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Accumulation of zinc, copper and manganese in soil fertilized with pig manure and urea in Southern State of Santa Catarina (Brazil)

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Abstract
This study evaluates changes in the Zn, Cu and Mn contents of a typical red clay Ultisol in the municipality of Braço do Norte, SC, Brazil during a corn (*Zea mays*) and oat (*Avena sativa*) crop cycle for a no-tillage system. The soil was fertilised with pig slurry and mineral fertilizer (urea), and swine deep bedding, at two rates: using the recommended dose of N and twice for the corn crop. Six measurements were made at depths of 0-15, 15-30, 30-45 and 45-60 cm, during the corn crop cycle in the 2007 / 8 harvest. In general, increases in the Zn, Cu and Mn contents occurred in soil with applications of pig manure. During the corn cycle, higher Zn, Cu and Mn concentrations were found in the surface layer (0-15 cm), and these values decreased with depth. For the treatment using fertilization with the deep bedding system twice the N recommendation (BD2x) in the soil surface layer, the highest Zn, Cu and Mn concentrations were observed. Although the levels of these elements were higher in the surface layer, their levels are not considered critical for environmental toxicity risks.

Key Words
Micronutrients, organic manure, sustainability

Introduction
Soil contamination with heavy metals has been recognized as a major environmental problem. Increasing concentrations of these metals in the soil may lead to their increased availability to plants. This availability and its vertical movement in the soil profile is controlled by soil attributes, and the varying mobility of these elements will be determined by the types and amounts of clay, pH, cation exchange capacity (CTC), MO contents, among others, which will influence the adsorption / desorption , precipitation / dissolution, complexation and redox reactions (Santos *et al.* 1999). Prolonged and / or excessive use of pig manure as organic fertilizer can result in the accumulation of Zn, Cu and Mn in the soil, and, as a consequence, in significant changes in the microbial community and phytotoxicity to plants (Simioni 2001). This is due to the chemical characteristics of wastes that are related to the nutritional composition of diets for pigs, which among other nutrients are rich in N, P and K, and have high concentrations of micronutrients such as Zn and Cu. It is estimated that 92-96% of Zn, 72-80% of Cu, (Bonazzi *et al.* 1994) ingested by animals are excreted and found in their feces and urine. Therefore, knowing the dynamics of these elements in soils is essential for assessing the environmental impact caused by the use of manure, since the extent of this impact is directly related to the ability of soils to retain these metals. This study aims to evaluate the leaching of Zn, Cu and Mn in Ultisol fertilized with deep bedding manure, pig slurry and chemical fertilizer in SPD in the municipality of Braço do Norte, Santa Catarina, Brazil.

Methods
The experiment was installed in the year of 2002 in an Ultisol, cultivated under a system of no-tillage with the succession oats / maize without the use of pesticides, in a rural property located at the Cachorrinhos Watershed River, in the city of Braço do Norte, at the coordinates 28° 15 'S and 49 ° 15' W. The climate of the city is a Cfa type, according to the classification of Köppen (Epagri 2000). The treatments were applied in experimental units (parcels) 4.5 x 6.0 m (27 m^2) in size, as follows: control with no fertilization (T), fertilization with swine bedding (BD), fertilization with pig slurry (PS), soluble nitrogen with urea application (AS). All the fertilization treatments were applied with doses related to one (1x) and two (2x) times the N recommended for cultures of oats and maize. The applied values were calculated based on the Chemical Commission and Soil Fertility (CQFS RS / SC 2004). The amount of N recommended for the cultures (30 kg/ha for oats and 90 kg/ha for maize) was based on soil analysis and expected productivity of maize. The swine deep bedding was manually applied on the soil surface, five days before planting the maize. The application of liquid swine manure and soluble fertilizer (urea) was according to the recommendation of the CQFS RS / SC (2004). The Zn, Cu and Mn contents during the course of the experiment were assessed at four depths (0-15, 15-30, 30-45 and 45-60 cm), 0,

7, 35, 53, 73 and 142 days after application of the deep bedding litter and the first application of pig slurry and urea. In each plot, 6 soil sub-samples were taken, with the help of a Dutch auger to form a composite sample. The material was transported to the laboratory, dried and then harrowed, thereby obtaining an air-dried soil sample. Measurements of Zn, Cu and Mn were done according to the method described by Tedesco *et al.* (1995), with extractions using KCl 1 mol/L and determined by atomic absorption spectrophotometry, performed at the Epagri Laboratory of Soils - Chapecó. The results in each soil layer and at different sampling dates were submitted to analysis of variance and the means were compared by the Tukey test at 5% of significance level.

Results

The analysis of variance showed that the application of pig manure promoted significant accumulation of Cu, Zn and Mn in the soil. This accumulation results from the overdose of Zn, Cu and Mn in the diets used, since the requirement for pigs ranges from 5 to 10 mg/kg for Zn and from 6 to 10 mg/kg for Cu. Simioni (2001) found a relationship between the levels provided by diets and those found in manure, where diets rich in Zn and Cu resulted in higher Zn concentrations in the manure. Figure 1 shows that during the corn crop cycle, Zn had limited mobility within the soil layers up to 60 cm, with which higher concentrations in the surface layer (0 - 15 cm) for all treatments.
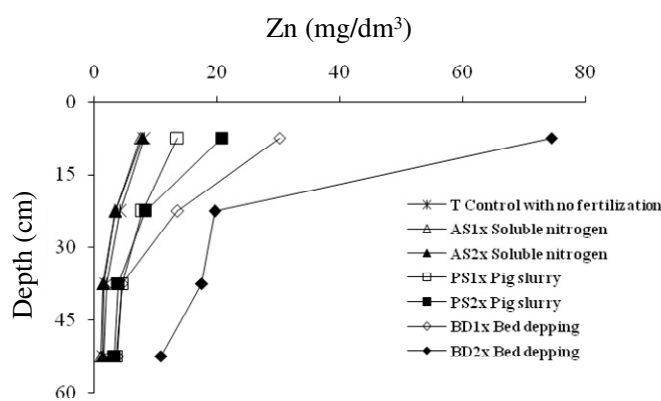
Figure 1. Zn concentration at depths of 0-15, 15-30, 30-45 and 45-60 cm.

The highest Zn concentration in the surface layer was for in the BD2x treatment, followed by BD1x, PS2x and PS1x, which significantly differ from each other. For all depths, the Zn concentrations for the treatments with mineral fertilizer showed no significant differences when compared to the control. The 15-30 cm layer also had the highest Zn levels for the treatment with BD and no differences were found for treatments with PS. In the 30-60 cm layer, the BD2x treatment differed from the others and there was no difference between the other treatments with organic fertilizers.

pH is one of the parameters with the greatest influence on the behavior of micronutrients in soils, because low values normally result in a higher availability, which may reach toxic levels. Araújo and Sobrinho (2000) studied Zn adsorption in several Brazilian soils and found a high correlation with organic carbon. Regarding the Cu contents in the soil (Figure 2), significant differences between treatments were also found. The highest Cu levels ($p < 0.05$) were observed for BD2x treatments in the surface layer, decreasing with depth. This Zn and Cu accumulation is consistent with data from L'Herroux *et al.* (1997), who also found increased levels and movement of these elements in the soil profile after four years of application of pig manure in France. These results differ from those found by Scherer and Nessi (2004) in the western state of Santa Catarina, on farms that had used pig manure for fertilization for 8 to 25 years. The authors observed higher Cu values in the 30 - 50 cm layer. According to the authors, this subsurface accumulation was due to the higher translocation capacity of this ion. For Zn, the highest contents were observed in the 0 - 10 cm layer.

Borkert *et al.* (1998) determined critical toxicity limits of these elements for some cultures. In general, legumes were more susceptible to Zn, while grasses were more susceptible to Cu. The critical limits established for corn were 300 mg of Zn/kg and 17 mg of Cu kg/soil. That is, the BD2x treatment presented Cu values close to or larger than the critical limit for the corn crop, at the 0-15 cm layer. Taking into consideration the standards set for European countries, which allows reaching up to 140 mg of Cu kg/soil and 300 mg of Zn kg/soil, the soil under study still con be used for the application of pig manure.
However, scientific works conducted in various parts of the world have shown that concentrations much lower

than the reported levels are able to negatively affect some components of the soil system. Baath *et al.* (1998) showed that 40 kg of Cu/ha (20 mg of Cu/kg soil) and 280 kg of Zn/ha (160 mg of Zn/kg soil) altered the biological diversity.
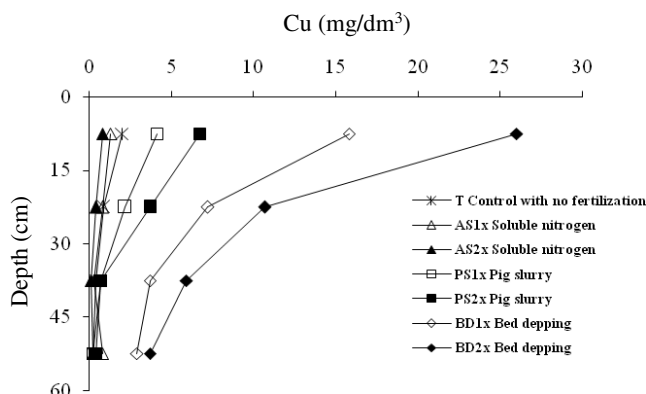
Figure 2. Cu concentration at depths of 0-15, 15-30, 30-45 and 45-60 cm.

For Mn, it was found that the BD2x treatment differed significantly from the others and promoted the accumulation of this element at the surface layer. In all treatments, decreased Mn contents at depth were observed (Figure 3). The largest accumulation at the surface layer is mainly due to the fact that Mn applied as fertilizer in a no-tillage system is retained in the organic fractions in a unavailable stable form (Moreira *et al.* 2006), which may also be related to a higher light incidence on the surface layers, increasing Mn solubility, which decreases in depth (Borkert *et al.* 2001).
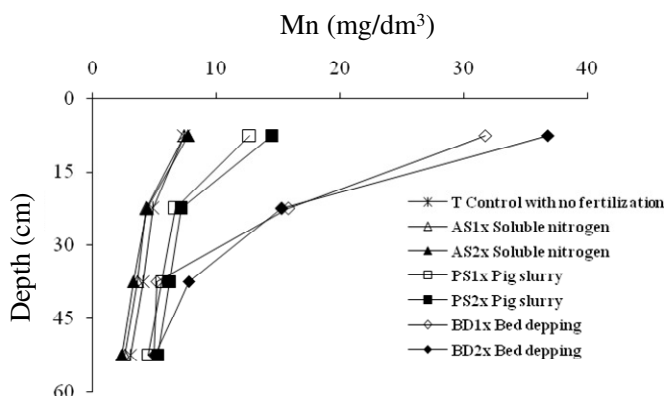
Figure 3. Mn concentration at depths of 0-15, 15-30, 30-45 and 45-60 cm.

Hargrove *et al.* (1982) observed higher Mn accumulation in weathered soil in southwestern USA under a no-tillage system when compared with a conventional system, attributing this difference to the deposition of plant residues. Brazil does not have legislation that determines the maximum Mn amount to be applied to soils. Sfredo *et al.* (2006), based on the Mehlich method, estimated Mn ranges in soil (Mg/dm^3) for the interpretation of their content in soils from the state of Paraná, and classified values above 30 as very high. Considering these rates, our research on fertilization with BD showed values that can be considered as very high. In a study conducted in the Rio Coruja / Bonito micro basin located at the municipality of Braço do Norte Mattias (2006), the authors observed that despite the large amounts of pig manure annually applied, the levels of heavy metals found were relatively low.

Conclusion
In general, increases in Zn, Cu and Mn levels were observed in the soil with pig manure applications, especially in the fertilization with swine bedding at a double dose, with the highest concentrations at the surface layer. The Zn, Cu and Mn contents added through pig manure were not considered critical to the environment.

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Aerobic decomposition and organic amendment effects on grain yield of triple-cropped rice in the Mekong Delta, Vietnam

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Abstract
The objective of this study was to determine whether soil aeration during decomposition of incorporated crop residues and application of organic amendments contributes to the improvement of soil quality and rice yield for sustainable intensive rice production in the Mekong Delta. A field experiment was conducted on triple-cropped rice during three consecutive crops with five treatments: (1) Conventional anaerobic decomposition of crop residues as a control (2) Air-drying of soil for three weeks before planting to foster aerobic decomposition of crop residues; (3) Air-drying of soil for three weeks combined with application of 10 Mg ha^{-1} compost of sugarcane filter cake (4) Air-drying of soil for four weeks before planting; and (5) Double-cropping of a rice-maize rotation.

The results showed that the intensity of soil reduction was highest in continuous submergence of triple-cropped rice with anaerobic decomposition of rice crop residues. All treatments with aerobic decomposition during three weeks with and without organic amendments, and double rice crops rotated with maize led to increased levels of soil labile organic carbon, available phosphorus and nitrogen mineralization compared to continuous triple rice with anaerobic decomposition. The mobile humic acid content in the soil was not different among treatments, due to high replicate variability. Consequently, through three consecutive crops, rice yield was improved compared to triple-cropped rice. The practice of drying soil for aerobic decomposition resulted in a higher amount of available soil nitrogen and increased rice grain yield, and it might benefit long-term sustainability of continuous rice cropping in the Mekong Delta.

Key Words
Triple rice, aerobic decomposition, rice rotation, organic amendments, rice grain yield

Introduction
In the Mekong delta, intensive triple rice cultivation inside dike built for flood control has led to soil degradation and a decline in rice yield. Continuous rice cultivation with the conventional practice of anaerobic decomposition of crop residues can enhance N binding to lignin-derived phenols which can result in limited soil N mineralization (Schmidt *et al*., 2004; Olk *et al*., 2009). Organic amendments promote longer-term N mineralization as a source of plant available N (Tamara *et al.,* 2006). This study aims at finding practical means to enhance soil nutrient supply for higher rice yield through crop residue management and crop rotation.

Methods
A field experiment was carried out during three consecutive rice crops in the first wet season 2007, the second wet season 2007 and the dry season 2007-2008 on an alluvial soil in Cho Moi district. Five treatments were arranged in a randomized complete block design with four replications, and four of them were triple-cropped continuous rice: (1) Conventional anaerobic decomposition of crop residues as a control (2) Air-drying of soil for three weeks before planting to foster aerobic decomposition of crop residues; (3) Air-drying of soil for three weeks combined with application of 10 Mg ha^{-1} compost of sugarcane filter cake (4) Air-drying of soil for four weeks before planting; Treatment (5) was Double-cropping of a rice-maize rotation. Analysis of variance was used to determine significant differences in soil variables and grain yield. Means were compared using LSD multiple range tests using MSTATC software. Results were considered statistically significant at P<0.05 level. Five soil samples were taken at random from each replicated plot (0-20cm). The soil samples were pooled to get one composite sample for each field plot. With four replications for each treatment, twenty soil samples were obtained at each soil sampling. Soil samples were collected at 10 days after planting before fertilizer application to determine labile C and carry out an aenarobic incubation to mineralizable N (Silveira *et al*. 2008). At two months after planting , the soil redox potential was measured in the field. Additional, soil samples were

collected ten days before grain harvesting for determining the contents of the mobile humic acid (MHA) fraction.

Results

During the dry season, soil reduction was less than during the wet season due to a high solar radiation and low water levels in the rice fields. A high intensity of soil reduction was found in continuous triple rice compared to the rice-maize rotation and the soil aeration few weeks before planting triple rice (Table 1). Soil labile organic carbon as well as N mineralisation increased significantly as a result of the aerobic decompostion of soil organic residues by rotation with upland crop or drying soil before rice planting. The MHA fraction tended to be high in triple rice, but there was no difference significantly among treatments (Figure 1, 2, 3). These results confirmed the finding by Olk et al.(2007) that continuous intensive irrigated rice led to reduce soil organic matter quality by accumulation of phenolic compounds which resulted in less available N in soil. By applying a period of aeration and organic amendment, soil nutrient supplying capacity increased and rice yield was improved in the triple rice system (Figure 4).

Table 1. Effect of soil management on the soil redox potential in a triple-cropped rice system.

Treatment	Eh (mV)	
	Crop 2 (Wet season)	Crop 3 (Dry season)
Triple-cropped rice	- 148a	-54a
Triple-cropped rice - 3 weeks aeration	- 89 b	21b
Triple-cropped rice - 3 weeks aeration + compost	- 89b	27b
Double-cropped rice-maize	- 86b	18b
Triple-cropped rice - 4 weeks aeration	- 72b	24b

Means followed by the same letters do not different at the 5% level of probability
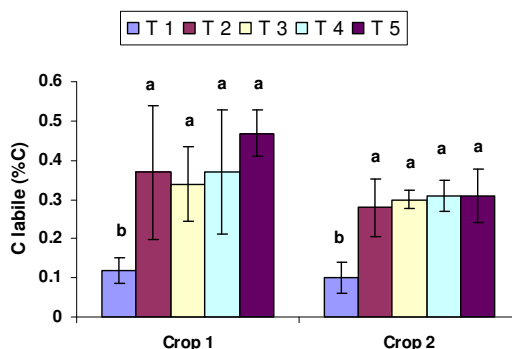
Figure 1. Effect of aerobic decomposition of crop residues and organic amendment on labile soil organic carbon l. T1.Conventional anaerobic decomposition of crop residues as a control; T2. Air-drying of soil for three weeks before planting to foster aerobic decomposition of crop residues; T3. Air-drying of soil for three weeks combined with application of 10 Mg ha^{-1} compost; T4. Air-drying of soil for four weeks before planting; and T5. Double-cropping of a rice-maize rotation. Means followed by the same letters do not different at the 5% level of probability. Bars are stadard deviation of the means.
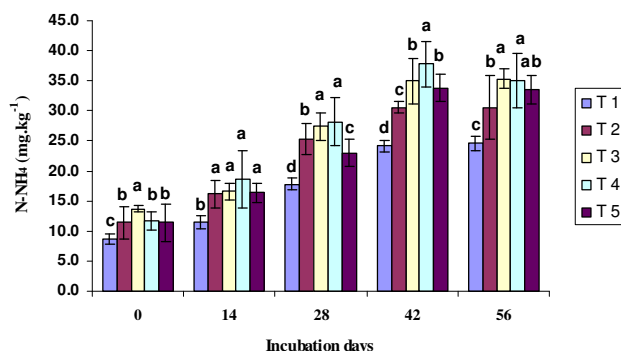
Figure 2. Effect of aerobic decomposition of crop residues and organic amendment on soil N mineralization. See Figure 1 for legend details.
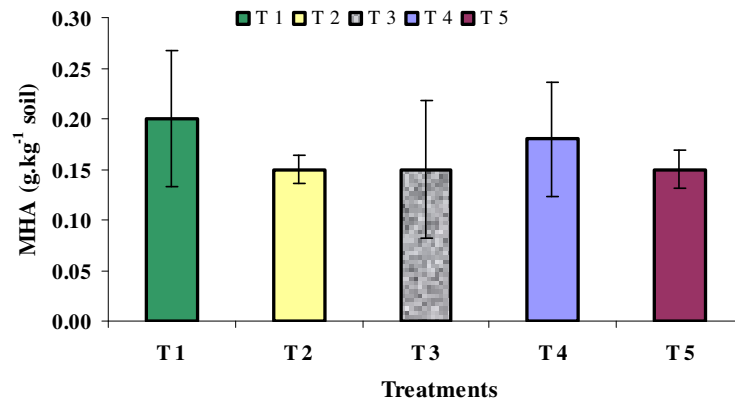
Figure 3. Effect of aerobic decomposition of crop residues and organic amendment on the quantity of the mobile humic acid fraction. See Figure 1 for legend details. Bars are standard deviation of the means.
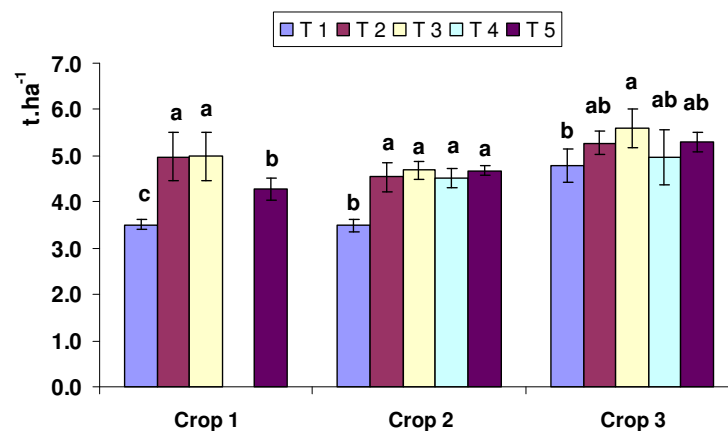
Figure 4. Effect of aerobic decomposition of crop residues and organic amendment on rice yield during three continuous rice crops. See Figure 1 for legend details. Means followed by the same letters do not different at the 5% level of probability. Bars are standard deviation of the means.

Conclusion

Soil aeration options for triple-cropped rice include aeration for three weeks before sowing to promote aerobic decomposition of crop residues, this same aerobic decomposition combined with compost amendment, and rotation of rice with maize, an upland crop. Compared to the conventional practice of anaerobic decomposition of crop residues, soil aeration provided a far less negative soil redox potential, improved soil quality as represented by soil N supply, and increased rice grain yield. An apparent decrease, i.e. enhanced mineralization, of the mobile humic acid fraction with increased soil aeration was obscured by a high variability among field replicates.

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An assessment of the health and ecological risk profiles of Sanjeevak and its fertilizing effect on cucumber biomass production

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Abstract
Permanent cultivation of the land is resulting in soil fertility decline in most agricultural systems in sub-Saharan Africa because most small-scale farmers cannot afford chemical fertilizers. The search for viable and cost-effective alternatives to improve soil fertility for sustainable crop production has resulted in renewed interests in the recycling of organic waste materials. However, concerns about health and environmental risks linked with their application to cropland may have restricted their use. The aim of this study was to assess the fertilizer value of Sanjeevak, its health and ecological risks and its effects on cucumber biomass production under greenhouse conditions. The results showed that the assessment of Sanjeevak revealed that none of the heavy metal and feacal coliform levels measured exceeded permissible limits for application to cropland. Equally, the study revealed that if applied at the proper agronomic rates; Sanjeevak can potentially be as effective as commercial fertilizer for crop production.

Key Works
Health and ecological risk profiles, cucumber, biomass production

Introduction
The search for viable and cost-effective alternatives for soil fertility improvement for sustainable crop production has resulted in the recycling of waste materials; including human and animal excreta. The fertilizing values of organic wastes such as animal manure and humanure are being used to varying extents for crop fertilization in many countries such as Zimbabwe, and South Africa. Hence, animal wastes combination such as Sanjeevak are being utilized for agricultural production. Sanjeevak is a fermented product made up of cattle faeces and urine; it has shown significant promises in field studies in India to improve seedlings development and the yield of various crops (Kate and Khadse 2002).

Objectives
The aim of this study was to evaluate the characteristics of Sanjeevak in terms of its heavy metal contents, total coliform concentrations; in comparison to the requirements for the agricultural use of wastewater sludge provided in the South African legislation. Also, the study reported herein was carried out to assess its fertilizing effects on growth parameters and biomass production of cucumber.

Materials and Methods
Sanjeevak preparation
Fresh dairy cattle droppings and urine were collected at the University of Stellenbosch experimental Farm. Cattle excreta and urine were mixed with water in the following proportions (1:1:18) and then fermented with molasses. The fermentation of Sanjeevak took place under aerobic conditions and kept at room temperature for a period of $\pm$ 45 days and replicated four times.

Analytical methods
Fifty-two days after sowing, all plant materials from each treatment (Control/Sanjeevak/Inorganic fertilizer) were harvested for plant height, shoot and root fresh and dry weight measurements. Total N, P and K concentrations were determined using atomic absorption spectrophotometer. Analysis was performed according to South African National Standard for the detection and enumeration and feacal coliform bacteria in wastewater (SANS 9308-3:2004).

Pot experiment
The treatments were 0.11% N, 0.007% P and 0.063% K; which translated to 1.1g N, 0.07g P and 0.63g K per 1000 ml of Sanjeevak. Mineral fertilizer of the same NPK concentrations as that of Sanjeevak was formulated as a source of inorganic fertilizer and translated into 3.14g NH_4NO_3, 0.3g KH_2PO_4, and 1.14g KCl per pot

experiment. The experiment had a total of three treatments for test crop, which were arranged in a randomized complete block design (RCB) and replicated ten times.

Results

The levels of heavy metals are generally very low in excreta, depending on the amounts present in consumed products. Equally, heavy metal contents in urine tend to be low depending on consumed food, probably because they are filtered by the kidneys when they enter the human body. This may explain the level of heavy metals recorded in Sanjeevak. Our results showed that the levels of feacal coliform (Table 2) found in Sanjeevak and heavy metal (Table 1) did not pose any potential health and environmental risks when used for cropland amendment (Table 3) (Snyman and Herselman 2006).

Table 1. Total concentrations (mg kg^{-1} dry weight) of heavy metals in dried Sanjeevak, compared to different classes of the pollutant in wastewater sludges (Snyman and Herselman 2006).

(mg/kg)	Pollutant Class			Sanjeevak
	a	b	c	
Arsenic (As)	< 40	40 - 75	> 75	n.d
Cadmium (Cd)	< 40	40 - 85	> 85	n.d
Chromium (Cr)	< 1200	1 200 - 3 000	>3000	0.03 ± 0.01
Copper (Cu)	< 1500	1 500 - 4 300	>4300	0.86 ± 0.18
Lead (Pb)	< 300	300 - 840	> 840	0.03 ± 0.01
Mercury (Hg)	< 15	15 - 55	> 55	1.76 ± 0.09
Nickel (Ni)	< 420	420	>420	0.14 ± 005
Zinc (Zn)	< 2800	2 800 - 7 500	> 7 500	4.74 ± 0.92

Table 2. Total feacal coliform counts in dried Sanjeevak (cfu/g weight dry matter), compared to microbiological classes in wastewater sludges (Snyman and Herselman 2006).

	Microbiological class			Sanjeevak
	A	B	C	
Feacal coliform (CFU/g dry)	1000 - 10 000	1×10^6 - 1×10^7	>1×10^7	1.2×10^2 - 2×10^4
Helminth ova (Viable ova/g dry)	0.25 - 1	1 - 4	> 4	N/A

N/A: Not Applicable

Table 3. Summary: Permissible utilization of sludge in agricultural applications (Taken from Snyman and Herselman 2006).

South African Sludge Classification		Is agricultural use an option?	Any additional restrictions and requirements	Notes
Microbiological class	A	Yes (i)	No	Could potentially be used as sealable product.
	B	Qualified yes (ii)	Yes	General restrictions/requirements apply.
	C	Maybe (iii)	Yes	General restrictions/requirements apply.
Pollutant class	a	Yes (i)	No	Could potentially be used as sealable product.
	b	Qualified yes (ii)	Yes	if the soil analysis is favourable.
	c	No (v)	Not applicable	May not be used in agricultural practices.

The effects of Sanjeevak application on cucumber growth and biomass production
Application of similar concentrations of Total NPK for both Sanjeevak and chemical fertilizer treatments, resulted in cucumber total biomass production increased relative to the control. Cucumber total biomass obtained 7 weeks after planting (WAP) was generally higher for both sources; with consistently greater yields from Sanjeevak. Equally, the heights of cucumber plants grown in Sanjeevak were greater and significantly different ($P<0.05$) from those of plants grown in inorganic fertilizer and the control (Figure 1). Cucumber root and shoot weights were greatest in Sanjeevak treatment. Taking the control as the baseline, cucumber biomass (Table 4) increases of about 3.5 and 2.2 times were obtained under Sanjeevak and inorganic fertilizer treatments respectively.
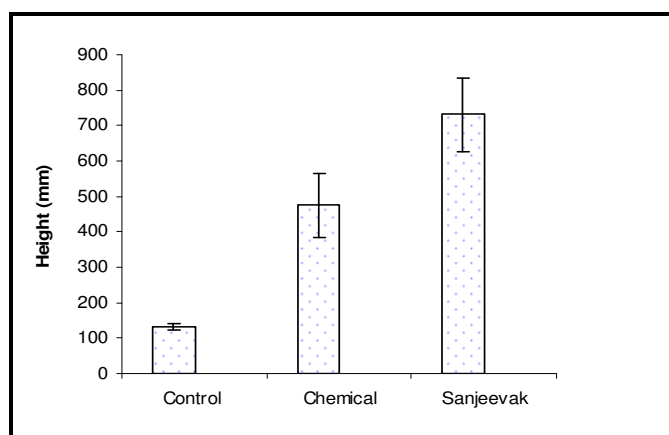
Figure 1. Effect of Sanjeevak vs. inorganic fertilizer on crop plant heights (mean ± standard error).

Table 4. Mean values of selected growth parameters of cucumber as affected by similar Sanjeevak and chemical fertilizer NPK application rate.

Treatment	Fresh biomass (g pot^{-1})		Dried biomass (g pot^{-1})		Total biomass (g pot^{-1})	
	Stems	Root	Stems	Root	Fresh	Dried
Control	13.49c	5.64b	3.09c	0.56c	19.13c	3.65c
Inorganic fertiliser	55.44b	5.78b	10.7b	1.04b	61.22b	11.74b
Sanjeevak	72.69a	13.47a	15.27a	2.43a	86.16a	17.7a

Means within each column followed by the same letter are not significantly different at $P<0.05$

Conclusions
In relation to the strictest current legislation that regulate the use of wastewater sludge for agricultural purposes, the assessment of Sanjeevak revealed that none of the heavy metals and feacal coliform levels measured exceeded permissible limits for application to cropland. In addition, the results revealed that the use of Sanjeevak can be as effective as commercial fertilizer as a source of essential nutrients for crops.

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Modern isotopic methods to investigate the fate and provenance of C sequestered into soils from livestock derived organic matter

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Understanding the fate of dung C in soils is challenging due to the ubiquity of plant-derived organic matter (OM), the source material from which both dung-derived OM and soil organic matter (SOM) predominantly originate. A better understanding of the fate of specific components of this substantial source of OM, and thereby its contribution to C cycling in terrestrial ecosystems, can be achieved through the use of labelled dung treatments. Bulk stable carbon isotope analyses are now used routinely to explore OM matter cycling in soils, and have shown that up to 20% of applied dung C may be incorporated into the surface soil horizons several weeks after application, with up to 8% remaining in the soil profile after one year. However, whole soil $\delta^{13}C$ values represent the average of a wide range of organic components with varying $\delta^{13}C$ values and mean residence times in soils. Several stable ^{13}C isotope ratio mass spectrometric methods have been developed to qualify and quantify different fractions of OM in soils and other complex matrices. Gas chromatography-combustion-IRMS (GC-C-IRMS) analyses have been applied to determine the incorporation and turnover of polymeric plant cell wall materials from C_4 dung into C_3 grassland soils using natural abundance ^{13}C isotope labelling.

The mean residence time of C pools increase with the application of manure. In the Hoosfield Classical Experiment at Rothamsted UK, annual applications of manure at a rate of 35 t ha^{-1} for 140 years resulted in a three-fold increase in soil organic C levels over that in unfertilised plots, and about 50% higher than unfertilised plots 104 years after manure addition had discontinued. This, and other, long-term studies indicate that manure can play a positive role in increasing soil C stocks in soils. However, other studies have concluded that dung application may have no effect or indeed a negative effect on soil C sequestration. Clearly, the dynamics of incorporation of dung C into soil are not well understood, but are highly variable in both space and time.

Natural abundance stable ^{13}C isotope labelling is one of the few proven techniques available for the examination of soil C dynamics in naturally functioning ecosystems. Isotope ratio mass spectrometry is widely used to determine the difference in natural abundance of ^{13}C between C_3 ($\delta^{13}C$ =-32 to -20‰) and C_4 ($\delta^{13}C$ = -9 to -17‰) vegetation which provides the basis for estimating the contribution of ^{13}C-enriched C_4 sources to SOM in ecosystems otherwise dominated by C_3 vegetation.

Naturally, the $\delta^{13}C$ values of cattle dung reflect the stable isotope values of their feed, therefore, cattle fed naturally ^{13}C-enriched C_4 species forage, i.e. *Zea mays*, produce a useful source of natural abundance ^{13}C-labelled dung that can be applied as a treatment to soils in C_3 ecosystems to explore cycling of dung C. Bulk $\delta^{13}C$ values of C_3 and C_4 dung-treated soil can be used in a simple mixing model to estimate dung C incorporation after dung deposition using stable C isotope determinations. A maximum of 20% and 12% dung C was determined in the top 5 cm soil horizon of dung-treated soils after autumn and spring applications. Incorporation of dung C in the spring differed from that in the autumn and was more rapid and fluctuated producing a sigmoid pattern of incorporation in the autumn. In the spring experiment, 8% of the dung derived C remained in the soil after 372 days providing direct evidence for the mechanism for increasing C stocks in soils treated annually with manures.

However, due to the diversity in decomposition dynamics and $\delta^{13}C$ values of individual biochemical components of dung, fluxes in bulk $\delta^{13}C$ values in C_4 dung treated soil may not imply a total loss or gain of dung C. Different components of plant-derived OM, and therefore dung, have a range of $\delta^{13}C$ values due to fractionations against the heavier isotope during biosynthesis. Cow dung is a complex mixture of biochemical components that are likely to decompose at different rates. The contribution of different biochemical fractions to dung estimated using gravimetric procedures showed that the major component is undigested lignocellulosic plant cell wall material. Cow dung derived from *Lolium perenne* and *Z. mays* forages was estimated as 20-30% hemicellulose, 20-30% cellulose, 7% lignin, 12% crude protein and 3-5% fats using the 'Forage Fibre Analysis' procedure. Analyses of dung carbohydrates analysed as alditol acetates using gas chromatography determined concentrations of up to 80% dry weight as sugars in dung due to the inclusion of the soluble components, which

may also derive from microbial debris. Lipids in dung were dominated by the 5β-stanols and C_{26} n-alkanol, with relatively minor contributions from carboxylic acids, wax esters and n-alkanes. Determining accurate concentrations of dung lignin is difficult due to the challenges presented by extraction of monomers with subsequent quantification against an internal standard. Lignin and lipids are depleted compared to bulk plant tissue, whilst cellulose and hemicellulose are 1-2‰ more ^{13}C-enriched. Off-line pyrolysis was used to extract lignin monomers from dung and dung-treated soils for stable ^{13}C isotope analysis using gas chromatography-combustion-IRMS (GC-C-IRMS). The m/z 44 ion current and instantaneous ratio of m/z 45/44 ions recorded for the off-line pyrolysate of lipid-extracted C_4 dung showing base-line resolved pyrolysis products, for which compound-specific δ^{13}C values could be obtained. Dung lignin-derived moieties in the pyrolysate were up to 7‰ ^{13}C-depleted relative to bulk dung, although syringol and 4-vinylguaiacol were ^{13}C-enriched up to 4‰ and 2‰, respectively. The ^{13}C-depleted values are in agreement with earlier studies, which indicated that plant tissues yield lignin products 2–7‰ depleted in ^{13}C compared with whole tissue. δ^{13}C values determined for lipids as n-carboxylic acids ($iC_{14:0} - C_{30:0}$) extracted from C_3 and C_4 dung also showed depletion of up to ca. 6‰ compared to bulk dung, with increasing depletion with hydrocarbon chain length in very long chain fatty acids (VLCFA) >C_{20}. Carbohydrate δ^{13}C values determined for arabinose, xylose, galactose and glucose extracted from dung and analysed as their alditol acetates were -10.4 ±0.5‰, -10.4 ±0.4‰, -8.3 ±1.6‰ and -11.5 ±0.6‰ respectively for C_4 dung (bulk δ^{13}C value -12.6 ±0.3). The variability in concentration and δ^{13}C values between individual components of dung-derived OM drives the need to develop and apply sensitive tools to determine their contribution to bulk values in order to understand C cycling soils treated with manures as soil improvers or under livestock management.

Using bulk and compound-specific stable IRMS, the spatiotemporal dynamics of whole dung C cycling and that of specific biochemical components of dung in the soil can be determined. Importantly, this work has shown that fluxes of carbon derived from polysaccharides, i.e. as cellulose or monosaccharide components, were more similar to the behaviour of bulk dung C in soil than lignin. However, lignin and its 4-hydroxypropanoid monomers were unexpectedly dynamic in soil. These findings provide further evidence for emerging themes in biogeochemical investigations of soil OM dynamics that challenge perceived concepts of recalcitrance of C pools in soils, which may have profound implications for the assessment of the potential of agricultural soils to influence terrestrial C sinks. Thus, by using bulk and compound-specific stable IRMS, the spatiotemporal dynamics of whole dung C cycling and that of specific biochemical components of dung in the soil can be determined.

Thus, to better understand the contributions made to SOM from different sources, in this case animal wastes, detailed biochemical understanding of the provenance and fate of individual components is required. This paper will provide a review of the state-of-the-art techniques for compound specific analysis of incoming organic materials to soils and quantify the contributions of animal residues to the SOM budget in pastoral agricultural systems.

Assessment of an automated method for determining particulate organic carbon in soil

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Abstract
A manual and an automated method of sieving soil to collect a particulate organic carbon (POC) fractions were compared. The manual method is potentially subject to operator influence whereas the automated method is not. Results revealed that the amount of carbon captured in the POC fraction was larger for the automated than manual method across the five soils examined. However, the magnitude of the difference in POC as determined by the two methods varied significantly with soil type. Variation between the results obtained by different operators were also higher for the manual than automated method. The automated methodology for sieving therefore provides more consistent data across operators but also gave higher POC values.

Key Words
Soil carbon, particulate organic carbon, sieve shaker

Introduction
It is now recognised that soil organic carbon (SOC) includes a variety of different materials with different susceptibilities to biological decomposition and mineralisation. Additionally, a variety of methods have been proposed to separate and quantify the allocation of SOC to these different components based on physical and/or chemical properties. One approach uses sieving to separate a dispersed sample of soil into >50 µm particulate organic carbon (POC) and organic material associated with particles ≤50 µm (Humus) (Skjemstad *et al*. 2002). This initial sieving process is then followed by photo-oxidation and/or solid-state ^{13}C nuclear magnetic resonance spectroscopy (NMR) to quantify the amount of charcoal (resistant organic carbon – ROC) present in these fractions. Although Skjemstad *et al*. (2004) were able to demonstrate the utility of this simple fractionation scheme by successfully substituting these measureable fractions into a variant of the RothC soil carbon model, the methodology is time consuming and operator dependent. As we move towards the routine measurement of these fractions of SOC (POC, Humus and ROC) and the extension measurement and modelling across Australia, a more rapid and operator independent methodology is required.

The main operator dependence in the SOC fractionation methodology occurs during the sieving process. During this process the effort applied to cause soil material to pass through the 50 µm sieve is dependent on the operator. A new automated sieve shaker system appeared to offer the potential to precisely define and control the sieving conditions and thus reduce any operator dependence from the sieving step within the SOC fractionation methodology. The purpose of this study was to compare results obtained from the existing manual sieving approach to those obtained using the automated sieve shaker for different soils fractionated by different operators.

Methods
A series of five different soil types varying in SOC content, clay content and pH were used for this study (Table 1). The soils were checked from the presence of carbonate and pretreated with H_2SO_3 to remove carbonates if required (SS8 and Weisenboden soils) according to Skjemstad and Baldock (2008). Approximately 10 g of soil was dispersed in 50 ml of sodium hexametaphosphate (5g/L) by shaking for 16 hours. The dispersed suspensions of soil were then sieved according to the previous methodology or placed onto the top of a 50 µm sieve housed within an automated sieve shaking system (Fritsch Vibratory Sieve Shaker Analysette 3) equipped with the capability to spray water over the sieves as it vibrates with a defined amplitude and velocity.

In the manual system, water was passed through the sieve while a rubber policeman was used to move the soil around. It is this step which accounted for the operator dependence as the rate of water flow, rate of movement of the rubber policeman and the force applied were all subject to variation between operators. In the automated system, the amplitude and velocity of the vibratory sieve shaker and the flow rate of water through the sieves were all controlled and could not be influenced by the operator. For both systems, sieving and water flow through the sieves continued until the solution exiting the sieves became clear. The volume of water required to achieve this condition varied between soils but was typically on the order of 300-500 ml. The material retained

on the 50 µm sieve (POC) was washed off the sieve into a container and dried at 60°C to constant mass and weighed. The ≤50 µm fraction (Humus) was collected in a beaker during the sieving process, transferred to a 500 ml polypropylene bottle, frozen, freeze dried and weighed. Total organic carbon contents of the POC (>50 µm material) and Humus (≤50 µm material) fractions were then determined using a LECO CR-144 carbon analyser. The POC fractions were first ground to a fine powder prior to organic carbon analysis.

To compare the manual and automated sieving methodologies, one operator analysed four replicates of all five soils using both methodologies and the acquired data was analysed as a 5 (soil type) x 2 (method of sieving) factorial design. To examine the operator dependence, three different operators analysed four replicates of three soils using both sieving methodologies and the data was analysed as a 3 (operator) x 3 (soil type) x 2 (method of sieving) factorial design. All statistical analyses were completed using Statistica 8 (Statsoft 2007).

Table 1. List of soils included in this study with some relevant soil properties.

Sample	Location	Depth (cm)	Classification	pH water	C g kg^{-1}	clay (%)
SS6	Tallagalla, Qld	0-5	Dermosol	6.6	71.4	45
SS7	Toowoomba, Qld	0-5	Ferrosol	5.9	143.0	16
SS8	Waco, Qld	0-10	Vertosol	8.2	28.0	61
SS10	Gympie, Qld	0-10	Chromosol	5.0	44.4	21
Weisenboden	Adelaide, SA	0-10	Vertosol	7.7	31.0	40

Results

Comparison of sieving methods

The data acquired by one operator across all five soils and both methods of analysis are presented in Figure 1. ANOVA indicated the presence of a significant interaction between soil type and method of analysis. For all soils, the automated method gave higher POC contents than the manual method; however, the magnitude of the difference between the two methods varied between the soil types. SS7 had a very large difference while little difference between the two methods was evident for the Weisenboden soil. The coefficient of variation for all soils, except the Weisenboden, was lower for the automated than the manual method of sieving.
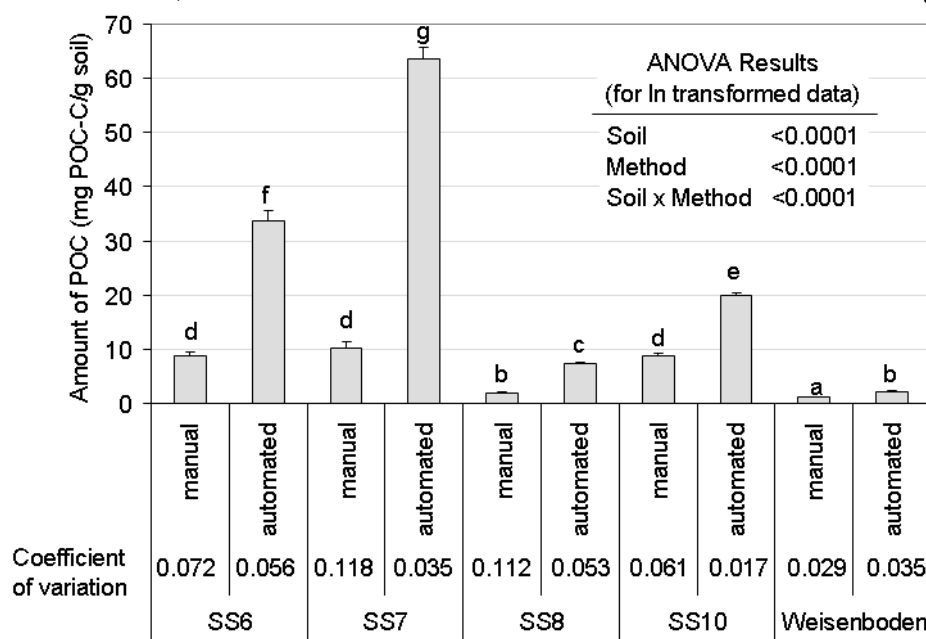
Figure 1. Comparison of manual and automated methods of POC fractionation. Error bars represent the standard deviation of the means. Statistical analyses were completed on natural logarithm transformed data to address an inhomogeneity of variance. Means with different letters had significantly different ln transformed values at p=0.05.

Comparison of results obtained by different operators analysing the same soil

The previous observation that more POC was obtained using the automated method persisted when three different operators analysed two soils using both sieving methodologies. Variation both within and between the various operators was lower for the automated method than the manual method of sieving. As a result, although the automated method gives a higher value for POC, the more consistent data was obtained across the operators using the automated method.
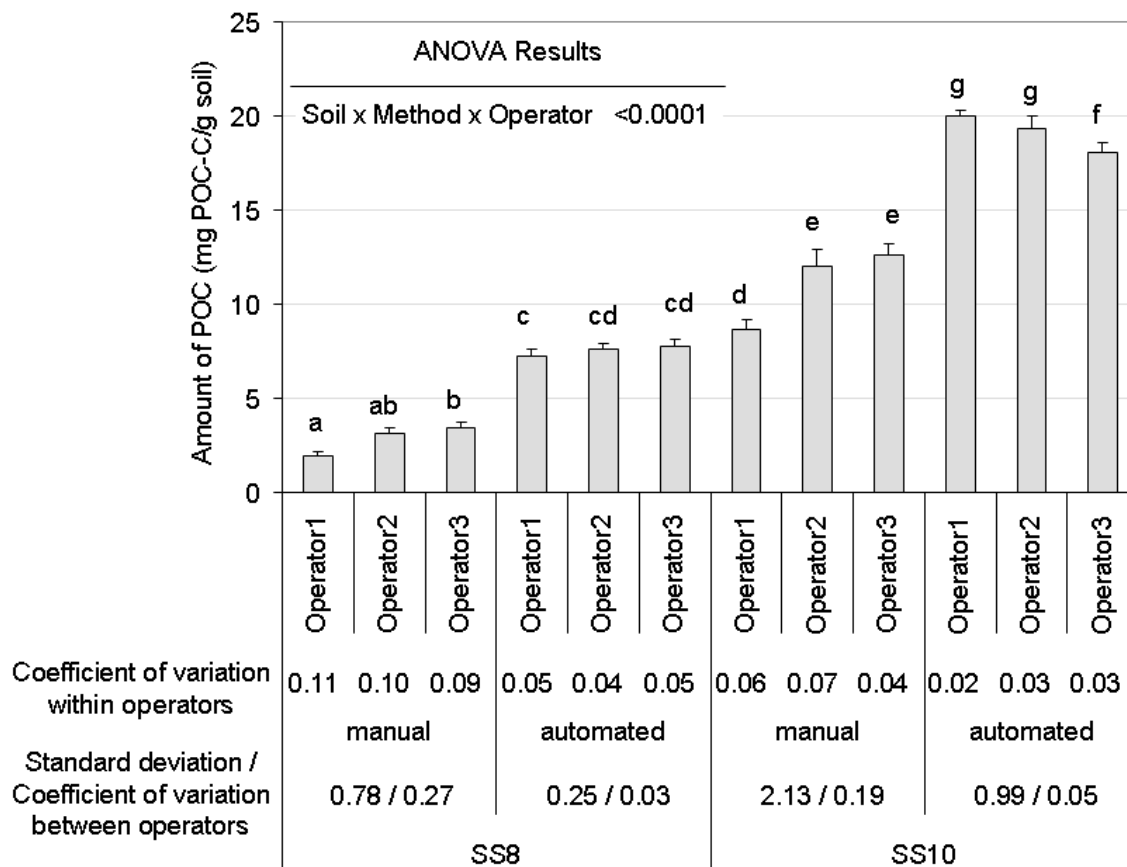
Figure 2. Comparison of operators using the manual and automated method of POC fractionation on two soils. Error bars represent the standard deviation of the four replicate determinations. All statistical analyses were performed on untransformed data. Means with different letters are significantly different at p=0.05.

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Baseline organic carbon stocks of Rwandan topsoils

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Abstract
Rwandan soil resources are very diverse. Yet, socio-economic drivers foster inappropriate land management and threaten soil quality. This manuscript quantifies the baseline topsoil (0-30 cm) organic carbon stocks (C_{stock}) of the country using analytical data comprised in the Rwanda Soil Information System. Based on data of 121 soil profiles, having measured soil organic carbon, volume of coarse fragments and bulk density values for all horizons within the upper 30 cm of the soil surface, the average C_{stock} in this tropical highland country amounts to 86.1 ± 4.7 Mg C/ha. Large differences in C_{stock} were identified as a function of soil reference group and land use. Especially the forested highlands have large potentials for organic carbon sequestration, though deforestation in favour of cropping activities clearly leads to significant carbon losses.

Key Words
Organic carbon stocks, reference groups, land use, Rwanda, soil survey database, data mining

Introduction
Central African soil resources are characterised by a large variability, ranging from stony, shallow or sandy soils with poor life-sustaining capabilities to deeply weathered soils that recycle and support large amounts of biomass (Bationo *et al.,* 2006). Socio-economic drivers within this largely rural region foster inappropriate land management, threaten soil quality and finally culminate into a declining soil productivity and increasing food insecurity. For the development of sustainable land use strategies targeting development planning and natural hazard mitigation, the decision makers need good baseline soil information. Because of the lack of bulk density measurements in many soil survey databases, estimates of organic carbon stocks generally rely on the use of pedotransfer functions filling gaps in datasets, yet increasing the uncertainty of the output results. This manuscript evaluates the quality and representativity of the Rwandan soil profile database and illustrates its potential value for developing baseline data for soil organic carbon stocks based on measured data.

Materials and Methods
Rwanda Soil Information System
The Rwanda Soil Information System comprises a soil profile database containing records for 1833 georeferenced soil profiles. All information was gathered from 1981 to 1989 during the national soil survey, which was realised through cooperation between the Rwandan Ministry of Agriculture, Livestock and Forestry and the Belgian Government. Based on unique combinations of parent material, profile development, soil depth, drainage, texture and physico-chemical properties, 276 different soil series were identified to characterise the Rwandan soilscape on 43 soil map sheets at a scale of 1:50,000 covering the entire territory (Verdoodt & Van Ranst, 2006a; Verdoodt & Van Ranst, 2006b). The soil profiles were sampled for a routine physico-chemical characterization of their horizons, using standardised methods, in the project soil survey laboratory in Kigali (Rwanda), and the soil science laboratory of Ghent University and of the Catholic University of Louvain-La-Neuve (Belgium).

Data quality control and analysis of representativeness
To control the quality of the stored information, the soil profile database was subjected to auditing routines based on (1) a confrontation of the spatial distribution of those attributes for which independent thematic layers exist (e.g. administrative maps, digital terrain model), and (2) theoretical limits set to each soil property, using correlations with other soil attributes, enabling the elimination of values outside the expected range (e.g. pH, granulometry). The representativity of the soil profiles was assessed by comparing the distribution of the soil profile population with respect to soil and land use types with the aerial extent of the soil reference groups, as reflected on the soil map, and the land use types characterizing the countryside.

Data handling and analysis
For all physico-chemical soil properties, weighted average parameter values characterising the mineral topsoil (0-30 cm) were calculated. Descriptive statistics were produced to illustrate range, mean and standard deviation of the measured parameters.

The C_{stock} (Mg/ha) within each horizon was calculated from the soil organic carbon content C_{conc} (g/kg), bulk density BD (g/cm³), coarse fragments CF (vol%) and thickness of the horizon d (cm) according to:

$$C_{stock} = C_{conc} \times BD \times (1-CF) \times d \times 0.1 \qquad (1)$$

Measured C_{conc} (Walkley and Black), CF (sieving > 2 mm) and BD (volumetric ring method) data were taken from the soil analytical database. Topsoil carbon stocks per unit area were then calculated by summing the C_{stock} of all horizons within 30 cm depth. Land use data were taken from the soil profile description, and pivot tables were generated highlighting the influence of soil type and land use on soil organic carbon stocks.

Results

Characterising the Rwandan soils
Rwanda, even though being a small (26,000 km²) landlocked country, hosts a great diversity in climatic, geologic, and geomorphic conditions. With its altitude ranging between 900 and 4500 m (Figure 1), it comprises both warm, semi-arid plains covered by savannah vegetation in the east to rainforest growing in the cool, humid (north) western highlands. Strongly weathered soils dominate the eastern and southern pediplains, whereas the soils in the valleys and highlands are subjected to regular rejuvenation through soil erosion and deposition of alluvium, colluvium, or even volcanic material. Besides nature conservation efforts within the 3 national parks, the land is generally used for agricultural production.
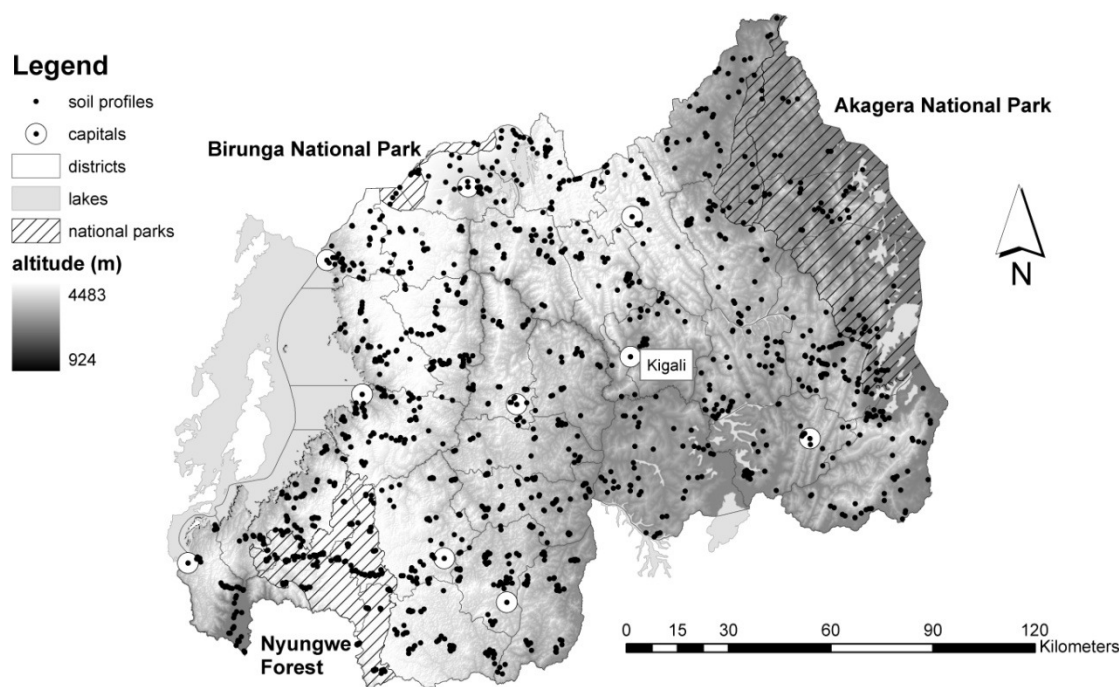
Figure 1. Distribution of the soil profiles.

Representativity of the Rwanda soil information system
Figure 1 shows the spatial distribution of the soil profile locations. The average sampling density was 1 profile for every 14 km², though large regional differences can be identified as the soil survey strategy focussed on pilot zones located within different geomorphologic environments. Cambisols (27%), Ferralsols (26%), Acrisols (14%) and Alisols (11%) dominate the profile database. The profile population furthermore comprises both cultivated and non-cultivated soils. Most soil profiles are under cropping (32%) or fallow (34%), followed by timber production (13%) and natural forests (13%). About 6% of the profiles was located within a natural reserve and 2% was exclusively used for pasture. This latter land use type seems to be underrepresented in the database, though in reality, many fallow lands are used for grazing as well.

After the initial quality control stage, 1518 soil profiles were retained for soil property modeling, albeit of varying completeness for individual properties. The diversity in soil formation factors is reflected in the large ranges of physical and chemical soil properties (Table 1).

Table 1. Ranges of a selected set of mineral topsoil (0-30 cm) physical and chemical soil properties comprised by the Rwandan soil profile database.

Description	Unit	N° of profiles	Average	Range
Physical soil fertility				
clay	%	1428	36 ± 15	2 – 85
silt	%	1428	21 ± 12	2 – 77
sand	%	1428	43 ± 17	0 – 90
bulk density	Mg m^{-3}	149	1.1 ± 7.4	0.5 – 1.7
moisture content at pF=2.5	%	208	30 ± 18	6 – 158
moisture content at pF=4.2	%	208	20 ± 13	3 – 122
Chemical soil fertility				
pH-H$_2$O	-	1448	5.1 ± 0.9	3.0 – 11.2
organic carbon	%	1450	2.92 ± 2.68	0.29 – 32.8
total nitrogen	%	1350	0.224 ± 0.392	0.028 – 12.850
available phosphorous	ppm	382	19.35 ± 44.39	0.00 – 372.00
exchangeable Ca^{2+}	cmol(+) kg^{-1} soil	1336	4.51 ± 6.79	0.00 – 92.80
exchangeable Mg^{2+}	cmol(+) kg^{-1} soil	1336	1.78 ± 2.98	0.00 – 51.07
exchangeable K^{+}	cmol(+) kg^{-1} soil	1336	0.42 ± 0.71	0.00 – 12.40
exchangeable Na^{+}	cmol(+) kg^{-1} soil	1336	0.22 ± 0.39	0.00 – 27.67
Soil mineralogy				
CEC-NH$_4$OAc	cmol(+) kg^{-1} soil	1343	17.90 ± 13.57	1.58 – 200.27
free Fe$_2$O$_3$	%	234	4.89 ± 3.71	0.00 – 28.31
amorphous Fe$_2$O$_3$	%	25	0.91 ± 0.76	0.13 – 2.73

Topsoil organic carbon stocks

Using the available data, the topsoil C$_{stocks}$ have been calculated for 121 profiles, representing 99 soil series which spatially cover 47% of the Rwandan soilscape. On average, 86.1 ± 4.7 Mg C/ha has been stored in the Rwandan topsoils. Yet, differences are large with values ranging between 14.5 and 240.4 Mg C/ha, measured in a stony, organic matter depleted cropland topsoil in the province of Gitarama, and in a forest topsoil of the Birunga volcanic range, respectively. The distribution is furthermore skewed with only 10% of the profiles having SOC$_{stocks}$ exceeding 150.0 Mg C/ha (Figure 2).
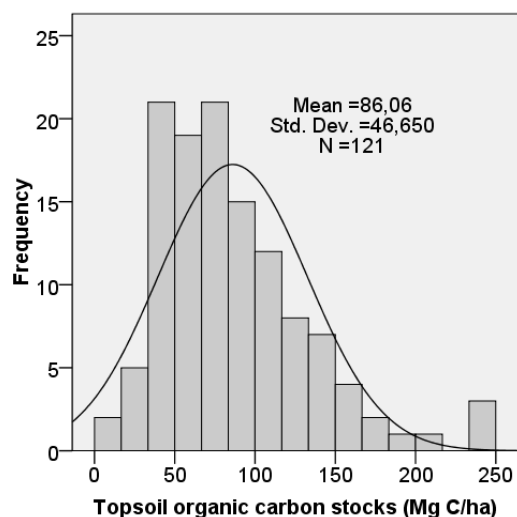
Figure 2. Histogram of the topsoil organic carbon stocks measured in 121 soil profiles of Rwanda

Analysis of the results as a function of soil type and land use illustrates that the Andosols are characterised by the highest C$_{stock}$ of 149.4 ± 44.2 Mg C/ha as the humiferous topsoil organic matter is stabilised by the presence of Al-humus complexes. Cropping activities reduce the C stocks, through enhanced organic matter mineralisation and erosion losses, though the topsoil stocks recorded in the '80s were still considerable. The lowest C stocks, on the other hand, have been reported in the Luvisols and Ferralsols, characterised by average C$_{stock}$ values of 55.5 and 59.4 Mg C/ha, respectively. Low topsoil stocks of the former reference group are

clearly associated with agricultural land uses, whereas the Ferralsols are characterised by low stocks, regardless of the land use type.

The C_{stock} values calculated from the Rwandan soil profile database thus roughly correspond to the Central African estimates for Ferralsols (58 ± 47 Mg/ha), Acrisols (65 ± 48 Mg/ha), and Cambisols (81 ± 50 Mg/ha) reported by Batjes (2008). The higher stocks measured in the Rwandan Acrisols and Cambisols can be explained by the positive impact of the relatively cool climatic conditions of this high altitude country on soil organic carbon contents.

Variations in altitude, topographic position and soil texture furthermore explain the moderate variation recorded within each reference group – land use type class. In future, the baseline dataset could be considerably enlarged (C_{conc} and CF measured for about 1428 profiles) if the missing BD data are estimated using regionally validated PTFs. This would allow a more comprehensive analysis of the topsoil organic carbon stocks in Rwanda as a function of several soil forming factors and the development of a topsoil C_{stock} map.

Table 3. Topsoil (0-30 cm) organic carbon stocks (Mg/ha) of Rwanda stratified according to the major soil reference groups and land use types.

Soil reference group	Land use					
	Forest	Grassland	Timber	Cropland	Savannah	*Average*
Andosol	164.9 ± 2.5	158.1 ± 71.7	162.5	114.1 ± 3.8	-	*149.4 ± 44.2*
Cambisol	148.8 ± 63.8	95.8 ± 45.0	98.9 ± 39.2	80.6 ± 51.5	-	*100.8 ± 49.0*
Alisol	-	124.4 ± 60.8	93.3 ± 24.8	87.7 ± 41.6	-	*95.5 ± 41.8*
Acrisol	170.3 ± 99.2	73.6 ± 25.8	76.2 ± 10.1	85.3 ± 44.3	34.4	*86.2 ± 48.0*
Ferralsol	52.9 ± 9.1	66.9 ± 26.7	68.3 ± 70.5	60.7 ± 20.1	43.6 ± 14.7	*59.4 ± 25.0*
Luvisol	-	89.8 ± 34.1	52.0	35.6 ± 14.6	-	*55.5 ± 33.0*
Average	*129.5 ± 68.7*	*92.7 ± 46.6*	*89.6 ± 37.3*	*71.8 ± 37.8*	*42.0 ± 13.6*	

Conclusion
The Rwanda Soil Information System is one of the most comprehensive soil resources databases of the African continent. It is a key instrument for the description of the physical environment that farmers face in the different agricultural regions of the country and for the development of baseline values for various soil properties. To that end, the dataset should be exploited to produce nationally and/or regionally consistent spatial estimates of key soil properties. With respect to topsoil organic carbon stocks, the database reveals a high potential for C sequestration, especially in the highlands. These soils, being prone to erosion, are subjected to significant C losses once deforested and cultivated. The value of the database also goes beyond national interest. In view of the large range of tropical environmental conditions covered by the dataset, the information can prove useful to the development of PTFs for physical and chemical soil properties, being of interest to the Central African highlands.

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Biochar-Ion Interactions: An investigation of biochar charge and its effect on ion retention

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Abstract

The method of measuring exchangeable cations as an approximation for cation exchange capacity was examined using a cow manure and green waste biochar. Both biochars were pre-treated by shaking with water over a range of times. Leachates were analysed, and the pre-treated biochars were then treated with two solutions ($0.1M$ $BaCl_2$ or $0.1M$ $CsCl$) to measure ion adsorption. Pre-treatment shaking had a significant effect on ion adsorption for both biochars. Ion adsorption for the green waste biochar was significantly increased with pre-treatment shaking, whereas it decreased for the cow manure biochar. Compulsive exchange of cations to determine the ability of a substrate to retain positively charged ions on its surface may not be an appropriate method for biochar.

Key Words

Biochar, cation exchange capacity, surface charge, electrostatic forces

Introduction

The summation of values from the compulsive exchange of cations (isomorphic substitution of calcium, sodium, potassium, and magnesium) is often used as a quantitative method for determining the ability of a substrate to retain positively charged ions on its surface (cation exchange capacity, CEC). This value can then give an indication of the surface charge of the substrate, depending on pH and the size of the exchanging ions. While some substrates can also have positive surface charge, and the net surface charge is the difference between these two charges, many soils favour a net negative charge. The two substrate properties that account for ion adsorption and retention are particle surface area and surface charge. Colloid surfaces within the substrate are the major sites of this isomorphic substitution and the ionisation of functional groups, resulting in the development of charge. Charge in soils can be both permanent and pH-dependant (Bohn *et al*., 2001). The surface charge of substrates can also be determined by the difference between pH_{KCl} and pH_{H2O} (Black and Waring, 1976; Kingston *et al*., 1972). Hence a net negative number would suggest a negative surface charge, and vice versa.

Substrates must maintain electrical neutrality, and so this is often maintained by H^+ and OH^- from (soil) water. Some substrates may have low exchangeable cations adsorbed to their surface, relying on H^+ to fulfil charge neutrality. So a measure of exchangeable cations for these substrates will produce low values. The measures of exchangeable cations for a cow manure and greenwaste biochar (obtained from Pacific Pyrolysis Pty. Ltd.) for this project were significantly different (45.6 vs 4.23 Cmol/kg). The relatively low value for the greenwaste biochar would imply little negative charge on its particle surface. However the pH difference for this biochar was -2.04, suggesting the potential for a substantial cation adsorption capacity. Biochar particles may also possess both positive and negative charge on their surfaces. These zwitterion-like properties may be due to inherent biochar charge, or it may occur through the adsorption of other zwitterions such as amino acids onto their surface.

It was hypothesised that ion adsorption of the two biochars in this project may vary according to particle surface charge. It was also hypothesised that the ion adsorption may be increased through the loss of ions from differing pre-treatment shaking times.

Materials and Methods

All shaking was performed in a temperature-controlled laboratory (20.1°C).

Experiment A: Pre-treatment of Biochars

- 100 ml of distilled water was added to 5g samples of 2 unground biochars and shaken end over end for 6 shake times (2, 8, 16, 32, 64, 120 hours; 6 replicates per time treatment).
- All samples were filtered with Advantec 5C filter papers (pore size 5 µm), with the leachate kept for analysis and the solid biochar material and filter papers kept for Ba/Cs treatments.
- A control of distilled water was filtered as above with the leachate kept for analysis and the filter papers kept for Ba/Cs treatments.
- Leachates were analysed using an ICP AES (Varian, Liberty 2, Environmental and Analytical Laboratory, Charles Sturt University, Wagga Wagga). Initially 2 samples from each biochar were qualitatively analysed by examining intensities across the full spectrum, to determine what elements may be present in the solutions.
- Standards were then made, and the identified elements quantitatively analysed.
- Leachate samples were also analysed through a UV VIS spectrometer for phosphate, and a segmented flow analyser for mineral nitrogen.

Experiment B: BaCl$_2$/CsCl Saturations

- 25 ml of 0.1 M BaCl$_2$ was added to biochar samples and filter papers retained from experiment A (pre-treatments) and shaken end over end for 2 hours (3 replicates/biochar).
- 25 ml of 0.1 M CsCl was added to biochar samples and filter papers retained from previous experiment (pre-treatments) and shaken end over end for 2 hours (3 replicates/biochar).
- 25 ml of 0.1 M BaCl$_2$ or 0.1 M CsCl was added to 5g samples of both biochars that had NOT undergone pre-treatment (3 replicates/biochar/solution).
- All samples were filtered with Advantec 5C filter papers (pore size 5 µm), with the leachate kept for analysis.
- Leachates were analysed for proportion of cation (Ba or Cs) remaining using ICP AES.
- Leachates were analysed for proportion of anion (Cl) remaining using an Ion Chromatograph (Dionex 1CS-2000, Environmental and Analytical Laboratory, Charles Sturt University, Wagga Wagga).

Results

Analysis of Pre-treatments

There was an increase in calcium desorption with increasing shake times for the green waste biochar, and the loss was significantly larger than the calcium desorption of the cow manure biochar. The loss of magnesium significantly increased with increasing shake times for both biochars, and this was significantly larger for the cow manure biochar compared to the green waste biochar.
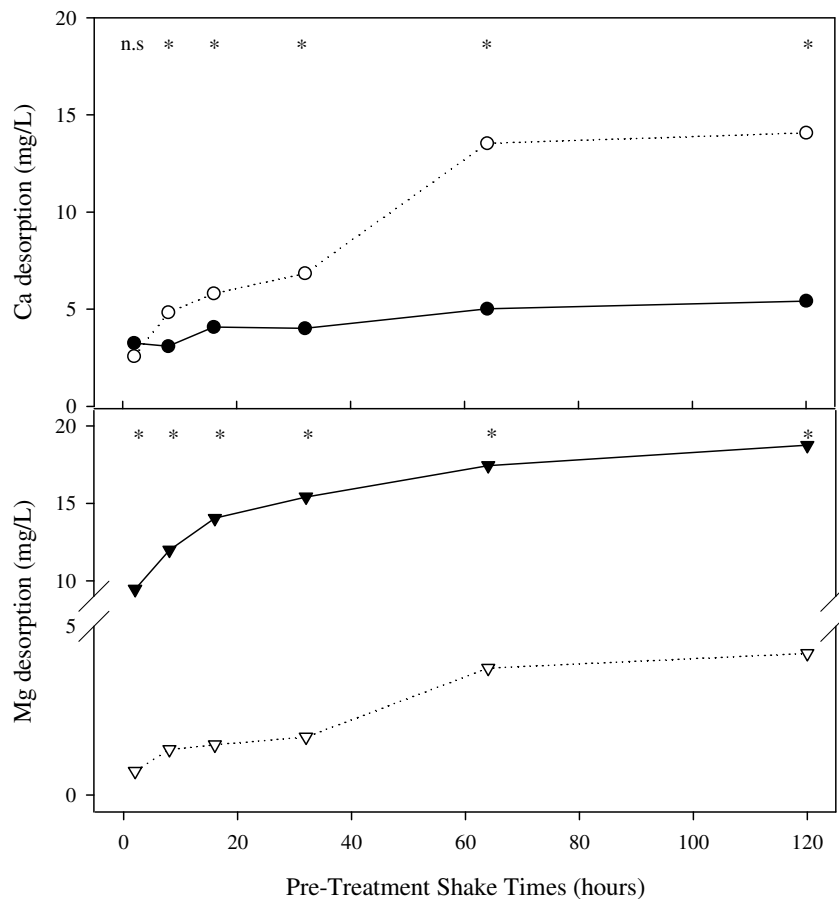
Figure 1. Amount of Calcium (○ and ●) and Magnesium (▽ and ▼) desorption for a cow manure biochar (solid lines) and green waste biochar (dashed lines) with different pre-treatment shake times (∗ indicate significant difference ($p<0.05$) between biochars, n.s. = not significant).

Analysis of BaCl$_2$/CsCl Saturations – Cations
The sorption of barium in the cow manure biochar was significantly greater for all pre-treatment shake times than in the green waste biochar. However, the sorption of barium in the cow manure biochar significantly decreased with the effect of pre-treatment shaking compared to no pre-treatment shaking, whereas the barium sorption in the green waste biochar significantly increased with pre-treatment shaking. There were similar trends for the cesium sorption in both biochars, with no significant difference between biochars at the 16 hour pre-treatment shake time.
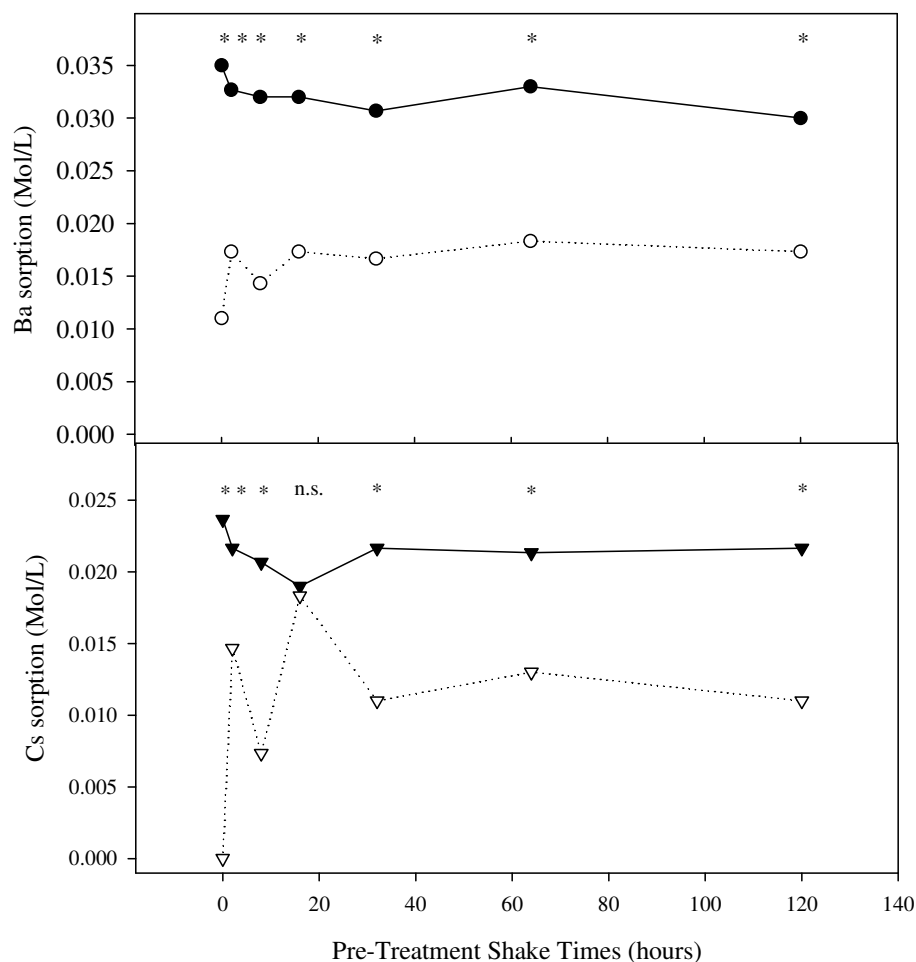
Figure 2. Amount of barium (○ and ●) and cesium (▽ and ▼) adsorption for a cow manure biochar (solid lines) and green waste biochar (dashed lines) with different pre-treatment shake times (∗ indicate significant difference (p<0.05) between biochars, n.s. = not significant).

Conclusion

The simple measure of compulsive exchange of ions may not be an appropriate method for the determination of the ion exchange capacity of biochar. The pre-treatment of biochars through shaking in water over differing times has manipulated the biochar particle-ion structure, thereby changing the potential for the biochar particle to adsorb ions.

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Biophysical controls over mineralization and sequestration of amended organic carbon in soil: Effects of intensity and frequency of drying and wetting cycles

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Abstract
Global climate change may enhance temporal and spatial variability of precipitation, which would likely increase frequency, intensity or both of wetting and drying (W/D) cycles in soils and then affect organic matter mineralization and SOC sequestration, but the direction of the change is still unclear. The objectives of this study were to assess the long-term effects of frequency and intensity W/D cycles on (1) soil water retention and pore size distribution, (2) main microbial agents and soil water repellency (3) organic matter mineralization rate and C sequestration. Soil physical properties such as porosity and pore size distribution, soil water content near saturation (-0.03 kPa) and soil microbial properties such as, soil water repellency, microbial biomass and its C:N are strongly affected by the number and intensity of W/D cycles. The bio- physical properties were correlated from each other and Soil mineralization rate of amended rice straw were also significantly correlated to the physical and biological properties. Such interaction resulted in the particulate fraction of organic carbon in soil being affected by the intensity of W/D cycles, suggesting that the increasing intensity of W/D cycles would enhance carbon sequestration through soil aggregation in a long run although it stimulates the Birch effect for a short time.

Key Words
Birch effect, W/D cycles, carbon sequestration, global climate change, soil biophysics

Introduction
Sequestration of soil organic carbon (SOC) has been considered as an important strategy to mitigate global climate (Lal, 2004). Many studies have been done on the rate and potential of SOC sequestration as affected by land use and soil management. However, the effect of global climate change on SOC sequestration is unclear. As model simulation predicted (IPCC, 2007), global climate change does not only cause the global warming, but also likely enhance the temporal and spatial variability of precipitation. The enhanced temporal and spatial variability of precipitation would likely increase frequency, intensity or both of wetting and drying (W/D) cycles in soils. Rewetting a dry soil causes a pulse of respiration (the "Birch effect"; Birch, 1958) and that the specific moisture status of soils is a key factor controlling organic matter decomposition (Orchard and Cook, 1983). Therefore, such increases in frequency and/ or intensity of W/D cycles in soils may affect organic matter mineralization and consequently SOC sequestration, but the direction of the change is still unclear (Borken and Matzner, 2009). Two mechanisms of the Birch effect should have dramatically different effects on SOC dynamics, particularly through multiple W/D cycles (Xiang et al., 2008). The microbial biomass mechanism suggests a reduction in SOC mineralization and an increase in SOC sequestration over time, while the substrate supply mechanism suggests an increase in the amount of SOC available to microbial attack and a decrease in SOC sequestration potential over time. Multiple W/D cycles can promote soil aggregation through both physical and microbial processes (Tisdall and Oades 1982), which has been considered as important mechanisms for physical sequestration of SOC (Six et al., 2002) because it can cause spatial inaccessibility of SOC for water and microbes (Lamparter et al. 2009). However, there are few supportive studies that demonstrate the feedback effects of soil aggregation on organic matter mineralization and the concomitant effects on SOC sequestration. We hypothesized that frequency and intensity of W/D cycles affect the microbiologically mediated soil aggregation, which in turn influences organic matter decomposition and physical protection of organic C through modification of soil pore size distribution. With extending incubation time to 120 days, the objectives of this study were to assess the long-term effects of frequency and intensity W/D cycles on (1) soil water retention and pore size distribution, (2) main microbial agents and soil water repellency (3) organic matter mineralization rate and C sequestration.

Methods

Soil sampling and core preparation

A soil derived from Quaternary red clay (Alumi-Orthic Acrisol or Udic Kandiusltult) was sampled, ground (<2 mm), air-dried and mixed with rice straw at a rate of 30 g straw/kg-soil. The mixture was filled into 100 cm^3 cylinders (46.4 mm in diameter and 59 mm high) to the field measured bulk density (1.2 Mg/m^3). The soil cores were covered at the lower end with nylon nets with 53 µm apertures for pre-incubation during which period the soil cores were placed sand box at a -0.03 kPa water potential for 7 d at 25°C to reduce priming effect and ensure the same initial conditions before the incubation experiment under wetting and drying cycles (W/D). W/D cycles were performed for a 1.5-*d* wetting at -0.03 kPa following with 1.5, 3.5 or 6.5- *d* drying, resulting in 40-W/D cycles in low drying intensity (S-LD), 24-W/D cycles in middle drying intensity (S-MD) and 15-W/D cycles in strong drying intensity (S-SD) treatments. Wetting was carried out from the bottom surface in airtight 1100 ml jars filled with 100 mm deep sand and with a -30 mm water table where soil respiration rate was measured. Drying was carried out in open air at 25 ^{o}C in the temperature controlled laboratory after the soil cores were moved out of the jars.

Incubation and experimental treatments

Three fixed soil cores before and after wetting on the sand table (-30 mm) were weighed and used to measure mineralization rate (SRR) at the sampling intervals. A set of nine soil cores were randomly sampled to ensure triplicates for each measurement at the same interval. The sampling was more frequent at the earlier stage than the later stage during the incubation period as changes in microbial activity and soil porous structure were expected to be stronger at the earlier stage. A set of three soil cores was used to measured soil microbial biomass (SMB) C and N, while another set of three soil cores was used first to measure soil water repellency (SWR) and then sampled to measure soil organic carbon (SOC), dissolved organic matter (DOC) and particulate organic carbon (POC). The remaining three soil cores were reserved in sealed, cool and dark condition till the end of the incubation to measure soil core volume and then soil water retention curve (SWRC) for calculation of pore size distribution.

Measurements

Soil cores after wetting at -0.03 kPa were weighed to calculate near saturation volumetric soil water content, θ_s as an indication of changes in soil pore characteristics. Soil core volume after drying was measured by determining changes in water volume after immersing the soil cores sealed with para film into pure water. The soil core volume measured was used to correct total soil porosity and porosities of different pore size classes. Soil pore size distributions are calculated from the water retention curves by applying Jurin's law The pore size classes were <1, 1-10, 10-30, 30-300 and > 300 µm corresponding to the soil water potentials of -300, -100, -60, -30, -10, -0.3 kPa for the soil water retention curve measurements.

To estimate soil respiration rate the evolved C-CO_2 trapped in 0.3 mol/L NaOH in the head space of the airtight jar was measured by titration with 0.1 M HCl following the addition of $BaCl_2$ (Bekku *et al*., 1997) during the 1.5 day rewetting period at the sampling times. The jars were vented every 12 hours by removing lids for about 2 minutes during the time when NaOH solution was replaced. Soil microbial biomass (SMB) C and N concentrations were measured using the chloroform fumigation-extraction method (Joergensen *et al*., 1995). SWR was then calculated following the approach of Hallett & Young (1999). Particulate fractionation of organic carbon was performed using a dense solution (1.8 Mg/m^3) following Sohi *et al*. (2001).

Results

Volumetric shrinkage of soil cores occurred along the metal ring wall within early 70 days of the incubation period and the magnitude of shrinkage followed the order S-SD> S-MD>S-LD. The median pore size fractions (10-30 µm) decreased with the increasing number of W/D cycles. The fractions of 30-300 and < 10 µm were conversely correlated with each other and to θ_s (Figure 1).

SRR during rewetting decreased over time during the incubation period (Figure 2) and the decay fitted well (R^2 > 0.94) to the first order exponential function. The estimated basal decomposition rate and decreasing amplitude was not influenced by drying intensity, but the decay constant was very significantly ($P < 0.01$) lower for S-LD than S-MD and S-SD, between which there was no significant difference. SMBC and SWR correspondingly changed with increasing number and intensity of W/D cycles (Figure 3). SWR and SMBC in all treatments were significantly correlated when the SMB-C measured at the first wetting was not included (R^2 =0.80, $P < 0.001$).
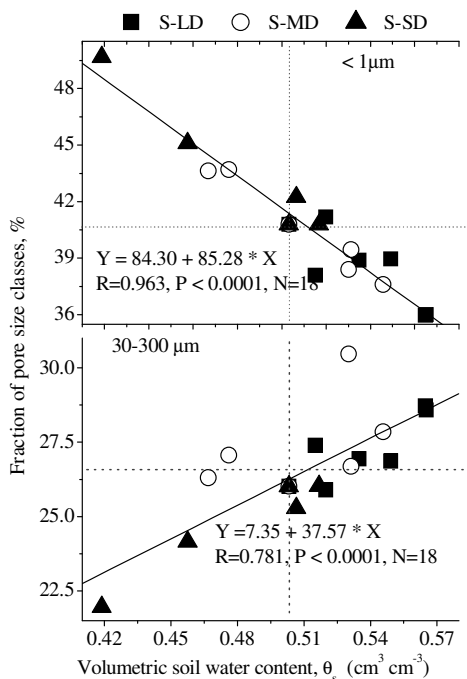
Figure 1. (Left). Percentage of different soil pore size classes (<1, 1-10, 30-300 and > 300 µm) in total porosity in relation to near saturated volumetric soil water content (-0.03 kPa), θs during incubation time and for the W/D treatments with low (S-LD, square), middle (S-MD, void circle) and strong (S-SD, triangle) drying intensity. The dot lines indicated the initial values θs and percentage of pore classes.
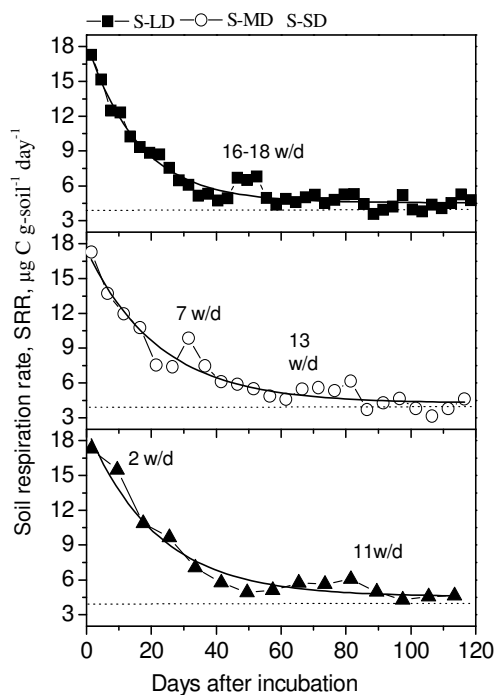
Figure 2. (Right). Soil respiration rate during the incubation period and the fitted line following first order exponential function in the W/D treatments with low (S-LD, upper, square), middle (S-MD, middle, void circle) and strong (S-SD, lower, triangle) drying intensity.

DOC content was constant during the incubation period. Both POC and SOC contents decreased over time and the dynamics were affected by drying intensity (Figure 4). The final POC content was greater in S-SD than in S-MD S-L. The final SOC content was greater in S-SD than in S-LD and S-MD.
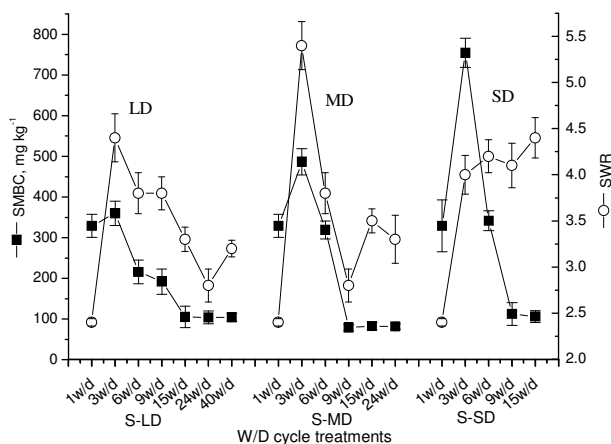
Figure 3. (left). Dynamics of soil microbial biomass carbon (SMBC) and soil water repellency (SWR) during the incubation period in the W/D cycle treatments with low (S-LD, left column), middle (S-MD, middle column) and strong (S-SD, right column) drying intensity.
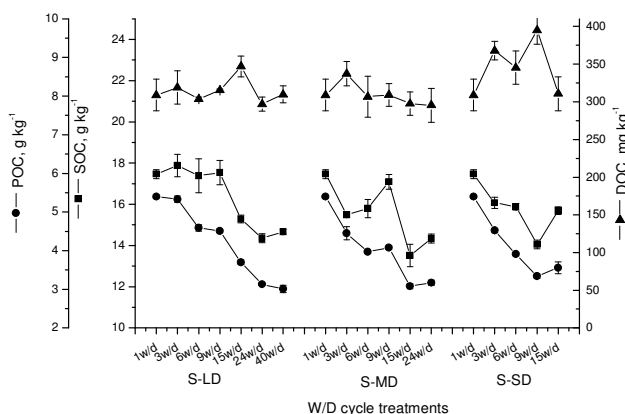
Figure 4. Dynamics of particulate organic carbon (POC), total soil organic carbon (SOC) and dissolved organic carbon (DOC) during the incubation period in the W/D cycle treatments with low (S-LD, left column), middle (S-MD, middle column) and strong (S-SD, right column) drying intensity.

SRR was significantly correlated to microbial biomass. SRR can be positively correlated to POC and negatively to SOC and DOC (SRR = 23.342-2.687 SOC-0.026 DOC+8.899POC, R2= 0.60. *P* = 0.003). In addition, SRR was also significantly affected by physical properties such as total porosity (R^2=0.86, P < 0.0001) and soil pore size distribution (Figure 5). In S-LD and S-MD, the decreases in SSR corresponded to the decreases in the

fraction of < 1 µm pore class and the increases in the fraction of 30-300 µm pore class before the maximum θ_s (9th W/D cycles), while after the maximum θ_s, the reductions corresponded to the increases in the fraction of < 1 µm porosity and the decrease in 30-300 µm pore class.
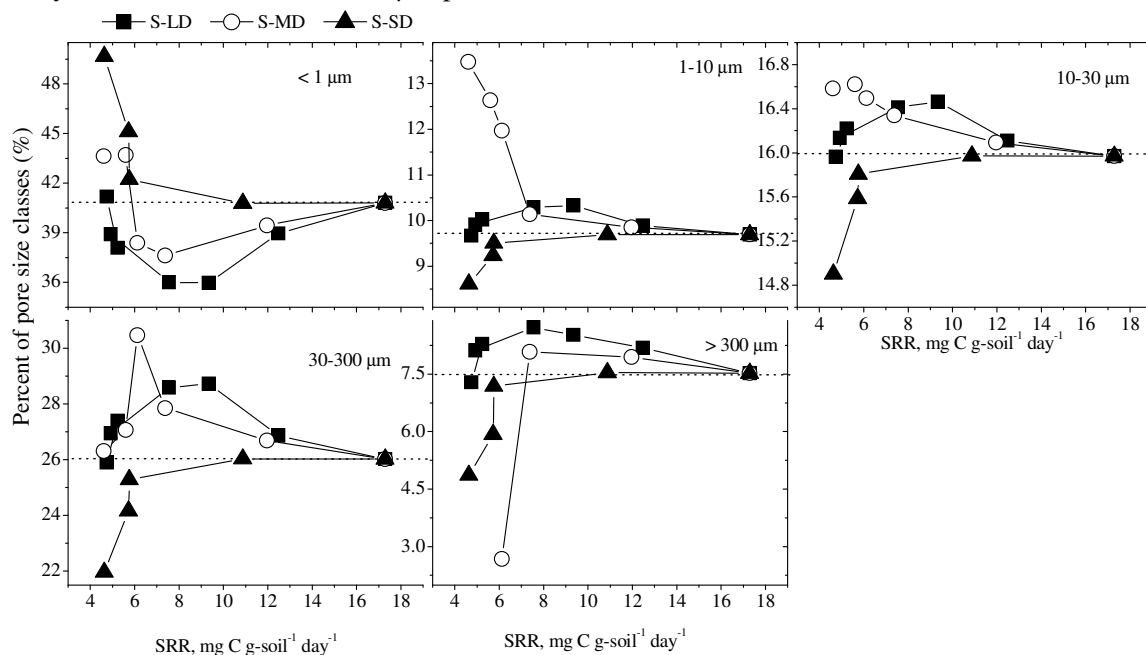
Figure 5. Fractions of the specified fractions of pore size class (<1, 1-10, 10-30, 30-300 and > 300 µm) in relation to soil decomposition rate (SRR) for the W/D treatments with low (S-LD, square), middle (S-MD, void circle) and strong (S-SD, triangle) drying intensity.

Conclusion

This study highlighted that the biophysical interaction during soil aggregation was affected by the number and intensity of W/D cycles. The increasing intensity of W/D enhanced the Birch effect at the early stage of incubation and physical protection of organic carbon after about two months due to increased micro-porosity (<1 µm). The results suggested that that the increasing intensity of W/D cycles would enhance carbon sequestration through soil aggregation in a long run although it stimulates the Birch effect for a short time.

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Can cell wall network explain crop residue decomposition and soil organic matter dynamic? A new insight into residue quality

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Abstract
This study aimed at determining the chemical characteristics of roots that regulate their C mineralization on the long term in soil. The chemical composition of maize roots from sixteen genotypes was characterized in details before soil decomposition. Roots were also incubated in soil for 796 days under laboratory conditions (15°C, -80 kPa). The chemical quality of maize roots differed markedly between genotypes notably in term of cell wall polysaccharides contents and quality, lignins contents and quality and esterified phenolic acids contents. Statistical relationships were established between the fate of C from roots and their initial chemical characteristics. The role of the intimate associations between the lignin fraction and cell wall polysaccharides in a cohesive network, and the role of esterified PCA as one of the main interconnecting agents between polymers in graminaceous cell walls, are of primary importance and could improve the prediction of residue decomposition in soils.

Key Words
Roots, decomposition, chemical quality, cell wall

Introduction
The intrinsic biochemical properties of crop residue, more commonly termed litter quality; strongly influence their decomposition in soil and the associated C and N fluxes (Swift *et al.* 1979). Quality of crop residue has long been approached through their initial C-to-N ratio which is now considered as a general index of quality mainly related to soil N dynamic (Vanlauwe *et al.* 1996; Heal *et al.* 1997). However, this ratio does not account for the availability of C and N, which is often essential to describe the decomposition kinetics (Recous *et al.* 1995). Crop residues have a complex composition with a soluble fraction and an insoluble fraction corresponding essentially to the cell walls. The cell wall composition and the quality of their constitutive polymers have a great effect on their decomposition in soil and on the associated C and N fluxes (Bertrand *et al.* 2006; 2009). The principal cell wall polymers are polysaccharides (such as cellulose and hemicelluloses) and lignin. In Gramineae, arabinoxylans represent the main type of hemicelluloses mainly substituted by arabinose and hydroxycinnamic acids, namely ferulic acid (FA) and p-coumaric acid (PCA), are the principal interconnecting agents between polymers (Kato and Nevis 1985). The chemical composition of cell wall polymers, as well as their interactions, influences the accessibility of these components to decomposers (Chesson 1988). Roots are one of the major sources of C contributing to soil organic matter build-up (Rasse *et al.* 2005), and the understanding of their kinetics of decomposition in soil needs to be improved. Indeed, few results were published concerning the effect of chemical quality on root decomposition in soil (Herman *et al.* 1977). Roots are particularly rich in cell walls and are more lignified than aerial plant parts (Machinet *et al.* 2009). Therefore the nature and the structure of these cell walls could significantly influence the kinetics of C mineralization in the medium and long terms. The aims of this work were (i) to better understand the role of cell wall chemical characteristics on root decomposition in soils and (ii) to improve the designing of parameters that could be used to describe residue quality in C models.

Methods
Soil and maize roots
Two sets of maize (Zea mays L.) brown-midrib isogenic lines, within the genetic background of inbreds F2 (F2, F2bm1, F2bm2, F2bm3 and F2bm4) and F292 (F292, F292bm1, F292bm2, F292bm3 and F292bm4), and a set of six maize hybrids (F7026bm3*F2bm3, Mexxal, Anjou 285, Anjou 258, Colombus and Manfusa) were cultivated in 2005 in experimental fields at the INRA Lusignan experimental station (49°26'N, 0°07'E, France) and were harvested at physiological maturity. Only the roots were kept for experiments and were cut to a diameter of 2 to 3 mm before incubation in an agricultural loamy soil.

Soil laboratory incubation
Soil samples and maize roots were mixed at a rate equivalent to 2 g C/kg dry soil and incubated for 796 days at 15°C. Inorganic N was added to the soil as KNO_3 to avoid N limitation during the decomposition process. Soil moisture was kept at a potential of -80 kPa throughout the incubation period by weighing at weekly intervals and readjusting with deionised water when necessary. A control incubation experiment was performed in the same way but without the addition of residues. Carbon mineralization was measured in the presence of a CO_2 trap (10 ml 1 M NaOH) at regular intervals up to day 796 after the beginning of incubation.

Chemical characteristics
Maize root residues before decomposition in soil were analysed for total C and N, soluble, neutral detergent fiber (NDF), acid detergent fiber (ADF) and acid detergent lignin (ADL) according to Goering and Van Soest (1970). Cell walls were extracted from maize roots by neutral detergent fiber (NDF) to remove cytoplasmic components (proteins, wax, pigments, tannin, etc…). Polysaccharides were analyzed according to Blakeney *et al.* (1983) on roots after NDF extraction (cell walls). The released monosaccharides were separated and quantified by high performance anion-exchange chromatography (HPAEC). Klason lignin was determined as the insoluble residue remaining after a two step sulphuric acid hydrolysis of the cell wall polysaccharides (Monties 1984). Lignin monomer composition was determined by thioacidolysis. This reaction enables the specific disruption of labile-ether inter-monomer linkages, which represent the non-condensed lignin fraction (Lapierre *et al.* 1986). Monomer products were analyzed as trimethylsilyl derivatives of guaiacyl (G) and syringyl (S) by capillary column gas chromatography. Ester-linked hydroxycinnamic acids (ferulic acid (FA) and p-coumaric acid (PCA)) were released by alkaline extraction and detected using a Waters photodiode array UV detector.

Results
The mineralization of maize roots varied markedly amongst genotypes and, as expected, was higher than that of control soil (Figure 1). At the end of the incubation (796 days), the total amounts of mineralized C were significantly smaller in F2bm1 (41.6 ± 2.2% of added C) than in Manfusa (70.1 ± 1.9% of added C) (P≤0.05). The observed differences in cumulative mineralized C over the entire incubation period resulted mainly from differences in the rates of C mineralization during the first 40 days. Total N contents of roots varied from 0.5 to 1.3% of dry matter. These contents lead to C to N ratio from 37 (F2bm1) to 97 (Manfusa). The NDS soluble fraction accounted for < 22% of dry matter; therefore cell wall contents were high. Glucose content of roots ranged from 30.7% to 41.1% while the arabinose to xylose ratio slightly varied between genotypes, indicating a similar level of xylan substitution by arabinose. The amount of Klason lignin (KL) varied from 15.2% to 19.4% DM and the S unit ranged from 25.1 to 90.5 µmol/g of cell wall, while the amounts of G unit varied from 21.2 to 54.2 µmol/g of cell wall (Table 1). Furthermore, the relative proportion of S unit was smaller than that of G unit in all bm3 mutants, leading to S to G ratios <1 which were only found in these genotypes. Ester-linked PCA were more abundant than ester-linked FA and ranged from 1.6% to 3.6% of cell wall (data not shown).

Simple correlation was performed to further establish the relationships between the cumulative amounts of mineralized C at different steps of decomposition and the initial chemical characteristics of maize roots. On the short term, the amounts of $C-CO_2$ were positively correlated with the soluble fraction over the first 10 days, and particularly highly correlated with the soluble C at day 3 (P≤0.001). Thus, the amounts of $C-CO_2$ were slightly but significantly negatively correlated with arabinose between days 3 and 7, the A/X ratio between days 7 and 14 and the KL/Soluble ratio between days 3 and 14 (P≤0.05). They were also negatively correlated with galactose during the whole incubation period. On the medium to long term, there was a negative relationship between the C mineralized and the Van Soest lignin/Soluble ratio from day 10 until day 796, and as expected the effect of lignin fractions on C mineralized became important. The amounts of mineralized C were strongly negatively correlated with the lignin fraction.

A multiple-regression analysis was attempted to explain more comprehensively the variations of the C mineralization kinetics observed among the 16 genotypes of maize roots. When using all chemical characteristics as explanatory variables, the best-fitting regression equation included the Van Soest lignin (LVS)/ Van Soest Cellulose (CVS) ratio, ester PCA and Van Soest Hemicellulose (HVS) according to the following equation (p<0.001, residual standard error RSE = 52.4, Figure 2).This three-variates-based equation accounted for 93% of the observed cumulative amounts of $C-CO_2$ (Figure 2).
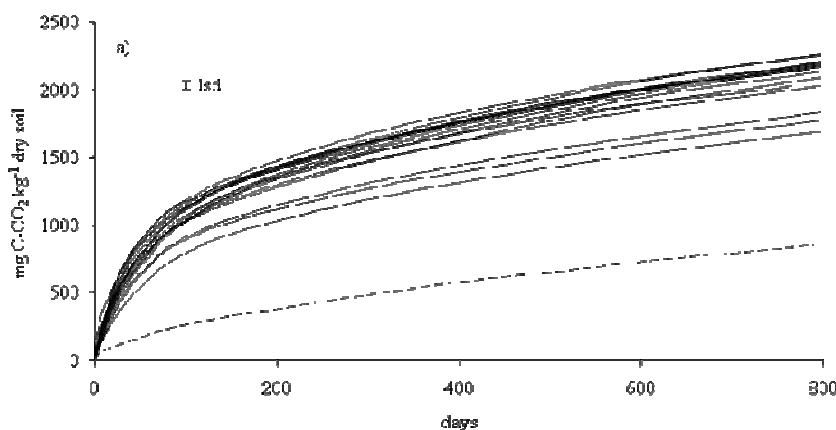
Figure 1. Cumulative amounts of carbon mineralized in control soil (without maize roots, dotted lines) and after addition of maize root (full lines). Data are means of 4 incubation replicates.

$$y = x + 0.04$$
$$R^2 = 0.93, p < 0.001$$

$$Y = 2001 - 2981 * LVS/CVS + 95.1 * ester PCA - 15.06 * HVS$$
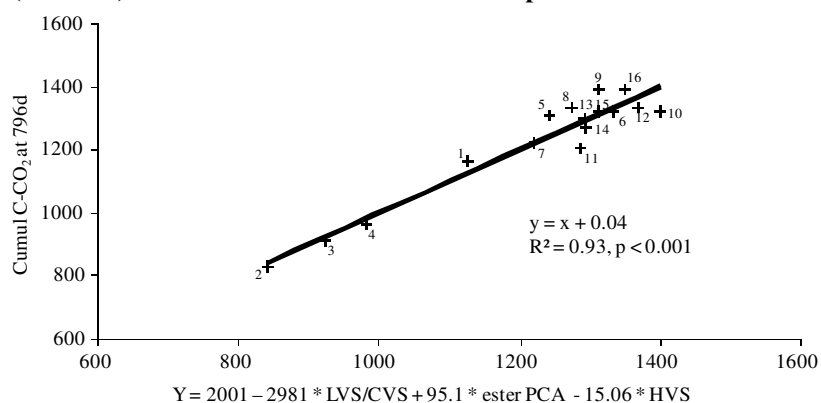
Figure 2. Relationships between the cumulative amounts of C mineralized after 796 days and equations of the multiple-regression model. Genotypes were identified by numbers 1 to 16.

Conclusion

The 16 maize root genotypes used presented significant variations in terms of chemical characteristics that translated into large differences in kinetics and cumulative C mineralization during their decomposition. This material was therefore very suitable for investigating relationships between quality and decomposition. The detailed analysis of chemical composition, by different methodes evidenced the role of soluble C on the short term, lignin fraction of the longer term, but also the importance of the intimate associations between the lignin fraction and cell wall polysaccharides in a cohesive network. The role of esterified PCA as one of the main interconnecting agents between polymers in graminaceous cell walls was shown by regression analysis, allowing to improve systematically the prediction of residue decomposition in soils despite its negligible quantitative importance in root tissues.

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Can organic amendments be used to improve the properties of bauxite processing residue sand?

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Abstract
The effects of adding of a range of organic amendments (biosolids, spent mushroom compost, green waste compost and green waste-derived biochar), at two rates, on some key chemical, physical and microbial properties of bauxite processing sand were studied in a laboratory incubation study. Addition of all amendments tended to decrease bulk density and macroporosity but increase total porosity, available water holding capacity and water retention at field capacity (-10 kPa). Addition of biosolids, mushroom compost and green waste compost all increased soluble organic C, microbial biomass C and basal respiration. The germination index of watercress grown in the materials was greatly reduced by biosolids application and this was attributed to the combined effects of a high EC and large concentrations of extractable P and NO_3^--N. We concluded that the increases in both water retention and microbial activity induced by additions of the composts is likely to improve the properties of residue sand as a growth medium during revegetation.

Key Words
Residue sand, biosolids, biochar, compost

Introduction
Alumina is extracted from bauxite by the Bayer Process and the material remaining (bauxite-processing residue) is disposed-of in large residue drying areas (RDAs) in a semi-dry state. The coarse-textured material (residue sand) is separated from the bulk of the fine-textured material (residue mud) prior to disposal. At Alcoa, the outer embankment of the RDAs are constructed with residue sand and these are subsequently revegetated with native plant species. In the development of effective closure strategies, minimising drainage from RDAs is critical. At present, drainage from RDAs can be recycled to the refinery but following closure, the drainage will need to be treated prior to release to the environment. The coarse-textured nature of residue sand exhibits little water holding capacity and allows rapid movement of infiltrating water to depth. Effective revegetation is important in this regard since transport of water from residue sand back to the atmosphere via transpiration greatly reduces downward percolation of water. It is therefore important to amend the sand in such a way that water holding capacity is increased, nutrient retention is favoured and sustainable plant growth is promoted.

Limitations to plant growth in residue sand include its highly alkaline (primarily due to NaOH and Na_2CO_3), saline-sodic nature, low water and nutrient retention and supplying capacities, its high leaching potential and negligible soil microbial activity (Jones and Haynes 2009). At present, the sand is amended with phosphogypsum (to help neutralise its saline-sodic nature) and inorganic fertilizers (N, P, K, Ca, Mg, B, Cu, Zn, and Mn) are applied prior to establishing a vegetation cover. Although these materials improve the chemical characteristics for plant growth, residue sand still exhibits low water and nutrient holding capacity and little biotic activity. We believe that adding other amendments such as organic matter would also be desirable since they could increase water holding capacity and nutrient supplying capacity and provide a medium where there is less drainage and better plant growth. In addition, organic matter amendment would stimulate soil biotic activity and the development of a self-sustaining below-ground ecosystem and this, in turn, is likely to increase the success of revegetation efforts, particularly in the long-term (Ussiri and Lal 2005).

The purpose of this study was to investigate the effect that addition of a range of organic matter amendments (biosolids, spent mushroom compost, commercially-produced green waste compost and biochar) to phosphogypsum-amended residue sand would have on key soil chemical, physical and microbial properties of residue sand.

Materials and methods
Materials and experimental design
Freshly deposited residue sand was collected from the residue storage area of the Alcoa Kwinana bauxite refinery, transported to the laboratory and air dried. Sieve analysis showed the material had a particle size

distribution of 1-2 mm = 12%, 0.5-1mm = 23%, 0.25-0.50mm = 42%, 0.10-0.25mm = 14% and <0.10mm = 9%. Phosphogypsum, obtained from Alcoa, was ground (<1mm) and thoroughly mixed with the residue sand at a rate of 2% v/v. The sand was rewetted to 70% of water holding capacity and incubated for 6 weeks. At the end of that period the sample was leached with 4 pore volumes of water to remove accumulated soluble salts. Biosolids were collected from the Oxley Creek Wastewater Treatment Plant (Brisbane) and spent mushroom compost was collected from a commercial garden centre. The green waste compost was produced commercially from shredded municipal green waste, shredded pine bark and poultry manure (3:2:1 v/v/v) and was sourced from Phoenix Power Recyclers, Yatala, Queensland. The biochar was supplied by BEST Energies, Australia and was produced by low temperature pyrolysis of municipal green waste. Organic materials were ground/sieved (< 2mm) prior to use. The four organic materials were added to the residue sand (3 replicates per treatment) at 40 and 80 g/L. On a volume basis, this is equivalent to 40 and 80 Mg/ha assuming a depth of 10 cm. Amendments were thoroughly mixed with residue sand samples (1L), placed in 2L plastic containers and rewetted to 70% of water holding capacity. The pots were arranged in a randomized block design and incubated at room temperature (24-30ºC) for 6 weeks. Containers were opened and mixed each week to ensure adequate aeration. At the end of the incubation, samples were split into two subsamples; one was stored at 4ºC for microbial and physical analysis and the other was air-dried and stored for chemical analysis.

Analyses
Organic C was measured by automated dry combustion using a Carlo Erba C, H, N analyser. Soluble C was measured in K_2SO_4 extracts using a Shimadzu 5000A soluble C/N analyser. Available P was extracted with 0.5 M $NaHCO_3$ (pH 8.5) (1:100 w/v for 16 h) (Colwell 1963) and measured colorimetrically. Extractable mineral N was extracted with 2 M KCl (1:100 ratio for 1 h) followed by colorimetric analysis of NH_4^+ and NO_3^--N. Microbial biomass C was estimated based on the difference between organic C extracted with 0.5 M K_2SO_4 from chloroform-fumigated and unfumigated soil samples using a K_C factor of 0.38. Basal respiration was determined by placing 30 g oven dry equivalent of moist soil in a 50-ml beaker and incubating the sample in the dark for 10 days at 25ºC in a 2-l air-tight jar along with 10 ml 1M NaOH. The CO_2 evolved was determined by titration. Bulk density was determined on naturally compacted samples, particle density by the pycnometer method and total porosity by the difference. Soil water content in samples was determined at -10 and -1500 kPa using a pressure plate apparatus. Pore size distribution was calculated as macropores (> 29 µm diameter; air-filled porosity at -10 kPa), mesopores (0.2-29 µm diameter; drained between -10 and -1500 kPa) and micropores (< 0.2 µm diameter; water filled pores at -1500 kPa).

Table 1. Some chemical and microbial properties of bauxite residue sand amended with organic materials at 40 or 80 Mg/ha.

Treatment[1]	Extractable P (mg/kg)	NH_4^+-N (mg/kg)	NO_3^--N (mg/kg)	Organic C (gC/kg)	Soluble organic C (gC/kg)	Microbial biomass C (mgC/kg)	Germination index (GI)
Control	11.8[a]	5.4[a]	1.0[a]	0.27[a]	nd	nd	83.4[b]
Biosolids (40)	460.6[b]	25.4[d]	296.6[b]	10.0[b]	126.8[b]	8.4[a]	47.6[a]
Biosolids (80)	966.1[c]	21.1[cd]	557[c]	16.9[c]	412.4[c]	20.4[c]	53.7[a]
Mushr. Comp. (40)[2]	50.2[a]	11.4[abc]	1.0[a]	9.0[b]	53.9[a]	16.0[b]	83.1[b]
Mushr. Comp. (80)	41.4[a]	17.9[bcd]	0.8[a]	14.6[bc]	145.1[b]	24.9[d]	86.6[b]
Greenw. Comp. (40)	27.3[a]	9.9[abc]	6.2[a]	10.8[b]	63.2[a]	11.5[a]	95.0[b]
Greenw. Comp. (80)	45.5[a]	13.3[abc]	12.4[a]	16.7[c]	95.5[b]	25.5[d]	73.2[b]
Biochar (40)	11.8[a]	11.8[abc]	1.3[a]	18.3[c]	nd	nd	78.7[b]
Biochar (80)	11.7[a]	7.6[ab]	1.8[a]	35.5[d]	nd	nd	83.6[b]

[1]Means followed by the same letter in a column are not significantly different at P≤0.05
[2]Mushr. Comp. = mushroom compost, Greenw. Comp. = Greenwaste compost

A germination test was carried out (in quadruplet) on filter paper in petri dishes. Two ml of aqueous extract (1/10 w/v) from each of the treatments was added to dishes. Ten seeds of watercress (Lepidium sativum) were placed on the filter paper and dishes placed in the dark at 28ºC. The germination index percentage with respect to control (distilled water) was determined after 5 days. The control GI value was considered as 100%. The statistical significance of experimental treatments was determined by Analysis of Variance Analysis using the Minitab Statistical Software Package and differences were calculated at the 5% level using Tukey's test.

Results and discussion
Very little research has addressed revegetation of residue sand although a large body of research has been concerned with revegetation of residue mud (Fuller *et al*. 1982; Wong and Ho 1993; Xenidis *et al*. 2005; Courtney *et al*. 2008). Although residue sand has similar chemical properties to residue mud, it has a lower

buffering capacity and a much greater particle size (Jones and Haynes 2009). The initial treatment of the residue sand with phosphogypsum was successful in reducing ESP from about 75% down to 15-20% and pH from 11.1 down to 8.1 (data not shown).

A more-than adequate supply of N and P following land application of biosolids is common (Pierzynski 1994) and in this study extractable P, NH_4^+-N and NO_3^--N were greatly elevated in the biosolids treatments (Table 1). The EC in saturation paste extracts was also elevated being > 1 mS m^{-1} in biosolids treatments and < 0.6 mS m^{-1} in the others (data not shown). The high soluble salts, extractable P and mineral N produced conditions inhibitory to germination and early seedling growth and as a result, germination index was 45-55% in biosolids treatments and >80% in the others (Table 1). The concentrations of extractable P in the biosolids treatments are likely to be inhibitory to growth of many Australian native plants (which are being used for revegetation) since Handreck and Black (2002) suggested optimum P levels were < 10mg kg^{-1} for species sensitive to P and < 40mg kg^{-1} for moderately sensitive species. Additions of both spent mushroom compost and green waste compost increased extractable P and NH_4^+-N levels (Table 1) demonstrating their important effect of improving soil fertility. Green waste biochar had no significant effect on extractable P or mineral N levels. This may be partially due to the source of biochar since Chan *et al*. (2008) showed that biochar produced from animal manure has a much higher nutrient content and greater effect on soil fertility than that produced from plant residues.

For brevity, results for physical properties of treatments are shown only for the 80 Mg ha^{-1} application rate (Table 2). Addition of organic amendments caused a reduction in bulk density and tended to increase total porosity (Table 2). This is characteristic of their effect when added to soils (Khaleel *et al*. 1981; Haynes and Naidu 1998). Their addition also caused a decrease in the percentage of total porosity occupied by macropores with concomitant increases in mesoporosity and microporosity. This is attributable to a greater percentage of small pores in the organic materials, compared to the coarse-textured sand, and/or organic material partially filling large voids previously present between these sand particles. This change in pore size distribution resulted in an increase in plant-available water and in water content at field capacity (i.e. -10 kPa) for all amended treatments. This is of particular practical importance since an increased water storage capacity will provide revegetating plants with a larger supply of water as well as reducing water fluxes down the profile.

As expected, the addition of biosolids, mushroom and greenwaste composts to the residue sand increased organic C, soluble C, microbial biomass C (Table 1) and basal respiration (data not shown). That is, their addition increased substrate C (i.e. soluble C) availability and as a result there was an increase in the size and activity of the microbial community present. Indeed, soluble C and microbial biomass C were below levels of detection in the control treatment. The increases in microbial activity are important in promoting a functioning below-ground ecosystem, the cycling of nutrients through organic pools and improving the fertility of residue sand. Charcoal C is essentially a biologically inert substance and as a result, soluble C and microbial biomass C were below the level of detection in the biochar treatments and basal respiration was very low.

Table 2. Physical properties of bauxite residue sand amended with organic materials (at 80 Mg/ha).

Treatment[1]	Bulk Density (Mg m^{-3})	Total Porosity (m^{-3} m^{-3})	Pore size distribution (%) Macropores (>29μm)	Mesopores (0.2-29μm)	Micropores (<0.2μm)	Available water (kg m^{-3})	Field Capacity (kg m^{-3})
Control	1.65[a]	0.46[a]	76[a]	11[a]	13[a]	51[a]	109[a]
Biosolids (80)	1.54[b]	0.48[ab]	63[c]	14[b]	22[c]	68[b]	177[b]
Mushr. Comp. (80)[2]	1.42[c]	0.54[c]	65[c]	19[c]	16[ab]	102[d]	190[c]
Greenw. Comp. (80)	1.46[c]	0.52[bc]	66[bc]	16[bc]	17[b]	85[c]	174[b]
Biochar (80)	1.44[c]	0.51[abc]	61[c]	25[d]	15[ab]	126[e]	199[c]

[1]Means followed by the same letter in a column are not significantly different at P≤0.05
[2]Mushr. Comp. = mushroom compost, Greenw. Comp. = Greenwaste compost

Conclusions

For revegetation of bauxite residue sand, waste organic materials such as biosolids, mushroom and green waste composts are potentially important amendments. Their addition not only improves physical conditions (particularly water storage capacity) of the medium but also increases fertility and stimulates microbial activity. There seems scope to mix, or co-compost, biosolids with some other material (e.g. green wate) in order to reduce its negative effects on soil chemical properties (e.g. excessive accumulation of salts, P and mineral N) to produce an amendment that would be more conductive to plant growth.

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Changes of nitrogen forms in a calcareous soil exposed to elevated CO_2 with two atmospheric temperature levels

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Abstract
Elevated carbon dioxide and other green house gases have increased the earth temperature in recent decades, thus may be affecting biochemistry cycles in soils. An experiment was conducted in a completely randomized design with factorial arrangement in the laboratory conditions. Soil was treated with one percentage of cow manure compost and 200 kg /ha of Urea. Soil samples were exposed to two levels temperatures (25 and 35) and two carbon dioxide concentrations (350 and 700 ppm) for a 60 day period of incubation with three replications. The results showed that elevated carbon dioxide at 25 and 35 ^{o}C had a different effect on total dissolved nitrogen. Elevated carbon dioxide at 25 ^{o}C had no significant effect on total dissolved nitrogen (TDN) while at 35 ^{o}C TDN was increased. Temperature and CO_2 had more effect on NO_3+NO_2 components of dissolved inorganic nitrogen than on NH_4. It seems that denitrification was higher in elevated CO_2 and high temperature treatments. Maximum and minimum rates of dissolved organic nitrogen (DON) occurred at 35 ^{o}C under elevated CO_2 faster than other treatments. This study revealed that elevated CO_2 and temperature enhanced nitrogen mineralization.

Key Words
Total dissolved nitrogen (TDN), total organic nitrogen (TON), nitrate, nitrite

Introduction
Fossil fuel combustion leading to elevated carbon dioxide and other green house gases may significantly increase earth temperature (Houghton *et al.* 1995). This may affect organic matter decomposition and mineralization of nutrients in soils. Phillips *et al.* (2002) showed an increase in organic matter degradation due to elevated atmospheric carbon dioxide. However in a three year experiment on a calcareous grassland soil Hungate *et al.* (1996) reported that carbon transformations in microbial biomass and organic carbon and nitrogen decomposition were not affected by increases in atmospheric CO_2. The authors further reported that soil nitrogen decomposition may vary due to increases in CO_2 among various ecosystems and even within a single ecosystem. Billings *et al.* (2002) investigated processes of the nitrogen cycle in desert soils exposed to elevated CO_2. They concluded that NH_4 volatilization is an important contributor to dissipated nitrogen gases in arid regions and low soil temperature limits microbial activity. The effect of elevated CO_2 on soil microbial activity was not similar in different seasons. It seems that temperature may be an important factor with respect to the CO_2 effect on nitrogen cycle in soil. The purpose of this work was to study the effect of temperature and CO_2 concentration on soluble forms of nitrogen in a calcareous soil in the north eastern of Iran.

Material and methods
An experiment was conducted in a completely randomized design with a factorial arrangement with two levels (25 and 35) temperatures and two carbon dioxide concentrations (350 and 700 ppm) during a 60 day period of incubation with three replications in the laboratory condition. Soil was initially treated with one percent of cattle manure compost and 200 kg/ha of urea. The pots contain 200 g of treated soil was transfer in CO_2 and temperature controlled chambers. In 0, 5, 10, 15, 30 and 60 days amounts of TDN, DIN, DON, sum of nitrate and nitrite and ammonium were measured in a 1:2.5 soil\water extract after 4 hour shaking time (Keeney and Nelson 1982; Cabrera and Beare 1993). Results were analyzed using MSTATC software and mean of treatment was compared using the Duncan test.

Results and discussion
The results showed that the highest and the lowest amount of total dissolved nitrogen (TDN) were for 35 ^{o}C at 350 and 750 ppm CO_2 concentrations. With increasing temperature, TDN decreased significantly at 350 ppm CO_2 concentration while temperature had different effect on TDN at 750 ppm CO2 concentration (Figure 1). It seems that nitrogen availability decreased when temperature increased from 25 ^{o}C to 35 ^{o}C at the low CO_2 concentration (350 ppm) due to increasing microbial activity.
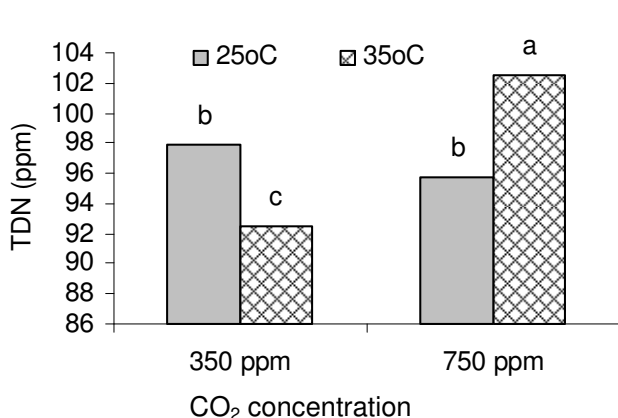
Figure 1. Effect of temperature and CO_2 concentration on total dissolved nitrogen (TDN).
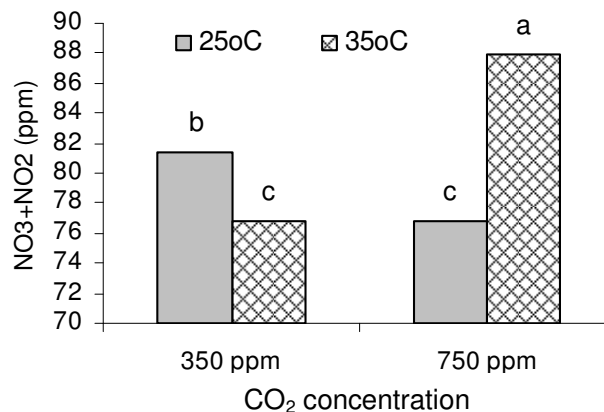
Figure 2. Effect of temperature and CO_2 concentration on $NO_3 + NO_2$ concentration.

It is also possible to assume that the higher temperature and 750 ppm CO_2 concentration increased the activity of some microorganisms responsible for nitrogen mineralization.

Since DIN is a major part of TND any changes in TDN concentration seem to be related in DIN. For this reason the effect of temperature and CO_2 concentration on DIN components (NH_4, $NO_3 + NO_2$) was quite similar to the TDN pattern. Changes in $NO_3 + NO_2$ concentrations also were similar to TDN and DIN at different temperatures and CO_2 concentrations (Figure 2) because ammonium concentration constituted only about 5 percent of DIN. In addition temperature and CO_2 concentration did not have a pronounced effect on ammonium concentration. Therefore, the most changes observed in DIN or TDN seems to be due to changes in $NO_3 + NO_2$ concentrations. Carnol *et al.* (2002) showed that nitrate production increased under an elevated CO_2 condition. They hypothesized that physiological adaptation or selection of nitrificatores could occur under elevated CO_2. The effect of temperature and CO_2 on $NO_3 + NO_2$ concentration during sixty days of incubation is shown in Figure 3. The results revealed that $NO_3 + NO_2$ concentration increased with incubation time in all treatments. Ammonium concentration showed a different pattern and its concentration decreased dramatically during incubation. Cabrera and Beare (1993) reported that nitrogen mineralization increased under higher CO_2 concentrations in a paddy soil. However some studies reported a negative effect of CO_2 on nitrogen availability (Cotrufo *et al.* 1994).
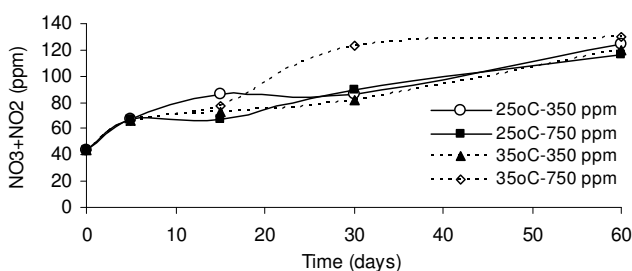
Figure 3. Effect of temperature and CO_2 on $NO_3 + NO_2$ concentration during two months of incubation.
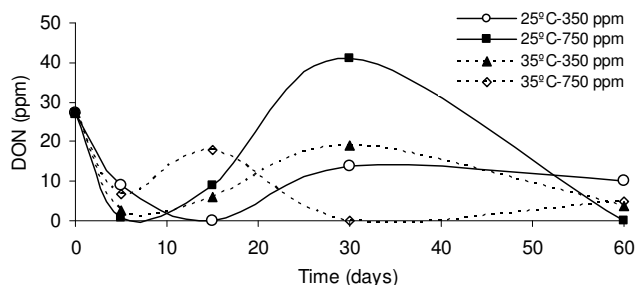
Figure 4. Effect of temperature and CO_2 on DON concentration during two months of incubation.

Our investigation showed that the maximum and minimum dissolved organic nitrogen occurred faster than for other nitrogen forms at $35^{\circ}C$ under elevated CO_2 (Figure 4). It may be concluded that elevated carbon dioxide with increasing temperature enhanced the rate of nitrogen biochemical reactions in soil.

Conclusion
The results revealed that the effect of elevated CO_2 on different forms of nitrogen was different at 25 and $35^{\circ}C$. Elevated CO_2 had a non significant effect on TDN concentration at 25 $^{\circ}C$ while TDN was increased at $35^{\circ}C$. TDN components were also affected by temperature and CO_2 concentrations. Changes in DIN were due to the changes in $NO_3 + NO_2$ concentration. In general, the results of this experiment demonstrated that temperature and elevated CO_2 may increase the nitrogen mineralization. However, in order to acquire a better perspective more research is needed.

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Characterization of almond orchards to assess soil fertility and organic matter dynamics to improve soil conditions by using organic amendments

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Abstract
The characterisation of soils in almond orchards from SE Spain has been carried out to assess fertility and organic matter content to improve soil properties by posterior use of organic amendments. The experimental area was divided into 14 plots. Samples of surface and subsurface were taken to analyse soil pH and electrical conductivity (EC), soil organic carbon (SOC), total nitrogen (N_t), calcium carbonate, bioavailable metals and available nutrients. The results highlight the low content of organic matter in the studied plots. The content in calcium carbonates and the alkaline pH make the nutrients partially unavailable for the crop. The application of organic amendments is one of the best solutions to improve soil quality and fertility. This procedure is not only a way of fertilization but a way of reusing a pig farm residue that is difficult to manage, pig slurry, thus fulfilling international guidelines of sustainable development.

Key Words
Soil properties, nutrients, organic fertilization, soil organic carbon

Introduction
In the Mediterranean Basin of Spain, almond trees have been cultivated for centuries (Zornoza *et al.,* 2009), Murcia (SE Spain) is one of the principal regions in almond production, as almond orchards require warm climate. This crop tolerates the lack of water and requires alkaline or neutral soils. To reach a good production of almond, keeping soil fertility, is needed so that nutrients are available for the plant. Inorganic fertilization has been carried out for years, although fertilization using organic amendments such us pig slurry and manure has also been introduced, which adds to the soil important contents of organic matter and nitrogen. This is important for the correct fertilization of soils and also improves its condition and structure. In fact, nutrient release increased more with organic amendment than with inorganic fertilizers (Goyal, 1998; Daudén *et al*., 2004). In this sense, in order to determine the proper dose of organic fertilizers to apply to the soil, and the nutritional necessities of the crop, it is necessary to characterize orchards soil. The results obtained are essential to fulfil the soil requirements for improved almond production.

Materials and methods
The study site is located in the village of La Aljorra, belonging to the municipality of Cartagena in the Murcia Region (SE Spain). The experimental area is an almond orchard of 8064 m². The climate of the area is semiarid Mediterranean with mean annual temperature of 18ºC and mean annual rainfall of 275 mm. A total of 14 plots (12 m x 30 m) were designed in the field so that sampling was representative of the surface area of the orchards. Plots are named alphabetically from A to N. The aim of this division in plots was to compare in the future the use of different organics amendments in order to determine the optimum dose for the necessities of soils and crops. The soil is a Typic Haplocalcid with clay loam to loam texture.

Soil sampling was made in September 2008. Three samples were taken per plot at two depths (0-15 cm, 15-30 cm depth). Soil pH and electrical conductivity (EC) were measured in deionised water (1:1 and 1:5 w/v, respectively). Soil organic carbon (SOC) and total nitrogen (N_t) were determined according to Duchaufour (1970). Calcium carbonate was assessed by the Bernard calcimeter (Porta, 1986). Bioavailable metals and available nutrients were extracted with DTPA and ammonium acetate, respectively, and measured using an atomic absorption spectrophotometer (AAnalyst 800, Perkin Elmer).

Results and discussion
As we can see on Figure 1, values of SOC ranged from 0.55 % to 1.80%, similar to the results obtained by Zornoza *et al*. (2009) in almond orchards in the province of Alicante, SE Spain, with similar soils and climatic conditions.
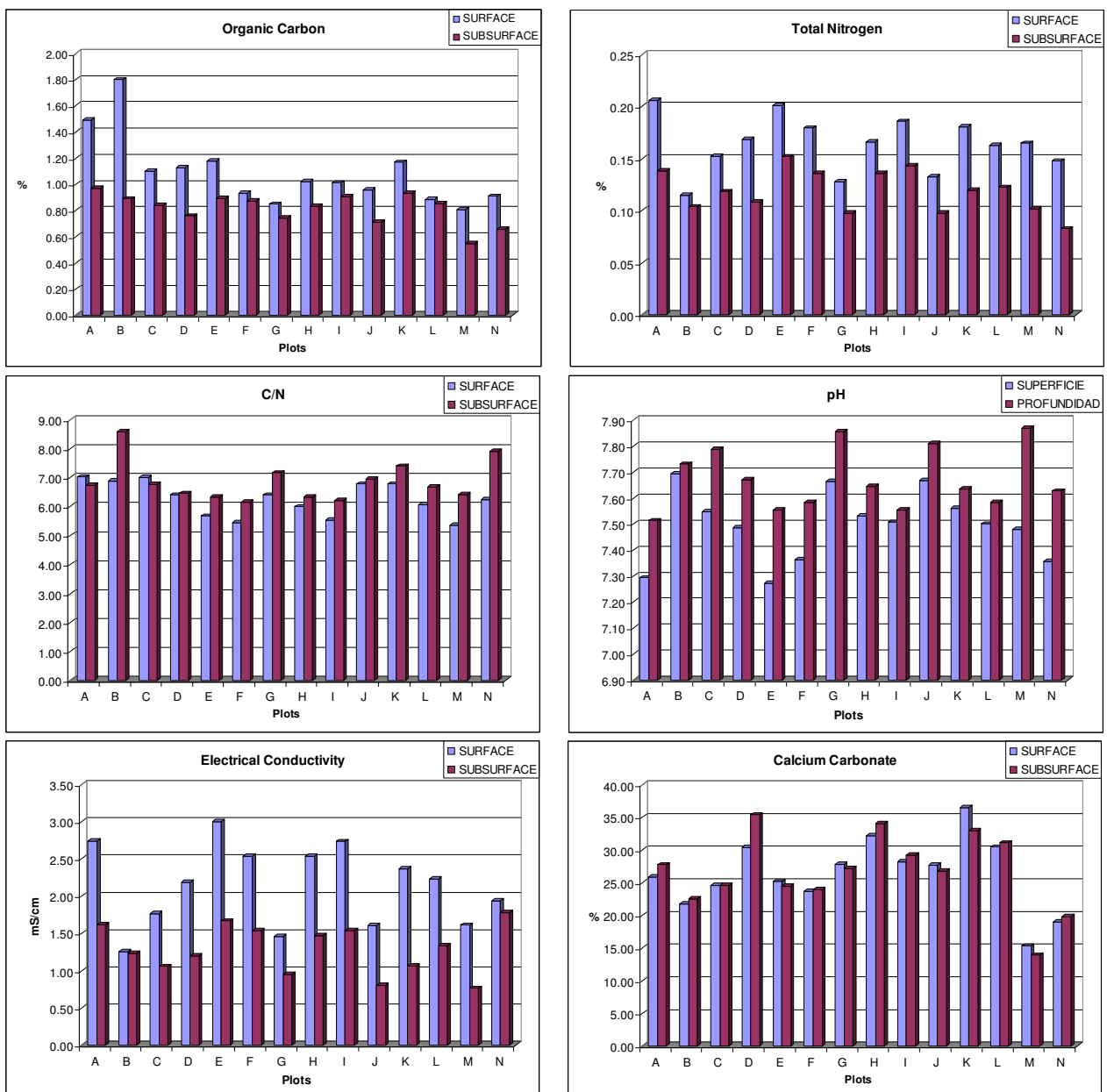
Figure 1. Physico-chemical characteristics of the different plots studied. Values are the mean (n=3).

Thus, we can consider that the soil organic matter content in the studied orchard is low. With regards to N_t, results show that percentages were quite high, considering these soils as medium for total nitrogen (Urbano, 1995). Therefore, we obtain C/N ratio quite low, what means that soil tends to the mineralization of organic matter and has a low to medium fertility, besides the organic rate could be increased by adding great amounts of organic matter to the soil (Cobertera 1993).

Values of pH and electrical conductivity indicate that we have moderately alkaline and slightly saline soils. This can be due to the use of irrigation water with high levels of salts. The content of calcium carbonate varies from 15% to 36% which are considered as normal to high values (Porta *et al*., 1999). The content of available micronutrients required for plant nutrition was quite low (Figures 2 and 3). In this type of soils, the level of carbonates and alkaline pH favour the immobilization of most nutrients, especially Fe.
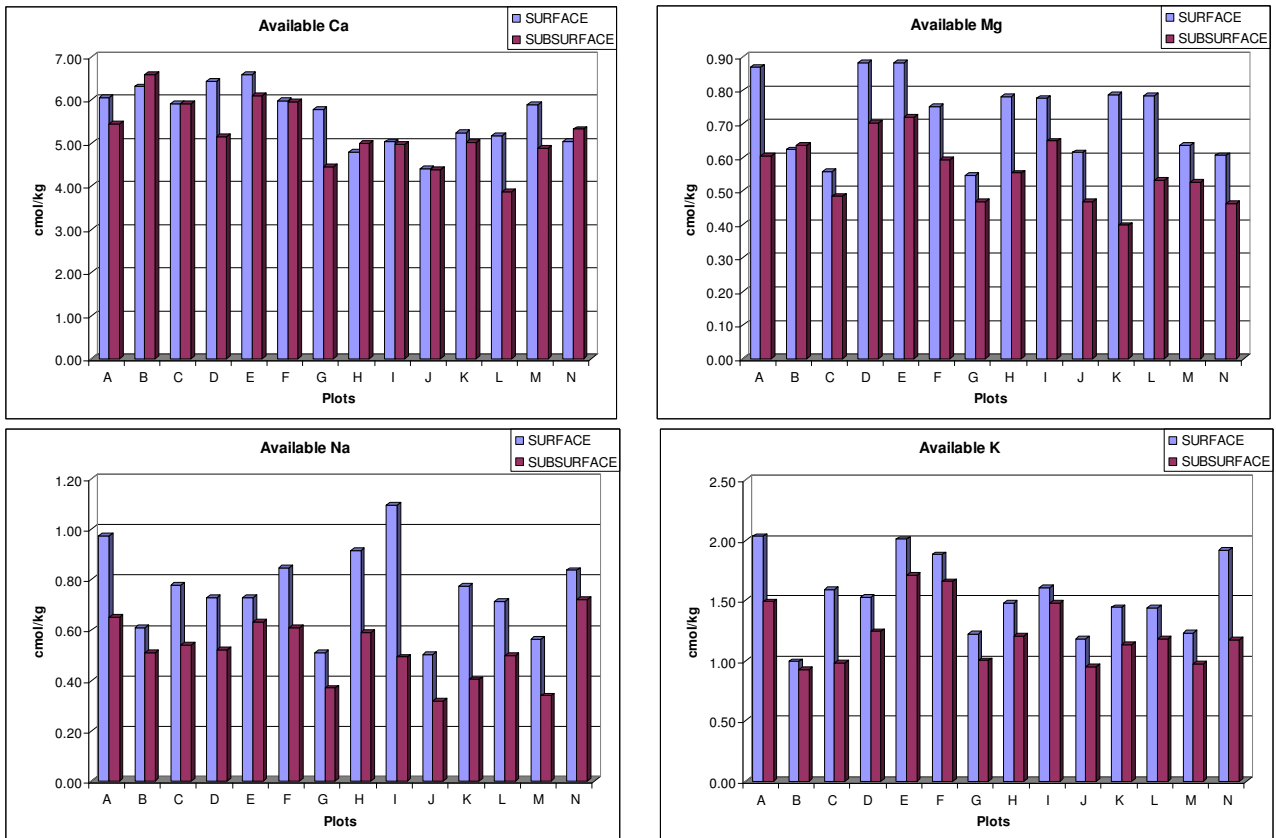
Figure 2. Bioavailable nutrients part 1. Values are mean (n=3).
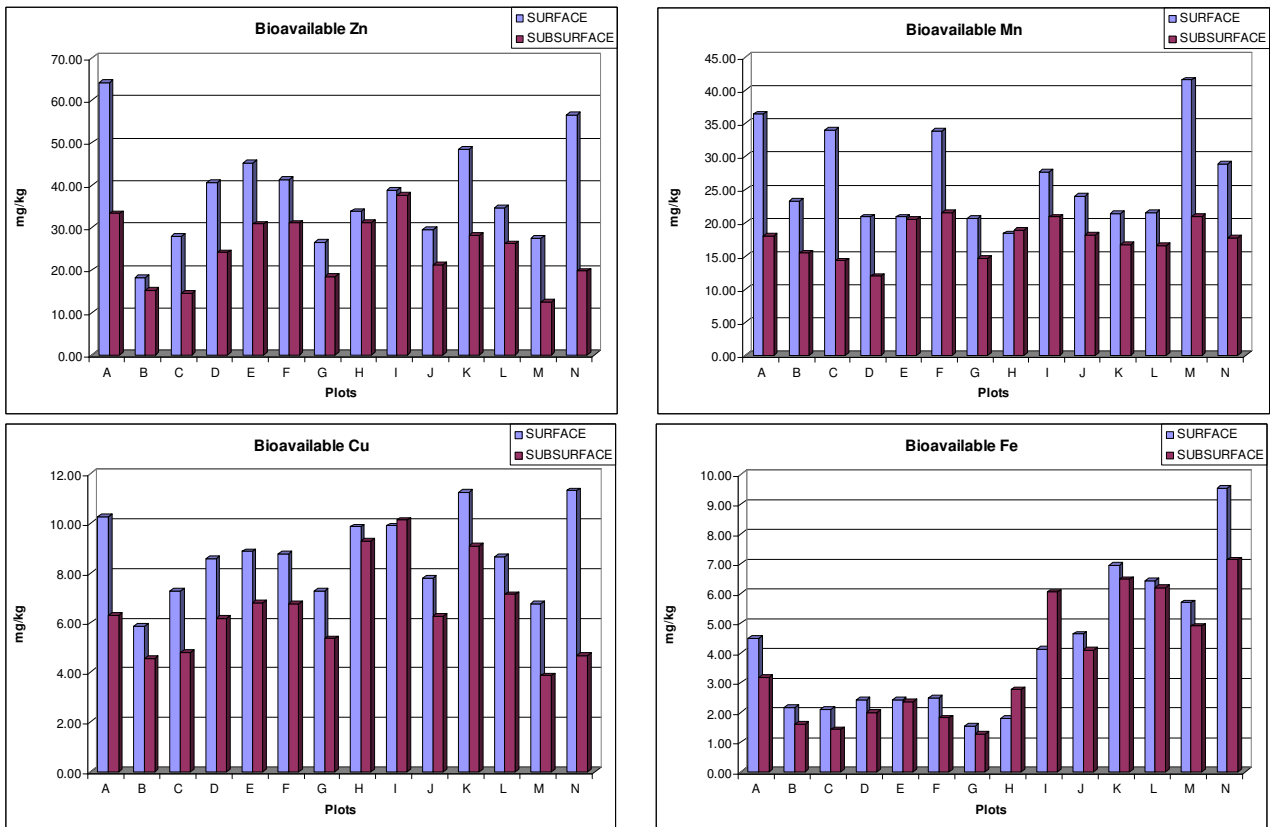
Figure 3. Bioavailable nutrients part 2. Values are mean (n=3).

Conclusion

The studied soils have some deficiencies in most properties required to support optimum production of the almond orchards. The content soil organic carbon is quite low, as well as the C/N ratio, There is a necessity to apply organic matter in order to improve soil conditions. The content in calcium carbonate and the alkaline pH of the soils immobilises nutrients so that the plant is not able to suitably assimilate them. The application of organic amendments such us pig slurry and manure, would add important quantities of organic carbon to the soil, which will enrich the soil continuously releasing nutrients at appropriate rates, favouring microbial activity and improving crop productivity. Contrary to inorganic fertilization, organic amendments would add higher quantities of organic matter. The use of these fertilizers is a way of utilising a residue generated in great amounts by farmers and which is very difficult to manage. This practice provides the basis of a sustainable procedure.

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Chemical mechanisms of soil pH change by agricultural residues

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Abstract

This paper reports the latest findings from studies on the role of organic matter in soil pH change. Soil pH changes induced by canola, chickpea and wheat residues in two soils with different initial pH (pH 4.4 and 6.2) were investigated under field conditions over 18 months. Changes in pH were related to ash alkalinity however, the relative contribution of canola residue to pH increase was greatly reduced at low initial pH. Furthermore, even at 2 months residue alkalinity had moved down the soil profile, particularly for chickpea. A subsequent incubation study examined the effects of separate soluble and insoluble fractions of these residues. The soluble fraction was the source of alkalinity within the first 2 days. For chickpea the increase in pH by the soluble fraction was greater than whole residue at 2 days however, this fraction subsequently acidified soil possibly due to nitrification of soluble N. These data highlight the need for a better understanding of residue chemistry and the interactions with the soil environment in order to predict the changes in chemical properties such as pH.

Key Words

pH, agricultural residues, organic matter, soluble alkalinity

Introduction

Soil acidification remains one of the key issues facing agricultural productivity and sustainability in Australia and around the world (Kochian *et al*., 2004). Agricultural residues and other plant materials can have a liming effect when added to soil in the absence of plants and leaching (Sakala *et al*., 2004; Tang *et al*., 1999; Tang and Yu 1999; Xu *et al*., 2006b). However, the chemical mechanisms for pH change by agricultural residues are not fully understood. While the quantity and timing of residue application is largely dictated by the farming system and the growing season, agricultural residues may be important for the development of pH gradients within soil profiles.

Increases in pH after the addition of residues are purported to occur due to the decarboxylation of organic anions (Tang and Yu, 1999; Yan *et al*., 1996). Other studies have suggested that basic cations which are released during decomposition increase the pH (Noble and Randall, 1999; Pocknee and Sumner, 1997), however experimental evidence for this does not exist. In fact, Yan and Schubert (2000) showed that the addition of cations as salts (e.g. Na_2SO_4) did not have the same liming effect as sodium malate. Nitrogen (N) cycling is considered a main mechanism for pH change, with the conversion of organic N to NH_4^+ consuming H^+ and subsequent conversion to NO_3^- releasing $2H^+$ (Xu *et al*., 2006a; Xu and Coventry, 2003). Leaching of nitrate results in net acidification and would otherwise be balanced by nitrate uptake by the plant. Furthermore, association/dissociation reactions of H^+ with residue surfaces, organic compounds and the soil matrix may also occur and will contribute to the pH change.

The net effect of these processes will be determined by the soil environment and the chemical composition of the residues. The excess cation content, indicative of ash alkalinity, represents the liming potential of residues (Noble *et al*., 1996). The temporal release of this alkalinity is largely controlled by edaphic factors such as initial pH, cation exchange capacity, organic matter content and texture which influence association / dissociation reactions and biological activity. In addition, microbial decomposition of residues is negatively correlated with C: N and is also inhibited in soils with low initial pH. The concentration and forms of N within residues will dictate the fate of N (mineralisation / immobilisation) and whether the N cycle results in acidification. Furthermore, chemical composition is also important since a high proportion (~50%) of alkalinity in plant materials is potentially immediately available (Sakala *et al*., 2004) and also soluble (Yan and Schubert, 2000) and may have the ability to move through the soil profile.

The aim of our recent experiments reported here was to investigate the role of organic matter in soil pH change in agro-ecosystems. In particular, we used both field and laboratory studies to (i) investigate soil pH changes after residue addition under field conditions, (ii) quantify the contribution of soluble and insoluble residue

fractions and (iii) evaluate the proposed mechanisms of pH change including the role of organic N mineralisation, initial soil pH, the chemical nature of residues (particularly C: N and excess cations) and decomposition rate. This paper highlights the main findings of two experiments.

Methods
Experiment 1
A field study was established in 2008 to examine pH changes after residue addition under field conditions. Two soils were collected from Victoria, a Podosol (Isbell, 1996) with a pH of 4.45 from Frankston (38°14'S 145°22'E) and a Tenosol (Isbell 1996) with a pH of 6.20 from Shepparton (36°28'S 145°36'E). Residues of field-grown canola, chickpea and wheat were collected, finely ground and incorporated at 1% w/w into the 0-10 cm layer of soil cores (30 cm long; 10 cm diameter). A set of cores was removed and destructively sampled at 5 times over 18 months. At each time, cores were sectioned into a range of depths and changes in pH (1:5 0.01M $CaCl_2$) and N form and pH buffer capacity were determined.

Experiment 2
A laboratory incubation study was established to determine the contribution of soluble and insoluble fractions of canola, chickpea and wheat to soil pH change. Finely ground residues of canola, chickpea and wheat (termed 'whole') and their fractions were added at 1% w/w to Frankston and Shepparton soils (outlined above). Fractionation of whole residues was performed using reverse osmosis water (1:10) at 70°C for 1 h, followed by centrifugation at 3700 g and filtration (Whatman #1). The 'insoluble' fraction was resuspended and extracted a second time and filtered extracts, termed the 'soluble' fraction, from each extraction were combined. Residues and their fractions were mixed separately with pre-incubated soils, packed into soil cores (25 g), placed in gas-tight chambers (Butterly et al., 2009b) and incubated at 25°C. Measurements were taken as described above.

Results
Experiment 1
Chemical properties of the residues are outlined below (Table 1). Soil pH changes were related to the alkalinity content of the residues (excess cation content), as illustrated in the Frankston soil (Figure 1). At 2 months after the residues were added, most of the alkalinity had been released (data not shown). The change in pH was attributed to the decarboxylation of organic anions. Alkalinity release from the added residues was reduced in the acidic Frankston soil compared to Shepparton soil, highlighting the importance of initial pH (Xu et al., 2006a; Xu et al., 2006b). Furthermore, the relative contribution of canola was different between soil types and highlights the important interactions between residue chemistry and the soil environment. This study also showed that some of the alkalinity within chickpea moved down the soil profile over the 2 month period. While to a lesser extent, canola and wheat residues also significantly increased the pH in the soil layer below they were added.

Table 1. Chemical properties of the residues.

Residue	C:N ratio	Ash Alkalinity (cmol/kg)
Chickpea	21:1	150
Canola	40:1	130
Wheat	64:1	45
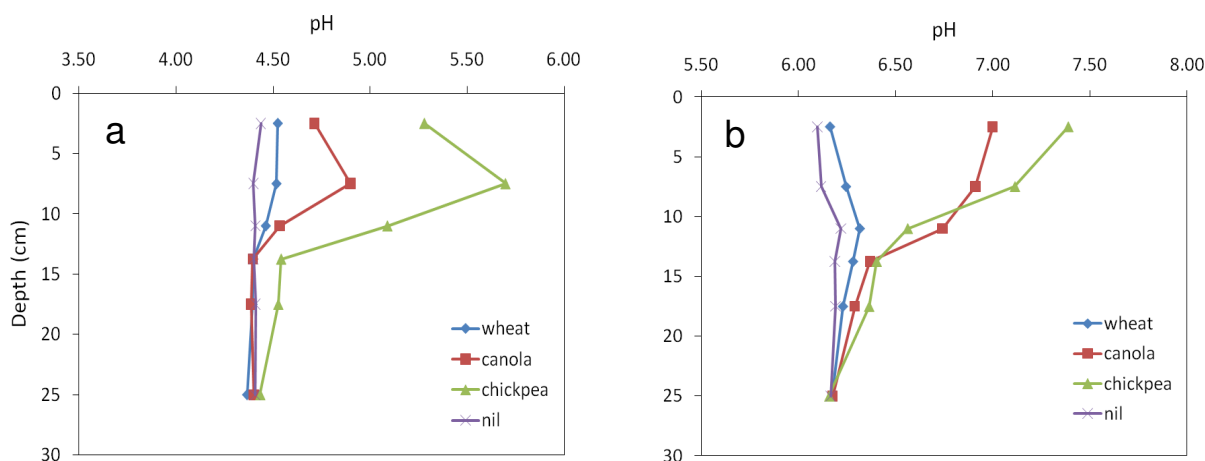
Figure 1. pH in (a) Frankston and (b) Shepparton soils at 2 months after the addition of canola, chickpea and wheat residues (Unpublished Data).

Experiment 2

This experiment confirmed that the soluble fractions of agricultural residues are important for pH change (Figure 2). This agrees with other studies which show that two-thirds of available alkalinity of a range of plant material is soluble (Sakala *et al*., 2004). This soluble fraction was the main source of alkalinity within the first 2 days. However, acidification occurred after 2 days in soil receiving the soluble fraction of chickpea most likely due to nitrification as the chickpea residue has a high N content (Table 1). The pH changes observed by whole residues were similar to those observed in the field study. While the potential alkalinity provided a suitable indicator to the relative liming potential of each residue, it was inadequate to predict the absolute pH change. For example, canola had more than 85% of the alkalinity of chickpea, but did not result in comparable change in pH (Figure 1). Further analyses of the chemical composition of the soluble fraction of each residue are required. In addition, quantifying changes in chemical composition of residues during decomposition would provide a useful link to studies which have examined the role of specific chemical functional groups using model compounds (Rukshana *et al*., 2009).
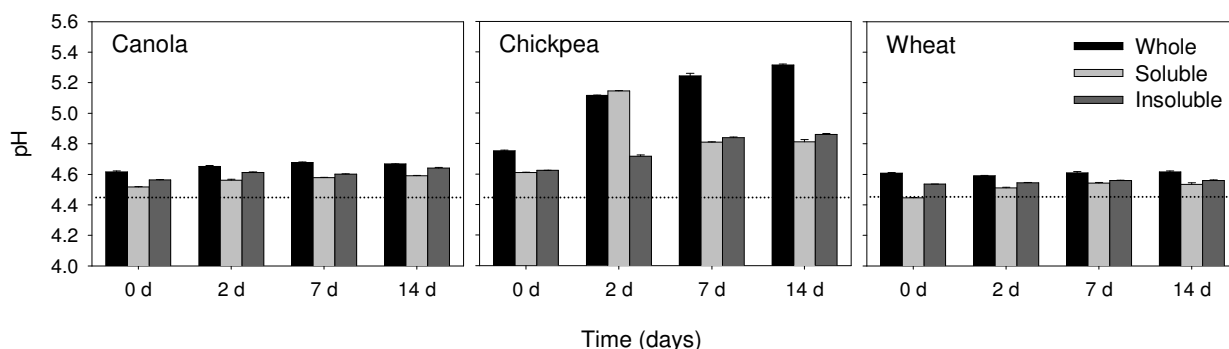
Figure 2. pH in Frankston soil after incubation with whole, soluble and insoluble components of canola, chickpea and wheat residues. Bars indicate standard error of the mean (n=3) and dotted lines the initial soil pH (Butterly *et al*., 2009a).

Conclusions

Soil pH changes after the addition of canola, chickpea and wheat were related to their alkalinity and N contents. The greatest increase in soil pH occurred after chickpea addition as it is easily mineralised (i.e. low C: N) and had the highest potential alkalinity than either canola or wheat. Ash alkalinity should be considered a coarse indicator of pH change, especially in the short-term since it was insufficient to predict the alkalinity contribution of canola. The soluble fraction contained a significant proportion of the total alkalinity for all residues. The soluble fraction was the main source of alkalinity within the first 2 days; however this fraction has the potential to acidify if it contains high concentrations or N. A better understanding of the biochemical process is required to accurately predict pH changes. Further studies should explore a wider range of agriculturally important residues and employ novel technologies to understand the interactions between residue chemistry and the soil environment.

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Composting green waste with other wastes to produce manufactured soil

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Abstract
Manufactured soil for landscaping purposes was produced by composting for 6 weeks (a) municipal green waste alone, (b) green waste amended with 25% v/v poultry manure or (c) green waste immersed in, and then removed from, a mixture of liquid grease trap waste/septage. During composting, temperatures reached 52ºC in green waste alone, 61ºC in poultry manure-amended and 78ºC in grease trap/septage-amended green waste. Following composting, each of the materials was split into (i) 100% compost, (ii) 80% compost plus 20% v/v soil and (iii) 70% compost plus 20% soil plus 10% coal fly ash. Addition of soil, or soil and ash, to composts increased bulk density, reduced total porosity and increased available water holding capacity. Bicarbonate-extractable P, exchangeable NH_4^+ and NO_3^-, EC and basal respiration were all markedly greater in the grease trap/septage-amended than poultry manure-amended or green waste alone treatments. Values for extractable P and EC were considered large enough to be damaging to plant growth and germination index (GI) of watercress was less than 60% for all grease trap/septage composts.

Key Words
Green waste, grease trap waste, compost, available water, available nutrients, microbial activity

Introduction
Municipal green waste consists of a range of materials including tree wood and bark, prunings from young trees and shrubs, dead and green leaves and grass clippings and it originates from both domestic dwellings and municipal parks, gardens and reserves. In most cities in the developed world, green waste is collected separately from other wastes and is mechanically shredded and then composted, either alone or with other organic wastes. It is used in products such as garden mulch, organic soil amendment, garden compost and soilless potting media. However, in Australia, the main use for the composted material is as "manufactured soil" used for field landscaping purposes in place of natural topsoil. Often, inorganic additives (e.g. sand, subsoil, fly ash) are blended with the composted material. Nevertheless, the inorganic component makes up only 10-30% v/v of the final product. The product is considerably cheaper than excavated natural topsoil and is therefore commonly used by landscape contractors.

The exact nature of the ingredients, other than green waste, the ratios at which they are mixed and length of the composting period have been arrived at by trial and error and differ appreciably between contractors. Whilst the above operations are commonplace in Australia, and may well have more widespread application, to date little scientific evaluation of the operations and the products produced has been performed. Indeed, although green waste is commonly composted (Bradshaw *et al*., 1996; Manser and Keeling, 1996) and a number of workers have investigated the properties of the composted material (e.g. Zaccheo *et al*., 2002; Brewer and Sullivan, 2003), there appear to be no reports, other than that of Belyaeva and Haynes (2009), on its use as the basis of the production of manufactured soils. The aim of this study was to compare composting intensity and the properties of manufactured soils produced through composting green waste alone or co-composting it with an easily-decomposable activator material such as poultry manure or grease trap waste/septage. Following initial compost production, the products were amended with 20% topsoil, or 20% topsoil plus 10% coal fly ash (to produce manufactured soil) and allowed to mature.

Materials and methods
Materials and composting
Municipal green waste was collected from Phoenix Power Recyclers, Yatala, Queensland, soon after it had been mechanically shredded. Recently-deposited fly ash was collected from the fly ash disposal lagoon at Tarong Power Station, 80 km west if Brisbane. Poultry manure was collected from a commercial egg producer. Liquid grease trap waste and septic tank waste were collected separately and deposited in a sealed lagoon at Phoenix Power Recyclers. The A and B horizon of a silt loam soil classified as a Clastic Rudosol (Isbell, 2002) was excavated from an unfertilized area under native vegetation. The compost treatments were, (1) 100% green waste (GW), (2) 75% green waste/25% poultry manure v/v (GWP) and (3) green waste immersed in a liquid mixture of

grease trap waste/septage for 6 hours and then removed (GWG). Two hundred litre samples of the mixtures were placed in 250 litre plastic composting bins. The experiment was replicated 3 times. Piles were turned every 7 days in order to ensure adequate O_2 levels inside piles. Temperature was monitored at a depth of 40 cm inside the piles at 0900 h each day. The water content of piles was maintained at 60-70% of their water holding capacity. After 6 weeks of composting each treatment replicate was split into 3: (i) 100% compost (Control), (ii) 80% compost plus 20% v/v soil (S) and (iii) 70% compost plus 20% soil and 10% fly ash v/v/v (SA). The resulting materials were thoroughly mixed and allowed to react and mature for a further 4-week period.
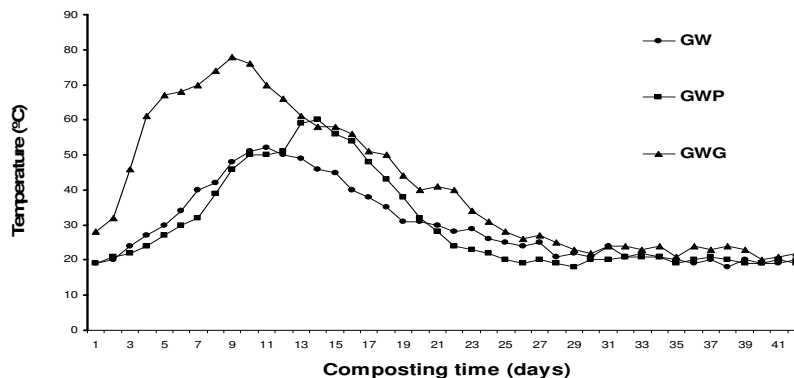
Figure 1. Temperature during composting in composts composed of green waste alone (GW), green waste plus poultry manure (GWP) and green waste plus grease trap waste (GWG).

Compost analyses
Ten subsamples were taken randomly from within each pile. Subsamples were bulked, homogenised and ground to pass a 5mm sieve. A part of each sample was stored at 4ºC for microbial and physical analysis and the rest was air-dried and stored for chemical analysis. Electrical conductivity and pH were analysed in a 1:5 (v/v) water extract using a glass electrode. Extractable mineral N was extracted with 2 M KCl (1:100 ratio for 1 h) followed by colorimetric analysis of NH_4^+ and NO_3^--N. Available P was extracted with 0.5 M $NaHCO_3$ (pH 8.5) (1:100 w/v for 16 h) (Colwell, 1963) and measured colorimetrically. Bulk density was determined on naturally compacted samples, particle density by the pycnometer method and total porosity by difference. Soil water content in samples was determined at -10 and -1500 kPa using a pressure plate apparatus.

A germination test was carried out (in quadruplet) on filter paper in petri dishes. Two ml of aqueous extract (1/10 w/v) from composts was added to dishes. Ten seeds of watercress (Lepidium sativum) were placed on the filter paper and dishes placed in the dark at 28ºC. The germination index percentage with respect to control (distilled water) was determined after 5 days. The control GI value was considered as 100%.

The statistical significance of experimental treatments was determined by Analysis of Variance Analysis using the Minitab Statistical Software Package and differences were calculated at the 5% level using Tukey's test.

Results and discussion
The composition of municipal green waste is typically dominated by shredded wood and bark, with high lignin and tannin contents respectively, and these components are not readily decomposed by microbial activity (Francou *et al.*, 2008). In addition, green waste is often left in stockpiles before shredding and/or composting. During these periods, much of the "soft" green waste decomposes thus further contributing to its slow decomposition during subsequent composting. As a result, temperatures during composting of green waste-alone only reached 52ºC for a short period and then declined (Figure 1). In order to initiate a more active phase of intense microbial activity during composting, the addition of a readily decomposable organic material is required. Addition of poultry manure at 25% v/v to green waste was shown here to both prolong the period over which temperatures were elevated as well as raise the temperature attained to 61ºC (Figure 1). The grease trap waste tended to coat the green waste thus offering a large surface area for microbial decomposition during composting (Coker 2006). Lipids are easily degraded under aerobic conditions (Wakelin and Forster 1977) and their high energy content resulted in composting rapidly achieving thermophilic temperatures. Maximum temperature reached was 78ºC (Figure 1).

Table 1. Some physical and chemical properties and germination index in green waste (GW), green waste plus poultry manure (GWP) and green waste plus grease trap waste/septage (GWG) – based composts to which nothing (Control), 20% topsoil (S) or topsoil (20%) plus coal fly ash (10%) (SA) had been added.

Treatment	Bulk density (m m^{-3})	Total porosity (m^3 m^{-3})	Available water (kg m^{-3})	EC (mS cm^{-1})	Extracable P (mg kg^{-1})	Germination index (%)
GW(control)	0.29a [a]	0.83d	133a	1.1b	616b	94bc
GW(S)	0.69d	0.70b	190ab	0.62a	212a	117c
GW(SA)	0.69e	0.66ab	273c	0.61a	183a	119c
GWP(control)	0.35b	0.79c	171a	1.1b	553c	85b
GWP(S)	0.58d	0.71b	258c	0.60a	228a	116c
GWP(SA)	0.69e	0.65ab	299c	0.64a	186a	145d
GWG(control)	0.35c	0.76c	129a	2.8e	2771f	54a
GWG(S)	0.66de	0.68b	174a	1.6d	1250e	57a
GWG(SA)	0.76e	0.64a	225b	1.3c	894d	61a

Means followed by the same letter within a column are not significantly different at p≤0.05

Composted green waste was characterized by a low bulk density and high total porosity (Table 1). The high macroporosity and relatively low available water holding capacity may limit its use in a field landscaping situation (Belyaeva and Haynes, 2009). The greater intensity of microbial decomposition induced by addition of poultry manure or grease trap waste/septage to green waste tended to result in a greater percentage of small particles being produced and this caused an increase in bulk density and a lowering of total porosity (Table 1). When added to the composted green waste, fine soil material (i.e. originating from a silt loam) and/or coal fly ash partially filled the macropores of the green waste resulting in an increase in bulk density, decrease in total porosity and an increase in percentage mesoporosity and thus available water holding capacity (Table 1). The substantial increases in available water holding capacity that resulted are likely to be of considerable benefit when the material is being used in a field landscaping application, particularly in the Australian context where droughts are common and most cities currently have water-use restrictions in place.

High concentrations of extractable P are a characteristic of green waste composts (Hue *et al*., 1994; Belyaeva and Haynes, 2009) because organic material has insignificant P-sorption capacity and therefore a relatively large proportion of their total P content (e.g. 30-40%) is extractable and potentially bioavailable. Concentrations of extractable P (Table 1) encountered in the GW and GP alone composts (183-616 mg kg^{-1}) are excessive whilst those in the GG compost are extraordinarily high (2771 mg kg^{-1}). These levels may well be harmful to plants, particularly Australian native plants that are adapted to low available P conditions. Handreck and Black (2002), for example, suggested optimum Colwell P levels were < 10mg kg^{-1} for native plants sensitive to P and < 40 mg kg^{-1} for plants moderately sensitive to P. Similarly, soluble salts (EC > 1.3 mS cm^{-1}) were extremely high (Table 1) and large concentrations of NH_4^+ and NO_3^- were also present in the GWG composts. That is, concentrations of NH_4^+-N ranged between 69 and 227 mg kg^{-1} and NO_3^--N between 68 and 80 mg kg^{-1} in GWG composts compared with between 1.9 and 14 mg kg^{-1} for NH_4^+-N and 0.26- 0.68 mg kg^{-1} for NO_3^--N in the other two composts (data not shown). The high levels of salts, P and mineral N probably all contributed to the low GI (< 60%) for the GWG composts. Thus, the high salt, P and N content of the grease trap waste/septage resulted in accumulation of these substances in the GWG compost. Values of GI less than 100% were also recorded for the GW alone and GWP alone composts and these were probably related to high soluble salts (> 1.0 mS cm^{-1}) and high extractable P (> 500 mg kg^{-1}) levels. That amendment of GW and GWP composts with soil or soil plus ash resulted in GI values > 100% demonstrates the importance of such amendment with regard to producing a suitable substrate for plant germination and growth. Such amendment lowers EC and extractable P (Table 1) by dilution and in the case of P also by adsorption. That is, both soil and fly ash contain mineral surfaces (e.g. Al and Fe oxides and aluminosilicates) that can specifically adsorb phosphate.

Conclusions
Green waste is an effective adsorbent material for grease trap waste/septage and the material composts rapidly at thermophilic temperatures. The resulting compost does, however, contain excessive levels of extractable P, high soluble salts and mineral N levels. There seems scope to dilute the grease trap/septage-amended compost with unamended green waste compost in order to lower soluble salts, extractable P and mineral N in the saleable product. Addition of inorganic materials such as subsoil or fly ash to composted green waste has several important positive effects including increasing available water holding capacity and reducing excessive concentrations of soluble salts and P that may have accumulated.

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Crop production, nutrient recovery and hydrology following cattle feedlot manure application

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Abstract

A field plot experiment was established on a sandy loam Typic Natrustalf, duplex soil in Northern NSW, Australia in 1997, to determine crop response, nutrient recovery, and impacts on surface and subsurface water flow following the application of feedlot manure and effluent. Over the three year study, treatments included a control, (nil manure), moderate annual manure applications (20-25t DM/ha applied every year), a high initial application (60 t DM/ha applied in year 1 only) and an inorganic fertiliser treatment (N, P, K applied every year). Both the moderate annual and high initial manure treatments received supplementary inorganic N fertiliser in years 2 and 3. Successive forage crops of sorghum (*Sorghum bicolour* cv. Super-Dan) and triticale (*Triticosecale spp*.cv. Madonna) were grown with highest total dry matter yields recorded by the manure and inorganic treatments. The highest recovery of N, P and S was in the inorganic treatment (63%, 48% & 32%) and K from the high initial manure treatment (269%). Supplemental N applied to the moderate annual manure treatment tended to increase nutrient recovery mainly through increased yield. Total cumulative surface runoff ranked in descending order was control>inorganic>moderate annual>high initial manure treatment. The high initial manure treatment also recorded the lowest total cumulative subsurface flow (95mm) compared to all other treatments (mean 150mm).

Key Words

Manure, crop production, nutrient recovery, hydrology

Introduction

In Australia, more than one million tonnes of feedlot manure is produced per annum (Lott *et al*., 1999) from intensive livestock industries. The value of manure as an ameliorant is more than its nutrient benefit alone. As an organic carbon source when applied to a degraded soil, it can significantly improve a soil's physical properties in addition to the chemical fertility. Improvement in infiltration, aggregation and bulk density, can reduce runoff and erosion from wind and water. These changes can also decrease the energy needed for tillage and improve seedling emergence and root penetration.

Eastern Australian feedlots operate in areas of higher rainfall and cropping intensity, but can have a greater magnitude of land degradation. To ameliorate and restore the soils productive capacity, information is required on the potential integration of manure (and/or effluent) and inorganic fertilisers on soil physical properties and soil water relationships in addition to their nutritional properties. As freight costs are often prohibitive for land application of manure great distances from the feedlot, information is also needed on safe application rates as the recommended rate of 25 to 30 t/ha per year is not always possible.

Methods

Site location, instrumentation and soil analysis

Fifteen runoff plots (20 * 5m) which allowed surface and subsurface water and sediment collection were installed on a duplex sandy loam Alfisol, Typic Natrustalf soil (Spodosol, suborder Brown AB) at the CRC Beef feedlot "Tullimba", Northern New South Wales, Australia ($30^o20'$S; $151^o12'$E). The A_1 horizon was a light grey loam of 0.10 – 0.15 m thickness, containing varying amounts of angular gravel. The A_2 horizon was a very pale, sandy loam to loamy sand, up to 0.3 m thick, usually having more gravel than the surface horizon. The B horizon was yellowish grey clay. Surface soil was acidic (pH_{CaCl2} 4.7 - 5.3) and pH became more alkaline with depth. Organic C, total N and Bray P concentrations are low. Soil bulk density ranged from 1.6 to 1.9 Mg/m^3, and the proportion of exchangeable sodium, especially in the lower slope positions, increased at depth, and exhibited clay dispersion and soil structural breakdown on wetting. Slope varied from 1.8 to 3.8% across the site.

Climate
Rainfall in the region is summer dominant (Oct – Mar) with average annual precipitation of 805 mm. Maximum temperatures generally occur in February, whilst minimum temperatures are below 0^oC in July and August generating an average monthly maximum of 15 frosts per month (Green 1993). Humidity is higher throughout the winter months (80 - 85%) and lower in November/December (65%).

Treatments and crop management
Experimental treatments that were applied over three years are summarised in Table 1. The inorganic fertiliser treatment received nutrients based on the estimated nutrient removal from a sorghum crop yielding approximately 20t DM/ha. Treatments were randomised and replicated twice, except for the no manure + effluent treatment. All manure treatments received irrigation in the form of effluent or clean water and the inorganic treatment received clean water only. Effluent shortages meant it was only applied in year 2 and there was no measured response so this allowed the plots designated to receive effluent to be used as additional replicates.

With different manure amounts applied in each year, nomenclatures shown in Table 2 were adopted to describe treatments. Successive crops of forage sorghum (*Sorghum bicolour* cv. Super-Dan) and triticale (*Triticosecale* spp. cv. Madonna) were grown with the seeds broadcast by hand and hand raked into the surface soil for the three year study. Cultivation was minimised being limited to a single light rotary hoeing after manure application, and immediately prior to sowing each crop. Herbicides and insecticides were applied as required.

Table 2. Treatments applied in each of the 3 years of the experiment. Brackets indicate kg N/ha applied as urea.

	No manure	Moderate annual	Moderate annual + N	High Initial + N	Inorganic
			Manure applied (t DM/ha)		
YEAR 1	0 t/ha	20 t/ha	20 t/ha	60 t/ha	Inorganic
YEAR 2	0 t/ha	25 t/ha	25 t/ha+ (120N)	0 t/ha + (180N	Inorganic
YEAR 3	0 t/ha	20 t/ha	20 t/ha+ (120N)	0 t/ha + (170N)	Inorganic

Plant biomass collection and analysis
Sorghum biomass was cut twice and triticale cut once in each year. Harvesting entailed cutting at approximately 80mm above the soil surface, subsampling and weighing, with all biomass removed from the site. Whole top samples were dried at 80^oC and ground to <2 mm. Multiple manure samples were taken prior to each land application and subsamples allowed application rate and chemical composition to be determined. Plant and manure samples were digested using the sealed container digest procedure of Anderson and Henderson (1986) for elements other than N. Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) was used to measure P, K, S, etc. Samples were digested according to Linder and Harley (1942) for nitrogen determination.

Results and Discussion
Biomass produced
Biomass production in a given environment is primarily influenced by nutrients and water supply. Total dry matter yields over three years were higher in manure and inorganic fertiliser treatments cf no manure, however yearly differences between treatments were recorded. Year 1 differences between moderate and high manure application rates may be due to higher mineralization within the high initial single application. No differences between treatments were recorded in year 2. In year 3, +N treatments yielded higher than manure only treatment, generating a 54% increase, up from 37.5% in year 2. Despite the application of fertiliser N to the high initial manure treatment, the triticale in year 3 displayed nitrogen deficiency symptoms. Research in the USA reported organic N mineralization during the second, third and fourth cropping years after initial application was usually about 50, 25 and 12 % of the first year (Midwest Plains Services 1993). Azevedo and Stout (1974) found that nitrogen in most types of manure was only 20-50 % as effective as commercial N fertiliser in increasing short-term crop yield. Hence, supplementing both moderate and high manure application rates with N fertiliser in years following manure application is necessary to avoid N limitation to crop growth.

Plant nutrient removal
Nutrient recovery in the inorganic treatment was higher than manure treatments for N, P, S and Na (Table 3). High dry matter yields and a readily available source of N were responsible for the highest N recovery (63%) in

the inorganic treatment. Nitrogen recovery in the manure treatments ranged from 38 to 53% and this was higher than found by Eghball and Power (1999) in a four years study on corn.

Table 3. Annual and 3 year total dry matter yield of forage sorghum and triticale.

	Treatment				
	No manure	Moderate annual	Moderate annual +N	High initial + N	Inorganic
YEAR 1	6784a[A]	10906b	10906b	23187c	23782c
YEAR 2	4117a	18444b	25346b	20247b	17233b
YEAR 3	3320a	10880b	16810c	14060c	16350c
GRAND TOTAL	**14221a**	**40230b**	**53062b**	**57494b**	**57365b**

[A] - Numbers within a row followed by the same letter are not significantly different (P>0.05) according to DMRT.

Phosphorus recovery ranged from 25 to 41 % in the manure treatments as compared to 94 % in the inorganic fertiliser treatment (Table 3). Of the manure treatments plus N, the single large application recovered 11% more P than annual applications potentially due to the longer mineralization period. The supplement of nitrogen made to the split application increased P recovery up to 5%, mainly due to increased yields. In this study, P recovery was much higher than Whalen and Chang (2001) who recovered 5-18 % of applied P manure by irrigated barley. However, their study had lower cropping intensity and poorer climatic conditions. Crops generally removed a much higher quantity of K than that applied, with manure and inorganic treatments exporting > 900 kg K/ha in three years. Recovery of K in the manure treatments ranged from 162 to 269%, whilst inorganic treatment recovery was 172%. Largest K removal was in the inorganic treatment, however the high initial plus N treatment recorded larger K recoveries due to less K applied compared with the inorganic treatment. Removal of whole plant tops highlights the potential export of significant amount of nutrient.

The amount of S removed by the crops ranged from 18 to 29% in the manure treatment and 32 % in the inorganic fertiliser treatment (Table 3). The low recovery of S in the manure treatments was due to a low crop yield and the lack of a balanced N supply. The moderate annual application of manure recovered a lower percentage of the applied S in the crop, as compared to the high initial application made at the start of the experiment. This is likely due to the longer time for the single application to be mineralised.
Overall, treatments can be ranked in descending order with respect to % recovery of applied N, P and S as inorganic fertiliser > high initial +N > moderate annual +N > moderate annual manure.

Table 4. Removal of nutrients (kg/ha) by forage sorghum and triticale over 3 years. The percentage of applied nutrient recovered by crops is shown in parentheses.

Nutrient	No manure	Moderate annual	Moderate annual +N	High initial + N	Inorganic
	Total nutrient removed (kg/ha/3 years)				
N	115	337 (38)	505 (45)	588 (53)	765 (63)
P	27	133 (25)	159 (30)	191 (41)	117 (48)
K	306	941 (162)	1153 (217)	1342 (269)	1445 (172)
S	15	46 (18)	59 (24)	65 (29)	76 (32)
Na	5	13 (3)	15 (4)	18 (5)	18 (6)

Hydrology
Lowest cumulative surface runoff and subsurface flow was in the high initial manure treatment and highest cumulative surface runoff was in the control treatment (Figure 1). Many factors control surface runoff, but it seems unlikely that treatment runoff differences could be due to soil cover as manure and inorganic fertiliser crop yield are similar, but the inorganic fertiliser treatment had a higher amount runoff compared to the manure treatments. The difference between the control and the inorganic fertiliser treatment may be partly due to the higher soil cover and root biomass in the inorganic fertiliser treatment. Although the slope varied from 2 to 4% across the experimental area it seems that slope did not have much influence on the amount of runoff from the various treatments. Rainfall intensity did not show a significant correlation with the amount of runoff. The most important factor determining runoff was infiltration capacity. In the third year runoff loss in the inorganic fertiliser treatment was much lower and the infiltration was higher compared to year 2 in this treatment. This was likely due to the decomposition of large masses of roots and stubble. This is supported by King (2001), who reported microbial carbon levels double that of the previous year in this treatment.
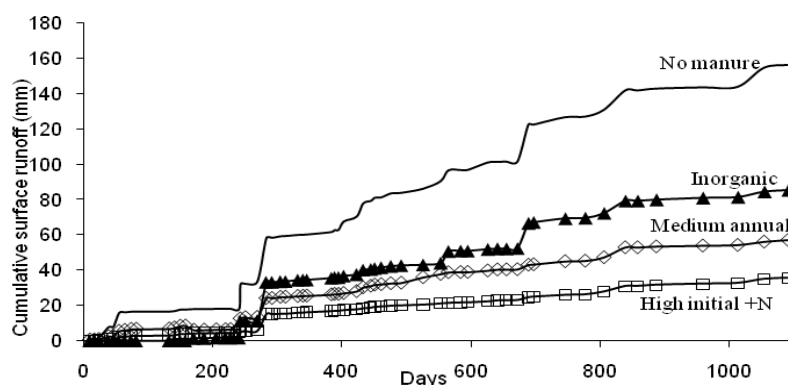
Figure 3. Cumulative surface runoff (mm) over 3 years

Subsurface flow represents a balance between infiltration, soil water retention capacity and rate of water uptake by the crop. There was no difference in cumulative subsurface flow between the control, inorganic and moderate annual manure treatments (mean 150mm loss). The most likely reason for this is that one of the replications of the moderate annual had a high amount of gravel (20%) in the upper surface and the depth to the B horizon was also shallow as compared to the other plots. It is likely that these two factors affected the result. Subsurface loss was lowest from the high initial+N treatment (cumulative 95mm).

Conclusion

The application or manure to land areas completes a natural nutrient recycling process. The nutrient and carbon containing product is commonly applied to land areas designated for crop production. Whilst manure application has been shown to increase crop yields and at high rates is comparable to inorganic fertiliser, nutrients in manure are unbalanced with respect to plant demand. Whether manure is applied at moderate rates annually or a large application is made once over a three year period, inorganic N (and often K depending on soil type) will need to be applied to meet crop demand (especially forage or pasture crops). The application of manure at high rates improves water infiltration as opposed to applying it annually, thus minimising surface and subsurface water flows. It appears a combination of high rates of manure applied once per three or four years and inorganic fertiliser (N), maximises crop yield and recovery of nutrient, whilst minimising water and dissolved nutrient losses.

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Crop rotation and fallowing can affect the functional resilience of microbial communities in a rainfed cropping system in southern Australia

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Abstract
The availability of biologically available carbon and soil moisture are the two key factors affecting the level of soil biological functions in southern Australian dryland cropping soils. In a long-term field experiment conducted on an alfisol, effects of crop rotation, fallowing and tillage treatments on soil microbial and chemical properties were investigated. Microbial biomass C and N and microbial activity were generally lower during the fallow phase of the rotation compared to continuous crop treatments. Crop rotation and fallow also influenced the catabolic diversity of microbial communities and the quantity of functional genes involved in N mineralization most likely due to differences in the quantity and quality of C inputs. The response of biological functions to stresses, e.g. repeated wet-dry cycles, differed between cropping systems with lower resilience in soils from a fallow-crop rotation than under continuous cropping.

Key Words
Microbial activity, resilience, catabolic diversity, microbial biomass, *amo*A, mineralization

Introduction
Soil biological functions in southern Australian dryland cropping soils are mainly regulated by soil moisture and the amount of biologically available carbon, and it is therefore critical that a regular addition of carbon sources occurs to maintain the functional capability. In the low rainfall Mediterranean region of southern Australia, fallowing every second or third year in a rotation has remained a common practice to supplement soil moisture and nutrient levels. The low productivity in the traditional crop-fallow systems with multiple cultivations combined with factors such as heavy grazing and wind erosion have resulted in low returns of organic matter to the soils with subsequent limitations to microbial activities and functions (Gupta *et al*. 2009). In these lower fertility soils, with soil organic C of ~0.5%, soil biota under a fallow-crop rotation generally experience boom-bust cycles of C availability. The depletion of carbon rich microsites can affect the distribution, diversity and metabolic status of microbial communities and can impact on the overall biological resilience. Crop management practices such as crop rotation, stubble retention and tillage influence the quality, quantity and location of crop residues.

In these Mediterranean environments, exposure to repeated wet-dry events is common during summer and can impact on the resilience of biological activity through physico-chemical stresses on microbial habitat and substrate availability. The stability of soil communities is a key to their continued functional capability when exposed to different external stresses. Stability depends on both resistance (i.e. ability to withstand disturbance) and resilience (i.e. ability to recover after the disturbance), i.e. resistance prevents further decline in ecosystem function and resilience allows its recovery (Figure 1A).

The measurement of a soil property reflects the capacity of soil to function at a particular time, whereas knowledge of a soil's resilience assists in the development of systems or practices that promote the recovery of degraded soils. In addition, a better understanding of the resilience of the system is also useful to understand the role of changing environments and climates on ecosystem function. The measurement of soil resilience involves quantifying short-term changes in specific biological properties (e.g. measures of the activity, diversity and population levels) following an exposure to disturbance or stresses, e.g. chemicals, wet-dry or freeze-thaw cycles (Morely and Coleman 1989; Kuan *et al.* 2007).

In this study we discuss the impact of 5 years of intensive cropping, no-till and optimum fertilizer input systems on microbial activity, diversity and resilience when compared to the traditional fallow-crop rotations on a Belah loam (alfisol) at Paringi, New South Wales, Australia.

Methods

Soil and site description
A long-term field experiment was established at Paringi (Kerribee station) in New SouthWales (WGS84 lon 142.37, lat -34.28) in 2002 with the aim to investigate the potential of improving rainfed farming systems in terms of productivity, profitability and overall soil biological health. Treatments included a combination of rotations (wheat, canola, fallow and grain legumes), tillage (no-till and conventional cultivation) and fertiliser inputs (district practice and high-input). Each treatment was replicated four times. The climate is a Mediterranean-type, characterised by hot dry summers and a winter-dominant, average annual rainfall of only 260mm. Soil is an alfisol (calcic Calcarosol). Soil chemical properties (0-10cm) at the start of the trial were pH(water) 7.6, organic C 0.68%, total N 0.06%, and clay content 10.6%. Surface soil samples collected prior to sowing (May) in 2007 were analysed for various microbial, biochemical, chemical properties.

Microbial biomass C, N levels and metabolic status of microbiota
Microbial biomass (MB) C and N (chloroform fumigation-direct extraction methods), substrate induced respiration (SIR) and Potential C and N mineralization were measured using methods described by Gupta *et al* (1994).

Catabolic diversity profiling
A measure of the ability of soil microorganisms to use a diverse array of added C substrates gives a profile of catabolic potential for microbial community. Carbon substrate utilization profiles of soil microbial communities were determined using the Microresp® method (Campbell *et al.* 2003) modified with specific carbon substrates selected for Australian soils (Gupta VVSR, Grains RDC report, Australia, unpublished).

Functional gene analysis:
DNA was extracted from subsamples of soils used for catabolic diversity (0.4 g soil samples) using the MoBio UltraClean soil DNA extraction kit (MoBio Laboratories, CA) and used to quantify the abundance of functional genes. Nitrogenase reductase (*nif*H) gene fragments were amplified using primers described by Rösch *et al*. (2002), and the ammonia monooxygenase (*amo*A) gene was amplified using primers described by Stephen *et al*. (1999).

Resilience analysis:
The stability of soil biological communities and processes was estimated using a laboratory based repeated wet-dry cycle assay standardised for Australian soils. Briefly, 120 g (dry wt equivalent) soil was weighed into 250ml polypropylene containers (Sarstedt Australia Pty Ltd) and bulk density adjusted to 1.3g/cc. Soil moisture was adjusted to -30kPa (100% field capacity (FC) or 60% water filled pore space). Duplicate samples were prepared for each field sample; one sample for resilience exposure and the other kept moist throughout the incubation assay. After soil moisture adjustment, all samples were pre-incubated for 5 days at 25 °C after which some of the samples were exposed to wet-dry (W-D) cycles where as others remained moist. The resilience samples were subjected to a series of 3 drying events (at 40°C), 3 days each, interjected with 4 days of wet condition (25°C). At the end of W-D cycles, soil moisture was adjusted to FC and incubated at 25 °C for 28 days. Subsamples at the start of the experiment (T1, at the end of pre-incubation), within 24h after W-D cycles (T2) and at the end of 28d post W-D cycle incubation (T3) were analysed for microbial activity, catabolic diversity and functional gene analyses. Stability parameters (resistance and resilience) were calculated using procedures described by Orwin and Wardle (2004). In order to overcome the interference from temporal changes in microbial activity measurements at different times, data for the W-D exposed samples were normalised against their counterpart samples that were not exposed to stress events.

Results
Average C inputs from above and below-ground crop residues were less than 1.5t C/ha/year. In the continuous crop rotations C residues were retained whereas during the fallow there were no C inputs. Legume crops in these environments generally added lower amounts of C compared with cereal crops. Grain yields of cereal crops were generally higher following fallows compared to the intensive cereal systems; mainly due to the extra stored soil water under fallow treatments. However, fallow-crop rotations only provided grain harvest in alternate years. The positive effect of stored water was highlighted because of the multiple seasons of less than average rainfall received during the trial.

Microbial biomass C ranged between 250 to 400ug C/g soil and accounted for 3-5% of soil organic C levels. In

the initial period of the field experiment, there was little difference in MB levels between crop rotations but after 5 years, soils from continuous crop rotations showed higher MB-C. MB was generally lower in the fallow phase of crop rotation (up to 25% lower than after wheat crops). MB-N ranged between 50-70kg N/ha; levels were highest after legume crops and lowest after the fallow phase. Soil respiration ranged from 25 to 45ug CO_2-C/g/day and was generally higher (>15%) in soils under continuous cereal cropping systems followed by the legume-cereal rotation and lowest in the fallow-crop rotation, in particular during and after the fallow period.
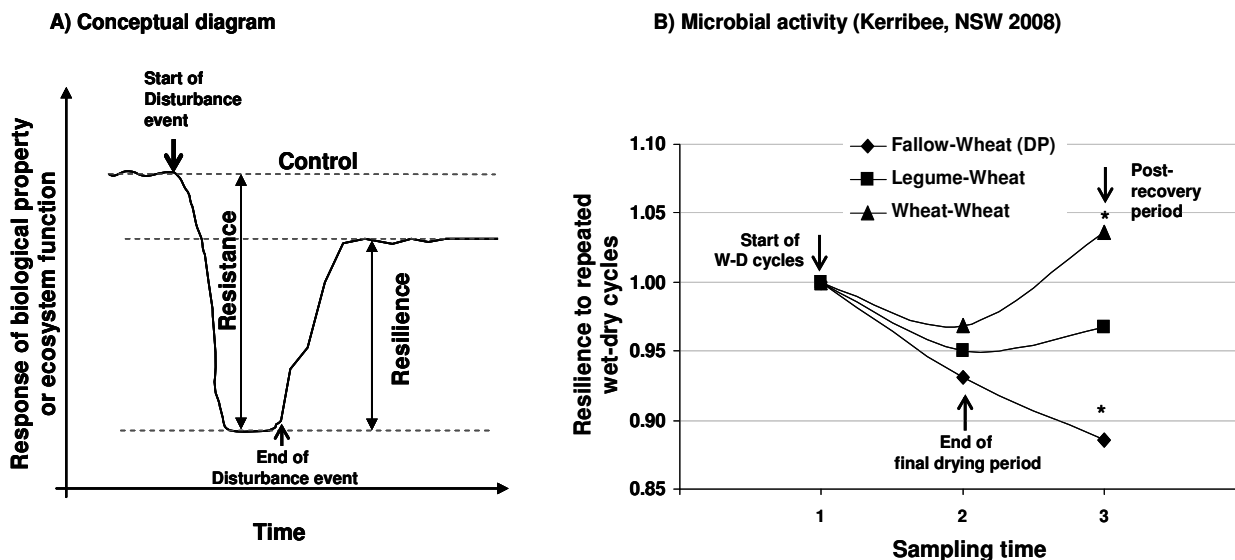
Figure 1. Stability of soil biotic communities - resistance and resilience. (A) The conceptual diagram is based on discussion by Herrick (2000) and Griffith *et al.* (2004). (B) Microbial activity resilience responses to 3 consecutive wet-dry cycles – after 6 years of three farming system practices (rotations and associated tillage practices). Microbial activity values normalised using data from samples that were not exposed to stress events.

Biological resilience (expressed as changes in microbial activity) was found to be lower in fallow-crop rotations than under continuous cropping (Figure 1B). Soil biota under fallow-crop rotations generally experience boom-bust cycles of C availability. The depletion of C rich microsites affects the distribution, diversity and metabolic status of microbial communities and reduces the overall biological resilience. The higher N content in the legume residues results in faster degradation and depletion of C rich microsites.
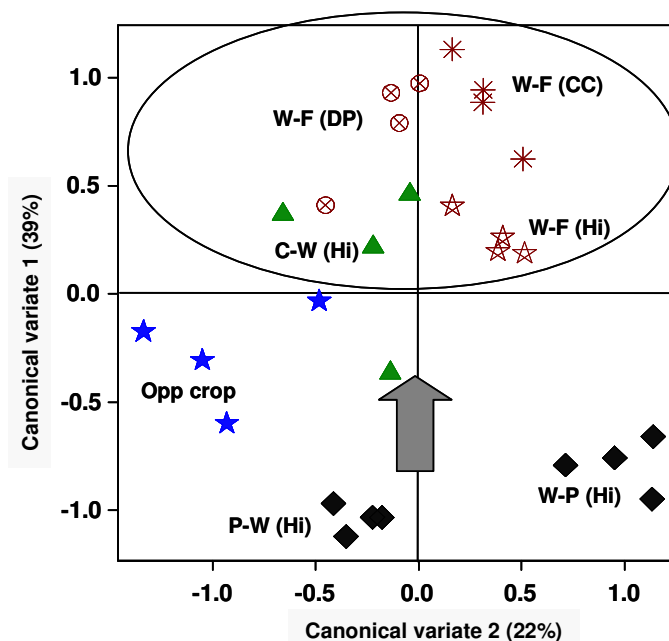
Figure 2. Canonical variate analysis of catabolic diversity profiles for microbial communities in surface soils after 5 years of different cropping systems at Kerribee, NSW, Australia. W=Wheat, F=Fallow, C=Canola, P=Peas, DP=District Practice, Hi=High inputs, Opp crop=Opportunity cropping i.e. crop type is selected based on seasonal conditions at the time of sowing.

Since the carbon availability, both in terms of quantity and quality, is one of the major regulatory factors influencing the biological processes, we measured the catabolic diversity of microbial communities. Community level physiological profiling using multiple C substrate usage showed significant differences between soils from different cropping systems. For example, all the treatments that had a fallow in rotation were different to intensive cropping treatments (Figure 2). Soil communities under the legume-wheat rotation were different from those under continuous cereal and canola. Differences in the quantity and quality of above- and below-ground crop residues for different crops resulted in the differences in catabolic diversity of microbial communities. Soils from continuous cropping systems generally indicated higher levels of N mineralization potential compared to those from fallow-crop rotations. Soils after legume crops exhibited a higher N mineralization potential. In general, soils from fallow-crop rotations had the lowest quantities of functional genes (e.g. *amo*A copy number for fallow-wheat < grain legume-wheat < continuous wheat). Exposure of soils to repeat W-D cycles resulted in a decline in the *amo*A copy number compared to those not subjected to stress, with the highest decline occurred in the legume-wheat rotation. After 5 years of intensive cropping there was no significant change in soil organic C (0.75 to 0.82%) and total N (0.065-0.073%) in the surface soils compared to pre-experimental concentrations. Soils under fallow-crop rotation showed a small decrease in the POM-C and POM-N (3-5%) whereas intensive cropping under no-till exhibited no significant change.

Conclusion

In the southern Australian rainfed region crop management practices that increased the C inputs from above and below-ground crop residues improved soil microbial activity and biological functions involved in C turnover and nutrient mineralization. Crop rotations that include a fallow season reduced the microbial biomass, catabolic and N mineralization potential and quantities of functional genes involved in N cycling. The decline in the biological resilience (expressed as changes in microbial activity) of soils under fallow-crop rotations could be attributed to the boom-bust cycles of C availability. Overall, the results suggest that there is a need for increased inputs of carbon to increase microbial populations, sustain biological functions for longer periods within the season and associated benefits.

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Decomposition rates of plant residues in Alfisols under different uses

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Abstract

In this study, we evaluated variations of decomposition due biochemical quality of crop residues and land use. Alfisols under different uses (woodland, grassland and cultivated soils) were mixed with alfalfa (*Medicago sativa* L.) and wheat (*Triticum aestivum* L.) in doses of 10 ton of dry matter per/ha, incubated in the lab, in triplicate. CO_2 emanated from the soils was measured after 20, 40, 60, and 80 hours of incubation, and the amount of released C was calculated (mg C/g soil). The difference between the amount of C added by the plant residue and C liberated as CO_2, was named residual C. The C loss was greater and residual C retained was lower ($p<0.05$) for Alfisols where alfalfa was applied than for those were wheat straw was added, which was a function of the biochemical composition differences between the alfalfa and wheat straw residues. Regarding the land use, residue C loss was greater ($p<0.05$) in woodland (*Haematoxylon Campechianum* and *Bucida buceras*) soils and lower in grassland (*Gramineae*), and cultivated soils (*Sorghum vulgare* and *Yucca sp.*). We conclude that the rate of decomposition increases in order of woodland > grassland > cultivated soils, and less residual C is retained.

Key Words

Crop residues, residue decomposition rates, Alfisols, land use

Introduction

Intensive management practices and low addition of organic residues may decrease the content of the soil organic matter (SOM), which negatively affects the sustainability of agricultural production systems. The management of organic residues has been a means of increasing the potential sink for carbon of cultivated soils (Six *et al.* 1999). There has been considerable research into the effects of organic residues, C/N relation, temperature, humidity, and management on decomposition rates; but there have been relatively few attempts to relate the soil C pool, as a result of management and soil characteristics, to decomposition rates in crop residue incorporation systems. Decomposition rates, mostly calculated from the net mineralization of C or N, usually, but not always, show an initial rapid mineralization, after which mineralization becomes much slower (Ajwa and Tabatabai 1994). Decomposition rates vary with the composition of the organic residues, the experimental conditions, and the nature of the soil (Hadas *et al*. 2004). Theng *et al*. (1989) points out that besides the aspects related to SOM quality, its decomposition rate may also be modified by the reaction of SOM on the surface of clays, or by physical barriers, such as materials that remain occluded inside the soil aggregates. These results were attributed to the mineral structure of clays, which is known to interact with organic C of the soil, thus protecting it from decomposition. The protective effect of clays on organic matter is significant, but the soil's respiration might depend on the re-supply of labile substrate apart from the organic carbon reserve (Wang *et al*. 2003). As a result, an understanding of the processes that control SOM dynamics and their response to crop residues management is essential for informed use of agricultural land. As a consequence, the aim of this research was to evaluate the variation of the decomposition by biochemical quality of crop residues under different uses in a representative area with Alfisols.

Methods

We selected six Alfisols from the State of Campeche in Mexico, and samples were collected under different use (medium forest, woodland, grassland and cultivated soils). Soils were classified according to Soil Taxonomy (Soil Survey Staff 2006) (Table 1). From each soil, 10 subsamples were taken from the surface 20 cm, in order to form composite samples. These were dried outdoors in the shade, ground and sieved through a mesh of 2mm. pH was measured with the potentiometric method, soil/water ratio 1:2, and electrical conductivity, with a conductimeter at a soil/water ratio of 1:5 (v/v).

Table 1. Classification and land use of soils.

Classification (Great Group)	Use	Scientific name
Ferrudalf	Woodland	*(Haematoxylon Campechianum)*
Ferrudalf	Woodland	*(Bucida buceras)*
Kandiudalf	Grassland	*(Gramineae)*
Kandiudalf	Yucca Crop	*(Yucca sp)*
Kandiudalf	Sorghum	*(Sorghum vulgare)*

Crop residues used were alfalfa (*Medicago sativa*, C/N ratio 13) and wheat straw (*Triticum aestivum* L., C/N ratio 77). Residues were previously dried at $65^{o}C$, ground and sieved through a 40 mesh sieve. Amounts of residue applied to soil were equal to 10 t /ha of dry matter; each treatment was repeated three times. In the plant residues, total N was determined by the semimicro-Kjeldahl method (Bremner 1965), and organic C by wet digestion with the Walkey and Black method (Nelson and Sommers 1982). Protein was estimated indirectly from the total N content (AOAC 1975). Total fiber content (hemicellulose, cellulose and lignin) was determined by the procedure of neutral and acid detergent fiber (Van Soest 1963). Soils were incubated according the Isermeyer method, quoted by Alef (1995) modified by Avilés (2000). Samples were incubated under 65% of field capacity at a temperature of $30^{o}C$ for 80 hours. CO_2 emanated from the soils was measured after 20, 40, 60, and 80 hours of incubation, and the amount of released C was calculated (mg C/g soil). The difference between the amount of C added by the plant residue and C liberated as CO_2, was named residual C. This was considered as an indirect measure of the C pool present in each soil. The residual C after incubation was related to each type of crop residue applied to soil. The tendency was described by a lineal function (y = -bt + a) where a is the amount of C added in the residue, b is the rate of carbon loss by decomposition, and y is the residual C. With the values of b determined from linear regression, a statistical means trial test was carried out (Tukey α=0.05) to determine if there were significant residue decomposition effects related to soil use.

Results

Soil pH values were from 5 to 8, and electrical conductivity was equal or less than 1 dS/m, thus, we avoided extreme values of acidity or alkalinity that could affect the decomposition processes. The characterization of residues applied is shown in Table 2. The C/N ratio of residues was 13 and 77 for alfalfa and wheat straw, respectively.

Table 2. Characterization of alfalfa (*Medicago sativa* L.) and wheat straw (*Triticum astevium* L.) residues.

Organic residue	Organic C %	N %	C:N	Protein%	Fibers[A] %	Hemicellulose	Cellulose	Lignin
						(-------------------%-------------------)		
Alfalfa	44.68	3.35	13	20.9	27.4	1.7	21.2	4.5
Wheat straw	46	0.6	77	3.8	71.1	23.1	39.6	8.4

[A]Percentage of fibers (hemicelluloses +cellulose + lignin)

In order to analyze the tendency of time of residence of plant residues evaluated for different conditions of land use, rates of residue decomposition were determined by regression of the carbon loss from 0 to 20, 40, 60, and 80 hours. The mean coeffecient of determination was $r^2 = 0.98$ for the 30 trials. Table 3 shows the the rate of residue C loss, coefficient *b*. The more negative is the value of the slope (b), the less is the amount of plant residue that remains after time t. There was a significant relation between the rate of plant residue loss and the residue C:N ratio for each condition of land use. Values of residue C loss with the application of alfalfa were -0.81 to -1.37 µg/g/day, and in contrast those obtained with wheat straw were -0.12 to -0.42 µg/g/day. The alfalfa residue (C:N=13) broke down quicker in time, so that C that remained was less compared to wheat straw (C:N=77). This was ascribed to the biochemical composition of the residues; alfalfa showed a C/N ratio, with more protein content (20.9%) and less fiber content (cellulose+ hemicellulose+lignin=27.4%), facilitating microbial decomposition (emanated C), thus diminishing residual C more rapidly than wheat straw.

In contrast, the biochemical composition of wheat straw showed a high C/N ratio (77), less protein content (3.8%) and more fiber content (71.1%), limiting the activity of microbial biomass and thus diminishing breakdown and retaining more residual C in the soil. Kumar and Goh (2000), mention that residues with a high C/N ratio decompose at a slower rate than those with a low C/N proportion. However, the biochemical features may only explain the initial decomposition rate of the residues, because C coming from the residue declines as time goes by (Trinsoutrot *et al.* 2000). Ladd *et al*. (1992) report that release as $C^{14}O_2$ of C^{14} applied to different soils, went from 15 to 27% after an incubation of 3 days, with significant differences among the studied soils. Similarly, Ajwa and Tabatabai (1994) point out that the amount of total mineralized organic C in soils treated with organic material, showed variations as a function of the kind of organic material that had been applied.

Table 3. Rates of carbon loss from added residues by each land use.

Land Use	Vegetation	Residue	C loss rate (value of b=rate) mg/g/day	MSD
Sorghum Crop	*Sorghum vulgare*	Wheat	-0.28a	
		Alfalfa	-1.36b	0.11
Grassland	*Gramineae*	Wheat	-0.42a	
		Alfalfa	-1.34b	0.16
Yucca Crop	*Yucca sp.*	Wheat	-0.37a	
		Alfalfa	-1.37b	0.09
Woodland	*Haematoxylon Campechianum*	Wheat	-0.12a	
		Alfalfa	-1.02b	0.19
Woodland	*Bucida buceras*	Wheat	-0.14a	
		Alfalfa	-0.81b	0.14

Mean values with different letters (a and b) in the same pair of rows are statistically different, Tukey (α=0.05). MSD=Minimum Significant Difference

Table 4. Rates of carbon loss from added residues by biochemical composition.

Plant residue	Land Use	Vegetation	C loss rate (value of b=rate) mg/g/day	MSD
Alfalfa	Woodland	*Haematoxylon Campechianum*	-0.81a	
	Woodland	*Bucida buceras*	-1.02b	
	Grassland	*Gramineae*	-1.34c	
	Sorghum Crop	*Sorghum vulgare*	-1.36c	
	Yucca Crop	*Yucca sp.*	-1.37c	0.18
Wheat	Woodland	*Haematoxylon Campechianum*	-0.12ab	
	Woodland	*Bucida buceras*	-0.14abc	
	Sorghum Crop	*Sorghum vulgare*	-0.28bcde	
	Yucca Crop	*Yucca sp.*	-0.37de	
	Grassland	*Gramineae*	-0.42e	0.12

Mean C loss rate values with different letters in the same column, for alfalfa and for wheat trials, are statistically different, Tukey (α=0.05). MSD=Minimum Significant Difference

In order to evaluate how the organic C pool of the soils was affecting the decomposition of plant residues, the C loss rates from each set of land use trials were compared for the two kinds of plant residue by ANOVA. The variance ratio (F) was significant ($p<0.05$) for both alfalfa and wheat straw trials (Table 4). Results showed that in woodland soils, the daily loss of C was from -0.81 to -1.02 μg/g with alfalfa and from -0.12 to -0.14 μg/g with wheat straw. In contrast, in grassland and cultivated soils (*Sorghum vulgare* and *Yucca sp.)* the values were from -1.34 to -1.37 μg/g with alfalfa and from -0.28 to -0.42 μg/g with wheat straw.

The application of a same residue to Alfisols under different use (from natural vegetation to intensive cultivation) show clear differences in the availability and recycling of organic matter in the soils, as well as in soil C pool level. In this sense, Lee *et al*. (2007) found that approximately 45% of added C with manure application was respired; and a large portion was retained in the soil. Campbell *et al*. (2005) showed that changes in SOC depend on the degree to which the soil has been degraded: the greater the previous degradation, the greater the likelihood that a change in management will reverse the process. The results obtained in this study, give us evidence that the decomposition of C that is added to the soil by means of the plant residues not only depends on the quality of the residue, but also by the land use, which is affecting the organic pool and plays an important role.

Conclusion

The C loss was greater and residual C retained was lower ($p<0.05$) for Alfisols where alfalfa was applied than for those were wheat straw was added, which was a function of the biochemical composition differences between the alfalfa and wheat straw residues. Regarding the land use, residue C loss was greater ($p<0.05$) in woodland (*Haematoxylon Campechianum* y *Bucida buceras*) soils and lower in grassland (*Gramineae*), and cultivated soils (*Sorghum vulgare* and *Yucca sp.*). We conclude that the rate of decomposition increases in order of woodland > grassland > cultivated soils, and less residual C is retained.

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Do Soil Microbes Know their Fractions?

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Abstract

The size and activity of the soil microbial community (SMC) is often correlated to the availability of carbon and nutrients. However, carbon exists in soils in a diverse range of pools/fractions that differ in their chemistry and rates of turnover.

Improved knowledge of the distribution of carbon (C) and nutrients (N and P) across different soil organic matter (SOM) fractions will potentially improve our understanding of drivers of the structure of the SMC, carbon utilisation and nutrient cycling functions, and predictions of nutrient mineralisation from SOM turnover.

Agricultural soils collected across Southern Australia, varying in soil type and management practices, were characterised for i) chemical composition via mid-infra red (MIR) spectroscopy; ii) distribution of carbon, nitrogen, and phosphorus in measurable SOM fractions; iii) the structure of the soil bacterial and fungal communities using community DNA fingerprinting; iv) the carbon utilisation potential of the soil microbial community (MicroResp). Using integrative multivariate analysis we explored stoichiometric relationships between abiotic and biotic properties of these soils. The results will provide greater insight into the relationship between SOM chemistry and the role of bacteria and fungi in nutrient cycling processes.

Key Words

Soil organic matter, stoichiometry, microbial community, carbon, nitrogen, phosphorus

Methods

Soil was collected from a range of long-term agricultural trials in Southern Australia (Hart, Harden, Hamilton, Junee reefs, Urrbrae, Waikerie, Yass). Management practices included permanent pasture, pasture-wheat/pea/fallow rotations, conventional tillage, stubble-burn, N or P fertilisation. Full details are described within Wakelin et al (2008). MIR spectroscopy was carried out according to Forrester *et al*., (2003). Soils were fractionated according to Sjemstad *et al*. (2004), providing >2mm buried plant residue (BPR), >53μm (POM) and < 53μm (HUM) size fractions respectively. Bacterial and fungal community structures were characterised using PCR-DGGE and catabolic potential was assessed using the MicroResp[TM] method (Campbell **et al**., 2003) as described in Wakelin *et al*., 2008.

Results and Discussion

Preliminary data indicate average C: N ratios of approximately 31, 15, and 10 for BPR, POM, and HUM respectively. The observed decreasing trend in C: N ratios across SOM fractions is consistent with increasing extent of decomposition. The data also demonstrated greater variability in the C: N ratio of plant residue inputs compared to component fractions of SOM. POM and HUM fractions, with consistently lower C:N ratios, are likely to contribute to N mineralisation, while the ratios of surface (SPR) and BPR materials are likely to lead to immobilisation.
Across these range of soils pH was found to be a stong driver of SMC structure and function. Further data analysis looks to identify the extent to which SOM chemistry correlates with SMC structure and function.

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Do texture and organic matter content affect C & N dynamics in soils exposed to dry/wet cycles?

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Introduction
Previous studies have reported both enhanced and reduced C and N cycling when soils of different compositions are exposed to repeated wet/dry cycles. The factors that determine the different responses are poorly understood. The objectives of this study were to determine how soil texture and organic matter content affect short-term C and N dynamics and the production of CO_2 and N_2O over a series drying and rewetting cycles, and then to use CO_2 and N_2O produced at constant moisture contents to calculate production during dry/wet cycles and compare this to actual production.

Materials & methods
Soil samples were collected from six paddocks on each of two soil types with contrasting textures (silt loam & clay loam) to produce an organic matter gradient for each. The soils (bulk density = 1.1 g/cm^3) were incubated aerobically for 92 days in gas tight chambers fitted with rubber septa for gas sampling. The experiment consisted of three phases (Figure 1):
1) Pre-incubation phase (14 days at field capacity [FC, -0.01 MPa])
2) Treatment phase (treatments as described below)
3) Recovery phase (soils returned to FC, 18 days).
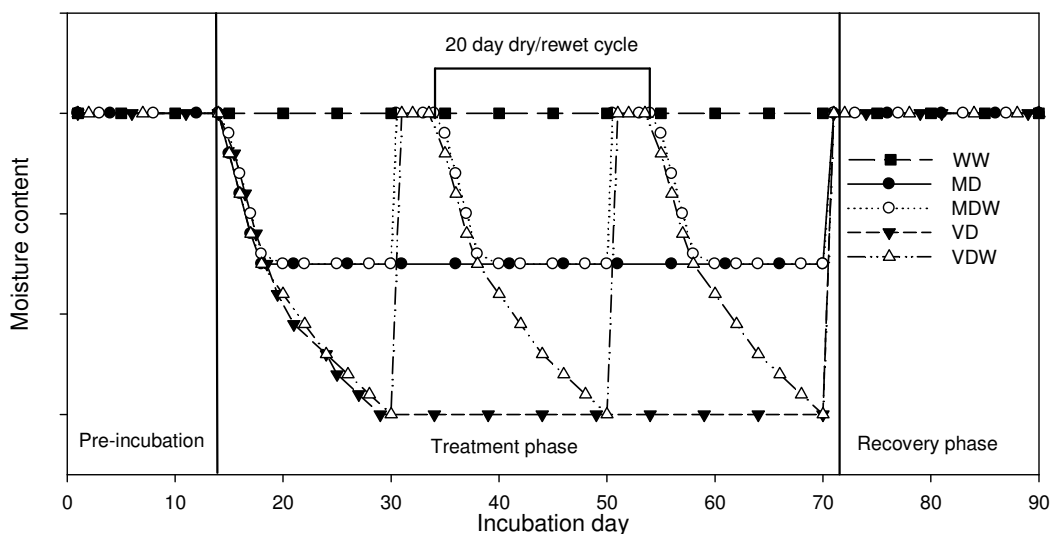
Figure 1. A schematic diagram representing the experimental phases and dry/wet treatments.

Three constant moisture and two dry/wet cycle treatments were imposed during the treatment phase (Table 1).

Table 1. Dry/rewet treatments.

Treatment name	Treatment ID	Moisture Treatment	Rewet treatment
Continuously moist	WW	FC	Maintained at FC
Moderately dry, rewet	MDW	120% WP	+ rewet
Very dry, rewet	VDW	80% WP	+ rewet
Moderately dry	MD	120% WP	- rewet
Very dry	VD	80% WP	- rewet

The dry/wet treatments (MDW and VDW) included three 20-day cycles each consisting of 16-day drying, rapid rewetting and 4 days at FC. Dry treatments (MD and VD) were dried down and incubated for duration of the treatment phase. Drying was achieved using silica gel, allowing continuous measurement of CO_2 (IRGA) and N_2O (GC) during the experiment. At the end of each phase soils were analysed for KCl extractable mineral N (Min N), and cold water (CWEC) and hot water (HWEC) extractable C.

Results and Discussion
Overall, total CO_2 production (cumulative C mineralised), HWEC and CWEC were positively related to the initial organic matter content (mg C/g soil), but this relationship was much more evident in the silt loam soils (Figure 2A, B & C). Progressively less C was mineralised with increasing frequency and intensity of drying (WW>MDW>VDW>MD>VD) in both soil types. There was evidence that, in the silt loam soils, HWEC and CWEC are substrates for the C mineralisation as their concentrations were elevated in the dry treatments at the end of the treatment phase and dropped sharply over the recovery phase, but again this relationship was less evident in clay loam soils (Figure 2D, E & F).

There were large differences in KCl extractable mineral N and N_2O emissions between the two soil types (i.e. textures). In the silt loam soils, mineral N increased with organic matter content and decreased with frequency and intensity of drying, and N_2O emissions were highest in the continuously moist (WW) and most intense dry/rewet (VDW) treatments (Figure 3A-C). In contrast there was a poor relationship between mineral N and organic matter content in the clay loam soils, but N_2O emissions were markedly higher in the dry/wet treatments (MDW, VDW) compared to WW, MD and VD treatments.

The total CO_2 production calculated from the constant moisture data showed a very good, positive linear relationship to CO_2 production measured during dry/wet cycles, with $R^2 = 0.96$ and 0.79 for silt loam and clay loam soils respectively (Figure 4A). All of the measured values fell well above the 1:1 line indicating that predictions based on constant moisture results underestimate the effects of repeated dry/wet cycles.

Much of the error in the calculated CO_2 production data arises from an underestimation of mineralisation when the dry soil is rewetted, especially during the first dry/wet cycle and an over estimation of the rate at which respiration decreases as the soil dries, especially in the first drying phase. There is evidence that the fit improves for subsequent dry/wet cycles (Figure 4C).

The N_2O emission data was inherently more variable than the CO_2 data. The clay loam soils tend to have much higher N_2O emissions than the silt loam soils, probably due to the finer texture of these soils leading to the creation of anoxic sites upon rewetting. The correlation between the calculated and measured N_2O emission data was poor, with actual N_2O emissions being, in some cases, several orders of magnitude higher than the calculated emissions (Figure 4B).

Conclusions
Not surprisingly, our results showed a positive relationship between soluble soil C fractions and total soil organic matter. There was also evidence that soluble soil C fractions were substrates for the C mineralised during dry/wet cycles. However, these relationships were more evident in silt loam soils than clay loam soils. This may be because clay loam soils have a greater affinity for sorption of dissolved organic matter, reducing its availability.

Soil N dynamics were greatly influenced by soil texture, particularly N_2O emissions. Fine-textured clay loam soils have a higher proportion of small pores than coarser textured silt loam soils and hence more anoxic sites, increasing N_2O production. Repeated drying and rewetting cycles, even of only moderate intensity, led to much higher N_2O emissions in these finer textured soils.

In order to use CO_2 production data from soils held at constant moisture contents to accurately predict CO_2 production in soils exposed to dry-rewet cycles, knowledge of the stress history for the soil would be required (e.g. size, duration and frequency of rainfall events, dry rates etc.).
Our results indicate that prediction of N_2O emissions in soils exposed to dry-rewet cycles using emission data from soils held at constant moisture contents would be very inaccurate, primarily due to the inherent variability of N_2O emissions in soils.
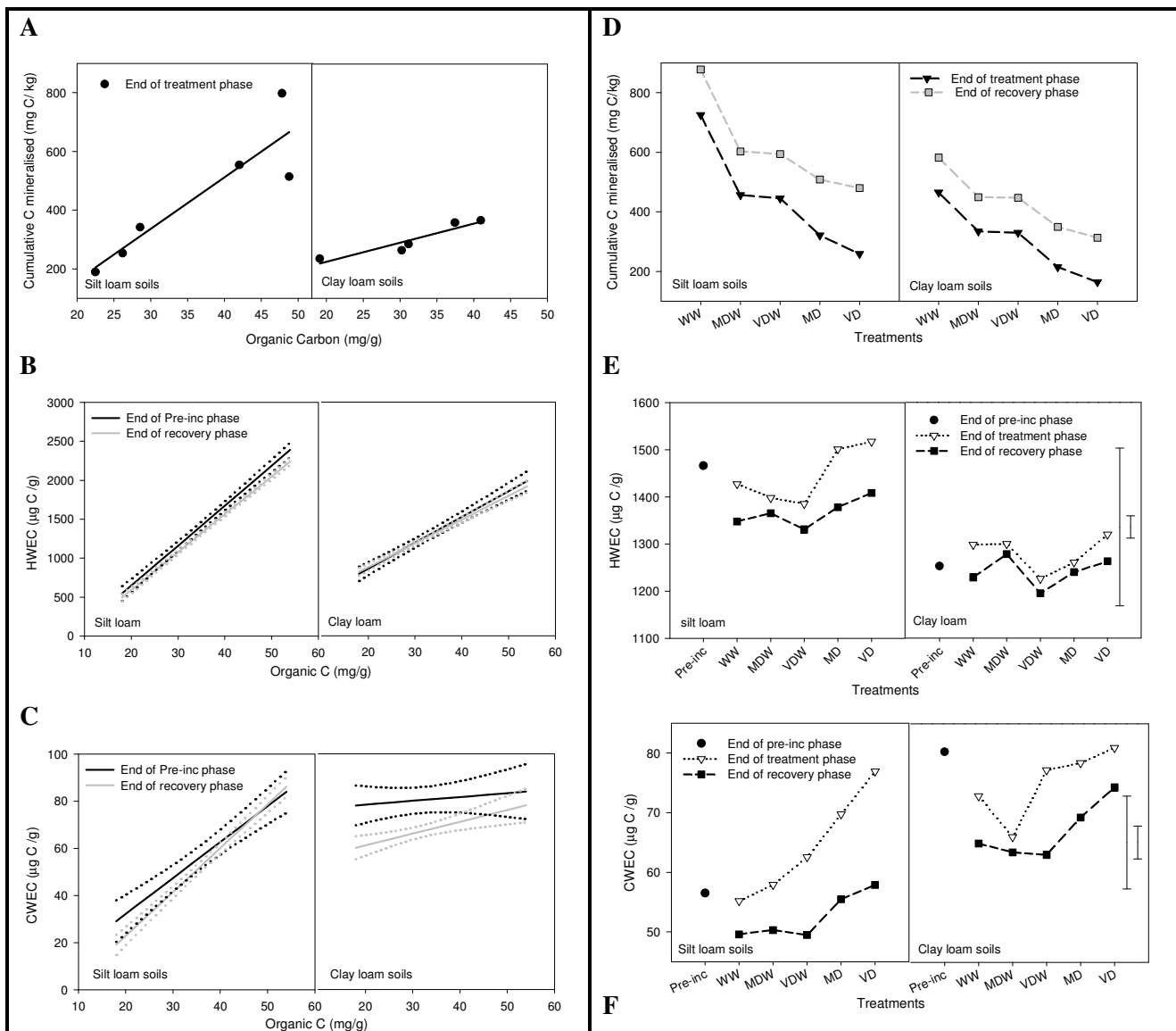
Figure 2. The effect of soil organic matter content on A) C mineralisation and B) CWEC and C) HWEC contents in silt loam and clay loam soils (the dotted lines are 95% Confidence Intervals), and the effect of dry/wet cycles on D) C mineralisation, and E) CWEC and F) HWEC contents in silt loam and clay loam soils (The short bar is the 5% LSD for comparing treatment means within each soil type; the tall bar is for comparing treatment means between soil types).
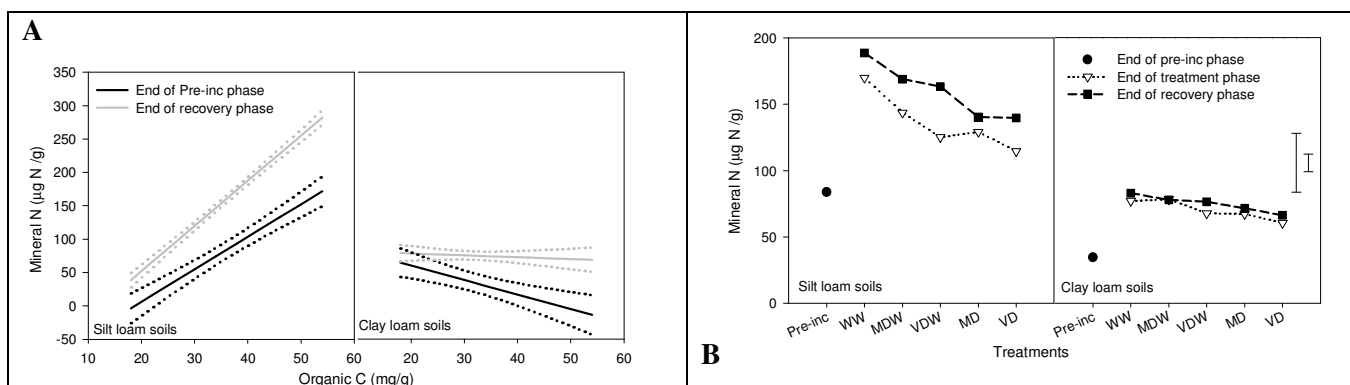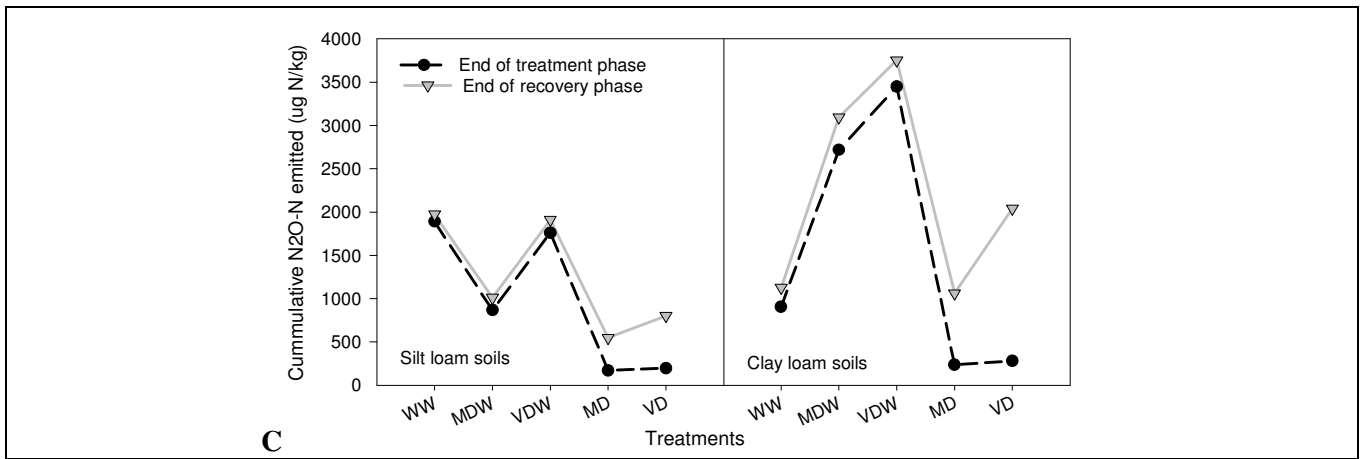
Figure 3. The effect of soil organic matter content on A) mineral N content and dry/wet cycles on B) mineral N content and C) N₂O emissions in silt loam and clay loam soils (the dotted lines are 95% Confidence Intervals and the short bar is the 5% LSD for comparing treatment means within each soil type; the tall bar is for comparing treatment means between soil types).
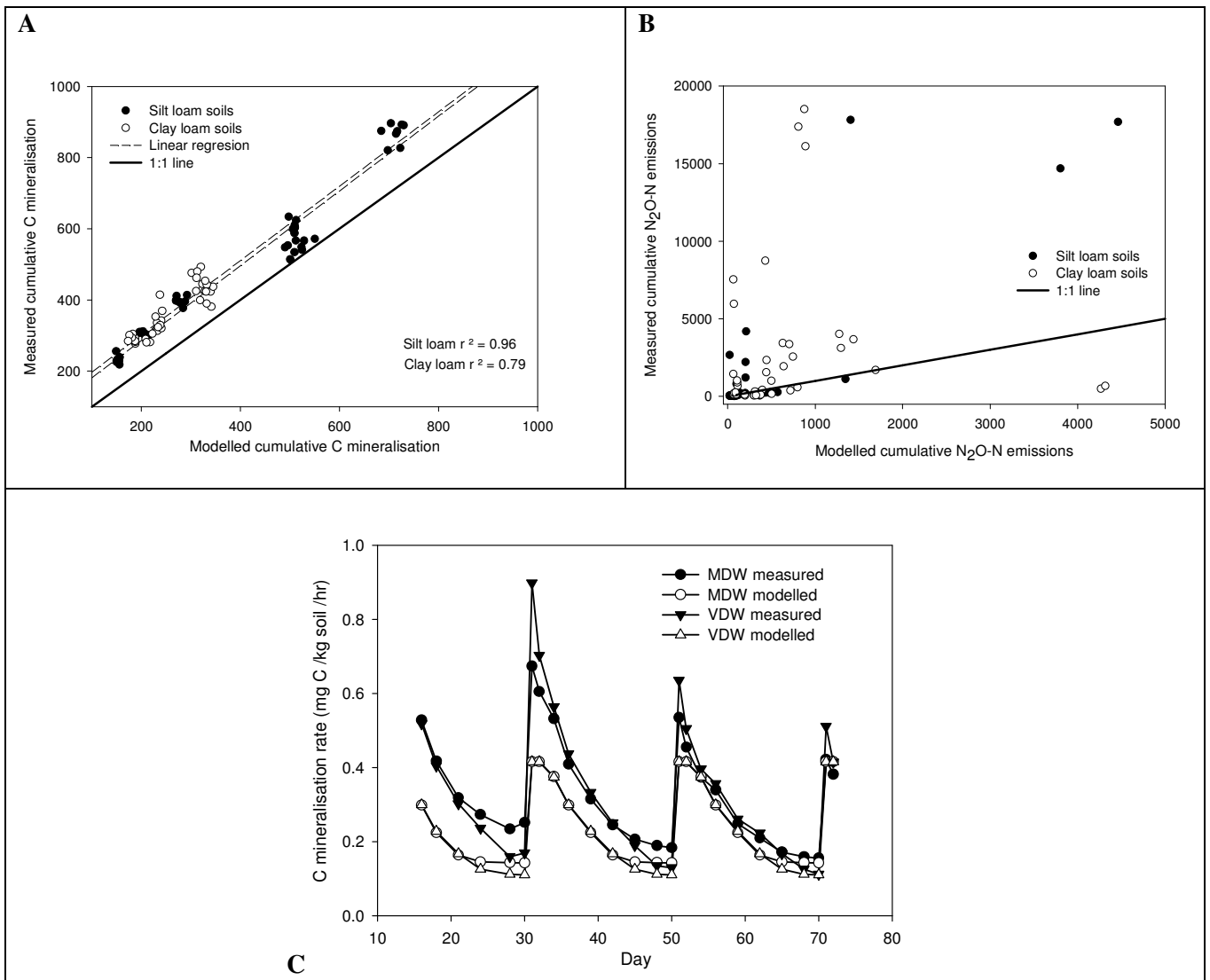
Figure 4. Comparison of calculated and actual A) cumulative C mineralisation B) cumulative N₂O-N emissions and C) mean C mineralisation rates.

Acknowledgements

Does Chicory inhibit or promote mineralisation?

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Abstract
Chicory is a perennial herb that has the potential to be incorporated into phased farming systems where lucerne is not well adapted. However, little is known about how chicory will influence the availability of N for the following cropping phase. A 16 week incubation study was conducted with chicory and lucerne plants that had been separated into leaves, stems, fine roots and coarse roots. From the beginning of the experiment all plant components of lucerne except for stems underwent net mineralisation. In contrast, the coarse roots were the only plant component for chicory to undertake net mineralisation from the beginning of the experiment. The stems for both chicory and lucerne did not undergo any net mineralisation during the 16 weeks of the study. Accordingly, the stems only released 1.1 % and 1.7 %, respectively, of N applied in plant material during the study. Despite having a C: N ratio approximately a third of the stems, chicory leaves only released 2.5% of N from plant material, which may be due to the delay in net mineralisation during the first 8 weeks of the incubation. Coarse chicory roots released 10.9 % of N from the plant material, although the C: N ratio was 32.3, which was double that of the lucerne roots. Therefore, chicory leaves actually inhibited net mineralisation during the first 8 weeks of the experiment while coarse chicory roots promoted net mineralisation in comparison to lucerne residues.

Key Words
Chicory, lucerne, net mineralisation, net Immobilisation, C: N Ratio

Introduction
Chicory (*Cichorium intybus*) is a perennial herb with the potential for incorporation into farming systems where lucerne (*Medicago sativa*) is not well adapted, such as acidic and waterlogged conditions (Dear and Ewing, 2008; Li *et al.,* 2008). Being a short-term perennial species, chicory could be combined with a highly productive annual legume in phased farming systems allowing farmers to adopt shorter and quicker pasture rotations (2-3 years), in comparison to a lucerne rotation that often requires longer rotations (4-5 years) (Kemp *et al.,* 2002). Chicory's responsiveness to and recovery of applied nitrogen (N) is extremely efficient in comparison to other pasture and crop species currently used in mixed farming systems. The ability of chicory to return N to the system for the following cropping phase will be dependent on how chicory influences mineralisation.

The timing and quantity of N mineralisation from pasture residues is affected by the maturity and species composition of the pasture (Angus *et al.,* 2006; Peoples *et al.,* 2001), timing of pasture removal (Dear *et al.,* 2009 In Press), and the biochemical characteristics of the residues (Constantinides and Fownes 1994; Kumar and Goh, 2003; Nourbakhsh and Dick, 2005). The key biochemical factors considered to affect plant residue decomposition are the C: N ratio, lignin, polyphenol and cellulose contents , and the ratio of lignin:N (Jensen *et al.,* 2005), polyphenol: N (Palm and Sanchez, 1991) and polyphenol + lignin: N (Constantinides and Fownes, 1994; Fox *et al.,* 1990).

To date there has been limited investigation into the residue quality and mineralisation of mature chicory plants. An incubation study was conducted to test the hypothesis that chicory roots, stems and leaves would mineralise either at a similar rate or faster than lucerne plants.

Methods
The Soil
Soil was collected from the 0 – 15 cm depth interval of a Red Chromosol soil (Isbell, 1996) derived from granite, located on the Charles Sturt University farm, Wagga Wagga. The area was under a pasture comprising of mixed annual broadleaf and grass species with little to no legume content, which has been the case for the past five years. The moist soil was passed through a 5 mm screen and mixed thoroughly with a cement mixer to obtain a homogenous sample.
Chemical analysis of the soil indicated the soil pH was 5.96 (1:5 1M KCl) and mineral N (NH_4^+, NO_3^- and NO_2^-) was 33.88 mg/kg. The exchangable cations were extracted and concentrations determined by atomic absorption

spectroscopy. The ECEC of the soil was 6.73 cmol+/kg, which was given by the sum of exchangeable Ca^{2+}, Al^{3+}, Mg^{2+}, Mn^{2+}, Na^+ and K^+ that were 4.51, 0, 0.64, 0.01, 0.02, 1.56 cmol+/kg, respectively. Field capacity of the soil was 18% gravimetric moisture content. To avoid drying the collected soil, subsamples were taken to determine the gravimetric moisture content. This measurement enabled the total mass of oven dried soil added to jars to be calculated.

The Plants
Established chicory and lucerne plants in their 3rd season were collected from the field in late September. Sampling involved excavating the entire plant including a large proportion of the roots. These plants were then prepared carefully for the various treatments.

Treatments
The chicory and lucerne collected served as plant treatments in addition to a no plant treatment, which was used as the control. Plant shoots were cut from the roots at the soil surface. The shoots were then separated into leaves and stems (primary stems). The roots were carefully washed free of any soil and separated into fine (< 1 mm diameter) and coarse (> 4 mm diameter) root fractions. Each plant species therefore had four separate plant fractions. Following separation each plant fraction was dried individually in the plant dehydrator at 80°C for 48 hours.

Nitrogen mineralisation was determined by an adaptation of the method described by Paul *et al*. (2001). A 1 g portion of the plant fraction was mixed thoroughly with 40 g of oven dry soil and then added to a 375 mL jar. The soil was then watered with deionised water to 90 % field capacity. On a weekly basis jars were opened for approximately 20 minutes to maintain adequate O_2 concentration within the jars. In addition, each week soil samples were re-wet to 90% field capacity weight with a fine spray of deionised water.

There were four replicates incubated for each treatment. Incubation jars were arranged in a completely randomised block design in a constant temperature (20°C) room. There were four blocks with one replicate in each block. All incubation jars were fully covered under aluminium foil to assist with the maintenance of constant temperature and low light intensity.

The duration of the experiment was 16 weeks with a total of 6 sampling times. Sampling of jars occurred immediately after the treatment application, 7 days later, 14 days later, 28 days later, 56 days later and at the completion of the experiment, 112 days after treatment application. At each sampling time incubation jars were distructively sampled by the addition of 200 mL of 1 M KCl for soil pH and mineral N analysis.

Results
The high C: N ratios of 48.1 and 45.2 for the chicory and lucerne stems, respectively, were significantly greater than all other plant fractions (Figure 1). The C: N ratios for coarse (32.3) and fine (37.3) chicory roots were significantly greater than that of the lucerne roots which were 16.1 and 17.2, respectively (Figure 1). The C: N ratio of the chicory leaves (17.5) was statistically the same as the lucerne roots (Figure 1). Whereas, the lucerne leaves had the significantly lowest C: N ratio of 11.2 (Figure 1). The quantity of N applied to jar for the chicory leaves, stems, coarse roots and fine roots was 2.4, 0.9, 1.3 and 1.1 mg/g, respectively. The quantity of N applied to jar for the lucerne leaves, stems, coarse roots and fine roots was 4.1, 1.0, 2.6 and 2.3 mg/g, respectively.

The mineral N for the control treatment remained relatively unchanged throughout the experiment (Figure 2). The control line in this experiment represents a significant boundary that separates net mineralisation and net immobilisation. Mineral N values exceeding the control indicate net mineralisation while values smaller than the control indicate net immobilisation. Therefore, all the plant fractions of lucerne except for stems underwent net mineralisation from the beginning of the experiment (Figure 2). In contrast, the coarse roots were the only plant fraction for chicory to undertake net mineralisation from the beginning of the experiment (Figure 2). Between week 8 and 16 chicory fine roots and leaves underwent net mineralisation (Figure 2). The stems for chicory and lucerne did not undergo any net mineralisation during the 16 weeks of the study (Figure 2).
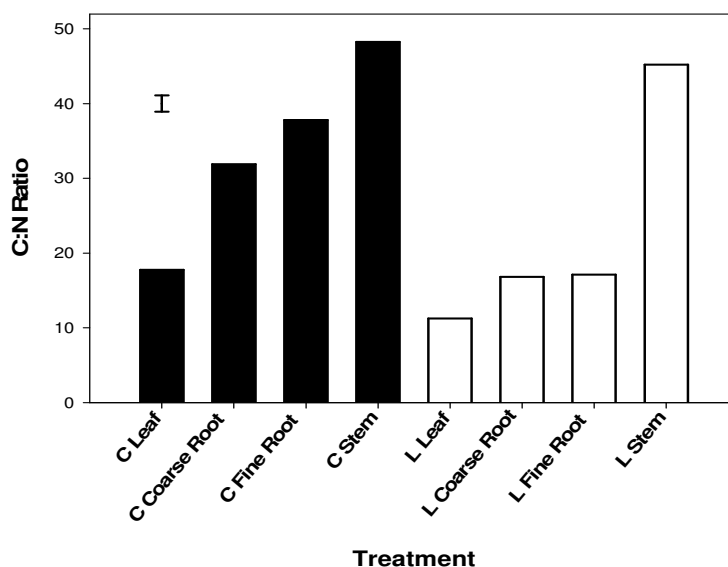
Figure 1. The C: N ratio of the leaves, coarse roots, fine roots and stems from 3 year old chicory (■)and lucerne (□) plants. Bars indicate L.S.D at p< 0.05.
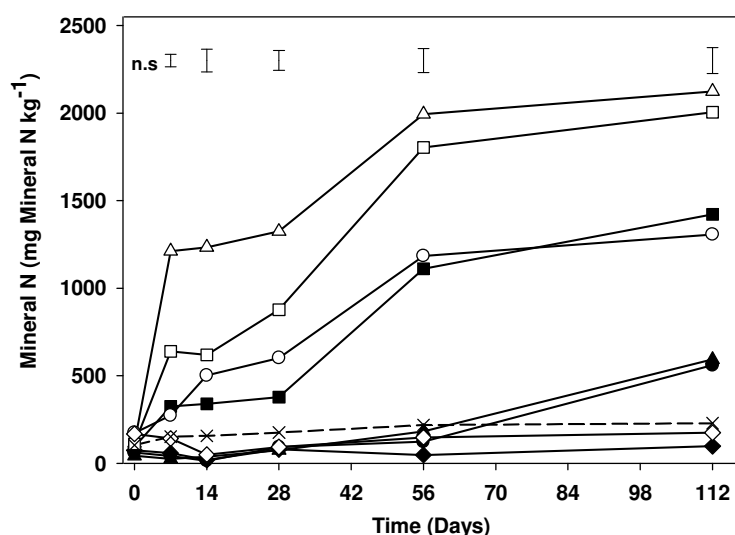
Figure 2. Mineral N concentration (mg/kg) of the soil at the six sampling times for the chicory (■) and lucerne (□) plants. Leaves, stems, coarse roots and fine roots are designated by triangles, diamonds, squares and circles, respectively. The control is designated by a cross and broken line. Bars indicate L.S.D at p< 0.05; n.s, not significant.

To give an indication of the mineralisation rate the proportion of N released from the 1 g of plant material was calculated and presented in Table 1. There was no significant difference in the proportion N released from the lucerne leaves (5.3 %), fine roots (6.5 %) and coarse roots (5.0 %) (Table 1), which all underwent net mineralisation from the beginning of the experiment. The fine roots of chicory also released 5.1% of possible N during the incubation despite only undergoing net mineralisation during the last 8 weeks of the experiment (Table 1). Although the chicory leaves (2.5 %) had a similar C: N ratio as lucerne roots the proportion of N released was not significantly different to the stem treatments, which were significantly lower than all other treatments (Table 1). In contrast, 10.9 % of the N applied in the coarse chicory root treatment was released, which was significantly greater than all other treatments (Table 1).

Table 1. The proportion of N released from the 1 g of plant material added following 16 weeks of incubation. Treatments designated with different letters within the table have released significantly different proportions of N during the incubation period (p< 0.05).

Treatment	Chicory (%)	Lucerne (%)
Leaf	2.5 a	5.3 b
Root (> 1 mm)	5.1 b	6.5 b
Root (< 4 mm)	10.9 c	5.0 b
Stem	1.1 a	1.7 a

Conclusion

Over the 16 weeks of the experiment lucerne behaved as expected with leaves, fine roots and coarse roots all undergoing net mineralisation, while lucerne stems with a high C: N ratio underwent net immobilisation. In contrast, chicory behaved a little differently. Chicory leaves, although having a similar C: N ratio as lucerne roots, underwent net immobilisation during the first 8 weeks of the experiment, which resulted in a lower proportion of N being released from the applied plant material. Coarse chicory roots on the other hand underwent net mineralisation, similar to lucerne roots, despite having nearly double the C: N ratio, which allowed it to release a significantly greater proportion of N from the applied plant material. In conclusion, chicory leaves inhibited net mineralisation during the first 8 weeks of incubation, whereas, coarse chicory roots promoted net mineralisation over the 16 weeks of the experiment in comparison to lucerne.

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Dynamics and fate of natural and waste organic material in soils: the role of the soil organic matter (SOM) recalcitrance in SOM turnover

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Abstract
Previous studies suggested that micropore surface area (MiS) of bio-macromolecules of biomass constitutes an important factor that explains their preservation in soil, that is, the preservation against biological degradation. On the other hand it has been reported that biochemical catalysis are limited in theirs action by the very complex macroscopic and microscopic structure of cell walls that limit mass transportation. Results of this work indicated the structure (nanostructure) of the cell wall playing a main role in the preservation of the organic matter in soil. Total microporosity and pore dimension correlated with biomass degradation. On the other hand chemical composition determined by CPMAS 13- NMR does not play a role in the definition of biomass recalcitrance.

Key Words
Biomasses, microporosity, organic wastes, recalcitrance, soil organic matter, surface gas adsorption

Introduction
The maintenance of soil quality is one of the main current challenges and a significant worldwide issue of the last two decades. Given that conservation and improvement of soil organic carbon (SOC) levels are crucial to preserving soil quality and fertility (Lal 2005), there is still a need to thoroughly study the global biogeochemical carbon cycle dynamics and to understand the key factors that determine transfer of carbon into the soil organic matter The transformation of plant detritus and organic wastes into recalcitrant HS that would then form the slow carbon pool has been known for a long time as an important mechanism for SOM stabilization. Nevertheless, Authors clearly demonstrated that the conventional SOM fractionation in humic acid, fulvic acid and humin have no explaining power in terms of the residence time of carbon in soil. Therefore, these kinds of SOM pools cannot explain carbon turnover rates in soil (Helfrich et al. 2006). Recent findings indicate that mechanisms that contribute at the same time to SOM protection against decomposition in soil are biochemical recalcitrance, chemical association and physical sequestration (Marschner et al. 2008). Marschner et al. (2008) specifies that, if biological recalcitrance allows plant molecules and organic molecules from biomasses to be preserved in soil, long-term stabilization of organic carbon, implies more complex mechanisms such as chemical association and physical sequestration with the mineral components of soil that are not yet understood.

The term 'recalcitrance' is used to describe the phenomenon by which plant tissues exhibit the natural resistance against microbial and enzymatic deconstruction (Himmel et al. 2007). Despite recent progress, the nature of plant biopolymer recalcitrance remains unclear and new methodological approaches such as analysis, for example, at the nanometer scale, may be promising tools to identify the ultrastructure and the chemical topography of plant cell walls (Himmel et al. 2007). Cell wall structure has e natural recalcitrance that limited enzymes activity (Himmel et al. 2007). It has been reported that biochemical catalysis are limited in theirs action by the very complex macroscopic and microscopic structure of cell wall that limit mass transportation (Himmel et al. 2007). In this study, the preservation of biomass organic matter has been investigated pointed out the role that nano-scale structure of the biomass plays in the preservation of the OM in soil and so the role that the organic matter of organic wastes play in the soil OM balance. Here we proposed preliminary results of a more large study under construction.

Methods
Biomasses
Different biomasses were selected for this work: plant residues, crop energy plants and lingo-carbohydrates complexes isolated after acid hydrolysis (Table 1). Other biomasses and organic wastes are under study. Biomasses were incubated in soil for long time (3 months) dosing an amount of 20 g C/kg soil dry matter. CO_2 evolution was detected by using NaOH trap and data reported as cumulative results.

CPMAS ^{13}C NMR spectroscopy
Cross-polarization magic-angle spinning ^{13}C nuclear magnetic resonance (CP MAS ^{13}C NMR) spectra on solid samples were acquired at 10 MHz on a Bruker AMX 600 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany). The spectra obtained were subdivided into four regions: alkyl C (0–50 ppm) (lipids, aliphatic polymers, and fatty acid; O-alkyl C (50–110 ppm) (polysaccharides and proteins); aromatic C (110–162 ppm) (lignin); carbonyl C (162–190 ppm) (carboxyl groups and amide carbonyls).

Micropore analyses
Micropore surface area (MSA) (half pore diameter of 0.22–0.72 nm) were determined by gas adsorption analysis of dried samples (0.5 g) using a porosimeter (NOVA 2200e, Quantachrome, Boynton Beach, FL, USA). Analyses were carried out by using CO_2 (273 K) and were preceded by a degassing procedure performed at 80 °C for 16 h. For calculation of micropore distribution, the nonlocal density functional theory method was applied to measure the CO_2 adsorption isotherms.

Result
Biomasses studied differed for both chemical composition and physical characteristics (Table 1 and 2). All biomasses were characterized by the high presence of microporosity surface (MiS) (pores of 0.3-1.5 nm of diameter). Data indicated that the recalcitrance, i.e. the natural resistance against microbial and enzymatic deconstruction was associated to the MiS. LCC complexes as expected, were less degraded in soil during incubation trials, and they were characterized by a high MiS. On the other hand biomasses characterized by young tissues, such as plant residues were largely degraded in soil and showed low MiS values.

Table 1. Microporosity surface and volume measured for biomasses studied.

	$S_{\mu p}$ (m^2/g) 0.3-1 nm	$S_{\mu p}$ (m^2/g) 1-1.5 nm	$S_{\mu p}$ tot (m^2/g)	$V_{\mu p}$ (cm^3/g)
Giant Cane[a]	39.93±1.08	1.59±1.16	41.52±0.08	0.014±0.00
Miscanthus [a]	48.11±2.01	3.98±2.62	52.10±4.63	0.018±0.002
Proso millet[a]	52.12±1.67	1.68±0.13	53.80±1.80	0.017±0.001
Sorgum[a]	36.46±3.46	1.76±0.66	38.22±2.79	0.013±0.001
Rivet wheat[a]	46.2±0.90	0.67±0.73	46.87±1.63	0.016±0.001
Wheat[a]	37.84±2.45	0.00±0.00	37.84±2.45	0.013±0.001
Wheat[b]	87.07±1.3	8.25±0.8	95.32±1.2	0.033±0.01
AlfaAlfa[a]	11.69±1.32	0.00±0.00	11.69±1.32	0.004±0.000
AlfaAlfa[b]	54.09±1.29	7.72±1.93	61.81±0.65	0.022±0.001
Pine needles[a]	35.16±5.18	0.25±0.36	35.41±5.53	0.0115±0.002
Pine needles[b]	82.47±2.46	7.73±0.93	90.20±3.39	0.0285±0.002
Leaves of beech[a]	51.91±0.74	7.32±5.11	59.23±5.85	0.0215±0.003
Leaves of beech[b]	82.35±4.36	10.83±0.67	93.18±3.68	0.0315±0.000
Wood of beech[a]	70.69±1.91	0.65±0.73	71.34±1.17	0.022±0.000
Straw mix	80.19±0.83	3.59±5.07	83.78±5.90	0.03±0.00

[a]Untreated plant.
[b]After acid hydrolysis with H_2SO_4 13.50 mol/L at 4°C for 24 h.

Degradability, measured as CO_2 (data not showed) produced during incubation tests, was not influenced by chemical composition. On the other hand MiS well correlated with degradability (r = -0.87, p<0.01). Results obtained can be discussed and interpreted taking into consideration that microporosity makes the enzyme inaccessible to organic molecules having a size larger than pores (Carpita and McCann, 2000; Adani *et al.* 2006; Adani *et al.* 2009; Papa *et al.* 2010). Therefore, the presence of a higher proportion in the biomass of fractions not accessible to the enzyme, i.e. higher MiS, could explain the lower degradability of biomass.

Conclusion
Results indicated that biomass is formed by a ultra-microporosity (pores below 0.8 nm) that limiting the enzyme activity preserved the OM from degradation. Therefore it can be concluded that the first step of OM preservation (humification ?) in soil consist in the preservation of the organic molecules.
Nevertheless, literature suggest that most likely chemical recalcitrance is not the only mechanism in the preservation of OM and that, more complex processes such as physical protection or interactions with mineral surface should be considered and could play a main role in OMN preservation.

Table 2. Area of CP MAS ^{13}C NMR bands.

	Aliphatic C bonded to other aliphatic chain or to H	O-CH$_3$ or N-alkyl-C O-alkyl-C di-O-alkyl-C	Aromatic-C phenol-C or phenyl ether-C	Carboxyl C + keto C
	0-50	50-115	115-160	160-210
		Band range (ppm)		
Giant Cane[a]	10.77	76.16	8.50	4.58
Miscanthus[a]	8.22	75.73	10.73	5.32
Proso Millet[a]	8.94	78.97	8.16	3.94
Sorghum[a]	11.31	75.71	8.00	4.98
Rivet Wheat[a]*(straw)*	10.26	73.10	10.09	6.55
Wheat[a] *(straw)*	10.02	78.01	7.70	4.27
Wheat[b]*(straw)*	20.56	42.46	29.40	7.59
Alfa Alfa[a]	27.14	56.95	6.17	9.75
Alfa Alfa[b]	44.36	30.93	13.01	11.70
Pine needles[a]	19.01	64.31	11.27	5.40
Pine needle[b]	40.47	29.50	23.24	6.78
Leaves of beech[a]	19.27	61.36	12.58	6.79
Leaves of beech[b]	34.24	32.85	25.28	7.62
Wood of beech[a]	5.86	80.60	9.09	4.44
Straw mix[a]	6.75	79.71	9.49	4.05

[a]Untreated plant.
[b]After acid hydrolysis with H$_2$SO$_4$ 13.50 mol/L at 4°C for 24 h.

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Effect of Fresh and Composted Organic Amendment on Soil Compaction and Soil Biochemical Properties of Citrus Orchards in the Mekong Delta, Vietnam

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Abstract

The objectives of this study were to evaluate the degree of soil degradation and the effect of organic amendment on improving soil properties and fruit yield of citrus orchards on alluvial soil. Sixty raised beds of citrus orchards were selected in a range of age from less than 10 years, 12-18 years, 22-28 years and 30 years. Soil samples were collected and analyzed for selected soil properties. The effects of 10 t ha^{-1} sugarcane filter cake compost plus *Trichoderma* spp. and 20 t ha^{-1} of fresh *Tithonia diversifolia* were studied in orange orchards where the raised beds had been constructed for more than 26 years. Both these organic treatments were combined with recommended inorganic fertilizer (250gN-200g P$_2$O$_5$ -120g K$_2$O.plant^{-1}), and compared with usual farmer practice (628g N-327g P$_2$O$_5$ - 64g K$_2$O.plant^{-1}). Soil analyses indicated that soil degradation occurred in 30 year old raised beds constructed. Soil aggregate stability was low and soil strength resistance was in the range of soil compaction. Soil organic matter, cation exchange capacity (CEC), and base saturation percentage were low compared to other raised beds (P<0.05).

Amendment with sugarcane filter cake compost (plus *Trichoderma* spp.) and fresh *Tithonia diversifolia* led to an increase soil organic matter content, available nitrogen and phosphorus, CEC, percentage base saturation, soil respiration, soil aggregate stability and to reduced soil compaction (P<0.05). Fruit yield was also improved with both treatments compared with the farmers usual practice, which gave low fruit yield (P<0.05) and resulted in poor soil quality in terms of soil physical and chemical properties. While both treatments enhanced fruit yield, the application of 10t.ha^{-1} of sugarcane filter cake was more effective than the application of 20 t ha^{-1} of fresh *Tithonia diversifolia*.

Key Words
Soil degradation, organic amendment, soil compaction, citrus fruit yield

Introduction
Adding fresh and composted organic substrates usually has beneficial effects on soil aggregate stability, humification and microbial activity (Bipfubusa et al., 2008). This study was carried out to clarify whether there was soil degradation in old raised beds citrus and whether fresh and composted organic substrate could improve soil physical chemical properties and fruit yield in orange orchards.

Methodology
Soil survey and soil sampling were carried out on sixty raised beds in citrus orchards that had been constructed for less than 10 years, 12- 18 years, 22-28 years and more than 30 years. Soil samples were analyzed for soil strength resistance, soil aggregate stability and some selected chemical properties. Four treatments were applied, with three replicates per treatment, arranged in a complete randomized block design: 1)10 Mg.ha^{-1} sugarcane filter cake compost (plus *Trichoderma* spp. Fungi); 2) 20 Mg. ha^{-1} of fresh *Tithonia diversifolia* plus reduced inorganic fertilizer; 3) Reduced inorganic fertilizer (250gN-200g P$_2$O$_5$ -120g K$_2$O.plant^{-1}); 4) A control treatment representing the usual farmers' practice (628g N-327g P$_2$O$_5$ - 64g K$_2$O.plant^{-1}). The changes of soil properties and fruit yield were recorded.

Results
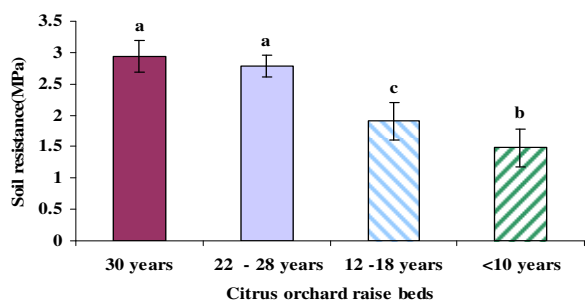
Figure 1. Soil compaction in raised beds of citrus orchards constructed for various lengths of time.
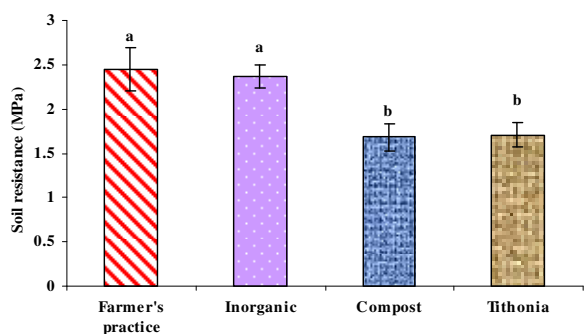
Figure 2. Effect of fresh *Tithonia* and sugarcane filter cake compost amendment on soil compaction in an orange orchard. Treatments: Compost -10 t ha^{-1} sugarcane filter cake compost ; Tithonia - 20 t ha^{-1} of fresh *Tithonia* ; Inorganic fertilizer - 250gN-200g P_2O_5 -120g K_2O.plant[-1]; Farmers' practice - 628g N-327g P_2O_5 - 64g K_2O.plant[-1].
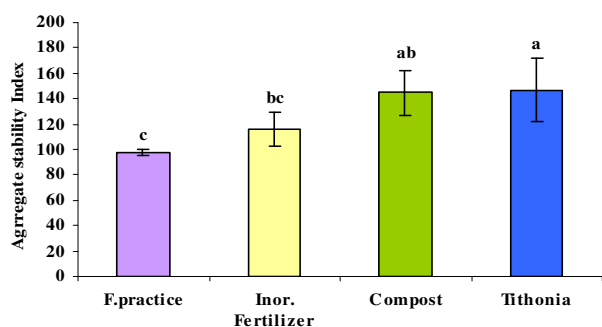
Figure 3. Effect of fresh *Tithonia* and sugarcane filter cake compost amendment on aggregate stability of soil. Treatments: Compost -10 t ha^{-1} sugarcane filter cake compost ; Tithonia - 20 t ha^{-1} of fresh *Tithonia* ; Inorganic fertilizer - 250gN-200g P_2O_5 -120g K_2O.plant[-1]; Farmers' practice - 628g N-327g P_2O_5 - 64g K_2O.plant[-1].
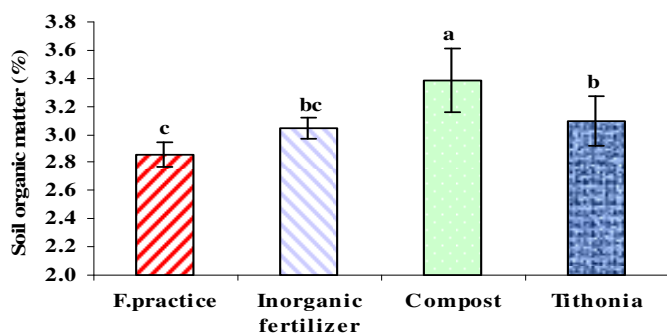
Figure 4. Effect of fresh *Tithonia* and sugarcane filter cake compost on soil organic matter. Treatments: Compost - 10 t ha^{-1} sugarcane filter cake compost ; Tithonia - 20 t ha^{-1} of fresh *Tithonia* ; Inorganic fertilizer - 250gN-200g P_2O_5 -120g K_2O.plant[-1]; Farmers' practice - 628g N-327g P_2O_5 - 64g K_2O.plant[-1].
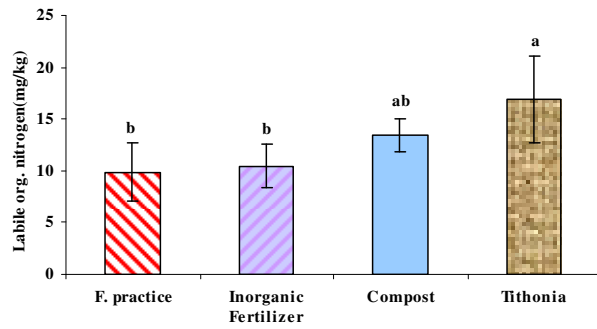
Figure 5. Effect of fresh *Tithonia* and sugarcane filter cake compost on labile organic nitrogen in soil.
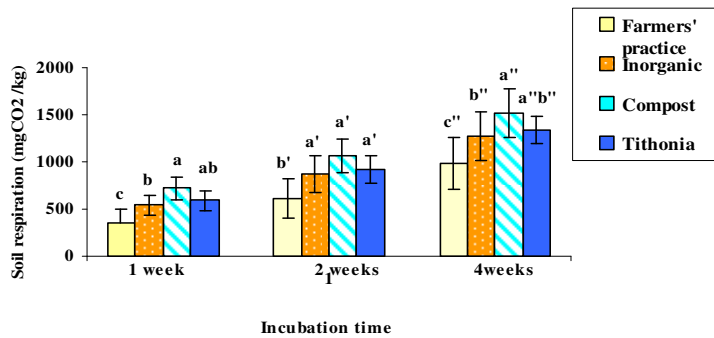
Figure 6. Effect of fresh *Tithonia* and sugarcane filter cake compost on soil respiration.
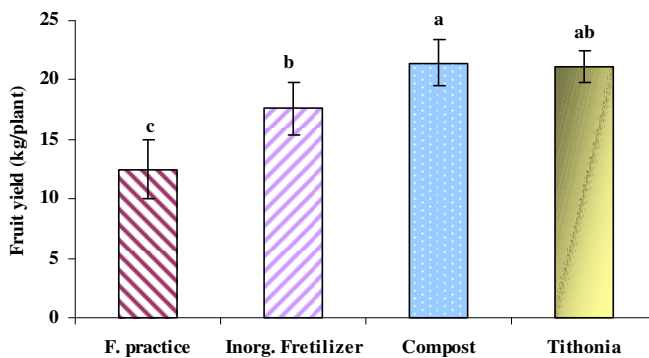
Figure 7. Effect of fresh *Tithonia* and sugarcane filter cake compost on orange fruit weight per plant. Treatments: Compost - 10 t ha^{-1} sugarcane filter cake compost ; Tithonia - 20 t ha^{-1} of fresh *Tithonia* ; Inorganic fertilizer - 250gN-200g P$_2$O$_5$ -120g K$_2$O.plant^{-1}; Farmers' practice - 628g N-327g P$_2$O$_5$ - 64g K$_2$O.plant^{-1}.

Conclusion

Old raised beds of orange orchards and high dosage of inorganic fertilizer used in the past lead to soil physical and chemical degradation. Soil amendment with fresh *Tithonia* and compost, which returned carbon to the soil, resulted in reduced soil compaction, increased aggregate stability, enhanced soil respiration, increased soil organic matter and labile organic nitrogen, and therefore increased fruit yield significantly.

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Effect of long-term compost application on humus composition of whole soils and their particle size fractions in a field subjected mainly to double cropping

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Abstract

The effect of long-term compost application (ca. 32 years) on humus composition of whole soils and their particle size fractions in a field subjected mainly to double cropping (upland and paddy crops) was investigated. Soil samples were collected from two plots of different types of management: (a) F plot, only fertilizer containing N, P, and K; (b) F + C plot, fertilizers plus compost. Each soil sample was divided into sand-sized aggregate, silt-sized aggregate, and clay-sized aggregate fractions by wet-sieving and sedimentation. In addition, coarse and medium sand-sized fractions were subdivided into "mineral particles" and "decayed plants" by a density fractionation. Compost application increased the amounts of total humus, humic acid, and fulvic acid in the whole soil and many size fractions, particularly, the silt-sized aggregate fraction. Their amounts of "decayed plants" were much larger than those of "mineral particles". On the other hand, the degree of humification of humic acids in the whole soils as well as many size fractions was decreased markedly by compost application. The findings indicate that in the continuous compost application field under study, the silt-sized aggregate fraction merits close attention as an important reservoir of soil organic carbon, including humic and fulvic acids.

Key Words

Paddy and upland fields, straw-cow dung compost, humic substances, humification

Introduction

A variety of organic amendments such as compost, farmyard manure, plant residues, food processing wastes, and sewage sludge is applied to various agriculture soils. Many investigators have observed the effects of these amendments on the physical, chemical, and biological properties, and fertility of soils in upland and paddy fields. However, the role of the amendments in the soils of double cropped (upland and paddy crops) fields needs to be further studied. Humus, which is composed of organic matter with differing origins and degrees of transformation, is one of the most important constituents of soils, and it affects various soil properties and the global carbon cycle. Particle size fractionation of soil makes it possible to separate organic matter. The objective of the present study was to gain a better understanding of the effect of continuous compost application on the quality and quantity of humus, using whole soils and their particle size fractions in a field subjected to long-term double cropping (paddy rice and barley).

Methods

Field experiment

The field experiments with different types of management were established in 1975 at Yamaguchi Prefecture Agricultural Experimental Station, Yamaguchi, Japan. The soil at this site was classified as gray lowland soil (FAO-UNESCO: Eutric Fluvisol). From the field experiments, we selected two plots (200 m^2 each): (a) F plot, only fertilizers containing N, P, and K were applied; (b) F + C plot, fertilizers plus compost were applied. The same plots were used as paddy fields for rice in summer and as upland fields for barley in winter until June 2001. The application rate of N, P$_2$O$_5$, and K$_2$O for each crop was 100 kg/ha. After harvest (June and November), rice straw-cow dung compost was applied at the level of 15 Mg/ha. However, since June 2001, these plots were used only as paddy fields, and the amounts of fertilizer and compost applied were reduced by half. In April 2007, to obtain an average soil sample in each plot, soils were taken from the plow layer (0-15 cm) of five sites across each of the two plots and mixed well. The soils were air-dried, gently crushed, and then passed through a 2-mm mesh sieve. These sieved samples were used for analytical determinations and physical fractionation.

Particle size fractionation

The particle size fractionation of the soil samples was carried out as described elsewhere (Tanaka and Shindo 2009). Firstly, the samples were divided into five particle size fractions, namely coarse sand-sized aggregate (212-2,000μm, CSA), medium sand-sized aggregate (53-212μm, MSA), fine sand-sized aggregate (20-53μm, FSA), silt-sized aggregate (2-20μm, SIA), and clay-sized aggregate (< 2μm, CLA) fractions, by wet-sieving and sedimentation. Secondly, the CSA and MSA fractions were subdivided into "mineral particles" and "decayed

plants" by a density fractionation (decantation) in water.

Humus composition
Humus composition was analyzed according to the method described in Kumada (1987). Humus was extracted with a mixture of 0.1mol/L NaOH + 0.1mol/L $Na_4P_2O_7$ (1:1). Then, the extracts were separated into humic and fulvic acids by addition of H_2SO_4. The contents of humic acid (HA), fulvic acid (FA), and total humus (HT) were determined by the $KMnO_4$ oxidation method. In the present study, 1 ml of 0.02 mol/L $KMnO_4$ consumed was calculated as corresponding to 0.48 mg carbon (Ikeya and Watanabe 2003). The degree of humification (darkening) of humic acid was determined using color coefficient (Δ log K) and relative color intensity (RF) values, where the Δ log K is the logarithm of the ratio of the absorbance of humic acid at 400 nm to that at 600 nm; the RF represents the absorbance of humic acid at 600 nm multiplied by 1,000, and then divided by the number of milliliters of 0.02 mol/L $KMnO_4$ consumed by 30 ml of humic acid solution.

Results
In the whole soils, the amounts of HT, HA, FA, and extracted humus (HE, HA + FA) were much larger in the F + C plot than in the F plot. Similar results were obtained for the extraction ratio (HE/HT) and the precipitation ratio (PQ, HA/HE). In the F + C plot, the amount of HA greatly exceeded that of FA.
The recovery of mass weight by physical fractionation was 97.0 for the F plot and 101% for the F + C plot. Thus, the percentage distribution of mass weight in the particle size fractions was corrected to a total of 100% (Table 1). In both F and F + C plots, the distribution of mass weight in the particle size fractions increased in the order of CLA < FSA < MSA < SIA < CSA and it did not largely differ between these plots. As expected, in the CSA and MSA fractions of both plots, the distribution values of "mineral particles" were much larger than those of "decayed plants".

Table 1. Percentage distribution of mass weight in particle size fractions.
F plot: only fertilizers containing N, P, and K were applied; F + C plot: fertilizers plus compost were applied; CSA: coarse sand-sized aggregate fraction; MSA: medium sand-sized aggregate fraction; FSA: fine sand-sized aggregate fraction; SIA: silt-sized aggregate fraction; CLA: clay-sized aggregate fraction; "M": "mineral particles"; "D": "decayed plants".

Plot	CSA "M"	"D"	MSA "M"	"D"	FSA	SIA	CLA
F	31.1	1.1	19.7	0.9	14.1	21.3	11.9
F + C	32.7	1.3	17.1	1.7	12.6	25.3	9.3

In both plots, the HT, HA, and FA contents of particle size fractions were much higher in "decayed plants" of the CSA and MSA fractions than in the other fractions (e.g. Tables 2 and 3). However, the values (%) of quantitative distribution of the HT, HA, and FA in particle size fractions, which were calculated from the data of mass weight distribution (Table 1) and of humus content of fraction (Tables 2 and 3), were much larger in the SIA and CLA fractions than in the other fractions. In the F + C plot, the distribution values of the HT, HA, and FA were larger for the SIA fraction than the CLA fraction, and the reverse was true for the F plot. The findings indicate that continuous compost application accumulated humus into the SIA fraction.

Table 2. Quantitative distribution (%) of total humus in particle size fractions and their total humus contents. See Table 1 for the abbreviations.

Plot	Total humus content of fraction (g C/kg fraction) CSA "M"	"D"	MSA "M"	"D"	FSA	SIA	CLA	Quantitative distribution (%) CSA "M"	"D"	MSA "M"	"D"	FSA	SIA	CLA
F	1.28	246	1.00	187	1.52	18.3	39.9	2.88	19.4	1.43	12.2	1.55	28.2	34.4
F + C	3.17	222	1.13	185	3.72	27.9	60.3	5.09	14.0	1.19	15.4	2.30	34.6	27.4

Table 3. Quantitative distribution (%) of humic acids in particle size fractions and their humic acid contents.
See Table 1 for the abbreviations. N.D: Not determined because the amount was very small.

Plot	Humic acid content of fraction (g C/kg fraction)							Quantitative distribution (%)						
	CSA		MSA		FSA	SIA	CLA	CSA		MSA		FSA	SIA	CLA
	"M"	"D"	"M"	"D"				"M"	"D"	"M"	"D"			
F	N.D	111	N.D	61.4	N.D	7.71	14.8	N.D	23.4	N.D	10.7	N.D	31.7	34.0
F + C	N.D	118	N.D	112	N.D	21.3	26.7	N.D	13.5	N.D	16.8	N.D	47.7	21.9

In the present study, the degrees of humification of the humic acids (HAs) extracted from the whole soils and several fractions were determined. According to Kumada (1987), the degrees of humification of soil HAs become higher as $\Delta \log K$ value decreases and RF value increases. The degrees of humification of HAs extracted from the whole soils and the SIA and CLA fractions were much lower in the F + C plot compared to the F plot. Compost application induced a decrease of humification degree of HA. In the case of F + C plot, the degree of humification was lower in the SIA fraction than in the CLA fraction. Such a definite relationship did not occur for the F plot. In both plots, the amounts in "decayed plants" were much lower than those in the SIA and CLA fractions.

Table 4. Degrees of humification of humic acids in whole soils and their particle size fractions.
See Table 1 for the abbreviations. $\Delta \log K$: the logarithm of the ratio of the absorbance of humic acid at 400 nm to that at 600 nm; RF: the absorbance of humic acid at 600 nm multiplied by 1,000, and then divided by the number of milliliters of 0.02 mol/L $KMnO_4$ consumed by 30 mL of humic acid solution.

Plot	$\Delta \log K$ value					*RF* value				
	Whole soil	CSA "D"	MSA "D"	SIA	CLA	Whole soil	CSA "D"	MSA "D"	SIA	CLA
F	0.696	0.940	0.756	0.657	0.638	40	14	31	50	52
F + C	0.807	0.939	0.893	0.806	0.719	28	15	21	29	37

Conclusion

Continuous compost application in a field subjected to long-term double cropping increased the amounts of HT, HA, and FA in the whole soil and many particle size fractions, particularly the SIA fraction. In contrast, the degree of humification of HA was decreased by this application. The findings indicate that for long-term compost application, the SIA fraction may play an important role as a reservoir of soil organic carbon, including humic and fulvic acids.

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Effect of sulfadiazine on soil nitrogen mineralization

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Abstract
Soil nitrogen (N) mineralization is important for soil fertility, and has been suggested to provide 20 to 80% of the N required by plants. Effects of antibiotic sulfadiazine (SD), a widely used antibiotic in livestock production, on the amount of net N mineralized in the soil were studied. The results showed that SD significantly inhibited the mineralization of N, and the inhibition increased with increasing SD concentration and reaction time. This suggested that soil fertility may be reduced with the presence of SD, with higher reduction rates when the concentration of SD increased from 0 to 2 mg/kg and during the first 21 reaction days.

Key Words
Nitrogen mineralization, sulfadiazine, soil

Introduction
Antibiotics are widely used in intensive livestock farming as growth promoters and/or to treat infectious diseases (Boxall *et al*., 2003), particularly for pig and poultry (Boxall *et al*., 2004). Tetracyclines and sulphonamides are the most widely used antibiotics due to their effectiveness and price (Boxall *et al*., 2004). It was estimated that annual consumption of antibiotics for livestock farming accounted for 95 tonnes in the European countries, of which 78 tonnes were for pig production (Diaz-Cruz *et al*., 2003). Since 2006, the EU countries have prohibited the use of antibiotics as growth promoters, but the use of such drugs for prevention and treatment of diseases is still allowed. And it has been reported that over ten thousand tons of antibiotic were used for prevention and treatment of animal diseases (Diaz-Cruz *et al*., 2003). The actual consumption of the veterinary drugs in most developing countries including China and many south-east Asian countries, such as Malaysia, is not known.

Most of the antibiotics are poorly assimilated by the animals. About 25 to 75% of the antibiotics are excreted via feces or urine as the parent compounds or their metabolites and enter the environment either directly by spreading as manure or after collection and storage in form of sludge (Diaz-Cruz, *et al*., 2003). The presence of traces of these antibiotic residues in the environment can induce the development of antibiotic-resistant pathogens, causing serious problems to human health (Hirsch *et al*., 1999). Currently, the environmental hazards of veterinary antibiotics have received greater attentions (Boxall *et al*., 2004; O'Neil *et al*., 2001). Residual concentrations of antibiotics have been observed in soils, surface and ground water (Hamscher *et al*., 2002; Kolpin *et al*., 2002; Simon, 2005). They may affect the beneficial bacteria communities in the environment. The fate of antibiotics in the soil and aquatic environments such as sorption and fixation, mobility and transport, eco-toxicity, resistance and degradation are well documented (Tolls, 2001; Figueroa, *et al*., 2004; Kulshrestha *et al*., 2004; Thiele-Bruhn, 2003; Kong *et al*., 2006; Wang and Yates, 2008), but information on the effect of antibiotics on soil nitrogen mineralization is scanty.

Nitrogen is important for efficient crop production. The main sources of N used by crops are from (i) mineralization of soil organic N, (ii) decomposition of plant residues or organic amendments such as manure, and (iii) addition of N as inorganic fertilizer. Inefficient use of the applied N to the soil is likely to cause undesirable environmental impacts from NO_3^- leaching or gaseous N losses by denitrification and/or volatilization. Accurate estimates of the contributions of soil N to crop production are needed to minimize environmental impacts and production costs from overuse of N fertilizer, (Rice and Havlin, 1994). Soil N mineralization has been shown to provide 20 to 80% of the N required by plants (Broadbent, 1984). Manure, as readily decomposable organic materials, is an important source of plant nutrients (Zaman *et al*., 2004), and has been shown to increase soil total N (Mikha and Rice, 2004) and to improve the nutrient status of the soil (Zaman *et al*., 2004). Currently, the use of manure as fertilizer for crop production has been widely practised. However, mineralization of soil organic matter and crop residue is a complex process, and is mainly via the activity of microorganisms. Sulfadiazine (SD) is broad spectrum bacteriostatic antibiotics, which inhibits dihydropteroate synthesis in the folic acid pathway (O'Neil *et al*., 2001), and reduces the reproductive functions of bacteria. Therefore, antibiotic residue in the livestock manure, when applied to the soil as fertilizer, may affect the

activity of microorganism and thus soil N mineralization. As mentioned earlier, that information on the effect of antibiotics on soil N mineralization is scanty, this study was conducted to provide such information.

Materials and Methods
Chemicals
Sulfadiazine (SD) (Sigma-Aldrich, USA) stock solutions were prepared at a concentration of 50 mg/L in deionised water, and further diluted to the experimental concentration standards in mobile phase to construct a standard calibration curve. Other chemicals of analytical grade were from Guangzhou Chemical Co., China.

Preparation of the soil samples
Red soils, widely used for the growing of vegetable, were collected from Dazhen village, Nanhai district, Foshan city of South China (23.08656 °N, and 113.10952°E) for this study. The sampling depth was 0-20 cm. Prior to the experiment, the soils were dried under open shade, ground to pass through 200 mesh screen.

Experimental procedure
Sulfadiazine (SD) was used as the model antibiotic for this study, to investigate the effect of SD on soil net N mineralization. The SD stock solutions were added into the soil samples to achieve the respective experimental concentrations of 0, 0.2, 0.5, 1, 2, 6, 10, 15 and 20 mg/kg. On day 7, the soils were sampled and stored for the study of net N mineralization. For the experiment on SD reaction times in the soil N mineralization, the concentrations of SD in the soil were 0, 0.5, 2, 20 mg/kg, respectively. On day 0, 7, 14, 21, 28 and 35, net N mineralizations of the respective treatments were determined.

Laboratory analysis of soil N mineralization
Soil samples from the treatments were shaken and extracted in 2 M KCl solution three times (15 min each in a serial extraction) to extract all available NH_4-N and NO_3-N. NH_4-N were analysed by Nessler's colorimetric method and NO_3-N were by Ion Chromatography Analyzer (Dionex ICS-90, USA) equipped with a Polysulfonate Ion Exclusion Column. The eluent of the ion analytical column contained the following: 8 mM of Na_2CO_3, 1 mM of $NaHCO_3$, and 45 mM vitriol. The amount of N mineralized in the soil at each sampling time was determined by subtracting the concentration of NH_4-N and NO_3-N in the soil at the beginning of the study from that at each sampling time and multiplying the dry weight of the total soil in each tube. Potentially mineralizable N (N_0) and the rate constant (k) were determined by laboratory incubation and applying a first-order exponential model, based on the leaching method proposed by Cabrera and Kissel (1988) as modified by Garcia (1992).

Results
Effect of SD concentrations on the soil N mineralization
Figure 1 presents the effect of different SD concentrations on soil net N mineralized. The result indicated that net N mineralized reduced with increased SD concentration. The inhibition of soil net N mineralized was more sensitive in the lower concentrations of SD than in the higher concentrations. The turning point of the inhibition effect (i.e. the point at which rapid inhibition ended and a more gradual inhibition began) was at 2 mg/kg SD. When the concentration of SD increased from 0 to 2 mg/kg, net N mineralized decreased from 0.170 to 0.148 mg/g, but when the concentration of SD increased from 2 to 20 mg/kg, net N mineralized decreased at a slower rate, from 0.148 to 0.142 mg/g. The above results suggest that soil fertility may be reduced with increasing SD concentrations, at a higher rate initially (0-2 mg/kg) than the subsequent higher SD rates (2-20 mg/kg).
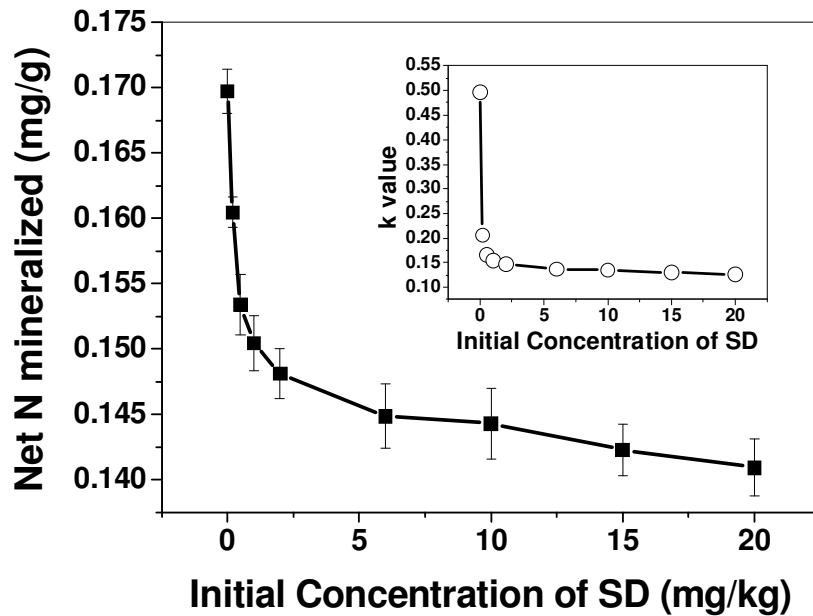
Figure 1. The effect of concentration of SD on soil net N mineralized.

SD reaction times on soil N mineralization

Net N mineralized remained almost the same with time in control and initially rapid (0-21 day) and then slowed down (21-35 day) in the SD treatment. There were significant differences in the net N mineralized rates (r value) between the control and SD treatments. This indicated that the soil fertility was influenced by both, the SD concentration and the reaction time. And the fertility decreased with the time, especially during the first 21 days.
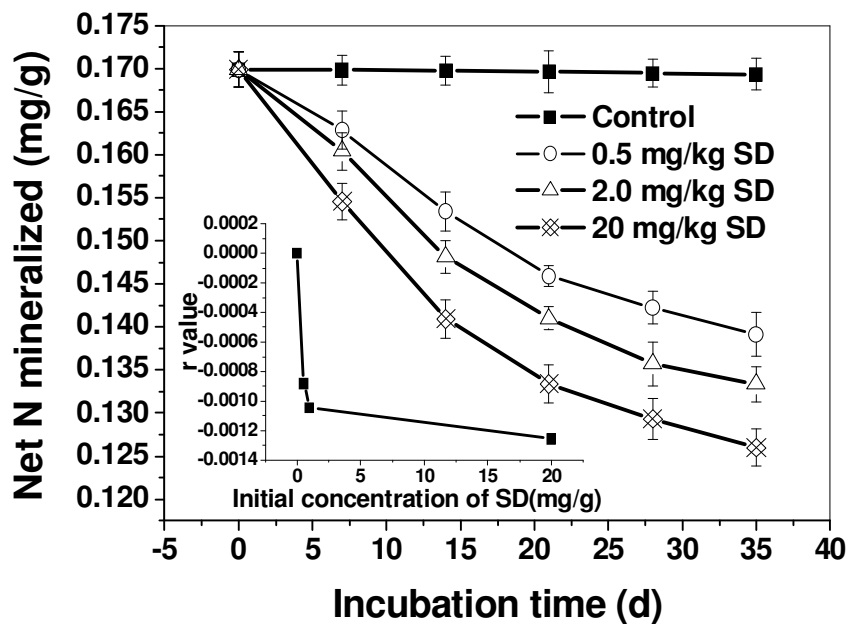
Figure 2. The effect of SD reaction time on the net N mineralized.

Conclusion

This study presented the effects of SD concentration and reaction time on the soil net N mineralized. Result showed the net N mineralized significantly affected by SD concentration and reaction time in the red soils used in this study. Higher SD concentrations resulted in lower net N mineralized. The amount of net N mineralized reduced with the time, initially rapid and later slowed down. This indicated that red soil fertility reduced with increased SD concentration and reaction time.

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Effect of temperature on soil microbial biomass, enzyme activities, and PLFA content during incubation period of soil treated with organic materials

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Abstract

This study was carried to evaluate the effect of temperature on soil microbial biomass, enzyme activities, and phospholipid fatty acid(PLFA) content during incubation period of volcanic (VAS)and non-volcanic ash soil(NVAS) treated with organic materials such as 2 types mixed pellet(OFPL) and powder organic fertilizers(OFPD), pig manure compost(PMC), and food waste compost(FWC). Soil microbial biomass N was high in NVAS treated with organic fertilizers and in VAS treated with PMC and FWC, respectively. At 75 days, PLFA content was higher in NVAS than in VAS. Urease activity in NVAS treated with OFPL followed the order of 10°C(75.0)>20°C(16.3)>30°C(4.6 ug NH_4-N/g/2h) at 150 days. It was decreased gradually at the high temperature and with time. Glucosidase activity was higher in NVAS than in VAS. The correlation coefficient between soil microbial biomass C and microbial activity indicators showed that PLFA was highly significant at r=0.91 in NVAS and for glucosidase was r=0.83 in VAS. Soil microbial activities showed differences in sensitivities depending on soil type and temperature.

Key Words

Volcanic ash soil, organic materials, PLFA, soil enzyme, microbial biomass C, N

Introduction

Environmental factors such as soil type (volcanic or non-volcanic ash soil, etc.), temperature, soil moisture, application of organic fertilizers play an important role in microbial activity. Soil microbial activity was low due to the properties of allophane in volcanic ash soil. When soil temperature was high, organic matter decomposed easily in soil, but some organic matter was resistant against decomposing process because of its constituents. Nutrient release from organic matter and soil microbial activity were affected by soil characteristic, temperature, and organic matter type. This study was carried out to evaluate soil microbial activities according to soil temperature in two soils treated with organic materials.

Methods

Treatment

Experimental soils were mixed well after adding water to 50% of soil moisture content and 2g of four organic materials added to volcanic (VAS) and non-volcanic ash (NVAS) soil (30g < 2 mm). The soils were incubated at 10, 20, 30°C. Soil samples were taken to analyses microbial biomass C and PLFA at 75 days, microbial biomass N and soil enzyme at 150 days. Soil samples stored immediately at 4°C for soil enzyme activity and biomass C, N and at -20°C for PLFA analysis.

Analysis

Dehydrogenase activity was measured by the triphenylformazan method (Rossel and Tarradellas 1991). Urease (Tabatabai 1976) and β-glucosidase (Garcia *et al.* 2000) activities were measured by the THAM buffer method. PLFA analyzed with GC‐FID instrument after Bligh/Dyer first-phase extraction (Bligh and Dyer 1959). Biomass C (Vance *et al.* 1987) and N (Amato *et al.* 1988) were measured by the Ninhydrin method.

Results

Soil microbial biomass C was high when soil temperature was high for both OFPL and OFPD treated VAS (Figure 1). Soil microbial biomass N was high in NVAS treated with organic fertilizers and in VAS treated with PMC and FWC, respectively (Figure 2). At 75 days, PLFA content was higher in NVAS than in VAS (Figure 3). Urease activity in NVAS treated with OFPL showed in the orders of 10 °C (75.0)>20 °C (16.3)>30 °C (4.6 ug NH_4-N/g/2h) at 150 days. It was decreased gradually with temperature and time, and was high at 10°C in VAS. Correlation coefficients between soil microbial biomass C and microbial activity indicators showed that PLFA was highly significant r=0.91 in NVAS as glucosidase r=0.83 in VAS (Table 1).

Table 1. Correlation coefficient between microbial activity indicators and microbial biomass C content.

Temperature (°C)	Non-volcanic ash soil				Volcanic ash soil			
	10	20	30	Average	10	20	30	Average
Biomass N	0.47	0.60	0.46	0.51	0.47	0.54	0.76	0.59
PLFA	0.93	0.83	0.96	0.91	0.90	0.44	0.25	0.53
Glucosidase	0.77	0.77	0.38	0.64	0.95	0.80	0.74	0.83
Urease	0.66	0.51	0.37	0.51	0.41	0.79	0.58	0.59
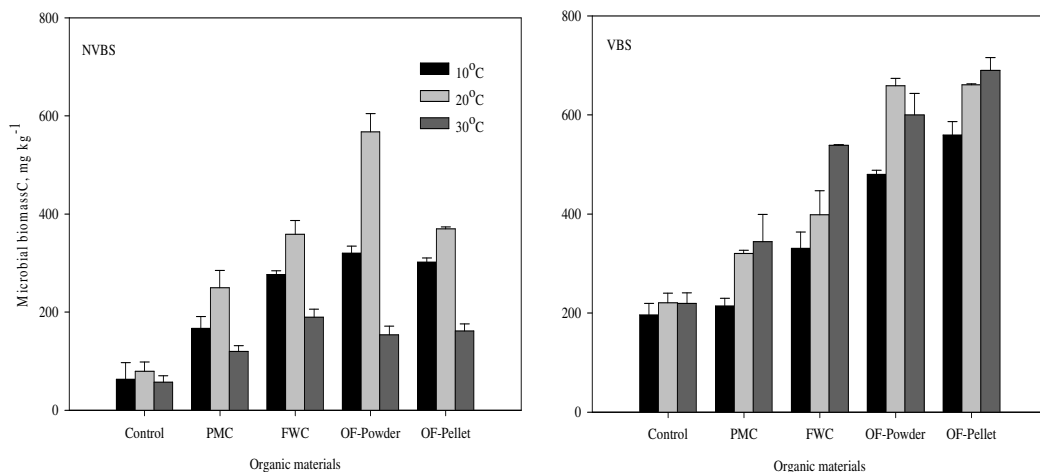
Figure 1. Soil microbial biomass C content after incubation at 75 days in NVAS and VAS.
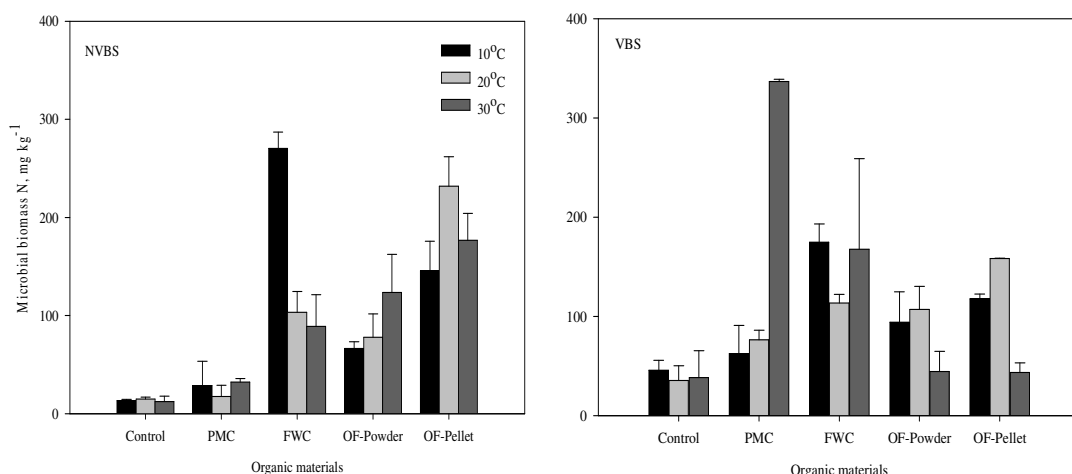
Figure 2. Soil microbial biomass N content after incubation at 150 days in NVAS and VAS.
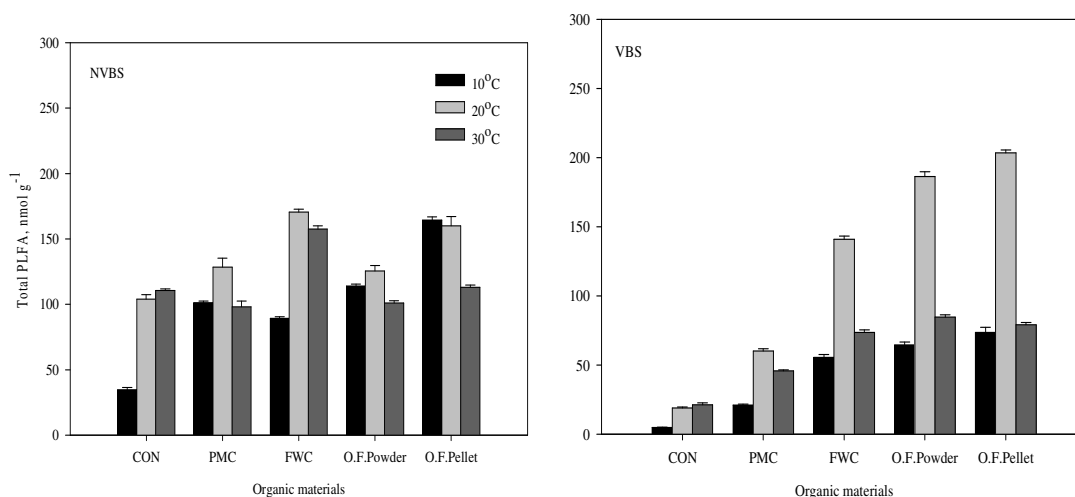
Figure 3. Total-PLFA content after incubation at 75 days in NVAS and VAS.

Conclusion

Soil microbial biomass C showed high when soil temperature was high and both OFPL and OFPD treated in VAS. Soil microbial biomass N was high in NVAS treated with organic fertilizers and in VAS treated with PMC and FWC, respectively. Urease activity decreased gradually with temperature and time. Glucosidase activity was higher in NVAS than in VAS. Soil microbial activity showed differences in sensitivity with soil type and temperature.

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Effects of Different Fertilizers on Soil-borne DDTs Dynamics and Its Impacts on DDTs Uptake by *Ipomoea aquatica*

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Abstract
A pot experiment was conducted to examine the effects of.various fertilizers on the dynamics of soil-borne DDTs and their subsequent impacts on DDTs uptake by a test plant. The results show that there was a significantly lower soil residual DDTs concentration in the iron-rich fertilizer-treated soil than in other fertilizer-treated soils. However, all the non-iron-rich fertilizers showed no significant effect on the reduction of soil DDTs on the last day of the experiment, as compared to the control. There was a close relationship between the soil residual DDTs and plant tissue DDTs. This suggests that the uptake rate of DDTs by the plant was dependent on the concentration of soil-borne DDTs. Application of iron-rich fertilizer enhanced the degradation of the soil DDTs and subsequently reduced the uptake of DDTs by the test plant. The findings obtained from this study have implications for remediation of DDTs-polluted soils.

Key Words
Fertilizer, DDT, pesticide, soil contamination, plant uptake

Introduction
The extensive application of dichlorodiphenyltrichloroethane (DDT) for pest control prior to the global restriction on its use resulted in widespread presence of this synthesized chemical and its metabolites, dichlorodiphenyldichloroethane (DDD) and chlorodiphenyldichloroethylene (DDE) (DDTs is frequently used to stand for the sum of DDT, DDD and DDE) in the environment (Longnecker, 2005). The Pearl River Delta in the southern China region is one of the global hotspots in terms of environmental contamination of persistent organic pollutants (POPs). This area has a long history of agricultural application of substantial amounts of organochlorine pesticides, including DDTs until their official ban in 1983 (Zhang *et al*. 2007). It is also likely that input of fresh DDTs has continued since 1983 as a result of the application of DDT-containing dicofol (Qiu *et al*. 2005).

The dyke-pond integrated cropping and aquaculture system has been long practiced in the Pearl River Delta (Ruddle *et al.* 1983). The fishpond sediments are potential sinks for DDTs and the sediment-borne DDTs could have adverse impacts on the quality of crop products due to elevated DDTs level in the plant tissues when the DDT-containing sediments are used for formulating topsoil layer on the dyke, which forms part of the routine operation in the dyke-pond system (Edwards 2008). The rate of DDT degradation in soils varies with environmental conditions, which could be affected by fertilizer applications. The objective of this work was to understand the effects of different fertilizer types on the dynamics of soil borne DDTs and subsequently the impacts on plant uptake of DDTs.

Materials and Methods
A representative fishpond located in the Shunde District of Foshan City was selected for this study. About 1000 kg of the bed sediment were collected from a depth of 0-30 cm after emptying the pond water. The sediment materials collected were air-dried and crushed to pass a 5 mm sieve before being used as the experimental soil for the pot trial. The sediment sample had a pH of 4.22 and an organic matter content of 2.26%. Total N, P and K were 1.890, 0.516 and 4.335 g/kg respectively. Available N, P and K were 0.312, 0.072 and 1.270 g/kg, respectively. The original soil contained 71 ng/g of DDTs. Prior to the growth experiment, an appropriate amount of technical DDT was added to the soil to simulate an on-farm application of DDT to raise the soil DDTs level to a theoretical concentration of DDT to 190 ng/g. A DDTs concentration of 186 ng/g was recorded on th 7th day of the pre-experiment incubation period.

Ipomoea aquatica, a vegetable that is commonly grown on the fishpond dyke, was used as the test plant in the pot experiment.
The four types of fertilizers used for different treatments are (1) organic fertilizer (chemical composition: 19.5

g/kg of nitrogen; 2.5 g/kg of phosphorus; 55.6 g/kg of K) , (2) compound fertilizer (chemical composition: 59.9 g/kg of nitrogen; 10.1 g/kg of phosphorus; 53.5 g/kg of K), (3) inorganic fertilizer and (4) Iron-rich trace element fertilizer (chemical composition: 40.3 g/kg of nitrogen; 6.7 g/kg of phosphorus; 58.6 g/kg of K; 1.9 g/kg of Fe^{2+}). No DDTs were detected from the fertilizers used in this experiment.

The experiment was conducted in a growth house equipped with temperature and light intensity controllers. Two controls and four treatments were set for the experiments: (1) Control 1 (C1): pond sediment only; (2) Control 2 (C2): pond sediment cultivated with vegetable; (3) Treatment 1 (T1): pond sediment with added organic fertilizer and cultivated with vegetable; (4) Treatment 2 (T2): pond sediment with added compound fertilizer and cultivated with vegetable; (5) Treatment 3 (T3): pond sediment with added inorganic fertilizer and cultivated with vegetable; and (6) treatment 4 (T4): pond sediment with added iron-rich trace element fertilizer and cultivated with vegetable. The experiment was performed in 4 replicates.

In each pot (height: 17 cm; inner diameter at the base: 20 cm; inner diameter at the top: 27 cm), 5 kg of the experimental soil was mixed with a relevant fertilizer. The pots were placed in the growth house randomly with temperature set at $27\pm1^{o}C$. 14 seeds were then sown in each pot. The plants were exposed to a photoperiod of 8 hours with light intensity set at 12000Lux each day during the entire period of the experiment. After 10 days following seed sowing, 8 healthy seedlings were selected to remain in each pot. Soil samples were taken from each pot on the 1st, 10th, 20th and 30th day after seed sowing. For each pot, 5-7 sub-samples of soil were collected using a soil sampler. The sub-samples were then mixed thoroughly to form a composite sample (approximately 200 g). The composite soil samples were air-dried, ground to pass a 0.25 mm sieve and stored at $4^{o}C$ in a fridge prior to chemical analysis.

On the 30th day of the experiment, the whole plant was harvested, washed and oven-dried at $55^{o}C$. The oven-dried plant residue from each pot was then weighed and finely ground prior to analysis.

DDTs in the soil and plant tissue samples were extracted using the procedures described in US EPA3510B (US EPA 1994) and measured using an Agilent HP-6890N GC-ECD system with a HP-5 fused-silica capillary column (30 m×0.25 mm I.D×0.25 μm). Helium was used as the carrier gas at 2 mL min−1 and nitrogen was used as the make-up gas 60 mL min−1. The oven temperature began at 165 °C for 2 min and increased to 265 °C (2 min hold time) at a rate of 6 °C min−1. Splitless injection of a 2 μL sample was performed. Injector and detector temperatures were maintained at 210 and 320 °C, respectively.

The detection limit ranged from 0.03 ng g^{-1} to 0.15 ng g^{-1} and the recoveries of surrogate standards ranged from 88.7 to 104%. The relative standard deviation (RSD) of replicate samples were less <15%. The statistical significance of difference between treatment means was determined by Duncan's multiple range test.

Results and Discussion
Change in soil-borne DDTs for the controls and treatments during the period of experiment can be seen from Figure 1. There was a trend that DDTs concentration decreased over time. After 10 days of growth experiment, approximately 45-55% of DDTs disappearred from the soils; there was a significant difference in residual soil DDTs ($P<0.05$) between C1 (pond sediment only) and C2 (pond sediment cultivated with vegetable) or any treatment; C1 had the highest concentration of soil-borne DDTs among the controls and treatments. There was no significant difference in residual soil DDTs ($P>0.05$) between C2 and T2 (pond sediment with added compound fertilizer and cultivated with vegetable), which had significantly higher ($P<0.05$) DDTs than the remaining three treatments i.e. T1 (pond sediment with added organic fertilizer and cultivated with vegetable), T3 (pond sediment with added inorganic fertilizer and cultivated with vegetable) and T4 (pond sediment with added iron-rich trace element fertilizer). These latter three treatments showed no significant significance in soil-borne DDTs among each others. On the 20th day of the experiment, there was no statistically significant difference in residual soil DDTs ($P>0.05$) among all the controls and treatments despite that the mean concentration of soil DDT varied markedly among each others.

At harvest (the 30th day of the experiment), T4 had the lowest residual concentration of DDTs (statistically significant at $P<0.05$) in the soil among all the controls and treatments. There was no significant difference ($P>0.05$) in residual DDTs in the soil among C2, T1 and T2, which had significantly lower soil DDTs, compared to C1 and T3. There was no significant difference ($P>0.05$) in residual DDTs in the soil between C1 and T3. Compared to the first 10 days, the decrease in soil residual DDTs was relatively slower during the

period from the 10th to 30th day of the experiment (Figure 1). Since DDT is not subject to water leaching and volatilization, it is likely that the loss of soil DDTs during the period of the experiment was mainly through degradation. The observed significantly lower soil residual DDTs in the iron-rich fertilizer-treated soil than in other fertilizer-treated soil generally agrees with previous work done by other authors that showed catalyzed degradation of DDT by reduced forms of iron (e.g. Boussahel *et al*. 2006). However, no significantly different ($P>0.05$) effect on the reduction of soil-borne DDTs by any non-iron-rich fertilizers was observed on the last day (30th day) of the experiment, as compared to the control (C2). As a matter of fact, the inorganic fertilizer treatment even resulted in a higher residual concentration of DDTs, relative to the control (Figure 1).
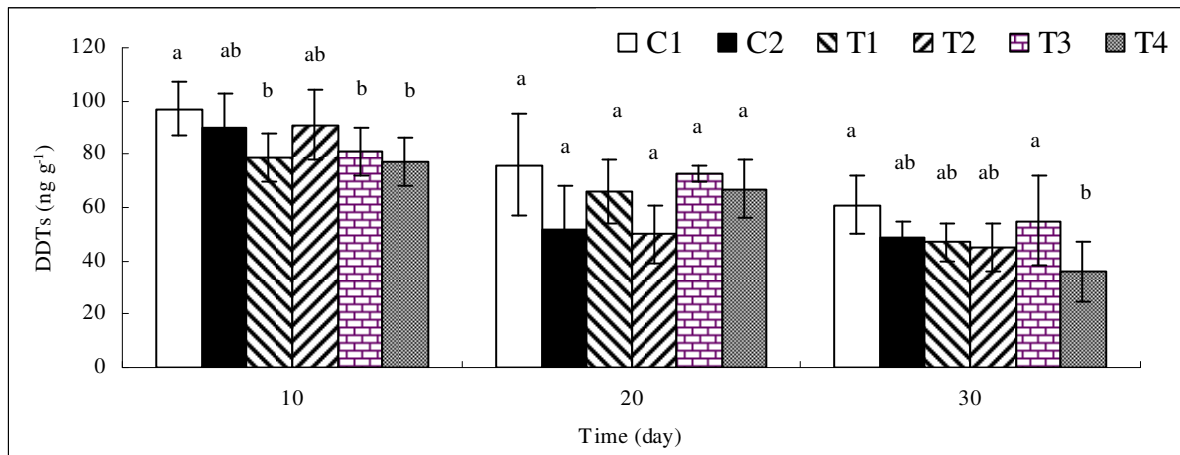
Figure 1. Change in soil-borne DDTs for the controls and treatments during the period of experiment

The concentration of tissue DDTs in *Ipomoea aquatica* at harvest is shown in Figure 2. There was a significant ($P<0.05$) difference among the control and various treatments. The mean concentration of plant tissue DDTs for the control and various treatments was in the following decreasing order: C2 >T3 > T1 >T2 >T4.
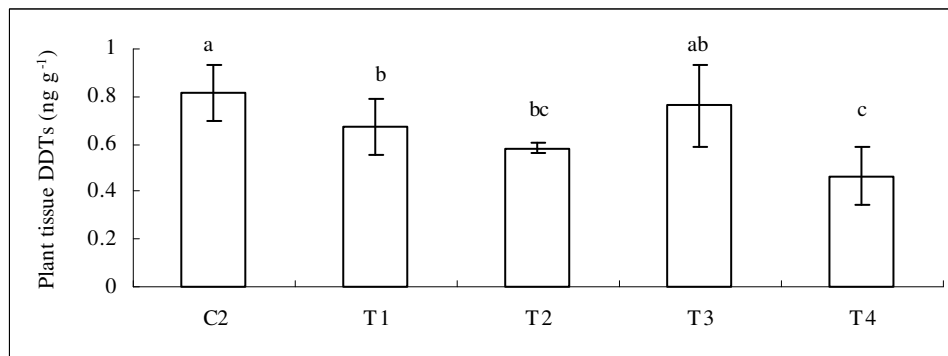
Figure 2. The concentration of tissue-borne DDTs of the Ipomoea aquatica for the control and various treatments at harvest

There was a close relationship between the soil residual DDTs and the plant tissue DDTs at harvest (Figure 3). This suggests that the uptake rate of DDTs by the plant was dependent on the concentration of soil-borne DDTs, i.e. the more residual DDTs the soil contained, the higher concentration of DDTs the plant tissue had.
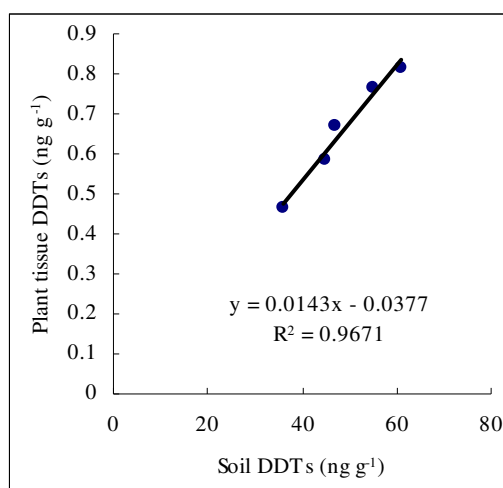
Figure 3. Relationship between soil residual DDTs and plant tissue DDTs at harvest.

The research findings obtained from this study have implications for the management of benthic sediment-turned soils in the dyke-pond integrated cropping and aquaculture production systems. Application of iron-rich fertilizers may enhance the degradation of the soil DDTs and subsequently reduce the uptake of DDTs by the test plant.

Conclusion
There was a significantly lower soil residual DDTs concentration in the iron-rich fertilizer-treated soil than in other fertilizer-treated soil. The uptake rate of DDTs by the plant was dependent on the concentration of soil-borne DDTs. Application of iron-rich fertilizer may enhance the degradation of the soil DDTs and subsequently reduce the uptake of DDTs by plants. The research findings obtained from this study have implications for the management of benthic sediment-turned soils in the dyke-pond integrated cropping and aquaculture production systems.

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Effects of Ionic Strength and Temperature on Adsorption of Atrazine, Deethylatrazine and Deisopropyatrazine in an Alkaline Sandy Loam

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Abstract

Atrazine is an agricultural herbicide used in large quantities and consequently companied with its two degradation products, deethylatrazine (DEA), and deisopropylatrazine (DIA), are commonly detected in groundwater and surface water. The retention of these compounds in vadose zone is highly related to their adsorption to soils. Laboratory studies were conducted to determine the sorption behaviour of atrazine, DEA, and DIA on a sandy loamy soil using the batch equilibration technique. The effects ionic strength (adjusted by $CaCl_2$ concentration) and temperature ($25\pm1°C$ and $40\pm1°C$) of absorption were also investigated. The adsorption isotherms of all three chemicals conformed to the Freundlich equation. Adsorption coefficients decreased in the order atrazine > DIA > DEA, and our calculated organic carbon normalized partition coefficients were 46.76, 46.00, 30.78 L/kg respectively. For atrazine and DEA, there existed a salting-out effect, their adsorption increased as ionic strength increased from 0 to 0.1 mol/L $CaCl_2$, but for DIA, its maximum adsorption occurred in 0.01 mo/ L $CaCl_2$ solution. The adsorption experiment also showed that more effective adsorption of atrazine, DEA and DIA at a lower temperature.

Key Words

Atrazine, deethylatrazine (desethylatrazine), deisopylatrazine (desisoprylatrazine), soil, adsorption

Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), a widely used herbicide in the world, is one among the 52 prior controlling pesticides in China. Because of the wide use of atrazine, byproducts of this compound are of particular interest (Bosch and Truman, 2002). Deethylatrazine (2-amino-4-chloro-6-isopropylamino-s-triazine, DEA) and deisopropylatrazine (2-amino-4-chloro-6-ethylamino-s-triazine, DIA) are the main biotic degradation products of atrazine in the soil environment (Jayachandran, 1994; Bosch and Truman, 2002), and both of them have been detected in surface and ground waters, and in some cases, at higher concentrations than that of atrazine (Seybold and Mersie, 1996; Ren and Jiang, 2002).

Assessment of pesticide adsorption during transport is a prerequisite for minimizing their potential mobility in the vadose zone. To our knowledge, no work dealing directly with temperature and ionic strength effect of atrazine, DEA and DIA adsorption on soils has been published. So, the main objective of the present study was to examine the adsorption characteristics of atrazine and its metabolites in a typical agricultural soil of Beijing. And the influences of ionic strength and temperature on the adsorption of atrazine, DEA and DIA are also demonstrated.

Materials and methods

Adsorption isotherms Adsorption isotherms for atrazine, DEA, and DIA were determined using the batch equilibration technique at $25\pm1°C$. Solution concentrations were prepared of each chemical in 0.01 mol/L $CaCl_2$, and ranged between 0.5 and 30 mg/L for all compounds.

Effect of ionic strength A procedure similar to the one described above was used, with the following modifications: solution concentrations were prepared with ionic strength were made from deionized water (0 mol/L) and 0.1 mol/L $CaCl_2$ solutions.

Effect of temperature The test was carried out the same way as the standard adsorption experiments, but equilibrated at $40\pm1°C$.

Results and discussion

Adsorption isotherms

All the isotherms were of L-type (see Fig. 1), i.e., were nonlinear with the curvature concave to the abscissa (Li *et al*. 2006), indicating a decrease in specific sorption sites when herbicide concentration in solution increases. The parameters of the Freundlich equation were well correlated with the experimental adsorption isotherms

obtained (Figure 1). The order of decreasing adsorption coefficients (Kd) was atrazine > DIA > DEA, in agreement with the results reported by Brouwer *et al.* (1990), Seybold and Mersie (1996) and Vryzas *et al.* (2007). Our calculated Koc values of 46.76, 30.78, 46.00 L/kg for atrazine, DEA, and DIA, were less than the Koc values reported by Brouwer *et al.* (1990) and Seybold and Mersie (1996), which may be due to the low content of clay and soil organic carbon, the high pH and CEC of our soil.

The Freundlich adsorption constant represents the degree or strength of adsorption (Seybold and Mersie 1996), our Kf values for adsorption of atrazine, DEA and DIA were1.2574, 0.7992 and 1.3201 respectively, are within the range of previously reported values. And the average slope 1/n is a measure of adsorption nonlinearity (Seybold and Mersie 1996), when the slopes are <1, indicate that the percentage of these chemicals adsorbed to the tested soil decreased as the initial concentration increased (Nemeth-Konda *et al.* 2002).
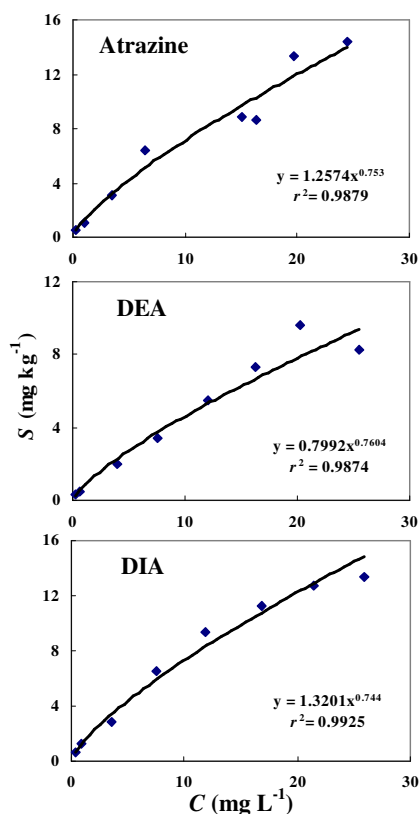
Figure 1. Freundlich isotherms for Atrazine, DEA and DIA adsorption.

Effect of ionic strength on pesticide adsorption
As can be seen, the shape of the isotherms from 0.1 mol/L $CaCl_2$ solution is the same shape as that obtained for pure water solution and for 0.01 mol/L $CaCl_2$ solution (Figure 2). Also, it clearly showed that, for atrazine and DEA, the adsorption increased with increasing ionic strength ($CaCl_2$ concentration in aqueous solution), which suggested that the role of electrostatic interactions in the adsorption process was significant. For a given concentration at equilibrium, the adsorption amount of atrazine on our test soil increased as ionic strength increased, which may be due to the occurrence of "salting out" effect that caused the solubility of atrazine in salt solution decrease. This phenomenon also reported by Spongberg and Lou (2000) and Ureña-Amate *et al.* (2005), the former synchronously pointed out that higher ionic strengths are often encountered in surface horizons when fertilizers and other compounds are applied. For DIA, with the ionic strength increased from 0 to 0.01 mol/L, the adsorption increased, while when the ionic strength increased from 0.01 to 0.1 mol/L, the adsorption onto the soil decreased, the adsorbed amount in 0.1 mol/L $CaCl_2$ background solution even less than that adsorbed when no $CaCl_2$ solution was used. The effect of salt concentration on pesticide sorption was complex, as had been explained by diffuse double-layer theory: Ions that form outer-sphere surface complexes show decreasing adsorption with increasing ionic strength, while ions that form inner-sphere surface complexes show little ionic strength dependence or show increasing adsorption with increasing ionic strength (McBride 1997; Anirudhan and Ramachandran 2007).
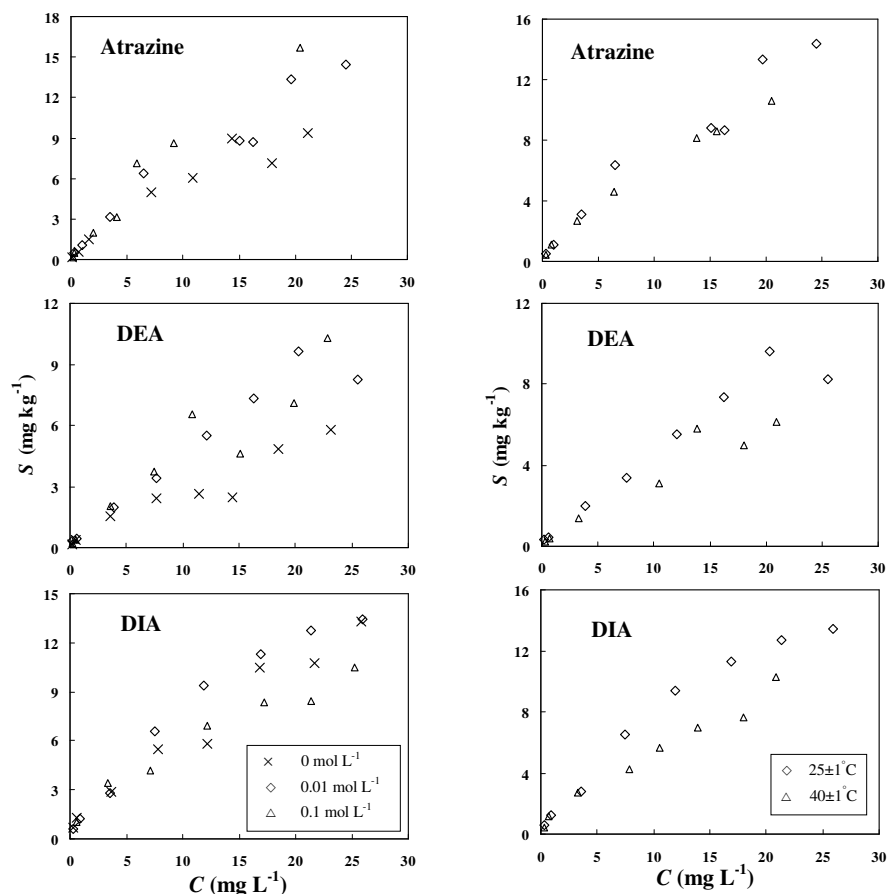
Figure 2. Adsorption isotherms of atrazine, DEA and DIA onto the tested soil for three different values of ionic strength at 25±1°C: (×) 0 mol/LCaCl₂; (◇) 0.01 mol/L CaCl₂; and (△) 0.1 mol/L CaCl₂.

Figure 3. Compared adsorption isotherms for atrazine, DEA and DIA in 0.01 mol/L CaCl₂ solution at 25±1°C (◇) and 40±1°C (△) on the tested soil.

Effect of temperature on pesticide adsorption

From Figure 3, again, all the isotherms were L-type, which suggested that the tested soil had an intermediate affinity for atrazine and its metabolites DEA and DIA and that no strong competition from the solvent for adsorption sites occurs (Ureña-Amate *et al*. 2005). Results showed that, with the increases of temperature, the Kf values were decreased for each chemical, while the variation of the exponents n had no clear trend. Kovaios *et al*. (2006) also reported that when temperature increased from 25±1 to 40±1°C, Kf values of atrazine decreased, but the n values increased. The same trend of decreasing Kf with increasing temperature was also reported by Ureña-Amate *et al*. (2005). As temperature increases from 25±1°C to 40±1°C, the adsorbed amount of chemicals at the same equilibrium concentration decreased, suggesting that adsorption is a process of release of activation energy.

Conclusions

In this study, the adsorption of atrazine, DEA, and DIA on a sandy loamy soil was measured using the batch equilibration technique. The Freundlich isotherms described adsorption well in all cases. Most of the isotherms were of L-type, indicating a decrease in specific sorption sites when herbicide concentration in solution increases. Generally, the adsorption coefficients (Kd) decreased in the order atrazine> DIA > DEA, which suggested that the metabolites have greater potential than the parent compound, atrazine, to move through our test soil and pose a threat to groundwater.

An increase in atrazine and DEA adsorption is accompanied by increasing ionic strength of the solution that represented by CaCl₂ concentration. A higher ionic strength would reduce the double layer thickness and result in a stronger interaction between the hydrophobic sorbate and the sorbent. The effect of temperature on the adsorption isotherms, in our case, is that by increasing temperature, adsorption decreases.

Further research will be undertaken to investigate the sorption behaviour of atrazine and its metabolisms in flow equilibrium condition and to estimate their potential migration to the groundwater.

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Effects of pH and Cadmium on Tetracycline Sorption to Soils

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Abstract
Batch sorption experiments were conducted to evaluate the sorption of tetracycline (TC) on soils as affected by pH and cadmium. Sorption isotherms of TC on soils in the presence and absence of Cd (II) were well fitted with the Freundlich equation. Sorption of TC strongly depended on environmental factors and soils characteristics. Lower pH facilitated TC sorption through cation exchange mechanism which also took place at pH above 5.5 where TC existed as zwitterion (H_2L^0) or anions (HL^- and L^{2-}). When pH was above 7, ligand-promoted dissolution of TC might occur due to the TC weakening the Al-O bond of aluminum oxide and Fe-O bond of iron oxide. The presence of Cd (II) increased TC sorption on soils, which was resulted from the decrease of equilibrium solution pH caused by Cd^{2+} exchange with H^+ ions of soil surfaces. The increase of TC sorption was also related to the formation of TC-Cd complexes and the bridge provided by Cd^{2+} between the soil and TC.

Key Words
Sorption, tetracycline, pH; cadmium, soil

Introduction
Sorption is an important process that affects the fate, transportation, bioavailability and toxicity of contaminants. TC is predominantly sorbed on soil clays and humic substances either mask sorption sites on clay surfaces or inhibit interlayer diffusion of TC. Sorption of TC decreased with increasing pH and sorption by clay appeared to be increased in the presence of Ca versus Na (Figueroa *et al.* 2004; Kulshrestha *et al.* 2004; Figueroa and MacKay 2005; Pils and Laird 2007). TC has multiple ionizable functional groups (Sassman and Lee 2005), sorption of TC significantly depends on environment elements and the properties of soil samples.

On the other hand, soils usually contain other contaminants such as heavy metals, which may affect sorption of TC. In recent years, some researchers focus on the interaction between metal ions and TC (Wang *et al.* 2008; Jia *et al.* 2008). Cadmium (Cd) as a nonessential element can result in adverse effects on animals and humans (Tu *et al.* 2007). High contents of Cd may be present in livestock additives because of contamination of mineral supplements (Nicholson *et al.* 2003). Thus, Cd can often coexist with TC, which may affect behavior of TC, however, little attention is paid to this possibly. The objective of this study is to investigate the sorption isotherms of TC on soils as affected by Cd and pH.

Materials and methods
Chemicals and soils
Tetracycline hydrochloride (98% purity) was obtained from Alfa Aesar. TC stock was prepared in methanol and stored at 4°C in the dark and refreshed every month. Calcium chloride anhydrous, sodium azide, oxalic acid dihydrate, $CdCl_2 \cdot 5/2H_2O$, HCl and NaOH were all reagent grade. Acetonitrile and methanol were HPLC grade. Solutions were prepared with high-purity water (18MΩ, Millipore Simplicity 185).
Three air-dried soils were gently crushed to pass through a 0.25 mm sieve. Three soil samples (0-20 cm) were collected from East Xinzhuang (Soil 1), North Tanggu Farm (Soil 2) and Northeast Dougu Town (Soil 3) respectively. The properties of soils were shown in Table 1. Cation exchange capacity (CEC) was determined by the method of ammonium acetate exchange. Organic carbon (OC) contents were determined using an Elementar Vario EI elemental analyzer (Germany) after the acid-treatment (1 M HCl). Particle size distributions were determined by laser particle size analyzer (Mastersizer 2000, Malvern Instrument Ltd. Malvern, UK). The content of total Fe and Al oxides in sediments and soils were determined by $HF-HClO_4-HCl$.

Table1. Some physical and chemical characteristics of the selected sediment and soil samples.

Samples	pH (1:2.5)	OC (wt.%)	CEC (cmol/kg)	Fe_2O_3 (%)	Al_2O_3 (%)	Particle size distribution (wt.%)			
						<0.002 mm	0.002-0.02 mm	0.02-0.25 mm	0.25-2 mm
Soil1	8.63	1.14	23.40	38.94	64.84	5.40	25.74	57.69	11.17
Soil2	8.39	1.90	24.06	38.66	67.02	1.20	16.54	57.69	11.17
Soil3	8.64	1.15	21.61	35.29	69.94	11.37	38.23	46.62	3.78

Sorption experiments

All experiments were conducted in 30 ml Nalgene polypropylene centrifuge tubes. According to preliminary experiment, 24 h was chosen as the equilibration time and the loss of TC was negligible. The prepared TC solution contained 0.01 M $CaCl_2$ to maintain a certain ionic strength and 1.5 mM sodium azide to inhibit biological activity, and was adjusted to pH 5.5 with HCl or NaOH. Twenty-five milliliter of different concentrations (from 5 to 150 mg/L) of TC solution with and without 10 mg/L of Cd (II) was added into each tube containing about 0.1 g soil. Soil 3 was selected to investigate the effect of pH on TC sorption with and without Cd (II) and were performed with a single TC concentration (30mg/L). Different pHs varying from 3.5 to 9.5 in one-unit increments were adjusted with 0.1 M HCl or 0.1 M NaOH. Sorbate-free control and Sorbent-free control tubes were prepared in the same manner. Duplicate experiments were conducted for all samples.

Concentrations of TC were determined by high-performance liquid chromatography system equipped with a UV detector (Germany Lumtech K-2600, Lumiere Tech Ltd.) using Inertsil ODS-3 C18 column (5 µm, 250×4.6 mm). Samples were eluted isocratically with a mixture of acetonitrile (23%) and 10 mM oxalic acid (77%), flowing at 1.0 ml/min. TC was measured by absorption at 360 nm. The amount of TC adsorbed was calculated by the difference between the amount of TC added initially and that remained in the aqueous after equilibration.

Results and Discussion
Sorption isotherms

The Freundlich isotherm model commonly used for quantifying equilibrium sorption of hydrophobic organic compounds (HOCs) by soils has the following forms:

$$q_e = K_F C_e^{n} \tag{1}$$

where q_e is the solid-phase concentration (mg/kg) and C_e is the liquid-phase equilibrium concentration (mg/L). K_F is the sorption capacity-related parameter ($(mg/kg)/(mg/L)^n$) and n is the isotherm linearity index. Figure 1 shows the sorption isotherms of TC on soils in the presence and absence of Cd (II) at pH 5.5. The Freundlich
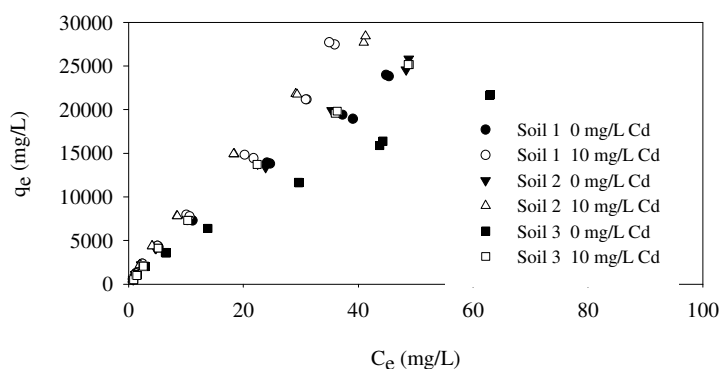
Figure 1. Tetracycline sorption isotherms on three soils in the presence and absence of Cd.

equation fits the sorption isotherms of TC with high correlation coefficients (r^2= 0.997-0.999) (Table 2), which suggests that the Freundlich equation can be used to sufficiently describe TC sorption to the soils with and without Cd (II). The organic carbon-normalized sorption coefficient (K_{FOC}) was calculated by dividing K_F values by the fraction of organic carbon (F_{oc}). The single point K_{oc} (L/kg) was calculated by the following equation:

$$K_{oc} = K_{FOC} C_e^{n-1} \tag{2}$$

Table 2. Freundlich sorption model coefficients for TC adsorption on soils in the presence and absence of Cd (II)

Samples	Cd (mg/L)	K_F [A]	K_{FOC}	n [B]	r^2	N [C]	Concentration-dependent K_{oc}		
							$C_e=0.005$ (mg/L)	$C_e=0.05$ (mg/L)	$C_e=0.5$ (mg/L)
Soil1	0	1106±44	970	0.826±0.025	0.999	16	2439	1633	1094
	10	1425±91	1250	0.999±0.049	0.997	16	1257	1253	1251
Soil2	0	1127±62	593	0.800±0.015	0.998	16	1711	1080	681
	10	1364±55	718	0.816±0.012	0.999	16	1903	1246	816
Soil3	0	778±21	676	0.802±0.007	0.999	16	1930	1223	775
	10	1072±43	932	0.813±0.011	0.999	16	2510	1632	1061

[A] 95% confidence interval of K_F; [B] 95% confidence interval of n. [C] number of observations;

The data in Table 2 show that the n values for TC by the soils varied from 0.800 to 0.826 with an average of 0.809. The differences of n values may be caused by different origins of soils. For all soil samples, higher C_e concentrations would result in lower K_{oc} values because of nonlinear sorption. When C_e was at 0.005 and 0.05 mg/L, the K_{oc} values for the three soils ranged from 1711 to 2439 L/kg with average at 2027 L/kg and from 1080 to 1633 L/kg with average at 1311 L/kg, respectively. When C_e was at the higher concentration (0.5 mg/L), the values of K_{oc} were much lower, ranging from 681 to 1094 L/kg.

Effects of Cd and pH on sorption of TC
When pH is 5.5, TC predominantly exists as the zwitterions (Sassman and Lee 2005), Cd (II) increased the sorption of TC on the three soils (Figure 2). Figure 2 shows that the K_d values was higher at lower pHs, because the cationic TC can combine with the negatively charged sites on soil surfaces, which increase the sorption of TC. K_d values of TC for Soil 3 in the presence of Cd (II) at different pHs were also shown in Figure 2. Cd suppressed the sorption of TC on Soil 3 when pH was below 4.5, this may be due to the competition of Cd (II) with TC and TC-Cd complexes. On the other hand Cd (II) promoted the sorption of TC on Soil 3 when pH was above 5.5, this may be due to Cd (II) acting as bridge between TC and Soil 3. This result was similar to the research on cosorption of TC and Cu (II) on soils conducted by Jia *et al.* (2008).
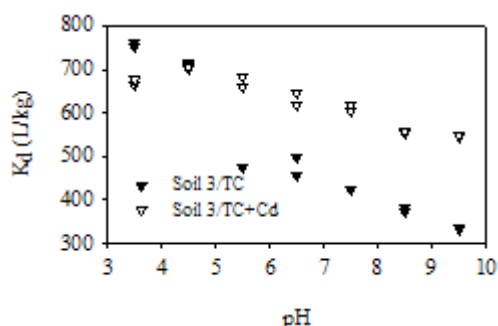
Figure 2. Effects of pH on TC sorption on Soil 3 in the presence and absence of Cd.

Relationship between soil properties and sorption isotherm
The pHs and CEC for three soils were similar, the differences of sorption capacities indicated that other properties played important roles. This experiment revealed that TC was less favor to be sorbed to Soil 3 which had obviously higher clay than others. A probable reason was that more ligand-promoted dissolution was occurring during TC sorption to Soil 3. Although Soil 1 and Soil 2 had more iron oxide content, they had less amount of aluminum oxide than Soil 3 (Table 1), which might result in the higher sorption capacity for Soil 1 and Soil 2. This result was consistent with sorption of TC to aluminum and iron hydroxides decreasing with increasing pH when pH was up to 7 (Gu and Karthikeyan 2005).

Possible sorption mechanism of TC in the absence and the presence of Cd(II)
Cation exchange has been reported as an important mechanism for TC sorption at acidic condition. pHs decreased with increasing concentration of TC (data were not shown), which suggested that cation exchange took place above pH 5.5, as the negative and positive charges on TCs were spatially separated and they might play their respective roles similar to that of soil cation and anion exchange sites (Sassman and Lee 2005). When pH was above 7, sorption of TC to aluminum and iron oxides decreased with increasing pH because of ligand-promoted dissolution. Ligand-promoted dissolution was more significant for aluminum oxides than for iron

oxides (Gu and Karthikeyan 2005). A possible explanation for the increase of TC sorption in the presence of Cd (II) could be that the equilibrium solution pHs were lower than those in the absence of Cd (II). The pH decreased in the equilibrium solution when Cd (II) was added, which was caused by Cd^{2+} exchanging with H^+ ions of soil surfaces. The cationic Cd could also combine with the negative charge sites on the soil surfaces, acting as a bridge between TC and soil particles (Pils and Laird 2007; Jia *et al.* 2008; Wang *et al.* 2008). Another reason might be related to the formation of TC-Cd complexes as well. The predominant TC species at solution pH between 6 and 8 were H_2L^0, HL^-, and L^{2-} (Sassman and Lee 2005), which could strongly combine with the Cd (II) to form CdH_2L^{2+}, $CdHL^+$, and CdL complexes. These TC-Cd complexes had less negative surface charge and more easily adsorbed on soil surfaces than TC itself at high pH conditions.

Conclusion

Sorption of TC on soils as affected by Cd (II) and pH were investigated in this study. Sorption of TC decreased with increasing pH, and basic conditions did not facilitate TC sorption, which suggested TC introduced into alkali soils would increase its environmental risk. When pH was above 7, aluminium and iron oxides might increase the mobility and bioavailability of TC due to ligand-promoted dissolution in soil pore waters. Cd enhanced TC sorption on soils at environmentally relevant pH values, thus reducing the mobility of TC. The results in this study can be potentially valuable in predicting the fate, bioavailability and risk of TC in soils. In addition, sorption of TC by different components of organic matter in soils needs further investigations.

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Effects of polyphenolic rich biomaterials on transformation of nitrogen in soils

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Abstract
Laboratory based studies showed that polyphenolic rich plant biomaterials (PRPBs) have the potential to slow down mineralisation of recently immobilised nitrogen (N) in soils. Five PRPBs were tested in this study and their rate of N immobilisation was compared with glucose as a standard C source. Among the range of PRPBs tested, PRPB2 was the most effective. Even at 0.5 or 1% rate of C (w/w) added, the PRPB2 showed prolonged immobilisation of N added at 340 kg N/ha. Using ^{15}N as a tracer, we measured over 85% of the recently immobilised N in PRPB2 being retained within soil organic matter until 98 days. Also, it was identified that addition of the PRPB2 to soil changed the fatty acid composition. Ongoing research is looking at the effectiveness of this plant material in protecting soil organic matter and the underlying mechanisms.

Key Words
Tannin, ^{15}N, N cycling, NO_3 and NH_4, dissolved organic matter

Background
Increased nitrogen (N) flow from agricultural land to waterways is now one of the major threats to water quality across the globe. Some of the N in lakes and rivers comes directly from the mineralisation of the N bound in soil organic matter (SOM). The rate of mineralisation of resident or recently added organic matter can be affected by manipulating enzyme and microbial characteristics in soils. It has been suggested that N cycling in grazed pasture system can be manipulated by increasing the tannin content in pasture plants. This can lead to greater partitioning of N from animal excreta into dung which is slowly mineralised over time. The tannins are polyphenolic compounds with the ability to form stable complexes with proteins and other compounds. Tannins in litter may slow decomposition rates and thereby nutrient cycling (Bradley *et al.* 2000). Tannins from various plant species have been shown to affect N mineralisation, induce toxicity in microbes and affect enzyme activities in soils (Schimel *et al.* 1996; Bradley *et al.* 2000). The aims of this study were to determine the effects of tannin rich biomaterials on the mineralisation and immobilisation of N in pastoral soils, and to evaluate if these materials affect the dissolved organic matter in soils. Results are reported from a series of laboratory experiments which were conducted to evaluate proof of concept, which then can be applied to and tested further in field studies.

Methods
Five polyphenolic rich plant biomaterials (PRPB) were used to examine the effects of their input on N cycling in two pasture soils varying in mineralogy and organic matter contents (Table 1). Four sets of experiments were carried out to evaluate a; the proof of concept in terms of effects of PRPB's on N cycling using a closed incubation system, b; efficacy testing at lower rates of application of the PRPB, c: use of ^{15}N tracer to study the incorporation of labelled N into soil organic matter as influenced by PRPB and its subsequent mineralisation, and d; characterisation of soil organic matter after the addition of PRPB application.

In the first experiment, four PRPBs that were characterised for tannin, C and N concentration (Table 2) were added to Bruntwood (allophanic) and Rangiatea (pumice) soils at the rates equivalent to 1.5 and 3% soil C. Glucose was used as a standard C source for comparison. Urea-N was applied @ 340 kg/ha. All treatments and a control with added urea-N were replicated (4), incubated at 20°C and 70% water holding capacity. A factorial design was used and sub-samples of soil from all treatments were collected at 1, 3, 14, 28, 42, 63 and 77 days intervals and analysed for extractable NO_3, NH_4, DON and DOC following the methods described by Ghani *et al.* 2007.

In the second experiment, rates of application of PRPB were reduced to the equivalent of 0.25, 0.50 and 1% soil C and an additional citrus based PRPB was added following the method described above. Subsamples of soil from each treatment were collected at 1, 3, 14 and 28 day intervals and analysed for extractable NO_3, NH_4, DON and DOC.

Table 1. Soil characteristics used in the incubation studies.

Soil properties	Bruntwood	Rangiatea
Soil Order	Volcanic ash	Pumice
% Total C (w/w)	8.4	4.6
% Total N (w/w)	0.8	0.4
Nitrate-N (µg/g soil)	7.5	5.5
Ammonium-N (µg/g soil)	0.5	0.5
Hot-water extractable C (µg/g soil)	2300	1550
Hot-water extractable N (µg/g soil)	350	170

Table 2. Some physical and chemical characteristics of the PRPB used in this study.

PRPB	% Moisture	% C*	% N*	Water-soluble C* (% of total C)	% Total tannin*
PRPM 1	5.1	52.9	1.3	1.0	7.1
PRPM 2	2.4	47.7	1.0	5.0	5.4
PRPM 3	13.5	50.4	2.5	2.5	0.4
PRPM 4	2.7	49.4	3.7	4.5	4.6
PRPM 5	3.0	48.0	2.5	7.0	5.2

*On dry weight basis

In the third experiment, ^{15}N-urea (99 atom %) was applied @ 200 kg N/ha to trace N incorporation into soil organic matter. A combination of closed and open incubation methods were used to examine N immobilisation and its subsequent mineralisation. The most promising PRPB treatment identified in the first two experiments was used along with glucose as a standard treatment. A control treatment did not receive any C source. All treatments were incubated in a closed incubation for 21 days to enhance immobilisation of the labelled N. At 7, 14 and 21 day intervals, sub-samples from each treatment were analysed for NO_3 and NH_4 to assess the level of incorporation of applied N. Also, ^{15}N in these soil samples was measured to get the accurate measure of incorporation of the applied N. At day 21, subsamples (30 g on oven dry wt. basis) from each of the treatments were packed into leaching columns. These columns were leached on a weekly basis and leachates were analysed for DOC, DON and NO_3 and NH_4. After each leaching, three replicate columns were destructively sampled for ^{15}N, total C and N analysis. At the conclusion of day 21 after the closed incubation system, soils organic matter fatty acids (C16-C20) from control, PRPB and glucose treatments were characterised using GCMS.

Results and discussion
Part 1. Effects of biomaterials
In contrast to glucose, the PRPBs had a small proportion (1-7%) of their total carbon in a water soluble form. Most of the C added as glucose was rapidly respired by soil microbes by day 14 when added at the lower rate i.e. 1.5% C (w/w basis) and by day 28 at the 3% C application rate (Figure 1). There was no difference in the rate of utilisation of added glucose between Bruntwood or Rangiatea soils. Application of PRPBs and glucose caused immobilisation of the added urea-N. The rate of immobilisation of added N was faster in glucose and PRPB2 treatments compared to other treatments (Figure 2). The range of immobilisation in the PRPB treatments illustrated the potential of using combination these treatments to retain more applied N in soils. PRPB2 was effective in lowering the concentration of DOC and DON in both soils (results not included). Effects of treatments for all other variables were similar in both soils therefore results from only one soil (Bruntwood) are presented.
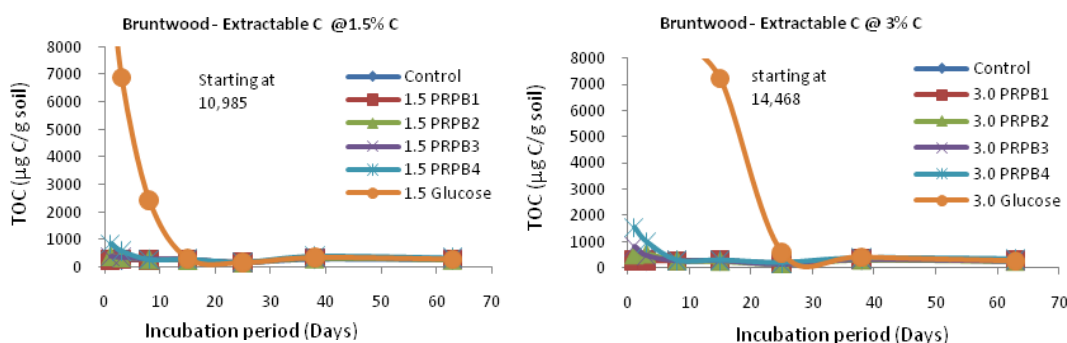
Figure 1. Influence of PRPB and glucose application on extractable C in soils.
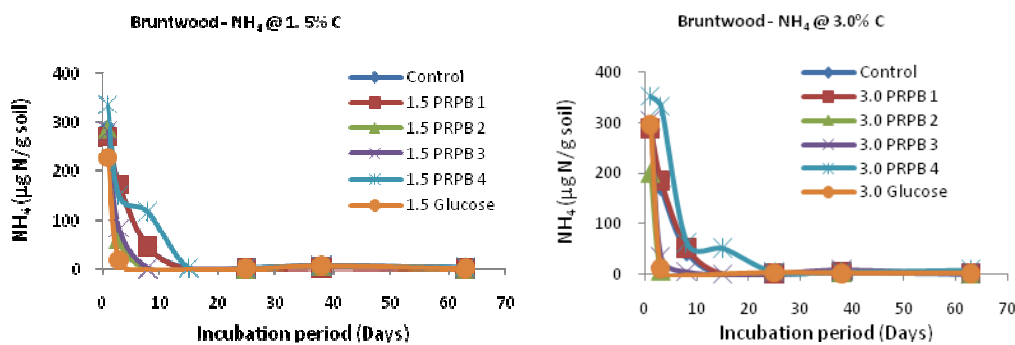
Figure 2. Effects of PRPB and glucose on the immobilisation of applied N in soils applied at 1.5. and 3% C (wt basis).

With the exception of glucose and PRPB2 treatments, none of the other PRPB treatments were effective in keeping the immobilised N in soil organic matter for any significant period of time at either application rate (Figure 3). Towards the end of the incubation period, PRPB 1, 3 and 4 treatments encouraged more mineralisation as the amounts of NO_3 was greater than the added N (Figure 2 and 3). The mode of action for immobilisation of applied N in glucose and PRPB2 is most likely to be through different mechanisms. In the glucose treatment, enhanced microbial activity due to availability of soluble C would be dominant but in the case of PRPB2, which has 25-40 times less soluble C (Table 2), complexing of N in protein may also be a reason for the prolonged immobilisation period.
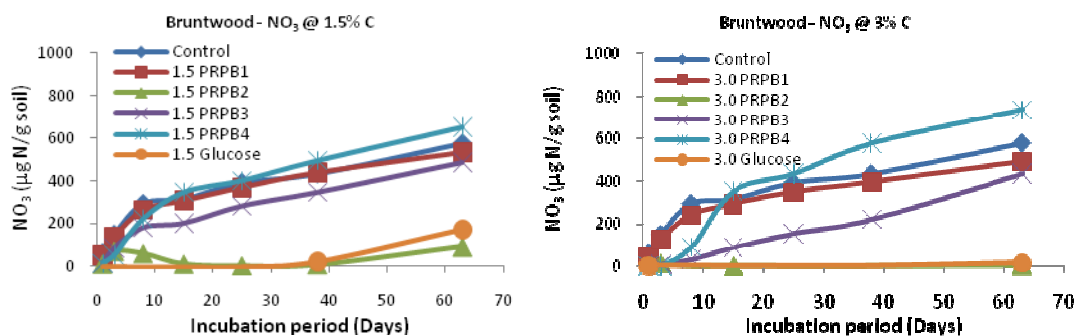
Figure 3. Effects of PRPB and glucose on the remineralisation of N in soils applied at 1.5 and 3% C (wt. basis).

Part 2. Efficiency of biomaterials
In the first experiment, rate of application for all treatments were too high for any practical use. Therefore, immobilisation efficacy of applied N caused by PRPBs was tested at lower rates of C application. The PRPB2 and glucose applied at lower rates of C (0.5 and 1% C) were equally effective in keeping the immobilised N into soil organic matter for a 4-8 week period. Addition of the citrus based PRPB treatment in the second experiment was least effective in causing immobilisation of added N (results not presented).

Part 3 and 4: How long was the recently immobilised N retained in soil organic matter?
Over 75% of the recently-incorporated Nin the control treatment was re-mineralised during the open incubation of 98 days. In comparison, only 12% of the recently incorporated N in soil organic matter from PRPB2 and glucose treatments was mineralised during the 98 days open incubation. For the first 75 days, N mineralisation from PRPB2 treatment was less than that of glucose treated soils (result not included in the text). The GCMS analysis showed that soil organic matter in the PRPB2 treatment had a slightly different make up of fatty acid compared to both control and glucose treatments (Figure 4).

Conclusions
The PRPBs can influence N cycling in soil systems. The concentration of tannin in the PRPB is not a good indicator of the potential of the specific PRPB to increase the period of immobilisation of the applied N in soil organic matter. Other chemical characteristics may help to indentify the efficacy of the PRPB in 'tightening' the N cycle. The PRPB2 showed considerable promise in immobilising the added N as well as protecting the immobilised N against microbial mineralisation for a longer period of time. Further work is required to evaluate the efficacy of PRPB2 in field experiments. Also, identification of the key chemical compounds that are responsible for protection of recently immobilised soil organic N is required.
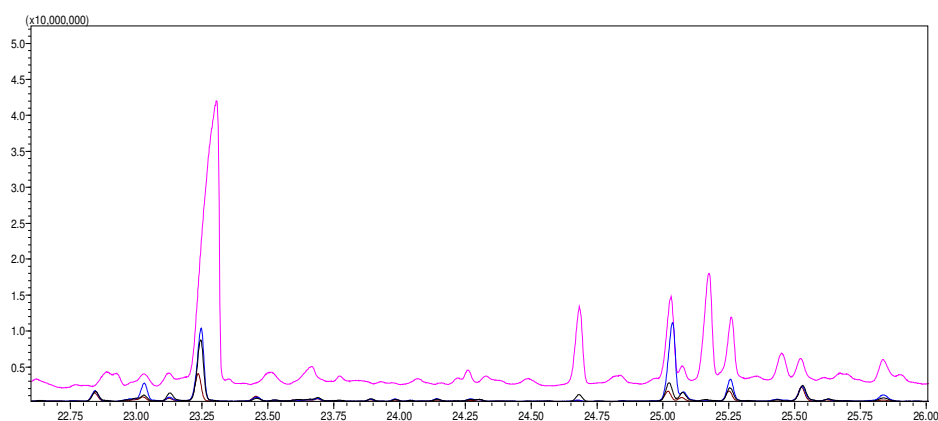
Figure 4. GCMS spectra showing chemical nature of soil organic matter when amended with PRPB2 (pink) and Glucose (blue) additions. The brown colour lines are for control treatment.

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Effects of tea genotype and slope position on soil soluble organic nitrogen pools

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Abstract
Soil soluble organic N (SON) pools, microbial biomass, and protease and asparaginase activities at the 0-15 cm and 15-30 cm layers in ten year old tea plantations of two genotypes - Oolong tea (*Camellia sinensis* (L.) O. Kuntze cv. huangjingui) (designated as 'OT') and Green tea (*C. sinensis* (L.) O. Kuntze cv. Fuyun 6) (designated as 'GT'), established at different slope positions. Concentrations of soil SON measured by 2 M KCl extractions under the OT plantation were generally greater than under the GT plantation, while concentrations of soil SON were greater in the middle position (MS) and lower position (LS) positions than in the upper position (US) position. Trends in soil microbial biomass C and N between the two genotypes and across the slope positions were similar to the SON pools. Soil protease and asparaginase activities were generally higher in the MS and LS positions than in the US position, while soil protease activities were higher under the OT plantation than under the GT plantation. Results from this study support that the genotype and the slope position are key factors controlling the availability of soil SON in tea plantations.

Key Words
Soil soluble organic nitrogen (SON), *Camellia sinensis* (L.) O. Kuntze, genotype, slope position, protease, asparaginase

Introduction
Soluble organic nitrogen (SON) is considered to play a vital role in ecosystem processes (e.g. Cookson *et al*., 2007). However, information on soil SON availability and associated microbial processes in tea orchards is scant. Tea (*Camellia sinensis* L. O. Kuntze) is one of the most important beverage crops in the world. Green, Oolong and black teas are the most common types, but differ genetically. Slope position is a key topographic factor influencing microclimate, species composition and ecosystem functions in many terrestrial ecosystems (McNab, 1993; Sariyildiz *et al*., 2005). It has been suggested that slope position affects soil particle distribution, soil temperature and moisture, and C and nutrient cycling processes in grasslands (e.g. Turner *et al.,* 1997) and forestlands (e.g. Sariyildiz *et al*., 2005). Different genotypes of tea cultivars vary with physiological processes and nutrient uptake and stocks (e.g. Kamau *et al*., 2008) and may respond differently to nutrient supply (Kamau *et al*., 2008). However, little is known about the effects of slope position and genotype on soil SON availability in tea ecosystems. In this study, it was hypothesized that: 1) different genotypes of tea cultivars affect the availability of soil SON directly through the inputs of root litters of varying quantity and quality and indirectly through influencing soil microbial biomass and enzyme activity and thus the production and transformation of soil SON; and 2) different slope positions influence the soil texture, the movement of carbon and nutrients and microclimatic conditions and thus availability of soil SON.

Methods
Site description and sample collection
Two adjacent tea plantations, established at the Research Station of Tea Research Institute (27°13′S, 119°34′E), Fujian Academy of Agricultural Sciences, Fujian Province, China, were selected for this study. The mean annual rainfall and temperature at this site are 1646 mm and 19.3 °C, respectively. The soil type is a Typic Alliti-Udic Ferrosols (Soil Survey Staff 1999). The research sites were located on two adjacent slopes facing in the same direction to the sun, with an average slope of 20°. The two slopes were developed into terrace land with the width of about 3-4 m. The area of each site measures 0.4 ha in which one was planted with Oolong tea (*C. sinensis* (L.) O. Kuntze cv. huangjingui) (designated as 'OT') and the other was planted with Green tea (*C. sinensis* (L.) O. Kuntze cv. Fuyun 6) (designated as 'GT'). The split-plot design was adopted for this particular study, with two major plots (i.e. OT and GT plots) and three secondary plots (i.e. upper, middle and lower slope positions). Each of the secondary plots had three 15×10 m^2 replicate plots with an interval of 3 m between each plot as a buffer area. Both OT and GT plantations were managed using conventional cultivation techniques. Fifteen soil cores were randomly collected from each plot at two depths (0-15 and 15-30 cm) in May 2008,

using a 7.5 cm diameter auger and bulked.

Chemical analysis
Total C (TC) and N (TN) of soils, leaf litters and roots were analyzed using an isotope ratio mass spectrometer with a Eurovector Elemental Analyser (Isoprime-EuroEA3000, Milan, Italy). Soil CEC, pH (soil:water 1:2.5) and particle size composition were measured using the methods described by Rayment and Higginson (1992). The 2 M KCl extracts were obtained using the modified version of methods described by Chen *et al.* (2005).

Soil microbial analysis
Soil microbial biomass C (MBC) and N (MBN) were measured by the chloroform fumigation-extraction method using an Ec factor of 2.64 (Vance *et al.*, 1987) and an EN factor of 2.22 (Brookes *et al.*, 1985). Soluble organic C and total soluble N in the K_2SO_4 extracts of the fumigated and unfumigated soil samples were determined by the high temperature catalytic oxidation method using SHIMADZU TOC analyzer (fitted with TN unit) (Chen *et al.*, 2005a). The activities of soil protease and L-asparaginase were estimated using the methods by Ladd & Bulter (1972) and Frankenberger & Tabatabai (1991), respectively.

Statistical analysis
Analysis of split plot design with two factors (main factor, genotype of cultivars; secondary factor, slope position) was performed on basic soil properties, SON pools, microbial biomass, enzyme activities, and PLFA profiling data using Statistica Version 6.1 (Statsoft, Inc.). Least significant difference (LSD, $P < 0.05$) was used to separate the means when differences were significant. Pearson linear correlations between SON pools, soil microbial biomass C and N, total soil N and enzyme activity were also conducted in Statistica Version 6.1 (Statsoft, Inc.).

Results
Concentrations of soil SON in KCl extracts (SON_{KCl}) ranged from 27.3 mg kg^{-1} to 54.1 mg kg^{-1} and comprising 33.5%-86.5% of total soluble N and 4.5%-15.0% of total soil N (Table 1). Concentrations of SON_{KCl} and SOC_{KCl} were higher in the MS and LS positions than in the US position at both depths (0-15 cm and 15-30 cm) under both the OT and GT plantations, and decreased with soil depth. In addition, concentrations of soil SON_{KCl} and SOC_{KCl} were higher under the OT plantation than under the GT plantation, and decreased with soil depth (Table 1). Concentrations of NH_4^+-N in KCl extracts were not significantly different among the slope positions except for the 0-15 cm layer under the GT plantation (Table 1), but were lower in the 0-15 cm layer under the OT plantation than under the GT plantation. Concentrations of NO_3^--N in KCl soil extracts were significantly higher at both depths in the MS position than in the US and LS positions under both OT and GT plantations, and were significantly lower under the OT plantation than under the GT plantation (Table 1). Trends in soil microbial biomass C and N between the two genotypes and across the slope positions were similar to the SON pools (Figure 1). Soil protease activities were generally higher in the MS and LS positions than in the US position at both depths under both tea plantations (Figure 2). Soil asparaginase activities showed a similar trend across different slope positions to that for the soil protease activity. Soil protease activities were generally higher in the 0-15 cm and 15-30 cm layers under the OT plantation than under the GT plantation, respectively, while there was no significant difference in soil asparaginase activity between the OT and GT plantations (Figure 2). Both soil protease and asparaginase activities decreased with soil depth.

Conclusions
It has been clearly demonstrated that the genotype and the slope position are key factors controlling the availability of soil SON in tea plantations. Concentrations of soil SON under the OT plantation were generally greater than under the GT plantation, while concentrations of soil SON were greater in the MS and LS positions than in the US position. Organic matter inputs (mainly root litters) of different quantity and quality under different genotypes of tea cultivars were largely responsible for the differences in the SON availability. The variation in soil SON availability at different slope positions may be attributed to different physical and chemical environments (clay content, moisture and soil total C and N etc.) resulting from the downward movement of soil and associated C and nutrients along the slope through the leaching and surface runoff due to the high rainfall and steep slope. Soil microbial biomass and organic N-related enzyme activities (protease and asparaginase) played a vital role in the production and transformation of SON under different genotypes and at different slope positions. Further studies should focus on how the quality and quantity of root and leaf litters affect the SON production, what key functional groups of soil microbial community are involved in the SON transformation and the chemical nature of SON as affected by the genotype and the slope position.

Table 1. Soil soluble inorganic N (NH$_4^+$-N and NO$_3^-$-N) and organic N (SON$_{KCl}$) in 2 M KCl extracts under adjacent Oolong tea and Green tea plantations in subtropical China*.

Soil soluble N and C	Oolong tea				Green tea			
	US	MS	LS	Mean	US	MS	LS	Mean
0-15 cm								
NO$_3^-$-N (mg kg^{-1})	0.3a	1.1a	0.0a	0.5b	1.3b	23.6a	0.0b	8.3a
NH$_4^+$-N (mg kg^{-1})	10.6a	10.6a	13.1a	11.4b	12.0b	23.5a	15.5b	17.0a
SON$_{KCl}$† (mg kg^{-1})	41.7b	52.8a	52.6a	49.0a	30.5b	54.1a	49.4a	44.7a
SOC$_{KCl}$‡ (mg kg^{-1})	460.6b	551.1a	548.1a	519.9a	272.6c	478.6a	369.6b	373.6b
C:N$_{KCl}$ ratio§	11.1a	10.4a	10.4a	10.6a	8.9a	8.8a	7.5b	8.4b
15-30 cm								
NO$_3^-$-N (mg kg^{-1})	0.5a	2.0a	0.0a	0.8b	3.5b	13.4a	1.2b	6.0a
NH$_4^+$-N (mg kg^{-1})	13.0a	12.9a	10.4a	12.1a	11.8a	14.2a	14.4a	13.5a
SON$_{KCl}$† (mg kg^{-1})	36.0b	48.2a	47.5a	43.9a	27.3b	41.8a	37.7a	35.6b
SOC$_{KCl}$‡ (mg kg^{-1})	442.5b	522.4a	509.8a	491.6a	239.3b	323.2a	268.2ab	276.9b
C:N$_{KCl}$ ratio§	12.3a	10.8b	10.7b	11.2a	8.8a	7.7ab	7.1b	7.8b

*Data in the column US (Upper slope), MS (Middle slope) and LS (Lower slope) under each tea cultivar are mean values (n = 3), which are compared among different slope positions within each tea cultivar and each depth; data in the column 'Mean' are mean values across different slope positions under each tea cultivar and within each depth (n = 18), which are compared between tea cultivars. These values are not different at the 5% level of significance if followed by the same letter.

†SON$_{KCl}$, soluble organic N in 2 M KCl extracts; ‡SOC$_{KCl}$, soluble organic carbon in 2 M KCl extracts; §C:N$_{KCl}$ ratio, the ratio of SOC to SON in 2 M KCl extracts.
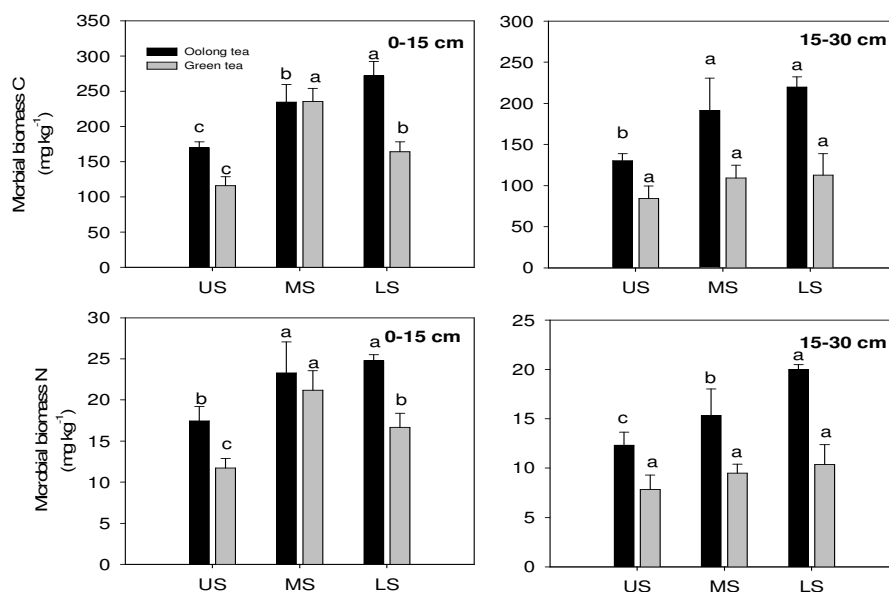
Figure 1. Soil microbial biomass C and N at different slope positions (US, upper slope; MS, middle slope; LS, lower slope) under adjacent Oolong tea and Green tea plantations in subtropical China. Error bars indicate the standard error of the mean (n = 3). Lower case letter indicate statistically significant differences among the slope positions under each tea cultivar.
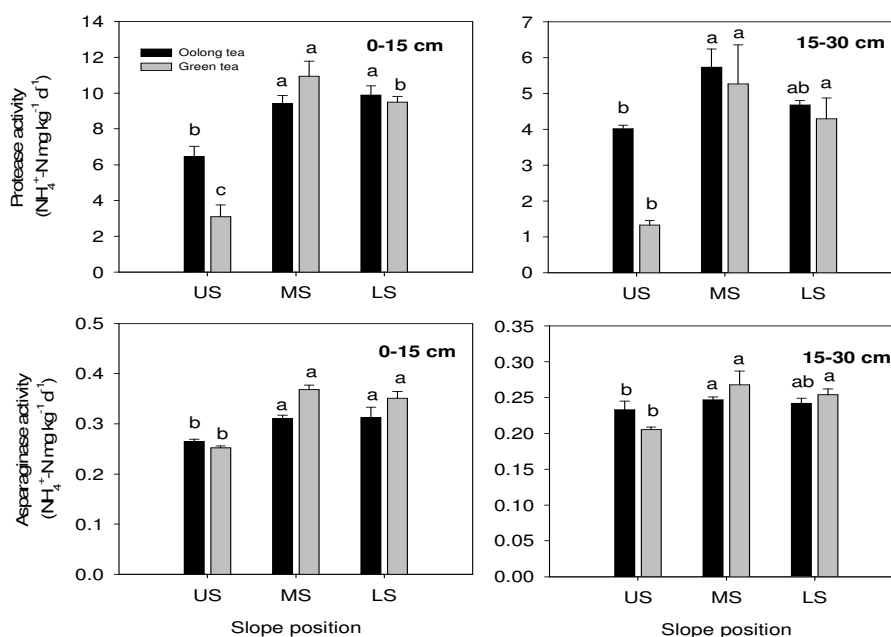
Figure 2. Activities of soil proteases and asparaginases at different slope positions (US, upper slope; MS, middle slope; LS, lower slope) under adjacent Oolong tea and Green tea plantations in subtropical China. Error bars indicate the standard error of the mean (n = 3). Lower case letter indicate statistically significant differences among the slope positions under each tea cultivar.

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Effects of tubificid worms on soil properties in ricefields with organic farming

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Introduction

Tubificid worms (aquatic oligochaetes) are one of the major benthos in lake bottom sediments and are known to disturb lake sediments (Davis, 1974) and influence lake ecosystems through increasing nutrient release to water from the bottom sediments (Fukuhara and Sakamoto, 1987). It is also known that tubificids present at high density in the ricefield rich in organic matter (Simpson *et al*., 1993) and increase nitrogen and phosphate in the submerged soil and the overlying water (Kikuchi and Kurihara, 1977). However, bioturbation and nutrient change by tubificid worms have not been quantitatively determined in ricefield soils.

In this study, we investigated the effects of tubificids on physical and chemical properties of ricefield with organic farming by field survey and in vitro experiments.

Key words

Tubificid, bioturbation, nitrogen mineralization, available phosphate, organic farming

Materials and methods

We measured the population density of tubificids in the winter-flooded and organically managed ricefield of Miyagi, Japan. Bioturbation by tubificids was estimated by soil thickness and weight transported over rice straw left last autumn in two no-tillage paddy fields with organic farming.

In order to analyze quantitative change of soil nutrients induced by tubificid activity, incubation experiment were conducted under continuous dark and dark/light (12/12 hours) at 30°C for 4 weeks using 300 mL vials with 7 cm depth of alluvial soil and 5 cm depth of overlying water. Concentrations of ammonium, phosphate and ferrous iron were measured in the soil with and without tubificids (*Branchiura sowerbyi*) (0-78 g/m on the basis of wet weight).

Results

The major species of tubificids were *Limnodrilus socialis* and *Branchiura sowerbyi* in the ricefields surveyed. The population densities of tubificids were higher in the two ricefields with organic farming (maximum densities: about 40,000 ind/m) than those of the conventional ricefields with application of agrichemicals. Surface soils were disturbed by feeding and excretion action of tubificids. Some 60 mm in thickness and 35 kg/m in dry weight of soils were transported over decayed rice straws left last autumn in the two no-tillage ricefields with high densities of tubificids.

Concentrations of ammonium nitrogen and available phosphate (Bray 2 extraction) in the soils significantly increased in proportion to tubificid densities under continuous dark and dark/light. Ferrous iron formation also increased in proportion to tubificid densities. It means that soil reduction through soil organic matter decomposition was stimulated by tubificid activity. Tubififids increased bioavailable nitrogen and phosphate in the submerged soil probably due to accelerating soil organic matter decomposition.
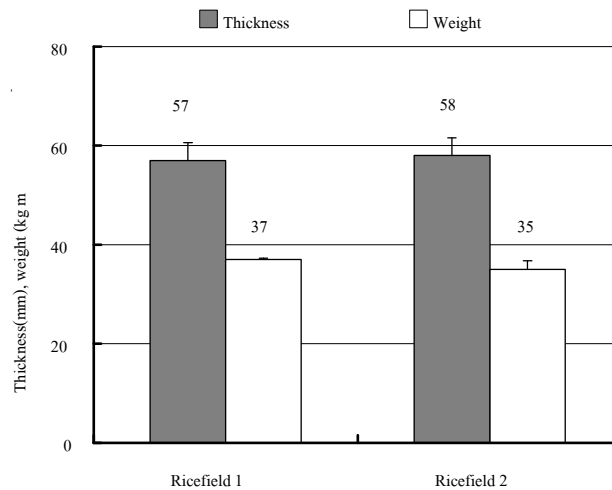
Figure 1. Soil mass transported over rice straws left on last autumn in the no-tilled ricefields.

Conclusion

Aquatic earthworm, tubificids increased in the ricefields with organic farming. Tubificid worms significantly disturbed surface soils and changed soil chemical properties in ricefields.

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Elevated CO_2 and nitrogen effects on dissolved organic carbon of two calcareous and non calcareous soils

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Abstract
Dissolved organic carbon (DOC) pools can be considered as suitable indicators of soil quality that are very sensitive to CO_2 levels, nitrogen fertilizer and plant residues. In this research controlled chambers were used to investigate the effects of elevated atmospheric CO_2 concentrations (350 vs. 760 ppm) under two level of nitrogen fertilizer (0 vs. 200 kg N ha^{-1}) and two different plant residues (alfalfa residue and wheat straw) on DOC of two calcareous and non calcareous soils. The results showed that elevated CO_2 significantly increased DOC in calcareous and non calcareous soils. In the soils that received high rates of nitrogen fertilizer, release of DOC at elevated and ambient CO_2 increased by approximately 30% compared to soils without nitrogen fertilizer. The amount of DOC tended to be affected by organic matter in both elevated and ambient CO_2. In calcareous soil exposed to elevated and ambient CO_2 concentrations of DOC in samples receiving high or no N fertilizer were always higher than for non-calcareous soil. We conclude that release of DOC in elevated CO_2 is controlled by multifactors such as soil organic matter, N and $CaCO_3$ levels of soils.

Key Words
Enhanced Carbon Dioxide, DOC, nitrogen fertilization, calcareous soils, C/N Ratio

Introduction
Increasing CO_2 levels are expected to have numerous direct and indirect effects on terrestrial ecosystems (Bazzaz 1990). Among those effects, changes of above ground plant processes such as photosynthesis, transpiration, biomass accumulation and microbial respiration (lekkerkerk *et al*. 1990; Norby 1994) have been identified. Few studies have documented the effects of an elevated atmospheric CO_2 on the dynamics of soil soluble organic carbon (Hill *et al*. 2005; Cheng *et al*. 1998) and most of these data were obtained from non calcareous soils. In addition, the application of nitrogen fertilizer during normal agricultural practices which leads to enrichment of ecosystems with nitrogen intensifies the importance of the fate of the applied nitrogen and its effect on DOC. It is generally believed that the amount of available nitrogen in the plough layer of agricultural soils usually meets the demands during the decomposition of straw and change the concentration of soil carbon (Christensen 1985)

The impacts of elevated CO_2 and nitrogen availability on soil DOC have shown contradictory and inconsistent results. In some cases, elevated CO_2 has been predicted to increase soil carbon storage. For example, Ross *et al*. 2002 suggested that increase in organic carbon in soil exposed to high CO_2 might have been caused by preferential metabolism by the decomposer populations of easily decomposable soil carbon. Indeed, Hu *et al*. 2001 reported an increase in available carbon for microbes under annual grasslands after 5 years of elevated CO_2. In other case elevated CO_2 has been observed to decreased soil carbon storage. Sowerby *et al*. (2000) concluded that in soil exposed to CO_2 soil carbon storage decreased more rapidly than in soils under ambient CO_2.

The objective of the present study was to quantify (i) the short-term effects of elevated CO_2 and nitrogen fertilizer on DOC, and (ii) different effect of elevated CO_2 in two calcareous soils. We hypothesize that dissolved organic carbon quickly decreases in elevated CO_2. We further hypothesize that nitrogen availability affects the response of soil DOC to elevated CO_2. The uses of calcareous and non calcareous soils enable us to distinguish the contributions of lime, CO_2 and nitrogen on DOC.

Materials and methods
Soil sampling
We used two mineral soils representing calcareous and non calcareous soils. These soils were obtained from 0-30 cm of Kardeh dam (Soil 1) and Saghravan zone (Soil 2) in Mashhad, Khorasan Razavi province, Iran. Soil samples were air dried, sieved (2mm) and stored at $4^{o}C$ until treatments were performed. Table 1 provides a summary of soils properties.

Table1. Physical and chemical properties of soil samples.

Soil property	Calcareous Soil (Soil 1)	Non calcareous Soil (Soil 2)
Clay (%)	20	25
Silt (%)	34	35
Sand (%)	46	40
pH	8.02	6.8
N (%)	0.111	0.13
$CaCO_3$ (%)	32.66	3.4
OC (%)	1.663	1.530
EC (dS/m)	3.53	2.9

Experimental design and Analytical procedures

A factorial, completely randomized design including two soil types (soil 1with 32% and soil2 with 3.4% lime), two CO_2 levels (350 and 760 ppm), two levels of nitrogen fertilizer as Urea (0, 200 Kg ha^{-1}), two organic matter residue treatments (wheat straw and alfalfa residues) and a control (without organic matter) with two replications were employed in this experiment. Three subsamples were made from each soil sample, one set of subsamples were mixed with wheat straw (2 mm in size, 2.5 %), another set were mixed with alfalfa residue (2 mm in size, 2.5 %) and a control treatment. Organic matter was applied uniformly to soil subsamples. Nitrogen fertilizer was applied to half of the subsamples. The experimental design consisted of 2 chambers (aluminum frame and clear plastic walls 120 ×240×70 cm high). The halves of samples were transferred to the chamber with 760 ppm and the other half were placed in the chamber with 350 ppm of CO_2. CO_2 measurements were performed several times a day for the first month and then daily afterwards. The use of closed chambers, as opposed to open-top chambers, ensure that concentrations rarely deviate more than 50 µmol ppm from their set point and that that CO_2 concentration homogeneous within the chamber (Barnard *et al*. 2005). Distilled water was applied to all samples to increase moisture content to 70 % of field capacity. The soils were checked every 2 to 3 days to keep soil moisture constant. To minimize the effect of environment both elevated and ambient chambers kept equal conditions during the experiment. Soil samples were analyzed after 0, 10, 20, 40, 60 and 90 days. A subsample of 10 g of soil was oven-dried at 105° C for 24 h for determining soil moisture. For DOC measurements, water samples were collected, filtered by 0.45-µm filters and were analyzed using TOC-Shimadzu V CPH analyzer (Shymadzu Coro., Kyoto, Japan).

Results and Discussion

The result of this study showed that DOC concentrations significantly increased in both soils exposed to elevated CO_2 compared with ambient CO_2 (Figure 1). The response of DOC concentrations was presumably caused by increased decomposer activity and quantity in elevated CO_2. Recent studies suggest that the activity and biomass of microorganisms appeared to be enhanced under elevated CO_2 (Wall 2001). Our findings are also in line with Kang *et al*. (2005) who found that elevated CO_2 increased DOC concentrations in wetlands, as soil microbes appeared to be affected. However, other studies detected that elevated atmospheric CO_2 did not affect the concentration of DOC in soil (Ross *et al*. 1995). For calcareous soil (Soil 1) the DOC concentration was almost 1.45 times greater than for non calcareous soil (Soil 2) for both elevated and ambient CO_2 (Figure 1). It seems that high amounts of $CaCO_3$, organic matter and higher pH in soil1 intensified microbial activity and resulted in increasing DOC (Filep *et al*. 2003).

Nitrogen fertilizer significantly affects the concentration of DOC in both calcareous and non calcareous soils (Figure 2). Nitrogen fertilizer application increased DOC significantly. The observed N-fertilization effect on DOC confirms our conclusion that microbial growth and activity may have increased, which may have allowed a partial release of DOC. Similarly, Sitaula *et al.* (2004) found that the application of N fertilizers had positive effects on organic matter decomposition and DOC release in forest soils. They indicated that high N addition might also have a direct effect on microbial activity and increase DOC mobility in soil. Curtis *et al.* (1995) also reported that soil nitrogen indirectly affects the release of organic nutrients such as DOC. The results also showed that DOC concentration in non calcareous soil is lower than for calcareous soil. It seems that the lower pH in non calcareous soil can be considered as a factor to amplify DOC adsorption by soil mineral particles and consequently DOC concentration decline in soil solution.
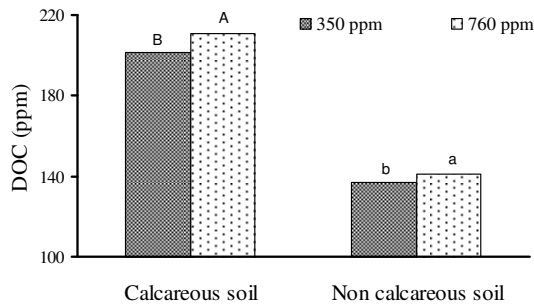
Figure 1. Influence of elevated and ambient CO_2 on DOC concentration (Means were separately compared in each soil).
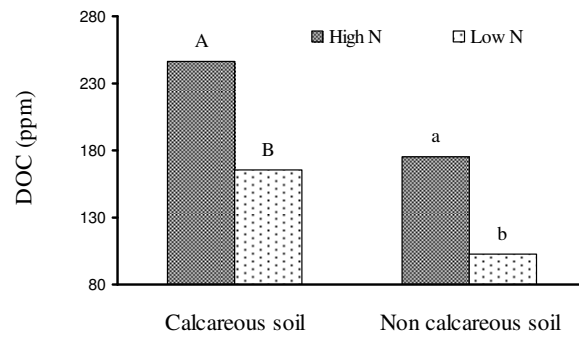
Figure 2. Influence of N availability on DOC concentration. (Means were separately compared in each soil).

In both soils N availability strongly influenced the effect of elevated CO_2 on DOC concentration (Figure 3). Although in both soils elevated CO_2 increased DOC concentration for high N availability treatments, for low N availability in the non calcareous soil elevated CO_2 caused DOC to decrease and it did not have a significant effect for the calcareous soil. The high availability of nitrogen increased microbial activity and DOC concentration in soil. Limited nitrogen availability for unfertilized treatments limited microbial growth which may have decreased accumulation of DOC (Hoosbeek *et al*. 2007). As it is obvious in Figure 3, elevated CO_2 had the greatest effect on DOC concentration for N treatments in calcareous soil (soil 1).
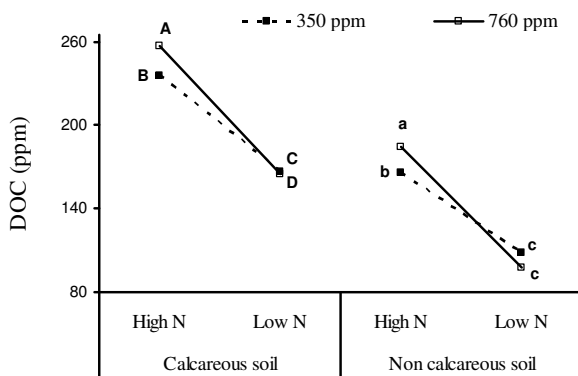
Figure 3. Interaction effects of CO_2 and N availability on DOC concentration. (Means were separately compared).
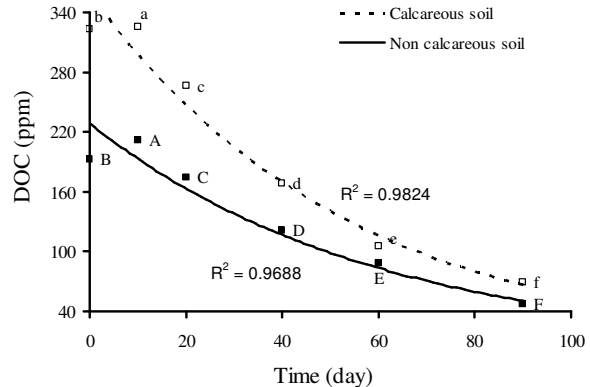
Figure 4. Exponential trends of DOC concentration with time.

The concentrations of DOC declined almost exponentially with time for elevated and ambient CO_2 in both soils (Figure 4). It seems that residue decomposition and emission of CO_2 from soils resulted in decreasing DOC concentration for both soils. The negative effect of time on DOC agrees with several similar studies (Karlik 1995; Anderson *et al*. 1999). Paustian *et al*. (1997) have shown that through time organic matters respired by soil microorganisms.

Conclusion

The results showed that CO_2 concentration had a same effect on DOC concentration for both calcareous and non calcareous soils and DOC concentrations increased in both soils for the elevated CO_2 treatment. Nitrogen fertilizer had a positive effect on DOC concentration of soil samples. Application of N fertilizer

increased DOC in all treatments. However in non-calcareous soil the concentration of DOC was lower than calcareous soil for all elevated and ambient treatments, possibly because of the higher pH in calcareous soil and consequent higher microbial activity. Additional research will be required to determine whether the composition and size of the soil microbial community will change under elevated CO_2 and for different N treatments in calcareous and non-calcareous soils.

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Evaluation of Nitrogen Availability from Raw and Treated Dairy Manures

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Abstract

There is minimal information on the composition of and amounts of potentially available nitrogen from treated manures. Knowing how nitrogen (N) availability differs with manure treatment will result in better N crediting guidelines. Twenty different dairy manures were sampled from five dairy farms and include raw, anaerobically digested before and after liquid-solid separation, non-digested separated liquids and solids, and composted bedded pack manures. The manures were incubated with five representative Wisconsin soils for 112 d. Manure potentially available N (PAN) differed by manure type and by soil. Generally, the treated liquids had significantly more ($P<0.05$) PAN than the raw liquids and the solids had significantly less ($P<0.05$) PAN than the raw liquids. N was immobilized in several of the solid manure types evaluated. The manure characteristics best correlated with PAN were acid detergent fiber (ADF) to total N (TN) ratio, neutral detergent fiber (NDF):TN, and NH_4-N:TN (r=-0.94, -0.93, and 0.90, respectively, $p<0.0001$). Using linear regression, PAN was best predicted by a model including NH_4-N:TN and organic N concentrations in manure as terms. This equation may assist in refining current University of Wisconsin-Extension first-year N availability estimates of treated, untreated, solid and liquid manures.

Key words

Potentially available nitrogen, dairy manure, nitrogen mineralization, nitrogen immobilization

Introduction

On-farm manure treatment systems are increasing in popularity among producers in the USA for various reasons, including more efficient transportation and storage along with reduced odor and lower pathogen levels in treated manure. Such treatment systems (anaerobic digestion, composting, and liquid-solid separation) alter the chemical and physical properties of manure, from nutrient concentrations to particle size and moisture content (Castellanos and Pratt 1981; Douglas and Magdoff 1991; Gordillo and Cabrera 1997; Shi *et al.* 1999; Chantigny *et al.* 2008; de Boer 2008). These properties have the potential to affect plant available nutrients when the manure is applied to agricultural fields.

Research on N availability of emerging dairy manure treatment systems is sparse. Additional research is necessary to determine if nitrogen availability guidelines should be modified to consider manure treatment or manure characteristics. The objectives of this study were: 1) to determine how much potentially available nitrogen (PAN) and N mineralization differs between raw and treated manures, 2) to assess manure compositional effects on PAN and N mineralization, and 3) to construct a model to predict potential N availability with various manure characteristics.

Methods

A laboratory incubation was conducted where five soils (four silt loams and one sand) were amended with 20 different raw and treated manures from five farms. Selected manure properties are provided in Table 1. Each manure was mixed with 40 g of each soil at a rate of 150 mg total N/kg with four replications except for two treatments, RW-RL and RW-SeL, where manure was applied at 100 mg total N/kg soil, because the large amount of liquid manure needed at the 150 mg total N/kg application rate would have created soil conditions greater than 60% water filled pore space. There was also an untreated control for each soil. Treated soils were incubated at 25°C for 112 days; moisture was maintained between 40 and 60% water filled pore space. At the end of the incubation soils were immediately air-dried. Ground soils samples were extracted with 2 M KCl in a 1:10 soil to solution ratio for one hour, filtered through Whatman no. 2, and analyzed for NH_4^+-N (Keeney and Nelson 1982) and NO_3^--N (Doane and Horwáth 2003).

Table 1. Selected manure characteristics and percent of total manure N that is potentially available averaged over five soils.

Farm-manure	Manure type	Total N	NH$_4$-N	Dry matter	NDF†	Total C: Total N	%PAN$_m$ ‡
		—— (g/kg dry matter) ——					(%)
5S-RL	Raw liquid	37.7	16.2	67	542.6	11.4	33.4 b§
5S-DL	Digest liquid	51.0	25.1	47	453.2	7.6	43.5 ab
5S-DSeL	Digested separated liquid	71.3	38.4	31	210.9	5.4	52.2 a
5S-DSeStL	Digested separated stored liquid	67.1	36.1	33	261.7	5.7	48.1 a
5S-DSeS	Digested separated solid	15.7	0.5	326	804.8	29.9	-14.6 d
5S-DSeCuS	Digested separated cured solid	21.7	1.7	323	790.3	20.5	0.4 c
CH-RL	Raw liquid	39.7	20.7	49	450.7	9.7	38.9 b
CH-DL	Digested liquid	79.3	52.5	26	200.9	4.6	57.6 a
CH-DSeL	Digested separated liquid	38.5	20.4	75	474.8	8.3	48.6 ab
CH-DSeS	Digested separated solid	21.8	5.4	262	721.9	19.9	17.0 c
RW-RL	Raw liquid	51.7	30.1	25	448.1	9.3	46.4 b
RW-SeL	Separated liquid	114.5	87.3	10	154.8	3	59.4 a
RW-SeStL	Separated stored liquid	112.1	32.1	28	517.6	5.2	46.1 b
RW-SeS	Separated solid	15.5	2.8	167	847.9	30.3	-15.6 d
RW-SeCoS	Separated composted solid	28.4	1.2	247	734.7	14.9	9.5 c
NP-CBP1	Compost bedded pack 0-30 cm	19.8	0.6	397	814.0	23.4	-13.3 b
NP-CBP2	Compost bedded pack 31-60 cm	23.1	5.4	377	814.0	18.7	9.3 a
NP-CBP3	Compost bedded pack 61-90 cm	21.3	4.6	383	725.4	18	12.5 a
MRS-RS	Raw solid-Scrape alley	30.7	15.0	138	780.6	2.2	41.8 a
MRS-RSA	Raw solid-Approachment	16.1	5.0	243	602.3	7.4	-2.8 b

† NDF, neutral detergent fiber.
‡ %PAN$_m$, percent of total manure N that is potentially available N.
§ Within a farm, %PAN$_m$ is significantly ($P<0.05$) different between manures with different letters.

Because two N application rates were used, all results were converted into percentages of total N applied. PAN from the soil and manure as a percent of total N applied (%PAN$_{m+s}$) was calculated as the sum of the NH$_4^+$-N and NO$_3^-$-N concentrations divided by the application rate by the equation:

$$\%PAN_{m+s} = [(NH_4^+\text{-}N + NO_3^-\text{-}N)_{treated}/ \text{ total N applied}] \times 100 \qquad \text{Eq. [1].}$$

%PAN$_{m+s}$ includes mineral N added with the manure and manure organic N that mineralized during the incubation as well as N that mineralized from the soil. PAN from the manure only (%PAN$_m$) is given as a percent of total N applied and was calculated as the inorganic N concentration in a treatment minus the inorganic N concentration in the control samples divided by the total N applied, as given the equation:

$$\%PAN_m = \{[(NH_4^+\text{-}N + NO_3^-\text{-}N)_{treated} - (NH_4^+\text{-}N + NO_3^-\text{-}N)_{control}]/\text{total N applied}\}\times 100 \qquad \text{Eq. [2].}$$

Note %PAN$_m$ includes both mineral N added with the manure plus the manure organic N that mineralized.

A mixed model for a completely randomized design was used to assess the affect of manure treatment and soil type on PAN$_m$ at the end of the incubation (PAN$_m$) with manure considered a fixed effect and soil a random effect. Mean separations were performed using Tukey's HSD with α=0.05. A t-test was used to determine if means of %PAN$_m$ were significantly ($P<0.05$) different than 0 or 40%. Relationships between %PAN$_m$ and manure characteristics were assessed by correlations. Stepwise multiple linear regression was used to determine the equations that best predicted %PAN$_m$. Mallow's Cp statistic was calculated to determine the best number of parameters to include in the linear regression equations.

Results

The %PAN$_m$ was analyzed for all soils combined at each dairy individually. At the 5S Dairy digested separated liquid (5S-DSeL) and digested separated stored liquid (5S-DSeStL) manure had significantly ($P<0.05$) greater %PAN$_m$ (52.2 and 48.1%, respectively) compared to the raw liquid (5S-RL; 33.4%); while %PAN$_m$ for the digested liquid (5S-DL) prior to separation (43.5%) was not different than the raw or digested separated liquids (Table 1). The digested separated solid (5S-DSeS) manure immobilized N as evidenced by the negative value for %PAN$_m$ (-14.6%). Curing (not active composting) the digested separated solid (5S-DSeCuS) reduced the

total C (TC):TN ratio and resulted in %PAN$_m$ of 0.4%, which was not significantly different than zero. Atallah *et al.* (1995) found that increasing storage time of cattle manure decreased N immobilization by increasing the stability of organic matter, explaining why curing of digested separated solids increased %PAN$_m$ in the present study.

Percent of PAN$_m$ from the digested liquid at the CH Dairy (CH-DL) was significantly greater than the raw liquid (CH-RL) (57.6 and 38.9%, respectively). Unlike the 5S Dairy, %PAN$_m$ from the digested separated solid at CH dairy (CH-DSeS) (17.0%) was significantly less than %PAN$_m$ from the raw liquid but was significantly greater than zero which is in contrast to the 5S Dairy. The digested separated solids immobilized N at 5S Dairy but not at CH Dairy. This difference might be attributed to 5S Dairy adding 10% fats to the anaerobic digester to improve biogas yield; addition of high C, low N material such as fat would decrease %PAN$_m$ if the fat were not completely digested.

The treatment system at the RW Dairy consisted of a liquid-solid separator only. The separated liquid sampled immediately after separation (RW-SeL) had the greatest %PAN$_m$ at 59.4%. The raw liquid (RW-RL) and separated stored liquid (RW-SeStL) had nearly identical %PAN$_m$, which is not surprising considering the neutral detergent fiber (NDF), dry mater, and NH$_4^+$-N concentration were similar as well. The separated solids (RW-SeS) initially immobilized N, but after composting (RW-SeCoS), %PAN$_m$ was 9.5%. During the composting process the TC:TN ratio of the solid was reduced by 50% and the NDF was reduced.

In a composted bedded pack system, bedding is added to the barn daily and the pack is actively composted by aerating it daily to a depth of about 30 cm. The pack was sampled in 30 cm increments prior to cleaning the barn. Percent of PAN$_m$ from the bottom two depths of the pack (NP-CBP2, and NP-CMP3) were not significantly different from each other and were significantly less than 40%, but were significantly greater than %PAN$_m$ from the first depth (NP-CBP1) where N was immobilized. The composting process for the first depth was not as complete as the lower two depths as evidenced by the greater TC:TN ratio and lower NH$_4$-N concentration.

Two raw solid manures from MRS Dairy were also evaluated with %PAN$_m$ from the scrape alley (MRS-RS) (41.8%) being significantly greater than manure from the approachment (MRS-RSA) which immobilized N (%PAN$_m$ of -2.8%). The large difference in %PAN$_m$ with these two raw solid manures is related to the large amount of straw that was visible in the approachment manure (MRS-RSA).

Manure separation is very influential on %PAN$_m$ with or with anaerobic digestion as a pre-treatment. Liquid-solid separators are effective in creating a separate liquid that has significantly lower dry matter, NDF, and TC:TN ratio along with greater NH$_4^+$-N concentration as a percent of TN compared to raw manure, which results in increased %PAN$_m$, while the separated solids have opposite properties and reduced %PAN$_m$. Using correlation analysis for all manures, %PAN$_m$ was significantly ($P<0.05$) correlated to dry matter, NDF, TN, ADF, and NH$_4^+$-N (r = -0.83, -0.82, 0.81, -0.80, and 0.78, respectively) along with other parameters however correlation coefficients were less. The negative correlations between %PAN$_m$ and NDF and ADF indicate that the greater the concentration of lignin, cellulose, and hemicellulose in manure creates greater microbial demand for N, subsequently reducing %PAN$_m$.

In an effort to provide a better prediction of %PAN$_m$, which could be used by farmers to credit manure N against crop needs, multiple regression analysis was used to develop a predictive model. A two-term model was determined to be superior to either a one or two term model. There were three good two-term models; parameters and R^2 values were: 1) ADF:TN + TC:organic N (ON) (R^2=0.913), 2) NDF:TN + TC:ON (R^2=0.915), and 3) NH$_4^+$-N:TN + ON (R^2=0.875). These three models were evaluated in a method similar to Doerge and Gardner (1988) to evaluate error and bias of predicted vs actual %PAN$_m$. While the third model had the lowest model R^2, predicted values with this model had the greatest correlation coefficient (r=0.93) with actual values compared to the first (r=0.90) and second (r=0.84) models. In addition, the first two models included parameters, NDF and ADF, which are not routinely analyzed for manure. The third equation might be a more practical estimation of %PAN$_m$ because all the parameters are routinely analyzed on manure samples and the predicted %PAN$_m$ most closely matched actual %PAN$_m$. The complete third equation is: %PAN$_m$ = 92.6* NH$_4^+$-N:TN + ON – 30.3.

Conclusions
Manure treatment significantly affects $\%PAN_m$ compared to raw manure; in general, treated liquid manures have greater and treated solid manures have lesser $\%PAN_m$. University of Wisconsin-Extension guidelines assume that 40% of TN is available if manure is incorporated, regardless of manure type, handling, and/or treatment. These data suggest that manure N availability guidelines should be updated to be applicable for all manure types. Results from this study suggest that $\%PAN_m$ might be predicted using NH_4^+-N:TN and ON. Further research is required to validate this research in a field setting.

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Impact of potassium humate on selected chemical properties of an Acidic soil

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Abstract

Potassium humates (KH) derived from lignite brown coal are alkaline, rich in carboxylic and phenolic groups, aromatic in nature provide favorable conditions for biological activity, chemical reactions and physical improvement of soil. They promote chemical reaction for cation exchange, increase pH buffering capacity of soils, bind and sequester phytotoxic elements and accelerate transport of nutrients to plants. A commercially available KH was used in this research to evaluate its effect on selected chemical properties of acid soil under laboratory condition. A soil was treated with different doses of KH (25, 50, 75, 100 kg ha^{-1} and control) along with P (control and 70 kg ha^{-1}) in the form of triple super phosphate (TSP). It was observed that when only P (T$_2$) was applied low pH values were found for this treatment. Whereas, the values of EC, pH, total carbon and effective CEC were significantly increased as the dose of KH increased over control, effect of T$_6$ (70 P$_2$O$_5$ and 100 KH kg ha^{-1}) was more pronounced. However no significant difference was found between T$_5$ and T$_6$ for EC, pH and effective CEC but there was a difference in total carbon. Results indicates that T$_6$ (70 kg P$_2$O$_5$ and 100 kg KH ha^{-1}) was a better treatment.

Key Words

Potassium humate, acidic soil, EC, pH, total C and Effective CEC

Introduction

Acidification of soil is a naturally occurring process. However, soil acidity is a major limitation to crop production on highly weathered and leached soils in both tropical as well as temperate regions of the world, (Sanches, 1976; Von Uexkull and Mutert, 1995). Main causes of acidification are leaching and nitrification due to excessive use of nitrogenous fertilization (Wild, 1988). Phytotoxicity of Al and Mn is often due to low pH of soil, and deficiency of Ca and Mg (Leeper and Uren, 1993).It has been proved that traditional liming treatments to be largely ineffective in short term duration because vertical movement of surface applied lime is slow (Pavan *et al.*, 1982; Richey, 1996), and costly (Cassel, 1980) especially within the root zone (Noble *et al.*, 1995; Bruce *et al*., 1988).Organic materials which are rich in Ca like Fulvic and humic acid based treatment to subsoil acidity denoted some considerable promises (Vander Watt *et al.*, 1991; Noble *et al.*, 1995). Humic substances are the most active fraction of humus, (Hayes *et al.*, 1989). HA is oxidized lignite brown coal that is used in the production of humic substances also known as humates. However, oxidized lignites are used as soil and plant amendments often on account of their high content of humic acids (30 to 60%). In addition, humates may provide an alternative to liming, ameliorating the soil organic matter that is responsible for the generic improvement of soil fertility and improved productivity (Kononova, 1966; Fortun *et al.*, 1989). The objective of this study was to evaluate the potential of commercially available KH derived from lignite brown coal on an acidic soil under rice cultivation.

Methods

The acid soil used in the 60 days incubation experiment was taken from a rice field located in Alor Kedah, The texture of the soil is a silty clay loam and belongs to the Kangkong (Inceptisols) soil series. The soil was sieved to pass 2 mm and 25g of it was placed in a vial. The layout of the experiment was completely randomized design with three replicates and six treatments. KH (0, 25, 50, 75 and 100 kg ha^{-1}) and phosphorus (0 and 70 kg P$_2$O$_5$ ha^{-1}) in the form of triple superphosphate were applied on the surface of the soil before watering; water was applied at field capacity level. At 15 days of incubation, soil samples were analyzed for EC, pH, total carbon and effective CEC.

The KH used in this study is alkaline. It was produced from Chinese lignite brown coal and is commercially available in Pakistan where it is used as a soil conditioner. It contains 55% humic acid and 12 % potassium oxide. Soil texture was determined using the pipette method (Gee and Bauder, 1982), total carbon was determined using LECO CR-412,effective CEC by BaCl$_2$ method (Hendershot and Duquette,1986), electrical

conductivity and pH at 1: 2.5 soil to water ratio (Chapman *et al*., 1961) were determined. Data were statistically analyzed using the Statistical Analysis System (SAS).

Results

The texture of the soil was a silty clay loam with pH, EC, total carbon and effective CEC typical of Kangkong series (Table 1). The N, C, S, H, O contents and C/N ratio of the potassium humate (KH) were 2.76 %, 38.44 %, 1.04 %, 3.40 %, 54.81 and 16.40, respectively. The phenolic, carboxylic, and total acidity were 194, 386 and 580 meq per100g, respectively (Table 2).

Table 3 1 shows that application of P alone (T_2) resulted in higher EC values in the 15-30 days incubation period compared to T_3 and T_4. T_6 increased the soil EC in comparison with the application of T_3, T_4 and T_5. Generally, the soil EC gradually increased with increase in incubation period. This observation is consistent with that of Albert *et al*. (2004).

Table 4 shows that pH increased with increasing rate of KH. Soil pH was lower with the application of 70kg ha^{-1} P_2O_5 in comparison with the control. Similarly, soil pH was also influenced by variation in incubation periods. The incubation of the treatments for 60 days resulted in a higher increase in soil pH as compared to other incubation periods. Similar findings have been reported by Albert *et al*. (2004).

Total carbon content in the soil is shown in table 5. It reveals no significant difference between control and T2.There was a corresponding increase in total Carbon as KH rate increase. The incubation period also resulted in an increase in total carbon. The results are supported by findings of Melero *et al*. (2007).

Effective cation exchange capacity (ECEC) data are presented in Table 6 and show that T2, T3 T4, T5 and T6 had significant effects on ECEC. Further it was observed that there was no significant difference between T5 and T_6. The results are supported by findings of Obviza *et al*., 1989, Cooper *et al*., 1998 and Mikkelson, 2005.

Table 1. Some chemical and physical properties of the acidic soil before conducting the experiment.

Soil property	Values
Texture	silty clay loam
pH (H_2O)	5.48
EC µS cm^{-1}	849
Total carbon % (w/w)	2.026
Effective CEC (cmol(+) kg^{-1})	9.44

Table 2. Elemental and functional group analysis of potassium humate (KH).

Nitrogen (N)	2.76 %
Carbon (C)	38.44 %
Sulfur (S)	1.04 %
Hydrogen (H)	3.40 %
Carbon nitrogen ratio (C/N)	16.40
Oxygen	54.81
Phenolic	194 meq 100g
Carboxylic	386 meq 100g
Total acidity	580 meq 100g

Table 3. Effect of potassium humate (KH) on EC (µS cm^{-1}) of an acidic soil.

Treatment	Incubation Period			
P_2O_5 + KH kg ha^{-1}	15 Days	30 Days	45 Days	60 Days
T_1 = 00 + 00	850d	849d	855d	852e
T_2 = 70 + 00	935a	944a	937b	932c
T_3 = 70 + 25	885c	892c	904c	921cd
T_4 = 70 + 50	898bc	910bc	929b	945c
T_5 = 70 + 75	910bc	918b	941b	961ab
T_6 = 70 + 100	921b	926b	962a	974a

Table 4. Effect of potassium humate (KH) on pH of an acidic soil.

Treatment	Incubation Period			
P_2O_5 + KH kg ha^{-1}	15 Days	30 Days	45 Days	60 Days
T_1 = 00 + 00	5.48d	5.49d	5.51d	5.50d
T_2 = 70 + 00	5.37e	5.41e	5.44e	5.48e
T_3 = 70 + 25	5.67c	5.70c	5.75c	5.76c
T_4 = 70 + 50	5.74b	5.80b	5.85b	5.89b
T_5 = 70 + 75	5.85a	5.89a	5.94a	6.01a
T_6 = 70 + 100	5.86a	5.91a	5.96a	6.03a

Table 5. Effect of potassium humate (KH) on total carbon of an acidic soil.

Treatment	Incubation Period			
P_2O_5 + KH kg ha^{-1}	15 Days	30 Days	45 Days	60 Days
T_1 = 00 + 00	2.025e	2.028e	2.029e	2.027e
T_2 = 70 + 00	2.033ed	2.036e	2.041e	2.038e
T_3 = 70 + 25	2.046d	2.055d	2.072d	2.084d
T_4 = 70 + 50	2.069c	2.083c	2.095c	2.120c
T_5 = 70 + 75	2.096b	2.119b	2.143b	2.177b
T_6 = 70 + 100	2.129a	2.153a	2.185a	2.213a

Table 6. Effect of potassium humate on ECEC (cmol(+)kg^{-1}) of an acidic soil.

Treatment	Incubation Period			
P_2O_5 + KH kg ha^{-1}	15 Days	30 Days	45 Days	60 Days
T_1 = 00 + 00	9.488c	9.479c	9.522d	9.441e
T_2 = 70 + 00	10.814b	10.605b	10.397c	10.454d
T_3 = 70 + 25	10.834b	10.620b	10.824bc	10.911c
T_4 = 70 + 50	10.841b	11.046ab	11.226ab	11.326b
T_5 = 70 + 75	11.031ab	11.358a	11.393ab	11.596ab
T_6 = 70 + 100	11.111a	11.482a	11.567a	11.786a

Means in column with different with different alphabets indicate significant difference at $P \leq 0.05$ using Tukey's test.

Conclusion

The treatment with 100 kg KH and 70 kg P_2O_5 ha^{-1} had significant effects on EC, pH and ECEC, and maximum values for Total carbon occurred for T_6 (100 kg KH ha^{-1}).

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Impact of soil amendments on organic carbon pools under a rice-wheat cropping system

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Abstract
Rice-wheat cropping is the dominant cropping sequence in the Indo-Gangetic plains (IGP) of India. An experiment was conducted to study the impact of continuous application of farmyard manure (FYM) and rice straw (RS), either alone or in conjunction with fertilizer nitrogen (N), under a rice-wheat cropping system on i) total soil organic carbon (SOC) and slow pool C, and ii) stabilization of cumulative input C. Application of FYM, after seven years of rice-wheat cropping cycles, increased total SOC and slow pool C at 0-0.15 m soil depth by 6.7 t/ha and 1.5 t/ha, respectively, with the highest effect when FYM, RS and fertilizer N were applied together. Incorporation of RS increased total SOC by 4.1 t/ha, with an insignificant effect on the slow pool C. There was no significant effect of fertilizer N application on total SOC and slow pool C. The slow pool C was strongly correlated with the total SOC. About 18.5% and 4.2% of the cumulative input C were stabilized as total SOC and slow pool C, respectively, due to application of FYM; values for RS were 17.9% and 3.3%, respectively.

Key Words
Farmyard manure, rice straw, nitrogen, slow pool C, C stabilization

Introduction
Rice–wheat cropping systems are of immense importance for food security and livelihoods in South Asia. About 85% of the rice-wheat area in South Asia is located in the IGP. Since the late 1990s, rice and/or wheat yields have stagnated or declined across the IGP (Ladha *et al*., 2003). Regmi *et al*. (2002) attributed the reduced productivity of the rice-wheat system to the decline in soil organic matter (SOM) and decreased soil fertility. Terrestrial ecosystem models, such as CENTURY (Parton *et al*., 1988), partition SOC into an active pool with turnover time ranging from 1-3 months, a slow pool with turnover time ranging from 10 to 50 years, and a passive pool with turnover time ranging from 400 to 4000 years. Most of the studies in the IGP are related to the management effect on the active or labile C pool and total SOC (Sekhon *et al.,* 2009; Benbi and Brar, 2009). Information about the impact of agricultural management practices on slow pool C, particularly under rice-wheat systems in the IGP, is very scanty. The present study was conducted to evaluate the impact of the application of FYM, RS and fertilizer N alone or in different combinations on (i) total SOC and slow pool C (particulate organic matter carbon [POM-C]), and ii) stabilization of cumulative C in the subtropical IGP of northern India after seven cycles of rice-wheat cropping systems.

Methods
Experimental Site
The experiment was set up in 1999 at the Punjab Agricultural University research farm, Ludhiana, India (30º 56' N, 75º 52' E). The experimental site is characterized by a semiarid sub-tropical climate. Soil texture is a sandy loam (60% sand, 17% clay and 23% silt) and the soil is classified as a Typic Ustorthents.

Treatments and Crop Management
The treatments viz. FYM (36.6% total C, 17% lignin and C:N ratio of 38.5), rice straw (46% total C, 10% lignin and C:N ratio of 71.9) and fertilizer N, were laid out in a randomized block design with four replications in plots of 15 m x 3.3 m (Table 1). Cumulative C inputs, during the seven cropping cycles, were calculated from organic sources (FYM and RS) as well as from crop contributions (roots, stubble and rhizodeposition) (Table 2).

Soil sampling and analysis
Soil samples were collected from 0-0.15 m soil depth after seven cycles of a rice-wheat cropping system using a core sampler with internal diameter of 70 mm. Each sample was a composite of six cores within a plot. The samples were air-dried and passed through a 2 mm sieve for analysis.

Table 1. Details of FYM, RS and fertilizer N treatments applied to wheat and rice grown in sequence.

Treatment	Rice	Wheat
T_1	Nil	Nil
T_2	120 kg N/ha	120 kg N/ha
T_3	FYM at 10 t/ha	Nil
T_4	FYM at 10 t/ha+120 kg N/ha	120 kg N/ha
T_5	Nil	Rice straw incorporated before wheat sowing
T_6	Nil	Rice straw incorporated before wheat sowing+120 kg N/ha
T_7	FYM at 10 t/ha	Rice straw incorporated before wheat sowing
T_8	FYM at 10 t/ha+120 kg N/ha	Rice straw incorporated before wheat sowing+120 kg N/ha

Total organic C and slow pool C

The amount of total soil C was determined by CHNS Elemental Analyzer (Vario EL III, Germany). The amount of inorganic C was determined titrimetrically, by digesting the soil with dilute HCl following the method of Bundy and Bremner (1972). The amount of total SOC was estimated by subtracting the amount of inorganic C from the total C. The amount of the total SOC was computed by multiplying the % total SOC with bulk density (g cm^{-3}) and depth (cm), and was expressed as t/ha. Particulate organic matter is the measure of slow pool C (Cambardella and Elliott, 1992). This pool was determined by the method described by Cambardella and Elliott (1992). The C stabilization % was estimated as:

$$\text{C stabilized (\%)} = \frac{SOC_{treatment} - SOC_{control}}{SOC_{cumulative\ input\ in\ treatment} - SOC_{cumulative\ input\ in\ control}}$$

Table 2. Cumulative C input (t/ha) from seven years of rice-wheat cropping cycles through FYM, RS and additions from stubbles, roots and rhizodeposition.

Treatment	Rice straw C	FYM-C	Roots-C	Stubble-C	Rhizodeposition-C	Total input C
T_1	0	0	2.97	0.71	5.9	5.9
T_2	0	0	5.79	1.45	11.6	18.8
T_3	0	27.5	4.55	1.06	8.8	42.0
T_4	0	27.5	7.29	1.80	14.4	51.0
T_5	18.0	0	3.50	0.80	6.8	29.1
T_6	26.8	0	6.19	1.54	12.3	46.8
T_7	24.3	27.5	4.72	1.07	9.2	66.8
T_8	34.4	27.5	7.33	1.81	11.5	82.4

Results and Discussion

Total SOC

Application of both FYM and RS significantly increased the total SOC (Table 3). After seven cycles of a rice-wheat cropping system, application of FYM and RS increased the total SOC at the 0-0.15 m soil depth by 6.7 t/ha and 4.1 t/ha, respectively, with the highest increase in SOC (7.9 t/ha) when all the three treatments were applied together. There was no significant effect of fertilizer N application resulting in no significant difference when applied with FYM or RS or FYM+RS from their individual application. The highest amount of cumulative C input (Table 2) under FYM+RS+N treatment may be attributed to the highest increase in total SOC under that treatment. Positive effects of FYM and RS application on SOC have been reported by several researchers (Yang *et al.,* 2005; Singh *et al.,* 2005).

Slow pool C

After seven cycles of a rice-wheat cropping system, application of FYM increased the slow pool C, as estimated by POM-C, at the 0-0.15 m soil depth by 1.5 t/ha, with the highest effect (2.5 t/ha) when all three treatments (FYM+RS+fertilizer N) (T_8) were applied together (Table 3). There was no significant effect of RS incorporation on the slow pool C. Plant residual lignin directly flows to the slow pool (Parton *et al*., 1987). The insignificant effect of RS on slow pool C could be attributed to the lower lignin content of RS as compared to FYM. Application of fertilizer N did not influence this pool. Mando *et al*. (2005) reported in a similar fashion that manure was the most effective in increasing POM-C when compared with urea, and straw with or without urea. Averaged across different treatments the slow pool C constituted 35-58% of the total SOC, similar to the

conceptual pool size described by the CENTURY model (Parton *et al*., 1988). Slow pool C was strongly correlated (r^2 = 0.76) with the total SOC.

Table 3. Influence of FYM, RS and fertilizer N application on total SOC and slow pool C (POM-C) after seven cycles of rice-wheat cropping system at the 0-0.15 m soil depth.

Treatment	Total SOC (t/ha)	Slow Pool C (POM-C) (t/ha)	C stabilization % (as slow pool C)	C stabilization % (as total SOC)
T_1	6.18a	3.58 (58)ab		
T_2	5.96a	3.27 (55)a	-2.4	-1.7
T_3	12.83c	5.08 (40)c	4.2	18.5
T_4	12.68c	4.45 (35)bc	1.9	14.4
T_5	10.32b	4.34 (42)bc	3.3	17.9
T_6	10.39b	4.35 (42)bc	1.9	10.3
T_7	13.79d	5.17 (37)c	2.6	12.5
T_8	14.11d	6.10 (43)d	3.3	10.4
LSD(0.05)	0.349	0.967		

Different small letters between rows indicate significant differences (P<0.05)
Values in parentheses indicate percentage of total organic C

Carbon stabilization
In the FYM treated plots, after seven cycles of a rice-wheat cropping system, 18.5% and 4.2% of the cumulative input C was stabilized as total SOC and slow pool C at the 0-0.15 m soil depth. Similarly, in the RS incorporated plots, 17.9% and 3.3% of the cumulative input C was stabilized as total SOC and slow pool C at the 0-0.15 m soil depth. The results suggest that FYM was slightly more effective, when compared to RS, in term of stabilization of C in the slow C pool. This may be attributed to the higher lignin content of FYM as compared to RS, as lignin directly enters into the slow pool (Parton *et al*., 1987). The N fertilization stimulates microbial activity and enhances C turnover (Raiesi, 2004), which explains the negative values of C stabilization in the fertilizer N applied plots.

Conclusion
Application of FYM at 10 t/ha/yr significantly increased total SOC stock (108%) and the slow pool C (42%), after seven years under the rice-wheat system. Although incorporation of RS alone had no effect on slow pool C, the combined application of RS with FYM and fertilizer N significantly increased slow pool C (70%) that would contribute to improving soil fertility as well as improve the total SOC stock under rice-wheat systems.

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Impacts of winery wastewater irrigation on soil and groundwater at a winery land application site

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Abstract

This study examines the impact of winery wastewater irrigation on Red Calcarosols or Red Kandosols typically found in the Riverine Plain of South Eastern Australia. The winery water composition is variable but generally has high organic matter concentrations (>2000mg/L total organic carbon), high potassium and sodium salts (up to 1000mg/L) with associated sodium adsorption (SAR) and potassium adsorption (PAR) typically having values >7. Over the 2005-2008 period, surface soil sodium and magnesium tended to decrease in concentration, calcium remained relatively constant and potassium doubled. Total organic carbon (TOC) and pH remained relatively unchanged. Surface soil potassium concentrations increased due to the high concentrations of potassium in grape juice and the winery using potassium-based cleaning agents for winery tank sanitization. However, concentrations remained unchanged in sub-surface soils. Soil solution samples obtained from Full Stop Wetting Front Detectors™ (FSWFD) indicated that salinity concentrations at shallow depths (30cm) were controlled by irrigation water composition, while at deeper depths (60cm), high salinity groundwater (14dS/m) was the major influence. Off site impacts in terms of nutrient movement to groundwater were found to be of low risk in the heavy clay soils of this study.

Key Words

Effluent, carbon, nitrate, pollution, potassium, salinity

Introduction

The aim of this work was to assess the sustainability of a winery wastewater land-based disposal system by determining impacts on soil and groundwater. The dynamics of nutrients, salt, and total organic carbon (TOC) in soils, soil solution samples and ground waters were monitored over an irrigation season and integrated with subsidiary longer term data, collected over a 3 year period prior to and after wastewater irrigation.

Methods

Field Site Description

The study was carried out at a winery (~80,000 tonne crush) land based wastewater disposal site in the Murrumbidgee Irrigation Area (MIA) near Griffith, New South Wales, SE Australia. A 67 ha portion of land was divided into irrigation bays of ~3 ha each. Water (~3 ML/ha) was applied to the bays by a border-check irrigation system traditionally used on farms in the area. Introduction of wastewater to the field was *via* a pipeline from the winery into an open irrigation channel. Irrigation control structures ('stops'), at the head of each irrigation bay could be opened to allow each bay to be flood irrigated individually. River water, the usual irrigation water in the region, could also be supplied to the channel to dilute the wastewater as required. Further details of the site are described in an environmental assessment (De Bortoli Environmental Assessment Report, 2005). Over the period of our study (May 2006 – March, 2007), the land was cropped with winter barley in 2006 followed by a fescue crop in January 2007.

Field Trial Monitoring and Sampling

Monitoring equipment was installed in three irrigation bays. Each site consisted of an area of approximately 2m x 2m in which were installed the following equipment: an automatically logged test well and piezometer and two Full Stop Wetting Front Detectors™ (FSWFD - 30 cm and 60 cm depth). In one bay, EnviroSCAN® Soil Moisture Monitoring Equipment was an additional installation.

Table 1. Chemical characteristics of surface and sub-surface soils at the field trial site.

Soil Interval	0-10 cm	60-90 cm
pH	8.1	9.2
Clay content (%)	60	50
TOC (g kg^{-1})	0.5-1.6	
Salinity (dS m^{-1})	0.14	0.49
CEC (cmolc kg^{-1})	10	> 10
ESP (%)	3.1	12.8

Soil Sampling
Surface soil samples were collected by the winery in 2005, 2007 and 2008 and we conducted a sampling campaign during the 2006/07 irrigation season; soil cores were collected on 21/11/06 after harvest of a barley crop, on 11/1/07 immediately before the planting of a fescue crop and on 7/3/07 during the growth of the fescue crop. Soil cores were taken to 90 cm depth and divided into four depth intervals: 0-10cm, 10-30cm, 30-60cm, 60-90cm. Observations were also recorded at an adjacent site without wastewater irrigation.

Soil Description
Dominant soils were Red Calcarosols or Red Kandosols (Isbell 1997) which, respectively, are calcareous throughout the solum or have a weakly structured or massive, clayey, B horizon (De Bortoli Environmental Assessment 2005). The main properties of the soil are reported in Table 1.

Water quality
The mid-season soil sampling (11/1/07) occurred after an irrigation consisting of winery wastewater diluted with channel water and the end of season soil sampling (7/3/07) immediately followed an irrigation that consisted of undiluted wastewater (Table 2).

Table 2. Chemical characteristics of irrigation water consisting of winery wastewater shandied with regular irrigation water (sampled 18/12/06), undiluted wastewater (sampled 13/2/07) and groundwater (sampled 14/2/07).

Water Quality Parameter	Diluted Wastewater	Undiluted Wastewater	Groundwater
EC (dS/m)	2.2	4.7	14
pH	9.6	4.4	7.6
Calcium (mg/L)	9.7	399.9	222.0
Potassium (mg/L)	594.8	801	62.9
Magnesium (mg/L)	48.2	72.0	365.7
Sodium (mg/L)	95.9	97.7	2814.4
TOC (mg/L)	190.5	2148	221.3
SAR + PAR	13	7	27.7

Results
Soils
Surface soil samples collected by the winery between 2005-2008 revealed that soil sodium and magnesium approximately halved in concentration, calcium remained relatively constant and potassium doubled (Figure 1). However, the available data indicated that changes in pH and TOC were insignificant. By 2008, observation of the soil indicated a more friable, aggregated structure, a darker brown colour and a greater number of earthworms than observed in earlier years and in adjacent soils that had not undergone wastewater irrigation. Overall, in spite of increased levels of potassium, which potentially may affect soil structural stability (Arienzo *et al*. 2009), the soil structure and biological condition did not seem to be negatively impacted.
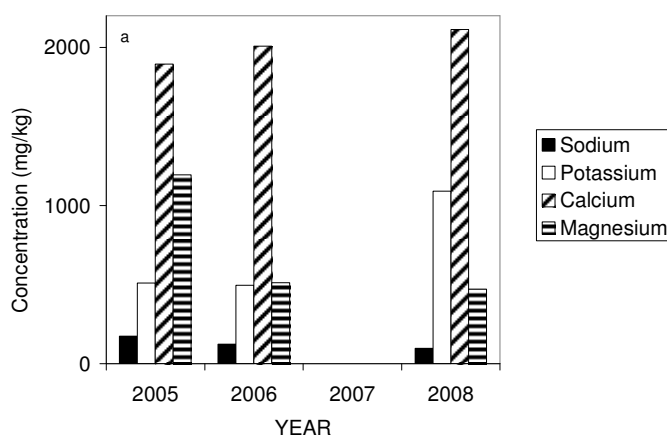
Figure 1. Changes in major cations prior to and proceeding three years of wastewater irrigation in surface soils at the land application site.

The soil samples we collected in 2006/07 indicate relatively low soil salinity in surface soils with large increases with depth (Figure 2).
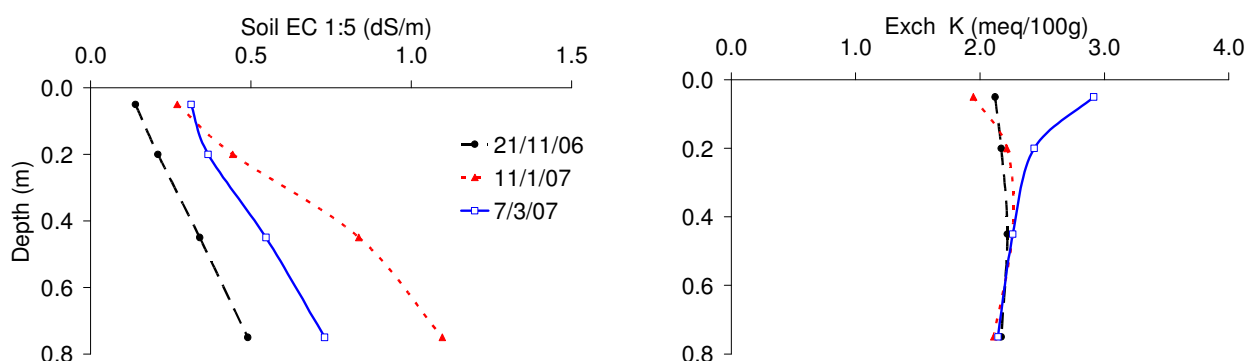
Figure 2. Soil EC$_{1:5}$ and exchangeable potassium vs. depth at three different dates throughout one irrigation season.

After a crop of barley had been harvested, grown by irrigating with regular channel water showed that soil electrical conductivity (EC$_{1:5}$) increased from 0.14 dS/m at the surface to 0.4 dS/m at 60-90 cm. Over the period of the irrigation season, surface EC$_{1:5}$ increased from 0.14 dS/m to 0.26 dS/m with large increases in sub-surface EC$_{1:5}$ to > 1 dS/m. The latter can be accounted for by shallow groundwater tables rising to 0.3 m below the soil surface due to irrigation. Exchangeable sodium matched the EC$_{1:5}$ trends. Surface levels of sodium increased marginally over the course of the irrigation period. Increases occurred from approximately 4 meq/100g to 10 meq/100g, mid season, then dropped back down to 6 meq/100g at the end of the season
Surface levels of potassium doubled over the course of the irrigation period from approximately 2 meq/100g - 4 meq/100g, with concentrations remaining unchanged below 20 cm (Figure 2).

Soil Solutions
Salt
Salt concentrations in soil solutions obtained from the 30 cm FSWFD were higher overall than in corresponding irrigation water but showed the same temporal trends (Figure 3).
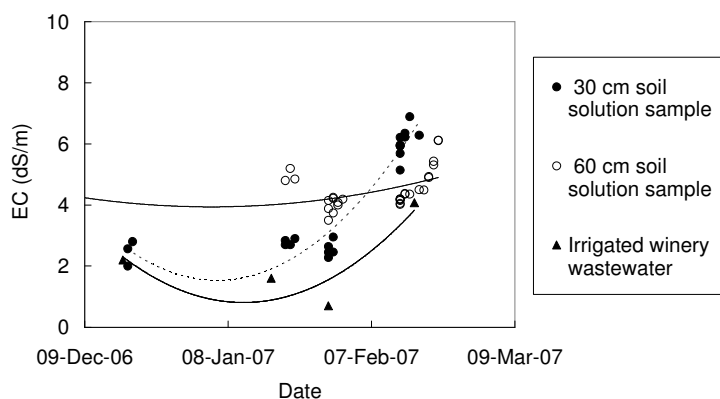
Figure 3. Trends in EC concentrations in soil solutions obtained from FSWFD at 30 cm and 60 cm depth over the 2006/07 irrigation season, compared with EC of corresponding irrigated wastewater.

This indicated, at shallow depths, soil solutions were dominated by the irrigation water salts with some additional salt residues being picked up from the soil profile as the wetting front progressed. In contrast, soil solutions obtained from the deeper detector (60 cm) displayed salt concentrations that were fairly constant over time. The solutions obtained at 60 cm probably represent irrigation water mixed with high salinity groundwater (Table 2) which had risen due to the irrigation.

Total Organic Carbon (TOC)
The similarity in TOC of irrigation water and soil solutions at 30 cm indicates little attenuation in TOC occurs between the surface and the 30 cm detector (Figure 4). This seems unlikely in these heavy clay soils and suggests preferential flow is occurring between the surface and 30 cm depth.
By Days 5 and 6 after the start of irrigation TOC in the 30 cm samples had declined to approximately 40% of its

initial value (Day 0) probably through degradation. Similar concentrations to the 30 cm soil solutions are seen in the 60 cm solution samples suggesting, that by Day 5, breakthrough has occurred. By Day 7 the shallower parts of the profile are drying, allowing aerobic degradation and further TOC decline, while the deeper depths remain wetted, thus anaerobic and TOC concentrations remain elevated.

Nitrate and Ammonia
Soil solution samples from the 30 cm depth FSWFD representing irrigation water May-Dec, 2006 clearly reflected the application of urea that was used to establish the barley crop. Maximum concentrations of nitrate and ammonia were 21.1 mg/L and 1.1mg/L respectively recorded the day after urea application. For the subsequent crop of fescue, established in January 2007 and irrigated with diluted or raw winery wastewater, almost identical results from the 30 cm FSWFD soil solution samples were observed compared with those seen previously. This suggests that the impacts of crop fertilization on NO_3 in soil solution are much more significant than irrigating with winery wastewater in these soils. Relatively small peaks of nitrate (maximum 3.6 mg/L) were detected directly beneath the crop in shallow groundwaters around the time of winery wastewater irrigation.
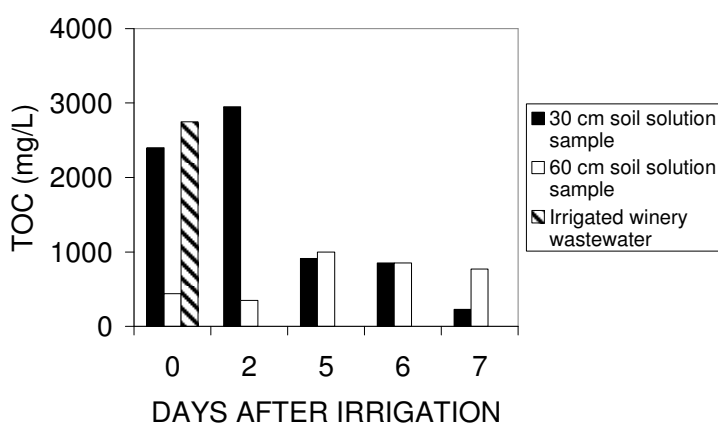
Figure 4. Distribution of TOC in soil solution samples collected from 30 cm and 60 cm FSWFD following irrigation, compared with TOC of irrigated wastewater.

Conclusions
Salt and potassium accumulation occurred during winery wastewater irrigation, but in these clay rich soils mobility was low and the accumulation was restricted to surface soils. Cropping and soil management of the site needs to be managed appropriately to utilise and remove excessive potassium levels. (Arienzo *et al.* 2009 review how this can be achieved). However, highly saline groundwater (>10dS/m) which rises during irrigation maybe a more significant threat to soil sustainability than the quality of winery derived irrigation water.
TOC in soil solution samples indicated that there was attenuation of TOC between 30 and 60 cm depth at the start of the irrigation schedule but that breakthrough occurred at lower levels after 5- 6 days. Then, as the paddock dried, TOC tended to persist at higher levels deeper in the profile compared with at the surface. Relatively small peaks of nitrate were detected beneath the crop in shallow ground waters around the time of winery wastewater irrigation, below the 10 mg/L NO_3-N, that are considered acceptable for potable water use.

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Investigations on Nitrogen Dynamics in Red Mediterranean Soils of Greece

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Abstract
Understanding the N dynamics in the soil-plant system is essential to successful N management. Red Mediterranean Soils (RMS) occupy a great part of the soils resources in Greece. However, there is still little information on the N fluxes in these soils. Surface samples were selected from 14 sites of N. Greece to represent RMS differing in culture history and soil characteristics. N mineralization potentials of these soils were measured, as well as N plant uptake was calculated in order to establish whether laboratory measurements of available N in soil were correlated with yields of unfertilized crops and with crop response to N fertilizer. In spite of the difference in No values among the soils tested, rates of mineralization were similar. Ammonium fixation is a property of many soils and a factor to be considered in practical agriculture. The C/N ratio alone is insufficient to predict the decomposability of the soil organic matter.

Key Words
N mineralization, Ammonium Fixation, C/N ratio

Introduction
Nitrogen is the key element to plant production and modern farming systems require an ample supply of N fertilizer necessary for maximum crop yield. Soil N dynamics is characterized by a series of transformation processes between organic and inorganic forms of N and the response of the N dynamic system to any stress such as N removal by crops and/or N fertilizer addition to soil.

Under normal soil conditions, inorganic N derived by mineralization process and the quantity of N fertilizer required for maximum yield, without leaving excesses that may be lost by leaching or other means, depends on an accurate estimation of the capacity of the soil to mineralize organic nitrogen. The relationship between total N and mineralized N has been widely studied (Cambell and Keeney 1982), but entirely different conclusions have often been reached. Native fixed ammonium is involved in the N dynamics of soil and may be an important component of the N fertility status of some agricultural soils ((Scarpf and Weier 1981). Carbon to nitrogen soil organic ratio is an indicator of the decomposing ability of soil organic matter and consequently of the N supplying potential of the soil (Xiaoping *et al.* 2007).

Greek soils have a wide range of mineralization potentials (Simonis and Setatou 1992) and native fixed ammonium was found to be the dominant N form in some soils (Setatou and Simonis 1994).

Red Mediterranean Soils occupy a great part of the soil resources in Greece. However there is still little information on the N fluxes in these soils. The purpose of this investigation is to study the N dynamics in representative RMS in Northern Greece.

Methods
Surface samples (0-30) were selected from 14 sites of N. Greece, to represent RMS differing in culture history and soil characteristics, measured by the standard procedures (Jackson 1958; Bremner 1965).Soil total N and inorganic N was determined according to the method of Stanford and Smith 1972.
In three of the soils the mineral status was determined by three different methods and in a pot experiment with ryegrass, three doses of ammonium sulfate (0 75, 150 mg/pot) were tested. Plant N uptake was calculated in order to establish whether laboratory measurements of available N in soil were correlated with yields of unfertilized crops and with crop responses to N fertilizer and to assess the value of such measurements for advisory purposes.

Results
Some basic characteristics of the soils tested are shown in Table 1. Total N of the soils ranged from 670 to 1820 ppm, while inorganic N varied from 60 to 128 ppm. Fixed ammonium ranged from 56 to 123 ppm and constituted 5.0 to 15.7 percent of the total N content of the soils tested. The distribution of C_{org}/N_{tot} ratios varied from 5.3 to 22.2. This suggests considerable variability in the quality of soil organic materials in contrast that all soil humus in mineral soils is of essentially the same composition stabilizing at a C/N ratio near 10:1.

Cumulative N mineralized during the incubation period followed the same general trend for all soils. The rate of mineralization was rapid at the beginning, then declined with the length of the incubation period (Figure 1). The cumulative N mineralized was linearly proportional to the square root of time ($t^{1/2}$), throughout the 30 weeks of intermittent incubations. The cumulative N mineralized – time curves found with the soils studied, were of similar shape to those obtained by other investigations working with RMS (Mattar *et al.* 1991).

The dry matter and N uptake by ryegrass grown in the pot experiment with the three soils were highly correlated with mineral N content of fresh soil (Min-N_f) and the increase in mineral content of re-wetted air-dry soils (MinN$_{ad}$).

Table 1. Some characteristics and N parameters of the soils tested.

Soil	Texture	pH 1:1	Org.N ppm	Org.C %	Total N ppm	Fixed NH$_4$-N ppm	Inorg N ppm	Exch NH$_4$-N ppm	Cumul N miner ppm	Fix NH$_4$-N total N	C/N
1	SC1	7.2	891	0.65	980	85	89	4	109.5	8.7	6.6
2	SC1	6.8	1741	0.97	1820	73	79	6	121.4	4.0	5.3
3	SC1	7.4	1050	1.15	1110	56	60	4	109.8	5.0	10.4
4	L	6.7	994	1.04	1090	90	96	6	112.0	8.3	9.5
5	SC1	6.7	734	0.82	810	73	76	3	148.0	9.0	10.1
6	SC1	6.2	652	0.88	780	123	128	5	107.0	15.8	11.2
7	SC1	7.0	504	0.55	610	100	106	6	118.6	16.4	9.0
8	SC1	6.0	1696	3.76	1820	111	124	13	108.6	6.1	20.6
9	SC1	7.2	560	1.49	670	104	110	6	113.4	15.5	22.2
10	CL	6.8	743	0.94	860	98	117	19	117.5	11.4	10.9
11	L	7.0	732	0.87	840	105	108	3	90.1	12.5	10.4
12	SC1	7.2	830	0.87	840	85	92	5	95.3	10.2	10.4
13	SC1	6.2	1195	1.28	1520	93	75	7	83.5	6.1	8.4
14	L	5.7	2125	2.60	2480	65	105	15	105.5	4.6	10.5
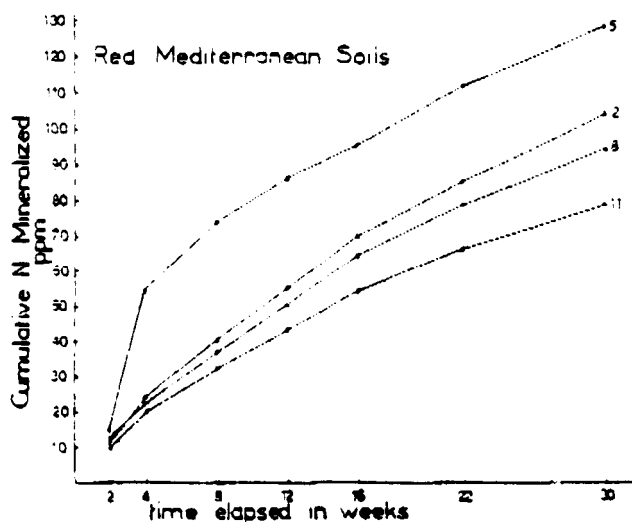
Figure 1. Cumulative N-mineralized with time for selected soils.

Conclusions

In spite of the difference in No values among the soils tested, rates of mineralization were similar. This suggests that the forms of organic N contributing to the mineralizable forms of N in Greek environments among soils are similar. Ammonium fixation is a property of many soils and a factor to be considered in practical agriculture. The C/N ratio alone is insufficient to predict the decomposability of the soil organic matter. Min-N_f and Min-N_{ad} can be used to predict available N for advisory purposes.

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Ionic Liquid Extractions of Soil Organic Matter

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Abstract
The ionic liquids dimethylammonium dimethylcarbamate (DIMCARB) and 1-butyl-3methylimidazolium chloride (Bmim Cl) can solubilise soil organic matter. Soil extractions with these materials showed that the organic matter recovered showed chemical properties that were consistent with humic substances. These extracts had a slightly different organic composition than the humic acids extracted using the traditional International Humic Substances Society (IHSS) method. The ionic liquids also solubilised some inorganic matter from the soil. Humic acids recovered with alkali were also partially soluble in the ionic liquids. DIMCARB appeared to chemically interfere with organic extract, increasing the level of nitrogen in the sample. It was concluded that the ionic liquid Bmim Cl may function as a useful solvent for SOM, and may be used to recover organic matter of a different character to that obtained with alkali

Key Words
Ionic liquids, humic substances, soil organic matter, extraction, characterisation

Introduction
The term 'ionic liquid' refers to a specific group of organic salts that melt at or below room temperature. These are called 'room temperature ionic liquids' (RTILs) or simply 'ionic liquids' (ILs). Ionic liquids have been investigated for their ability to dissolve and extract natural organic compounds (Zhao *et al*. 2005), proteins (Fujita *et al*. 2005), carbohydrates (Liu *et al*. 2005) and lignin (Tan *et al*. 2009). Given that soil organic matter (SOM) is likely to contain all of these compounds, or at least fragments of them, it is reasonable to conclude that ionic liquids may solvate part, if not all of the organic matter in soil.

The ionic liquid dimethylammonium dimethylcarbamate or 'DIMCARB', was chosen for study as a potential SOM extractant. Unlike other ionic liquids, DIMCARB is able to be removed by distillation thus providing a means of recovering extracted material from the ionic liquid. The ionic liquid 1-butyl-3methylimidazolium chloride or 'Bmim Cl' was also chosen because this material has been used to dissolve cellulose and is commercially available (Swatlowski *et al*. 2002).

Method
Soil Preparation
Dalmore clay soil, a peaty clay with up to 17.6% organic matter from the Koo-Wee-Rup area in Victoria, was used in this study. After removing of organic debris, the soil was dried in a vacuum oven at 40 C overnight to remove free water. A fine grind of this sample was prepared for extraction.

Humic Acid Extraction
A standard International Humic Substances Society (IHSS) method (Swift, 1996) for extracting humic materials with alkali solution was followed, with a modification of the final step to "clean up" the humic acids by removing inorganic matter.

Whole soil (200 g) yielded 3.42g of dried humic acids. The sample of humic acid was washed six times in concentrated HCl (32% w/w), followed by washing in distilled water. After each washing, recovery of the humic acids was achieved by centrifugation. Waste acids were neutralised and discarded. After washing in acid, washing in water was repeated until pH increased to the point where the humic acids would start to redissolve. The recovered humic acid was air dried and stored in a dessicator (1.92 g).

Synthesis of DIMCARB
DIMCARB was synthesised following a method published by Kreher *et al* (2004).
Dimethylamine and carbon dioxide gases were fed to a three neck RBF resting in ice bath and connected to a 1.5ft spiral condenser from which DIMCARB was collected as a distillate.

Soil Extraction with DIMCARB
A sample of soil (50 g) was combined with DIMCARB (250 ml) in a stoppered conical flask, and stirred overnight at room temperature. The Soil / DIMCARB mixture was transferred to 30 ml glass centrifuge tubes and centrifuged. The supernatant was decanted and vacuum filtered through glass filter paper. Filtered extracts were combined, placed under high vacuum to boil off and collect the DIMCARB. The mass of dry soil extract recovered was 1.42 g.

IL extraction with Bmim Cl
Two 1 g samples of acid washed soil (HCl) were prepared. One sample was placed in a vacuum oven (110ºC for 2 hrs) to remove water, this was labelled 'oven dry soil'. The other sample was allowed to equilibrate with moisture in the air and was labelled 'air dry soil'. Both samples were then treated with the following extraction method. Bmim Cl (20 g) was melted and dried in vacuum oven (110ºC for 4 hrs). Using a high speed glass centrifuge tube, soil (1 g) was added to of molten Bmim Cl (10 g). This was then sonicated (70ºC for 4 hours). Whilst still hot, the mixture was centrifuged (20,000 rpm for 30 mins). The supernatant was recovered and deionised water (10 ml) was added. This was shaken and then allowed to stand overnight. Precipitated solids were settled using high speed centrifugation (as above), and the supernatant poured off and set aside. The remaining solids were washed in deionised water, centrifuged, and the supernatant discarded. This step was repeated three times to remove the ionic liquid. The sample was then freeze dried.
The two dried organic extracts weighed 0.15 g (oven dry soil), and 0.12 g (air dry soil).

Results and Discussion
DIMCARB Extract
The dark brown solid recovered from the DIMCARB extraction (1.42 g) represented 2.84% of the original soil sample. Thermal gravimetric analysis showed this to have an ash content of 21.8%. The extraction recovered 1.11 g of organic matter (OM), or 22.9% of all the OM in the soil sample (4.85 g OM in 50 g of soil). The solid state carbon-13 nuclear magnetic resonance of whole soil, humic acid (obtained by the traditional IHSS method) and DIMCARB extract are shown in Figure 1. While the differences are not striking, the DIMCARB extract does appear to show more prominent O-alkyl absorbance than the humic acid extract. The carboxyl region is prominent, and consistent with a humic substance spectrum. Elemental analysis of this organic extract showed a higher level of nitrogen was present in the DIMCARB extract (~ 4%) compared with the humic acid extract (~2%).

Bmim Cl Extract
The solid state carbon-13 nuclear magnetic resonance of whole soil, humic acid (obtained by the traditional IHSS method) and the two Bmim Cl extracts are shown in Figure 2. As with the DIMCARB extract, the O-alkyl absorbance region is more prominent than the humic acid extract. The spectra of both extracts are consistent with a humic substance spectrum. TGA results showed 66.1% ash was present in the 'air dry' sample and 72.5% ash for the 'oven dry' sample and use of this ionic liquid carried considerable quantities of ash along with the organic matter. Further investigation to de-ash the organic matter is required.
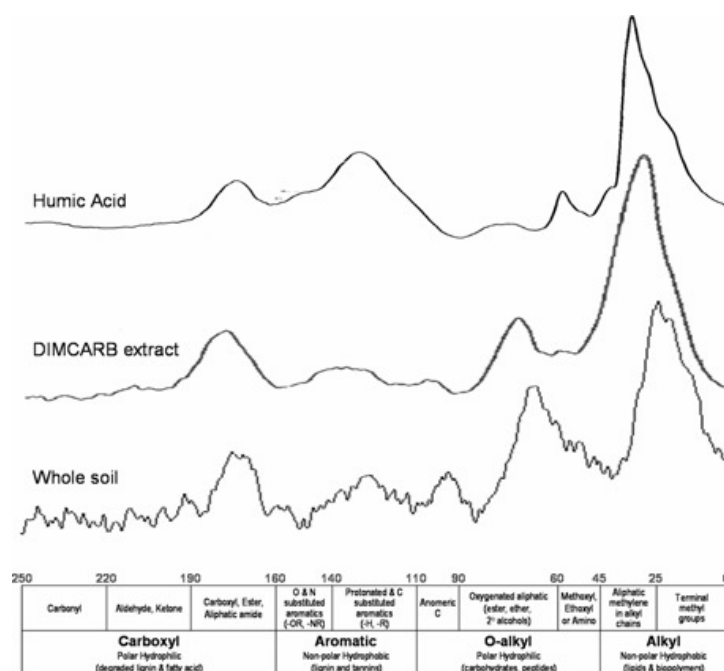
Figure 1. Solid State ^{13}C NMR spectra and chemical shift assignments (ppm) for Humic Acid, DIMCARB extract and whole soil.
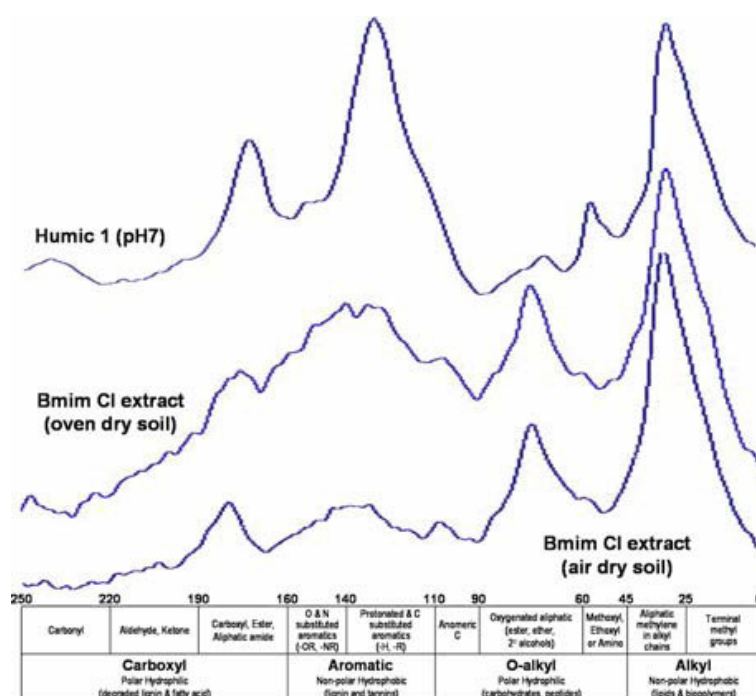
Figure 2. Solid State ^{13}C NMR spectra for humic acid (pH 7), and extracts of soil obtained with Bmim Cl.

Conclusion

The dimethylammonium dimethylcarbamate (DIMCARB) extraction of an organic matter rich soil was found to give a good yield of OM, and contained organic carbon types that seemed to be more representative of the SOM. However, it was also determined by microanalysis that DIMCARB is a reactive medium that interacts with the SOM and changes it chemically through the addition of nitrogen.

The second extraction solvent investigated utilised the ionic liquid, 1-butyl-3methylimidazolium chloride (Bmim Cl). Experimental evidence indicated that this ionic liquid is capable of solvating and extracting SOM. The Bmim Cl extracts were found to contain an excellent representation of the types of organic carbon found in SOM, with higher oxygenated alkyl content than the humic acids recovered with alkali. The extracts were, however, very high in ash content, although this issue may be addressed by further developing the method.

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Long-term effect of farmyard manure and N on the distribution of zinc and copper in soil fractions under pearl millet – wheat cropping system

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Abstract

A long-term field experiment was initiated in November, 1967 to study the response of N on pearl millet (*Pennisetum typhoides*)-wheat (*Triticum aestivum*) cropping sequence for various doses and modes of farmyard manure (FYM) application. Increasing levels of FYM from 0 to 45 Mg /ha increased the exchangeable, carbonate bound, oxide bound, organic bound and residual fraction of both Zn and Cu in surface (0-15 cm) and sub-surface (15-30 cm) soil. FYM applied during the winter (rabi) season caused a greater increase in all Zn and Cu fractions as compared to summer (kharif) application. The percent contribution of different Zn and Cu fractions towards total Zn and Cu in surface and sub-surface soil revealed the following order: exchangeable < carbonated bound < oxide bound < organic bound < residual.

Key Words

Long-term, FYM, pearl millet, wheat, zinc, copper, fractions

Introduction

Organic amendments, such as FYM are known to improve soil physical properties (Marinori *et al*. 2000). Organic matter is an important soil constituent influencing a number of constraints linked with crop productivity. The loss of soil fertility, in many developing countries, due to continuous nutrient depletion by crops without adequate replenishment poses an immediate threat to food and environmental security. Intensive cropping and tillage system have led to substantial decreases in soil organic matter levels of much prime land in the world. This decrease in soil organic matter levels seems to be associated with the decline in soil productivity.

The importance of micronutrients has been realized during the past three decades when widespread micronutrient deficiencies were observed in most of the soils of India, where intensive agriculture is practised. The micronutrient deficiency in soil is either due to continuous removal of micronutrients from the soil by recently introduced fertilizer responsive and high yielding varieties of crops, or use of micronutrient free high analysis fertilizers.

Estimation of only total content of micronutrient cations in soil does not provide any information regarding the mobility, plant availability, chemical reactivity and biological effects. Elements such as Zn and Cu present in soils are found in a variety of physicochemical forms/fractions (Berti and Jacobs, 1996, Sekhon *et al*. 2006)). To assess their impact in agriculture it is essential to identify which forms are actually present in soil, as the mobility and bioavailability of these elements are governed by dynamic processes, and not the total element contents (Kuo *et al*. 1983). Organic matter redistributes applied Zn in less soluble fraction under a field-capacity moisture regime (Sekhon *et al*. 2006). FYM application increased Cu more in the organic fraction as compared to the oxide-bound fraction (Rupa *et al*. 2001). The objective of this investigation was to determine the effect of long-term application of FYM and N on the dynamics of Zn and Cu fractions in soil.

Methods

A long-term field experiment was established in November, 1967 to study the response of fertilizer N at various doses of FYM and their modes of application in pearl millet (*Pennsisetum typhoides*) - wheat (*Triticum aestivum*) cropping sequence. The experimental field soil was classified as a mixed Typic HaplusteptThe experimental site is located in north-west India between 29.16°N latitude and 75.75°E longitude with a mean annual precipitation of 443 mm. Farmyard manure was applied at 15, 30 and 45 Mg /ha under three modes i.e. applying to each summer (kharif) crop (June), applying to every winter (rabi) crop (November) and to both the crops. One FYM control plot (where no FYM was applied) was also maintained. These 10 treatments were allocated in the main plots and each main plot was divided into three sub-plots receiving fertilizer N at 0, 60 and 120 kg N /ha in each season through urea. Urea was applied in each crop in two split applications. The sub-plot

size was 10x6 m and each treatment was replicated four times. Surface (0-15 cm) and sub-surface (15-30 cm) soil samples from each plot were collected after the harvest of wheat crop in April-2004. Soil samples were air dried, grounded to pass through a 2 mm sieve and stored for further analysis. Different fractions of Zn and Cu in soil were estimated by following the method of Tessier *et al*. (1979) and modified by Jeng and Singh (1993).

Results

Increasing levels of FYM from 0 to 45 Mg /ha increased the exchangeable-Zn (0.55 to 0.98 mg/kg), carbonate bound-Zn (0.81 to 1.21 mg/kg), oxide bound-Zn (7.12 to 11.12 mg/kg), organic bound-Zn (1.22 to 3.15 mg/kg) and residual-Zn (67.07 to 91.69 mg/kg) contents surface soil (Table 1). Similarly in sub surface soil also increasing levels of FYM increased all the fractions i.e. exchangeable-Zn (0.39 to 0.85 mg/kg), carbonate bound-Zn (0.94 to 1.33 mg/kg), oxide bound-Zn (4.05 to 9.03 mg/kg), organic bound-Zn (0.69 to 2.54 mg /kg) and residual-Zn (50.27 to 74.62 mg /kg) . Farmyard manure applied in winter showed a greater increase in all the Zn fraction as compared to its application in summer. Higher values of all the fractions were observed especially when FYM was applied in both the seasons. Surface soil has higher content of all Zn fraction except carbonate bound-Zn (Table 1). Application of N from 0 to 120 kg /ha also increased all the fraction of Zn both in the surface and sub-surface soil layers. The amount of Zn in different fractions as a percent of total Zn at both depths followed the order: Exchangeable < carbonate bound < organically bound < oxide bound < residual. The exchangeable Zn fraction contributed least towards total Zn i.e. 0.72 to 1.03 % and 0.69 to 1.11 % in surface and sub-surface soil, respectively. Residual fraction contributed highest i.e. 84.01 to 87.36 % and 82.34 to 89.23 % in surface and sub-surface soil, respectively.

Table 1. Long-term effect of FYM and N application on different fractions of Zn in soil after 37 cycles of pearl millet-wheat cropping sequence.

Treatment	Zn fractions (mg/kg)				
	Exchangeable	Carbonate bound	Oxide bound	Organically bound	Residual
FYM levels (Mg /ha)					
0	0.55	0.81	7.12	1.22	67.07
15	0.73	0.95	9.55	2.06	74.74
30	0.87	1.09	10.63	2.54	82.52
45	0.95	1.21	11.12	3.15	91.69
LSD (0.05)	0.05	0.10	0.37	0.17	1.55
Modes of FYM					
Kharif	0.70	0.91	9.27	2.04	77.34
Rabi	0.77	1.00	9.50	2.23	78.27
Both	0.89	1.14	10.04	2.46	81.41
LSD (0.05)	0.05	0.09	0.32	0.15	1.34
N levels (kg /ha)					
0	0.72	0.99	9.61	2.15	78.21
60	0.79	1.00	9.50	2.21	78.99
120	0.82	1.05	9.70	2.36	79.82
LSD (0.05)	0.09	NS	NS	0.30	2.68

Table 2. Long-term effect of FYM and N application on different fractions of Cu in soil after 37cycles of pearl millet-wheat cropping sequence.

Treatment	Cu fractions (mg/kg)				
	Exchangeable	Carbonate bound	Oxide bound	Organically bound	Residual
FYM levels (Mg /ha)					
0	0.17	0.39	5.20	0.55	13.40
15	0.39	0.70	6.34	1.07	18.53
30	0.51	0.89	6.74	1.58	21.24
45	0.67	1.09	7.15	1.96	21.93
LSD (0.05)	0.05	0.08	0.37	0.14	0.82
Modes of FYM					
Kharif	0.37	0.63	6.02	1.02	18.25
Rabi	0.42	0.69	6.43	1.31	18.35
Both	0.52	0.99	6.63	0.56	19.74
LSD (0.05)	0.45	0.08	0.32	0.12	0.71
N levels (kg /ha)					
0	0.43	0.74	6.18	1.28	18.21
60	0.44	0.77	6.35	1.26	19.02
120	0.44	0.80	6.55	1.33	19.10
LSD (0.05)	NS	NS	NS	NS	1.43

Application of FYM increased the Cu content of soil. It increased the exchangeable-Cu (0.17 to 0.67 mg/kg), carbonate bound-Cu (0.39 to 1.09 mg /kg), oxide bound-Cu (5.20 to 7.15 mg /kg), organic bound-Cu (0.55 to 1.96 kg/mg) and residual-Cu (13.40 to 21.93 mg /kg) contents in surface soil. Similarly, in sub-surface soil also Cu increased all fractions exchangeable-Cu (0.12 to 0.48 mg /kg), Carbon bound-Cu (0.74 to 1.87 kg/mg), Oxide bound-Cu (3.83 to 6.16 mg /kg), Organic bound-Cu (0.37 to 1.60 mg /kg) and Residual-Cu (7.47 to 12.43 mg /kg) with increasing levels of FYM from 0 to 45 Mg /ha. Farmyard manure applied in winter showed a greater increase in all the Cu fractions as compared to its application in summer. Nitrogen application also had a positive effect on the build up of all fraction of Cu in soil. The percent contribution of Cu towards total Cu (sum of all 5 fractions) in surface and sub-surface soil followed the order: exchangeable < carbonated bound < oxide bound < organic bound < residual. The exchangeable Cu fraction contributed least towards total Cu i.e. 0.86 to 2.37 % and 0.96 to 2.44 % in surface and sub-surface soil, respectively (Table 2). The residual Cu fraction contributed the most to total Cu i. e. 65.20 % to 71.23 % and 53.60 % to 60.47 % in surface and sub-surface soil, respectively. Generally Exchangeable, carbonate bound and organically bound fractions of Zn and Cu contribution increased and residual fraction of Zn and Cu contribution decreased with increasing level of FYM at both depths.

Conclusion
Increasing levels of FYM from 0 to 45 Mg /ha increased all Zn and Cu fractions (exchangeable, carbonate bound, oxide bound, organic bound and residual) in surface and sub-surface soil. The contribution of both Zn and Cu towards total Zn and Cu followed the order: exchangeable < carbonated bound < oxide bound < organic bound < residual. Hence, the application of FYM is essential for maintaining soil fertility.

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Long-term effects of applied organic manures and inorganic fertilizers on yield and soil fertility in a wheat-rice cropping pattern

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Abstract
An 11 years study was conducted to investigate the effects of nine treatments of organic manures (PM: Poultry manure and FYM: Farmyard manure) in combination with chemical fertilizers (NPKSZn) on crop productivity and soil fertility in a wheat-rice experiment in Bangladesh.. Organic manures had direct and residual effects on rice and wheat yields, but the effect of PM was dominant. Plots with FYM plus 75% NPKSZn produced equivalent or higher yields as 100% NPKSZn. The PM direct to wheat produced 12 % higher yield than 100% NPKSZn. After 3 crop cycles, soil pH was increased in plots with PM and unchanged in inorganic fertilizers and FYM. Percent OM (organic matter) was reduced (13 to 19%) with inorganic fertilizers and increased (7 to39%) with organic manures. Percent total N (Nitrogen) was unchanged in OM plots, but reduced in others. Available P (Phosphorus) increased dramatically in PM plots and was reduced in control plots. Exchangeable K (Potassium) was reduced in control and inorganic fertilizer treatments, but was sustained for others. After 9 years, %OM, % total N and exchangeable K were reduced further in inorganic treatment and increased in OM treatments. The soil pH increased in PM receiving treatments.

Key Words
Wheat, rice, organic matter, nitrogen, potassium, phosphorus

Introduction
Rice is the staple food grain in Bangladesh and covers about 80% of the total cropped area accounting for over 90% of total grain production of Bangladesh. Wheat is the second most important food grain and is commonly grown after rice. Over 85% of the total wheat area of the country is preceded by transplanted monsoon rice grown from July to December (Saunders, 1991). Rice and wheat yields have either remained stagnant or declined (Bhuiyan, 1994; Duxbury *et al*., 2000) in South Asia. Modern varieties give higher crop yields but respond to more nutrients than local varieties because of higher amount of potential biomass production. The farmers of the country use only about 102 kg nutrients/ha (70 kg N, 24 kg P_2O_5, 6 kg K_2O, 2 kg S+ Zn) annually (Islam *et al*., 1994), while the crop removal is 200 kg/ha. Consequence of soil fertility is declining. Soil organic matter content in Bangladesh soil is not only poor but it is declining gradually. Studies by Bhandari *et al*. (2002) attributed the reduced productivity of the rice-wheat system to declining SOM, decreased soil fertility, occurrence of nutrient imbalances, and inappropriate fertilizer practices. Previous research considered that the continued use of mineral fertilizers may result in decline of soil quality and productivity, while other studies have indicated positive and no noticeable effects on soil productivity. In most long-term experiments, a combination of mineral fertilizers and farmyard manure has generally given the best crop yield and soil quality (Wang *et al*., 2004; Chalk *et al*., 2003). Singh *et al*. (1983) reported that application of poultry manure alone was about 1.5 times more effective than compost alone in increasing yields of rice and maize as well as building up more available Zn in soil than did compost alone. Sharma and Saxena (1985) indicated that incorporation of poultry manure or FYM in to the soil increased maize yields besides improving soil P indices. Application of poultry manure in Bangladesh is rarely practiced, and the effect of poultry manure application on the wheat-rice cropping pattern or on soil fertility has not previously been documented. The present investigation was therefore, undertaken to observe the performance of the integrated use of poultry manure (PM), farm yard manure (FYM) and chemical fertilizer to sustain soil fertility and productivity in a wheat-rice cropping pattern.

Methods
A permanent plot experiment in the wheat-rice pattern initiated in November 1997 at Wheat Research Centre (WRC), Dinajpur, Bangladesh ($25^0$38' N, $88^0$41' E, 38.2 m above sea level) on a sandy loam on a Old Himalayan piedmont plain. At the beginning of the experiment, the soil was low in available N, medium in available P, low in exchangeable K, medium in available S and medium in Zn. The soil reaction was acidic. The experiment consisted of 9 treatments laid out in a randomized complete block design with 4 replications. The

treatments for wheat were: control (T_1), 100% NPKSZn (T_2), 75% NPKSZn (T_3), 75% NPKSZn+FYM (T_4), 75% NPKSZn+FYM (T_5), 75% NPKSZn (T_6), 75% NPKSZn+PM (T_7), 75% NPKSZn+PM (T_8) and 75% NPKSZn (T_9). In case of rice, the treatments were control (T_1), 100% NPKSZn (T_2), 75% NPKSZn (T_3), 75% NPKSZn (T_4), 75% NPKSZn+FYM (T_5), 75% NPKSZn+FYM (T_6), 75% NPKSZn (T_7), 75% NPKSZn+PM (T_8) and 75% NPKSZn+PM (T_9). For rice, FYM (Farm yard manure) and PM (Poultry manure) were excluded from the treatment T_4 and T_7 to observe residual effects in rice of FYM and PM, respectively. FYM and PM were included to T_6 and T_9, respectively to see the direct effects of FYM and PM in rice. Wheat and rice received FYM and PM in the treatments T_5 and T_8, respectively to evaluate the effect of double application of organic manures per year for each of those crops. One hundred percent rates of recommended chemical fertilizers for both wheat and rice were 26kg P, 33kg K, 20kg S and 4 kg Zn ha^{-1}. However, the 100% recommended rate of nitrogen was 100 and 70kg ha^{-1} for wheat and rice, respectively. Organic manures, both PM and FYM were incorporated @ the rate of 10t ha^{-1} to soil 4-5 and 15 days before seeding wheat and transplanted monsoon rice, respectively. The dry matter FYM was added at 69.52, 128.12 and 58.60 ton ha^{-1} FYM to wheat, both crops and rice, respectively. The dry matter PM was added as 85.69, 162.89 and 77.20 ton ha^{-1} PM to wheat, both crops and as rice, respectively. Chemicals fertilizers were applied using recommended times and methods for the crops. Wheat seed @ 120 kg ha^{-1} was sown at the optimum time (last week of November) every year and the crop was harvested at maturity (Normally 112 days after sowing). Thirty to thirty- seven-day old seedlings of monsoon rice were transplanted on the last week of July every year and the crop was harvested at maturity in the 1st week of November. Weeding was done once for wheat after 1st irrigation and rice 25 days after transplanting. Three irrigations were applied to wheat at 17, 50 and 70 days after sowing (DAS). The rice was grown with natural monsoon rain, but one irrigation was given the 1st week of October (if necessary). Plant protection measures viz. insecticide and fungicide sprays, were not necessary since the wheat crop remained free from insect and pathogen attack. The monsoon rice requited, Marshal, an insecticide @ 1.0 litre ha^{-1} which was applied twice to control stem borer.

The surface soil (0-15cm) was sampled at the beginning from the experimental site and from individual plots after completing 3 and 9 crop cycles and chemically analyzed to determine %total N, available P, exchangeable K, available S, %organic matter and pH. Data were statistically analyzed with MSTAT following the F-test and mean comparisons were made by DMRT at the 0.05% level.

Results and discussion:

Soil fertility

The soil pH, % OM, %total N, available P, exchangeable K and available S content of soil significantly responded to the application of organic and inorganic fertilizers (data are not shown). After 3 crop cycles, soil pH was unchanged in control, only inorganic fertilizers and FYM receiving treatments and increased in PM treatments compared to initial soil test results. The soil pH was increased significantly (P< 0.05) in FYM and PM treatments compared to 100% NPKSZn treatment after 9 crop cycles. Considering organic manure treatments, pH was higher in PM treatments than FYM treatments. The mean (mean of PM treatments) soil pH was 0.54 units higher than mean of FYM treatments. The results suggest that organic manures could increase pH of low pH soils by addition of base cations. This result concurs with the findings of Whalen *et al.* (2000) who reported that cattle manure amended soil had significantly higher pH than non amended soil and the pH of Beaverlodge and Fort Vermillion soils increased from 4.8 to 6.0 and 5.5 to 6.3, respectively. Percent organic matter was reduced from 13 to 19% and 18 to 24% in plots where organic manures were not added and increased 7 to 39% and 30 to 62% in plots where organic manures were applied after 3 and 9 crop cycles, respectively. The prominent increasing trends were for plots with PM relative to those with applied FYM. The results indicate that continuous application of organic manure could cause % OM to accumulate in soil although the decomposition rate of OM in high humidity and temperature condition in subtropic region is quick. This investigation is similar to that of Rekhi *et al.* (2000) who reported that an initial low level of OC was raised to a medium level after 3-yrs rice-wheat cropping with the GM or FYM application. Percent total N was unchanged in almost all organic manure receiving treatments except for FYM applied as double application (FYM for both wheat and rice) after 3 crop cycles and increased 11 to 39% after 9 crop cycles relative to initial. In contrast, total N was reduced in the control (25%), 75%NPKSZn (13%) and 100% NPKSZn (13%) plots after 3 crop cycles and further reduced (30 to 35% than initial) in control and where only inorganic fertilizers were used after 9 crop cycles. Reduction of % total N in control and inorganic fertilizers treatments is a consequence of reducing %OM and possibly higher the removal of N from soil. During the cropping period, soil available P was sustained in 100%NPKSZn, reduced in control and 75%NPKSZn, and increased in organic manures in combination with chemicals fertilizer treatments. It was noticeable that available P content increased dramatically in plots where PM was applied. The results indicate that addition of PM had added higher amounts

of P to the soils. After 3-crop cycles, the exchangeable K content was reduced in control and plots where only inorganic fertilizers were added and , it was sustained in plots where organic manures were added. After 9-crop cycles, the exchangeable K was further reduced in control and inorganic fertilizer treatments and increased in organic manure receiving treatments. The available S content was also sustained or even increased irrespective the treatments. The results agree with the findings of Venkatesh Bharadwaj and Omanwar (1994) and Kaushik *et. al.* (1984) who reported an increase in available N, P and K due to FYM application. Also Sharma and Saxena (1985) reported that incorporation of poultry manure or FYM to the soil improved soil P indices.

Grain yields
Grain yields (wheat and rice) significantly responded to added chemicals fertilizers and organic manures in each year (data are not presented). The 75%NPKSZn treatment produced significantly higher yields than control and lower yield than 100%NPKSZn and organic manure treatments during the cropping period. The yields were statistically higher in almost all PM receiving treatments [75%NPKSZn plus poultry manure direct to wheat (residual to rice), double application (poultry manure both in wheat and rice) and residual to wheat (direct to rice)] compared to 100%NPKSZn except in1998-99 and 2002-2003 for wheat and in 1999, 2000 and 2005 during 11-yrs study. Crops were lodged and severity of damage was higher in high input receiving treatments in years that yields were low in PM treatments. The treatments that received FYM [75%NPKSZn plus farmyard manure direct to wheat (residual to rice), double application (farmyard manure both in wheat and rice) and residual to wheat (direct to rice)] produced equivalent or higher yields than 100%NPKSZn. In the 11-yr study, the mean yield was 16 (581 kg ha^{-1}), 11 (361 kg ha^{-1}) and 7% (246 kg ha^{-1}) higher for wheat and 9 (320 kg ha^{-1}), 9 (347 kg ha^{-1}) and 6% (236 kg ha^{-1}) higher for rice for PM direct to wheat, double application and residual to wheat treatments, respectively compared to 100% NPKSZn alone if the abnormal yield in PM as direct to wheat in the 2002-2003 wheat growing season was not considered. The FYM double application gave 6 and 5 % higher yield of wheat and rice, respectively than 100%NPKSZn treatment. The mean yield for wheat and rice was more or less equal for 100% chemical fertilizers, FYM direct to wheat and residual to wheat. The higher yields of crop in organic manures as direct or residual with 75%NPKSZn over only 75%NPKSZn treatment and equivalent or higher yield over 100%NPKSZn was contributed by greater number of spikes/m2 or panicles hill-1 and grains spike-1 or panicle-1. The result suggest that both PM and FYM have potential to increase crop yields as direct or residual by supplementing nutrients to crops and increasing availability of nutrients in soils. The crop yields and nutrient availability were higher in PM plots than FYM plots indicating PM was more effective in producing crop yields and providing nutrients because of its higher nutrient content than FYM (BARC, 1997).

Conclusion
From the experimental results it can be concluded that the combined use of organic manure with inorganic fertilizers performed better than inorganic fertilizers alone to sustain soil fertility and system productivity. PM could be used instead of FYM to get higher yields and to better sustain soil nutrient availability. From the soil analysis results it can be concluded that continuous application of organic manures could enhance the % OM content in soil although the decomposition rate of OM in high humidity and temperature condition in sub-tropical regions is quicker.

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Management of soil quality and carbon sequestration with long-term application of organic amendments

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Abstract

Soil organic matter is of central importance in maintaining soil quality and is also now receiving attention due to the potential for carbon sequestration in soils. Here we aimed to assess the effects of organic and inorganic amendments on soil quality in a rice-wheat cropping system in the Indo-Gangetic plains of eastern India and to evaluate the carbon sequestration potential of such management approaches. Soil samples were collected from a 19 year old long-term fertility experiment in West Bengal and results showed that there were significant increases in nutrient availability with the application of farm yard manure (FYM @ 7.5 t/ha), paddy straw (PS @ 10 t/ha) and green manure (GM @ 8 t/ha) along with inorganic fertilizer. Microbial biomass C and mineralizable C were also increased by the addition of organic inputs. Continuous cultivation, without application of organic inputs, significantly depleted total C content by 39-43% when compared with the addition of organic amendments. There was a significant increase in non-labile C fraction by the amendments when compared with control. There was a net loss of C by 5.6% due to continuous cultivation without any amendment and 26.1%, 17.7% and 6.3% of the C applied through FYM, PS and GM respectively was sequestered.

Key Words

Soil quality, soil organic carbon, carbon pool, manure, paddy straw

Introduction

Soil quality is an integrated characteristic determined by biological, chemical and physical soil properties defining a soil's capacity to function (Karlen *et al.* 1997). Maintaining or increasing soil organic matter (SOM) is critical to achieving optimum soil function. In many parts of the world, organic wastes represent an inexpensive and plentiful resource for the treatment of soil quality. However, investigation of the options for the application of organic wastes and their efficacy in improving soil condition are needed to assess their potential to partially or fully replace inorganic fertilizers.

Soil organic carbon (SOC) is the most frequently reported soil attribute from long-term agricultural studies and is commonly selected as the key indicator of soil quality and agronomic sustainability because of its impact on other physical, chemical and biological elements of soil quality (Reeves, 1997). Long-term fertility experiments (LTFE) play an important role in understanding the complex interaction involving plants, soils, climate and management practices and are the primary source of information to determine the effects of cropping systems, soil management, fertilizer use, and residue utilization on the quantitative and mechanistic changes soil quality as well as on SOC pools (Leigh and Johnston, 1994; Rasmussen *et al.,* 1998).

Rice (*Oryza sativa* L.) - wheat (*Triticum aestivum* L.) cropping is the dominant cropping sequence in the Indo-Gangetic Plains, and occupies nearly 50% of its cropped area (Singh and Khan, 2000). Use of organic amendments such as FYM, rice straw and green manure is known to improve soil productivity in rice-wheat cropping (Ghosh *et al.,* 2009) and has the capacity to add SOC and to improve soil condition. However, little work has quantified the impact of long-term organic amendments on SOC quantity and pools in intensively managed Indian soils and such studies are particularly scarce in the Indo-Gangetic region. Therefore the present study was undertaken to assess the long term effect of different management practices on soil quality and carbon sequestration using a 19 years old LTFE with rice-wheat cropping systems in West Bengal, India.

Methods

Site description

A long-term field experiment was initiated in 1986 for the All India Coordinated Research Project on Cropping Systems at the University Teaching Farm, Bidhan Chandra Krishi Viswavidyalaya, West Bengal, India (23˚N,

89˚E, 9.5 m msl); along the new alluvial soil zone in the hot humid sub-tropic Indo-Gangetic plains of eastern India. The experimental soil was characterised with pH 7.2, oxidisable organic C 8.8 g/kg, bulk density 1.2 Mg/m^3 and cation exchange capacity 22.0 $cmol_c/kg$.

Experimental design and treatments
The experiment was laid out in randomised block design with four replications with the following treatments: Fallow (no cultivation since the inception of the experiment) (T_1), Control (conventional cultivation without any fertilizer or amendments) (T_2), 100% recommended dose of inorganic fertilizer (NPK) (T_3), NPK + farm yard manure (FYM @ 7.5 t/ha) (T_4), NPK + paddy straw (PS @ 10 t/ha) (T_5) and NPK + green manure (*Sesbenia sesban*) (GM @ 8 t/ha) (T_6). Soil samples were collected from three different depths (0-.15, .15-.3 and .3-.45 m) 7-10 days after rice harvest, including the fallow and analysed for selected soil quality parameters (physical, chemical and microbiological).

Soil analyses
Soil pH, bulk density, total C, available N, extractable P and exchangeable K was analysed following standard methods. Carbon mineralization (Min-C) was evaluated by incubation using alkali traps (Anderson, 1982). A chloroform ($CHCl_3$) fumigation-extraction method was used to determine microbial biomass C (MBC) (Voroney and Paul, 1984).
Cumulative C inputs, during the 19 cropping cycles, were calculated from organic sources (FYM, PS and GM) as well as from crop contributions (roots, stubble and rhizodeposition) (Table 1). Fractions of SOC were estimated through a modified Walkely and Black method as described by Chan *et al.* (2001) which allowed separation of total C into the following four fractions of decreasing oxidizability: Fraction I ($C_{frac\ 1}$, very labile); Fraction II ($C_{frac\ 2}$, labile); Fraction III ($C_{frac\ 3}$, less labile) and Fraction IV ($C_{frac\ 4}$, non-labile).

Table 1. Cumulative C input from different treatments.

Treatment	Stubble biomass C	Root biomass C	Rhizode-position C	Aquatic biomass C	Crop C input	FYM/PS/GM C	Cumulative C input
	(Mg/ha)						
Control	1.52	10.6	11.8	13.3	37.2	0.0	37.2
100% NPK	3.04	24.5	29.6	13.3	70.4	0.0	70.4
NPK+FYM	3.42	27.0	34.2	13.3	77.9	9.49	87.4
NPK+ PS	3.42	26.4	33.3	13.3	76.4	7.98	84.4
NPK+GM	3.23	25.8	32.5	13.3	74.83	6.31	81.1

Results and discussion
Effect on soil quality
Results showed that upon cultivation with or without fertilizer, there was a little increase in pH over the fallow i.e. uncultivated soil. Soil bulk density (BD) under different treatments ranged between 1.13 to 1.25 Mg/m^3 and the highest value (1.25 Mg/m^3) was associated with fallow (T_1) and 100% NPK (T_3) (Table 2). Application of fertilizer with and/or without organic amendments caused significant increases in available N, P and K content in all the treatments over the control except for K under T_5. The increase in extractable P with T_4 treatment might be due to incorporation of FYM with inorganic fertilizer, since FYM upon decomposition produces some organic ligands, which helps to increase the availability of P to plants.

Table 2. Changes in soil quality parameters under different treatments after 19 years of cultivation.

Treatment	pH	BD (Mg/m^3)	Av. N (kg/ha)	Extrac. P (kg/ha)	Exch. K (kg/ha)	MBC (µg/g soil)	Min-C (mg CO_2/24 h. g soil)	Total C (%)
T_1	6.57[b]	1.25[a]	132[d]	35.0[e]	162[d]	483[d]	0.17[a]	1.61[c]
T_2	7.20[a]	1.13[c]	152[c]	48.8[d]	173[c]	250[e]	0.09[b]	1.12[d]
T_3	6.90[a]	1.25[a]	165[ab]	95.9[a]	199[a]	486[d]	0.15[ab]	1.60[c]
T_4	7.03[a]	1.19[b]	167[a]	95.5[a]	186[b]	531[c]	0.15[ab]	1.95[ab]
T_5	7.00[a]	1.19[b]	158[bc]	73.7[c]	159[d]	776[a]	0.13[ab]	2.00[a]
T_6	7.03[a]	1.16[b]	158[bc]	90.1[b]	191[b]	565[b]	0.11[ab]	1.83[b]
$SE_m(\pm)$	0.089	0.011	2.30	1.07	1.95	3.58	0.020	0.438

Means followed by common letter are not significantly different (p<0.05) by Duncan's Multiple Range Test (DMRT).

Changes in the physical and chemical properties of the soils were associated with changes in the soil biological properties. Microbial biomass carbon (MBC) content of the soils under different treatments (Table 2) varied from 250 to 776 µg/g soil constituting about 3.05% of the TOC content of the soil. The highest and the lowest values were associated with T_5 and T_2 treatment respectively. The greater magnitude of MBC with PS compared to GM or FYM might be due to the presence of decomposition resistant fibre fractions in the former compared with the latter. Similarly Rasmussen *et al.* (1998) reported that addition of organics caused a substantial increase in the MBC in soil. The relative amount of mineralizable C (Min-C) content of the soils under different treatments was as follows: $T_1 > T_3 > T_4 > T_5 > T_6 > T_2$ (Table 2). There was, however, no significant difference among the fertilizer treatments compared in the study. Because of intensive cultivation for the last 19 years, there was a significant decline in this form of C in soils, the magnitude of decrease in control treatment being 48.2% of the fallow.

Effect on C sequestration
Continuous cultivation, without application of organic inputs, significantly depleted total C content by 30% when compared with fallow (Table 2). Application of FYM, PS and GM as a supplement with NPK not only added C to the soil but also increased plant C input in the soil through root residue, stubble, rhizodeposition (Table 1).
The fractions of OC extracted, were significantly different among the treatments. Both PS and GM significantly increased the more labile $C_{frac\ 1}$ by 28% and 25%, respectively; and both PS and FYM increased labile $C_{frac\ 2}$ significantly by 97% and 69%, respectively, when compared with control. All the treatments increased $C_{frac\ 4}$ significantly when compared with control, with the highest increase under T_4 (136%) followed by T_6 (101%) > T_5 (80%) > T_3 (71%). When compared with fallow, continuous cultivation, without any amendment (T_1), decreased the $C_{frac\ 1}$, $C_{frac\ 2}$ and $C_{frac\ 4}$ significantly by 17-43%. Among the organic treatments, only T_4 and T_6 significantly increased the $C_{frac\ 4}$ by 35% and 15% respectively (Table 3).

Table 3. Fractions of SOC (g/kg) under different treatments.

Treatment	Soil organic carbon fraction (g/kg)											
	$C_{frac\ 1}$			$C_{frac\ 2}$			$C_{frac\ 3}$			$C_{frac\ 4}$		
	0-.15	.15-.3	.3-.45	0-.15	.15-.3	.3-.45	0-.15	.15-.3	.3-.45	0-.15	.15-.3	.3-.45
T_1	4.30	2.43	1.89	1.77	1.41	1.43	1.13	2.23	0.33	2.72	3.69	5.54
T_2	3.77	2.00	1.30	0.83	0.54	1.37	1.60	1.10	1.37	1.78	3.47	1.59
T_3	4.17	1.63	1.37	1.07	1.39	1.39	1.50	0.89	1.93	2.98	5.13	3.55
T_4	4.43	1.76	1.50	1.70	1.88	1.04	2.00	1.00	1.95	3.04	7.59	5.49
T_5	4.23	3.45	1.37	2.44	0.98	1.95	1.86	1.82	0.85	2.05	5.29	4.96
T_6	4.77	2.15	1.95	1.50	0.85	1.17	1.73	0.91	1.50	2.48	6.79	4.48
T X D	***			**			**			***		
LSD (0.05)	0.249			0.365			0.401			0.350		

Higher values of labile fractions under NPK+PS (T_5) may be ascribed to the higher polysaccharides (cellulose and hemicelluloses) content of PS that could lead to the higher production of that fraction as compared to that of FYM and GM. The largest effect of NPK+FYM (T_4) treatment on less labile/non labile fraction may be attributed to the higher lignin and polyphenol content of FYM that could lead to formation of more stable complex with protein of plant origin and thus made FYM-C more resistant to decomposition (Tian *et al.,* 1992). The significant increase in MBC with application of organic amendments along with inorganic fertilizer probably resulted from a more conducive environment for microbial growth (Grego *et al.* 1998). When compared with fallow, the amount of sequestered C was higher (2.47 Mg/ha) under T_4 followed by T_5 (1.41 Mg/ha) > T_6 (0.4 Mg/ha). There was a net loss of C by 5.57 due to continuous cultivation without any amendment. The result showed that 26.1%, 17.7% and 6.3% of the C applied through FYM, PS and GM were sequestered. This indicates that among the organic amendments, C applied through FYM was sequestered more than that of PS, followed by GM. This may be attributed to the higher lignin and polyphenol content of FYM (17.5% and 1.08%) than that of PS (11% and 0.60%) and GM (8.9% and 0.32%). Addition of these organic amendments also increased plant C input in the soil (Table 1) and when the plant C inputs were included with C inputs through organic amendments, then the percentage of C sequestration reduced to 14.5%, 10.0% and 3.7 % due to the FYM, PS and GM application, respectively. After 19 years cropping cycles, the existence of a strong positive linear relationship ($R^2 = 0.98$) between stable C ($C_{frac\ 4}$) and cumulative C input indicates that soil of the present study still has the capacity to sequestered more C with the increase of C input through organic amendment as well as crop C input.

Conclusion

Management practices such as application of fertilizer and organic amendments played important roles in maintaining soil quality and C sequestration and thereby greenhouse gas mitigation in the Indo-Gangetic plains of eastern India. Addition of organic residues with inorganic NPK fertilizers significantly increased the nutrient content of the soil. Continuous cropping decreased total C as well as its labile and non-labile fractions. The labile C fractions dominated in the near surface soil layers, but decreased significantly in the deeper layers where the recalcitrant C fraction was significantly dominated down to .45 m depth. The result has clearly shown that even in intensive cropping, application of NPK + organic amendments could build up more C as compared to that of fallow and among the organic inputs, FYM is proved more beneficial than PS and GM.

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Mapping micro-spatial patterns of C, and Fe and Al-oxides in gleysols: A means of understanding SOM-mineral interactions

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Abstract
To fully understand the role of mineral interactions in the sequestration of soil organic matter (SOM) these processes need to be studied at the micro-scales over which they occur. The spatial patterning of iron oxides as a result of redox reactions makes gleysols an ideal medium in which to study such processes. This paper outlines the methods being used in an on-going study of SOM – mineral interaction in gleysols. A combination of soil micromorphology, SEM-EDS, and selective dissolution using oxalate and citrate dithionite on undisturbed soil sections is teamed with sequential extraction of bulk soil samples also using oxalate and citrate dithionite, ICP-OES, FT-IR and CN analysis. The results of this study are still being collected, but will be presented in August once the study is complete.

Key Words
Soil organic matter, mineral interactions, gelysol, stagnosols, micro-analysis

Introduction
The stabilisation of SOM through its interaction with Fe and Al oxides is well documented (Eusterhues *et al*., 2005; Wagai and Mayer, 2007; Wiseman and Püttman, 2005), but not well understood (Kögel-Knaber *et al*., 2006). The nature of the interaction between organic matter (OM) and Fe/Al oxides is determined by the chemical characteristics of the OM and the type of mineral phases present. The reactive surfaces of Fe and Al oxides are often presumed to account for sorption and stabilisation of OM (Kaiser *et al*., 2000), but recent research has suggested that simple sorption processes do not stabilise the bulk of SOC as the maximum sorption ratio of Fe oxides is only 0.22 g OC/1 g of Fe Wagai and Mayer, 2007). Ternary OM - Fe-oxide - clay associations (Wagai and Mayer, 2007) and the formation of unidentified chemical bonds (Spielvogel *et al*. 2008) have been suggested as possible mechanisms for stabilisation.

Gleyed (waterlogged) soils are characterised by highly localised patterns of Fe (hydr)oxides concentration and depletion, related to the reduction and mobilisation of Fe in anaerobic regions and its reprecipitation as Fe (hydr)oxides in oxidising areas of the soil. The spatial and temporal distribution of oxidising and reducing conditions in gleyed soils is linked to groundwater and soil water chemistry, microbial activity, OM distribution, aggregation and void patterns (Lovely, 1991; Ottow, 1970). In a gleyed soil where reducing and oxidising conditions alternate, the microbially mediated reduction and oxidation of Fe (hydr)oxides can lead not only to the stabilisation of carbon but also to its release as dissolved organic carbon (DOC) (Stemmler and Berthelin, 2003), CO_2 and CH_4.

The turnover of carbon in peaty gley soils is, therefore, highly complex with temporal and micro-spatial variation due to localised redox conditions. Few studies have investigated the chemical composition of the OM stabilised by Fe/Al oxides in gleyed soils (Kaiser *et al.*, 2000; Spielvogel *et al.*, 2008), and as far as we can establish, the complex spatial pattern of oxidising and reducing conditions over very small scales has not been considered in previous research using bulk soil chemical properties. Analysis of the distribution of SOC, Fe, Al, and other minerals (e.g. Si and Mn) in undisturbed gley soils over scales of µms to mms, carefully related to bulk SOC chemistry can provide a means of studying the complex processes of SOC chemical stabilisation *in-situ*. To this end the study combines direct micro-spatial analyses and bulk soil chemical techniques to map the relative distribution and concentrations of C, Fe and Al in gleysols in order to study carbon storage associated with Fe oxides and clay minerals and better understand the mechanisms of stabilisation.

Methods

Soils with contrasting hydrological regimes (gleysol, stagnosol and gleyic cambisol) were sampled from an experimental forest, Harwood Forest, Northumberland, UK, in which above and below ground carbon stocks have already been well characterised (Zerva *et al*., 2005). Undisturbed soils samples were taken from the top soil (10-20 cm) and sub soil (20-30 cm) using kubiena tins together with closely spatially associated bulk samples.

Concentrations of Fe, Al and Mn have been determined for bulk soils and extracted bulk soil residues (after microwave-assisted HNO_3/HBF_4 digestion) and for bulk soil and thin section extract solutions using ICP-OES. Bulk soil samples are also being analysed to determine concentrations of weakly and strongly crystalline Fe/Al oxides and associated with organic matter fractions by sequential selective extraction using oxalate and citrate-dithionite. Additionally, to study the chemical characteristics of the stable OM, extract solutions were purified and analysed using FT-IR spectroscopy. Carbon, nitrogen and OM contents were also measured for the bulk soils/residues.

The undisturbed samples were freeze-dried, resin impregnated under vacuum and then bonded to glass slides and lapped to produce thin sections with a thickness of 30 µm following standard procedures (www.thin.stir.ac.uk). Thin sections are currently being described micromorphologically following the terminology of Stoops (2003). Void space, organic matter, and iron depletion and concentration features, such as those shown in Figure 1, are in the process of being mapped and counted using point counting techniques with a spatial interval of 1.5 mm. The range of organic and iron features identified micromorphologically will then be analysed using SEM-EDX to quantify and map C, Fe, and Al distributions. Selective dissolution of the soil thin sections using oxalate and citrate dithionite will be followed by repeat micromorphological examination and SEM-EDX to determine the micro-spatial distribution of weakly and strongly crystalline Fe/Al oxides and their association with soil organic matter.
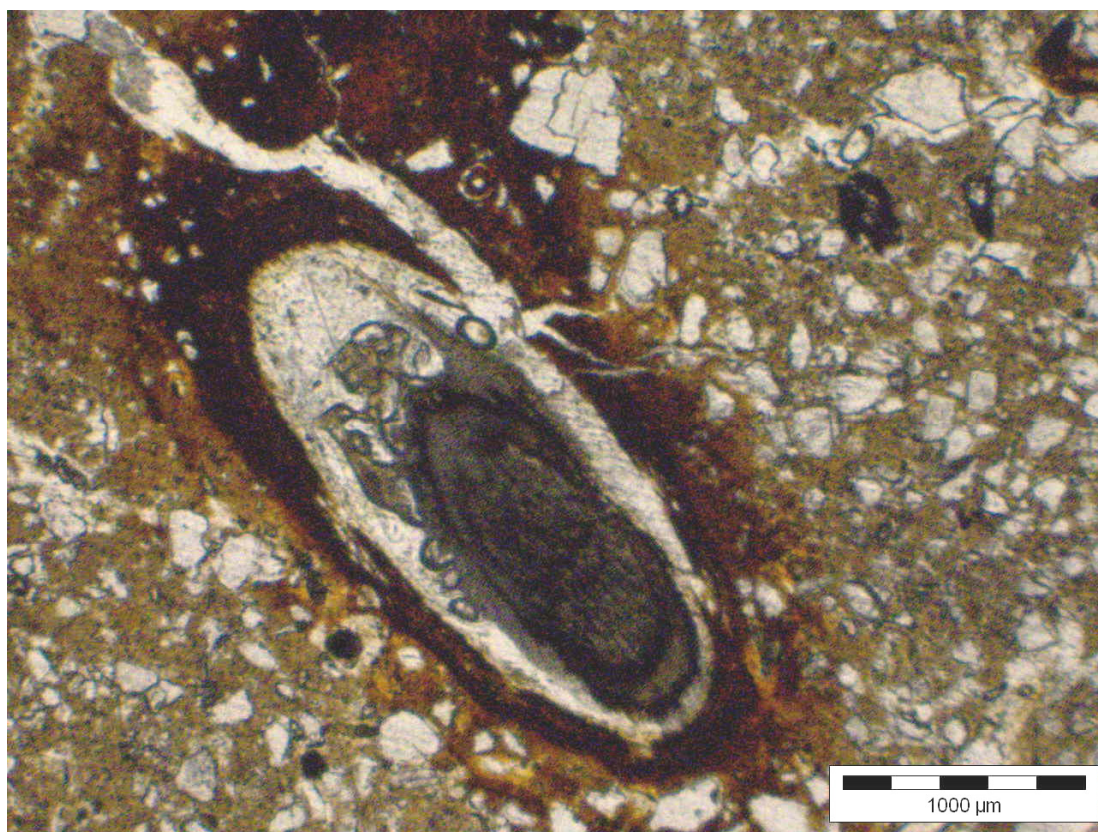
Figure 1. Amorphous iron oxide impregnation surrounding and within the organic tissues of a partially decomposed root.

Results

This is a scoping study that is on-going (due to report March 2010) hence results to date are preliminary and incomplete, but the final findings of the project will be presented at the WCSS in August 2010 once the study has been completed.

Acknowledgements

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Microbial properties and carbon dynamics in a heterogeneous soil landscape under different cropping systems and fertilizer regimes

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Abstract

In order to reveal impacts of different cropping systems and fertilizer regimes on soil microbial properties and carbon dynamics, plots with 10 years of mono-cropping maize and rye were compared in a traditional field trial. Additionally, a more complex long-term field experiment was initiated, resembling typical periglacial landscape features with different soils, cropping systems and fertilizer regimes, and were firstly characterized for soil ecological conditions. After 10 years of mono-cropping, evidence was provided for unchanged soil organic matter and nitrogen contents but differences of organic matter content in several soil fractions. Carbon turn-over of different substrates in the mono-culture rye system was more intense compared to the maize system. Soil microbial properties did not differ significantly after ten years of mono-culture, however, evidence for differences in bacterial community composition were revealed. Further studies will be conducted to reveal interrelations between cropping systems, organic matter application to soil, soil organic matter fractions, microbial activities, and carbon turn-over.

Key Words

Microbial biomass, CO_2 respiration, microbial communities, rye, maize, fermentation slurry

Introduction

Crop management practices are known to determine the quantity and quality, as well as seasonal and spatial distribution of plant residues entering soil. Consequently, several scenarios of land use change are well studied in this respect, e.g., carbon fluxes after land use change from cropland to grassland (Alberti *et al*., 2006). Especially for systems of cropping energy plants, which are fast-growing crops planted for the specific purpose of producing energy from all or parts of the resulting plant, rarely any studies do exist about the impacts on soil carbon dynamics (Ma *et al*., 2000). Therefore, combined studies of soil microbial properties (biomass, activity, structure) and pools of soil organic matter (SOM) are performed in systematic field trials, comparing different cropping systems and fertilizer regimes. Our study is intended to contribute knowledge for understanding the impact of land use management on soil carbon dynamics by detailed soil microbiological and chemical analyses.

Methods

First exploratory studies were conducted on traditional field trials located at ZALF Research Station Dedelow, NE Germany, providing 10-years of mono-cultures of maize and rye considered to decrease or sustain SOM content in the long-term, respectively. Subsequently, a long-term field experiment (CarboZALF-D, Dedelow) was initiated in 2009, resembling typical periglacial landscape features and a range of different soil types and soil properties, and were firstly characterized for soil ecological "starting conditions" (2009: completely under maize). At the beginning of the 2010 vegetation period, 14 experimental field plots will be analysed providing variants of soils (Luvisol, Kolluvisol), cropping systems (wheat *vs*. energy maize), and fertilizer regimes (100% mineral fertilizer, 50% to 50% mineral fertilizer and biofermentation slurry, 100% slurry).
Soil microbial biomass (C_{mic}) was determined by a substrate-induced respiration method (Anderson and Domsch, 1978) at 20°C using an automated infrared gas analysis system (Heinemeyer *et al*., 1989). Soil *basal* CO_2 *respiration* was measured hourly under continuous aeration of the samples, using the automated infrared gas analysis system over a period of at least 8 up to 18 h at 20°C. The *ecophysiological quotients* qCO_2 and C_{mic} / C_{org} ratio were calculated. *Bacterial, fungal and actinomycetal contributions to soil microbial biomass* were determined by phospholipid fatty acid analysis (Frostegard *et al*., 1993; Maassen *et al*., 2006). The *bacterial community composition* was analyzed using terminal restriction fragment length polymorphism of 16S rRNA genes (Ulrich and Becker, 2006).
The *content and the composition of soil organic matter* were analysed in two steps: firstly, coarse organic particles were separated from soil samples in four replications by using electrostatic attraction of a charged glass surface (Kaiser *et al*., 2009). Subsequently, dry weight per kg soil was estimated. In the second step, physically unbounded, macro-aggregate and micro-aggregate occluded organic particles, as well as water-soluble OM

fractions were sequentially separated by a combination of ultrasonic treatment, density separation, sieving, and water extraction. *Carbon mineralization dynamics* were investigated under laboratory conditions in soil samples from the maize and rye cropping systems using ^{14}C-labelled maize and rye root substrates. For this purpose a continuous-flow incubation device (microcosm) was constructed, as described by Chen *et al.* (2009).

Results

Studies on field trials at ZALF Research Station revealed soil carbon and nitrogen contents that were not different after 10-years monoculturing maize and rye. Correspondingly, the content of soil microbial biomass under mono-cultures of maize and rye (97 and 100 µg C_{mic} g^{-1} soil, respectively) did not differ. Furthermore, soil basal respiration was 0.11 and 0.13 µg CO_2-C g^{-1} h^{-1} under maize and rye, respectively, also without a significant difference. However, the mineralization rates of ^{14}C-plant residues *in vitro* were two times higher in soil from the rye system compared to soil from the maize system (Figure 1). During 26 days of incubation, 22% and 44% of added ^{14}C-substrates were mineralized in soils from maize and rye systems, respectively.
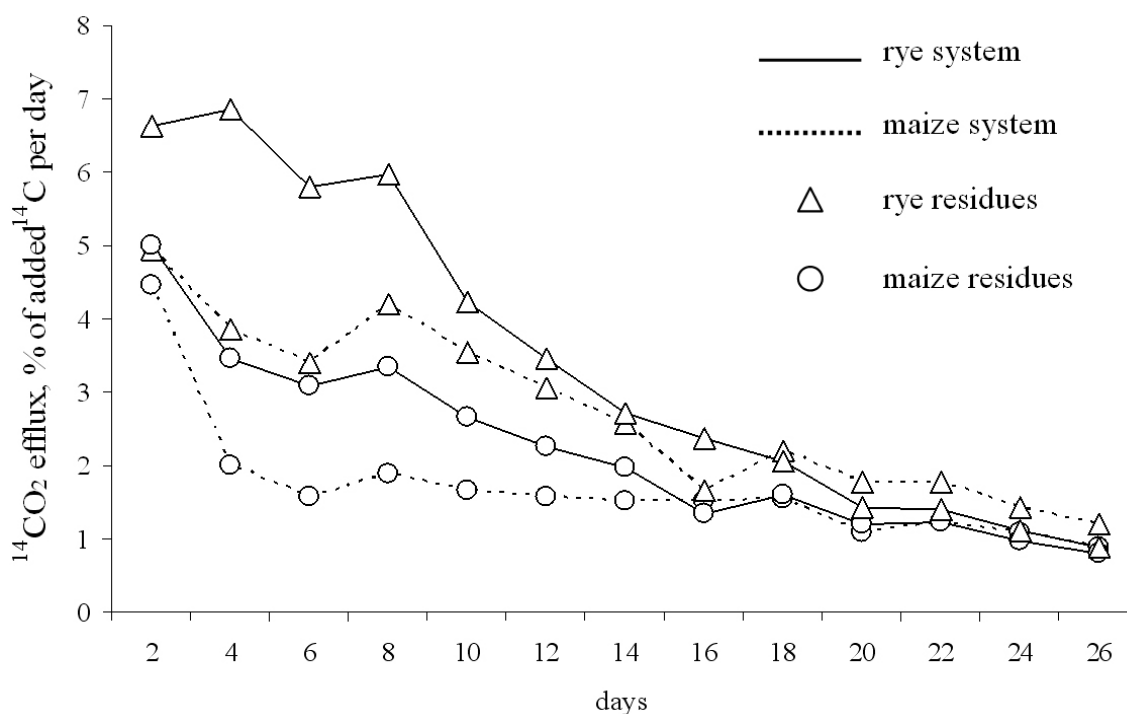
Figure 1. Mineralization rates of ^{14}C-labelled, rye and maize roots residues in soils from rye and maize mono-cropping systems.

Particulate organic matter content derived after water extraction was about by two times higher in soil under mono-culture rye compared to soil under maize. The highest amount of SOM was extracted from soil micro-aggregates in the maize cropping system, while the amounts of SOM extracted from macro-aggregates as well as water-soluble fractions were similar in soils under maize and rye cropping systems. Overall, the highest significant differences in organic matter content in soils under maize and rye cropping systems were found in fractions obtained by ultrasonic dispersion of soil micro-aggregates. Concerning microbial community composition (fungi, bacteria, actinomycetes), results from bacterial community analyses revealed differences in variants, most clearly for the maize versus the rye and rotation systems – but mixed clusters were also present.

Conclusion

From our studies on traditional field trials we can conclude, I) soil organic matter contents did not differ after 10 years of mono-cropping maize and rye, but differences of SOM contents in soil fractions were detected. II) Carbon turn-over of different substrates in the mono-culture rye system was more intense compared to the maize system. III) Soil microbial properties did not differ significantly after ten years of mono-culture, however, evidence for differences in bacterial community composition was detected. Further studies are required to reveal interrelations between land use, soil organic matter fractions, microbial activities and carbon turn-over. For this reason, a new long-term field experiment (CarboZALF-D, Dedelow, NE Germany) was initiated, resembling typical periglacial landscape features and a range of different soil types and soil properties. Different cropping systems and fertilizer regimes will be established in 2010 and consecutively studied.

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Mineralization dynamics and biochemical properties following application of organic residues to soil

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Abstract

The reliability of soil application of organic residues as an effective strategy for sustainable management of soil organic matter requires a thorough evaluation of the impact of amendment on C and N mineralization and size and activity of soil microbial biomass. In this work three soils were amended with three plant residues and five animal by-products and analysed for CO_2 evolution, extractable NH_4^+ and NO_3^-, water extractable C and N, microbial biomass C and protease and β-glucosidase activities. Mineralization patterns depended on the nature of the residues and the properties of soils. Cumulative extra respiration was higher (16-24% of added C) for animal residues than for plant residues (9-12 % of added C). Animal by-products caused a significant increase in the content of mineral N and water soluble C and N, while plant residues produced an immobilization of mineral N. The application of wastes caused an increase in the size and activity of soil microbial biomass, indicating an enhanced capacity of the soil to carry out ecosystem functions. Overall results suggest that plant residues are more effective soil amendments and favour C sequestration, while animal residues are effective organic fertilizers.

Key Words

Organic residues, soil organic matter, mineralization, soil microbial biomass, enzyme activity

Introduction

Soil organic matter (SOM) is a critical component of both natural and managed ecosystems. The decline of SOM caused by the intensification of agricultural practices is among the main threats to soil fertility and quality (Matson *et al.,* 1997). In the Mediterranean area the decrease of SOM during last decades is estimated at around 50% of the original content, with 74% of the land covered by soils containing less than 2% of organic C (Van Camp *et al.,* 2004).

The maintenance of soil agronomical and environmental functions implies a sustainable management of SOM. Among the management practices aimed to the preservation and increase of SOM, application of organic residues represents a valuable option because it allows for soil fertility enhancement, soil quality conservation, environmental protection and sustainable recycling of organic residues. Nevertheless, the suitability of soil application of organic residues requires a thorough evaluation of the impact of exogenous organic matter on C and N mineralization and size and activity of soil microorganisms. Dynamics and amount of mineralization plays a key function for availability of nutrients, release of toxic elements and soil C sequestration, while soil microorganisms exert fundamental functions determining the degree of soil quality, such as improvement of soil structure, decomposition of organic compounds, synthesis of humic substances, C and nutrient cycling, enhancement of nutrients and water uptake, protection of crops from pest and disease, bioremediation of toxic metals and other harmful compounds. In this work a series of laboratory assays was designed to study mineralization dynamics and chemical and biochemical properties of soil following amendment with different plant and animal residues. In particular, the impact of organic residue characteristics and soil properties was evaluated in order to optimise soil amendment as effective strategy for sustainable management of SOM and soil conservation.

Methods

Three plant residues (straw, cotton and olive mill waste) and five animal by-products (meat bone meal, two different blood meals, horn and hoof meal and hydrolyzed leather) were added (0.5% on dry weight basis) to three moist soils and incubated at 20 ºC for one month. Main properties of soils and residues are reported on Table 1 and 2, respectively.

Table 1. Chemical and biochemical properties of the selected soils.

Site	Sand	Silt	Clay	pH	CaCO₃	C_{ORG}	N_{TOT}	C_{MIC}
	(%)					(%)		(mg kg⁻¹)
S. Martino	69	28	3	8.3	74	0.57	0.05	114
Jumilla	52	21	27	8.0	42	1.04	0.10	119
Lodi	67	21	12	6.7	-	20	0.21	205

Table 2. Main properties of organic residues.

Organic residues	Abbreviation	pH	C_{ORG}	N_{TOT}	C_{ORG}/N_{TOT}	K	P
			(%)			(%)	
Meat and Bone Meal	MBM	5.9	46.0	11.1	4.2	0.3	2.7
Blood Meal	BLM	6.7	52.6	16.4	3.2	0.7	0.2
Blood Meal 2	BLM2	6.6	49.3	15.6	3.2	0.3	0.4
Horn and Hoof Meal	HHM	7.5	51.3	17.0	3.0	0.1	0.2
Hydrolysed Leather	HL	5.2	42.0	13.2	3.2	0.4	1.4
Straw	STRAW	6.5	49.6	0.2	201	0.4	0.0
Cotton	COTTON	6.2	45.2	1.5	30.5	1.5	0.2
Olive Mill Waste	OMW	5.2	55.1	1.1	48.7	2.4	0.1

During incubation the CO_2 evolution of the amended soils was measured every four hours by means of an automatic chromatographic system for gas sampling and measurement (Cayuela et al., 2006). At the end of incubation, soil samples were analysed for water extractable C and N, K_2SO_4-extractable NH_4^+ and NO_3^-, microbial biomass C (Wu *et al.,* 1990), protease (Alef and Nannipieri, 1995a) and β-glucosidase activity (Alef and Nannipieri, 1995b).

Results

On the whole the addition of the residues to the soil produced, after a short lag-phase, an exponential increase in the soil respiration rate, reflecting the growth of microbial biomass, followed by a steady decrease, indicating the depletion of available substrates (Figure 1). Cumulative extra CO_2-C (Cumulative CO_2-C from amended soil minus cumulative CO_2-C from control soil) ranged from 9.1 to 24% of added C (Table 3).

Table 3. Cumulative extra CO_2-C in amended soils (% of added C).

Organic residue	Soil			Mean
	San Martino	Jumilla	Lodi	
MBM	19.3	21.3	27.7	22.8
BLM	13.3	11.8	22.1	15.7
BLM2	15.5	17.0	21.6	18.0
HHM	24.3	23.2	24.4	24.0
HL	15.0	17.0	21.2	17.7
STRAW	8.0	5.6	20.1	11.2
COTTON	8.3	7.9	19.2	11.8
OMW	6.1	6.6	14.6	9.1

The dynamics and amount of mineralized C were affected by the nature of chemical constituents of residues. Cumulative extra respiration was higher (16-24% of added C) for animal residue (mainly constituted by proteins) with respect to plant residues (mainly constituted by ligno-cellulosic components - 9-12 % of added C) (Table 3). Carbon mineralization was also affected by the complexity of chemical constituents of residues as the different dynamics of BLM, MBM and HHM (Figure 1) reflected the predominant kind of proteins (globular, collagen, keratin) present in the residues.

Also soil properties greatly affected C mineralization. For instance cumulative extra CO_2-C derived from straw was about four times higher in the Lodi soil with respect to S. Martino (Table 3). Microbial biomass, pH and texture were the main soil properties affecting C mineralization.

All residues caused a significant increase in water soluble organic C (data not shown), an indicator of soil quality for plant growth (Zsolnay, 1996).
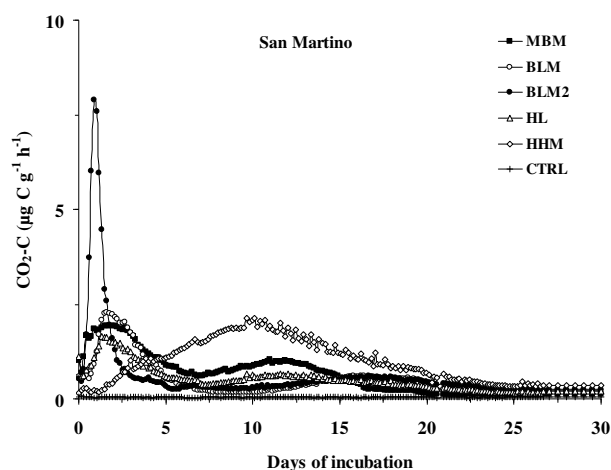
Figure 1. Dynamics of CO$_2$ evolution in S. Martino soil amended with animal residues.

Water soluble N was increased with respect the control in the animal residues treated soils, while it was decreased in the soils treated with plant residues (data not shown).

Animal by-products caused a significant increase in the content of net extractable mineral N (extractable mineral N from amended soil minus extractable mineral N from control soil) ranging from 13 to 33% of the N added with the residue, indicating an increase in the mineral N available for plant, but also an increased risk of nitrate leaching. On the contrary, plant residues caused an immobilization of mineral N and therefore a possible N supply deficiency for plants (Table 4).

Table 4. Net extractable mineral N in amended soils (% of added N).

Organic residue	Soil			Mean
	San Martino	Jumilla	Lodi	
MBM	47.9	40.2	9.8	32.6
BLM	29.0	22.3	22.7	24.6
BLM2	1.4	27.2	8.1	12.3
HHM	7.5	19.2	12.6	13.1
HL	5.1	23.9	9.1	12.7
STRAW	-394	-172	-221	-262.5
COTTON	-63.1	-29.1	-36.7	-43.0
OMW	-90.9	-38.5	-57.6	-62.3

The application of wastes caused an overall increase in the size and activity of soil microbial biomass, indicating an enhanced capacity of the soil to carry out ecosystem functions. The importance of the characteristic of amendments was evident in the case of the two blood meals; despite they derived from the same starting material their soil application caused the minimum and maximum increase in the size of microbial biomass (Figure 2).
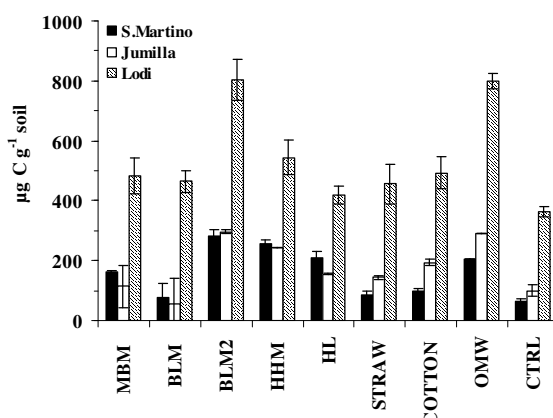
Figure 2. Microbial biomass C in control and amended soils after 1 month incubation. Bars represent standard deviation.

All residues caused an increase in the enzymatic activity. In particular animal by-products caused the highest increase in the protease activity (3-10 fold increase), a key enzyme in protein degradation (Alef and Nannipieri, 1995a), while β–glucosidase activity, the rate limiting enzyme in the microbial degradation of cellulose to glucose (Alef and Nannipieri, 1995b) was mostly stimulated by straw and cotton (1.4-3 fold increase) (Figure 3).
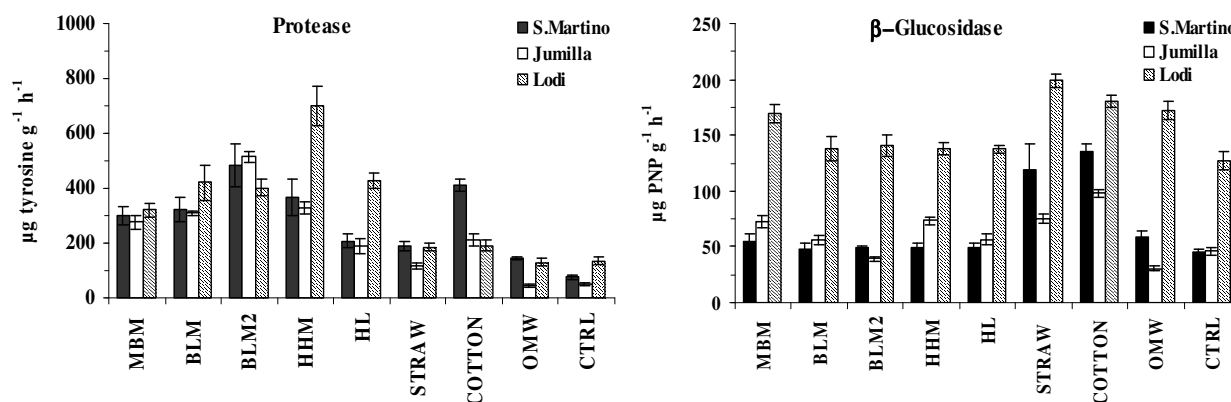
Figure 3. Protease and β-glucosidase activity in control and amended soils after 1 month incubation. Bars represent standard deviation. PNG: para nitro phenol.

Conclusion

Results showed that the decomposition of organic residues varied greatly according to the characteristic of the residues and was soil specific and largely related to the soil biochemical and textural characteristics.
Mineralization data suggest that plant residues are best suited as soil amendment and for promoting soil C sequestration, while animal residues are more indicated as organic fertilizers.
The general increase in microbial size and activity represents an enhancement of soil capacity to carry out fundamental ecosystem functions.
Results of the present study underline the importance of researches for the optimization of soil addition of organic residues in order to increase beneficial effects of soil amendment (enhancement of soil fertility and quality, substrate for soil microorganisms, soil C sequestration, closure and proper functioning of elements cycle, environmental decontamination) and avoid negative environmental impacts (NO_3^- leaching, soil N deficiency). In this perspective laboratory studies can provide rapid assessment of the effect of several factors on mineralization and biochemical properties. Results from these studies can be used as the first step to design appropriate field management strategies.

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Model carbon compounds differ in their effects on pH change of soils with different initial pH

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Abstract
Laboratory experiments were carried out to investigate the mechanisms of soil pH change using organic compounds. Carbon (C) compounds commonly found in plant material (citric acid, ferulic acid, glucose and glucosamine hydrochloride, potassium and sodium citrate) were selected based on the type and number of functional groups and applied to two soils differing in initial pH. Organic acid (R-COOH) addition instantly decreased soil pH via H^+ dissociation followed by an increase in pH through decarboxylation. The ability of soil to return to the original pH was less with increased rate of acid addition and was not restored at the highest addition rates. Organic anions increased pH of both soils. Soil pH increased with increasing proportion of organic anion when organic acids and anions were added together to the soil. Glucose (R-OH) did not significantly change pH. In comparison, glucosamine hydrochloride (R-NH$_2$) addition had no major effect on soil pH in Frankston soil (initial pH 4.44) as nitrification was inhibited at low pH, whereas in Shepparton soil (initial pH 6.20), pH subsequently decreased due to nitrification. Therefore, the results demonstrated that C compounds in plant material and initial soil pH regulates the direction and magnitude of pH change.

Key Words
Association/dissociation, mineralisation, alkalisation, organic salt, C rates

Introduction
Organic compounds in plant residues may have a substantial effect on soil pH depending on the nature of the chemical functional groups (Rukshana *et al.* 2009). Some functional groups may be the source of H^+ after dissociation and thus acidify soil (Brady and Weil 2002). Others may be basic or neutral. During decomposition of organic matter chemical reactions are related to the quantities and types of organic chemical functional groups and structural components present in organic compounds (Essington 2004). Association/dissociation of protons from organic compounds is an important process resulting in soil pH change (Xu *et al.* 2006). The amounts of H^+ released or consumed by the added organic matter will determine the change in soil pH. The association/dissociation of functional groups of organic matter depends on mean pKa values of the organic matter and initial pH (Ritchie and Dolling 1985; Tang and Yu 1999; Xu *et al.* 2006). Moreover, the proportion of organic compounds in plant residues varies between species (Gunnarsson and Marstorp 2002) and also plant components (e.g. leaves, shoot) (Yan and Schubert 2000). We hypothesized that the change in soil pH after addition of C compounds would be related to the chemical nature of the compounds and, therefore, neutral functional groups (glucose) would not affect pH whereas acidic (R-COOH) and basic N containing (R-NH$_2$) compounds would significantly change soil pH.

Method
Soils and C compounds
Soils were collected from Frankston (Podosol) and Shepparton (Tenosol), Victoria, Australia (Isbell 1996). Glucose, citric acid, ferulic acid, glucosamine hydrochloride, potassium citrate (K-citrate) and sodium citrate (Na-citrate) were selected as they represent compounds commonly found in plant residues and differ in the type and number of chemical functional groups. Glucose is a simple carbohydrate with neutral OH and CHO groups. Citric acid is low molecular weight organic acid containing acidic carboxyl (R-COOH) functional groups. Glucosamine hydrochloride is a basic nitrogenous compound that contains an amino group (R-NH$_2$). K-citrate and Na-citrate are organic anions in the salt form. Ferulic acid is a phenolic compound containing hydroxyl and carboxylic groups.

Experiment 1

The aim of this experiment was to investigate soil pH changes by a range of C compounds. Citric acid, ferulic acid, glucosamine hydrochloride and glucose were added to pre-incubated soil at 0.5 g C/kg soil. Soils were thoroughly mixed and 25 g soil was packed into individual plastic cores (bulk density of 1.4 g cm^{-3}) with 3 replicates. The soil cores were transferred into glass incubation chambers (2009) and incubated for 30 days at 25 ^{0}C. Soil water content was maintained at 80% field capacity. At 0, 1, 3, 7, 15 and 30 days, a set of cores was destructively sampled for analysis. Soil pH was determined using moist soil after extraction in 0.01 M CaCl$_2$ (1:5) by shaking end-over-end for 1 h following centrifugation at 3500 rev min^{-1} for 10 min.

Experiment 2

The purpose of this experiment was to determine the change in soil pH by either an organic acid (citric acid) or anion (K-citrate) at different rates of addition during direct shaking with soil for 384 h. Citric acid and K-citrate were added separately at rates of 0, 0.2, 0.5, 1.5 and 3 g C/kg soil into vials containing 5 g soil, adjusted to 25 mL with 0.01 M CaCl$_2$ (1:5). Soil pH was determined at 1, 24, 96, 192, and 384 h using air-dried soil as described above.

Experiment 3

This experiment aimed to simulate the effect of percent dissociation of an organic acid on pH change. Different ratios of organic acid (citric acid) or salt (tri-Na-citrate) were added to pre-incubated soil using stock solutions at a rate of 0.25 g C/kg soil to give acid: salt ratios of 100: 0, 90: 10, 75: 25, 50: 50, 25: 75, 90: 10 and 100: 0. To ensure equal sodium concentration, Na$_2$SO$_4$ was added to balance the sodium in each treatment. The incubation procedure and pH determination were performed as experiment 1 except that samples were taken at 2 and 30 d.

Statistical analysis

Results were analysed by analysis of variance (ANOVA) and significant differences (*P*<0.05) between means were tested using post-hoc Tukey tests using GENSTAT 11th Edition (Lawes Agricultural Trust).

Results

Experiment 1

Addition of organic acid (citric and ferulic acid) to soil instantly decreased pH due to H$^+$ dissociation (Figure 1). However, the magnitude of the pH decrease was much greater with addition of citric acid compared to ferulic acid. In subsequent incubation, pH slowly returned to the original level as organic anions were decomposed, consuming H$^+$ ions. Glucose did not significantly change pH as it is a neutral compound. Glucosamine hydrochloride did not change pH immediately after addition to either soil, but in the Shepparton soil, pH decreased over time due to rapid nitrogen mineralisation through adequate conversion to nitrate (data not presented). No effect of glucosamine on pH in Frankston soil was observed due to the inhibition of nitrification. The magnitude of the pH change was greater in the Shepparton soil which was related to its lower buffer capacity than the Frankston soil.
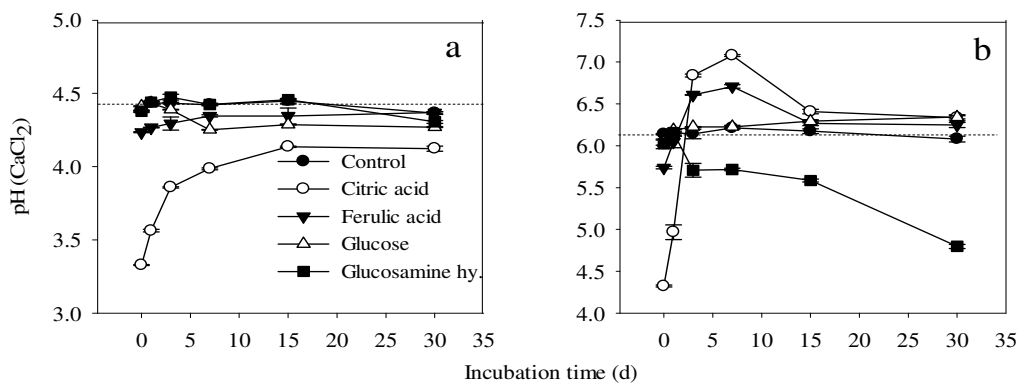
Figure 1. Soil pH changes over a 30 d incubation period after the addition of model C compounds to a) Frankston and b) Shepparton soils. Bars represent the standard error of the mean (n = 3) where they are greater than symbols. Dotted lines indicate the initial pH of the soil (Exp. 1).

Experiment 2

The addition of citric acid immediately decreased pH in both Frankston and Shepparton soils (Figure 2). The magnitude of the soil pH decrease was greater with increased rate of C addition. Over time the pH was slowly restored to the original level and the degree to which pH was restored was less with increased rate of acid addition. Soil pH did not return to the original level at higher rates as H^+ dissociation was much greater than H^+ association. In the Shepparton soil, the magnitude of pH increase was higher over time compared to the Frankston soil.
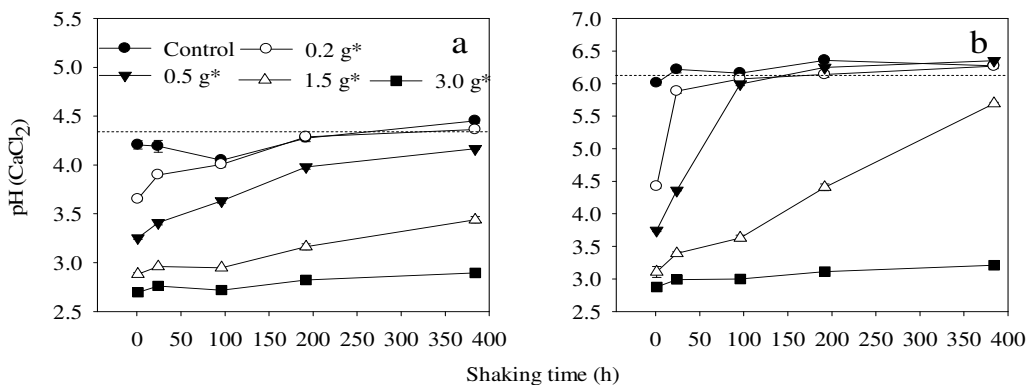
Figure 2. Soil pH changes during 0-384 h shaking after the addition of citric acid at different rates to a) Frankston and b) Shepparton soils. Asterisk (*) specify C/kg soil and bars represent the standard error of the mean, n = 3. Dotted lines indicate the initial pH of the soil (Exp. 2).

In the Frankston soil the addition of K-citrate at rates of 1.5 and 3.0 g C/kg increased pH over time but this was not observed at lower rates (Figure 3). Conversely, in the Shepparton soil pH was greatly increased at the lowest rate of 0.2 g C kg soil compared to the control and there were smaller increases in pH at higher rates of addition compared with the lowest (0.2 g C/kg).
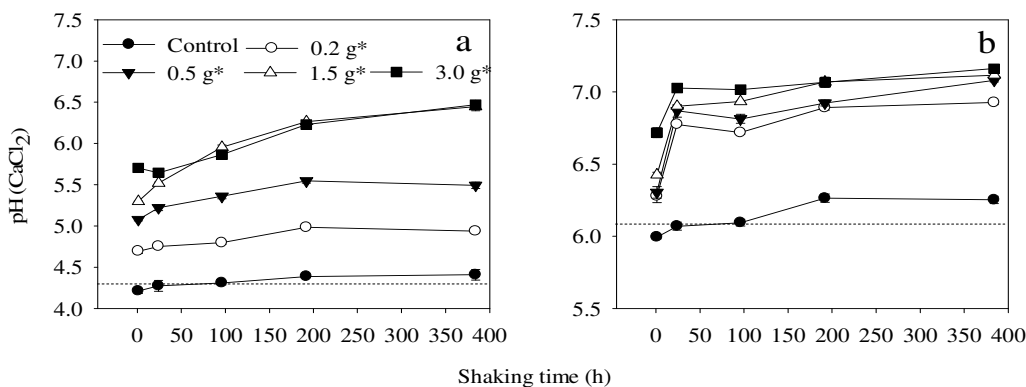
Figure 3. Soil pH changes during 0-384 h shaking after K-citrate was added at different rates to a) Frankston and b) Shepparton soils. Asterisk (*) specify C/kg soil and bars represent the standard error of the mean, n = 3. Dotted lines indicate the initial pH of the soil (Exp. 2)

Experiment 3

Increasing citrate-to-citric acid ratio linearly increased soil pH of the two soils at days 2 and 30 (Figure 4). The pH of the Shepparton soil was higher than the initial pH at 2 d even where 100% citric acid was added. However, in the Frankston soil, pH at day 2 was lower than the initial pH where 50% C was added as citrate. Organic acid addition to soil immediately decreased pH, followed by an increase in pH and magnitude of pH increase was much greater in Shepparton soil compared to Frankston soil. Therefore, at 2 d pH was greater than initial pH in the Shepparton soil and lower than the initial pH in Frankston soil up to a ratio of 50:50. Soil pH increased over time in Frankston soil. However, in Shepparton soil, pH decreased at 30 d compared to 2 d at lower ratios of salt addition (0: 100, 10: 90 and 75: 25) and followed by increasing pH with increasing salt ratio (50; 50, 75: 25, 90: 10 and 100: 0).
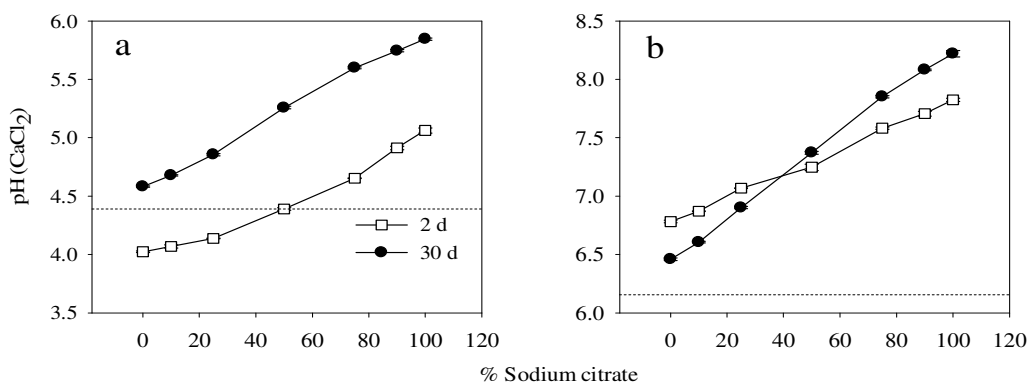
Figure 4. Effect of citrate-to-citric acid ratio on soil pH changes 2 and 30 d after Na-citrate and citric acid were added at a total C rate of 0.25 g/kg to a) Frankston b) Shepparton soil. Citrate: acid ratios are 0: 100, 10; 90, 25: 75, 50: 50, 75: 25, 10: 90, 0:100. The standard error bars were smaller than the symbols. Dotted lines indicate the initial soil pH (Exp. 3).

Conclusions

Organic compounds commonly found in plant residues have significant impacts on soil pH. Organic acids (R-COOH) reduced soil pH immediately after addition to soil due to H^+ dissociation from carboxyl groups followed by an increase in pH due to decarboxylation of the organic anions. Therefore when organic anions (K-citrate) were added to soil, pH immediately increased through decomposition of organic anions. The combined application of organic acid and anion increased soil pH, the pH increase being proportional with increasing organic anion-to-acid ratio. Glucose (R-OH) did not significantly change pH as it is neutral compound. Glucosamine hydrochloride (R-NH$_2$) decreased pH over time as a result of nitrogen mineralisation through adequate conversion to nitrate (data not presented) in the Shepparton soil. Conversely, glucosamine hydrochloride addition to the Frankston soil had no major effect on soil pH as nitrification was inhibited at low pH. Moreover, the magnitude of soil pH change was greater with increasing rate of C addition. This study showed that the addition of model C compounds to soil can increase, decrease, and did not change pH and the extent and direction of the pH change was associated to the nature, application rate and decomposition of C compounds, and the initial soil pH. Therefore, the composition of C compounds in plant materials will be vital in determining the direction and magnitude soil pH change.

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Modelling soil strength and its effects on winter wheat dry matter production

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Abstract
In order to apply irrigation water efficiently, it is of critical importance to understand how lack of water is stressing a crop. Soil strength can sometimes retard growth even when water is present in soil at relatively high matric potentials (e.g. >-80kPa). Accordingly we have modified a computer simulation model of soil water dynamics under a growing wheat crop to include the calculation of soil strength, as determined by the resistance to penetration. The combined model requires the moisture release curve (but can be derived from soil textural data), daily rainfall, temperature and potential evaporation and the agronomy of the crop and soil data. With this information, estimates of penetrometer pressure were simulated well compared with measured values in artificially strengthened (compacted) and weakened (irrigated) soils. Our aim was to develop a versatile model that could be used to infer effects of soil strength on a wide range of crop yield data from many different field trials.

Key Words
Computer simulation model, soil strength, drought, crop dry matter, matric potential, yield

Introduction
When crops or plants are exposed to drought they are subject to a number of abiotic stresses that sometimes act simultaneously to reduce growth. Certain stresses are inter-related: growth can be reduced by drought or an increase in soil strength (Masle and Passioura, 1987; Whitmore and Whalley, 2009) which is itself dependent on the soil water status (e.g. Greacen, 1960). The high correlation between soil strength and soil water potential has made it difficult to disentangle the effects of these separate stresses on plant growth except in laboratory experiments where it has been demonstrated that even under well-watered conditions, soil strength can reduce plant growth significantly (Masle and Passioura, 1987). In a series of recent articles Whalley *et al*. (2006; 2008) have demonstrated these effects in field-sown wheat.

Methods

Modelling
Whitmore and Whalley (2007) have shown how penetrometer pressure, *Q*, can be related to soil moisture status and bulk density:

$$\log_{10} Q = 0.35421 \log_{10}|\psi_i S_i| + 0.9313\rho_i + 1.262$$

(1)

where ψ_i is the matric potential at depth *i*, S_i is the relative saturation and ρ_i is the bulk density. We have implemented a fully-implicit finite difference solution to Richard's equation (Richards, 1931) in one dimension for water flow in unsaturated soil in order to calculate ψ and *S*. In this way we can obtain a dynamic record of the change in soil strength during the growing season. Nitrogen supply from soil, and crop growth are as described by Whitmore (2007, 1995 respectively). Parameters for the water model can be derived from published pedotransfer functions (Wösten *et al*., 1999)

Sensitivity analysis
The sensitivity of the combined model to changes in texture, meteorological variables, bulk density and soil organic matter was tested by varying parameters in combination and examining the effect on penetrometer pressure in the spring under a growing crop.

Field data
Gregory *et al*. (2007) distinguished the effect of strong soil on winter wheat (<u>Triticum aestivum</u> cv. Clare) from drought by compacting the soil artificially in three contrasting soils at Silsoe in Bedfordshire, UK. Compaction was achieved by driving an 11 tonne tractor over plots 0, 1, or 8 times. The effect of compaction in unsaturated soil is to increase the bulk density and to reduce the number of large pores. Soil strength was recorded in both years on all plots with a Bush hand-held recording penetrometer (Findlay, Irvine Ltd, Penicuik, Midlothian, UK) fitted with a cone with a 30° angle and 130 mm² base area. Meteorological data was taken from the nearby

Woburn meteorological station (Lat: 52° 2′ N; Long: 0° 36′ W). Properties of the soils used to evaluate our model of soil strength are given in Table 1.

Table 1 Properties of the experimental fields.

Field name	Site	Soil	Org. C %	Sand %	Silt %	Clay %	ρ
Cashmore	Silsoe	Sandy loam	1.9	73	13	14	1.4
Cashmore	Silsoe	Sandy clay loam	2.5	65	15	20	1.3
Boot	Silsoe	Clay	2.6	12	22	66	0.90

Results

Model

Mean squared differences between measurement (Gregory *et al*., 2007) and model were minimised on differences with log-transformed values of penetrometer resistance in soil; the transformation was used in order to stabilise the variances. Figure 1 plots the goodness of fit to data obtained during the 2004-2005 growing season under a crop of winter wheat. The root mean square error of prediction of Q was 485 kPa for measurements made during the growing season between November and June.
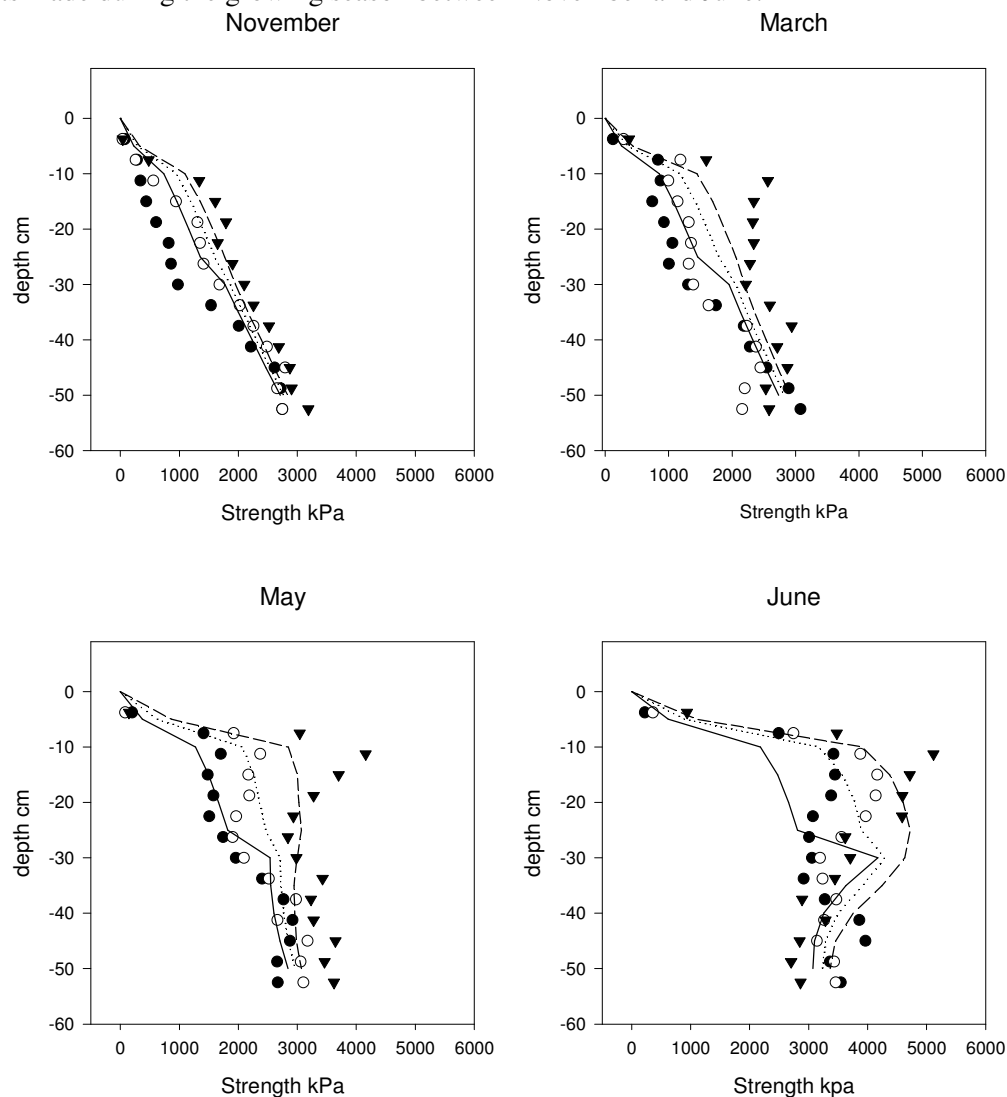
Figure 1. Fit of the model to measurements of penetrometer pressure under a field of growing wheat during 2004-5 on a sandy clay loam soil at Woburn. Symbols: measurements; lines: model. Closed circles, no compaction, open circles, one pass from a 10 tonne tractor; triangles, 8 passes. Solid, dotted and dashed lines, 0,1 &8 passes respectively.

With these data and those from other experiments on winter wheat (Whalley *et al*., 2006; 2008), we were able to infer the effect of soil drying prior to anthesis on final yields of crop dry matter.

Sensitivity analysis
Modelled *Q* is somewhat sensitive to changes with rainfall but not to temperature or evaporation (Figure 2). Note that these are for typical values in southern England. In parts of the world where evaporation or temperature have greater ranges, *Q* might vary more. In general, rainfall can probably be measured with sufficient accuracy for this model, but the issue in practice will be whether appropriate, i.e. on-site rainfall data is available. Data from a distant meteorological station might differ from the actual local conditions. *Q* changed by about 15% with a change in clay from 10 to 50% (Fig 2). *Q* was not sensitive to changes in soil organic matter (SOM, data not shown) nor to changes in silt content in isolation (data not shown). Clay and SOM can almost certainly be obtained with sufficient accuracy for use in this model. Both quantities vary extensively over short distances in space, however (eg Watts *et al*., 2006). Penetrometer resistance is quite sensitive to changes in bulk density (Fig 2). A change in bulk density of 0.15 units, from say 1.3 to 1.45 results in a change in *Q* of almost 18% assuming all other factors such as clay content held constant. The changes in *Q* are more marked at the denser end of the range tested and the 70% change in ρ shown in Figure 2 can result in a 100% change in *Q*.
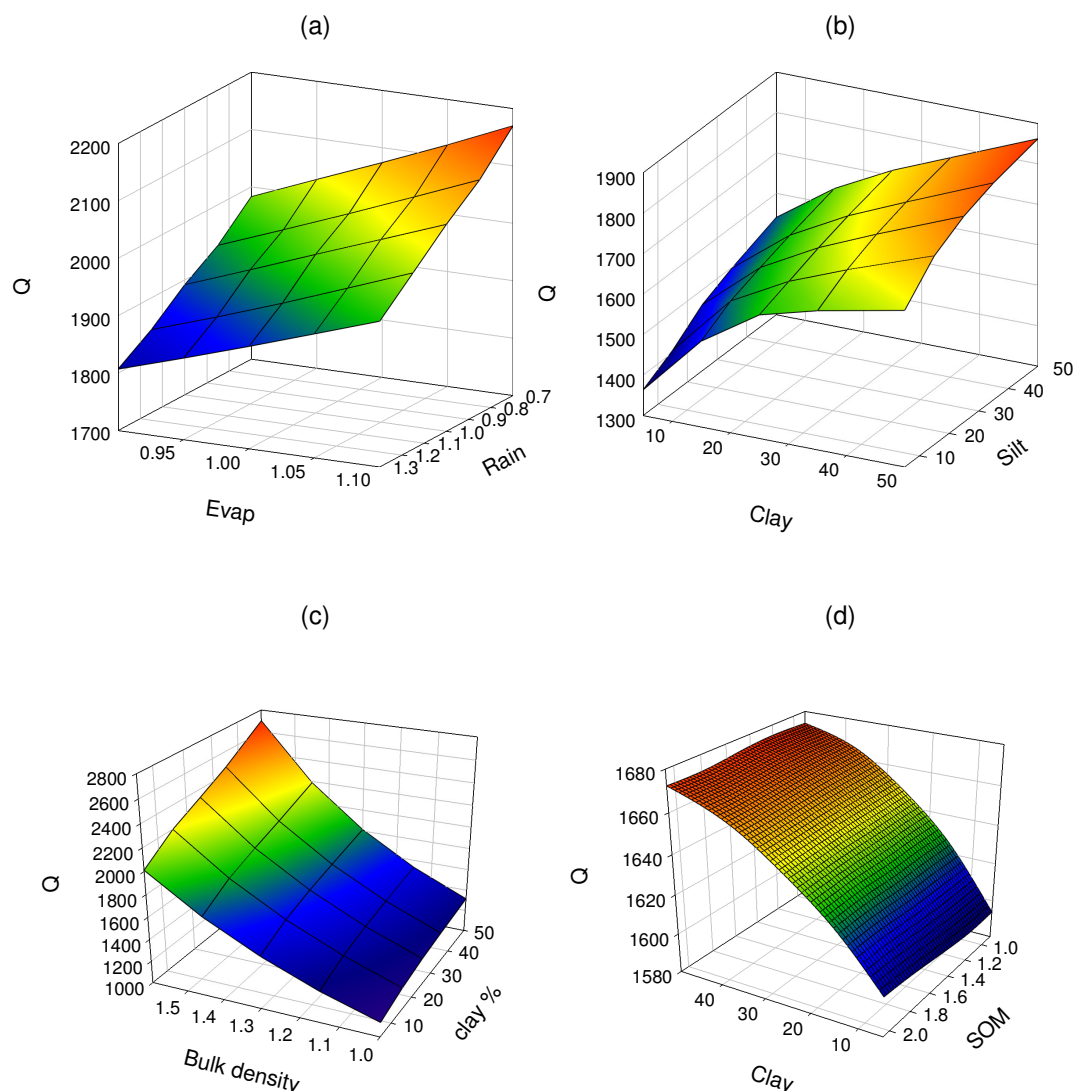
Figure 2. Sensitivity of *Q* in the model to changes in rain, evaporation (a), clay and silt (b), bulk density and clay content of soil (c), clay and SOM content (d).

Conclusions
Penetrometer pressure, *Q*, was predicted well by our model, and so we may regard the model as a useful means to estimate soil strength under crops grown in standard agricultural practise during the critical period of interest when the soil is dry enough to impede root growth but not so dry that crop is permanently wilted.

The data needed to run the model can be obtained with sufficient accuracy for us to have confidence in the values of *Q* predicted. In use, most effort should be put into obtaining good estimates of rainfall and the bulk density of a soil.

The next steps of this work are to compare the effects of both matric potential and soil strength in the field on crop yield and to try to assess the most effectiveness manner of irrigation.

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Nitrogen Release from Poppy Waste and Biosolids at Low Temperature

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Abstract
An incubation experiment was conducted over 56 days at 12.5°C and constant soil moisture to compare nitrogen mineralisation between organic soil amendments available to the agricultural industry in Tasmania. Treatments incorporated with soil were poppy mulch (PM, seed head and stem residues after alkaloid extraction), poppy seed waste (PSW, seed residue after oil extraction), anaerobically digested biosolids (ADB), lime amended biosolids (LAB), lime and an unamended control. At day 28, mineralisation of the total nitrogen applied in the ADB, PSW and LAB treatments was 29%, 36% and 44% respectively. Values increased to 35%, 48% and 62% respectively at day 56. However, the PM treatment (and to a lesser extent the lime and control treatments) exhibited a drawdown of nitrate over the same period.

Key Words
Poppy waste, biosolids, nitrogen mineralisation

Introduction
Many organic soil amendments used in agriculture are a source of both carbon and plant available nutrients. However, amendment availability and logistical limitations rather than the demand for nutrients and organic matter often determine application timing and rate for agriculture use (Bünemann *et al.* 2006). Inorganic fertiliser contains nutrient formulations for direct uptake by plants. Conversely, prediction or calculation of plant available nutrients in organic amendments is more problematic because they are generally waste products with a variable and dynamic composition. In Tasmania, lime amended biosolids (LAB), anaerobically digested biosolids (ADB), poppy mulch (PM) and poppy seed waste (PSW) are available for agricultural use. Total nitrogen for each product is generally 3 %, 4.6 %, 1.6 % and 5.1 % respectively, most of which is in organic form. The Tasmanian state biosolids guidelines (Dettrick and McPhee 1999) suggest that only 25 % of the organic nitrogen contained in biosolids is mineralised in the first twelve months following application. Calculated application rates are based on this assumption. However, a study conducted by Eldridge *et al.* (2008) in NSW found up to 50 % of total N in land applied biosolids was mineralised in the first 2 months after application. They further suggested that a one size fits all model may not be appropriate for biosolids mineralisation calculations (Eldridge *et al.* 2008). No published research has been found on the mineralisation rates of PM and PSW as they are waste products of a primary industry that provides alkaloids for pharmaceuticals, and seeds for edible oil, culinary purposes and in the manufacture of paints and cosmetics.

Incubation experiments have been conducted by Flavel and Murphy (2006), Burgos *et al.* (2006) and Hseu and Huang (2005) to investigate N mineralisation of various soil-applied organic amendments. Incubation temperatures (and times) used for the amended soils were 15°C (142 days), 28°C (280 days) and 30°C (336 days) respectively. Although these studies were conducted between 20 and 48 weeks, most changes occurred within the first 4 weeks following incorporation. N mineralisation studies conducted specifically on biosolids-amended soil by Smith *et al.* (1998) concluded that biosolids type, soil temperature and time from incorporation were dominant factors in determining release rate and nitrate formation. The incubation temperature in this experiment was 25°C, with subsequent biosolids studies by Smith and Durham (2002) and Rouch *et al.* (2009) using 25°C and 20°C respectively. Aside from the study by Flavel and Murphy (2006) the temperatures in the other studies mentioned ranged between 20 and 30°C, temperatures most favourable for the nitrification process (Brady and Weil 1999).

However, in cool temperate climates, soil preparation for crop production or pasture renovation traditionally occurs in autumn or spring at which time soil amendments are also applied and incorporated. Therefore, the objective of this study was to determine the rate of N release from amended soils at a temperature more typical of this climate at these times of year.

Methods

An incubation study was undertaken in a growth chamber over 56 days at a temperature equivalent to the 'autumn' and 'spring' season in Tasmania. A randomised complete block design with three replicates was used. Treatments included control (unamended), LAB, ADB, PM and PSW. Two other controls of $NaNO_3$ and NH_4Cl at 1% w/w soil were included for observing denitrification and mineralisation respectively (Rouch *et al*. 2009). A further control soil plus lime ($CaCO_3$ at 4% of LAB wet rate) was used to determine the effect (if any) of calcium on the release of nitrogen in the absence of the biosolids treatment (i.e. LAB). Each replicate included seven samples for removal and analysis at days 0, 3, 7, 14, 28, 42 & 56. Overall, there were 8 treatments x 3 replicates x 7 sample times. Treatment preparation was derived from Smith *et al*. (1998) with application rates based on treatments being incorporated in the soil to a depth of 10cm at a wet weight equivalent rate of 7.5 dry solid (DS) t/ha, assuming a bulk density of 1 g/cm^3. Although measured bulk density for this soil *in situ* was 1.4 g/cm^3, the lesser value was used to reflect the state of soil immediately following cultivation. Soil to a depth of 10cm was collected from an agricultural site near Cressy, Tasmania, sieved to < 4mm and stored at 4°C. The soil had been previously classified as a 'brown' Sodosol (Cotching *et al*. 2001). The gravimetric moisture content (GMC) of the soil at field capacity (FC) was determined using 'Haines' apparatus (Haines 1930) and calculated as 33%. 1.5 kg sub-samples of field moist soil (20% GMC ≈ 61% FC) were spread loosely at an even thickness on a 35 cm x 40 cm stainless steel tray. Each amendment was then evenly distributed over the soil samples at the required DS rate and mixed by hand using a broad spatula turning the soil in a uniform motion. Both biosolids products were mixed into a slurry with 40ml of distilled water before incorporating in the soil. 40 ml of distilled water was added to all other treatments (including control) to maintain a minimum of 70% field capacity. 7 x 50g samples for each replicate were weighed out in 125ml plastic bottles with loose fitted lids (for gaseous exchange) and incubated in the dark at an average of 12.5° C. The selected temperature was a calculated average of data obtained from http://www.bom.gov.au/climate/averages/ for 5 sites around Tasmania with similar soils: Cressy, Cambridge, Campbell Town, Ross and Palmerston. The treated and untreated soils were tamped down in the bottles (7 light taps on a bench) to achieve a similar bulk density (i.e. similar height in container). No additional water was added to the samples over the incubation period due to minimal moisture loss.

Samples from plots removed at each time period were frozen at -19 °C until analysis. Frozen samples were thawed to room temperature before weighing (10 – 15 g), drying at 105 °C for 24 hours, and reweighing to determine GMC. 5 g of each moist sample was also weighed into a 125 ml PPE screw top container and mixed with 2M KCl solution at a 1:10 ratio (w/v) for 1 hour. Extracts were then filtered through Whatman No. 42 filter paper, analysed colormetrically for NH_4 and NO_3, with results corrected for moisture using GMC. The total inorganic N content was calculated as the sum of NH_4 and NO_3 extracted from each sample throughout the incubation and the net mineralised N from the applied products was calculated as the difference between inorganic N in each treatment and the control soil (Burgos *et al*. 2006).

Results

The organic products used in the experiment were analysed prior to commencing the trial with results shown below in Table 1. The moisture results were used for final correction of samples prior to incubation. Brady and Weil (1999) suggest that the lower the C:N ratio of residues added to soil, the higher the microbial activity and subsequent mineralisation. Therefore mineralisation extent and rates should follow the sequence ADB > LAB > PSW > PM. They also suggest that if the C:N ratio exceeds 25:1, the microbes will source nitrogen from soil reserves, simulating the priming effect often associated with introduction of organic residues to soil (Brady and Weil, 1999).

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Table 1. Characteristics of organic amendments and the soil

	Units (DMB)	LAB	ADB	PM	PSW	Soil
Moisture	% (w/w)	70.1	80.3	55.1	10.8	20.0
pH (H_2O)		13	6.6	7.3	5.5	7.3
Organic C	% (w/w)	15.0	13.6	26.1	34.6	2.0
Ammonia	mg/kg	1300	4300	8.6	46	<1.0
Nitrate	mg/kg	1.7	1.2	<1.0	20	7.9
Nitrite	mg/kg	1.2	<1.0	1.6	6	<1.0
Total N	% (w/w)	3	4.6	1.6	5.1	0.15
Total N_{DS}*	kg/ha	225	345	120	383	1500
Total P	mg/kg	18000	11000	9300	15000	340
Ca	mg/kg	248000	20700	89400	23600	7790
C:N Ratio†		5:1	3:1	16:1	7:1	13:1

Total N_{DS}* - Total N in 7.5 dry solid tonnes / ha of organic amendment, C:N Ratio† - assumes total C ≈ organic C.

However, results in Figures 1 & 2 show the sequence to be PSW > LAB > ADB > PM and that even with a low C:N ratio of 16:1 (well below the suggested cap of 25:1), the PM treatment exhibited a nitrogen drawdown for 42 days of the 56 day incubation. The lime treatment was not significantly different to control.
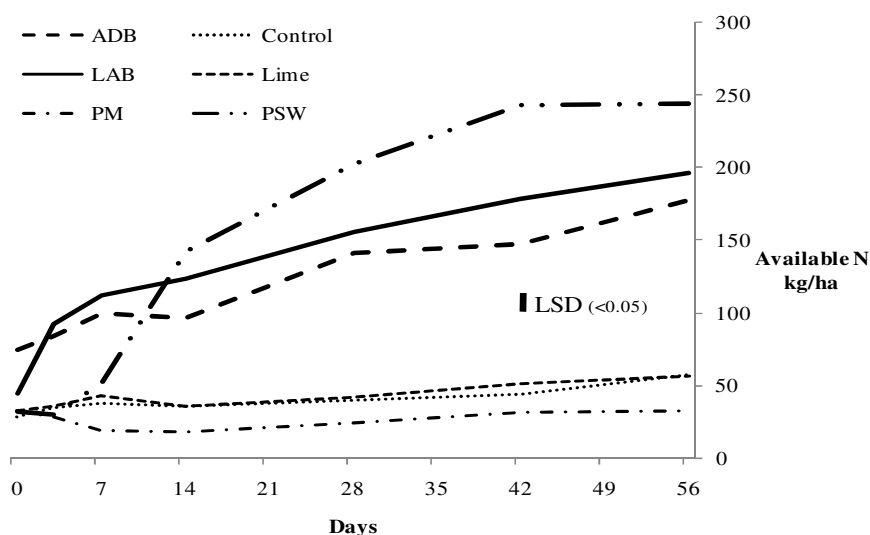
Figure 1. Total mineralised nitrogen from soil applied amendments
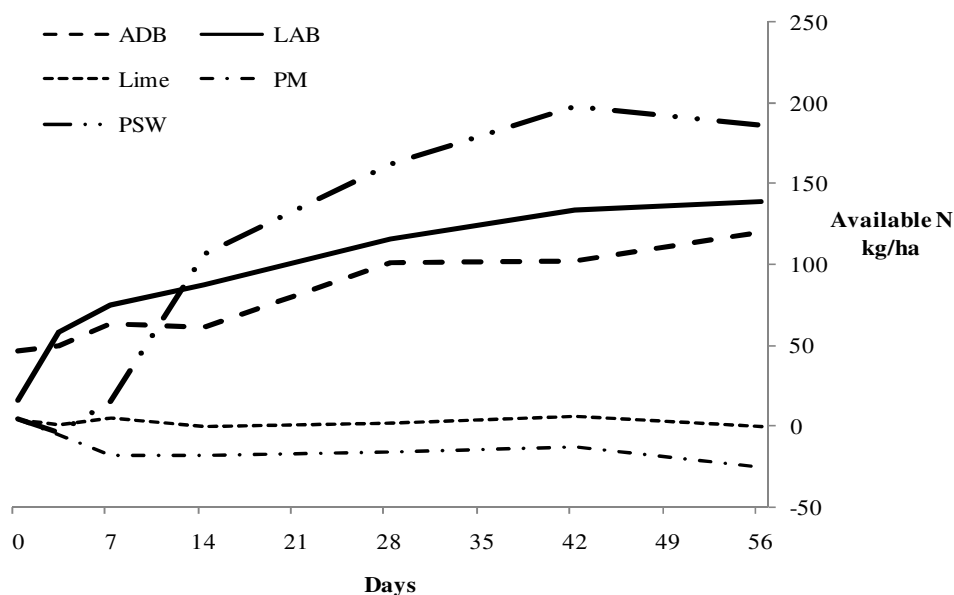
Figure 2. Mineralised nitrogen from soil-applied amendments relative to the control

After 28 days, the nitrogen mineralised from the PSW, LAB and ADB treatments was 162, 116 and 102 kg/ha greater than the control (Figure 2), representing 36 %, 44 % and 29 % of the total nitrogen applied with each organic amendment. Relative to the control, the available nitrogen increased to 186, 139 and 120 kg/ha by day 56 (48 %, 62 % and 35 % respectively) (Figure 2).

Conclusion

The results of this study confirm the suggestion by Eldridge *et al.* (2008) that one size does not fit all with respect to estimating nitrogen mineralisation, particularly from biosolids. The results also demonstrate that predictions of mineralisation extent and rates may not be reliably based on the C:N ratio of the applied product, which Griffin and Hutchinson (2007) found for compost. Although this study was conducted at a temperature less than the most conducive range for nitrogen mineralisation, the results show that plant available nitrogen can still be mineralised from amendments applied and incorporated in the soil in autumn and spring. If amendments were applied in the summer, the rate of mineralisation would probably be greater, at least initially. This indicates that timing of application is essential in ensuring that mineralisation of nitrogen coincides with plant requirements.

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No-tillage crop rotations, C sequestration and aspects of C saturation in a subtropical Ferralsol

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Abstract

We assessed the 17-years contribution of no-tillage crop rotations to C accumulation in bulk soil and in physical fractions up to 20-cm depth of a subtropical Ferralsol of Brazil. The wheat-soybean succession was the reference. The alfalfa system with maize at each three years showed the highest C accumulation (0.44 t/ha/yr). The bi-annual rotation of ryegrass (hay)-maize-ryegrass-soybean sequestered 0.32 t C/ha/yr. Among the two bi-annual crop-based systems of black oat-maize-wheat-soybean and hairy vetch-maize-wheat-soybean, the legume vetch-based system, although having lower C addition, sequestered more C (0.28 t/ha/yr) than the grass black oat-based system (0.16 t/ha/yr). Most of the C accumulation took place in the mineral associated fraction (71 to 95 %, in the 0-5 cm layer) compared to the particulate organic matter fraction. There was a linear relationship between annual C input and total and fraction C stocks, and no evidence for C saturation could be confirmed yet. Crop-forage systems and crop-based systems with legume represent viable strategies to increase soil organic C stocks in no-tillage soils of subtropical Brazil, in a C addition range whose contribution is not limited by an eventual C saturation.

Key Words

Crop-forage rotation, physical fractionation, alfalfa, legumes

Introduction

The conversion of conventional to no-tillage farming is far from being the ultimate possible achievement in terms of SOC accumulation in subtropical Brazilian soils. The challenge now is to develop and improve crop rotation schemes with high phytomass-C inputs that maximize the benefits of no-tillage as a strategy to promote CO_2-C sequestration and soil quality. The cultivation of forage species has shown benefits in terms of SOC accumulation (Franzluebbers *et al.*, 2001), possibly because of the high photosynthate accumulation in roots stimulated by grazing or hay cut. The cultivation of legume cover crops has also been reported to increase SOC stocks in no-tillage soils (Sisti *et al.*, 2004).

In discussions about soil as a C sink generally rises the question whether soils have or not a finite capacity of C storage, the so called C saturation, in which the steady-state C pool no longer increase regardless of increases in annual C input (Stewart *et al.*, 2007). This issue remains to be better clarified and more studies are required in order to come to consistent conclusions about it, especially for tropical and subtropical soils.

The objective of this study was to assess the long-term contribution of no-tillage crop rotations of wide range of phytomass-C addition, some including forages (hay) or winter cover crops, to the accumulation of organic C in bulk soil and in associated physical fractions of a subtropical Ferralsol; and thus infer about the capability of those rotations to promote C sequestration and to reach an eventual C saturation level.

Methods

Field experiment and soil sampling

The study was based on a long-term field experiment (17 years) conducted in the experimental station of ABC Foundation for Agricultural Assistance (Ponta Grossa-PR, Brazil), on a sandy clay Ferralsol (FAO). Climate is subtropical, classified as Cfb (Köppen). The experiment was established during the winter of 1989. Crop rotation treatments are distributed in 7.0 × 10.5-m plots, according to the randomized complete block design, with four replicates. Six crop rotation systems were selected: (i) Wheat (*Triticum aestivum* L.) in winter – soybean (*Glycine max* (L.) Merr) in summer [W-S], representing the reference or base-line system; (ii) Black oat (*Avena strigosa* Schreb.) in winter – maize (*Zea mays* L.) in summer – wheat – soybean [O-M-W-S], with black oat as winter cover crop; (iii) Hairy vetch (*Vicia villosa* Roth) in winter – maize – wheat – soybean [V-M-

W-S], with hairy vetch as legume winter cover crop; (iv) Hairy vetch – maize – black oat – soybean – wheat – soybean [V-M-O-S-W-S], with hairy vetch and black oat as cover crops; (v) Ryegrass (*Lolium multiflorum* Lam.) in winter – maize – ryegrass – soybean [R-M-R-S], where ryegrass is hayed; (vi) Alfalfa (*Medicago sativa* L.), with maize cropping each three years [A-M]. Samples from the 0-5, 5-10 and 10-20 cm layers were collected with spatula in December 2006 at two sampling points per plot. Undisturbed soil cores were collected in each layer for determination of soil bulk density.

Estimate of annual C addition, soil C analysis and physical fractionation
The mean annual C addition was estimated from historic information about grain yield or aboveground dry matter yield (including hay) (Molin, 2008). The total C addition (shoot and root) was calculated according to the procedure suggested by Bolinder *et al.* (2007), with some modifications.

Samples were analysed by dry combustion to determine total organic C (TOC). The granulometric physical fractionation was based on dispersion with hexametaphosphate solution and size-separation of particulate organic matter (POM) (>53 μm) (Cambardella and Elliott, 1992). POM was analysed by dry combustion. The C in mineral associated fraction (min-C) was determined from the difference between TOC and POM-C. The TOC stocks were corrected against the equivalent mass of soil in W-S reference system (Sisti *et al.,* 2004). The stocks of POM-C and min-C were also corrected. To calculate the annual C sequestration rate in the 0-20 cm layer of each crop rotation system, the W-S was considered as the base-line system.

Results
Total organic carbon
According to the TOC content in the whole 0-20 cm layer (Figure 1), cropping systems were separated into four main groups: A-M (52.2 t C/ha) > R-M-R-S = V-M-W-S (average of 49.7 t C/ha) > O-M-W-S = V-M-O-S-W-S (average 47.1 t C/ha) > W-S (44.7 t C/ha), demonstrating the C accumulation capacity of the two forage-based systems of alfalfa and ryegrass and of the legume-based bi-annual crop rotation with vetch. These C stocks are partly related to the annual C addition of each crop rotation, as can be viewed from the linear regression between annual C addition (shoot plus root) and the TOC stock in the 0-20 cm layer (Figure 2). The A-M system had the highest annual C addition (8.25 t C/ha) and thus showed the highest TOC stock, while the W-S system, with the lowest C addition (5.08 t C/ha), showed the lowest TOC stock.
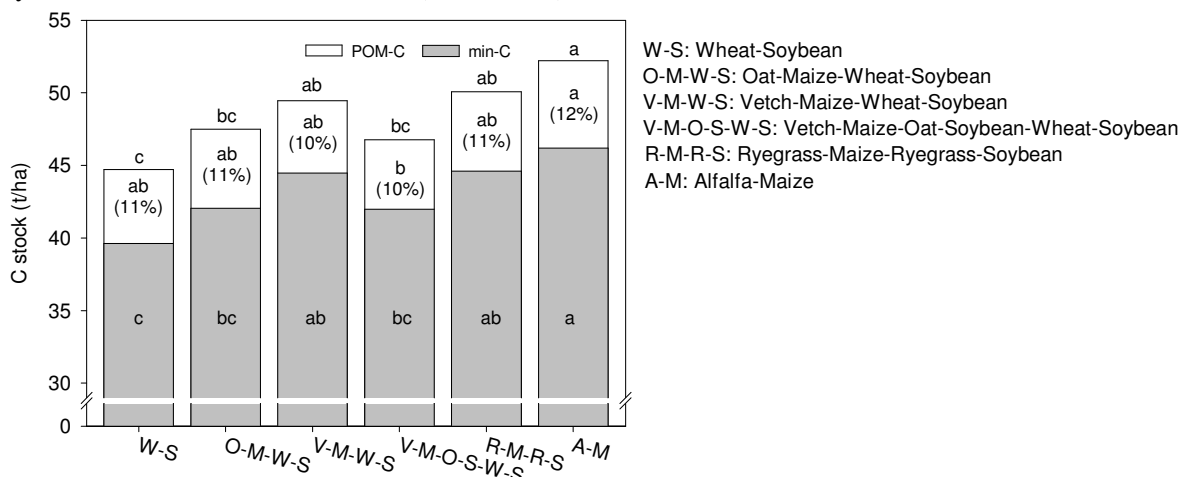
Figure 1. Organic C stock in whole soil, in particulate organic matter fraction (POM-C) and in mineral associated fraction (min-C), in the 0-20 cm layer. Numbers in parenthesis are the percentage of total C stock in the POM-C fraction. Letters compare crop rotation systems, according to Tukey's test (*P*<0.10).

Among the systems with oat or vetch winter cover crops, the V-M-W-S system contained almost 2 t/ha more C than in O-M-W-S system (Figure 1). This is intriguing by considering that V-M-W-S had 8 % less C addition (Figure 2) but 4% more C in soil, throwing some light to the hypothesis that the legume based system was more efficient in converting added C into soil organic matter C. Drinkwater *et al.* (1998) observed that quantitative differences in C addition did not account for the observed changes in SOC stocks across three crop rotations, but suggested that qualitative differences in plant and litter composition had a significant impact, and this would explain why legume-based systems retained more SOC although showing lower C addition. In line to this idea, it is important to considered the contribution that proteinaceous legume-N might have on organo-mineral interaction and thus C stabilization. Kleber *et al.* (2007) have recently proposed a conceptual model of organo-

mineral interaction in which nitrogenous (proteinaceous) organic compounds are believed to be preferentially adsorbed on mineral surfaces; a proposal reinforced by the fact that mineral associated organic matter generally have low C:N ratio compared to the bulk soil organic matter (Diekow *et al.,* 2005). But until now all these are speculations that remains to be clarified in future studies seeking to deeply understand the role of legumes into C sequestration processes in no-tillage soils.
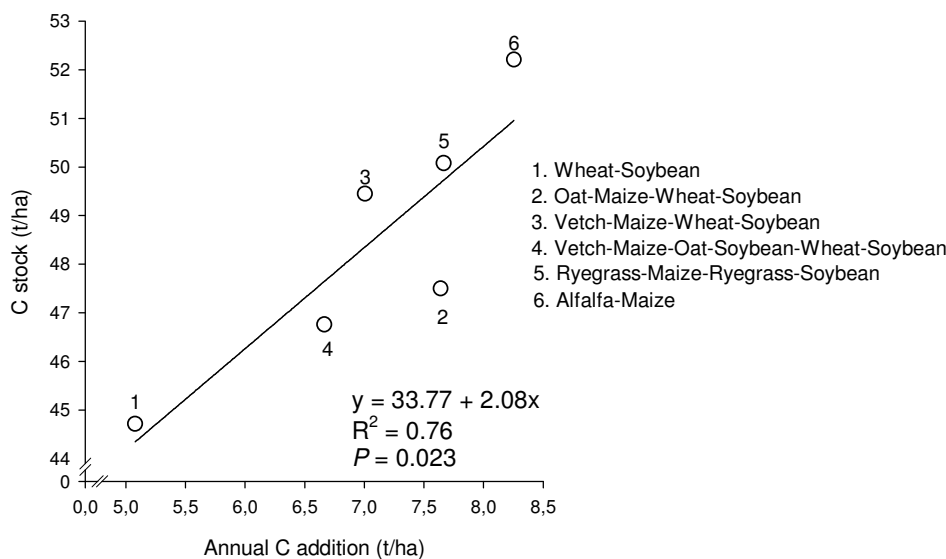
Figure 2. Relationship between annual C addition (shoot plus root) and total organic C stock (TOC) in whole soil of the 0-20 cm layer.

The tri-annual V-M-O-S-W-S rotation, although being a legume-based system, showed lower C stocks compared to the bi-annual V-M-W-S or O-M-W-S. That relies on the fact that in V-M-O-S-W-S system maize is cropped in one and soybean in two out of three summers, while in the bi-annual systems maize and soybean are cropped in the same proportion. Since soybean has a lower phytomass production compared to maize, this rendered a smaller average annual C addition and C stocks in V-M-O-S-W-S system (not shown).

Taking the W-S as the base-line system, the changes in SOC stocks varied from 4.5 % increment in V-M-O-S-W-S to 16.7 % increment in A-M system. Considering the 17 years of experimental duration, the average annual C sequestration rate ranged in the following order: V-M-O-S-W-S (0.12 t C/ha) < O-M-W-S (0.16 t C/ha) < V-M-W-S and R-M-R-S (average of 0.30 t C/ha) < A-M (0.44 t C/ha).

Organic carbon accumulation in physical fractions
The min-C represented most (89 %) of the TOC stock in the 0-20 cm layer (Figure 1). It was also the fraction that stored most of the C sequestered by each cropping system, in proportions that reached 71 to 95 % of the total C sequestration in the 0-5 cm layer and in proportions that were even higher for the two deeper layers and the whole 0-20 cm layer (not shown). This highlights the fundamental role of the mineral associated organic matter fraction in contributing to C sequestration by no-tillage crop rotations. Two major stabilization mechanisms of organic matter are involved: (i) the direct organo-mineral interaction through ligand-exchange process and (ii) the occlusion of organic matter, even of that directly associated to mineral surfaces, inside stable microaggregates. Denef *et al.* (2007) found in a previous study in two subtropical Brazilian Oxisols the mineral associated C (in microaggregates inside macroaggregates) stored most of the C accumulation obtained by adopting NT against CT and concluded that this was a very important long-term stabilized fraction for C sequestration. Although most of the accumulation ultimately occurs in the min-C fraction, one has to consider the role of POM in serving as a "bridge" fraction between the free POM fragments recently derived from plant residues and the min-C pool. Plant residue C does not immediately follows the path to become stabilized on mineral surfaces or microaggregates, but instead it first rely on the physical protection offered by macroaggregates when it is still in the POM form, so that later it can be slowly incorporated into microaggregates and mineral associated fractions instead of being promptly mineralized (Six *et al.,* 2000).

Soil C saturation

With a range in annual C input (5.08 to 8.25 t C/ha/yr), there was a clear trend of a linear relationship between annual C input and C stocks in soil, and this was observed for the TOC (Figure 2), POM-C and min-C pools (not shown) in 0-20 cm layer. No evidence for C saturation in bulk soil could be confirmed, but it was possible to conclude that if C saturation exists for this soil, it will occur at C inputs far beyond than those obtained even in the best rotation systems practicable in agricultural systems in Southern Brazil.

Conclusion

The crop-forage rotation systems of semi-perennial alfalfa and annual ryegrass contribute more to soil organic C sequestration than rotation systems bases only in crops (wheat, soybean and maize) and winter cover crops (black oat or vetch). A significant contribution of C input comes from root and aboveground material like leaf-falls from those species. In crop-based systems, the rotation with legume winter cover crop (vetch) contributes more to soil C accumulation than the rotation with grass winter cover crop (black oat), although the later has higher C input. No clear evidence can so far be presented to explain why legumes contribute more than grasses cover crops to soil C accumulation. Most of the C accumulation due to crop rotation takes place in the mineral associated fraction. The turnover of the particulate C pool inside macroaggregates is crucial to further C accumulation in the mineral fraction. No evidence for C saturation in total as well as in physical fraction C pools is found for this subtropical Ferralsol after being subjected to 17 years of no-tillage crop rotations of wide range of phytomass-C addition. If C saturation exists for this soil, it will occur at C inputs far beyond than those evaluated in this study and practicable in agricultural systems in Southern Brazil.

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Novel use of thermal analyses to meet soil C monitoring in agriculture

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Abstract
Concerns exist about the application of the current methods where total organic carbon (TOC) analytical data is extrapolated from very small sample aliquots to quantify significant land areas. Extending the limits that allow larger amounts of soil to be determined for TOC assists in smoothing natural variability as well as reducing costs. Furthermore, soil carbon (C) comprises a range of organic matter (OM) with varying residence times. The main types can be characterised by different ignition temperatures allowing carbon pools to be distinguished for varying soils using thermal techniques. The added reliability and information rendered can support infrared measurements which can also be used to differentiate carbon.

Key Words
Soil carbon monitoring, dry combustion, soil carbon characterisation, thermogravimetric analysis

Introduction
A major obstacle to realising broad scale soil C monitoring is the uncertainty of how representative soil C analyses are of a larger area or indeed the near neighbourhood (Goidts *et al.* 2009). Contributing to this has been the need for sample processing (drying, grinding, sieving, splitting etc.) to isolate the fine C rich fractions. For these reasons, huge emphasis has been directed towards the most reliable and cost effective analytical methods to quantify soil carbon. This aspect can be much improved by scaling up the amount of soil material processed for each C determination. Even then, spatial statistical analysis methods are a vital component and should additionally assist in managing costs. An important goal is the capacity to estimate with confidence, from a fixed set of data, the C contribution from an entire parcel of agricultural land. Different farming practices can then be assessed in terms of their effectiveness on long term soil carbon management.

Thermogravimetric analysis (TGA) has traditionally been used to characterise chemical decomposition of materials and can be done in oxidative and inert atmospheres. In soil science, it has been widely used for the mineral fraction but for soil C applications it offers inadequately tested potential where dehydration, denaturing or oxidation report as separate events. For this type of application, qualitative analyses are the obvious outcome but quantification of organic matter is an achievable aim also. It appears that dehydration and carbonate decomposition are energy rather than time dependent (Kasozi *et al.* 2009), lending the technique to resolution of these constituents as well as organic matter, on the basis of temperature.

Methods
Sampling was done with a 3.78mm (i.d.) push/vibra corer. Soils were extruded and placed in PVC split-tubing for air drying before sectioning into horizons (0-10 cm 11-20 cm etc.) and processing in the generally accepted ways (McKenzie *et al.* 2000). The cross-sectional areas of the aliquots removed with the probe could then be used as a pro rata to determine C values for the larger stratum. To maintain comparability in the 3rd dimension, equal weights were collected and then submitted for TOC and TGA analysis.

Total organic carbon determinations were initially carried out with a vario Max CN (Hanau, Germany) elemental analyser (EA) on samples in the range 0.5 to 0.75g range. As EA is an accepted standard for % C determination, it formed a basis for comparisons. Experimentation was carried out on as large amounts of soil as feasible using a post-combustion gas analysis technique.

TGA analyses were conducted on a TA Instruments 2950 supplied with either a N_2 or O_2 atmosphere. The temperature program involved ramping to 200^oC over 10 min. followed by a further ramp to 700^oC over 50+ min.

Results

Comparisons were made between combustion methods applied to identical soils (homogeneity and treatment). EA and TGA were correlated and indicated the need for refinements to the C to OM conversion factor (exceeded 1.8) which in much of the loss on ignition (LOI) work has also been regarded as too low (Sutherland 1998). However TGA can be considered a quasi LOI that provides a wealth of additional information. Occurrence of mass-loss events within the organic groups could be manipulated by varying the temperature ramps and atmospheric composition. These preliminary TGA results indicated that a combination of analyses using oxidising and non-oxidising atmospheres reveals interesting differences in the spectrum of carbonaceous soil constituents. An example of a soil with 2% organic C is shown on Figure 1. The falling curve plots the absolute mass loss while the peak trace results from the differential mass change and this is sensitive to heterogeneity in the organic composition. The thermal pattern is similar to that derived by Laird *et al.* 2008. Similar to EA, the TGA microbalance and system as a whole is limited to very small amounts of material, usually in the range of 100 mg. Such small sample sizes may be disadvantageous for quantification in soils but is compensated with mass spectral data on carbon species.
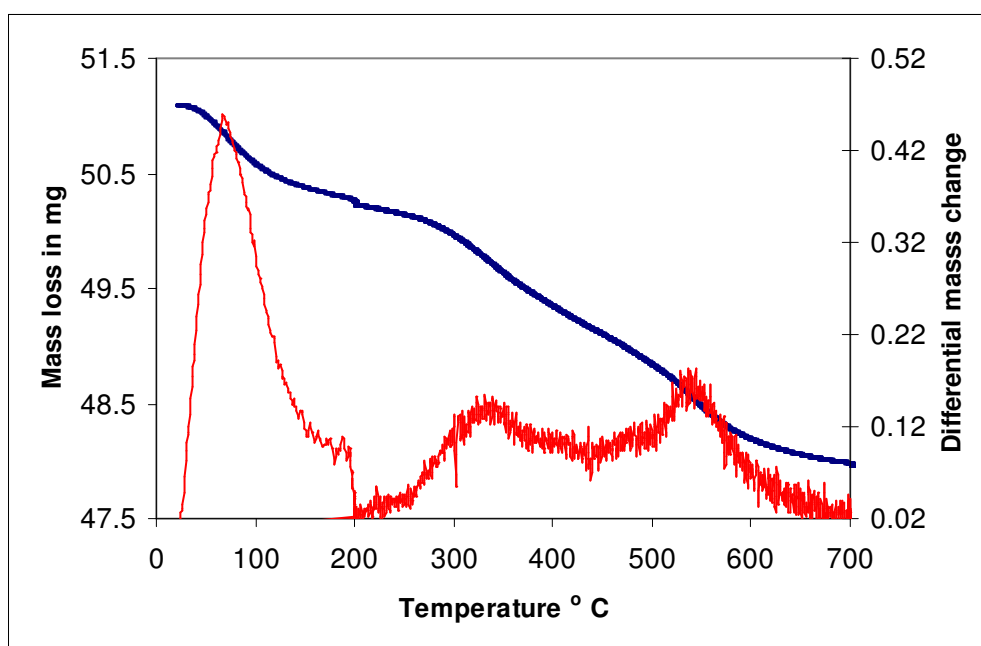
Figure 1. Loss of H$_2$O indicated between ambient and 200°C followed by two pulses of OM loss over 250 to 650°C.

Conclusions

Thermal methods still serve as among the most reliable carbon analysis methodologies although, indirect determinations provide speed and cost benefits. Scaling up the amount of soil carbon that can be oxidised will be an important factor in the smoothing of the inherent variability found in most soils and should assist in cost reductions. TGA has played an integral part in developing an improved set of analytical tools and provided further insights into soil C.

While carbonates commonly form part of soil C, these early experiments have focused on carbonate free soils to limit the number of variables to organic C types. Continuation of this work with a wider analytical scope will include inorganic C as it is legitimate to include this component when monitoring soil C on farms.

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Organic amendments in horticultural production

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Abstract
Mineralization of organic amendments applied to soils in field conditions has been little studied in Uruguay. Ours objectives were: a) to document the amount of the most frequently organic amendments applied to soil for intensive productions; b) to know the range of N concentration in soils of commercial greenhouses at crop plantation; and c) to characterize in situ the nitrogen mineralization from organic amendments and their effects on tomato yield under greenhouse conditions. Dairy or poultry litters were applied to representative soils of the two horticultural zones in Uruguay, at the rate usually applied and at the half of that rate. Soil mineral N was monitored periodically and crop yield was measured. The organic amendment most frequently applied in the North Zone was dairy litter, at rates ranging from 30000 to 55000 kg/ha and in the South Zone, was poultry litter, at rates from 10000 to 31250 kg/ha. The mineral N in the soils ranged from 30 to 496 mg/kg. In the greenhouse experiments N mineralization was closely related to soil temperature and soil physical characteristics. Crop yields were higher in soils with lower amounts of organic amendments. More field studies are needed to improve organic amendment recommendations.

Key Words
Decomposition rate, mineralization, immobilization

Introduction
The incorporation of organic amendments to improve the physical properties of degraded soils is a common practice in intensive production in Uruguay. However, the application of organic amendments is performed regardless their chemical and physical characteristics or history of application of organic materials. In addition, inorganic fertilizers are also frequently applied. Improper use of amendments may limit the production of crops due to nutrient imbalances excessive amounts of some nutrients or deficiencies induced by others, disease problems arising from the risk of environmental pollution by excess nutrients accumulated in the soil may cause deterioration in soil quality.

The prediction of the amount nitrogen mineralized from organic amendment is necessary to improve N recommendations. The mineralization of organic amendments is a microbial process that depends on the nature of the amendment (C and N content, C/N ratio, and fiber, lignin and soluble C content) (Trinsoutrot *et al.* 2000; Calderón *et al.* 2004) as well as environmental factors (temperature and humidity) that promote increased microbial activity (Kowalenko *et al.* 1978; Kelley and Stevenson 1987; Paul and Beuchamp 1996). Soil characteristics (texture, pH) have been reported as other factors that affect the mineralization of organic materials (Hassin, 1994). These are factors determining the release or immobilization of N and other nutrients (Eghball 2000). Therefore the estimation of N mineralization, in order to adjust N availability for crops and requirements is important, not only in economic but also environmental terms Although incubation studies are normally used to estimate the mineralization rates from organic materials under laboratory conditions (del Pino *et al.* 2008), studies under field conditions need to be done. Therefore, the objectives of this study were: a) to document the amount of organic materials applied frequently to soils for intensive plant productions; b) to know the N concentration in soils in commercial greenhouses previously under crop plantations; c) to characterize the decomposition and release of nutrients from organic amendments in situ and their effect on yield in actual greenhouse tomato production.

Methods
Greenhouse survey
Twenty five greenhouses in the South Zone and twenty in the North Zone were surveyed during the spring of 2007 and 2008. The farmers were asked about the type of amendment used, amount, and time before planting crops. In the South Zone, composite soil samples from the 0-15 cm depth were taken and analyzed for NH_4^+ and NO_3^- (Table 1).

Greenhouse experiments
Two greenhouse experiments were conducted during 2007 and 2008 in the North Zone and during 2008 in the South Zone of Uruguay. The soils were a sandy soil and a clay soil, respectively, being representative of the horticultural zones of the country.

Three treatments were applied to plots arranged in a randomized complete block design with three replicates. The treatments were three rates equivalent to 0, 300, and 600 kg N/ha of poultry or dairy litter. The poultry litter was obtained from a local commercial farm and consisted of a mixture of poultry feces and rice hull bedding. The dairy litter compost was taken from an unsheltered pile and consisted of a mixture of relatively fresh and old feces and forest bedding, including soil. The organic amendments analyses are shown in Table 2. Two or three weeks after organic amendment application, the tomato crop was planted at a rate of 25,000 plant/ha. All culture practices, except organic amendment application were those conducted by the farmers. Crop harvests were made during May to Jun in the North, and from January to April in the South.
After treatment application, soil samples were taken at 1, 15, 30 days, and each month during the growing season, using plastic 5 cm diameter and 15 cm depth tubes inserted in each plot. For each sample, NH_4^+ and NO_3^- were determined. For all treatments soil temperature was maintained.

Table 1. Selected characteristics for soils used in the study.

	Sandy soil	Clay soil
Total sand (g/kg)	907	118
Total lime (g/kg)	5	591
Clay content (g/kg)	88	291
pH (H_2O)	7.3	7.7
Org. C (g/kg)	8.1	13.0
NO_3^- (mg/kg)	33.0	102.0
NH_4^+ (mg/kg)	6.0	7.0
K ($cmol_c$/kg)	0.34	0.52
Ca ($cmol_c$/kg)	6.23	9.8
Mg ($cmol_c$/kg)	1.36	4.5
Na ($cmol_c$/kg)	0.48	0.76
P-Bray-1 (mg/kg)	108	323

Table 2. Chemical and physical characteristics of the organic amendments used in the experiments.

	Unit	Broiler litter	Dairy litter compost
Dry matter	%	70	47
Density	g/cm^3	0.24	0.70
pH[A]		7.73	6.29
Total C	g/kg	283	178
Soluble C	g/kg	50	16
Total N	g/kg	17.7	8.8
C/N		16	20
NO_3^- -N	mg/kg	131	36
NH_4^+ -N	mg/kg	77	14
Total P	g/kg	14.5	1.5
K	g/kg	7.8	2.9
S	g/kg	2.65	0.91
Ca	g/kg	23.0	7.9
Mg	g/kg	3.2	2.5
Na	g/kg	1.6	0.2
Lignin	g/kg	166	109
Polyphenols	g/kg	253	29
Ash	g/kg	178	727

[A]pH was determined on 1:1 water to dry organic amendment ratio

Results

Greenhouse survey
The type of organic amendment most frequently applied in greenhouses in the North Zone was dairy litter, in amounts ranged from 25 to 55000 kg/ha. In the South Zone, the most frequently used organic amendment was poultry litter, and the amount usually applied ranged from 10000 to 31250 kg/ha. Other sources of organic

amendments were poultry manure, which amount ranged from 5500 to 26000 kg/ha. Other organic amendments applied were poultry feathers, horse manure, or composts from different origin. The average application rates of those materials were 60000, 25000, and 17000 kg/ha, respectively.

The mineral N in the soils for the South Zone ranged from 30 to 496 mg/kg (Figure 1). This amount of N is greater than the amount that can be removed by a tomato crop, assuming a N concentration in tomato fruit of 16 g/kg and 5.6% dry matter.
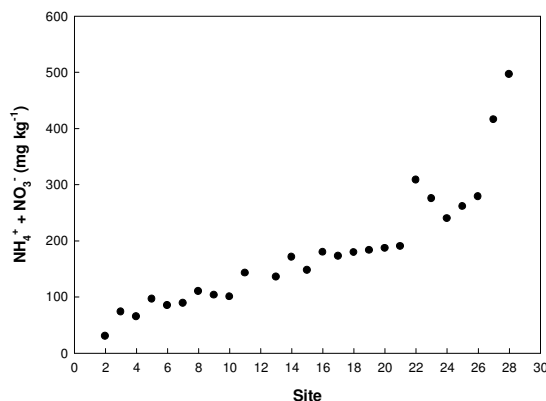
Figure 1. Mineral nitrogen in 0-20 cm soils from greenhouses, before planting crop.

Greenhouse experiments-Nitrogen mineralization

Soil temperature ranged from 10 to 45°C during the field study. Nitrogen mineralization was closely related to soil temperature (Figure 2) or sampling date (Figure 3). There was a trend for amended soils to present greater amount of mineral N than control soils, especially in the period following the application. Net N mineralization was determined by subtracting the N mineralized in the control plots from the amended soils and dividing the difference by the total amount of N applied. About 20% of applied total dairy litter N and 30% of the poultry litter were mineralized in 2007 and 2008. The low N mineralization of the dairy litter may be explained by the relatively high C/N ratio, and the low N content of the material. This determined the net immobilization of N during the growing season.
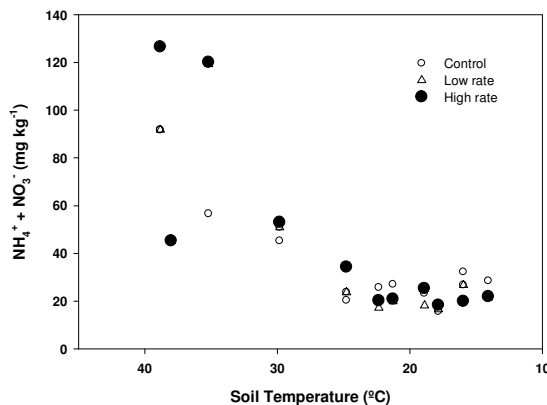
Figure 2. Relationship between nitrogen mineralization and soil temperature in soils receiving dairy litter in rates of zero, half rate (300 kg N/ha) and full rate (600 kg N/ha).
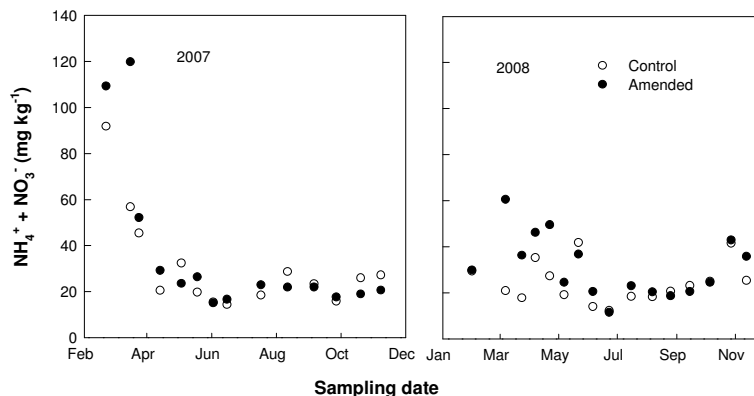
Figure 3. Relationship between nitrogen mineralization in amended and unamended soils and sampling date for the Sandy Soil in 2007 and 2008.

Tomato Yield

Tomato yield was similar for both zones and there were significant differences between treatments (Table 3). In the North Zone experiment, tomato yields for the control or the full rates were lower than half rate. At the SouthZone, the yield was higher in the control or half rate, comparing with the full rate. These results may indicate that the organic amendments applied in full rate may supply excessive nutrients to the crop.

Table 3. Tomato yield for North Zone and South Zone.

Organic N amendment rate kg/ha	North	South Mg/ha
Control	74b	77a
Half	79a	81a
Full	76b	69b

Conclusion

Our results show that reduced organic amendment application may produce best yields and decrease the risk of excess of nutrients. More studies are needed to develop organic amendment recommendations.

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Profile distribution of soil organic carbon under different land use type in Sanjing Plain

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Abstract
To understand the dynamic changes of soil organic carbon (SOC) after different durations of cultivation, soil samples down to a depth of 120 cm were collected in layers from lowland and upland fields having been reclaimed for 5-25 years, with adjacent undisturbed wetland and forestland as the controls. The study of the vertical distribution of SOC and its relationship with soil pH showed that the SOC content in undisturbed wetland and cultivated lowland rice fields had a marked decrease from 0-10 cm to 40-60 cm and a smaller change downward, and a similar variation trend was observed in undisturbed forestland and cultivated soybean fields, only with the difference that the SOC content in 0-10 cm layer was much higher in forestland than in wetland, and lower in soybean fields than in rice fields. For undisturbed wetland, the SOC content in surface layer was decreased by 49.3% and 14.3% after being reclaimed for 10 and 25 years, and for undisturbed forestland, 81.9% and 68.3% of SOC in surface layer were lost after being reclaimed for 5 years and 18 years, respectively.

Key Words
Soil organic carbon (SOC), pH, land use, Sanjing Plain

Introduction
Soil organic carbon (SOC) is a main factor affecting soil quality and agriculture sustainability. Being a source and sink of plant nutrients, SOC plays an important role in terrestrial C cycle (Freixo *et al*., 2002). Land use type has a deep effect on SOC storage, since it affects the amount and quality of litter input, litter decomposition rate, and stabilization of SOC. The SOC loss from irrational land use often leads to some negative impacts on both terrestrial and aquatic ecosystems, and on atmospheric environment (Reeder *et al.*, 1998; Bronson *et al.*, 2004). The Sanjiang Plain, one of the largest freshwater marshes in China, has been experienced intensive cultivation over past 50 years. About 3.8 Mha of its native marshland has been converted into cultivated land, resulting in a significant change in hydrological properties of the Plain (Liu and Ma, 2000). Many researches were made on the dynamics of methane emission due to this land use change (Ding *et al*., 2004), but the effects of the land conversion on SOC remain largely unknown. With the cultivated lowland and upland and adjacent undisturbed wetland and forestland as test objects, this paper studied the dynamic changes of SOC under different land use type in Sanjiang Plain.

Methods

Sampling sites
The undisturbed wetland and forestland and cultivated lowland and upland in Sanjiang Honghe Farm were selected as test objects, with their sampling sites listed in Table 1.

Table 1. Description of sampling sites.

No.	Land use type	Reclamation history
Site 1	Wetland	Undisturbed
Site 2	Lowland rice field	Reclaimed for 10 years
Site 3	Lowland rice field	Reclaimed for 25 years
Site 4	Forestland	Undisturbed
Site 5	Upland soybean field	Reclaimed for 5 years
Site 6	Upland soybean field	Reclaimed for 18 years

Soil sampling and analysis
Soil samples were taken from the depths of 0-10 cm, 10-20 cm, 20-40 cm, 40-60 cm, 60-90 cm and 90-120 cm, and duplicates were installed at each sampling site. Soil organic carbon content was determined by TOC 5000A

autoanalyzer, and soil pH was measured in 1:2.5 soil:water suspension by using Elico Digital EC meter. Statistic analyses were made with SPSS 10.0.

Results
Soil organic carbon
The SOC content in undisturbed wetland and cultivated lowland rice fields had a marked decrease from 0-10 cm to 40-60 cm and a less change downward (Figure 1a). In 0-10 cm layer, there was a significant difference in SOC content ($P < 0.01$), with the sequence of undisturbed wetland > lowland rice field reclaimed for 25 years > lowland rice field reclaimed for 10 years. Compared with that in undisturbed wetland, the SOC content in the 0-10 cm layer in the lowland rice fields having been reclaimed for 10 and 25 years was decreased by 49.3% and 14.3%, respectively.
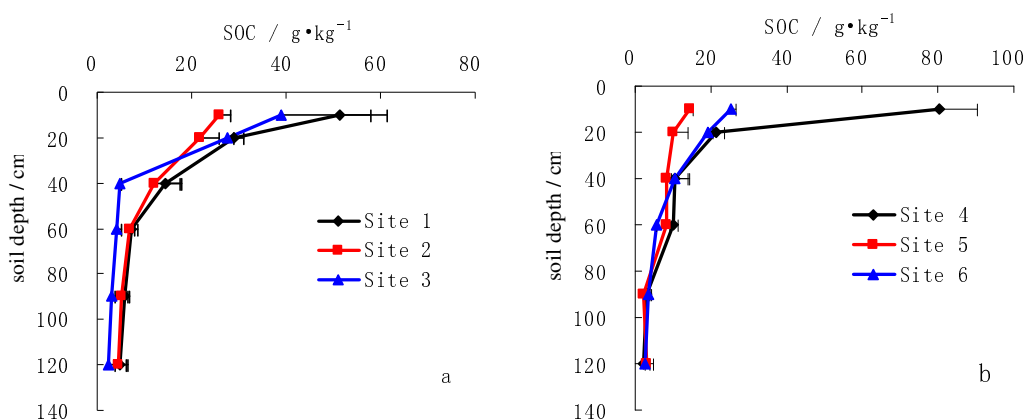
Figure 1. Vertical distribution of SOC under different land use types in Sanjiang Plain.

A similar distribution pattern of SOC was observed in undisturbed forestland and cultivated soybean fields (Figure 1b), only with the difference that the SOC content in the 0-10 cm layer was much higher in forestland than in wetland, and lower in soybean fields than in lowland rice fields. Compared with that in undisturbed forestland, the SOC content in the 0-10 cm layer in the soybean fields having been reclaimed for 5 and 18 years was decreased by 81.9％and 68.3%, respectively.

The higher storage of SOC in surface layer was closely related with the accumulation of plant materials, while the differences in the dynamics of SOC in this layer should have close relations with the amount and quality of plant residues, as well as the environmental and soil conditions (Needelman *et al.*, 1999).

Soil pH
Soil pH decreased with depth in undisturbed wetland, but had a uniform vertical distribution in cultivated lowland rice fields. It was higher throughout the profile in the rice field with a longer reclamation history than in that with a shorter one. In 0-10 cm layer, there was a significance difference in soil pH, with the sequence of undisturbed wetland > lowland rice field reclaimed for 25 years > lowland rice field reclaimed for 10 years (Figure 2a). On the contrary, the soil pH in undisturbed forestland and the soybean field having been reclaimed for 18 years was increased with depth, and in 0-10 cm layer, soil pH was decreased in the sequence of soybean field reclaimed for 5 years > soybean field reclaimed for 18 years > undisturbed forestland (Figure 2b).

The different distribution patterns of soil pH suggested that reclamation had different effects on soil acidity of wetland and forestland, especially that in surface layer, which should have definite effects on SOC storage. Regression analysis revealed that there was a significant negative correlation between soil pH and SOC in undisturbed forestland and the soybean field having been reclaimed for 18 years, indicating that the higher soil pH after reclamation led to a decreased SOC storage, probably due to the enhanced mineralization of SOC by soil microbes (Motavalli *et al.*, 1995).
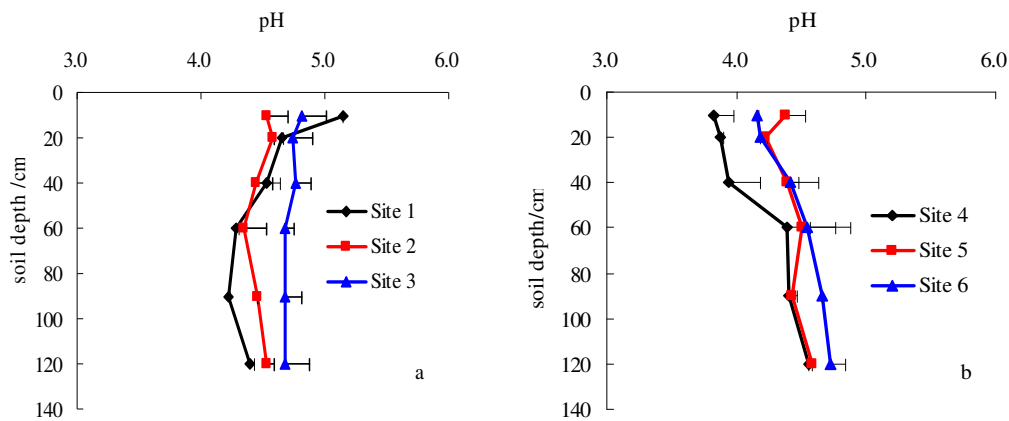
Figure 2. Vertical distribution of soil pH under different land use type in Sanjiang Plain.

Conclusion

A similar vertical distribution pattern of SOC, *i.e.*, decreased markedly from 0-10 cm to 40-60 cm and less changed downward, was observed in undisturbed wetland and forestland and in their reclaimed fields. The only difference was that the SOC content in 0-10 cm layer was much higher in forestland than in wetland, and lower in soybean fields than in rice fields. Reclamation made a great loss of SOC in surface layer, with a loss rate of 49.3% and 14.3% in wetland after reclaimed for 10 and 25 years, and 81.9% and 68.3% in forestland after reclaimed for 5 years and 18 years, respectively.

Land use type had a significant effect on soil pH. In surface layer, soil pH was decreased in the sequences of undisturbed wetland > lowland rice field reclaimed for 25 years > lowland rice field reclaimed for 10 years, and soybean field reclaimed for 5 years > soybean field reclaimed for 18 years > undisturbed forestland. The variations of surface soil pH under reclamation could be one of the factors inducing the SOC loss.

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Quantifying heavy metal inputs from organic and inorganic material additions to agricultural soils in England and Wales

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Abstract
Heavy metal inputs to agricultural soils in England and Wales were estimated from all major sources, including atmospheric deposition, biosolids, livestock manures and footbaths, composts, anaerobic digestates, industrial 'wastes' (including paper crumble, food 'wastes', water treatment sludges), ash (from poultry manure incineration) and canal/river dredgings. Across the whole *agricultural land area*, atmospheric deposition was a major source of metals ranging from 8 to 85% of total inputs, with livestock manures and biosolids also important sources as a result of the large quantities of these materials applied. Metal addition rates at the *individual field* level from pig and poultry manures and composts were similar to (and sometimes greater) than those from biosolids. Moreover, metal inputs from 'new' materials which are increasingly being applied to agricultural land (e.g. food wastes) also sometimes exceeded those from biosolids. The study has provided baseline information upon which to develop and focus future policies limiting heavy metal inputs to and accumulation in topsoils.

Key Words
Heavy metals; organic materials; agricultural soils; inventory, soil quality

Introduction
The soil is a long-term sink for the group of potentially toxic elements often referred to as heavy metals. Leaching losses and plant offtakes are usually relatively small compared with the total quantities entering the soil from different diffuse and agricultural sources. As a consequence, they slowly accumulate in the soil over long periods of time, which can have implications for the quality of agricultural soils. Therefore, reducing heavy metal inputs to soils is a strategic aim of soil protection policies in England and the EU (Defra, 2009; EC, 2002). However, information on the significance and extent of soil contamination from heavy metals in different material additions is required so that appropriate actions can be effectively targeted to reduce inputs to soil.
A previous version of the "Agricultural Soil Heavy Metal Inventory" (Nicholson *et al*., 2003) identified atmospheric deposition as the principal source of most metals entering soils at a national level, with biosolids (treated sewage sludge) and livestock manures also significant sources, albeit to limited land areas. Subsequently, a number of important changes have taken place which are likely to have affected heavy metal inputs to agricultural soils in England and Wales. These include reductions in the maximum permitted levels of trace elements in livestock feeds, decreasing metal atmospheric deposition rates, the increased recycling of organic materials such as compost to agricultural land and the application of 'new' materials (e.g. anaerobic digestate, paper crumble etc.) which are likely to be of increasing importance in the future.
In this paper, we discuss the effects of these changes on the relative importance of the different sources of metals at a *national* and *individual field level*, and the implications for agricultural soil quality.

Methods
This paper presents a quantitative inventory of heavy metal inputs (zinc - Zn, copper - Cu, nickel -Ni, lead - Pb, cadmium - Cd, chromium - Cr, arsenic - As and mercury - Hg) to agricultural soils in England and Wales. The major sources included were atmospheric deposition, biosolids (i.e. treated sewage sludge), livestock manures and footbaths, composts (green and green/food), anaerobic digestates, industrial 'wastes' (including paper crumble, food 'wastes', water treatment sludges), ash (from poultry manure incineration), canal/river dredgings, inorganic fertilisers and lime, agrochemicals, metal corrosion, lead shot (from recreational shooting) and irrigation water. The inventory was based on recently published data on the heavy metal contents of the above materials and estimated quantities applied to agricultural land, including data from a survey of metal concentrations in *c*.190 livestock manures sampled between 2007 and 2009. The relative importance of the different sources of metals at a *national* level was estimated from the total quantities of materials applied to agricultural land and their typical metal concentrations. Relative importance at the *individual field* was based on a typical rate of material addition per hectare of farmland, which for most organic materials was equivalent to *c*.250 kg N/ha (Defra/EA 2008). We also assessed the implications of these input rates in terms of the time required to reach soil metal limit concentrations where biosolids are recycled to agricultural land (DoE 1996).

Results

Inventory of heavy metal inputs

Estimated total annual heavy metal inputs to agricultural land in England and Wales (Table 1) were lower than those previously reported (Nicholson *et al*., 2003) mainly due to lower estimated inputs from atmospheric deposition. Inputs from atmospheric deposition, which were previously based solely on a national monitoring network (Alloway *et al*., 2000), were adjusted to correct for a potential over-estimate of the contribution of dry deposition, as well as allowing for reductions in deposition since the original measurements were taken (1995-98). Nevertheless, atmospheric deposition still accounted for *c*.20-30% of the total annual inputs to agricultural land for Zn, Cu, Ni, Cd, Pb and As, and *c*.80% for Hg.

Livestock manures were estimated to account for *c*.30% of Zn, Cu and As inputs, but were a less important source of the other metals. Biosolids contributed between 10% (Cd) and 40% (Cr) of total metal inputs, and composts less than 5% of total inputs (except for Pb). Industrial 'wastes' (including paper crumble, food 'wastes', water treatment sludges and canal/river dredgings) were an important source of Ni (22%), Pb and Cd (*c*.10%), whilst inorganic fertilisers (mainly phosphate fertilisers) and lime contributed *c*.30% of Cd and Cr inputs.

Table 1. Estimates of total annual metal inputs (t/yr) to agricultural soils in England and Wales from different sources.

Source	Zn	Cu	Ni	Pb	Cd	Cr	As	Hg
Atmospheric deposition	1010	330	70	100	6	20	8	9
Livestock manures	1070	380	20	40	2	30	10	<1
Biosolids	700	360	40	170	2	100	7	2
Industrial wastes[1]	180	80	50	50	2	20	2	<1
Compost[2]	120	60	10	60	<1	10	<1	<1
Anaerobic digestate	<10	<10	<1	<1	<1	<1	nd	nd
Footbaths[3]	30	10	nd	nd	nd	nd	nd	nd
Fertilisers and lime	150	60	30	10	7	70	5	<1
Ash[4]	150	40	nd	nd	nd	nd	nd	nd
Plant protection products	20	<10	nd	nd	nd	nd	nd	nd
Irrigation water	<10	<1	<1	<1	<1	<1	<1	<1
Corrosion	30	nd	nd	nd	nd	nd	nd	nd
Lead shot				[3250][5]				
Total	**3450**	**1330**	**220**	**430**	**19**	**255**	**31**	**11**

nd: no data

[1]Including paper crumble, food 'wastes', water treatment sludges, canal/river dredgings

[2]Including green compost and green/food compost

[3]Only includes the proportion of footbaths disposed directly to land. Metals in footbaths disposed to slurry/manure stores are assumed to be included in the contribution from livestock manures

[4]Ash from the incineration of poultry litter

[5]Not included in total due to uncertainty of estimate

Although atmospheric deposition was an important source of heavy metal inputs to agricultural land on a national scale, metal addition rates at an *individual field* level were small compared with other sources. For some metals (Zn, Cu, Cr and As), the highest metal addition rates at a field level were from biosolids (applied at 6.5 t dry solids/ha/yr, *c*.250 kg total N/ha/yr), although Zn and Cu addition rates from some pig and poultry manures (applied at 250 kg total N/ha/yr) were of a similar magnitude (Figure 1). Metal addition rates from composts (applied at 20-30 t fresh weight/ha, *c*.250 kg total N/ha/yr) were similar to or greater than those from biosolids. 'Wastes' from food production (e.g. dairies, soft drinks manufacture etc.) are generally low dry matter liquids and as a results are commonly applied at high rates to agricultural land (*c*.180 m³/ha). Consequently, Ni and Cd addition rates with these materials were estimated to be higher than from biosolids (Figure 1). Similarly, water treatment sludges were also estimated to add high rates of metals, in particular Ni, to agricultural soils. Anaerobic digestate (applied at 30 t fresh weight/ha or *c*.250 kg total N/ha/yr) did not add significant quantities of metals at the field level compared to many of the other sources considered. Notably, metal addition rates from all the sources discussed here were below the current maxima for biosolids application to agricultural soils (DoE, 1996).

Implications for soil quality

The above field level heavy metal addition rates were used to estimate the time (number of years) required to

raise topsoil metal concentrations from background values (i.e. mean concentrations in England and Wales; McGrath and Loveland, 1992) to the maximum permissible concentrations for heavy metals stipulated in the Code of Practice for Agricultural Use of Sewage Sludge(DoE, 1996), assuming that all fields received inputs from atmospheric deposition and had the same rate of metal loss via crop offtake and leaching. The limiting metal for most organic and inorganic material additions was Zn, with the limit value of 200 mg/kg soil reached after approximately 100 years of biosolids, pig slurry and compost additions. Clearly, these times would decrease if soil Zn concentrations were already above background values, if more than one material was applied in a year, or if application rates or input material Zn concentrations were higher than those assumed here. In comparison, it was estimated to take >1,000 years for cattle farmyard manure (FYM) applications to raise topsoil Zn concentrations to the limit value. For food 'wastes', the limiting metal was generally Cd, where the maximum permitted concentration of 3 mg/kg soil was estimated to be reached after *c*.250 years.

Conclusion

In response to concerns over the impact of heavy metal inputs on long-term soil fertility and the potential transfer of certain metals to human diets, an updated inventory of heavy metal inputs to agricultural soils was compiled for England and Wales. Whilst atmospheric deposition was a major source of total heavy metals inputs to agricultural land at the national level, livestock manures and biosolids were also important sources because of the large quantities of materials applied. The results also showed that metal addition rates at the field level from some pig and poultry manures and composts were similar to (and sometimes greater than) those from biosolids. Moreover, metal inputs from 'new' materials which are increasingly being applied to agricultural land (e.g. food 'wastes') also sometimes exceeded those from biosolids. This study has provided baseline information for the development of strategies to reduce heavy metal inputs to agricultural land and to effectively target policies for minimising long-term accumulation in soils.

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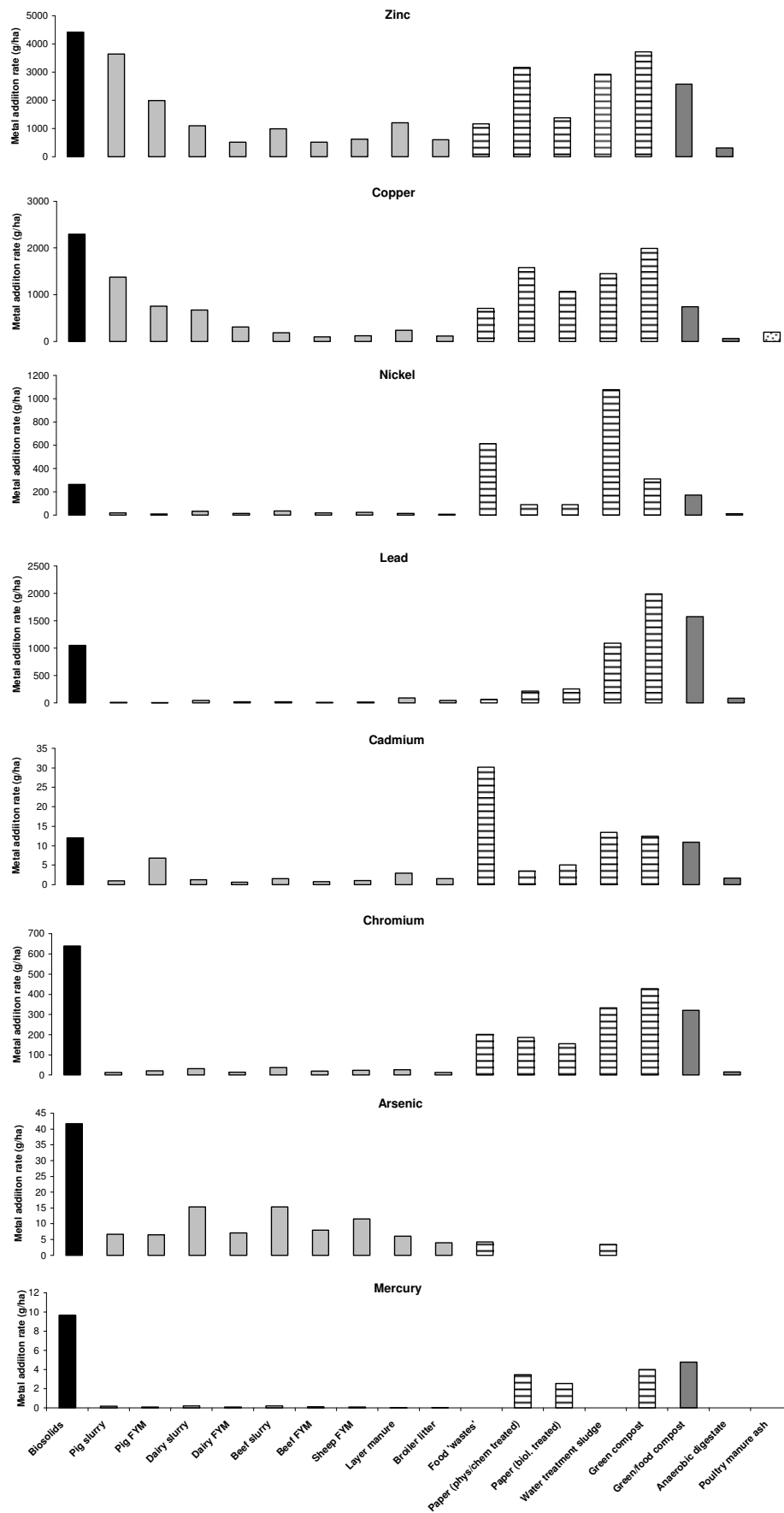
Figure 1. Estimates of metal addition rates (g/ha/yr) from selected organic and inorganic materials applied to agricultural land in England and Wales at typical rates.

Relationship between organic matter retention and soil carbon in irrigated mixed farming systems

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Abstract

Understanding the relationship between farming systems and long-term trends in soil organic carbon (SOC) levels is of significant current interest, both for improving soil health and estimating the potential for sequestering greenhouse gases. This relationship was investigated for the mixed irrigated cropping and pasture farming systems in NW Victoria and southern New South Wales, Australia, using a sample of 13 paired paddocks, each with a high and low organic matter retention history. At each paddock, the annual average organic matter (OM) produced and not removed was estimated over the previous 10 year period. The difference in this value at each paired site was compared to the current difference in SOC at each paired site. This relationship showed that 70% of the variability in the difference in SOC at each paired site could be explained by the difference in the estimated average annual amount of OM remaining on or in the soil over the preceding ten year period.

Key Words

Soil carbon, soil organic matter, soil health, carbon sequestration

Introduction

Soil organic matter (SOM) has long been considered central to soil health and maintaining soil productivity (Magdoff and van Es, 2000). The soil also holds a vast stock of carbon (C) and agriculture is often considered to have run down these stores releasing significant quantities of greenhouse gases. For these reasons there is considerable debate about the role that farming systems plays in increasing or decreasing soil organic carbon (SOC) levels. The study of SOC dynamics is difficult because trends in SOC occur slowly, while actual measurements can be quite inconsistent due to spatial variability and short-term climate effects.

For these reasons short-term trials are not good indicators of long-term soil C trends, but indicate dynamics in more labile pools. Long-term experiments provide the best information on C trends, although such experiments are rare and often do not have management systems relevant to current farmer practices. The development of new long-term trials is important, but they will only be able to include a limited quantity of farmer practices, and it will take a decade or more before firm conclusions can be drawn. Paired sites have been used for a number of SOC studies (e.g. Harms and Dalal, 2003). This approach is useful as it enables comparison of a wide range of possible farming systems without the delays involved in establishing new experiments. However, as with many other methodologies, considerable care and scientific understanding is required in applying paired site studies if misleading conclusions are to be avoided. Conclusions from paired-site studies, as with any experimental data, also need to be contextualised for the conditions that applied, and the results not extrapolated to other situations.

Ensuring all conditions, as far as is reasonable, are the same in both parts of a paired site, except the parameter to be investigated, is of paramount importance in any paired site study. The definition of the population to be studied also needs to be clearly defined, and sites where the hypothesised relationship is expected to be different need to be excluded from the population, or a variable included as a covariate. This is particularly true of soil texture properties in the study of SOC dynamics, as both the rate of C accumulation and the SOC equilibrium value are expected to be different as textures range from sandy to clay. Climate conditions and soil water are also important variables.

This study has taken the approach of using a sample of 13 paired paddocks, each with a 'high' and 'low' organic matter retention history, to develop the relationship between the differences in the estimated average annual amount of OM remaining on or in the soil over a preceding ten year period, to the current difference in SOC at each paired site.

Methods
This study is based on a sample of thirteen paired paddocks that were selected by district agronomists to represent the irrigated mixed farming industry of northern Victoria and southern NSW. Paired paddocks were required to be adjacent and agronomists were requested to only select sites where there were no apparent differences in soil type or land form for a reasonable distance on each side of the adjoining boundary. The assumption in this analysis is of near homogeneity at each paired site of all other factors (e.g. soil texture) and variables except those being studied. Site consistency was reasonably supported by measurement of particle size analysis from three bulked samples on each paddock.

Each paired site was chosen by the agronomists, following discussion with the growers, to represent one paddock with a history of higher average annual amount of OM remaining on or in the soil over the preceding ten year period (referred to as 'High OM Scenario') relative to the corresponding paddock in each pair (referred to as the 'Low OM Scenario'). Rotation and approximate yield histories were collected from the grower for the past 10-20 years. This data was converted into an estimated annual quantity of OM retained at the paddock (including roots) using published data on the harvest index and root to shoot index that most closely reflected the site and farming system. Rotations included OM input practises such as subterranean clover dominant pasture or lucerne and low OM input practises such as annual cropping with residues burnt. Other rotations and management used in the study include winter cropping (wheat, barley, oats, faba beans, canola), double cropping (combinations of oaten hay/maize, soybeans/barley, soybeans/sub clover silage), summer cropping (maize, rice, soybeans), orchards (apples), stubble retention versus stubble burnt or bailed, and the application of composted pig manure. All sites used in the study were predominantly irrigated systems.

Soils were sampled at three locations and three depths (0-10, 10-20, 20-30 cm) in each paddock. Sampling sites were selected to be reasonably close to the adjoining paddock to minimise any soil differences, but avoided any edge effects. Total carbon was determined using a high frequency induction furnace and infrared detection (LECO CR12 analyser). The various relationships were assessed using linear regression. Where the regression analysis indicated the presence of outliers these were removed and regression analysis on the remaining data indicated that the regression assumptions of constant variance and normal distribution for the residuals were reasonably satisfied by the data.

Results
Soil textures for the paired sites are plotted on a soil texture triangle in Figure 1. The lines link the High and Low OM Scenario paddocks at each site. Soil texture differences were negligible within most paired paddocks, although at three paired sites (labelled in orange) slightly larger texture differences were found. Carbon modelling of the sites suggests that difference in soil texture, for the clay range found (20 – 50%), will be expected to have only a small impact on C sequestration rate (data not shown). At each paired site, the estimated annual OM retained at the paddock (from above and below ground sources), averaged over the 10 years prior to the soil measurements, was higher in the High OM Scenario paddocks compared to the corresponding Low OM Scenario paddocks (Figure 2). The sites included a wide range of differences in OM retained, possibly reflecting the difficulty agronomist had in predicting the quantity of OM retained. However this enabled a wide range of values for the regression analysis.

Across all 24 paddocks, the value of estimated annual OM retained at the paddock (from above and below ground sources), averaged over the 10 years prior to the soil measurements explained 58% of the variability in measured SOC values (Figure 3). Unexplained variability in this relationship is likely to reflect previous rotation history prior to the ten years considered, and other climatic, site and management factors, and any inaccuracies in estimation of OM retained or SOC measurement.

Although soil C is constantly in flux due to changes in OM inputs and climatic condition, and can take many decades to reach an equilibrium level, provided there exists a cause and effect relationship between OM retained and SOC, this medium term (i.e. 10 year) average annual OM input relationship (Figure 3) provides an indication of the rate of OM input in these systems required to maintain a specific SOC level. For example, for these soil types to maintain SOC levels at around 1%, OM retained needs to be maintained at approximately 4 to 5 t/ha per year, whereas to maintain SOC levels at 2.5%, OM retained needs to be approximately 11 t/ha per year. This OM input includes all plant residues (roots and shoot), manures or any other organic material.
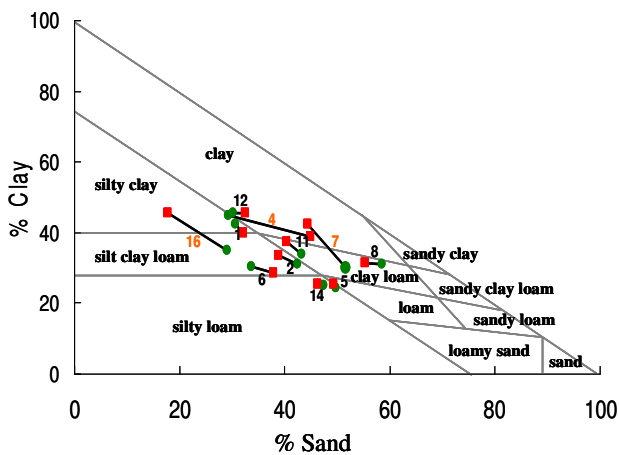
Figure 1. Australian Soil Texture Classification Triangle showing soil textures (0-10 cm) of High (●) and Low (■) OM Scenario paddocks in the paired paddock study (paddocks 13 and 15 not included because measurements not taken). Numbers on diagram refer to the site code. Clay and sand components are graphed, while the silt content is the unaccounted for component from 100% after clay and sand is accounted for.
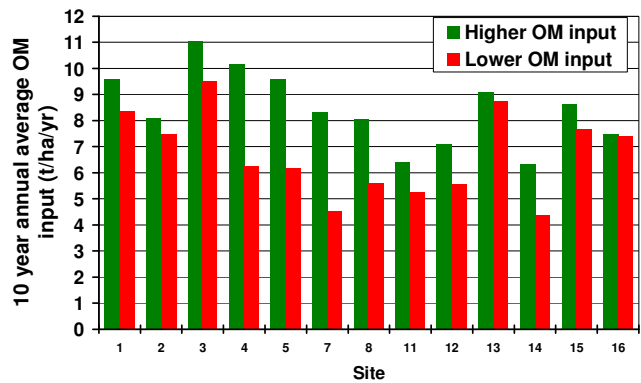
Figure 2. Average annual OM input over a ten year period, versus TOC (%, 0-10 cm) for 13 paired paddocks. Green bars are High OM Scenario paddocks; Red bars are Low OM Scenario paddocks.

$$y = 0.195x + 0.19$$
$$R^2 = 57.9, P < 0.001, n = 24$$
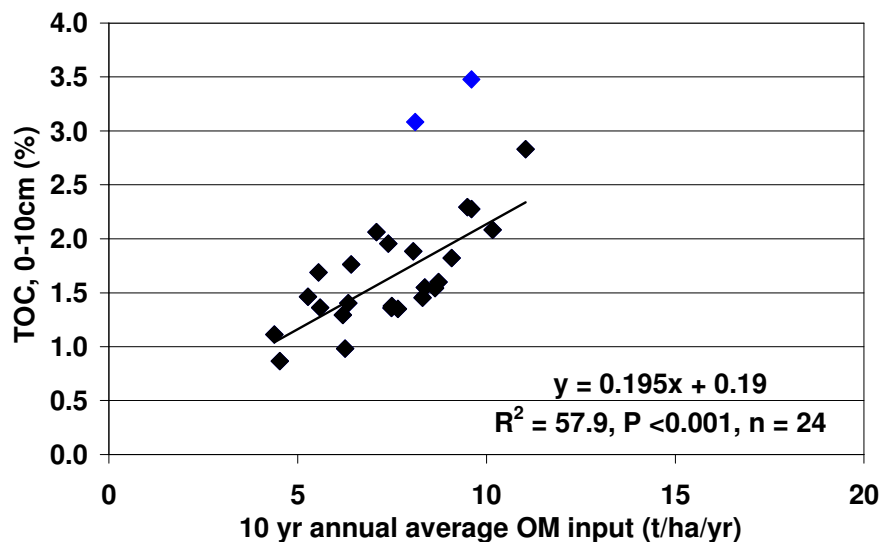
Figure 3. Average annual OM input for ten years, versus TOC (%, 0-10 cm) for 26 paired paddocks. Blue points represent paddocks 1H and 2H (outliers), not included in the analysis.

To remove from the analysis variability caused by differences between the various paired sites, the relationship has been developed between the differences in estimated average annual OM retained over the past 10 years between the paddocks at each paired site, and the corresponding current differences in measured SOC values (0-10 cm) between the paddocks at each paired site. This relationship shows that 70% of the variability in the measured difference in SOC can be explained by the difference in estimated 10 year average annual OM retained (Figure 4). If there exists is a cause and effect relationship between SOC and OM input, then this relationship suggests a useful rule of thumb for these sites. This is that for every extra 1 t/ha/year of organic matter retained that is continued for at least 10 years, it can be expected that SOC values after 10 years will be approximately 0.28% higher than they would have been otherwise.
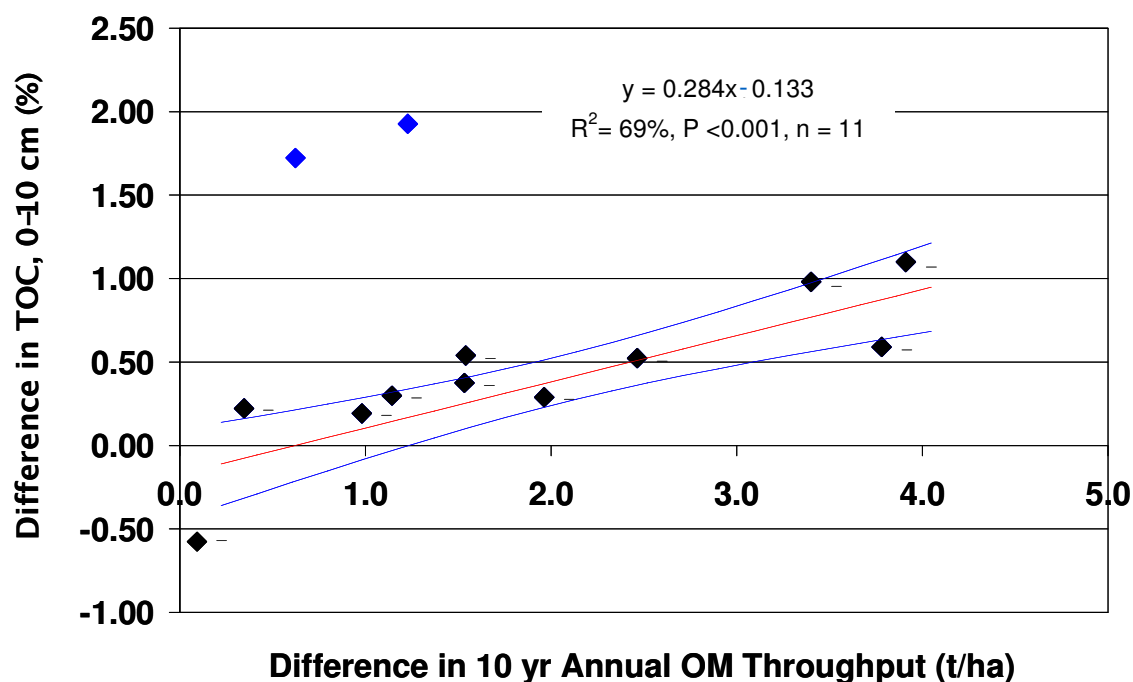
Figure 4. The difference in estimated average annual OM retained (over a 10 year period) between High and Low OM Scenario paddocks at each paired paddock, versus the current measured difference in TOC between High and Low OM Scenario paddocks. Two outliers (sites 1 and 2 shown as blue points) are not included in the regression. 95% confidence intervals are shown as blue lines.

Conclusion

The study of SOM dynamics is difficult and many different methodological approaches, such as short- and long-term experiments, modelling, and paired site studies, are all required to obtain a full picture of the issues involved. This project took the approach of using farmers' paired paddocks to develop the relationship between the estimated quantity of OM retained over a 10 year period, and C-sequestration. Despite the complexity of the factors affecting the amount of OM required to increase TOC levels, this study has shown a positive relationship between the difference in the estimated amount of OM retained and the difference in measured SOC level. However this relationship is only applicable to the irrigated mixed farming systems within the study region.

Considering the various difficulties in all approaches to studying soil carbon dynamics, using strategically selected paired sites to develop the relationships between differences in organic matter retained on site and the corresponding change in soil carbon, for specific agroecological zones, soil types and management, may provide a useful methodology to support other soil carbon monitoring techniques.

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Relative contribution of naturally-occurring carbonates and soil organic carbon to soil aggregation dynamics

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Abstract

Carbonates in the topsoil of many Mediaterranean soils interact with soil organic carbon (SOC) and aggregation dynamics, by decreasing organic matter mineralization and enhancing aggregate stability. The relative contribution of SOC and carbonates in two Mediterranean soils were studied. We hypothesized that SOC-carbonates interaction can alter aggregation hierarchy and that the relative role of these cementing agents can change depending on aggregate-size fractions. Topsoil (0-20 cm) of a carbonated (Typic Calcixerept) and a non-carbonated (Typic Haploxerept) soil were forced to pass a 250 μm sieve and incubated at 25 ºC for 63 days with the following treatments: carbonated (C) or non-carbonated (NC) soil with (ST) and without (NST) maize straw. Aggregates dynamics in the non-carbonated soil was controlled by organic matter, according to aggregation hierarchy (Six *et al.* 1998). Unlike the non-carbonated soil, we observed that carbonates had a major role in macroaggregate (>250 μm) formation at low SOC content in C.NST. Maize straw addition enhanced macroaggregates percentage in C.ST compared to C.NST. Microaggregates (50-250 μm) within macroaggregates percentage was similar in both treatments at day 21, but it was greater in C.ST than in C.NST thereafter. No effect of carbonates was observed in macroaggregates >2000 μm in the carbonate-rich soil. We concluded that carbonates presence in the carbonate-rich soil can interfere with SOC dynamics by modifying the aggregation hierarchy of soils as that described in the non-carbonated soil.

Key Words

Aggregate-size distribution, naturally-occurring carbonated soil, carbonates, soil organic carbon

Introduction

Soils of Mediterranean climate can have carbonates accumulation at some depth, as it happens in the Ebro Valley of Spain. Lithogenic or primary carbonates, originated from the calcareous parental material, are the main source for the formation of secondary or pedogenic carbonates in these soils. Evapotranspiration in arid and semi-arid soils enhances precipitation of secondary carbonates (Lal and Kimble 2000). Soil structure results from the arrangement of primary particles into micro- and macroaggregates, creating a pore space. The association of primary particles and aggregates is mediated by different cementing agents depending on soil conditions: organic matter, inorganic cations, carbonates, clay, and soil biota. Carbonates contribute to soil organic carbon (SOC) protection and aggregate formation and stabilization (Bronick and Lal 2005).SOC dynamics and aggregation dynamics are closely related when organic materials are the main binding agents of soil (Six *et al.* 2000). Carbonates can decrease SOC mineralization and enhance aggregation due to increased cationic bridging effect by Ca^{2+} and precipitation of secondary carbonates that forms coatings around primary particles and organic residues, acting as a stabilizing agent (Baldock and Skjemstad 2000; Lützow *et al.* 2006). Consequently, positive correlation of aggregate stability and SOC quality and quantity may change in carbonated soils (Bouajila and Gallali 2008).

In this work, we used a naturally-occurring carbonate-rich soil to study aggregation dynamic and contribution of SOC and carbonates to soil structure in medium-term incubations with maize straw addition. Many authors have studied the role of SOC and carbonates in aggregate formation and stability adding external sources of calcium to carbonate-free soils (Muneer and Oades 1989, Wuddivira and Camps-Roach, 2007), however few studies have used carbonated soils (Bouajila and Gallali 2008). We hypothesized that the relative role of carbonates and SOC in aggregation dynamics may change depending on aggregate-size fractions and that SOC-carbonates interaction can change aggregate hierarchy of the carbonated soil.

Methods

Site description and sampling

Surface soil (0-20 cm) was collected from a toposequence of the Oja River in La Rioja (Spain), with different carbonates content. The carbonate-rich soil in Rodezno (C) is a Typic Calcixerept (Soil Survey Staff 2006) with

a loam texture (38% sand, 44% silt, and 18% clay), total organic carbon content of 8.8 g/kg, and carbonates content of 220 g/kg. The non-carbonated soil in Castañares (NC) is a Typic Haploxerept (Soil Survey Staff 2006) with a loam texture (47% sand, 38% silt, 15% clay) and total organic carbon content of 7.6 g/kg. The two soils have been conventionally cultivated with a rotation based on wheat (*Triticum aestivum* L.), pea (*Pisum sativa* L.), and sugar beet (*Beta vulgaris* L.) or potato (*Solanum tuberosum* L.) for the last 50 years. The climate in the area is sub-humid Mediterranean.

Samples were collected in different points at each soil and mixed to get a composite sample. The incubation protocol was adapted from Denef *et al.* (2001). After collection, field-moist soils (10-12% w/w) were gently forced to pass through a 250 µm sieve to reduce macroaggregates and recover only microaggregates (<250 µm) and sand, silt and clay primary particles. The 250-1000 µm sized sand and particulate organic matter fractions were kept and remixed with the 250 µm sieved soil. The following treatments and their combinations were studied with 3 replicates: (i) carbonated soil (C) or non-carbonated soil (NC) and (ii) with (ST) or without (NST) maize straw. In total, 60 soil cores were incubated at 25 ºC for 63 days. Soil subsamples, equivalent of 91 g dry soil, were placed in aluminium cylinders (diameter = 6.7 cm, height = 2.15 cm) closed at the bottom by a nylon mesh of 53 µm. They were carefully packed to obtain a bulk density of 1.2 Mg/ha. The soil cores were suspended in a sealed 1 l glass jar with 20 ml of deionized water in a beaker at the base to minimize desiccation. The added maize straw was only stems and leaves (C/N = 60) ground to the size of 200-500 µm (Cosentino *et al.* 2006). Soil subsamples were mixed with 353.89 mg of straw to obtain 1.75 mg C/g soil in each core. The soil cores were incubated at field capacity. The cores with maize straw were wetted up to field capacity with NH_4NO_3 solution to keep the sample C/N ratio around 10 and minimize N limitation during straw decomposition. In the same way, the cores without straw were wetted with deionized water.

Aggregate-size distribution measurements
Aggregate-size distribution was analysed at days 21, 42 and 63 according to Six *et al.* (2002). Soil cores were wet sieved following the method of Elliott (1986) to obtain large macroaggregate (>2000 µm), macroaggregate (250-2000 µm), microaggregate (50-250 µm) and silt plus clay (<50 µm) fractions. Approximately half of the soil core was submerged in deionized water on top of a 2000 µm sieve for 5 min before sieving. Each soil subsample was manually sieved by moving the sieve up and down 3 cm, 50 times in 2 min. The material passing through 2000 µm sieve was poured onto the next µm sieve and sieving was repeated. Fractions recovered in each sieve (2000, 250, and 50 µm) were oven-dried at 50 ºC.

The macroaggregate fraction (>250 µm) was used to isolate microaggregates within macroaggregates (Six *et al.* 2002). Macroaggegates were immersed in deionized water on top of a 250 µm sieve and shaken with 50 glass beads (diameter = 4 mm). A regulated continuous water flow through the sieve allow to flush all material <250 µm onto a 50-µm sieve, separated from the horizontal shaker, 125 rev/min). After all macroaggregartes are disrupted, only coarse sand and POM remained on the 250 µm sieve. Material remaining on 50 µm sieve was wet sieved to obtain water stable microaggregates. The two fractions were also oven-dried at 50 ºC. A subsample of microaggregates within macroaggregates and free microaggregates were used to separate sand between 50-250 µm. The percentage of soil mass in each aggregate-size fraction was determined (soil mass in the fraction/total soil mass in the subsample) after sand corrections for comparison among treatments and soils.

Data were analysed using ANOVA (univariate linear model). Treatment means were compared using significant differences (P<0.05), and post hoc analysis was performed by Duncan test (P<0.05). All statistical analyses were performed using SPSS 16.0software (SPSS Inc. 2008, Chicago IL).

Results
In the non-carbonated soil, fresh organic matter addition (i.e. maize straw) enhanced Magg formation, according to the aggregation hierarchy described by Six *et al.* (1998). Organic residues increased soil microbial activity, resulting in a greater production of organic binding agents, and macroaggregates percentage increased in NC.ST compared to NC.ST (Fig 1). As organic matter is decomposed, organic binding agents are gradually degraded and macroaggregates percentage decreased in NC.ST. After macroaggregates dispersion, microaggregates amount per macroaggregates mass unit was also greater in NC.ST than in NC.NST due to fresh organic matter addition (Table 1).

Table 1. Percentage of soil mass in large macroaggregate (LMagg, >2000 μm), macroaggegate (Magg, >250 μm), and microaggregate within macroaggregate (mMagg, 50-250 μm) fractions. Studied treatments: carbonated (C) or non-carbonated (NC) soil with (ST) and without (ST) maize straw. Values in the same column followed by different letters are significantly different at P<0.05 according to ANOVA.

	Incubation day		
	21	42	63
LMagg (>2000 μm)			
C.NST	0.23 ± 0.08 b	0.16 ± 0.07 b	0.15 ± 0.02 b
C.ST	7.53 ± 0.26 a	11.92 ± 1.64 a	6.77 ± 1.28 a
Magg (>250 μm)			
NC.NST	1.28 ± 0.08 c	1.46 ± 0.16 c	1.12 ± 0.16 c
NC.ST	3.93 ± 0.64 b	2.41 ± 0.20 bc	2.43 ± 0.30 b
C.NST	4.35 ± 0.55 b	3.05 ± 0.23 b	2.74 ± 0.13 b
C.ST	8.88 ± 0.97 a	8.64 ± 0.59 a	9.74 ± 0.52 a
mMagg (50-250 μm)			
NC.NST	0.96 ± 0.33 c	1.1 ± 0.48 c	1.11 ± 0.04 c
NC.ST	4.95 ± 0.84 b	2.72 ± 0.73 c	3.68 ± 0.59 c
C.NST	32.89 ± 0.05 a	29.64 ± 0.40 b	30.46 ± 1.97 b
C.ST	29.86 ± 1.93 a	38.17 ± 1.19 a	39.24 ± 1.02 a

LMagg and Magg percentage in expressed as aggregates amount per soil sample mass unit. The percentage of mMagg is expressed as microaggregates amount per macroaggregates mass unit.
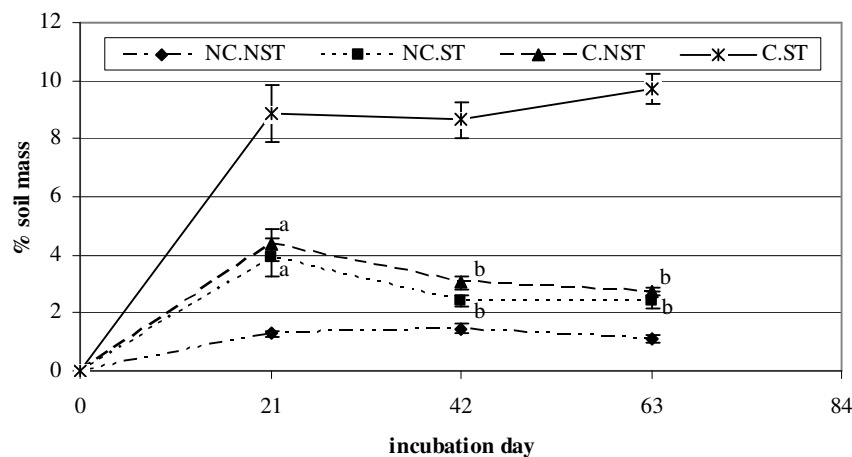
Figure 1. Percentage of soil mass in macroaggegate (>250 μm) fraction at incubation days 21, 42, and 63. Studied treatments: carbonated (C) or non-carbonated (NC) soil with (ST) and without (ST) maize straw. In each treatment, values followed by different letters are significantly different at P<0.05 according to ANOVA.

Comparing to the non-carbonated soil, two major differences were observed in the aggregation dynamics of the carbonate-rich soil. First, greater macroaggregates percentage in C.NST than in NC.NST (Table 1) indicates the role of carbonates in macroaggregation. Carbonates mediated in aggregation most likely due to cationic bridging effect of Ca^{2+} (mineral-mineral and mineral-organic matter linkages) and precipitation of secondary carbonates coatings (Clough and Skjemstad 2000; Baldock and Skjemstad 2000). Second, macroaggregates percentage was also greater in C.ST than in NC.ST. In addition, unlike the NC.ST, macroaggregates amount remained almost constant in C.ST during this short incubation (Figure 1). These results suggest that there is an interaction between fresh organic matter and carbonates that increased macroaggregates water stability. Shang ant Tiessen (2003) proposed that carbonates precipitation (i.e. coatings) may play a major role in the stability of more labile organic matter, resulting in an enhanced stability of aggregates.

Although macroaggregates percentage was greater in C.ST than in C.NST, similar microaggregates amount per macroaggregates mass unit was observed in both treatments at day 21. Microaggregates percentage was greater in C.ST than in C.NST thereafter (Table 1). In addition, microaggregates percentage was greater in C.NST and C.ST than in NC.NST and NC.ST. This indicates that carbonates rather than organic matter largely contribute to microaggregates fraction. The role of calcium in clay and organic matter flocculation into colloidal aggregates may be responsible of microaggregates formation and stabilization mechanisms (Muneer and Oades 1989). Moreover, fresh organic matter addition may improve this mechanism, increasing microaggregation.
When only large macroaggregate fraction (>2000 μm) was studied, no significant effect of carbonates was observed in C.NST (Table 1). Large macroaggregate formation in C.ST was due to organic matter addition only.

Conclusion

In the carbonated soil, both soil organic carbon and carbonates contribute to the aggregation dynamics. Carbonates controlled macroaggregates formation at low soil organic carbon content in C.NST; however, maize straw addition promotes fresh organic matter-carbonates interaction that enhanced macroaggregates formation and water stability in C.ST. Microaggregates formation was also largely related to carbonates aggregation mechanisms in C.NST and C.ST. We conclude that carbonates are the dominant binding agents of the naturally-occurring carbonated soil with low organic matter content. When fresh organic matter is added, interaction between carbonates and SOC affected aggregation dynamic of this soil. Aggregate hierarchy appeared to be altered when SOC is not the major stabilizing agent of soil. More research is needed to understand the relative role of SOC and carbonates on different aggregate-size fractions, in order to adapt the aggregate hierarchy model to carbonated soils. Research on this subject will also help to study mechanisms for organic carbon and inorganic carbon stabilization in soils.

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Residual effects of topsoil replacement depths and organic amendments on soil organic carbon levels of reclaimed wellsites

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Abstract

The reclamation success of abandoned wellsites in agricultural areas depends on their capacity to sustain levels of soil quality similar to those which existed prior to soil disturbance. A study conducted from 1997-2000 examined the effect of four (0, 50, 100 and 150%) topsoil replacement depths (TRD) and five amendment treatments [compost, manure, alfalfa (*Medicago sativa* L.) hay, wheat (*Triticum aestivum* L.) straw, check) in the reclamation of three natural gas wellsites in south-central Alberta. In 2007 (10 yr after establishment) the three wellsites were sampled to examine the residual effects of reclamation treatments on soil organic carbon (SOC). The compost-amended plots (averaged over all TRDs) in 2007 maintained higher SOC than the straw and check plots (by 11-15%). The results showed that where topsoil is scarce (e.g. in the reclamation of older wellsites) initial investment in organic amendments can have a residual effect on soil quality, as indicated by SOC.

Key Words

Soil reclamation, organic amendments, soil organic carbon, natural gas wellsites.

Introduction

In mid-2009, Alberta=s oil and gas infrastructure included over 212,000 capable wells (Energy Resources Conservation Board 2009). As these wells are depleted and abandoned over time, the wellsites, many of which are leased from agricultural landowners, need to be returned to >equivalent land capability= (Alberta Environment, 1995, 2008), i.e. to levels of production similar to those which existed prior to soil disturbance. A study conducted from 1997-2000 examined the effect of four (0, 50, 100 and 150%) topsoil replacement depths (TRD) and five amendment treatments [compost, manure, alfalfa (*Medicago sativa* L.) hay, wheat (*Triticum aestivum* L.) straw, check) in the reclamation of three wellsites in south-central Alberta (Strathmore, Hesketh and Rosedale). Larney *et al*. (2003) looked at crop response to the various reclamation treatments. Of the 20 treatments (four TRD x five amendments), the reclamation capacity of the 100% TRD-compost treatment ranked highest, being 19% higher than the baseline treatment (100% TRD-check). The lowest-ranking treatment overall, was the 0% TRD-straw treatment which yielded 64% of the baseline treatment. Crop yield responses to organic amendments were larger when the recipient soil was lower in organic matter.

Changes in soil properties reflect the success or failure of reclamation practices on abandoned wellsites. Larney *et al*. (2005) examined the effect the four TRD treatments and five amendment treatments on soil properties. TRD treatment differences were consistent across all wellsites, with 30 to 32% higher soil organic carbon (SOC) on the 150% TRD compared to the 0% TRD. After 40 mo (June 1997–October 2000), the average amounts (*n* = 3 wellsites) of added C conserved near the soil surface were: compost (65 ±10% SE) > manure (45 ±16% SE) > alfalfa (28 ±11% SE) > straw (23 ± 6% SE). Zvomuya *et al*. (2006) found that low carbon to nitrogen (C/N) ratio amendments, particularly compost and alfalfa, were the most effective for improving grain N concentration and uptake.

The above results point to enhanced crop performance and soil quality as a result of reclamation treatments over the short-term duration of the initial study (4 yr, 1997-2000). However, questions remained about the longevity of the soil treatment (TRD, organic amendments) effects on these wellsites. To answer this question, we carried out a follow-up study in 2007 which involved returning to the three wellsites, relocating the plots and taking soil samples. Our objective was to examine, 10 yr after establishment, the residual effects on soil organic carbon (SOC) of the initial reclamation treatments.

Methods

Study sites and design

This study is described in greater detail by Larney *et al*. (2003, 2005). Briefly, three abandoned natural gas

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wellsites (Strathmore, Hesketh and Rosedale) were selected in south-central Alberta in the spring of 1997. The soils were Orthic Dark Brown or Black Chernozems. Surface soil texture was loam to clay loam. The experimental design was a split-plot, with topsoil replacement depth (TRD, at 0%, 50%, 100% and 150%) as the main treatment and organic amendment (compost, manure, straw, alfalfa and check) as the sub-treatment, replicated four times. Each main plot was 8 x 10 m in area with sub-plots of 8 x 2 m.

Topsoil replacement depths and amendments
Two-lift soil stripping was carried out on all three sites by an experienced operator on a bulldozer. This is the selective recovery and stockpiling of all available topsoil (mostly Ap horizon material) in the first lift and 'good quality' subsoil (mostly B horizon material, some Ap horizon material, minimal C horizon material) in the second lift. Soils were redistributed uniformly (subsoil followed by topsoil) across the sites to meet the required replacement depth for topsoil of 60% of the control soil depth (Alberta Environment 1995). It was assumed that the depth of topsoil existing following replacement represented the 100% TRD treatment. The 0% TRD was achieved by removing and stockpiling all of the topsoil layer. The 50% and 150% TRD treatments were accomplished by removing half of the topsoil layer depth from the 50% TRD plots and spreading it evenly over the 150% TRD plots. After TRD main plot treatments were established, amendments were applied as one-time sub-treatments in late June/early July 1997 as follows: (1) compost derived from straw-bedded cattle feedlot manure; (2) fresh feedlot manure; (3) straw (wheat); (4) alfalfa hay and (5) check (unamended). Compost and manure were applied at 40 t/ha (dry wt.), and straw and alfalfa at 14.6-17.0 t/ha (dry wt). Amendments were with two passes of a rototiller to 10 cm depth. Apart from manure at Strathmore (15.6 t/ha of C), the amendments added similar amounts of C (6.6-9.9 t/ha).

Management and soil sampling
Spring wheat (*Triticum aestivum*) was the test crop at all three sites throughout the initial four year study period (1997-2000). After harvest in 2000, the wellsites were land-farmed in the same manner as the adjacent field area by the owners. In 2007, soil samples were taken from each plot to determine SOC at 0-15 cm, 15-30 cm, and 30-60 cm. Total C was measured on fine-ground material in an elemental analyzer (Carlo Erba, Milan, Italy). Inorganic carbon was measured by the method of Amundson *et al*. (1988). Organic carbon was determined as the difference between the total carbon and the inorganic carbon. Statistical analyses were performed using the GLM procedure (SAS Institute Inc., 2006).

Results
Soil organic carbon (SOC) was significantly affected by TRD in 2007 for all three depths at Strathmore, the 0-15 cm depth at Hesketh and the 0-15 cm and 30-60 cm depths at Rosedale (Table 1). The trend was for lower SOC in the 0% TRD compared to the others. The lack of topsoil on the 0% TRD resulted in lower SOC at the 0-15 cm depth and this extended deeper in the profile since a deeper layer (inherently lower in SOC) would be sampled for the 30-60 cm depth on the 0% TRD compared to the 100% or 150% TRDs due to the lack of topsoil.

Residual effects of the organic amendments were significant for the 0-15 cm depth at all three sites (Table 1), but did not extend to deeper layers. At Strathmore, the compost treatment (20.4 g/ kg) was significantly higher than the straw and check treatments (17.8-18.1 g/kg) but not the manure or alfalfa. At Hesketh, the compost and manure treatments (24.0-24.5 g/kg) were significantly higher than the straw (21.7 g/kg) treatment but not the alfalfa or check. At Rosedale, the compost treatment (19.9 g/kg) was significantly higher than the straw, alfalfa and check treatments (17.5-17.6 g/kg) but not the manure treatment. Residual effects of compost and manure were not significantly different from each other at any of the three sites, while alfalfa was as good as both manure and compost at two (Strathmore, Hesketh) of the three sites. The check treatment was as good as manure and compost at the Hesketh site only (the one with the highest background level of SOC). SOC on the straw treatment was significantly lower than compost at all three sites. None of the TRD x amendment interaction effects were significant (Table 1).

Table 1. Effect of topsoil replacement depth and amendment on organic carbon concentrations at Strathmore, Hesketh and Rosedale, 2007.

	——— Strathmore ———			——— Hesketh ———			——— Rosedale ——		
	————————————————— Depth (cm) —————————————————								
	0-15	15-30	30-60	0-15	15-30	30-60	0-15	15-30	30-60
	————————————————— g/kg —————————————————								
Topsoil replacement depth (TRD) (%)									
0	16.9c†	9.9b	5.5ab	21.4c	13.5a	10.8a	16.1b	8.2a	6.6ab
50	18.6b	9.6b	4.5b	22.5bc	13.6a	11.2a	18.5a	8.1a	4.2c
100	20.0a	11.6a	6.8a	26.0a	14.8a	11.5a	18.8a	8.6a	7.8a
150	20.4a	12.1a	5.8ab	23.4b	13.5a	11.3a	19.8a	9.1a	4.5bc
Amendment									
Compost	20.4a	11.3a	5.5a	24.0a	14.2a	10.9a	19.9a	8.4a	6.3a
Manure	19.1ab	11.0a	5.9a	24.5a	13.6a	11.6a	18.9ab	8.8a	5.6a
Straw	18.1b	10.4a	5.5a	21.7b	14.0a	10.9a	17.5b	8.6a	6.0a
Alfalfa	19.3ab	10.9a	5.7a	23.4ab	14.0a	11.4a	17.6b	8.3a	5.5a
Check	17.8b	10.3a	5.6a	23.1ab	13.5a	11.1a	17.6b	8.5a	5.5a
P-value									
TRD	<0.001	<0.001	0.009	<0.001	0.32	0.87	<0.001	0.37	0.004
Am	0.005	0.32	0.97	0.05	0.94	0.86	0.007	0.97	0.96
TRD xAm	0.54	0.36	0.12	0.96	0.71	0.82	0.79	0.96	1.00

TRD = topsoil replacement depth; Am = amendment. †Within TRD or amendment, means followed by different letters are significantly different according to LSD (0.05).

Soil organic matter content is considered one of the most important soil quality indicators (Gregorich *et al*. 1994). Although C mass additions were not that different among amendments, the C added as compost or manure raised SOC levels and, more importantly, maintained them for 10 yr, while C added as straw or alfalfa was less effective. Cox *et al*. (2001) also reported that compost was of greatest benefit in improving soil quality on an eroded soil in Washington compared to straw or coal ash. They found that compost significantly increased SOM and plant available P, as well as reducing bulk density and improving water infiltration.

The status of C on the decomposition spectrum is important in the ability of organic amendments to enhance SOC levels. Compost- or manure-C is in a much more stable form than straw- or alfalfa-C. Most of the readily decomposable C had already left the compost and manure before they were soil-incorporated, leaving mostly stable C, which was able to raise SOC levels significantly. In contrast, the greater part of organic C in straw and alfalfa was readily decomposable, rapidly breaking down once mixed with soil, and the remaining C was less capable of raising SOC.

Conclusion
The study demonstrated that residual effects of one-time applications of organic amendments (e.g. compost, manure, alfalfa) on SOC were found 10 yr after application. It is hoped that results from this research will promote increased use of organic amendments (particularly compost) in wellsite reclamation in Alberta. The livestock industry produces large volumes of manure and its return to the soil as compost in reclamation scenarios in the oil and gas industry is a good fit.

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Soil biodegradation of aerial and underground litter of *Miscanthus*, a perennial energy crop

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Abstract
To predict the environmental benefits of energy crop production and use, the nature and fate of biomass residues in the soil need to be quantified. Our objective was to quantify *Miscanthus x giganteus* biomass recycling to soil (senescent leaves, roots and rhizomes) and to assess how harvesting time and N fertilization affect their characteristics and subsequent biodegradability. The quantification of aerial and belowground biomasses and their sampling were performed on 2- and 3-year-old Miscanthus stands, either fertilized with 120 kg N ha^{-1}year^{-1} or not fertilized, in autumn (maximal biomass production) and winter (maturity). Plant biomass was chemically characterized and incubated in optimum decomposition conditions (15°C, -80kPa) for 263 days, for C and N mineralization. C mineralization kinetics was analyzed in relation to litter quality.

Key Words
Miscanthus, litter quality, soil biodegradation, carbon and nitrogen cycles

Introduction
The concerns of global fossil fuel depletion and environmental pollution from its combustion are driving the search for carbon-neutral, renewable energy sources. The use of ligno-cellulosic plant biomass as an energetic source is an alternative which is fully investigate nowadays. Substituting fossil fuels with crop biomass will require selection of the most suitable plant species and adequate management to meet the environmental constraints. Several species that produce high biomass from low inputs would be good candidates for energy production. Amongst these, the genus *Miscanthus*, which is a perennial rhizomatous grass, with a great adaptability to different environments and a high yielding potential (C$_4$-plant) appears as a good candidate (Heaton *et al*., 2004). New practices and/or the development of new energy crops will also modify the quantity and quality of crop residues entering the soil system and therefore affect the nutrient cycles (mainly Carbon (C) and Nitrogen (N)) (Bertrand *et al*., 2009; Amougou *et al*., 2010). The aim of our study was therefore to establish the relationships between *Miscanthu*s litter quality (aerial and underground parts) and their rate of decomposition in soil as a function of the agricultural practices (date of harvest and N fertilization rate).

Methods
Site and field experiment
Miscanthus sampling was realized at the INRA experimental station of Mons en Chaussée Northern France). The soil is a deep silt loam (Orthic Luvisol) with 19.9% clay, 2.0% silt, 7.8% sand, 0.3% CaCO$_3$ and pH of 7.8. The climate is oceanic temperate with annual precipitation and temperature means of about 713 ± 49 mm and 11 ± 1°C respectively since the establishment of the Miscanthus crop (spring 2006).
The field experiment design consisted of a randomized block design with (i) two Nitrogen rates (0 kg N ha^{-1} (0N) and 120 kg N ha^{-1}(120N)) added as urea ammonium nitrate solution applied each year at the beginning of growth (April), and (ii) two harvest dates, an early harvest in autumn (October) and a late harvest in winter (February-March). This gave four treatments: autumn/0N, autumn/120N, winter/0N, winter/120N. Each treatment had 3 replicates. The Miscanthus rhizomes were planted in April 2006 at a density of 15,625 plants ha^{-1}.

Sampling of aboveground and belowground biomass
The study concerned the 2007 and 2008 growing seasons, i.e. the plantation second and third years. At each harvest date (autumn 2007 and 2008, winter 2008 and 2009), 3 whole Miscanthus plants were destructively sampled from each 0N and 120N treatment plot. Each plant had 26 stems on average. Stems and leaves were weighed to obtain fresh weight and were then separated, subsampled and dried at 80°C for 48 hours for dry matter determination. The dry weight of the stems was then added to that of leaves to determine total aerial dry matter. The rhizomes were sampled to determine the below-ground biomass to a depth of 30 cm. The rhizomes + associated roots were cleaned of soil by manual washing on a sieve to avoid dry matter loss. The roots were then separated from the rhizomes by hand. The rhizomes were manually cut into small pieces (5-10 cm). Senescent leaf fall was monitored through the autumn-winter 2007-2008 and autumn-winter 2008-2009 periods

using a nylon net (mesh size 1 cm × 1 cm) in the 0N and 120N treatments. The yields of the different plant parts were then expressed in ton dry matter per hectare (t DM ha^{-1}). Subsamples of roots, rhizomes and leaves were kept for an incubation experiment and biochemical analysis; there were dried at 35°C for a week.

Chemical characteristics of the litters
Chemical characteristics were determined on leaf, rhizome and root samples from the first year of sampling only (2007). The total Carbon (C) and Nitrogen (N) concentrations of the plant parts were determined using an elemental analyzer. The total neutral sugar content of the plant samples was determined using the method described by Blakeney *et al.* (1983). The NDS-soluble fraction was determined using the method described by Goering and Van Soest (1970). The NDF fraction, designated as cell walls, was then dried for one week at 30°C and ground to 80 μm prior to Klason lignin determination. Klason lignin (KL) was determined as the acid-insoluble residue remaining after sulphuric acid hydrolysis of cell wall polysaccharides (Monties, 1984).

Incubation study
The soil from the field site was sampled from the top 5-10cm layer of one plot. It was sieved to 2 mm and stored at the incubation temperature (15°C) for a week prior to incubation. The rhizomes, roots, necrotic rhizomes and senescent leaves were hand cut into pieces 4-5 mm long and 5 mm wide prior to incubation. They were added at a rate equivalent to 2 g C kg^{-1} dry soil, mixed into the moist soil and incubated at 15°C, for 263 days for C mineralization and 114 days for N mineralization. Potassium nitrate was added to the soil to ensure that decomposition would not be N-limited (Recous *et al.*, 1995). Soil moisture was maintained throughout the incubation period by weighing at weekly intervals and adding deionised water when necessary. A control treatment was performed in the same way but without the addition of residue.
Carbon mineralization was measured from soil samples equivalent to 100 g dry soil, incubated in the presence of a CO_2 trap with four replicates per treatment. Mineral N was determined on separate soil samples with three replicates per treatment.

Results
The total aboveground biomass measured at autumn harvest was 20 to 22 t DM ha^{-1} for year 1 and 24 to 26 t DM ha^{-1} for year 2, declining to 14-15 and 19-20 t DM ha^{-1} at winter harvest, respectively. The aboveground biomass increased significantly between year 1 and year 2 except for the autumn/0N treatment, while N treatment had no significant effect (data not shown). The amount of senescent leaves collected over the winter was about 3 t DM ha^{-1} and did not vary between year 1 and year 2 or between N treatments. Belowground biomass was not significantly affected by harvest date or N treatment, and amounted 15 to 20 t DM ha^{-1} depending on the treatment.
Aboveground biomass sampled in winter accumulated significantly ($P \leq 0.05$) smaller amounts of N (22 to 41 kg N ha^{-1}) than the autumn sampled ones (90 to 118 kg N ha^{-1}), indicating that N lost from aboveground parts during winter amounted on average to 68 ± 7 kg N ha^{-1}. Application of fertilizer N had no effect on N accumulated in aboveground parts, except for autumn sampling in year 2, where the N content was significantly higher for the 120N treatment than for 0N. Total belowground parts sampled in winter accumulated higher amounts of N than those sampled in autumn, but the differences were not significant except for the winter/120N treatment in year 2, which exhibited higher N content than the winter/0N treatment.

Figure 1 presents cumulative C mineralization for rhizome, necrotic rhizome, root and senescent leaf obtained from the winter/0N treatment, incubated for 263 days. As expected, the cumulative CO_2 produced in the residue-amended soils was greater than in the control soil and ranked as follows: rhizome > necrotic rhizome = senescent leaf > root > control. At the end of incubation (263 days), the net mineralization of residue-C was significantly higher for rhizome (59% of added C) than for necrotic rhizome (51% of added C), leaf (53% of added C) and root (30% of added C) ($P \leq 0.05$). The observed differences at day 263 resulted mainly from differences in C mineralization during the first 30 days (Figures 1a). Over the 242-263 day interval, the rates of C mineralization were not significantly different ($P < 0.05$) between senescent leaf (1.6 mg C kg^{-1} day^{-1}), rhizome (1.4 mg C kg^{-1} day^{-1}) and necrotic rhizome (1.2 mg C kg^{-1} day^{-1}), but all these were significantly higher than for root (0.8 mg C kg^{-1} day^{-1}) and control (0.4 mg C kg^{-1} day^{-1}). These results suggest that at the end of incubation the residues were still decomposing.
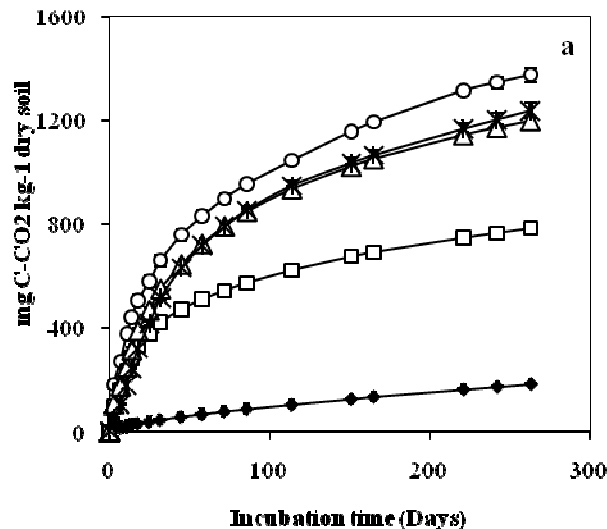
Figure 1. Kinetics of C mineralized in soils (a) without residues (control soil, *black diamond*) and after addition of rhizome (*white circle*), necrotized rhizome (*white triangle*), root (*white square*) (winter/0N treatment) and senescent leaf (*black star*). Data are means (*n* = 4)

Table 1. Correlation coefficient (r) between *Miscanthus* × *giganteus* residues initial chemical characteristics (rhizome, root, necrosis rhizome and senescent leaf from all treatments) and cumulative C mineralized. *, **, ***, Significant at the 0.05, 0.01 and 0.001 probability levels respectively; "ns" means not significant.

Days	3	7	14	32	58	86	114	200	263
% N	0.79***	0.81***	0.77**	ns	ns	ns	ns	ns	ns
NDS-soluble	0.82***	0.80***	0.83***	0.83***	0.71**	0.65**	0.62**	0.70**	0.68**
Total sugars	ns	ns	ns	0.57*	ns	ns	ns	ns	ns
Klason lignin	ns	ns	ns	-0.83***	-0.92***	-0.93***	-0.93***	-0.92***	-0.92***
(Klason lignin/total sugars) ratio	ns	ns	ns	-0.89***	-0.93***	-0.94***	-0.94***	-0.92***	-0.92***

Simple linear regressions were performed to establish relationships between the cumulative amounts of mineralized C over time and the initial chemical characteristics of the Miscanthus residues. To do this, rhizome, root, necrotic rhizome and senescent leaf from all treatments were considered together (Table 1). In the very short term (3 to 7 days), $C-CO_2$ is positively correlated with N concentration ($P \leq 0.01$) and with the NDS-soluble fraction. The correlation between NDS fraction and $C-CO_2$ remains highly significant up to day 32, then begins to decrease but remains significant until day 263 (P<0,01). There is no correlation between mineralized C and the total sugars fraction except at day 32 ($P \leq 0.05$). Mineralized C is strongly negatively correlated with Klason lignin from day 32 to day 263 ($P \leq 0.001$). Total sugars are positively and more clearly correlated with mineralized C at day 263 for rhizome ($R^2 = 0.66$) and necrotic rhizome ($R^2 = 0.79$) than for root ($R^2 = 0.33$), for which a negative correlation is obtained (data not shown).

Conclusions

We saw that a *Miscanthus giganteus* crop is characterized by a large amount of organic plant biomass that is potentially recycled in the soil, and that the amount, quality and therefore subsequent decomposition of these biomasses depend on harvesting strategy and to a lesser extent on N fertilization, if any. From an environmental point of view, harvesting the Miscanthus aerial biomass early (before plant maturity) in order to harvest plant biomass larger in amount and more easily enzyme-fractionable in term of biochemical quality would deprive the soil from the annual input of organic matter as leaves that fall during the winter, while also depriving the rhizomes of several months of accumulation of nutrients that are necessary for subsequent plant growth cycles.

Miscanthus leaves, roots and to lesser extent rhizomes are characterized by a high lignin content compared to other types of crop residues, inducing potentially low rates of mineralization, i.e. a high rate of organic C storage in the soil, which may be a positive criterion for this crop in terms of its impact on soil fertility. However, too few data are as yet available on Miscanthus residue quality and decomposition, particularly on the

amount and extent of recycling of roots in the soil and on rhizome decay over the life of the Miscanthus plant. It also seems important to be able to predict the fate of the organic C stored in belowground parts when an old Miscanthus crop is destroyed.

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Soil carbon distribution and soil physical properties as affected by rice-barley long-term double cropping system in Korean paddy fields

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Abstract

Cropping system and organic matter affect crop productivity and soil chemical-physical properties. This study was carried out to evaluate the effects of a double cropping system in paddy fields in Korea. Rice mono cropping systems, rice-barley double cropping system with and without barley straw were evaluated from 1990 to 2009. Soil organic carbon and physical properties such as bulk density, cone index, aggregate distribution at different soil depths were investigated.

The amount of total soil organic carbon of up to a depth of 30 cm in a rice-barley double cropping system was higher than for a rice mono cropping system. The amount of total soil organic carbon in the upper 12-cm depth of soil from the fields with removal and recovery of barley straw did not significantly differ. Bulk density and cone index were found to decrease under the rice-barley double cropping system. On the other hand, the bulk density of the upper 30-cm depth of soil from fields with recovery of barley straw was significantly different from the other treatments.

The rice-barley double cropping system was more effective than the rice mono cropping system in increasing soil organic carbon for the improvement of soil fertility and physical properties in paddy fields of Korea. Furthermore, barley straw recovery in the rice-barley double cropping system with rice straw recovery was not effective in increasing soil organic carbon and improving physical properties.

Key Words

Rice, Barley, Double cropping, Soil carbon, Physical properties

Introduction

The level of agricultural productivity in Korea, a small country, has been increased by the double cropping system. Most rice and barley straw is utilized as feed for livestock by recovering straw from the fields. Double cropping rice-barley is an effective cultivation technique for improving soil chemical, physical properties and productivity compared to the mono cropping system. Improving soil organic carbon and physical properties with different cropping systems involving retention of organic materials is important in maintaining productivity and reducing global warming increasing by carbon sequestration in the long term in paddy fields.

Materials and Methods

1) Treatments (1990~2009)
  - Mono culture : Rice mono cropping
  - Rice-Barley (Removal): Rice-barley double cropping system without barley straw
  - Rice-Barley (Recovery): Rice-barley double cropping system with barley straw
2) Fertilizer and organic matter schemes

Cropping system	1990~1998 (kg ha^{-1})			1999~2009			Barley Straw (Mg ha^{-1})
	N	P$_2$O5	K$_2$O	N	P$_2$O5	K$_2$O	
Rice mono cropping	90	70	80	90	45	57	
Rice-Barley (Straw removal)	90	70	80	90	45	57	
Rice-Barley(Straw recovery)	90	70	80	90	45	57	45

3) Rice straw recovery in all treatment
4) Soil Properties
  . Soil series: Pyeongtaeg *(mixed mesic, Typic Haplaquepts)*
  . *Fine silty loam (somewhat poorly drained fine silty)*

Results
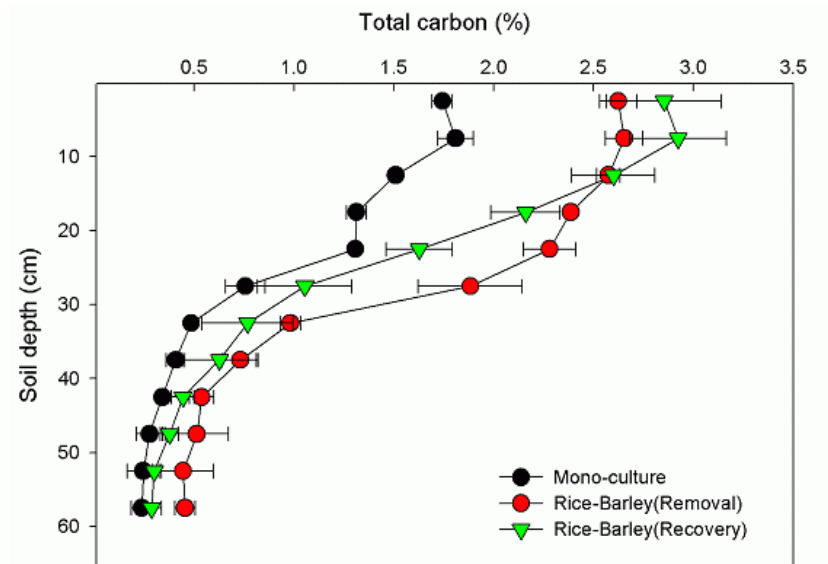
Figure 1. Changes in soil organic carbon concentration with soil depth under different cropping systems for a long term rice paddy field.
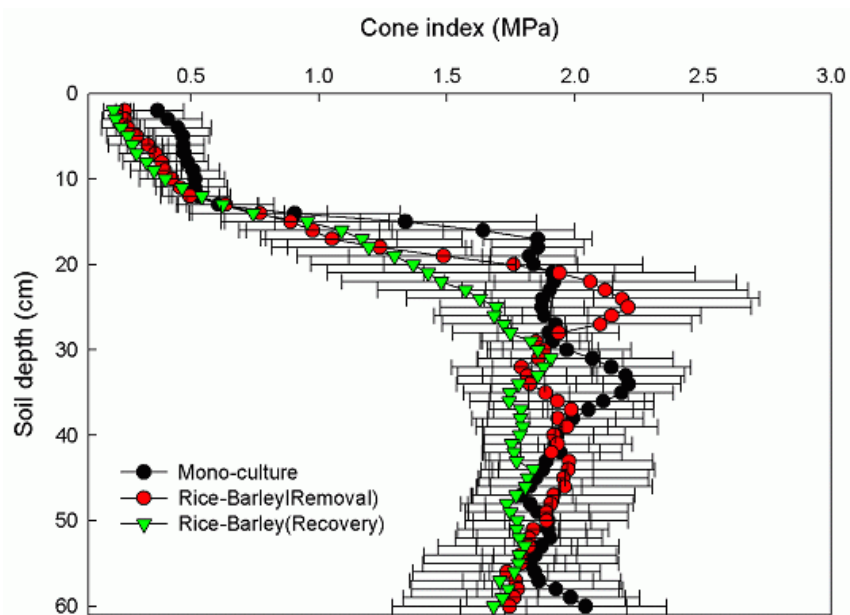
Figure 2. Changes in cone index with soil depth under different cropping systems in a long term rice paddy field.
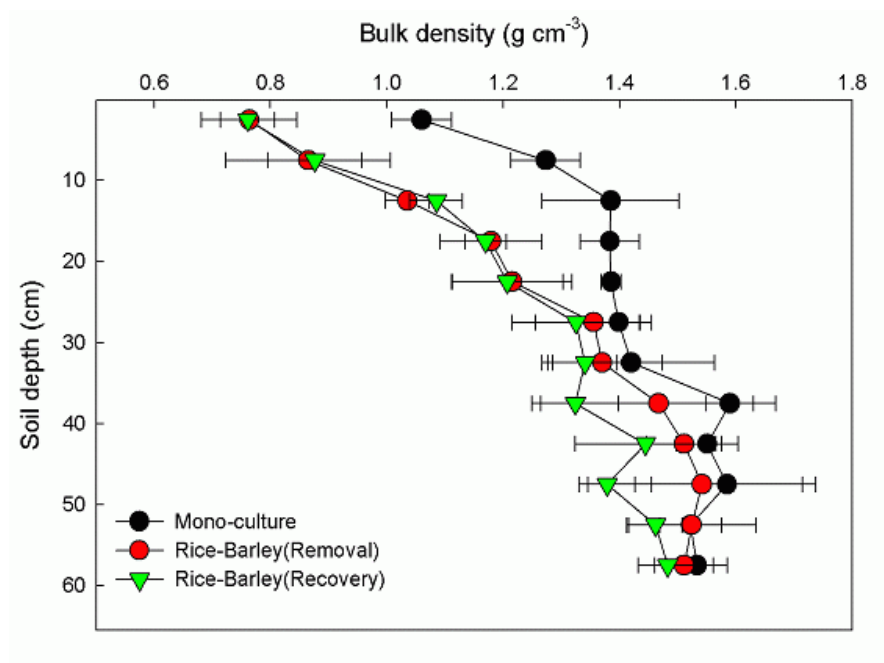
Figure 3. Changes in bulk density with soil depth under different cropping systems in a long term rice paddy field.

<Rice mono culture>   <Rice-barley (Removal)>   <Rice-barley (Recovery)>

Figure 4. Soil profiles for different cropping systems in a long term rice paddy field.

Conclusion

The rice-barley double cropping system is an important cultivation method for organic matter application in paddy fields. Continuous rice-barley cultivation increases the soil carbon concentration in the upper 30-cm soil layer with a corresponding decrease in bulk density. The rice-barley cropping system could be a good management practice to substantially improve yield by increasing carbon storage in the soil profile. Soil organic carbon and soil physical properties under the rice-barley double cropping system with recovery of rice straw did not significantly differ from that of fields without recovery of barley straw. Further work is needed to evaluate the maintenance of productivity and the best management practice for soil fertility under a double cropping system in long term paddy fields.

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Soil carbon sequestration affected by no-tillage and integrated crop-livestock systems in Midwestern Brazil

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Abstract

Conservation management systems can improve soil organic matter stocks and contribute to atmospheric C mitigation. This study was carried out in a 15-year long-term field experiment established on a tropical Oxisol in Dourados/MS, Brazil, to assess the potential of tillage systems [conventional tillage (CT), no-tillage (NT) and no-tillage integrated crop-livestock (ICL)] for mitigating atmospheric C. For that, the soil organic carbon (SOC) accumulation in the 0-100 cm depth and the C equivalent (CE) costs of the different management systems were taken into account for comparison with the CT. More SOC accumulation was observed in NT and in ICL systems because of the lesser oxidative environment compared to CT. SOC accumulation rate in NT was 0.21 Mg ha^{-1} yr^{-1} higher in the 0-30 cm layer, and lower rates were observed below 30-cm depth. ICL system accumulated three times more SOC in the 0-30 cm layer than NT. Probably, this greater SOC accumulation in ICL system is due to greater amounts of forage root mass compared to crops like soybean, wheat, oat, which were cultivated in NT systems. SOC accumulation rates increased by 30% when SOC was assessed up to deep layers (i.e. 100 cm depth) as the result of carbon addition in deep layers by tropical forage. These results indicated that ICL system can be a better strategy to provide C mitigation in Midwestern Brazil compared to no-tillage alone.

Key Words
Global warming, C mitigation, C addition, C equivalent costs

Introduction
Soil is an important terrestrial C reservoir which plays a significant role in the global C cycle. However, use and management it may function either as a C source or sink. The increase of the soil organic matter stock can be a strategy for mitigating the potential greenhouse effect (Lal 2004). The adoption of no-tillage management systems (NT) in subtropical Brazilian soils has lead to soil organic carbon accumulation indicating that NT soils can function as an atmospheric C sink (Bayer *et al*., 2006). Nowadays, integrated crop-livestock system (ICL) has been a good alternative to practice NT in tropical soils, mainly because it can provide high C addition and permanent soil cover. However, soil carbon sequestration should consider the carbon equivalent costs relative to each management system like consumption of diesel and fertilizers (Lal 2004). The objective of this study was to evaluate C sequestration rates in NT and ICL systems in a long-term field experiment that has been carried out for 15 years in a tropical Brazilian Oxisol.

Methods
Experimental area
The study was carried out in a 15-year long-term field experiment located at Embrapa Western Region Agriculture in Dourados, MS, Brazil (24º 19'S e 54º 49'W and altitude of 430 m). Annual average temperature is about 23 ^{o}C and precipitation about 1635 mm concentrated in summer season. Soil is an Oxisol with 630 g kg^{-1} of clay, 210 g kg^{-1} of silt and 160 g kg^{-1} of sand in 0-20 cm layer. Original vegetation was Savannas constituted by grass and bush distributed randomly in the landscape. The experimental area had been previously cultivated using CT system for 20 years with annual grain production. The following management systems were tested: conventional tillage (CT) applied with heavy disk, no- till (NT) with a three-year crop rotation (rape/maize/oat/soybean/wheat/soybean) and integrated crop-livestock (ICL) with two years of cropping (oat/soybean) followed for two years of pasture (*Brachiaria decumbens*) both using NT.

Soil sampling
Four samples per plot were taken for determination of organic carbon and bulk density at 0-10, 10-20, 20-30, 30-40, 40-50, 50-60, 60-70, 70-80, 80-90 and 90-100 cm depth. We used a spatula for taken samples of organic carbon and volumetric rings for bulk density. Thereafter, soil samples were air dried, ground to pass a 0.05-mm mesh and analyzed by wet combustion for measuring organic carbon concentration while soil bulk density was determined using core method with the soil inside the core being dried to 105°C for 24 hours.

Carbon sequestration

To estimate the annual atmospheric C sequestration rate of NT and ICL systems we considered the SOC accumulation in the different soil management systems as well as the hidden C equivalent (CE) costs due to tillage operations, fertilization and pesticide use for the whole period of 15 years. CT system was taken as reference for calculation of SOC accumulation and sequestration rates. To calculate CE costs due to tillage operations we considered that each liter of consumed diesel did release 0.8 kg of $C-CO_2$ and each kilogram of applied N, P_2O_5 and K_2O did release 1.3, 0.2 and 0.15 kg of $C-CO_2$ (Lal, 2004). Pesticide use did contribute with 6.3 kg of $C-CO_2$ kg^{-1} of a.i. These costs were individually calculated for each management systems and taken into account to obtain the carbon sequestration rate. In this study, the carbon costs relative to fossil fuel consumed during tillage operations (26 kg CE ha^{-1} y^{-1}) were added to C sequestration rate of NT and ICL systems because it considered the amount of CO_2 that not was released to atmosphere by replacing CT to NT or ICL systems.

Results

Management systems affected the total SOC stocks between 0 to 30 cm and 0 to 100 cm layers (Table 1). The greatest SOC stocks were observed for the NT and ICL systems and the lowest ones for the CT system in both layers. Compared to the CT system, NT and ICL systems did show an SOC stocks increment of 3.2 and 10.1 Mg ha^{-1} in the 0 – 30 cm layer, respectively. In the 0-100 cm layer, these increments decreased to 2.0 Mg ha^{-1} in the NT and increased to 13.7 Mg ha^{-1} in the ICL system. These results have shown the important contribution of conservation management systems to increase SOC stocks in tropical soils as well as in temperate and subtropical soil as reported by studies of Six *et al.* (2002) and Diekow *et al.* (2005). The less oxidative environment and the physical protection mechanism imparted by the stable aggregates support SOC accumulation in soils under NT and ICL, while the mobilization of soil in CT system has lead to its exposure to microbial activity and climate effects (Conceição *et al.*, 2007). The addition of forage residue and their roots in ICL system provided enough input for the accumulation of organic C in deep layers. These results are in agreement with those reported by Noble *et al.* (2008).

Table 1. Stocks and accumulation rates of carbon, equivalent costs and carbon sequestration rates in management systems in the 0-30 and 0-100 cm soil layers.

Management systems	Stocks C	C accumulation rate	C equivalent costs	C sequestration rate
	Mg ha^{-1}	----------------- Mg ha^{-1} ano^{-1} --------------		
----------------------- 0 - 30 cm -------------------------				
CT	52.1 (±11.6)	-	0.074	-
NT	55.3 (±1.0)	0.21	0.126	0.11
ICL	62.2 (±8.5)	0.67	0.033	0.66
----------------------- 0 - 100 cm -----------------------				
CT	102.1 (±15.5)	-	0.074	-
NT	104.1 (±5.9)	0.13	0.126	0.03
ICL	115.8 (±11.6)	0.92	0.033	0.91

CT = conventional tillage; NT = no- till; ICL = integrated crop-livestock.

CE costs were higher in NT systems than in the others management systems (Table 1 and 2). The reason for this was because two crops were cultivated in the NT system needed nitrogen fertilizer (maize and wheat), which had a high carbon cost that reached in a 15-year period about 806 kg C ha^{-1} y^{-1}. ICL showed the lowest CE cost due to the no need of fertilization in the pasture cycle and reduced use of pesticides and fossil fuel. In the total experimental period, the use of herbicide was reduced in the ICL system because cover straw controlled weeds. Total CE were about 126.3, 74.9 and 33.6 kg CE ha^{-1} y^{-1} for NT, CT and ICL, respectively.

The great carbon costs reduced significantly C sequestration rate in NT system, which showed values lower than 0.11 Mg ha^{-1} y^{-1} (Table 1). However, ICL system reached C sequestration rates of about 0.66 and 0.91 Mg ha^{-1} y^{-1} in the 0 - 30 cm and 0 - 100 cm layers, respectively showing that this system can be a good strategy to mitigate green house effects by agriculture. The ICL system in this region contributed to mitigate about 50 Mg CO_2 ha^{-1} in 15 years.

Table 2. Carbon equivalent (CE) costs relative to consumed diesel, fertilizers and pesticides for each management system.

Input	C equivalent cost[2]	Total carbon equivalent cost		
		CT	NT	ICL
	kg CE unit[-1]	---------- kg CE ha^{-1} y[-1] ----------		
Fossil fuel (L)[1]	0.80			
- power harrowing		14.2	0	0
- harrow leveling		11.8	0	0
- sowing		2.6	3.0	2.3
- pesticide application		3.6	3.6	1.8
- harvest		16.0	16.0	8.0
Sub-total		*31.9*	*22.6*	*12.1*
Fertilizers				
- N (kg of N)	1.30	0	53.7	0
- P$_2$O$_5$ (kg of P$_2$O$_5$)	0.20	12.2	17.2	6.2
- K$_2$O (kg of K$_2$O)	0.15	9.2	11.2	4.7
Sub-total		*21.4*	*82.1*	*10.9*
Pesticides (kg of a.i)	6.30	21.6	21.6	10.6
TOTAL		**74.9**	**126.3**	**33.6**

[1]Based in the consumetion of diesel estimated by Portela *et al*. (1980). [2]Based in Lal (2004). CT = conventional tillage; NT = no- till; ICL = integrated crop- livestock.

Conclusion

Integrated crop-livestock systems promotes atmospheric C mitigation by reducing C costs due to tillage operations and fertilization and because it increases soil organic C accumulation in comparison to soils which are conventionally tilled. In crop- livestock systems the soil organic C accumulation occurs also in deep soil layers, affected probably by the use of tropical pasture. The balance of soil C in NT system does not necessarily result in atmospheric C mitigation because the benefits of increasing soil organic C stocks may be counterbalanced or surpassed by the C equivalent costs related to the applied N-based fertilizers.

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Soil organic matter loss following land use change from long-term pasture to arable cropping: Pool size changes and effects on some biological and chemical functions

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Abstract

Effects of tillage on soil organic matter (SOM) and soil functions dependent on SOM (C and N minerization, cation retention) were examined in trial that was established (in 2000) to identify practices that conserve SOM following cultivation of pasture to grow annual crops. During the 2000-07 period, soil C stocks declined by about 12 Mg/ha (a decrease of ~14% compared with pasture). Total soil C stocks were not affected by tillage type (intensive, minimum, no tillage) after seven years of continuous cropping.

The results confirm that mineralization potential can decline by about 50% within a few years of pasture cultivation. This reduction in mineralization potential is large relative to the decline in total C and N (~20%), indicating labile part of SOM depleted. There was little difference in mineralization between tillage treatments or between disturbed and intact soil cores. The results suggest that changes in total and mineralizable organic matter following change in land use were mainly due to change in plant type from perennial grass returning large amounts of OM to the soil in above ground resideues and roots to an annual crop with smaller inputs. The effects of soil disturbance associated with the establishment of the annual crops appear to have only a small effect on toatla and mineralizable OM.

Key Words

Tillage, pasture, carbon, nitrogen, mineralization, disturbance

Introduction

Soil organic matter (SOM) generally makes up a small fraction of the mass of mineral soil, but it can have a profound influence on soil biological and chemical functions. Most of the N in soil is in organic form and the rate at which it mineralizes has a strong influence on N availability to plants. Because SOM has a high density of negatively charged sites compared with mineral material, it makes a disproportionately large contribution to soil cation exchange capacity (CEC). Management-induced changes in SOM could, therefore, have a significant effect on the retention and leaching of cations such as K, Ca, and Mg. The Millenium Tillage Trial was initiated in 2000 at Lincoln, Canterbury, New Zealand to identify tillage and cover crop practices that maintain SOM following the conversion of long-term pasture to arable cropping. The objectives of this paper are to: (1) examine effects of these management practices on total C and N stocks; (2) identify SOM fractions depleted under arable cropping; and (3) quantify effects of management-induced changes in SOM on key soil biological and chemical functions.

Materials and methods

Trial description

Trial was established in spring 2000 on a Wakanui silt loam (immature Pallic soil or Orthic Tenosol) that had been under sheep-grazed ryegrass/clover pasture for >14 years. The trial was designed as a split plot experiment with tillage as main-plot and cover crop (+/- winter forage crops) as sub-plot treatment. Each treatment was replicated three times in an incomplete Latin square. Main plot size was 28 m x 18 m (sub-plots 28 m x 9 m). The tillage treatments were (1) intensive tillage (mouldboard plough to ~20 cm, maxi-till, grub, harrow, roll); (2) minimum tillage (maxi-till, grub, harrow, roll (tillage depth ~ 10 cm)); and (3) no-tillage. All tillage operations were carried out using standard commercial equipment.

Spring-sown main crops (the crop sequence was barley, wheat, pea, barley, pea, barley, barley, barley) were followed by winter cover crops (oats or forage brassicas) or winter fallow (minus cover crop sub-plot). All crops were sown using a Great Plains Direct Drill. Fertiliser (N and P) was applied to the spring crops to ensure these nutrients were not limiting. The spring crops were irrigated using a sprinkler that applied water at approximately 6 mm/h. Irrigation was not usually required for the winter cover crops, but it was occasionally applied at sowing to improve plant establishment. Spring-sown crops were harvested at grain maturity (late summer-early autumn; late January to early March).

Each autumn, a winter forage crop (oat in 2001; forage rape in other years) was sown on the plus cover crop sub-plots with either intensive, minimum, or no-tillage, as described above for the spring crops. The minus cover crop subplots were also cultivated, but no crop was sown (i.e., plots remained fallow over winter). Cover crops were grazed using sheep in spring (prior to spring cultivation). Plots representing the previous land use (i.e., pasture) were included in the trial as a control. To maintain consistency with the trial design, these plots were split into pasture and fallow sub-plots. The fallow sub-plots were maintained plant-free during the experiment using herbicides (i.e., not cultivated) (hereafter this treatment is referred to as "permanent fallow"). The pasture sub-plots were grazed by sheep (typically 10 times per year and 20 sheep per plot), with all animal dung and urine returned to the plots. The pasture and fallow sub-plots were irrigated in summer (water application rate was the same as for the arable crops). Management (irrigation, fertilizer, grazing regime) of the pasture plots remained essentially the same as before the trial.

Changes in soil C and N
Soil samples were collected before initiation of the trial in 2000 and again in 2007 (0-7.5, 7.5-15, 15-25, and 15-30 cm). A total of 7 cores (5 cm diameter) were taken per plot. Bulk density and soil C and N (Leco TruSpec C/N analyzer) were determined in each depth increment. Total stocks of C and N were estimated by the equivalent mass method (Ellert *et al*. 2001) based on a 3500 Mg/ha soil mass (i.e., ~ pasture soil mass to 25 cm depth at the start of the trial). The particle size distribution of C and N in soil samples from the 0-7.5, 7.5-15, and 15-25 cm layers was measured after soil dispersion by ultrasonic vibration. The sand fraction (>50 μm) was separated by sieving and the 20-50, 5-20, and <5 μm fractions were obtained using standard sedimentation methods. The size separates were analyzed for total C and N (Leco TruSpec C/N analyzer).

Exchangeable cations and CEC
Exchangeable cations and CEC were determined using the ammonium acetate method. Exchangeable cations (Ca, Mg, K, Na) extracted in 1 M NH$_4$OAc were measured by inductively coupled plasma spectroscopy. Effective CEC was estimated by summing the exchangeable cations.

Carbon and N mineralization
Intact soil cores (0-15 cm depth; 5 cm diameter) were extracted in spring 2005 when the soil was close to field capacity. Half of the cores were maintained intact while the other half was disturbed by passing the soil through a 4 mm sieve. These disturbed cores were then refilled to the original bulk density (all material retained on the sieve was returned to the soil). The soil cores were incubated in 5.5 L air-tight plastic containers (3 cores per container) for 100 days at 20°C. Carbon dioxide evolution was measured periodically (usually every 2 to 3 days) by determining the concentration of CO$_2$ in air samples removed from the containers using a syringe. After each measurement, the headspace was flushed with air to return the CO$_2$ concentration to ambient levels. Nitrogen mineralized during the 100 day incubation was determined as the difference between post- and pre-incubation mineral N.

Results and discussion
Average-to-good yields of spring-sown main crops were obtained during the experiment with generally little difference between the tillage treatments (data not shown). Although in some years winter cover crop yields were somewhat less under no-tillage (partly due to slug damage), inputs of organic matter to the soil in crop residues are unlikely to have differed much between tillage treatments. As cover crop yields and, by extension, organic matter returns in plant residues and sheep dung were low in many years, there was usually no difference in SOM between the plus and minus cover crop treatments (not shown).

The total mass of C (top 3500 Mg/ha of soil) under pasture in 2007 was 87 Mg/ha (Table 1), slightly higher than the initial value (84 Mg/ha) in 2000. Alter 7 years of continuous cropping, loss of SOM was similar for all tillage treatments (average 12 Mg C/ha). The tillage treatments had lower C concentrations than pasture soil in the top 7.5 cm. Re-distribution of SOM was evident under intensive tillage. This treatment had lower C levels in the top layer but higher levels deeper in the profile compared with minimum and no tillage. Greatest SOM loss was observed in the permanent fallow (~17 Mg C/ha less than pasture in 2007), emphasizing the importance of plant inputs in maintaining SOM. Our results show that, while soil under no tillage may have more organic matter near the soil surface than intensively cultivated land, the total quantity of SOM in the profile may be similar regardless of tillage intensity.

Table 1. Effect of management treatments on C concentrations in the top 25 cm and on total C stocks in 3500 Mg/ha soil mass in 2007. Standard deviations are in parentheses.

Treatment	C concentration (g/kg)			Total C stock (Mg/ha)
	0-7.5 cm	7.5-15 cm	15-25 cm	
Pasture	36 (2.2)	27 (2.2)	19 (1.8)	87.3
Permanent fallow	24 (1.6)	21 (1.3)	16 (0.8)	70.5
Intensive tillage	24 (1.4)	24 (1.4)	22 (1.4)	76.6
Minimum tillage	29 (1.5)	26 (0.7)	17 (1.9)	75.6
No tillage	29 (1.6)	22 (1.2)	16 (2.6)	73.9

Size fractionation data confirmed that SOM was concentrated in the colloidal fraction (<5 µm). However, SOM associated with this fine-sized material changed relatively little following cultivation of pasture. Most of the C lost after cultivation was derived from the > 50 µm fraction, which is commonly referred to as particulate organic matter (POM), and from the 5-20 µm size fraction. Changes in POM-C in response to land use change have been shown previously (Skjemstad *et al*. 2004). The nature of the organic matter in the 5-20 µm fraction requires further investigation, but our preliminary results suggest that at least part of it is POM-like in character.

Organic matter mineralization, measured five years after the start of the trial, did not differ significantly between intact and disturbed cores (Table 2), contrary to the common belief that physical disturbance stimulates microbial activity. Over the 100 day incubation period, C mineralization in pasture soil averaged 3120 kg/ha, compared with only 1150 kg/ha in cropped treatments. The decline in mineralizable C following cultivation was large relative to the change in total C. Effects of tillage treatments on C mineralization were small. As observed for total C (Table 1), the permanent fallow had lowest levels of mineralizable C. Nitrogen mineralization also showed a large decline under arable cropping and, again, there was little difference between tillage treatments. Over the 100 day incubation, pasture soil mineralized about 200 kg N/ha, compared with ~100 kg/ha under arable cropping. Mineralization of N was similar for intact and disturbed cores. The results confirm that the mineralizable fraction of SOM is rapidly depleted after pasture is cultivated. The decline in SOM may, on a large extent, be due to lower organic matter inputs from arable crops vs perennial pasture species. Based on our observations, physical disturbance (cultivation) does not appear to accelerate the decomposition of SOM.

Table 2. Effects of the management treatments on C and N mineralization, measured using intact and disturbed soil cores.

Treatment	C mineralized (kg/ha)		N mineralized (kg/ha)	
	Intact	Disturbed	Intact	Disturbed
Pasture	3015	3221	203	191
Permanent fallow	861	848	76	74
Intensive tillage	1048	1058	88	77
Minimum tillage	1155	1233	93	99
No tillage	1273	1111	111	91
LSD (0.05)	226		28	

The decline in SOM under permanent fallow and arable cropping had a detectable effect on effective CEC and exchangeable cation composition (Table 3). In permanent fallow (C loss of ~17 Mg/ha), there was a decline in total exchangeable cation (Ca + Mg + K + Na) equivalents of 47 $kmol_c$/ha (0-25 cm depth), a decrease of 20% compared with pasture. Loss of cation exchange capacity resulted in selective release of cations with lower affinity for SOM (K, Na, Mg).

Table 3. Effect of management treatments on total amounts of exchangeable cations in the top 0-25 cm soil layer.

Variable	Pasture	Permanent fallow	Intensive tillage	Minimum tillage	No-tillage	LSD (0.05)
Exch. Ca (kg/ha)	3410	2935	3259	3226	3320	449
Exch. Mg (kg/ha)	377	246	290	268	289	55
Exch. K (kg/ha)	836	536	366	357	375	242
Exch. Na (kg/ha)	256	135	164	174	164	46
ΣCa+Mg+K+Na ($kmol_c$/ha)	234	186	203	200	206	

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Soil quality and vegetable growth as affected by organic amendments to a tropical Oxisol during transition to organic farming

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Abstract

Changes in soil properties and vegetable growth were quantified during the transition from conventional to organic farming. Four treatments (2 composts, urea and control) were applied to an Oxisol in Hawaii. Two crops, Chinese cabbage and eggplant were grown sequentially as test crops. Hot-water soluble carbon, dehydrogenase activity and CEC were increased by compost amendments. CO_2 respiration rate did not correlate with the soil amendments. Nitrogen nutrition was the main factor that improved growth and carotenoid content in cabbage. The urea treatment promoted better growth of cabbage, while compost was effective for eggplant, suggesting N from organic inputs requires time to mineralize and to become available to crops.

Key Words

Compost, soil quality, hot-water soluble C, cabbage, eggplant

Introduction

During the transition from conventional to organic farming, N availability may decrease due to a shift in biological activities and N sources could not be immediately available for plant use (Petersen *et al*. 1999). Consequently, crop yields may be lower than those under conventional practices (Mäder *et al.* 2002). Predictably, total soil N would increase with organic amendments, but extractable P and exchangeable K often increased as well (Bhat and Sujatha 2006). Perhaps because of improved soil quality, organically grown crops often contain more vitamins (especially vitamin C), phenolic compounds, and carotenoids than conventionally grown crops (Adam 2001; Rembialkowska 2004). Being in the Tropics, Hawaii's soils are dominantly Oxisols and Ultisols, which are inherently low in plant nutrients. Furthermore, past sugarcane and pineapple cultural practices used large amounts of synthetic N fertilizers, which acidify the soil, decrease effective CEC and basic nutrients (Ca, Mg, K) (Hue *et al*. 2007; Hue 2008). Given such potentially poor growing conditions, tropical soils would be fittingly suitable for evaluating the effects, if any, of organic amendments on soil and crop responses. Thus, this study was conducted to quantify changes in properties of an Oxisol in Hawaii, where vegetables might be grown organically.

Methods

Site location, soil and amendment properties

The trial was conducted on an Oxisol (Rhodic Haplustox, clayey, kaolinitic, isohyperthermic, Wahiawa Series) located at the Poamoho Experiment Station ($21^o32'11"$ N – $157^o56'24"$ W) of the University of Hawaii. The site receives approximately 1000 mm of annual mean precipitation, and is situated 265 m above sea level. The mean temperatures are: 27 ^{o}C in summer (May-September) and 21 ^{o}C in winter (October – April). In the unamended state, the soil has a bulk density of 1.12 Mg/m^3, a cation exchange capacity (CEC) of 11 $cmol_c$/kg as extracted with 1 *M* ammonium acetate, pH 7.0, a soil pH (1:1 in water) of 5.5, 2.2% total organic carbon and 0.2 % total N.

Four treatments were applied and incorporated into the soil to a depth of approximately 15 cm: (1) control (only plowing), (2) urea at 0.50 Mg/ha providing 140 mg N/kg, (3) a redwood- based commercial compost (Rwd compost) having 0.34% N fortified with a composted chicken manure (2.1% N) (total amount of the Rwd compost used was 17 Mg/ha), (4) a University of Hawaii compost (UH compost, 1.0% N) made of grass clippings and tree trimmings, lime and phosphate rock, fortified with the same composted chicken manure (total amount of the UH compost used was 13 Mg/ha). Both treatments (3) and (4) provided approximately 140 mg/kg total N. The plot size was 5 m x 10 m and drip irrigation was used. The experiment had a randomized complete block design with 3 replications per treatment.

Two weeks after treatment and irrigation applications, tomatoes (*Lycopersicon esculentum*) were planted. However, weeds, especially Guinea grass (*Panicum maximum*) became a serious problem, crowding out tomato seedlings, yielding poor stands. For this reason, the tomato crop was removed, and weeds were mechanically

mowed. Subsequently, sunnhemp (*Crotalaria juncea* cv. Tropic Sun) was planted to all plots for 5 weeks, thereafter was plowed under as a green manure. A week later, black plastic sheets were placed on the surface of all plots to control weeds; and Bok Choi cabbage (*Brassica rapa* Chinensis group) were planted. Insects were controlled by periodically spraying with a commercial *Bacillus thuringiensis* (Bt)-derived biocide or with neem (*Azadirachta indica*) oil. The cabbage was harvested 6 weeks later. The soil was then idled for 4 weeks, before eggplant (*Solanum melongena*) was transplanted and grown for 7 weeks as a second crop.

Sampling and chemical analysis
The soil samples were collected after cabbage harvest from all 12 plots by mixing 3 or 4 small cores (1-15 cm depth) taken within each plot. The samples were air dried and screened to pass a 2-mm sieve. Soil pH was measure in 1:1 (soil: water by weight). Mehlich-3 extractable nutrients were measured with an inductively couple plasma spectrometer (AtomScan-16 ICP, Thermo Jarrell-Ash/Fisher Scientific,Waltham, MA), (Mehlich, 1982). Total C and N in soil samples and N in plant samples were measured by dry combustion using a LECO CN-2000 analyzer (Leco Corp., St. Joseph, MI). Other nutrients in plant samples were measured using ICP (Hue *et al.* 2000). Cation exchange capacity was measured as proposed by Sumner and Miller (1996); dehydrogenase activity was measured as proposed by Tabatabai (1982); hot-water soluble carbon was measured by the Mn-pyrophosphate complex method proposed by Bartlett and Ross (1988); total carotenoids in leaves were measured as proposed by Gross, 1991; and soil CO_2 measurement was measured by incubation as described by Zibilske (1994).

All samples were analyzed in triplicate and standard errors were determined. Analysis of Variance was performed to establish the significance ($P < 0.05$) and LSD was used to compare treatment means. Statistical software used was either SAS 9.1 or WinStat (an add-in to MS Excel).

Results
Amendment effects on soil properties
Adding compost or urea to this Oxisol certainly altered many soil properties, especially those representing soil biological and chemical characteristics (Table 1).

Table 1. Soil quality as measured by hot-water soluble C, dehydrogenase activity, CO_2 production, total C, N, and C/N ratio as affected by the additions of urea or composts to an Oxisol of Hawaii.

Treatment	Hot-water C mg/kg	Dehydrogenase mg TPF/kg	CEC cmol$_c$/kg	Total C %	Total N	C/N	CO_2 mg/g/day
Control	180 b	146 b	12.6 b	2.29 b	0.22 b	10.4	0.89 a
Urea	211 b	139 b	11.9 b	2.38 b	0.27 a	8.8	0.93 a
Rwd compost	385 a	192 a	13.7 a	2.82 a	0.26 a	10.8	0.90 a
UH compost	371 a	172 ab	13.9 a	2.27 b	0.22 b	10.3	0.72 b
LSD	129	34	0.84	0.36	0.038	---	0.14

LSD = least significant difference; different letters following numbers within a column indicate differences ($P < 0.05$).

For example, hot-water soluble carbon, increased from 180 mg C/kg in the control to 385 mg C/kg in the Rwd compost. Concentrations of dehydrogenase enzyme activity also increased significantly with the compost treatments and correlated positively with soluble C (Table 2). In contrast, CO_2 production, which ranged from 0.72 to 0.93 mg/g soil/day did not correlate well with any treatments (i.e., compost vs. urea) nor with biological activities. Total organic carbon, ranging from 2.27% to 2.82%, also was not a good indicator of the soil amendments: only the Rwd compost showed a slight increase (Table 1). Total C/N ratio also did not change with the organic inputs, averaging 10.5, but dropped slightly to 8.8 with the addition of urea. Cation exchange capacity (CEC), increased significantly with the additions of compost, being the highest (13.9 cmol$_c$/kg) in the UH compost and lowest in the urea treatment. Regarding soil nutrients that may affect plant growth in the short term, soil test data show that the UH compost significantly increased pH, P, Ca and K (Table 3). Such nutritional enhancements, however, were probably due to the quality of the amendment because the UH compost had lime ($CaCO_3$) and phosphate rock added during its preparation. The addition of the Rwd compost also slightly increased extractable P, K and Fe relative to the control (Table 3). In general, the soil seemed to be marginal (pH 5.5, 30 mg/kg P and 1280 mg/kg Ca as extracted by the Mehlich-3 solution) for crop production, especially vegetables, based on the interpretations for Hawaii soils (Yost *et al.* 2000; Hue and Fox 2009).

Table 2. Correlation among soil-quality indicators after additions of urea or composts to an Oxisol of Hawaii.

Treatment	Hot-water C	Dehydrogenase	CO_2	Total C	CEC
Hot-water C	1	0.93*	-0.54 ns	0.53 ns	0.90*
Dehydrogenase activity	0.93*	1	-0.33 ns	0.71 ns	0.89*
CO_2	-0.54 ns	-0.33 ns	1	0.41 ns	0.70 ns
Total C	0.53 ns	0.71 ns	0.41 ns	1	0.33 ns
CEC	0.90*	0.89*	-0.70 ns	0.33 ns	1

* Significant at $P < 0.05$; ns = non significant.

Soil amendment effects on vegetable growth and leaf nutrients

As a consequence of insect damage, we had to combine all 3 replications of cabbage together to obtain some estimated yields, which ranged from 3.50 Mg/ha in the UH compost treatment to 8.50 Mg/ha in the Rwd compost treatment, with an overall average of 5.68 Mg/ha. On the other hand, nutrient analysis of cabbage leaves shows differences among the treatments (Table 4). Cabbage grown in the two compost treatments had 3.01 and 3.20% N. Interestingly, total carotenoids in cabbage leaves were highest in the urea treatment (125 µg/g), followed by the UH compost (90 µg/g) and lowest in the control (62 µg/g). Perhaps, good N nutrition yielded good growth, which in turn provided higher levels of carotenoids.

Table 3. Soil properties as measured by pH, EC, Mehlich-3 extractable nutrients as affected by additions of urea or composts to an Oxisol of Hawaii.

Treatment	pH	EC	P	Ca	Mg	K	Fe	Mn	Zn
		dS/m	←--mg/kg--------------------→						
Control	5.51	0.23	37	1278	221	190	53	596	18
Std. Err.	0.06	0.02	13	51	30	33	6	40	1.3
Urea	5.74	0.94	30	1806	303	213	44	637	20
Std. Err.	0.11	0.14	10	340	27	28	4	24	5.0
Rwd compost	5.80	0.29	53	1434	264	279	60	593	18
Std. Err.	0.05	0.05	18	245	24	38	6	58	2.1
UH compost	6.23	0.68	200	3718	410	518	44	565	25
Std. Err.	0.19	0.00	19	123	41	75	4	26	3.3

pH and electrical conductivity (EC) were measured in 1:1 soil:water.

Table 4. Total carotenoids and leaf nutrients in Chinese cabbage (*Brassica rapa*, Chinensis group) grown on an Oxisol amended with urea or composts.

Treatment	Carotenoids	N	P	K	Ca	Mg	Fe	Mn	Zn
	µg/g	<--------------------%----------------- >					< ---------µg/g--------->		
Control	62 b	2.80	0.43	5.99	3.19	0.61	109	139	98
Std. Err.		0.47	0.06	0.14	0.32	0.01	4	7	34
Urea	125 a	3.64	0.40	6.01	3.05	0.61	84	175	75
Std. Err.		0.30	0.02	0.32	0.39	0.01	4	28	15
Rwd compost	73 b	3.01	0.43	5.75	3.52	0.62	99	159	73
Std. Err.		0.16	0.04	0.07	0.34	0.02	6	11	7
UH compost	90 ab	3.20	0.43	6.17	2.78	0.56	112	166	69
Std. Err.	LSD = 34	0.20	0.02	0.08	0.33	0.06	19	17	6

LSD = least significant difference; different letters following numbers within a column indicate differences ($P < 0.05$).

After crops were changed from cabbage to eggplant, and leaf insects were controlled by biocides, yields of the second crop were reliably obtained (Table 5). Eggplant yields were highest in the UH compost treatment (5013 kg/ha) followed by the urea, Rwd compost and control, respectively. These fruit fresh weights seemed to correspond well with N nutrition, which was highest in the UH compost treatment (3.80% N), suggesting that N mineralization in this treatment has approached or reached its optimal potential (approximately 6 months after application).

Table 5. Fruit fresh yield and leaf nutrients in eggplant (*Solanum melongena*) grown on an Oxisol amended with urea or composts.

Treatment	Fruit yield Kg/ha	N	P	K	Ca	Mg	Fe	Mn	Zn
		<----------------%---------------------->					< ---------μg/g------>		
Control	3013 b	3.00	0.37	2.52	2.40	0.43	61	147	28
Std. Err.		0.18	0.03	0.36	0.48	0.04	16	23	2.6
Urea	3626 ab	3.48	0.34	2.77	2.86	0.47	86	140	26
Std. Err.		0.21	0.02	0.10	0.21	0.02	31	33	3.5
Rwd compost	2333 b	3.22	0.41	2.79	2.32	0.39	69	143	33
Std. Err.		0.16	0.02	0.16	0.06	0.01	25	16	4.8
UH compost	5013 a	3.80	0.38	2.60	2.51	0.44	143	195	29
Std. Err.	LSD = 1811	0.21	0.03	0.05	0.19	0.05	47	34	2.5

LSD = least significant difference; different letters following numbers within a column indicate difference (P < 0.05).

Conclusion

Switching from conventional to organic farming provide opportunities as well as challenges in getting good crop yields and making profits. These challenges include weeds, insects, and plant nutrient requirements. On the other hand, soil quality as measured by such parameters as hot-water soluble C, dehydrogenase activity, and CEC, was improved by adding organic amendments, especially to low-fertility soils of the Tropics.

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SOM Pools: Fact or fiction, functional or fanciful

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Abstract
There are many models of the dynamics of soil organic matter (SOM) and almost as many ways of conceptualising its composition. But concepts need to be parameterised and model behaviour needs to reproduce reality. Modern methods attempting to measure SOM composition are showing great promise for parameterising these models but one simple approach is often overlooked, using what we already know. For example, the behaviour of SOM under different agricultural systems, for different soil types, or in different regions is often well understood and for a model to be credible, it must reproduce this behaviour. Whilst this is generally accepted, modellers are not always aware of the value of this data for building their model, rather than just for testing their model. It is possible to deduce, *a priori*, the apparent SOM composition from observed changes in measured total C and C:N ratio. Form follows function, or in this case, SOM composition can be deduced from soil behaviour. This is demonstrated using simple deductions applied to a long term dataset to predict changes in SOM and crop productivity.

Key Words
APSIM, simulation, soil organic matter

Introduction
Interest in modelling of soil organic matter (SOM) has been increasing with awareness of its importance for soil health, plant nutrition and the global carbon balance. Many models of SOM processes have been developed and show great promise for describing observed dynamics in natural, forestry and agricultural systems. To describe the nature of the SOM, model developers usually describe the bulk SOM as consisting of a collection of pools, each of which reflects a collection of organic components which behave in a certain manner. Each of these pools often varies from the other pools in terms of its rate of turnover, size and N content. One of the most important decisions of any modeller is how to distribute C and N across these various pools. There is increasing interest in methods to provide direct measures of modelled pools (e.g. Skjemstad *et al*. 2004) and these are showing promise in easing the task of modellers. There is however other information available to model users that should be taken into account. This information revolves around soil function. The behaviour of SOM under different agricultural systems, for different soil types, or in different regions is often well understood. For any model to be credible, it must reproduce this observed behaviour. This is generally accepted. However, modellers are not always aware of the additional value of this data for building their model. This short paper will demonstrate a simple case where the known behaviour of a soil was used to deduce the required parameterisation of a model, *a priori*.

Methods
The model used in this example was the Agricultural Production Systems Simulator (APSIM) (Keating *et al*. 2003). APSIM's component-based design allows individual models to interact via a common communications protocol on a daily time step. Models are available for many major crop, pasture and tree species as well as the main soil processes affecting agricultural systems (e.g. water, C, N and P dynamics, and erosion) (Probert *et al*. 1998). APSIM also provides a flexible agricultural management capability enabling the user to specify complex crop rotations and land management regimes. APSIM Version 7 was used.

Testing of the APSIM modelling capability was undertaken using the detailed data from the cropped catchment within the Brigalow Catchment Study (BCS) (Cowie *et al*. 2007) near Theodore, Queensland, Australia (24.81° S, 149.80° E). This study had been established to investigate the change in catchment water balance and decline in soil fertility after clearing of native Brigalow (*Acacia harpophylla*) forest. Brigalow is a leguminous tree, and soils within these forests contain large amounts of C and N. The data set includes crop production and organic matter decline, runoff and deep drainage and chloride leaching (Radford *et al*. 2007, Thornton *et al*. 2007). The BCS includes data for three soil types occurring within three catchments with contrasting land use (uncleared, pasture, cropping). To simplify this analysis, only the most common soil type (upper clay)(see Cowie *et al*. (2007)) within the cropping catchment has been used. The cropping catchment was cleared in 1982 with the

first crop being planted during the summer of 1984. Crops during the period to March 2005 were wheat (*Triticum aestivum*) and sorghum (*Sorghum bicolor*) and no fertiliser was applied.

Configuration of the model was undertaken using a wide range of available information. Agronomic records of sowing dates, cultivar selection, plant populations, tillage and weed spraying were used to reproduce the historical management. Long term soil moisture measurements were used to infer soil hydrological parameters. Long term air temperature and solar radiation data for the Brigalow Research Station (Australian Meteorological Bureau Station Number 035149) was combined with rainfall from the catchment monitoring station.

The APSIM-SoilN model includes pools to account for fresh organic matter, microbial biomass, humic and inert C within the soil (Probert *et al*. 1998). All default parameters (Probert *et al*. 1998) describing the rates and efficiencies of C flows between pools were retained as these had been previously tested on relevant datasets within the study region. Parameterisation of these soil organic matter pools followed a multi-step process making use of data from a variety of sources. Long term soil C data are available for the BCS (Radford *et al*. 2007) to a depth of 0.3 m (0-0.1, 0.1-0.2, 0.2-0.3 m). This is the depth to which most roots are found in Brigalow forests and to where the majority of C is lost after clearing. Total soil C was partitioned into pools so as to reproduce the two main emergent behaviours of the soil C and N during the BCS: (1) a rapid (~9 years) early phase of C decomposition after clearing of the forest followed by a longer slower decline, and (2) a steady increase in soil C:N ratio over time. The soil C lost during the rapid phase of decomposition would, by definition, need to be assigned to the faster soil pools. It is assumed that this C would be mostly in the form of fresh organic matter in natural systems. The increase in soil C:N ratio is likely to be the result of changes in soil C composition from a system dominated by low C:N ratio labile soil pools, to a state consisting mostly of more resistant or inert pools with higher C:N ratios. The process therefore was as follows:

We assumed that the majority of soil C during the period of slow C decline resides within the inert and humic pools. Crop residues decompose rapidly in these systems and microbial biomass constitutes a small fraction of the total C. If we further assume, that the inert C can be represented by measurements of charcoal C (Skjemstad *et al*. 2004) and that the N content of this pool is low, we can estimate the size and C:N ratio of the humic pool during this later period of decline as the bulk of the N would be contained in the humic pool. Charcoal C was partitioned between the surface layers such that the resultant C:N of the humic pool in each layer was similar. This resulted in an average C:N for the humic pool of 12.8 and this was subsequently applied across the entire soil profile.

The C:N of the humic pool remains constant within the APSIM model as does the amount of inert C. This being the case, the partitioning of the initial soil C can be performed on the basis of the relative value of the bulk soil C:N and the C:N for the humic and fresh organic matter pools. Or put another way, the partitioning of C into various pools of differing N content must reproduce the measured C:N of the soil as a whole. Prior to clearing, large amounts of fresh organic matter would have been present in surface soil within the native plant community. We set the C:N of fresh organic matter to a value of 8 based on the ratio of losses of C and N from the profile and have assumed that much of this material will be lignin from partially decomposed organic matter in a native plant community at a climax state. The C:N of the humic pool is taken from step i above. The parameterisation derived from this logic is shown in Table 1. This configuration should provide a linked decline in soil C and N, and thus the observed change in bulk soil C:N over time as the faster, low C:N pools decline. The final data required for model initialisation concerns the input of C and N to the soil surface after clearing of the native vegetation. Bulldozers were used to fell trees and these were left on the ground for many months before burning, raking of unburnt coarse woody debris, and cultivation (Cowie *et al*. 2007). Surface litter and felled foliage, bark and twigs from standing trees would have been susceptible to decomposition in the period before burning. Coarse woody debris would not have decomposed significantly in the period before it was burned and removed. Measurements of total C and N content of surface litter and standing vegetation have been made for brigalow forests (Moore *et al*. 1967; Dowling *et al*. 1986). From this data we estimate that approximately 40 t ha-1 of biomass with a C:N ratio of approximately 30 would have been on the soil surface subsequent to clearing.

Results
APSIM was able to adequately describe the major processes and resultant changes in soil C and N content within the surface (0-0.3 m) soil layers. The observed and predicted time courses of crop productivity and soil fertility are demonstrated in Figure 1. Clearing of native vegetation resulted in a rapid decline in soil C and N in

the surface 10 cm and these trends are captured by the model (Figure 1a,b). The model was also able to predict the levels of C and N within the soil once the rapid losses of labile material had been completed and the input and decomposition of soil organic matter approached a new equilibrium. Predictions of general productivity are similar to observation though the yields in some seasons showed large discrepancies (Figure 1c). Some of these can be attributed to the impacts of weeds, pests and diseases which are not represented within the model. It is therefore not unexpected that the model would significantly over-predict measurement in some seasons. The impact of declining fertility upon productivity has previously been illustrated using the observed time trends in protein content of wheat grain (Radford *et al.* 2007). A very similar trend can be observed in the measured and predicted wheat grain protein contents (Figure 1d). This gives confidence that impact of declining fertility upon crop growth is being captured by the dynamic model. In general, the emergent behaviour of the soil in terms of C rundown, N mineralisation and subsequent crop productivity has been reproduced by the model.

Conclusion

This paper highlights the issue of parameterisation of SOM models. Whereas others have explored the use of targeted laboratory techniques to parameterise individual soil C pools (Skjemstad *et al.* 2004; Roxburgh *et al.* 2006), we have demonstrated that simple logic applied to emergent soil behaviour can be used in a similar way. Form follows function, or in this case, SOM composition can be deduced from soil behaviour. The choice between these two approaches to parameterising soil C pools is similar to that available in soil hydrology, where soil hydraulic properties can be obtained from laboratory or functional measures. Both approaches are valid (Williams *et al.* 1991). The differing rates of decay of C and N, the resultant changes in soil C:N ratio, and the decline in crop productivity are all well understood for these systems and so model parameterisation should take all these factors into account in a simple yet meaningful way. For example, failure to account for the changes in N mineralisation with changing soil C composition will impact upon predictions of crop production, which is the source of C input into the soil. Modelling of soil C and N should combine attempts to measure soil C composition with considerations of soil function and the method employed above provides a framework for such considerations.

Table 1. **Initial C and N pools (kg ha^{-1}) for layers in the surface 0.3 m.**

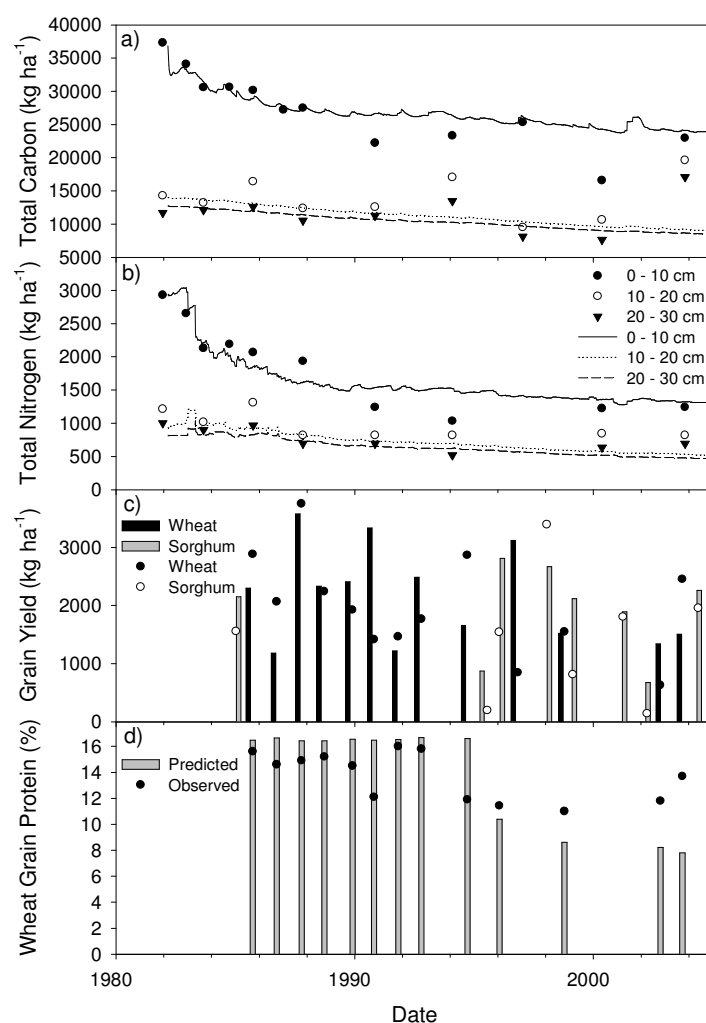|	0-0.1 m	Depth 0.1-0.2 m	0.2-0.3 m	Total
Carbon (kg ha^{-1})				
Inert	7590	2460	2600	12650
Humic	17348	10933	9556	37837
Microbial	867	546	477	1890
FOM	11600	94	92	11786
Total	37405	14033	12725	64163
Nitrogen (kg ha^{-1})				
Humic	1355	854	746	2955
Microbial	108	68	59	235
FOM	1450	2	2	1454
Total	2913	924	807	4644

Figure 1. Observed and predicted time courses of a) soil carbon and b) total soil nitrogen (observed as symbols and predicted as lines, see legend) as well as c) grain yield and d) wheat grain protein content (observed as symbols, predicted as bars).

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Specific response of soil fungi and bacteria to carbon availability indicated by the transformation dynamics of soil amino sugars

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Abstract

Microorganisms in terrestrial ecosystems are usually in dormancy due to carbon starvation. Labile carbon sources enhance microbial assimilation of extraneous N but carbon availability regulates the specific response of fungus and bacterium populations as well as the community structure of the microbiota. The dynamics of ^{15}N incorporation into fungus-derived glucosamine (GluN) and bacterium-originated muramic acid (MurN) can reflect the ever-active response of these two populations during the immobilization of extraneous $^{15}N-NH_4^+$. For glucose amendment, the more rapid ^{15}N transformation into MurN than GluN indicated that bacteria were more competitive initially than fungi, but the successional growth of fungi was dominant over time, resulting in the continuous increase of ^{15}N enrichment in GluN. However, the addition of maize stalk was of more benefit to the reproduction of fungi and retarded the rapid growth of bacteria in soil, thus the ^{15}N enrichment in GluN and MurN was increased initially and then became stable. After being incubated with maize stalks for 18 weeks, the assimilation capacity of reproduced fungi to simple substrates was enhanced while that of bacteria was weakened in soil microcosms. The findings indicate that soil fungi and bacteria respond to different carbon sources specifically.

Key Words

Amino sugar, ^{15}N transformation, carbon availability, bacterium and fungus, response

Introduction

Native microorganisms in terrestrial ecosystems are usually in dormancy and restricted in reproduction mostly due to carbon deficiency (Mondini *et al*., 2006). Therefore, the assimilation of nutrients, especially N by soil microorganisms is highly depended on carbon availability (Paul and Clark, 1996). If large amounts of inorganic N remained in soil, there would be an environmental risk due to N losses. Labile carbon sources enhance microbial assimilation of extraneous N but the carbon availability regulates the specific, response of fungus and bacterium populations as well as the community structure of the microbiota (Brant *et al*., 2006; Schneckenberger *et al*., 2008; Rasul *et al*., 2009). Because amino sugars are recognized as microbial residue biomarkers with heterogeneity, i.e., muramic acid (MurN) is uniquely derived from bacteria and glucosamine (MurN) is mainly of fungus origin (Parsons, 1981; Zhang *et al*., 1999), the dynamics of inorganic N incorporation into these two compounds can reflect the ever-active response of different communities to the added nitrogen. However, this can only be done when newly incorporated N (labeled) can be differentiated from soil inherent N (unlabeled) by the isotope tracing technique (He et al., 2006). Therefore, laboratory incubations with ^{15}N-labeled ammonium were conducted with addition of either glucose or maize stalk as carbon sources. The ^{15}N enrichment in GluN and MurN was traced periodically and the specific response of bacteria and fungi to different carbon availability was evaluated.

Methods

Soil and incubations

A fresh surface (0-20 cm) Mollisol sample was collected from Gongzhuling, Jilin Province, China (124º48´E, 43º30´N) and sieved to <2 mm. Portions of soil were weighed into plastic containers and $^{15}NH_4^+$ solution was added once a week at 0.1 mg N/g soil each time. For the organic material amendment, maize stalk (<2 mm, 452 mg C/g) was mixed initially with soil samples at the weight percentage of 4%, while for glucose amendment, glucose was added at 1 mg C/g soil together with $^{15}NH_4^+$ once a week till the 18th week to ensure equal carbon input between the two treatments. The incubated soils were sampled after 1, 2, 4, 6, 9, 12, 15 and 18 weeks, respectively.

In the other incubation, the soil sample was first incubated with NH_4^+ addition once a week with maize stalk as the carbon source. After 18 weeks, glucose plus $^{15}NH_4^+$ was added into the microcosm once a week and the incubated soils were sampled after 1, 2, 4, 6 and 9 weeks, respectively.

Analysis of soil amino sugars and the determination of ^{15}N enrichment
The air-dried soil samples were ground to <0.25 mm and the pretreatments of amino sugars including hydrolyses, purification and derivatization were conducted using the method of Zhang & Amelung (1996). The amino sugar derivatives were separated on a DB-5MS column and the ^{15}N incorporation into individual amino sugars was identified by gas chromatography/mass spectrometry (GC/MS) (He et al, 2006).

Calculations and statistic analysis
The ^{15}N enrichment in each amino sugar was expressed by the term of atom percentage excess (APE) and calculated as follows:

$$APE = (Re - Rc)/[1 + (Re - Rc)] \times 100$$

Where Re is the isotope ratio of incubated samples and $Re = [A_{(F+1)}/A_{(F)}]$ (A is the area of the selected ion). Rc represents the corresponding ratio obtained from original samples analyzed on the same GC/MS assay (He *et al*., 2006).
The effect of carbon availability on the ^{15}N enrichment of individual amino sugars at different sampling time was analyzed using a one-way analysis of variance (ANOVA) and LSD method at a 95% confidence level.

Results

Specific response of fungus- and bacterium-derived amino sugar to different C sources
When glucose plus ^{15}N-labeled NH_4^+ was added into the soil samples in a week, the ^{15}N enrichment in MurN increased rapidly and then tended to reach the maximal level of 42 after 9 week incubation. The extraneous ^{15}N incorporation into bacterial MurN was more rapid at the first week in maize stalk amendment and showed no significant difference compared with that in glucose amendment (P>0.05). However, the plateau of ^{15}N enrichment in MurN was found shortly after the incubation with the value less than 13 for maize stalk treatment. The ^{15}N enrichment for fungal GluN increased also for glucose amendment but the velocity and magnitude were much lower than those for MurN. The transformation from $^{15}NH_4^+$ into GluN for the first two weeks was more rapid for the maize stalk amendment than for the glucose treatment and it became stable after 9-week incubation with the maximal magnitude of 15%, which was much lower than that for the glucose amendment (Figure 1). Interestingly, there were different responses of fungal and bacterial amino sugars to different C source addition.
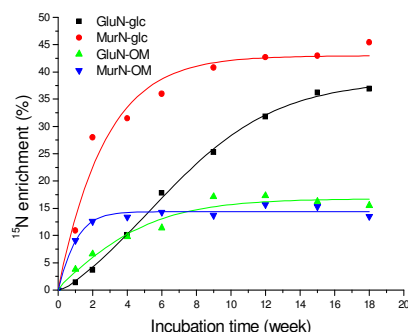

Figure 1. [15]N enrichment of muramic acid (MurN) and glucosamine (GluN) during incubations amended with maize stalk (OM) or glucose (glc).
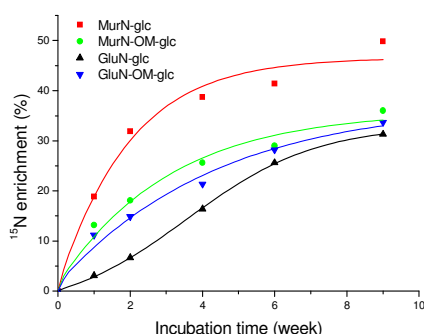
Figure 2. [15]N enrichment of muramic acid (MurN) and glucosamine (GluN) after glucose-$^{15}NH_4^+$ addition into the soil microcosm amended with maize stalk (OM-glc).

Specific response of fungus- and bacterium-derived amino sugars to the change of C source
When glucose plus $^{15}NH_4^+$ was added into the soil samples having been incubated with maize stalk and NH_4^+, the ^{15}N enrichment in both MurN and GluN was increased rapidly the first 4 weeks and then tended to become stable. In this case, the magnitude of ^{15}N enrichment between the two compounds showed no significant difference during the whole incubation (P>0.05). Compared with the incubation with glucose addition initially, the ^{15}N incorporation into bacterial MurN was decreased significantly (P<0.05); whereas, the ^{15}N enrichment for fungal GluN was significantly higher, especially before the first 6 weeks (P<0.05).

Conclusion

The availability of C sources determined the microbial immobilization of extraneous N and the specific response of bacteria and fungi as well as the changes in the community structure was indicated by the ^{15}N enrichment dynamics of heterogeneous amino sugars. Active carbon, for instance, glucose and the labile components including soluble saccharide, organic acids and amino acids released from maize stalk, enhanced

nitrogen assimilation and the transformation of the structural compounds; whereas, the recalcitrant carbon in organic residue can only enable survival of the microorganisms in soil matrices and thus the nutrient transformation was restricted. The significant higher 15N enrichment of MurN than GluN for glucose amendment reflected explicitly that bacteria were more competitive initially than fungi to assimilate the substrate of high availability, but the successional growth of fungi was dominant over time. However, in the maize stalk amendment, the nutrient competition between bacterium and fungus populations was diminished because fungi have higher ability to span microsites and decompose more recalcitrant substrates to compensate intensive carbon requirement, leading to the relatively retarded growth of bacteria. Therefore, the less available substrate of crop residue was of more benefit to the biodiversity of soil microorganisms, especially the reproduction of fungi in the soil microcosms. As a result, the assimilation capacity of the stimulated fungi to simple substrates was enhanced while that of bacteria was weakened. The findings indicate that soil fungi and bacteria respond to different C sources specifically. In order to reduce the environmental risk of extraneous N losses from both agricultural and natural ecosystems, enough C sources with different availability should remain.

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The agronomic utilisation of organic soil amendments

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Abstract
Organic amendments are becoming more commonly used in Australian agriculture despite a lack of scientific research to support the claims of manufacturers or to guide land managers in their application. These products have an influence on the carbon cycle in the soil in that they can be both a source of carbon and increase the rate of nutrient and carbon mineralisation in the soil. Three organic amendments, a seaweed extract (SWE), a liquid meat, blood and bone (LMBB) and a liquid humate (LH), were applied at two rates at the start of three consecutive cropping seasons in a complete randomised block design, in two fields in the Trangie area of the Macquarie Valley, situated in central western NSW, Australia. Soil samples were regularly collected from the experimental fields and analysed for microbial biomass, total carbon and resilient carbon (<53 µm soil fraction). Results indicate that there may be a stimulation of microbial biomass in the soil, potentially causing a decrease in total carbon content, but an increase in resilient carbon.

Key Words
Microbial biomass, soil carbon, seaweed extract, humates, meat blood and bone meal

Introduction
Research has shown that the application of organic amendments can influence soil biological processes, soil carbon pools and the performance of crops (Atiyeh *et al.* 2002; Mondini *et al.* 2008; Rathore *et al.* 2009). However, there is a lack of scientific research into the utilisation of these products in broadacre agriculture in Australia. The available findings in scientific literature suggest that to perceive the benefits of organic amendments, the application rates must be significantly higher than those suggested by the manufacturers (Edmeades 2002). However, some of these products may potentially help improve or sustain soil health at relatively low application rates, through stimulating biological activity, enhancing nutrient and carbon cycling in the soil and potentially increasing the amount of organic carbon in the soil. The aim of this work is to identify any changes to soil carbon, structural and biological properties resulting from the addition of a number of organic amendments to the standard inputs of conventional broadacre irrigated agriculture.

Methods
Products were applied prior to planting each season for three consecutive growing seasons at two rates in a randomised complete block design in two fields in the area around Trangie in central western NSW. The fields were located on two properties, Byron and Buddah. The soil at Buddah is a grey vertosol, while the soil at Byron is a brown chromosol. SWE was applied at 20 and 40 L ha^{-1}, LMBB at 30 and 60 L ha^{-1}, and LH at 5 and 10 L ha^{-1}. The products were applied as an additional input to the standard operations of the farms. Soil samples were collected from 0 to 50 mm depth prior to harvest in the first two seasons and prior to the application of organic amendments and at monthly intervals during the third season. Samples were analysed for microbial biomass carbon (MBC), using a chloroform fumigation (Sparling *et al.* 1993), and for total carbon content, using an Elementar VarioMax CNS Analyser. Plant performance indictors, including boll retention in cotton, will be collected during and at the end of the third season of the field experiment.

Results
No significant difference in any of the measured soil properties was observed between the treatments. A rate effect was observed for both LMBB and the SWE, with both these showing an increase in microbial biomass with increasing application rates in November 2008 and September 2009 for LMBB (Figure 1). The higher application rate of 40 L ha^{-1} of SWE showed a lower microbial biomass in 2008 than at the rate of 20 L ha^{-1}, while in 2009 this result was reversed (Figure 1). In 2008 the LH treatment resulted in a greater microbial biomass for the higher application rate of 10 L ha^{-1} compared to the LH applied at 5 L ha^{-1} with the reverse occurring in 2009 where the lower rate had the greater microbial biomass.
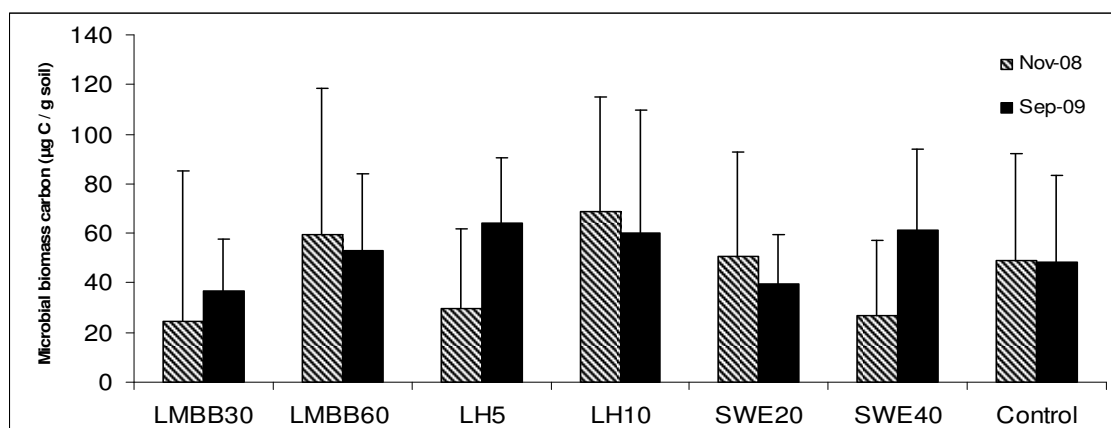
Figure 1. Microbial biomass carbon from soil samples collected from the Byron experimental field. November 2008 samples collected six months after the application of organic amendments and two weeks prior to harvest. September 2009 samples collected eight weeks after the application of organic amendments. LMBB30: liquid meat, blood and bone at 30 L ha^{-1}; LMBB60: liquid meat, blood and bone at 30 L ha^{-1}; LH5: Liquid humate at 5 L ha^{-1}; LH10: Liquid humate at 10 L ha^{-1}; SWE20: seaweed extract at 20 L ha^{-1}; SWE40: seaweed extract at 40 L ha^{-1}.

Although no significant difference in tillering was observed in September 2009, tillering was higher in all treated plots (Figure 2). Similarly, although not significant an increase in average plant height in treated experimental plots was observed in September 2009 (Figure 2). Results are pending, to be completed by December 2009, for MBC, total and resilient soil carbon and crop yields for both experimental fields.
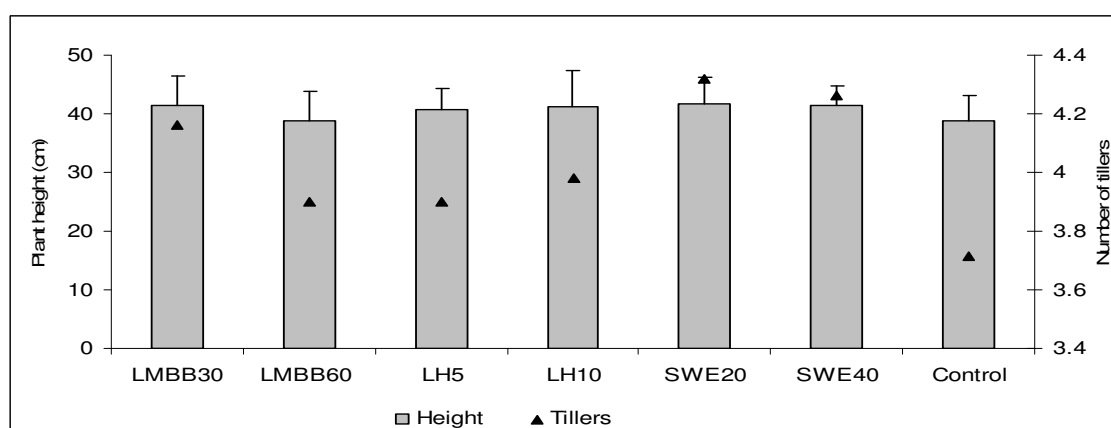

Figure 2. Wheat plant heights and average number of tillers per plant from the experimental field at Byron in September 2009 eight weeks after application of organic amendments. LMBB30: liquid meat, blood and bone at 30 L ha^{-1}; LMBB60: liquid meat, blood and bone at 30 L ha^{-1}; LH5: Liquid humate at 5 L ha^{-1}; LH10: Liquid humate at 10 L ha^{-1}; SWE20: seaweed extract at 20 L ha^{-1}; SWE40: seaweed extract at 40 L ha^{-1}.

Discussion

The application of organic amendments appears to have a rather transient influence on microbial biomass. However, this has an influence on the total carbon content, potentially influencing the amount of resilient carbon in the soil. The stimulation of microbial activity and increased biomass resulting from the application of organic amendments is a common finding in research (Marinari *et al.* 2007; Mondini *et al.* 2008). The results of this study suggest that the application of organic amendments may increase the level of microbial activity in the soil, and that this effect increases with increasing rates of application. However, the application of both the SWE and the LH appeared to have the opposite effect in September 2009 compared to November 2008.

Of the three organic amendments utilised in this research, LMBB is has the greatest nutrient potential, containing approximately 8% nitrogen. The manufacturers of the SWE claim that it contains less than 0.1% nitrogen and the LH less than 0.5%. This would suggest that the increase in plant height and tillering resulting from the application of LMBB is possibly due to the nutritive effects of the organic amendment, while those resulting from the SWE and LH could possibly be related to plant-growth promoting activity of these amendments. The application of SWE aims to increase plant biomass through the actions of the plant-growth promoting hormones cytokinin and auxins, which are present in this type of product (Rathore *et al.* 2009). The activity of humic molecules has also been shown to have a similar influence on some crops (Eyheraguibel *et al.*

2008) and thus may be responsible for the increased height and tillering of the wheat. However, the application of the LH may also have resulted in an improvement in soil structural condition, which may have led to enhanced plant performance. Results pending will determine the structural condition, total carbon content and resilient carbon content of the soil from 0 to 50 mm depth.

Conclusion

Although pending results are critical to drawing conclusions from this research, the findings thus far indicate that the application of organic amendments as an additional input to conventional irrigated farming systems can result in improved crop performance. The stimulation of microbial activity may lead to an increase in the rate of mineralisation occurring and the rate of organic matter decomposition occurring in the soil. If adequate organic matter is not available to microbial species as a source of carbon, there is the potential that the more resilient forms of carbon in the soil may be utilised, thus leading to a decline in soil carbon content over time. This is most likely to occur where the organic amendments provide a source of easily available energy to microorganisms, such as LMBB. If properly managed there is also the potential to increase the amount of stable humic substances in the soil through increased decomposition of organic matter. The application of organic amendments must therefore be further investigated to ensure that they do not lead to a decline in soil health.

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The composition and diversity of prokaryotic and eukaryotic communities from an Australian Vertisol: An experimental study

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Abstract
Biological diversity in soils has been linked to many functional processes. A conjoint measurement of biodiversity of all three Domains (Archaea, Bacteria and Eukarya) has seldom been attempted in soils. We measured biodiversity of bacteria and eukarya (fungi, micro- and mesofauna) under controlled laboratory conditions, studying the dynamics of a detrital food web in a self-mulching Vertisol from New South Wales, Australia. Previous site use history (including vetch in the rotation) had a greater impact on biotic diversity than short-term additions of stubble.

Key Words
Soil food web, biodiversity,16S rRNA, prokaryotes, eukaryotes, microfauna

Introduction
Soil disturbances caused by natural or human activities have direct impacts on ecosystem properties and function, such as nutrient cycling and physical and chemical complexity. Soil, one of the largest reservoirs for bacteria on earth, and its processes are greatly influenced by bacterial, fungal and faunal community structure, activity, and stability (Whitman *et al.* 1998; Coleman & Whitman 2005). The use of molecular, culture-independent based techniques has led to a new understanding of microbial diversity (Hugenholtz *et al.* 1998; Janssen 2006). Most approaches exploit sequence variation in the small subunit of the ribosomal RNA gene (ssu rRNA). Using DNA extracted from whole soil communities, ssu rRNA sequence variation can be used to rapidly profile the community structure and diversity within each of the three domains (DGGE, TRFLP, SSCP, ARISA etc). Detailed analysis of near full-length ssu rRNA gene clone library sequences can then be used to determine the composition of species within soil microbial environments, an essential step towards understanding the role of these communities and their effects on ecosystem processes.

Detrital food webs have been analyzed in a wide range of soils and ecosystem types. Many of these have been described and analyzed in agricultural and forested lands, usually in heavily-textured soils, such as sandy loams or loamy sands in Alfisols, Mollisols, and occasionally in Ultisols (Wardle 2002; Coleman *et al.* 2004). To our knowledge, no detrital food-webs have been investigated in heavy clay soils, such as self-mulching Vertisols. To identify differences in the composition and diversity of the bacterial and eukaryotic communities in an agricultural soil, we carried out a study using a self-mulching Vertisol from eastern New South Wales, Australia.

The objective of this study was to measure the prokaryotic and eukaryotic diversity in an Australian Vertisol that had varying previous histories of land-use. In pursuing this study, we hypothesized that treatments that had vetch grown in the crop rotation would have more available organic and inorganic N, and this would be reflected in a more speciose array of bacteria, fungi and soil micro- and mesofauna as well.

Methods
Soil and site description
Vertisol soils were taken from two field sites at the Australian Cotton Research Centre, Narrabri, NSW. The previous history of the sites was as follows: one site had cotton-wheat-cotton (designated cwc) in summer-winter rotation. The other field had cotton-wheat-vetch-cotton rotation (designated cwvc). Samples (10kg apiece, of 0-10 cm soils) were shipped to Adelaide, sieved and air dried before use. The pH was near neutral, soil organic carbon ranged from 0.95 to 1.03 % in the two treatments. Total nitrate-N for the cwvc treatment was 50 mg/kg, while the cwc rotation was nearly 142 mg/kg. All other inorganic characteristics were very similar.

Handling of soil, setup of the experiment
Triplicate samples of each soil type were set up in 5 cm. dia x 5 cm depth PVC cores to a bulk density of 1.2 in four permutations: cwc soil alone; cwc soil with 1 g. wheat stubble sprinkled on top of it (cwcs); cwvc soil alone; cwvc soil with 1 g. wheat stubble on top (cwvcs). Replicate cores were moistened to field moisture capacity and maintained there, and others were subjected to a wetting and drying regime.

Soil DNA extraction
Samples of soil from individual cores were taken at the end of the experiment (40 d) and mixed community DNA was extracted from duplicate 0.4 g soil samples using the MoBio UltraClean soil DNA extraction kit (MoBio Laboratories, CA). Mechanical disruption via bead-beating (FastPrep FP100; Bio101) was used to increase recovery of DNA from the heavy-textured soil. Following DNA extraction, the duplicate aliquots of DNA were combined giving a final volume of 100uL in Tris-buffer. The bacterial cultures were re-grown at the UGA sequencing facility for isolation of plasmid DNA and the 16S rRNA gene inserts were partially sequenced using the primer 27F. Quality checks of the sequences, editing, chimera analyses, and alignments were carried out as described in Jangid *et al.* (2008).

Fungal PCR-DGGE
DGGE was used separate the mixture of fungal sequences within the PCR based on sequence variability (binding strength) and used the Ingeny phorU system (Ingeny International, The Netherlands).

Extraction and enumeration of the soil mesofauna
Protists were identified in dilution-well plates with inverted microscopy, using bacterial (*Pseudomonas* sp.) broths to feed the protozoans. Nematodes were extracted in modified Baermann funnels over 48 h and preserved in 4% formalin (Coleman *et al.* 1999). They were counted in trophic groups and analyzed accordingly.

Results
Bacterial diversity, 16S rRNA gene libraries
We sampled four soil treatments, with three replicates taken per treatment for a total of twelve*.,* Between 70-80 clones from the 16S rRNA gene library for each soil sample resulted in good quality sequences (Table 1). Our low PCR cycle amplification resulted in a very low frequency of chimeric sequences, a total of 14, amongst the 937 sequences analyzed, resulting in a total of 923 sequences (Table 1) that were analyzed further. LIBSHUFF comparisons of the replicate libraries indicated no significant difference between them. Thus, the methods for extracting DNA and cloning were reproducible, and the samples generally appeared to be representative of each site. However, all three replicates of cwc were different, $p = 0.002$. Sequences from the replica cores were then combined for further analyses. Because all libraries contained sequences from bacterial groups that were difficult to lyse (e.g., *Actinobacteria*), cell lysis during the extraction was considered complete.

Phylogenic groups represented in clone libraries
Close to one-half of the sequences within each library were only distantly related to cultured organisms. These clones were placed by RDPquery into the "unclassified" group (Table 1), indicating that they possessed less than 80 % sequence similarity to a sequence from a type stain in the RDP database.

In spite of their low similarity to genes from cultured organisms, many of these clones were closely related to other environmental clones obtained from soil. Thus, the composition of these libraries was similar to that found in other soil communities, and these communities are well represented in the data bases. The large number of unclassified clones was due to poor representation of soil bacteria among the type strains in culture collections. Many of these clones represented deep branches of phyla with only a few cultured representatives, such as *Acidobacteria*, *Nitrospira* and *Chloroflexi*.
For clones that were classified by RDPquery, the most abundant phylum was *Proteobacteria*, which consisted of 37% of the total number of clones (Table 1). Amongst them, the *β-Proteobacteria* was the largest proteobacterial group within all the libraries (12%) and included clones similar to many common soil bacteria, such as nitrifying bacteria and *Rhizobiaceae*. The second most abundant phylogenetic group was *Firmicutes*, with about 19% of clones. The third most abundant phylum was *Acidobacteria*. The fourth largest phylum, 8.6% of clones, represented another well known soil group, *Bacteroidetes*. The remaining phyla present within the libraries included *Planctomycetes*, *Verrucomicrobia*, and *Gemmatimonadetes*. Each consisted of less than 3% of the clones.

Table 1. Australian Vertisol microbial analyses, showing Taxa and experimental treatments: 1-3 = soil alone; 4-6 = soil plus straw; 10-12 = vetch soil alone; 13-15 = vetch soil plus straw.

Phylum	Treatments												
	1	**2**	**3**	4	5	6	**10**	**11**	**12**	13	14	15	
Acidobacteria	**11**	**4**	**9**	5	9	8	**13**	**7**	**13**	12	9	7	
Actinobacteria	**5**	**5**	**8**	9	9	3	**7**	**11**	**5**	5	4	6	
Bacteroidetes	**4**	**9**	**3**	10	11	9	**3**	**6**	**4**	4	8	9	
Firmicutes	**2**	**0**	**1**	2	2	1	**2**	**1**	**0**	0	0	0	
Gemmatimonadetes	**3**	**5**	**3**	6	4	2	**3**	**1**	**2**	2	1	2	
Alphaproteobacteria	**8**	**5**	**10**	19	8	8	**3**	**1**	**2**	2	13	8	
Betaproteobacteria	**8**	**6**	**5**	9	8	7	**16**	**3**	**15**	15	7	12	
Deltaproteobacteria	**4**	**3**	**3**	3	1	6	**3**	**0**	**4**	3	1	4	
Gammaproteobacteria	**6**	**5**	**5**	5	3	9	**3**	**8**	**2**	2	3	3	
Unclassified Proteobacteria	**4**	**2**	**4**	2	4	2	**6**	**1**	**6**	8	8	6	
Verrucomicrobia	**2**	**4**	**5**	2	4	1	**1**	**5**	**0**	0	2	0	
Others	**25**	**23**	**28**	12	19	13	**16**	**27**	**26**	23	14	22	
Total (all taxa)	**82**	**71**	**84**	84	82	69	**76**	**71**	**79**	76	70	79	923

Diversity indices
The soil bacterial community was very diverse. The Shannon indices for each library were 0.88-0.93 of their maximum values, and the Chao1 estimators were much higher than the number of sequences examined. Similarly, the rarefaction curves failed to plateau, even when similar libraries were combined. For these reasons, the libraries only sampled a small portion of the bacterial diversity present in the samples.

Fungal numbers and diversity
Crop and stubble treatments significantly (p <0.001) affected fungal community structure (data not shown).

Mesofaunal numbers and diversity
Nematodes were more diverse in soils with a previous history of vetch in the field rotation history; only stubble treatments in wetting-drying regimes were significantly separated (Figure 1).
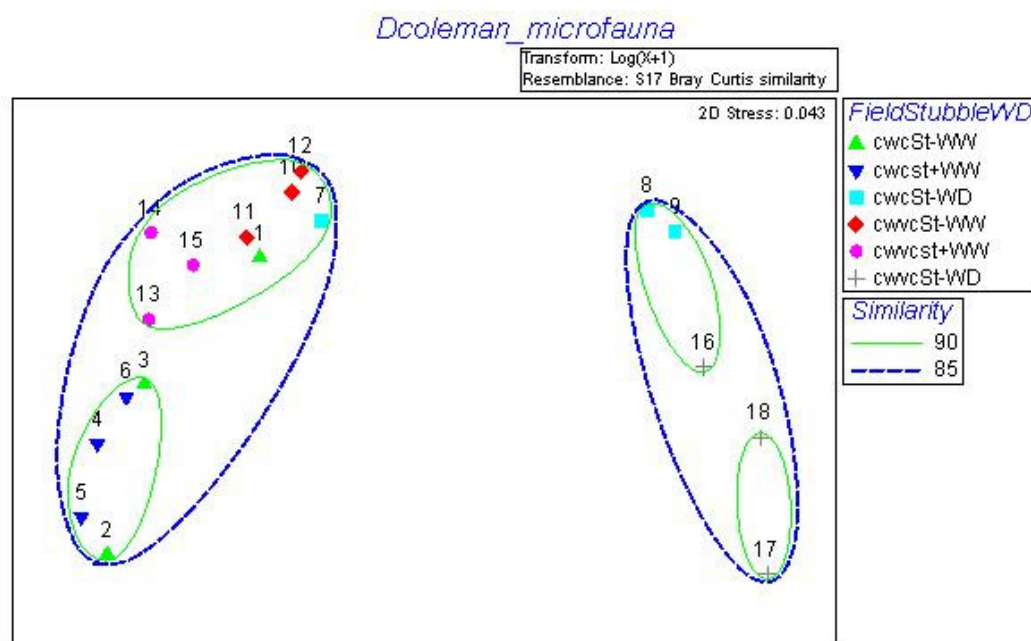

Figure 1. PCA-plots of nematodes in Narrabri Vertisol microcosms.

Conclusion
The Rep Clones that were significantly greater (p< 0.01) in the vetch rotation were: Proteobacteria-Betaproteobacteria and Proteobacteria-unclassified bacteria. Proteobacteria-Alphaproteobacteria, and Gemmatimonadetes. Only Bacteroidetes and Alphaproteobacteria were significantly lower in straw-amended soils. Site history seems to have greater influence than short-term carbon additions in these experimental conditions.

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The mean turnover time of biochar in soil varies depending on biomass source and pyrolysis temperature

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Abstract

The rate of turnover (decomposition) of biochar carbon (C) is the major determinant of its value in long-term C sequestration in soil. However, little research has been undertaken to quantify the mean turnover time of biochar applied to soil and its effect on 'native' soil C. In order to precisely quantify the magnitude and rate at which biochar C is decomposed in soil and released as CO_2, we have initiated a long-term incubation experiment using a novel method based on measuring the inherent differences in $\delta^{13}C$ signature between biochar and soil. Briefly, biochars from a range of C_3-biomass sources (bluegum wood and leaves, paper sludge, poultry manure on rice hull, and cow manure) produced at different temperatures (400°C or 550°C) and activation level (activated or non-activated), were applied to a clay-rich soil (Vertisol) from a C_4-pasture (*Astrebla* spp.) field. Soil-respired CO_2-C and microbial-C and their associated $\delta^{13}C$ values have been measured over 2.3 years to date, and are continuing. Results show decomposition of biochar C varied depending on biomass source and pyrolysis temperature and only 0.3% to 6.0% of the applied biochar C was decomposed in the first 2.3 years of incubation. Biochar application enhanced decomposition of 'native' soil C; this priming effect on soil C was higher in soil amended with leaf or poultry manure biochars than wood biochars. Microbial biomass C was not affected by the biochar treatments, except for the low-temperature poultry manure biochar treatment which significantly increased microbial biomass C as compared to the control. Our estimates of mean turnover time of biochar-C, determined by fitting the two-pool kinetic model to the cumulative CO_2-C evolved under ideal conditions in the laboratory, ranged from approximately 100 to 1300 years between biochar types. The low-temperature (400°C) manure biochars decomposed substantially more quickly than the high-temperature (550°C) biochars.

Key Words

Biochar carbon turnover, soil carbon turnover, natural ^{13}C abundance, microbial biomass, priming

Introduction

There is growing interest in the use of biochar (black C) as a soil amendment, with potential to increase soil C, improve soil properties, reduce greenhouse gas (GHG) emissions, and enhance agricultural productivity. Because the pyrolysis process produces biochar that can provide long-term C sequestration in soil, and also generates renewable bioenergy, it is said to be a "carbon negative" process (removing more CO_2 from the atmosphere than is emitted). Desktop calculations of whole of life GHG balance of biochar production and utilisation for a range of biochar scenarios, compared with conventional practices, have shown that biochar C turnover rate is one of the major factors affecting the GHG mitigation value of its application to soil (Cowie, unpublished). Review of the literature has indicated that very little is known about turnover rate of naturally-produced or manufactured biochar (e.g. Schmidt and Noack, 2000; Lehman *et al*., 2006). The biochar remaining in soil following fire events in natural and managed ecosystems (black C) is considered an inert pool of soil C (i.e. highly resistant to biological degradation), which could accumulate over the course of centuries or millennia. Because of its long residence time, black C is considered to play a vital role in long-term sequestration of C in soil (Skjemstad *et al*., 2001; Preston and Schmidt, 2006). It is likely that manufactured biochar will have similarly slow turnover time when applied to soil. However, contradictory degradation rates of both (natural and manufactured) biochar types have been reported in the literature (Bird *et al*., 1999; Hamer *et al*., 2004; Kuzyakov *et al*., 2009). The recalcitrance of biochar against biological degradation also is likely to depend on pyrolysis temperature. For example, the aromaticity of biochar has been shown to increase with increasing production temperature (Baldock and Smernik, 2002). Clearly, research is needed to accurately quantify mean turnover time and understand stabilisation mechanisms of biochar C in soil. For the present study, biochars from a range of C_3-vegetation sources ($\delta^{13}C$ ~ -22 to -29 ‰) were incorporated into a clay-rich soil (Vertisol) collected from a paddock under C_4-vegetation (Mitchell grass, *Astrebla* spp., with $\delta^{13}C$ ~ -14 ‰) and are being incubated for up to 5 years. In this paper, we report the results obtained in the first 2.3 years of incubation.

Methods

Soil and biochar material and their preparation for incubation

Soil for this study was collected from a paddock (top 10 cm depth) at Toorak Research Station (TRS) in Julia Creek (Queensland) (21°016′S, 141°784′E). The soil is classified as a Vertisol and contains 0.42% organic C and -14.1‰ $\delta^{13}C$ signature (Table 1). Biochars from a range of C_3-biomass sources (blue gum wood and leaves, paper sludge, poultry manure on rice hull, and cow manure) were prepared at different temperatures (400ºC or 550ºC) and activation level (activated or non-activated) (Table 1) by Best Energies, Australia.

Table 1. Biochar treatments (T1 to T12) along with total carbon content (%) and $\delta^{13}C$ signature (‰) of the biomass, the corresponding biochar and the soil used in the experiment.

Biomass source	Pyrolysis temperature (°C)	Activation treatment	Biomass / Biochar (% total C)	Biomass / Biochar (‰ $\delta^{13}C$)
(T1) Blue gum wood	400	Activated	47.9 / 73.2	-27.6 / -28.5
(T2) Blue gum wood	550	Activated	47.9 / 83.9	-27.6 / -28.8
(T3) Blue gum wood	400	Non-activated	47.9 / 72.8	-27.6 / -28.4
(T4) Blue gum wood	550	Non-activated	47.9 / 83.3	-27.6 / -28.8
(T5) Blue gum leaves	400	Activated	50.1 / 67.8	-28.2 / -28.2
(T6) Blue gum leaves	550	Activated	50.1 / 74.1	-28.2 / -28.2
(T7) Paper sludge	550	Activated	33.5 / 32.0	-23.6 / -21.7
(T8) Poultry manure	400	Non-activated	39.3 / 46.8	-24.9 / -25.0
(T9) Poultry manure	550	Activated	39.3 / 46.0	-24.9 / -25.1
(T10) Cow manure	400	Non-activated	20.0 / 21.5	-27.4 / -27.5
(T11) Cow manure	550	Activated	20.0 / 18.8	-27.4 / -27.9
(T12) Non-amended soil			0.42	-14.1

Incubation experiment

The soil (650 g, air-dried, 2 mm sieved) from a paddock under C_4-vegetation, adjusted to ~ 70% of water holding capacity using a dilute inorganic N solution, and inoculated with 1.4 g of a microbial-rich <2mm moist soil, was placed in plastic containers in triplicate. Ten days after preconditioning of the moist soil to ensure development of microbial populations, different biochar materials (ground to <2 mm) were homogenously mixed with the soil to a concentration of 8.2 g biochar per kg of soil (oven-dried basis), corresponding to 10.2 t biochar per ha to a depth of 10 cm (bulk density 1.25 t m^{-3}). A control treatment of soil without biochar was also included. Just before refilling the containers, 2 ml of nutrient solution (containing N, P, K, Ca, Mg, S, Cu, Zn, Mo, Co, Na) in appropriate concentrations was sprayed onto biochar-amended and non-amended soils and then uniformly mixed. Following amendments, containers were placed in 5-L sealed buckets containing (i) 100 mL of water to maintain a water-saturated atmosphere, and (ii) 30 mL of 2 M NaOH to trap microbial-respired CO_2. The sealed buckets were then placed in a dark room and incubated at 22±1°C.

Analyses

Soil-respired CO_2 is being monitored by periodically removing NaOH from sealed containers and then measuring trapped CO_2 by titration with HCl. The CO_2 trapped in NaOH is precipitated with $SrCl_2$ aqueous solution as $SrCO_3$ for $\delta^{13}C$ analysis using an IRMS (Harris *et al*., 1997). The biochar-derived and soil-derived C is determined from a ^{13}C mass balance equation (Rochette *et al*., 1999; Schweizer *et al*., 1999).

The mean turnover time of decomposing biochars was determined by fitting the two-pool model to the cumulative biochar-derived CO_2-C evolved. To determine soil microbial biomass C, moist soil samples (23–24g) were fumigated for 10 d in with chloroform containing amylene (0.006% v/v) as a stabiliser, followed by extraction with 80 ml of 0.5 M K_2SO_4. The corresponding non-fumigated soil samples were also extracted with 0.5 M K_2SO_4 in the same way on the day of fumigation. Organic C in the filtered 0.5 M K_2SO_4 extracts was determined by the dichromate digestion method of Vance *et al*. (1987).

Results

➤ Carbon content of biochar increased as pyrolysis temperature increased from 400°C to 550°C for bluegum biomass, but not for the poultry and cow manures (Table 1).

➤ The $\delta^{13}C$ of biochar was depleted by up to -1.2‰ compared to $\delta^{13}C$ of biomass, except for biochars from leaves (no change in $\delta^{13}C$) and paper sludge ($\delta^{13}C$ enrichment of -1.9‰) (Table 1).

➤ The $\delta^{13}C$ of paper sludge biochar was higher by 3.3 to 7.1‰ compared with the other biochars probably due to the presence of ^{13}C-enriched carbonate (Table 1).

➤ The rate of C mineralisation from biochar-amended and control soils decreased with time (Figure 1).
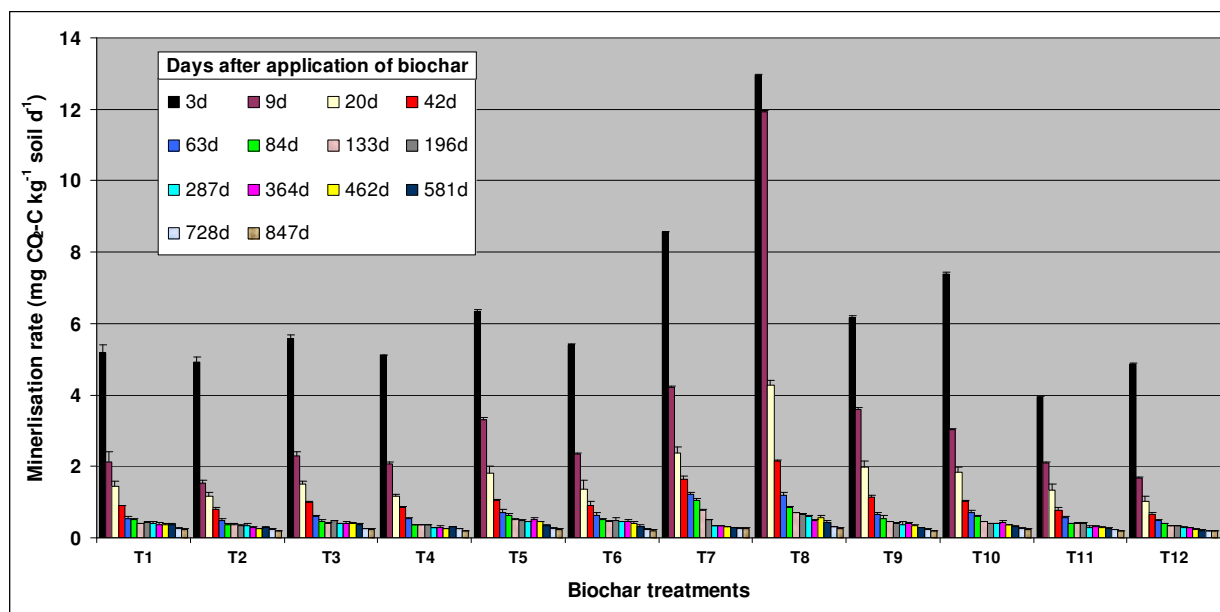

Figure 1. The rate of mineralisation of carbon in biochar-amended and non-amended (control) soils at different times of incubation (3d to 847d, see legends). Details of treatments, T1 to T12, are presented in Table 1. The bars show 1 standard error of means of three replicates.

➤ In the first 2.3 years of incubation, decomposition of biochar C in soil ranged from 0.3% to 6% of biochar C applied, depending on biochar type (data not shown).

➤ On cumulative basis over 2.3 years, biochar application enhanced decomposition of 'native' soil C; this positive priming effect on soil C was higher in soil amended with leaf or poultry manure biochars than wood biochars (data not shown).

➤ Microbial biomass C was not affected by the biochar treatments, except for the low-temperature leaf and poultry manure biochar treatments, which significant ($P < 0.05$) increased soil microbial biomass C as compared to the control (Figure 2).

➤ Our estimates of mean turnover time of C in biochars, determined by fitting the two-pool kinetic model to the cumulative CO_2-C evolved under controlled and optimal conditions of soil moisture and temperature in a laboratory, ranged from approximately 100 to 1300 years, with poultry manure showing fastest turnover and wood biochar the longest residence time (data not shown).

Conclusion

This study has found that the rate of decomposition of biochar varies with biomass source and pyrolysis temperature. While some biochars (e.g. wood biochars synthesised at 550°C) are highly stable in soil environment with mean turnover time >1000 years, other biochars can also survive in soil for >100 years. In general, biochars that decomposed faster also increased microbial biomass and turnover of native soil C more than other biochars. Turnover times in the field are likely to be slower than measured in this laboratory study, which intentionally employed conditions of moisture and temperature ideal for decomposition. The stability of biochar C and its influence on native soil C should be further tested under a range conditions likely to be experienced in the field.
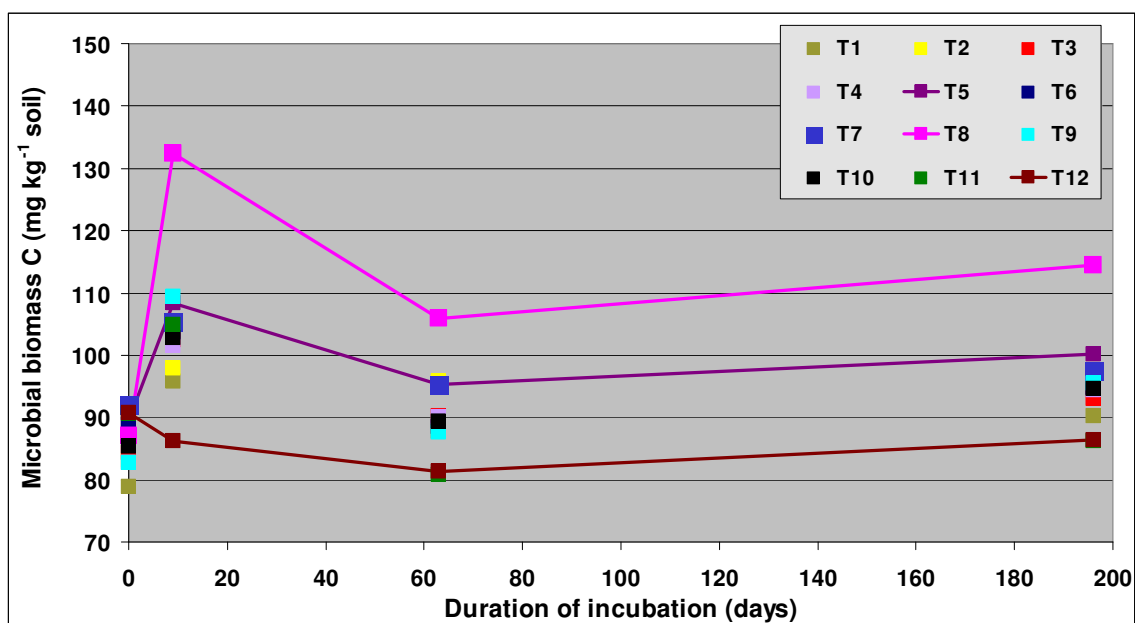
Figure 2. Biochars influence on microbial biomass C during 196 days of incubation. The treatment numbers shown in legend are explained in Table 1. Averaged over 196 days, microbial biomass C in biochar-amended soils shown by symbol plus solid line is significantly higher at *P* < 0.05, as compared to control (T12).

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Using maize as a reference plant material and natural ^{13}C for field assays of soil carbon dynamics

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Abstract

Sustainable agriculture should maintain soil organic carbon to prevent soil degradation and erosion, but soil C management still requires basic data on soil C dynamics under many climates, soil types and land uses. We applied a simple field method for the measurement of soil carbon dynamics, based on the natural ^{13}C labelling technique of carbon inputs. The method implies the addition of locally produced maize material into the soil with C3 crops, in a simple, light and cost-effective design, and the kinetic analysis of soil ^{13}C/[12]C. In Chile the approach was applied on a nine years fertility experiment with no till conditions sustaining a wheat-oat rotation, and followed thereafter for 5 years. The experimental site is located in the Andes pre-mountain (36º55'S, 71º53'O). The soil is of volcanic origin (medial, amorphic, mesic, Typic Haploxerands) and the crop rotation wheat-oat. The labeling technique showed that a very low amount (about 1 t ha^{-1}) was incorporated to the soil (new C) during the time-period of the experiment (4 years). The ratio of remaining C/ added C after 4 years was very low (0.03) suggesting that the high carbon content of the soil can therefore be considered as due to a large amount of passive carbon, or to ancient carbon inputs, that have saturated the sorption capacity

Key Words

C dynamics, no-till, volcanic soil, C4 plant residues, C crops, long-term experiment

Introduction

Preventing soil degradation should be a central goal of sustainable agriculture, especially under intensification or colonization of new lands. The maintenance of a sufficient organic carbon content in soil surface layers is one of the major ways to prevent soil degradation. Organic carbon may act directly by improving the physical properties of the superficial layer, thus reducing soil erosion or structure destruction, and indirectly by increasing the physical and chemical fertility. The enhancement of plant growth therefore increases soil C in a positive feedback process (Tiessen *et al*., 1994). Soil management and the management of crop residues (above- and below-ground parts) is the major way of controlling soil C. For instance reduced tillage is reported to increase soil C to various extends, especially in the uppermost soil layer, which is the most sensitive to degradation (Balesdent *et al*., 2000; Dolan *et al*., 2006). In Chile, about fifty percent of the Chilean agriculture production occurs in Andisols. At present no –till management is the main practice for Chilean farmers in the Andes pre-mountains. While soil carbon dynamics and the fate of plant residues and is well documented in some countries and crop productions, there is still a need for references under many climates, soil types and land uses. To better predict the effect of the practices of C management over a wide range of situations, specific long term experiments would be required. Unfortunately, such trials cannot be implemented at each place, and would need long durations and high sensitivity, because of the dilution of added C into the existing organic matter. Undoubtly, the isotope labelling of carbon inputs is the best tool to quantify and forecast the fate of C (Coleman and Fry, 1991; Zagal, 1994). This is the conventional interest of tracers to investigate systems under dynamic regimes.

The natural ^{13}C labelling technique (Balesdent and Mariotti, 1996) has proven to be a very powerful tool to quantify soil organic matter dynamics and trace C inputs (IAEA, 1998). It is based on the natural difference in ^{13}C/^{12}C ratio between C4 plants and C3 plants. The change of vegetation from one type to the other provides a natural labelling of new carbon incorporated into the soil by the vegetation. The dynamics of soil C can be there measured by the analysis of 13C/12C in soil organic matter. The latter is determined by high-resolution stable isotope ratio mass spectrometry. The method may be applied to the analysis of total soil C, but also to organic separates to decipher processes of C transformation and analyse relevant compartments of soil organic matter. The method is very powerful but unfortunately limited to places where vegetation has changed from the C3 to the C4 type.

The objective of this study was to apply the natural ^{13}C technique in a volcanic soil under no-till management where production is dominated by C3 plants, by applying C4 plant material and following its fate by ^{13}C/^{12}C measurements, in simple controlled field experiments, as a complementary tool of soil studies, allowing for quantification ofsoil organic matter dynamics

Methods

The experiment is located in the VIII region of south central Chile (36° 55' S;71° 59' W) at the Andes pre-mountains. The soil is classified as medial, amorphic, mesic, Typic Haploxerands. The climate is humid Mediterranean, with a precipitation over 1400 mm. Mean temperature is between 12,5° and 13,9°C (Del Pozo, 1999.)

The experiment has a completely randomized block design with 3 replicates. It is a long-term no till experiment (at present thirteen years old) with different sources of N and P fertilizer; with a crop rotation wheat-oat, and with the following treatments: T1. Control (no nitrogen), only triple superphosphate (TSF). T2. TSF + Chilean Salpeter. T3. Urea + Ammonium mono phosphate (MAF). T4. Urea + MAF + 500 kg ha^{-1} CaCO$_3$. T5. Urea + MAF +1000 kg ha^{-1} CaCO$_3$. Nitrogen rate is 150 kg ha^{-1} (applied in two occasions); P rate is 150 kg ha^{-1} (as P$_2$0$_5$); K rate 120 kg ha^{-1} (as K$_2$0).

Maize residues were applied in the main no tillage experiment, establishing 4 m^2 specific sub-plots (isotope reference plots). To develop the methodology measurements were concentrated on treatments TSF + Chilean Salpeter and Urea + MAF +1000 kg ha^{-1} CaCO$_3$. The main plots (fertilizer treatments) with C3 crop are used to measure unlabelled isotopic composition (these plots are analyzed for the C and ^{13}C only). The sub plots are geo-referenced and staked. The material used was leaves and stems harvested by hand (600 m^2), cut in cm pieces and air dried at existing outside conditions. Moisture content was determined before application and a sub-sample taken for C and ^{13}C analysis. Before maize residues application, C3 crop residues were a removed. Due to the high content in organic matter (8-10%) high amounts of maize residues were applied in only 4 m^2 (e.g. 7 kg m^{-2}) in one or two more operations. Maize C is incorporated every two years at the same place. This is a cumulative labelled-C addition, for a better sensitivity and time-integration of processes. Plots should be followed at least 5 years at the yearly time-step, considering that the first year is establishment time.

The soil is typically analyzed before crop return and the new maize addition. Soil samples are taken in one m^2 at the center of the subplots. One quarter is used each year, an properly marked, in order to provide an unbiased and representative estimate of soil C and residue C. Samples were dried and completely reduced to a size finer than 0.2 mm by a step-by step reduction of sample aliquots. Organic C and delta^{13}C were analyzed by EA-IRMS in a specialized laboratory (University of Ghent, Faculty of Bioscience Engineering, ISOFYS laboratory). Soil bulk density has been measured. Twenty four (24) measurements (3 replicated blocks x 4 years x labelled+unlabelled) is the minimum set of measurements per treatment.

The proportion f of residue C in soil C will be determined as

$$f = (\text{delta}^{13}C_{labelled\_plot} - \text{delta}^{13}C_{unlabelled\_plot})/ (\text{delta}^{13}C_{maize} - \text{delta}^{13}C_{crop})$$

The amount of residue-C remaining is:

$$C_{residue} = C \times f, \text{ where C is the density of soil C (t/ha)}$$

Carbon, N and delta^{13}C content of maize DM were also determined by using EA-IRMS. Crop yields were recorded during the experiment. The change in stable carbon isotope signature was interpreted as follows: the delta^{13}C of reference plots under C3 plants was considered as unaffected by time and the values for all years were pooled, providing n=24 independent measurements for each horizon. Two outlier data were removed from the dataset. The delta^{13}C of labelled plots was considered as dependent on time only and n=6 independent values of replicates plots were used for each year. This enabled to calculate the 95% confidence interval on the difference between labelled and unlabelled plots, with a comfortable number of degrees of freedom.

Result

Table 1 shows unlabeled and labelled total C contents and delta ^{13}C values in the soil. The results indicate the very high content of total C in this volcanic soil, characteristic that dilutes the input of new C. Despite of this effect an increase in carbon isotopic signature could be measured.

Table 1. Unlabeled and labeled total C contents and delta ^{13}C values in the soil (n=24).

Soil depth (cm)	Unlabeled total C (t/ha)	Labeled Total C (t/ha)	Unlabeled delta ^{13}C (‰)	Labeled delta ^{13}C (‰)
0 to 5	31,14	33,23	-26,61	-26,40
SD	(3,67)	(2,18)	(0,34)	(0,28)
5 to 10	28,27	29,05	-26,32	-26,23
SD	(3,12)	(2,64)	(0,38)	(0,39)
10 to 20	40,89	40,22	-25,79	-25,76
SD	(7,05)	(6,82)	(0,30)	(0,30)
20 to 40	58,67	54,24	-25,17	-25,11
SD	(15,02)	(11,72)	(0,37)	(0,31)

In fact, following the interpretation described in the section Methods, the signature demonstrated a progressive trend versus time in the 0-5 cm in accordance with the, whereas the amount of maize-derived-C in the horizons below was much smaller, and not significant below 10 cm (Figure 1).
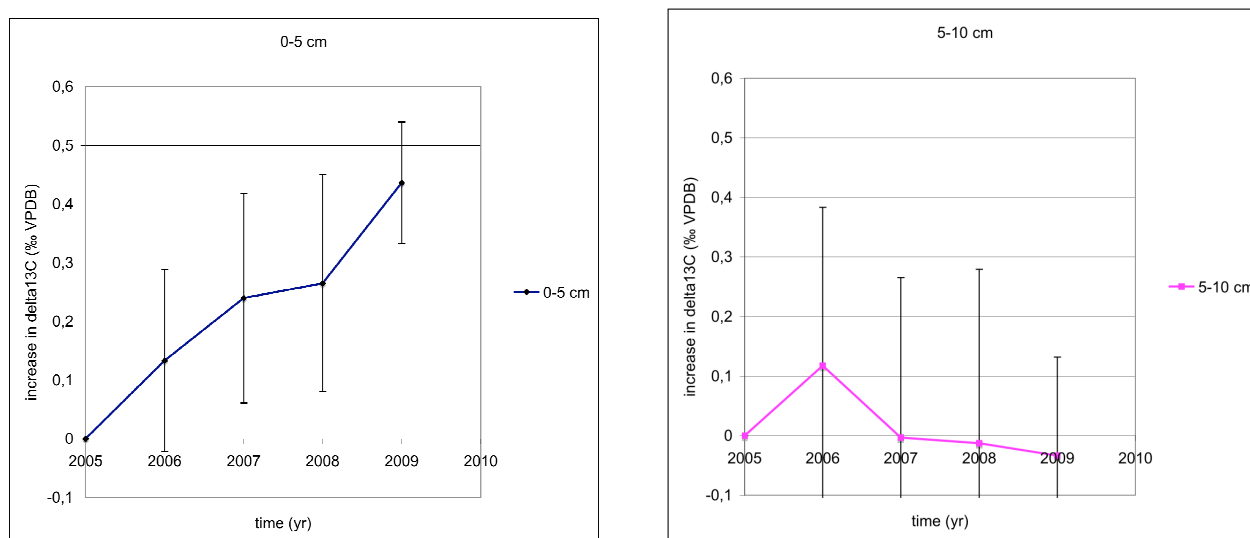

Figure 1. Mean and 95% confidence interval on the difference in delta^{13}C between maize-labelled and unlabelled plots.

This enabled to estimate minimum and maximum estimates of the amount of maize-derived carbon in the soil. Table 2 provides this estimate at the end of the experiment in 2009
The increase in delta ^{13}C is relatively low to the very high dilution in the large pool of preexisting organic matter (100 t C ha^{-1} in the top 20 cm; Table 1).

This amount can be related to the cumulated amount of added carbon residues (29 t C ha^{-1}).
The ratio of remaining C/ added C after 4 years is 0.97/29 = 0.033 and is lower than (<0.2). This conventional ratio means that plant material decays as rapidly in this type of soil as in other soils. The high carbon content of the soil can therefore be considered as due to a large amount of passive carbon, or to ancient carbon inputs, that have saturated the sorption capacity.
Further interpretation will be done by using the RothC model (Jenkinson and Rayner, 1977) of soil organic carbon dynamics, and the need for a specific calibration in this type of soil will be evaluated. The study also demonstrated that with appropriate experimental design, methods of sampling and analysis, a confidence interval as low as ±0.15 ‰ VPDB could be obtained on the change in delta^{13}C of the bulk soil.

Table 2. Contribution from maize residue to soil organic carbon (4 years).

	Maize-derived C (t ha^{-1}) in 2009		
	minimum (conf. 95%)	mean	maximum (conf. 95%)
0 to 5 cm	0,74	0,97	1,21
5 to 10 cm	0,00	0	0,26
10 to 20 cm	0,00	0	0,12
20 to 40 cm	0,00	0	0,00
0 to 10 cm	0,74	**0,97**	1,46
0 to 40 cm	0,74	**0,97**	1,58

Conclusion

The labeling technique showed that a very low amount was incorporated to the soil (new C) during the time-period of the experiment (4 years) and the ratio of remaining C / added C was very low suggesting that the high carbon content of the soil can therefore be considered as due to a large amount of passive carbon, or to ancient carbon inputs, that have saturated the sorption capacity.

Acknowledgements

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Validation of Most Probable Number technique for determination of *Salmonella* Typhimurium in compost, according to EPA 1682/06

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Abstract
To validate the Most Probable Number technique (MPN) according to the method EPA1682/06 from the U.S. Environmental Protection Agency, in compost and chicken manure, these matrices were inoculated with *Salmonella* Typhimurium ATCC#14028, defining a double blinded study. In order to include all parameters established for a validation process, 504 samples were used: 252 compost samples and 252 chicken manure samples. The detection limit was 0.8 cells/g for compost and 2 cells/g for chicken manure. In addition, the critical level was 5 UFC/g and the correlation between the results obtained from MPN and Absence/Presence techniques, was a high one, showing an r^2 of 0.972.

Key Words
Organic fertilizer, *Salmonella* sp. validation and critical level

Introduction
The development of diseases related to the presence of pathogens such as *Salmonella* spp. in biomaterials and organic manure has brought to consideration the relevance of control measures and above all, it has favored their regulation. This regulation favors the elaboration and application of these agricultural products. The importance of finding detection techniques that allow identification and quantification of *Salmonella* spp. and more so, one which allows avoids effects from interferent microorganisms, permits a guarantee over the results given. The objective of this work was to validate the Most Probable Number technique (MPN) according to the method EPA1682/06 from the U.S. Environmental Protection Agency, in compost and chicken manure inoculated with *Salmonella* Typhimurium ATCC#14028 and to determine the inclusiveness for *Salmonella* spp. after inoculating the samples with 30 different microorganisms (EPA, 2006).

Methods
Using a double blinded study, in order to include all parameters established for a validation process, 504 samples were used, distributed as follows: 252 compost samples and 252 chicken manure samples. These were used for the determination of sensitivity, specificity, relative exactitude, and positive and negative predictive values. Inclusiveness was determined using the critical level and methods correlation with 114 samples distributed in: 88 compost samples and 26 chicken manure samples; these were inoculated with different concentrations of *Salmonella* Typhimurium. For the critical level and the methods correlation finding, samples were inoculated with 5, 10, 20 and 100 cfu/g (colony forming unit per gram), meanwhile, to find the inclusiveness, 100 UFC/g of *Salmonella* Typhimurium were inoculated so they could be processed using the Absence/Presence technique (ICONTEC, 1998) and MPN (EPA, 2006). The inclusiveness was determined by employing 30 interfering strains commonly found in soil.

Results
The reported results for both methods, indicate that, for compost, sensitivity, specificity, relative exactitude, and positive and negative predictive values, a 100% was reported for every parameter, while for the chicken manure a sensitivity of 94.5% , specificity and positive predictive value of 100%, negative predictive value of 96.9% and relative exactitude of 93.7% were obtained, making these results "almost perfect".

The detection limit was 0.8 cells/g for compost and 2 cells/g for chicken manure. In addition, the critical level was 5 UFC/g and the correlation between the results obtained from MPN and Absence/Presence techniques, was a high one showing an r^2 of 0.972.

Considering the inclusiveness, a high recovery of *Salmonella* spp. was found in regard to the 30 strains employed in this study, since 83.33 % of these overcame the demanded percentage (+/- 30 %), by the NTC 5014:2001 and the remaining 16.67% (commonly reported in the literature as interfering), allowed the recovery of *Salmonella* spp. even if they did not comply with the demanded percentage.

Validation of the method was achieved fulfilling every demanded parameter and it shows a high inclusiveness, obtaining trustworthy results in samples which had a great variety of microorganisms.

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Water retention properties of maize stem residue as affected by particle size and decomposition in soil

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Abstract
The aim of this study was to investigate the effects of crop residue particle size and decomposition on water retention properties. Two pieces of 0.5 and 5 cm length of intact maize stem were chosen as experimental model. Maize particles were incubated in soil during 49 days at 24°C to alter the characteristics of stem particles by decomposition. Maximum water retention and residual humidity of particles were established by immersing the particles at three decomposition stages (undecomposed, decomposed after 14 days and after 49 days) for different duration of time until stable weight. We observed that 0.5 cm particles absorbed the same amount of water per g of residue as 5 cm particles. Decomposed particles absorbed more water than undecomposed ones for both particle sizes. Similar trends were obtained for residual water. We hypothesized that higher maximum water absorption and lower residual water retention in decomposed particles were due to an increase in residue porosity during decomposition. Particle size affected C mineralization with significant higher mineralization for 0.5 cm particles (29% of added C) than for 5 cm particles (21% of added C). The consequences of water retention properties on residue mulches are discussed in the context of conservation agriculture.

Key Words
Crop residue management, Physical properties, Granulometry, Specific surface, C dynamics

Introduction
For integrated and sustainable agricultural management, it is crucial to understand the processes involved in decomposition of crop residues. The dynamics of decomposition is controlled by many factors. Among these factors, physical characteristics and location in soil determine the contact between soil and residue. Some studies showed that decreasing the residue particle size and incorporating residue into soil, increase area in contact with soil and make degradable components more accessible to decomposer micro organisms (Anger and Recous 1997). Conversely leaving crop residues in mulch at the soil surface such as in no tilled systems greatly affect the dynamics of water in and below the mulch, and the decomposition of the mulch itself becomes highly dependent on environmental conditions, particularly moisture (Coppens *et al.* 2007). To understand and model residue mulch decomposition and associated C and N dynamics, it is necessary to determine residue physical properties, particularly those related to water dynamics and their relation to decomposition. To answer these questions, we selected maize stem as experimental model because it is frequently involved in rotations, particularly in conservation agriculture.

Materials and Methods
Characterization of crop residues
The maize stems were collected at the INRA experimental station in Mons (80) on 10 July 2006. We eliminated the nodes of stems because nodes have very different chemical and physical features compared to internodes. The maize internodes were then cut into two different particle sizes: 5 cm length (T5 treatment) and 0.5 cm length (T0.5 treatment). The shape and geometry of the 5 cm and 0.5 cm particles are presented in Figure 1.
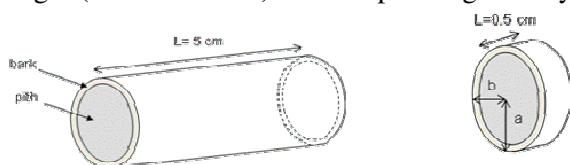

Figure 1 Schematic diagram of two particle sizes, 5 cm and 0.5 cm.

Physical and chemical properties of residue
The particles were characterized by their geometry, specific surface, potentially available contact surface and volume. For characterizing the geometry of the particles, we designed the shape of the residue as close as

possible to their exact shape (Figure 1), in order to estimate the volume and specific surface of the two sizes. The geometrical shape of maize stem was not exactly a cylinder, because both ends of the stem particles are of elliptical shape. Van Soest (1963) analysis indicated that maize stem was composed of 24% soluble, 26% hemicelluloses, 43% cellulose and 7% lignin components. While soluble C at 20°C was 25% of dry matter and C/N was 183.

Maximum water retention and residual humidity
To our knowledge, there is no standardized and published protocol to examine water retention and residual humidity for crop residue, so, the first step was to set up a protocol before using it for particles at different stages of decomposition. The strategy was to immerse particles in 1200 ml deionized water for different time durations (t) and note their weight after removal from water. The water absorption by each particle size was calculated using difference between initial weight and weight after immersion, the maximal water retention being the maximal difference obtained at a given time. Once the protocol was established, then it was applied to all stages of decomposition for the two sizes.

To assess the residual humidity of particles, the previous particles having maximal water retention were placed sequentially at 40°C until constant weight, 80°C until constant weight and 120°C until constant weight. The protocol for residual humidity measurements was deduced from this experiment. It was calculated as the difference in water content of particles at 40°C and 120°C. The duration of drying was selected as 48 hours at both temperatures (40°C and 120°C) for 0.5 cm particles. While this duration for 5 cm particles was 96 hours at 40°C and 144 hours at 120°C to determine residual water content.

Incubation Experiment
The soil was also collected at the INRA experimental station in Mons, France. The main characteristics of the soil were: 16.8% clay, 76.3% silt, and 3.8% sand. Organic carbon content was 8.70 mg C g^{-1} of soil and soil pH (H_2O) was 7.6. Incubation experiment was conducted during 49 days at 24 ± 1°C by mixing soil samples and maize internodes added to soil in amount equivalent to 4 g C kg^{-1} of dry soil. A control soil without residue added was included. The dynamics of C mineralization was followed at 3, 7, 10, 14, 21, 28, 36, 42 and 49 days after the beginning of the incubation by replacing CO_2 traps periodically. The concentrations of CO_2 trapped in NaOH solution were measured by continuous auto- analyzer (TRAACS 2000, Bran and Luebbe).

Results
Physical characteristics of particles
Several physical characteristics changed with decomposition stage as particle mass decreased with decomposition. The average mass of particles decreases rapidly from t=0 to t=14 and more slowly from t=14 to t=49. The volume of particles was almost same at the different decomposition stages. The density of particles decreased with time (Table 1).

Table 1. Physical characteristics for two sizes of particles (T0.5 and T5) at three stages of decomposition (t=0, t=14 days and t=49 days): the mass of particles (M), the volume of particles (V) the density of particles (D), the degraded mass (md), the volume of created pore (Vp), the supplement volume of water absorbed (Vw) and the residual humidity (wR).Values are mean of 10 replicates (± SE). Symbol nr means "Not relevant".

	Decomposition stage					
	t=0		t=14 days		t=49 days	
Treatment	T0.5	T5	T0.5	T5	T0.5	T5
M (g)	0.13±0.03	0.88±0.15	0.09±0.01	1.05±0.06	0.08±0.01	0.83±0.08
V (cm3)	0.82±0.09	6.75±1.05	0.84±0.09	10.42±1.01	0.83±0.17	8.58±0.84
D (g/ cm3)	0.16±0.02	0.13±0.01	0.11±0.01	0.10±0.01	0.09±0.01	0.10±0.01
md (g)	nr	nr	0.03±0.0	(-)0.17±0.2	0.05±0.0	0.05±0.2
Vp (cm3)	nr	nr	0.20±0.2	(-)0.97±1.2	0.29±0.2	0.30±1.3
Vw (cm3)	nr	nr	0.23±0.2	2.57±0.9	0.02±0.2	2.88±1.8
wR %	5.18±1.16	7.71±0.48	2.36±0.85	4.27±0.14	3.73±0.43	4.55±0.13

Effect of decomposition stage on water retention properties
Preliminary experiment showed that the maximal water retention was obtained at different durations of immersion, depending on the particle size, i.e. 2 hours for 0.5cm particles and 30 hours for 5cm particles. We applied the experimental procedure set up above to particles removed from soils at different stages of decomposition (t=0, t=14 and t=49). Undecomposed 5 cm particles (t=0) absorbed 0.37 g of water/cm^3 of

residue, particles at t=14 absorbed 0.49 g of water/cm^3 of residue and at t=49, particles absorbed 0.63 g of water/cm^3 of residue, i.e. 23 % (t=14) and 40% (t=49) more water than undecomposed particles (Figure 2). We observed that undecomposed residue particles (t=0) absorbed less water than decomposed particles. The same trend was obtained whether results were expressed by mass or by volume. Conversely, for the 0.5cm length particles, undecomposed particles (t=0) absorbed 0.40 g of water/cm^3 of residue, decomposed particles (t=14) absorbed 0.67 g /cm^3 of residue and decomposed particles (t=49) absorbed 0.42 g water/cm^3 of residue (Figure 2). Therefore the increase in water retention at t=49 was not similar to the pattern observed for the 5 cm length particles.

Residual water content decreased with decomposition, from 8 % (g H$_2$O/100 g DM) at t=0 to 5% at t=49 for T5; from 5% at t=0 to 4% at t=49 for T0.5. The hypothesis is that the increase in porosity with decomposition allowed the water contained in the residue to be evaporated (Table 1).
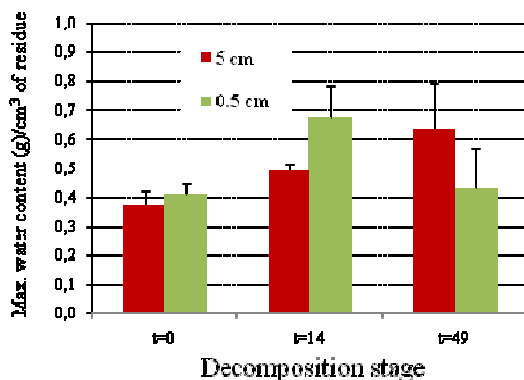

Figure 2 Maximum water absorption for 5 cm and 0.5 cm particles at different stages of decomposition measured after 30 hours and two hours of immersion respectively.
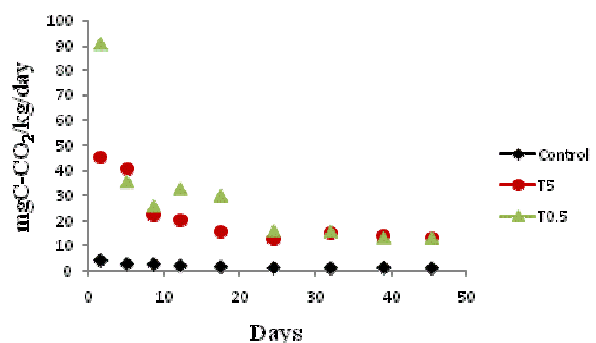
Carbon mineralization
The C-CO$_2$ mineralized from control soil was regular with a mean rate of 2.0 mg C per kg soil per day. After 49 days a total of 87.5 mg / kg of soil organic C were mineralized to CO$_2$ (Figure 3a). When maize residues were added to the soil, we observed a large increase in C mineralization (Figure 3a). The maximal rates of C mineralization peaked already at day 3 for the two amended treatments with the highest rate being obtained with the smaller size. The rates of C mineralization decreased continuously over time until the end of incubation and there were no significant differences in rates between the two residue treatments over the 20-49 day period. They remained significantly higher than the control soil (Figure 3b).

(a)

(b)
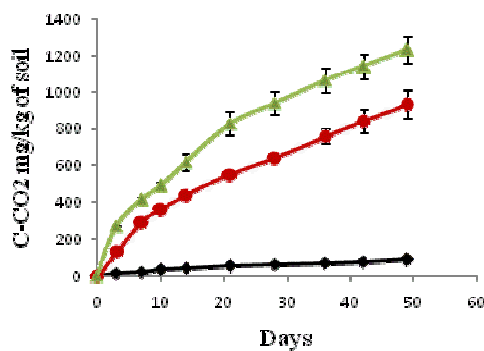
Figure 3a: Cumulative C mineralization. Each treatment has 4 replicates.

Figure 3b: Rate of C mineralization. Each treatment has 4 replicates.

Conclusion
According to literature (Findeling *et al.* 2007; Coppens *et al.* 2007), both physical processes that drive mulch decomposition are first the contact between the soil and the residue particle to be decomposed and secondly the water content of mulch in relation to rainfall. Our results confirmed that the particle size of crop residues has an important effect on residue decomposition as it increases the effective contact between the particle and the soil.

The absorbed water content of residue was found to depend on the particle size and on the stage of decomposition. The particle size affected the kinetic of absorption: the larger was the particle, the longer was the time to reach the maximum water content. The maximum water absorbed per volume unit was constant for different size of particles and it increased with decomposition stage. This can be qualitatively explained by the creation of new pores during decomposition process. This study shows that the effects of particle size on retention properties are determined by the quantity of vegetal material (volume or mass). This feature differs from the effects of particle size on decomposition which are essentially determined by the contact interface between the soil and the residues to be decomposed. The difference in amount of water retained between different sized particles at different decomposition stages implies that size, decomposition stage and rate of mulch cover per surface area will have a significant effect on the interception of rain. This amount of water received to the mulch plays an important role in determining the decomposition and mode of N release (Seneviratne *et al.* 1997).

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Carbon Dynamics in Organic Production Systems

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Abstract

Carbon accumulation and biological activity is being monitored for organic production systems of intensive vegetable production, broad acre arable farming, beef grazing and for uncultivated virgin soil at two depths (0-10 cm, 10-20 cm). The organic matter content and biological activity decreased with increasing soil depth. The total and bioavailable carbon levels, basal respiration and substrate induced respiration were higher under organic production systems than for virgin soil. All these values were higher for vegetable production than for the other two systems. The difference among organic production systems was more pronounced for basal respiration than for substrate induced respiration. The higher carbon levels and biological activity in soils under vegetable production is attributed to the copious application of organic compost to this system. Carbon dynamics of these systems will be monitored in the long term.

Key Words

Basal respiration, substrate induced respiration, organic farming, organic carbon

Introduction

In many countries including Australia and New Zealand, there has been increasing interest in organic production systems. In Australia, the growth in organic production is estimated at 15-25% annually and is expected to continue because of strong domestic demand and also because of Australia's ability to supply expanding markets overseas, especially in Asia (Alexandra and May 2004). While the economic prospects can be promising for Australian organic production, many growers face particular challenges due to high climatic variability, inherent low soil fertility soil and large distance between farm and input sources (Malcolm *et al.* 1996).

Organic farming systems are generally characterised by an ecological management system that aims to promote and enhance biodiversity, biological cycles (nutrient cycles) and soil biological activity (Kristiansen and Merfield 2006). Soil biological health is a central principle of organic agriculture and is vital to sustainable agriculture (Widmer *et al.* 2006). Soils under organic production systems are generally rich in organic matter and biological activity (Drinkwater *et al.* 1995; Marinari *et al.* 2006; van Diepeningen *et al.* 2006). However, this is not always the case with findings indicating no difference in soil biological activity between farming systems such as conventional, organic and biodynamic (Burkitt *et al.* 2007; Nachimuthu 2008; Penfold *et al.* 1995; Watson *et al.* 2002b). Soil biological properties were also strongly influenced by crop management practices rather than type of farming system as a whole (Nachimuthu 2008). Large quantities of organic compost are used in vegetable production systems in Australia including organic production systems as a source of nutrients and also to enhance the physical and biological fertility of soils (Chan *et al.* 2008; Wells *et al.* 2000). In contrast, the broad-acre organic production system receives low inputs and soil fertility levels decline so that the sustainability of the farming system is being questioned (Penfold 2000).

With this in view, an investigation was initiated to study the carbon dynamics on a fully certified organic farm in western Victoria which has multiple enterprises of intensive vegetable production, broad acre arable farming and beef grazing and uncultivated virgin soil. The aim of this study is to compare carbon accumulation and biological activity between these production systems in long term. The present paper discusses the preliminary findings of this study.

Methods and materials

Soil samples

Soil samples were collected at two depths (0-10 cm and 10-20 cm) from various organic production systems viz., vegetable production, broad acre arable farming and beef grazing systems and for uncultivated virgin soil during January 2009. The farms are located near Minimay, Victoria 36.72 °S, 141.18 °E. Soil is acidic with pH of about 5.5. Farms were converted to organic production system 5 years ago. The broad-acre area was pastureland until 2007.
Three samples from each system were taken. The samples were air dried, ground and passed through a 0.2 mm sieve for the analysis of total and bioavailable organic carbon contents.

Organic matter and biological activity measurements
The total organic matter and bioavailable or easily degradable organic matter contents were measured by loss on ignition and dichromate oxidation methods (Blakemore *et al.*, 1977)
Biological activity was monitored by measuring basal respiration and substrate induced respiration (respiratory response on the supply of glucose) (Anderson and Domsch 1978). Soil was broken in small clumps and stones, large invertebrate animals, stones and roots were removed before the soil moisture was adjusted to approximately 75% field capacity where microbial respiration is optimal. The moistened sample was incubated in air tight respiration jars at 25 ^oC for two days and then CO_2 evaluation was measured. These respiration rates were measured by trapping the evolved CO_2 from soil samples using 0.05M NaOH. The amount of CO_2 trapped was measured by back-titration with 0.03M HCl.

Sodium hydroxide solution has an affinity for CO_2. It is absorbed and forms sodium carbonate in solution.
$$2NaOH + CO_2 = Na_2CO_3 + H_2O \qquad (1)$$
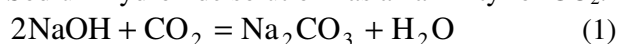
This equation indicates that one mole of CO_2 combines with 2 moles of NaOH
The mixed solution of Na_2CO_3 and NaOH cannot be titrated directly with HCl because both would react. Barium chloride is added to precipitate the carbonate.
$$Na_2CO_3 + BaCl_2 = BaCO_3 + 2NaCl \qquad (2)$$
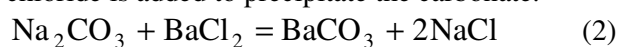
Because the solution in the flask remains alkaline until the end point is reached, the barium carbonate does not react with the acid. Thus the acid only reacts with the residual NaOH.
$$NaOH + HCl = NaCl + H_2O \qquad (3)$$
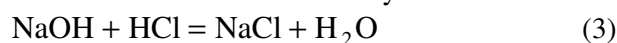
This equation indicates that one mole of HCl reacts with one mole of NaOH. Thus the moles of acid used for titration gives the moles of NaOH remaining after absorption of CO_2.

Results, discussion and conclusion
The organic matter content and biological activity as measured by basal and substrate induced respiration for the virgin soils and soils collected from various organic production system (Table 1) indicated that organic matter content and biological activity decreased with increasing soil depth which could be linked to the higher amount of organic matter available in top soil (Ge *et al.* 2010). The total and bioavailable carbon levels, basal respiration and substrate induced respiration were higher under organic production systems than virgin soil. These values were higher under vegetable production than for the other two systems. The level of activity and size of the microbial biomass may differ according to the management practices that have been used (Bulluck *et al.* 2002; Toyota and Kuninaga 2006). The organic production systems received off farm organic inputs such as organic compost and composted manure which could be the reason for higher biological activity than for virgin soil.

The substrate induced respiration was higher than basal respiration and there was a greater difference with land use in the later than the former, indicating that biological activity was limited by bio-available carbon in the soils. The higher substrate induced respiration than basal respiration indicates that the indigenous soil microbial population can readily adapt and multiply with respect to changes in soil environment such as addition of organic or inorganic amendments (Nachimuthu 2008). While the results are from an early phase of investigation and only the long term study will help us to state categorically which system is better, the observed difference or lack of difference in soil biological activity among different farming systems in this study might be attributed to the length of time the farms has been under organic management (Monokrousos *et al.* 2006; Zaller and Kopke 2004) together with the nutrient content and quality (Marinari *et al.* 2006; Shepherd *et al.* 2002; Stockdale *et al.* 2002) and quantity of organic matter added (Watson *et al.* 2002a). The increases in the accumulation of carbon and biological activity in soils under vegetable production in this study is attributed to the copious application of organic compost and composted manure to this system. This confirms the earlier findings that vegetable production system in Australia receive higher inputs to enhance soil fertility (Chan *et al.* 2008; Wells *et al.* 2000) and that there is large difference in soil carbon status between broad-acre and vegetable production systems.

Table 1. Organic matter content and biological activity for soils under various systems

Soil	Depth (cm)	Total organic matter (g/kg soil)	Bioavailable organic matter (g/kg soil)	Basal respiration (g CO_2/mg soil/min)	Substrate induced respiration (mg CO_2/g soil/min)
Virgin soil	0-10	2.38	0.82	8.91	23.3
	10-20	1.02	0.47	3.41	7.81
Vegetable	0-10	10.22	3.35	42.3	123.1
	10-20	7.28	2.11	34.2	87.5
Grazed beef	0-10	6.23	1.98	15.6	75.6
	10-20	2.12	0.89	7.81	17.6
Broad acre	0-10	4.21	1.14	11.2	35.3
	10-20	1.23	0.75	2.54	11.2

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Effects of biosolids on P sorption and phosphorus buffer capacity

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Abstract
Biosolids from sewerage treatment works represents a potentially valuable source of plant nutrients, particularly P. The application of biosolids to land can add P, change pH and increase the organic matter in the soil, all of which may affect the P sorption capacity. The objectives of the experiments described here were to determine the effects of biosolids application on P sorption capacity for two soils. Soils from farms at Tichborne, and Manildra, were used from biosolids treated and adjacent untreated sites on the same farm. The addition of biosolids reduced the P sorbed at a solution concentration of 0.2 mg P/L in each soil. There was desorption of P at a solution concentration of 0.2 mg P/L in the Tichborne biosolids treated soil and the sorption at a solution concentration of 0.2 mg P/L was lower in the non-treated Tichborne soil than in the non-treated Manildra soil. The PBC, measured as the P sorbed on increasing the P concentration of the equilibrium solution from 0.2 to 0.3 mg P/L, decreased in the Manildra soil and increased slightly in the Tichborne soil. For both soils the isotherms shifted along the x axis indicating that less P was adsorbed at a solution concentration of 0.2 mg/L.

Shifting of the isotherms on adding biosolids seems to be more important than changing their slope (PBC). With future application of biosolids, P sorption should be monitored to ensure that any decreased capacity of the soil to sorb P does not result in groundwater or surface water P pollution.

Key Words
Pollution, residual value, fertilizer

Introduction
Sewage wastewater contains mostly water (99%), human waste and chemicals which have been disposed of down the sewer. This wastewater is treated at a sewage treatment plant (STP) where effluent (liquid) and biosolids (solid) are produced. Once considered waste, sewage sludge or biosolids were disposed of into the ocean, incinerated or put into landfill, which potentially created problems for the environment. An awareness of the potential for health risks, pollution of waterways and contamination of land has resulted in the production of less noxious sewage effluent and biosolids. Biosolids are potential fertilisers or soil conditioners in soils deficient in nutrients and organic matter. Presently, with tighter restrictions being placed on the disposal of biosolids, they are beneficially used in agriculture, land rehabilitation, forestry and composts with only a small percentage going into landfill.

There are several treatments used by STPs to remove the nutrients from the effluent to meet discharge limits. Treatments include the addition of metal salts such as those of iron (Fe), aluminium (Al) and calcium (Ca) to remove P, and biological nutrient removal where microbes in the sewage remove the nutrients such as N and P. Some STPs use both techniques as it has been found to be most effective. Digestion of the sewage may also occur in some STPs under aerobic, anaerobic or anoxic conditions. Aerobic digestion involves the aerating of wastewater and the microbial breakdown of organic matter in biosolids into carbon dioxide and water. At this stage oxidation of chemicals applied to the wastewater for removal of P may occur, such as the oxidation of Fe(II) to Fe(III), which improves the capacity to remove P. Nitrification also occurs in the wastewater. This is followed by the anoxic process in which denitrification occurs so that N originally present in the wastewater is lost as N_2 gas. During the anoxic process sedimentation of solids also occurs. Anaerobic micro-organisms decompose the organic matter in the sewage biosolids into methane gas and carbon dioxide. As a result of the addition of chemicals to improve the quality of the effluent for discharge, high concentrations of Fe, Al and P may occur in the biosolids.

Sorption reactions in the soil are affected by pH. In high pH soils P sorption occurs on Fe and Al hydrous oxides, clay minerals, Ca and Mg carbonates and phosphates and Ca organic matter complexes but in low pH soils P sorption occurs on Fe and Al hydrous oxides, clay minerals, Fe and Al phosphates and Al organic matter complexes (Holford 1989). Organic matter, in the form of organic compounds (eg. humic acid), may compete with the P for P sorption sites, which may lower phosphate sorption and increase P availability in the soil

(Iyamuremye and Dick 1996).

The application of biosolids to land can change both the pH of the soil and increase the organic matter in the soil, both of which may affect the P sorption capacity of the soil. The main objectives of the experiments described here were to determine the effects of biosolids application on P sorption capacity for a range of soils and to determine the residual effects of biosolids application on the P characteristics of soils.

Materials and Methods
The soil samples were provided by NSW Agriculture and were taken from the top 15 cm of the soil profile in February 1999. There were no replicate samples so statistical analysis of the results was not possible.
Soils from farms at Tichborne, and Manildra, were collected from biosolids treated and adjacent untreated sites on the same farm. The history of the biosolids application and the type of the biosolids are presented in Table 5. The treated soils received one application of lime amended biosolids (biosolids that have been treated with lime) and dewatered biosolids applied together.

Table 5. History of biosolids application to the soils.

Location	Biosolids application
Tichborne	August 1997: Lime amended biosolids (10 dry t/ha) and aerobically and anaerobically digested biosolids (10 dry t/ha).
Manildra	September 1995: Lime amended biosolids (6 dry t/ha) and aerobically digested, dewatered biosolids (10 dry t/ha).

Soil analyses
Phosphorus sorption isotherms were measured on the soils using Rayment and Higginson's (1992) method. Known concentrations of KH_2PO_4 solutions in a background of 0.01M $CaCl_2$ were equilibrated with the soil. The concentrations of the equilibrating solutions were chosen so that 50 mL aliquots of solution P added to the soil were at rates of 0, 5, 10, 15, 20 and 25 mg P/kg soil. 50mL of equilibrating solution was added to approximately 5 g air-dried soil (<2mm) in 100mL extraction bottles. The bottles were shaken end-over-end for 17 hours at 25 °C. The solutions were then filtered through Whatman 42 filter papers and P determined colorimetrically with a Shimadzu UV-120-01 spectrometer using the Murphy and Riley (1962) method. Isotherms were used to determine the amount of P that was sorbed at a solution concentration of 0.2 mg P/L, which is assumed adequate for the growth of a range of crops (Beckwith 1965).
The phosphorus buffering capacity (PBC) was calculated by:
PBC (mg P/kg) = P sorbed at 0.3 mg P/L (mg P/kg soil) – P sorbed at 0.2 mg P/L (mg P/kg soil).

Results
The addition of biosolids reduced the P sorbed at a solution concentration of 0.2 mg P/L in each soil (Table 6). There was desorption of P at a solution concentration of 0.2 mg P/L in the Tichborne biosolids treated soil and the sorption at a solution concentration of 0.2 mg P/L was lower in the non-treated Tichborne soil than in the non-treated Manildra soil (Table 6).
The PBC, measured as the P sorbed on increasing the P concentration of the equilibrium solution from 0.2 to 0.3 mg P/L, decreased in the Manildra soil and increased slightly in the Tichborne soil (Table 6). In both soils the isotherms have shifted along the x axis indicating that less P is adsorbed at a solution concentration of 0.2 mg/L (Figure 4).

Table 6. Soil pH, P sorption at a soil solution concentration of 0.2mg P/L and phosphorus buffer capacity for soils with and without biosolids.

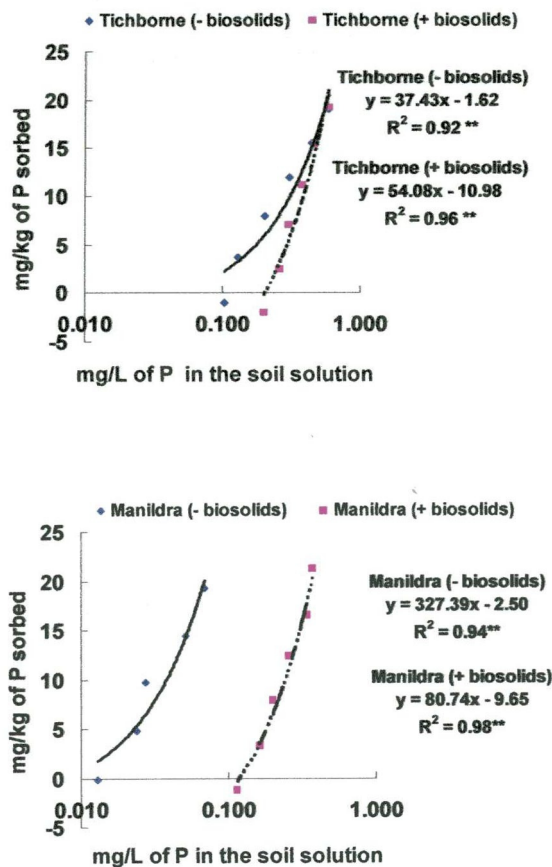| Location	pH $CaCl_2$		P Sorption (mg P sorbed/kg soil at solution concentration of 0.2 mg P/L)			Phosphorus buffering capacity (mg P sorbed/kg/0.1 mg/L)	
	Minus biosolids	Plus biosolids	Minus biosolids	Plus biosolids	% Change in Sorption	Minus biosolids	Plus biosolids
Tichborne	5.4	5.9	5.9	-0.2	-103	3.7	5.4
Manildra	5.0	5.6	63.0	6.5	-90	32.7	8.1

Figure 4. Effect of biosolids addition on P sorption isotherms in soils from Tichborne and Manildra.

Discussion

The changes in P sorption capacity of soils up to 6 years after biosolids application indicate the considerable residual benefits of applying biosolids to these soils. In all soils analysed there was a decrease in the P sorbed by the soil following the application of lime amended and dewatered biosolids, although the extent of the decrease varied. The results are in agreement with those of Barrow (1974) who reported that previous additions of P on phosphate adsorption of soils displaced isotherms to the right, reduced the slope of the isotherms (PBC) and P adsorption of the soil.

In a previous study (Davis, unpublished) there was an increase in bicarbonate P following addition of biosolids. At an application rate of 7.5 dry t/ha, 50% of the bicarbonate P was derived from biosolids and at 60 dry t/ha this increased to approximately 90%. The reduced P sorption following the addition of biosolids could be due to P derived from the biosolids occupying sorption sites or to organic matter blocking P sorption sites. The most noticeable feature of the paired isotherms (Figure 1) is the shift to the right along the x-axis when biosolids were added to the soil, rather than a large change in the slope of the isotherms. This indicates that P is being sorbed from the added biosolids to a much greater degree than a decrease in sorbing sites which would change the slope of the isotherms. Øgaard (1996) reported that the application of animal manure resulted in a reduction in P adsorption, and that desorption occurred in soils with high available P. The soils in the present study were all deficient in P prior to biosolids application, but in some instances desorption still occurred. The adsorption of P from biosolids would shift the equilibrium between P in solution and P sorbed to the extent that desorption occurred when determining the isotherms.

The reduction in the soils capacity to adsorb P could limit further biosolids application as saturation of P sorption sites could lead to P being leached or removed by surface runoff. This hazard is unlikely to eventuate with the application practices currently used in NSW.

Conclusions

There is a residual P effect from biosolids application affecting P sorption. The application of biosolids decreased the sorption of P and shifts the P sorption isotherm thereby decreasing the P sorption of the soil at a particular concentration. Shifting of the isotherms on adding biosolids seems to be more important than

changing their slope (PBC). With future application of biosolids, P sorption should be monitored to ensure that any decreased capacity of the soil to sorb P does not result in groundwater or surface water P pollution.

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Producing biochars for New Zealand soils

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Abstract

To understand the potential impacts of biochar on New Zealand soils, it is crucial to assess its capability to achieve a desired soil outcome. The present research is focused on (i) the characterization of biochars obtained from different types of feedstocks and pyrolysis conditions, (ii) the use of pre-treatments to enhance surface activity of biochars, and (iii) the simulation of long-term geochemical weathering of a mineral-rich ash biochar so that its fertilizing value can be assessed. The results obtained indicate that the different properties of the biochars produced are controlled to a large extent by process conditions (e.g., high or low temperature) and feedstock (e.g., low and high mineral ash content). Surface charge of biochars from eucalyptus and pine bark increased after treating the feedstocks with alkaline tannery waste. This effect was more evident with the biochar made from hard-wood bark. Up to 18 and 14% of K and P originally present in biochar made from biosolids were lost through intense weathering, whereas less than 1% of N was leached from the system. The knowledge acquired in this study is valuable to recognize, not only the different characteristics of the fresh biochars produced, but also their potential changes over time.

Key Words

Biochar characteristics, activation, surface charge, weathering

Introduction

Biochar-production technologies that convert biomass (short-term biodegradable carbon) into a more durable form (e.g., charcoal) and, at the same time, produce bioenergy, may provide the ideal greenhouse gas (GHG) mitigation solution for New Zealand's unique mix of pastoral and forestry land-uses. However, research needs to be conducted to ensure the sustainability of biochar-amended soils across New Zealand before this technology can be adopted by end users. Specifically, within the biochar and soil science stream, it is crucial to develop a predictive capability for the beneficial application of biochar in the diverse land-use systems of New Zealand. To attain such an objective, the physical, chemical and biological mechanisms behind its impact in soil functions must be fully understood. This study is focused on the physical and chemical properties of different biochars – obtained from very diverse types of feedstocks, different pyrolysis conditions, and with and without chemical activation – with the objective of understanding their potential impacts on New Zealand soils.

Methods

Pretreatment and pyrolysis conditions were varied with different feedstocks. Biochars from different forest (pine, eucalyptus, willow, poplar, Chinese silver grass), agricultural (corn stover) and urban (sewage sludge) waste streams were produced using a rotating drum kiln at 550 °C. Pine, poplar and willow were pyrolysed at 400 °C, corn stover at 350 and 400 °C; and pine and eucalyptus barks were treated with alkaline tannery waste before pyrolysis at 550 °C to promote surface activity. The biochar produced from biosolids was weathered using a modified Soxhlet reactor during a 300-h period to evaluate its long-term geochemical evolution. Carbonaceous materials were characterized by: SEM imaging, and solid-state ^{13}C NMR and FT-IR spectroscopy. Elemental composition, pH, effective cation exchange capacity, and yield were determined. For specific biochars, a characterisation using XPS spectroscopy was carried out, and acid group contents and BET were determined. For the weathering study, the leaching kinetics and the transformations within the solid phase were examined.

Results and Discussion
Influence of process conditions and type of feedstock on biochar properties
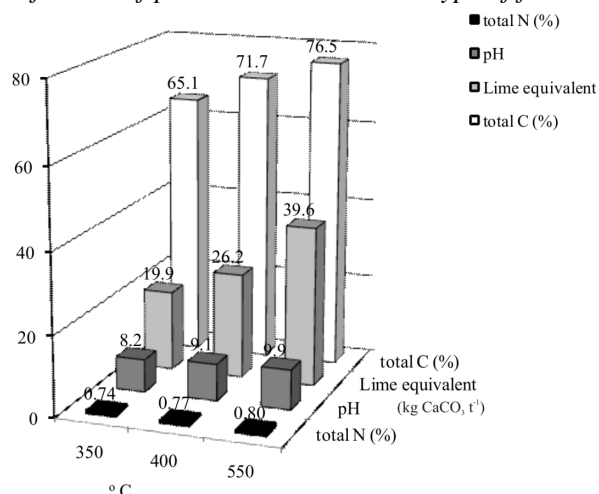

Figure 1 Changes in several chemical properties of biochars produced from corn stover at increasing temperatures.
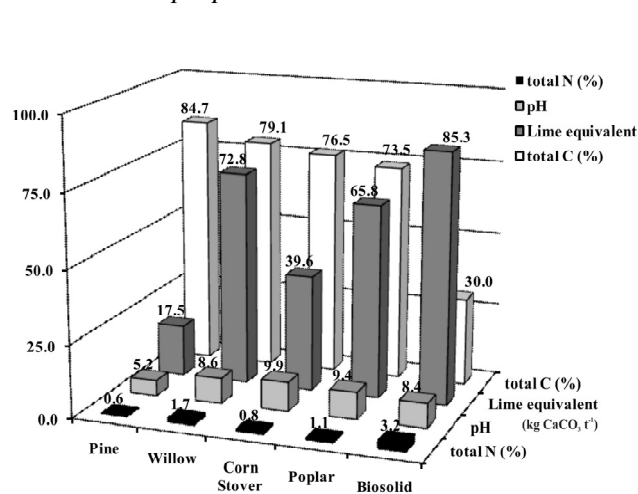

Figure 2. Chemical properties of bichars produced from different feedstocks at 550°C

Pyrolysis at increasing temperatures produced an increase in pH, lime equivalence, and C and N concentrations, as expected (Figure 1). On the other hand, product yield, the amount of carbon fixed, and H and O concentrations decreased with increasing temperatures (data not shown). This resulted in lower O/C and H/C ratios in the high temperature biochars than in the low temperature ones, indicating a greater degree of condensation of the former. Solid-state ^{13}C NMR spectra, acquired using both cross and direct polarization techniques, showed the increasing aromaticity of the chars with increasing temperature (data not shown). Different types of feedstocks had varied effects (Figure 2). The composition of the starting material had a large effect on the biochars produced at lower temperatures (350°C), but as heat increased (up to 550°C) this effect was less pronounced (data not shown).

Influence of alkaline pre-treatments on the surface activity of biochars
Biochars were produced by pyrolysis of fibrous debarking waste from eucalyptus and pine that either had, or had not, been pretreated with diluted (L) or undiluted (S) alkaline float tannery waste. Biochars made from treated eucalyptus feedstocks (L-EU and S-EU) contained less fixed carbon (39 and 37%, respectively) than the respective control (Ctr-EU; 40 %). However, they showed greater change in chemical characteristics than those from pine (L-PI and S-PI, respectively), which showed minimal decrease in C content compared to their control (Ctr-PI; 43%). The differences were mainly attributed to different types of lignin (S-type/G-type) in pine and eucalyptus. Biochars made from treated eucalyptus feedstocks had higher surface charge than the corresponding control, the highest value being in the L-EU biochar (Figure 3). L-PI and S-PI biochars also showed a higher surface charge than the corresponding control biochar (Ctr-PI), although values were always smaller than in the EU samples (Figure 3). The specific surface area of the biochars decreased with the alkaline treatments (from > 135 m^2 g^{-1} to < 9 m^2 g^{-1}) (data not shown).

In subsequent filtration experiments, in which NH$_4^+$ sorption and desorption properties were studied, treated biochars sorbed greater NH$_4^+$ from a 40 mg N L^{-1} stream than untreated biochars, with higher retention in the eucalyptus samples (Figure 3). The amount of NH$_4^+$ retained was not directly related to the new surface charge generated. Desorption of the sorbed NH$_4^+$ was low, especially in treated biochars (0.1-2 % out of total retained) compared to untreated biochars (14-27%) (data not shown). The results obtained indicate the contribution of other mechanisms of NH$_4^+$ retention, in addition to electrostatic interactions. They also suggest that a decrease in surface area does not necessarily imply a decrease in surface charge.
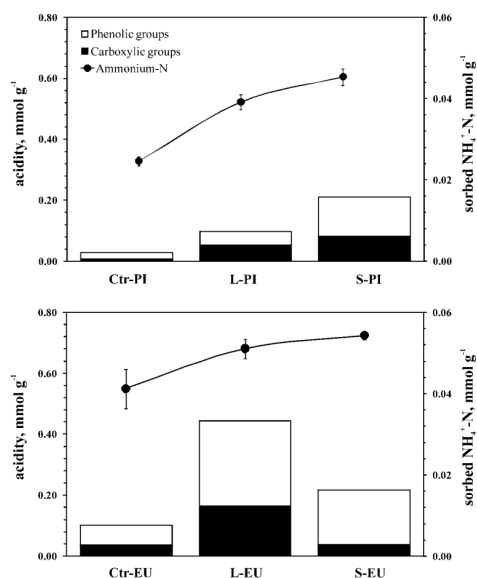
Figure 3. Surface functional groups of the different biochars and NH_4^+-N sorption after filteration with 1 40 mg N L^{-1} waste stream.
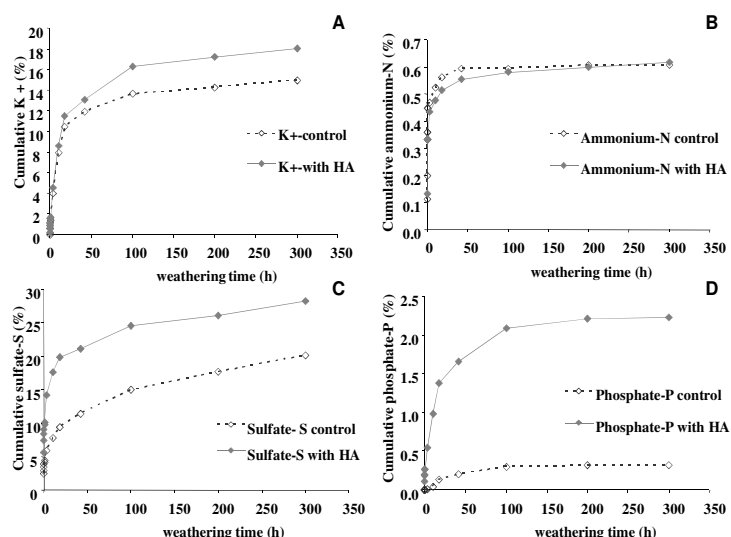
Figure 4. Cumulative amounts of (A) K, (B) NH_4^+-N, (C) SO_4^{2-}-S, and (D) PO_4-P in the weathering solutions.

Simulated long-term geochemical weathering of a high mineral ash biochar

The weathering process of a biochar produced from sewage sludge was studied with and without the presence of humic acids (BC-B and BC-HA, respectively). The pH values of the BC-B leachates rapidly decreased from ~ 9 to neutrality in the first hours, and the pH at the end of the experiment was 7.8. The BC-HA leachates had an initial pH of 7.5 and fluctuated between 7.0 and 7.4 during the rest of the experiment. The overall amount of dissolved organic C (DOC) in the weathering solutions was as low as 0.3 and 0.8% of the initial total C, for the BC-B and BC-HA, respectively. Substantial K (15 and 18 % for the BC-B and BC-HA treatments, respectively) and S (20.2 and 28.3 %) were released within 300 h of geochemical weathering (Figure 5A-B). The solubilisation of less readily soluble salts (e.g., P salts) was particularly promoted by the presence of HA. Once leached and their ionic activity in solution reached saturation, new precipitates were formed at the inner surface of the flask, probably as a Ca-phosphate salt. This would explain why the amounts of P and Ca recovered in the leachates (e.g., 2.2 % of P in the BC-HA) (Figure 5C-D) were far below the decrease in P and Ca detected in the solid fraction (e.g., 14 % of P decrease in the BC-HA). Less than 1% of the total N was leached out of the system at the end of the experiment, with a predominance of NH_4^+ over NO_3^-. As the C/N ratio of this biochar was < 11, the results reveal the presence of very recalcitrant forms of N.

According to XRD analysis (data not shown), there were a few crystalline minerals present in the biochar: quartz, trace amounts of albite, Ti-magnetite and olivine. In addition, trace amounts of calcite were detected in the fresh biochar and the BC-B sample, but disappeared in the BC-HA after weathering. The oxygen containing functional groups present at the outer surface of the biochar particles were analysed by XPS. The C 1s core level spectra (curve fitted data) obtained for fresh and weathered biochar samples are shown in Figure 5. For these materials, the C1s spectra contains four signals attributed to, to aliphatic/aromatic carbon group (CHx, C-C/C=C) (284.6 eV), hydroxyl and ether groups (-C-OR) (285.8 eV), carbonyl groups (>C=O) (287.2 eV) and carboxylic groups, esters and lactones (-COOR) (288.8-288.9 eV). Generally, the XPS results showed that the BC-HA biochar had a higher proportion of hydroxyl-ether groups than the other two biochars. The two weathered biochars displayed higher concentrations of carbonyl and carboxylic groups than fresh biochar. This could be originated through biochar oxidation and, in the BC-HA, also from the added HA.
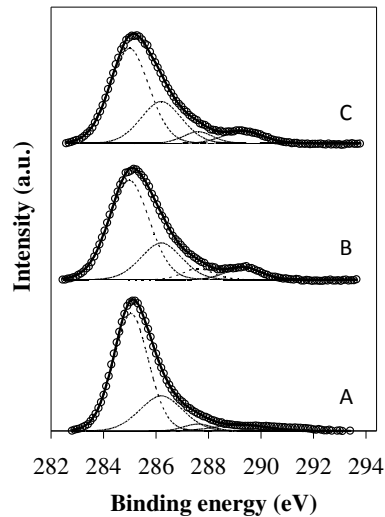
Figure 5. C 1S core level spectra of (A) fresh biochar, (B) BC-B,and (C) BC-HA.

Conclusions

This research represents a first step in the identification of the factors with the greatest influence on the final properties of biochars. This knowledge is crucial for fine-tuning the biochar production systems and the conditions under which the biochars will be beneficial to soils and to plant growth. Provision of an additional value to biochars, other than the sequestration of a stable C form in soils, may be critical for the economic feasibility of biochar production systems. Biochars with greater surface activity, and thus, suitable as filtering material, could be obtained through chemical activation, by use of an alkaline waste from the tannery industry. This could be attained with negligible impairment to the final fixed carbon. Mineral-rich ash biochars, such as those produced from biosolids, have been shown to represent an important source of P and K nutrients, but not of N. This may have key implications for the use of such biochars as fertilisers. The knowledge acquired in this study is valuable for recognising the different characteristics of the fresh biochars produced, and also any potential changes in them over time.