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A chronosequence of bauxite residue sand: weathering and vegetation response

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Abstract

We aimed to identify the edaphic characteristics limiting vegetation performance on rehabilitated bauxite residue storage areas. A chronosequence (up to 25 y) of rehabilitation sites was investigated at Alcoa of Australia's residue storage areas at Kwinana and Pinjarra, Western Australia, where gypsum-amended residue sand has been rehabilitated with native vegetation or pasture. Vegetation diversity and biomass were assessed within 6-m squares from which soil samples from different depths in the residue profile were taken for analysis. An exponential decline with time in maximum electrical conductivity (EC) was demonstrated using quantile regression while a progressive reduction in spatial variability of EC with time was also evident. Vegetation biomass index was more strongly related to age of residue than to period since establishment, indicating a diminishing limitation with time of some edaphic factor such as salinity. Additional sites will allow identification of such factors systematically through the environmental envelope approach using quantile regression. The present data, in confirming that simple parameters for assessing rehabilitation progress show consistent trends with time, indicate the potential value of these sites for providing additional more complex chronosequences such as evolution of secondary minerals, accumulation and humification of organic matter, and the development of complex microbial communities, all of which probably have an effect on ecosystem stability.

Key Words

Bauxite residue, chronosequence, weathering, rehabilitation vegetation, pedogenesis

Introduction

Bauxite refining produces considerable volumes of residue, which is generally managed by establishing a vegetation cover for visual amenity, dust and erosion control, and water management purposes. Vegetation has been established on bauxite residue with varying degrees of success due to the high pH and sodicity of the 'soil' medium. Assessments of vegetation success on bauxite residue have received attention (Wehr *et al*. 2006) and although some general factors governing the success are widely applicable, other factors are site specific owing to the varied elemental content of bauxite residue at different locations worldwide and the influence of climate.

In Western Australia, Alcoa's bauxite residue is separated into sand and mud fractions, with the sand fraction (> 150 μm) being used for constructing embankments within which the mud is dry-stacked. The embankments are ameliorated with gypsum to reduce sodicity and sequester alkalinity before vegetation is established – either a grass pasture or native species from a scrub/woodland ecosystem that occurs locally.

Measuring the establishment and long-term resilience of the vegetation in relation to residue properties is needed to demonstrate adherence to environmental standards as well as to reveal the soil factors exerting most influence on vegetation performance as the bauxite residue undergoes pedogenic alteration through natural weathering and leaching. To measure the success of vegetation establishment a chronosequence of sites is required for which accurate records are available of bauxite residue deposition and amendment history and of vegetation establishment. In this study we describe the establishment of such a database of rehabilitation sites from which the progress of vegetation establishment is assessed in relation to soil development in the bauxite residue.

Methods

Site selection and soil sampling

Seventeen sites at Alcoa of Australia's Kwinana and Pinjarra residue storage areas, of various ages of deposition and vegetation, were selected with the aid of a GIS database of botanical monitoring plots. These 6 × 6-m plots were originally made to monitor the establishment success of the rehabilitation vegetation since 2003. Additional plots were made in older and more recent areas where no botanical monitoring had been conducted.

Samples of the litter layer and the 0–2 cm mineral layer were collected with a trowel, and the 2–10 cm, 10–20 cm, 20–50 cm, and 50–80 cm layers were collected by driving a 9-cm PVC pipe into the soil, then extruding and dividing the cored sample into the abovementioned profile layers. Eight such samples were taken on each 6 x 6 m plot, spaced evenly over the site, and these were mixed to obtain a composite sample for each layer. At four sites, the eight samples of six layers were kept separate for an assessment of spatial variability. Samples were air-dried and passed through a 2 mm screen.

Vegetation assessment

Individual plants rooted within the 6 × 6-m plots were identified by species and measured at their widest extent in two perpendicular directions as well as a measurement of their height. An index of vegetation performance was calculated from width × width and width × width × height. Such indices of shrubby vegetation correlate very closely with total plant biomass (Raison *et al*. 2003). Ephemeral weedy vegetation was measured by height and % cover of the plot, and analogous indices of vegetation performance were calculated from these measurements.

Chemical analyses

Electrical conductivity (EC) of a 1:5 soil:water extract was measured according to Rayment and Higginson (1992). pH_{water} and pH_{KCl} were measured on 1:2.5 soil:solution extracts according to Gautheyrou and Pansu (2006).

Results and discussion

The sites show a distinct trend of reducing EC over time as seen in the raw values of EC for all depths, with the upper boundary of EC values, represented by the 95th quantile, very closely following an exponential decay with time (Figure 1). This is consistent with the leaching of soluble salts (probably mostly sodium sulfate) from the gypsum-amended residue sand. (About 50 Mg/ha gypsum had been mechanically incorporated to a depth of 1–1.5 m on all sites prior to vegetation establishment).

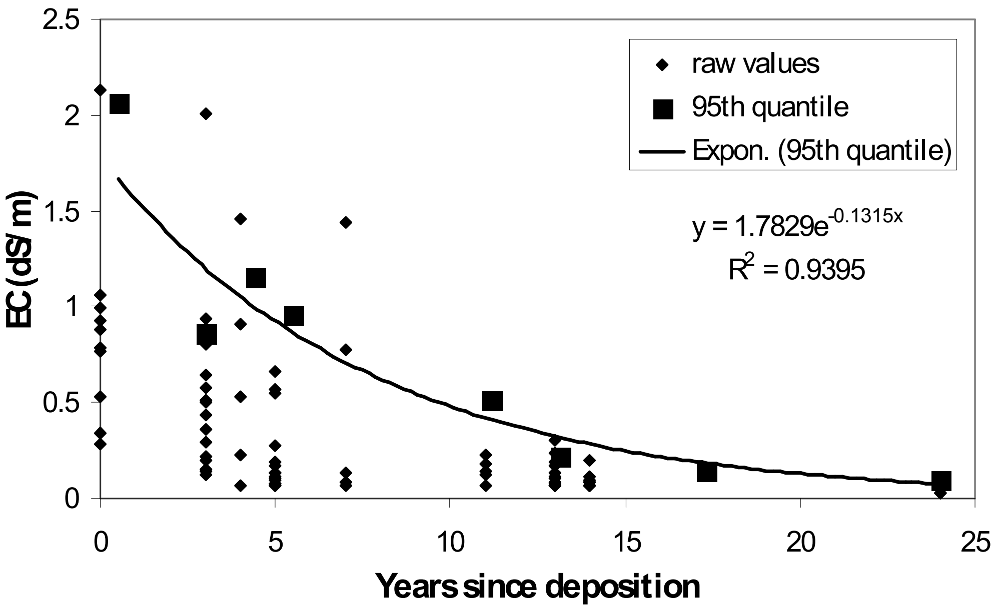

Figure 1. The decline in EC (individual values for different depths at each site and the 95th quantile) with increasing age of bauxite residue sand. .

Besides the general decline in EC with time, the spatial variability of EC within sites also decreased substantially with age regardless of the vegetation type established on the site (Figure 2). These data confirm the expectation of a progressive decline in salinity through seasonal leaching. The large spatial variability shown at the youngest rehab site in Figure 3 is probably because gypsum incorporation was achieved mechanically and thorough mixing was difficult to achieve.

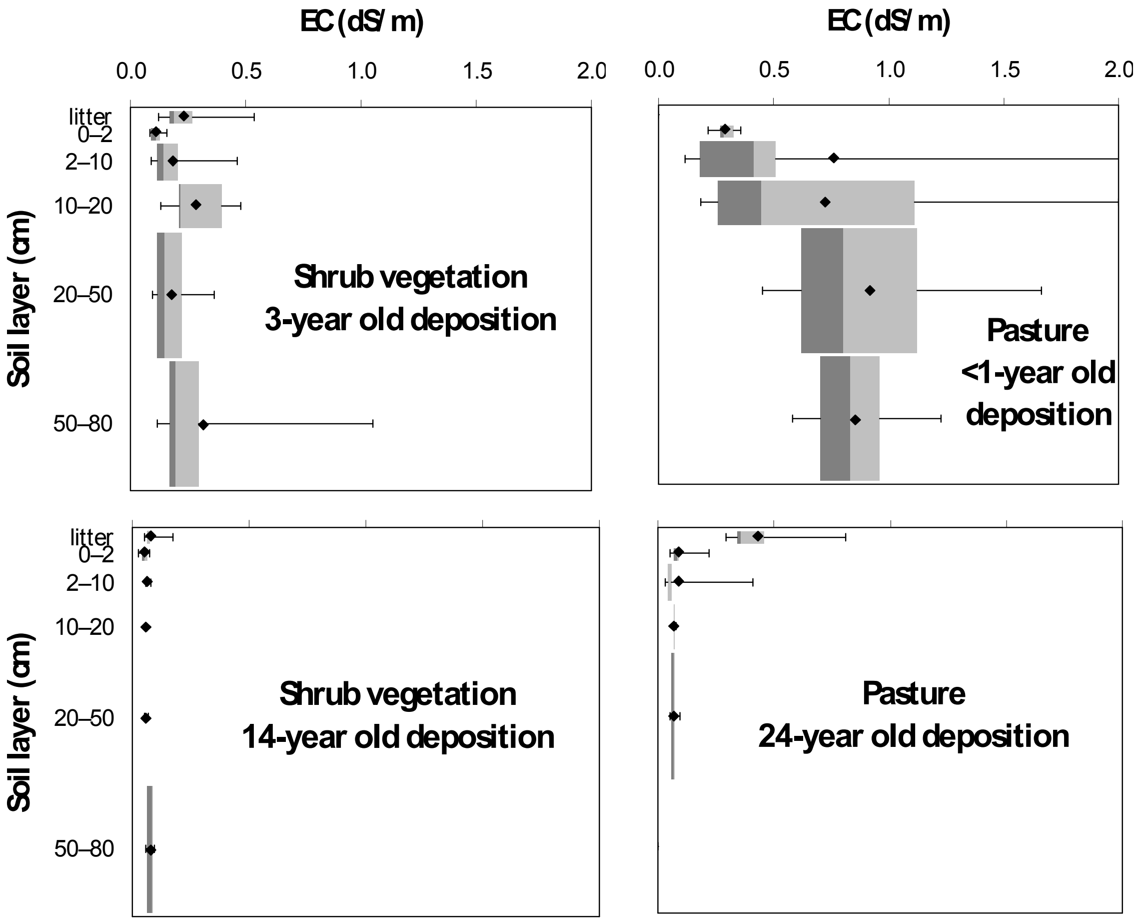

Figure 2. The spatial variability of soil layer EC within 6 × 6-m plots of scrub/woodland or pasture vegetation on different ages of deposition of bauxite residue sand. Data are represented as box and whisker plots, with boxes delineating the 25th, 50th, and 75th quantiles, and whiskers showing the range. Points show the mean.

The index of vegetation biomass was positively correlated with the age of deposition of the bauxite residue but not correlated with the age of the vegetation itself, when assessed on those sites that had been planted with the same suite of native species (Figure 3). This indicates that plant productivity is limited by some edaphic factor(s) given its lack of correlation with vegetation age. The pH data (ranging between values of about 6 at the surface and 8 at depth) did not show any clear trend with time, probably as a result of buffering by calcium carbonate formed through reaction of applied gypsum with residual alkalinity and CO_2. We have sampled too few sites at this stage to enable the use of an environmental envelope approach for identifying limiting factors (Fey and Mills 2009) and additional sites will be examined for which a wider variety of soil properties will be determined. Other researchers have emphasised the importance of leaching bauxite residue prior to the successful establishment of vegetation (Meecham and Bell 1977; Woodard *et al*. 2008). Once salinity has largely been removed, however, it is probable that the relatively high pH levels will result in deficiencies of one or more trace elements. Low availability of Mg is also potentially limiting in amended bauxite residue, although the key factors limiting vegetation growth after gypsum amendment and leaching remain to be identified.

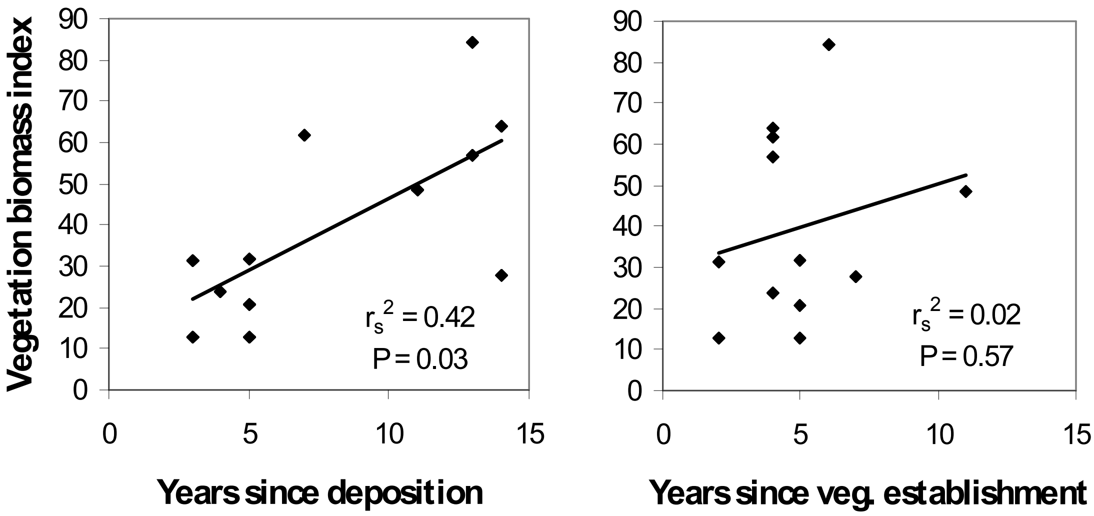

Figure 3. The correlation (Spearman rank correlation) of vegetation biomass index at each site versus years since the deposition of the bauxite residue sand and years since the vegetation was established. Only comparable sites that were vegetated with native scrub/woodland species are included in this analysis; pastured sites have been excluded.

Conclusions

The results confirm an expected pattern over time of both improved vegetation cover and ameliorated soil chemical status due to leaching of soluble salts. The study will now be expanded to include more soil properties and assessment at more sites. The chronosequence should also prove useful for examining microbiological processes affecting nutrient cycling. Ultimately it may be developed as a model of how ecosystem sustainability can be verified through temporal monitoring to reveal the parallel development of soil quality and vegetation.

Acknowledgements

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Agricultural recultivation of brown coal mining areas – initial soil physical properties after site construction

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Abstract
We investigated the agricultural recultivation of open cast brown coal mining areas in Lusatia, Eastern Germany. Lignite mining activities lead to large-scale disturbance of soils. Recultivation efforts attempt to regenerate mining areas for new agricultural land use options. The mainly sandy substrate used for recultivation is excavated from depths of several meters and is therefore devoid of recent soil organic matter. However, some lignite fragments are present. The substrate itself has poor soil structure. During the excavation, deposition and management process the substrate is subjected to strong mechanical stresses. This practice leads to more or less compacted soils/substrates, which may result in reduced yields of agricultural crops. In this context, we investigate the effect of different organic soil additives in combination with different recultivation crop rotations to improve soil structure for enhanced agricultural productivity and land use. Our experimental site was heaped up and levelled off in 2006/2007. On each of the experimental sub plots undisturbed soil samples have been taken to characterise the substrates according to their mechanical and hydraulic parameters before the application of any recultivation measures. We present results of the initial soil physical properties of the site.

Key Words
Precompression stress, dynamic loading, static loading, air conductivity, Technosols, anthropogenic site

Introduction
Open cast lignite mining activities result in the deposition of substrates, which have covered the brown coal. These overburden sediments of Quaternary and Tertiary origin are subsequently used to recultivate the post mining landscape (Pflug *et al.* 1998). The Quaternary substrates utilized for agricultural recultivation in our study originates from depths of several meters below the former soil surface. These substrates have not undergone pedogenetic processes, are unstructured, more or less devoid of organic carbon and have calcium carbonate contents of up to 4%. During dry periods the substrate is susceptible to intense hardening processes (i.e. hard setting) and during wet periods the mechanical stability is low (Stock *et al.* 2007). During wetting, the effective stress between soil particles decreases and becomes neutralised with increasing water saturation of the substrate. During drying increasing pore water suctions propagated by water menisci induce the movement of soil particles towards each other and consequently lead to a compressive deformation of the soil (Krümmelbein *et al.* 2007). Because of the lack of contemporary organic matter and poor soil structure the substrate is very susceptible to compaction (Stock *et al.* 2007), especially at high water contents. This natural process is intensified by the technical process of excavating, depositing and levelling off of the substrate on the recultivation sites using heavy machinery. The substrates are deposited on dams of several meters in height. Afterwards a heavy crawler, which induces strong mechanical stresses is used to level off these dams. Compacted areas often show poor soil functionality, which induces low agricultural productivity as well as negative environmental impacts such as water erosion (Krümmelbein *et al.* 2006; Hakansson 2005). High bulk density and a small interaggregate (macro-) pore volume cause productivity problems due to decreased aeration and modified hydraulic properties and nutrient fluxes. Soil water storage capacity and groundwater recharge are decreased due to soil compaction (Horn & Smucker 2005), which is especially problematic in typical dry summer periods in Lusatia. The recultivation sites are constructed as anthropogenic soil landscapes and are supposed to be constructed homogeneously according the utilised substrates. The technical processes are also applied uniformly on all recultivation sites of one open cast mining pit. In this investigation results of the status-quo-sampling before the application of any recultivation measures are shown.

Material and methods

Experimental area:

The experimental area is situated in Lusatia, Brandenburg, Germany (E14°35', N51°47') and belongs to the largest lignite mining area in Germany. The site of a total size of about 6 ha is supposed to be prepared homogenously according the utilised substrate and technical processes. It was constructed in winter 2006/2007, therefore the moisture content of the utilised substrate presumably was relatively high. The mean annual precipitation in the experimental area is about 570 mm with comparably dry summers and wet winters. Before the first sampling, the site had only experienced slight fertilization to supply the subsequent seeded clover-grass-mixture with nutrients. No recultivation treatment has been applied at this time. After the first sampling the experimental area was divided into 25 subplots, which were treated with various recultivation strategies (different organic soil additives, partly deep loosening, different crop rotations). The recultivation strategies will be investigates in terms of accumulating soil organic matter, developing improved soil structure stability as well as soil water balance. The mean content of calcium carbonate in the experimental area is 2.3% and the mean pH value ($CaCl_2$) is 8.4. The classification of texture according to the German system (2000 > sand> 63 µm; 63 µm > silt > 2 µm; clay < 2 µm) (Ad-Hoc-Arbeitsgruppe Boden 2005) is overall sandy and ranges from pure sand to loamy and silty sand.

Soil sampling:

Two sampling campaigns were planned, one directly after establishing the site (S1) and a second one after two years of recultivation (S2). For S1 on each subplot undisturbed samples were collected from a soil profile in three depths (15-19 cm, 45-49 cm, 75-79 cm). For purposes of clarity, only the results of one depth (45-49 cm) and eight (I - VIII) of the 25 subplots are shown (S1).

For the determination of static and dynamic precompression stress (n = 5) and air permeability (n = 15), undisturbed soil samples of a volume of 235 cm³ and for the determination of saturated hydraulic conductivity undisturbed samples of a volume of 100 cm³ were used.

For S2 eight soil profiles will be chosen to take samples in spring 2010. The same parameters as for S1 will be determined.

Measurements:

Bulk density (n = 15) was determined by drying the soil samples at 105°C for 24 h (Hartge & Horn 2009). For the determination of precompression stress and air permeability the samples have been equilibrated to a standard matric potential of -6 kPa prior to the laboratory measurements. Static and dynamic precompression stress was measured using a drained multistep-oedometer (n = 5). The loading steps were 20, 40, 50, 60, 80, 100, 120, 150, 300 and 400 kPa. For the determination under dynamic loading stepwise increasing loads were applied in loading cycles. One loading cycle consists of 30 s loading and 30 s unloading, 20 cycles were applied per load step. The method is described in detail by Krümmelbein *et al*. (2007). Precompression stress values have been determined graphically according to Casagrande, 1936 (Kezdi 1980).

Results

The soil bulk density of the soil profiles I-VIII varies between 1,35 g/cm³ and 1,90 g/cm³ (Figure 1).

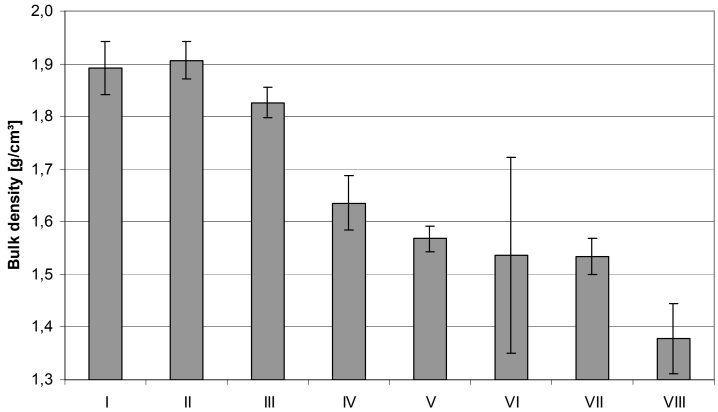

Figure 1. Soil bulk density of the profiles I-VIII (40-45 cm depth). Error bars show standard deviation, n=15.

The values of static precompression stress vary between 30 kPa and 70 kPa (Figure 2). The values of dynamic precompression stress show the same trend as the static ones but in generally about 10-20 kPa higher.

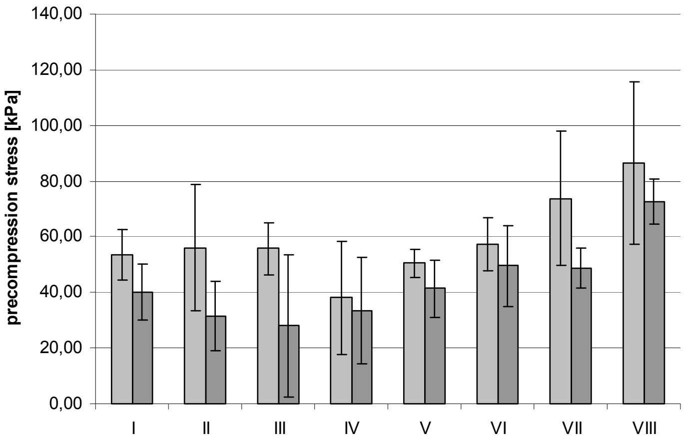

Figure 2. Precompression stress [kPa] of the profiles I-VIII (45-49 cm depth). Light grey: dynamic determination; dark grey: static determination. Error bars show standard deviation, n=5.

Discussion

The results presented in Figures 1 and 2 illustrate that the spatial heterogeneity of all the measured parameters is high, even though the preparation of the site is "assumed to be homogenous". These differences are mainly due to the technological processes of piling up and levelling off substrate dams of several meters height using heavy crawlers. The differences in bulk density not only result from the shape of the dams (higher bulk densities in former dam-areas, lower bulk densities in the former gaps between the dams) but also from the number of wheelings of the caterpillar. Furthermore, varying water contents of the substrate during levelling off influenced the substrate's effective soil strength, thus the amount of compaction (Fazekas and Horn 2005). Unfortunately, no water content of the substrate during site construction is available. To characterize soil physical properties, some authors determine bulk density and draw conclusions concerning soil functions, e.g. from hydraulic or air permeability and soil stability properties (Assouline 2006). It is assumed that the mechanical stability of soils and substrates increases with increasing bulk density (e.g. Rücknagel *et al.* 2007; Krümmelbein *et al.* 2006). Our results show that this is not necessarily the case for substrates, which have poor structure and additionally are homogenized during transport, deposition and levelling. We even found a negative correlation between bulk density and precompression stress. Our results prove that especially on strongly disturbed sites like our experimental area, that it is not possible to derive definitive soil characteristics such as air permeability or precompression stress from other parameters, (e.g. bulk density). In our study, soil functions such as air permeability are neither correlated with soil texture nor to bulk density (not shown). The dynamically determined values of precompression stress show the same trend as the static ones but are generally about 10-20 kPa higher, which is due to the time-dependency of the settlement. Precompression stress increases with decreasing loading time (Fazekas and Horn 2005). The concept of precompression stress assumes that mechanical loading of a soil below the precompression stress will completely be converted into elastic deformation (Horn 1989). Our results show that during the 20 loading cycles of each loading step and even if the applied load is kept below the precompression stress there was a slight additive settlement effect, which defines the deformation as partly plastic (not shown). Therefore cyclic loading can lead to compaction even though the load is kept below the precompression stress of the soil (Krümmelbein *et al.* 2007; Peth & Horn 2006).
In summary, it can be stated that a site, which has been anthropogenically constructed to be "technically homogeneous" is not necessarily the case because it may simply illustrate a "visual" homogenous distribution of soil physical parameters. Even if the texture of the substrate is similar across the total area, considerable differences in soil hydraulic and soil mechanical parameters can be expected to occur because of the technical compaction processes on the substrate, which is structureless and mechanically instable before site construction.

Outlook

The second soil sampling and measuring campaign in spring 2010 will allow to draw conclusions concerning the development of soil physical properties in dependence of the applied recultivation practice.

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Biosolids application for revegetalization of an abandoned nickel mine from New Caledonia

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Abstract
Old nickel mines from New Caledonia expose large surfaces without any plant cover. The lack of topsoil and the natural low fertility of soils were not favourable to plant growth in these places. In order to limit erosion and environment impact for the lagoon, it is important to restore the vegetation of these degraded sites. Numerous plantation programs have been established with process including fertilizers or organic amendments such as poultry litter.
In this study, sewage sludge had a positive impact on the growth of the different indigenous species planted in the experimental site. The tree heights were significantly higher after two growing years. The efficiency of sewage sludge was slightly better than poultry manure but it was not significant.
These results indicate that biosolids were as useful as poultry litter for fertilisation of ultramafic soils for mine site remediation.

Key words
Sewage sludge, lateritic soil, fertilisation, vegetal growth, *Carpolepis laurifolia*, *Grevillea exul rubiginosa*, *Gymnostoma deplancheanum*.

Introduction

New Caledonia is a small south Pacific island with a high plant diversity and high endemism. The plant specificity is partly linked to the ultramafic soils which were characterized by a poor concentration in nutrients (N, P, K) and high levels in heavy metals like Ni, Co Mn (Becquer *et al.* 2003). Moreover, since the 60s, nickel exploitation processes have removed vegetation on large surface with no rehabilitation program. It results in numerous places, free of topsoil, with a poor fertility, and subsequently, with high difficulties for a plant reinstallation. These soils are usually considered as toxic for plants. Revegetalization programs with plantations are essential for the remediation of mine sites.
Nevertheless, in order to facilitate the plant installation and growing, it is important to increase the soil fertility. In New Caledonia, chicken litter (with fertilizers) is often used as an organic amendment. Numerous authors have tested sewage sludge to replace fertilizers for plant cover restoration (Blechschmidt and al 1999; Delschen on 1999).
The aim of this study consisted of verifying that these biosolids promote plant establishment on a lateritic soil. A field experiment was conducted in an old mine location, comparing the traditional use (chicken litter) with sewage sludge amendments.

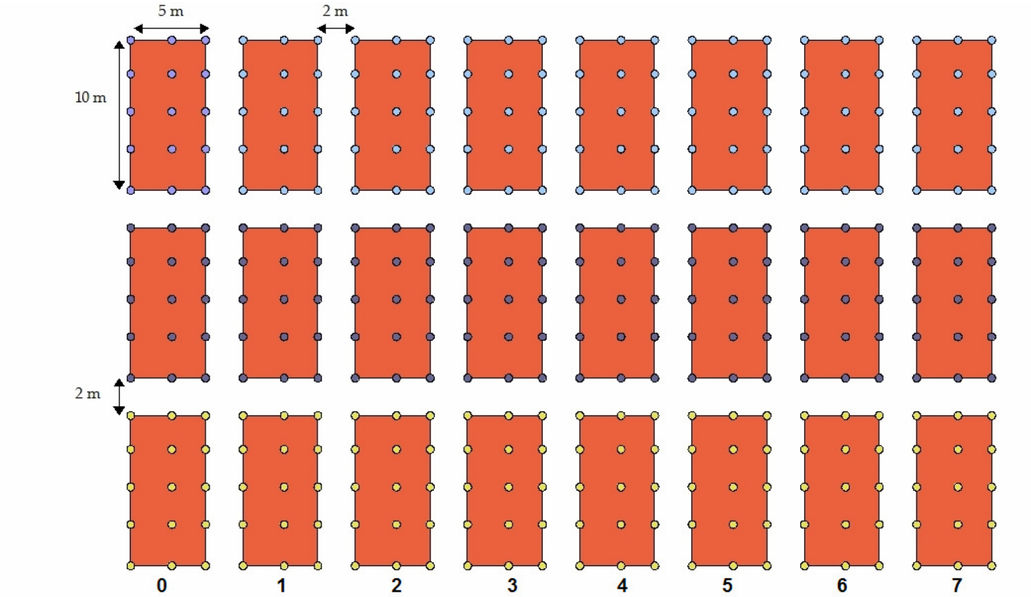
Methodology

Experimental design

The experimental site was located in an old mine (mine Claudette, Mont Dor, New Caledonia) characterised by a rocky soil totally free of topsoil. In this sloping area, 24 plots (5x10m) were delimited for the different amendment treatments. Plots were separated with a 2 m passages in order to limit material transfer from one plot to another.

The sewage sludge used for this study came from the activated sludge treatment plant of Koutio, New Caledonia. This sludge, obtained with a compression filter, was taken at the outlet of the water treatment plant, put in single-dose packets and directly transported to the experimental site. This sludge was characterized by a low level for heavy metals (in accordance with European policy) and 1.0% P and 4.6% N. Poultry litter and fertilizer were obtained from a commercial dealer.

In each plot, 15 seedlings were sown as described in the Figure 1 corresponding to a plant density around 1600 seedlings per hectare. Three local species (*Carpolepis laurifolia*, *Grevillea exul rubiginosa*, *Gymnostoma deplancheanum*) received either poultry litter or sewage sludge. The amendment level was calculated in order to provide the same nitrogen quantity (10g of nitrogen/kg) from each source (sewage sludge, poultry litter and fertiliser). Then, this organic matter was either spread on the top or mixed into the soil with or without fertiliser.



Treatment	0	1	2	3	4	5	6	7
OM	P	P+F	P	P+F	SS	SS+F	SS	SS+F

Figure 1. diagram of the planting methodology. P: poultry; SS: sewage sludge; F: fertiliser.

Vegetation measurements and sampling

All sown seedling were individually followed during their growth. Their heights were measured at the beginning of the experiment and twice a year from August 2007 (the beginning of the experiment). The survival rate was estimated by counting the individuals in each plot.
Ramification number from Carpolepis was also measured.

Statistical analysis

The effects of amendments on trees heights and mortalities were evaluated using a one-way ANOVA or a Kruskal-Wallis one-way ANOVA on the ranks when normality or equal variance tests failed. Comparisons of mean heights of a single plot between two measurement periods were conducted using a t-test. All the statistical analyses were carried out with SigmaPlot v11 software.

Results

During the experiment a high mortality was observed for *Grevillea* planted plots (until 100%). *Carpolepis* had the highest survival (70%).

During the first 6 months, no significant effects were observed on growth either for sludge or for poultry litter. Significant growth was observed after the first year for all treatments with no significant difference, between organic matters. A significant effect was observed for fertiliser additions for *Carpolepis*.

Discussion

For agricultural soils, since the early 70s (Hinesly *et al.* 1972; Kirkham 1974), and forestry (Bramryd 2002; Selivanovskya and Latypova 2006; Wang *et al.* 2004; Egiarte *et al.* 2005), sewage sludge has been used as a fertilizer. It provides an interesting option for lateritic mine soil restoration. Some authors have already demonstrated the role of biosolids for the establishment of a vegetal cover on mine sites, mine spoils or old quarries (Seaker and Sopper 1983; Blechschmidt *et al.* 1999; Delschen 1999; Kahl *et al.* 2000; Rate *et al.* 2004; Dudeney *et al.* 2004). Nevertheless, the current study showed that sludge did not result in immediate growth of plants. This delay may be due to the mineralization time as described by Garcia *et al*. (1991). Moreover, a high mortality was found at our site, and de Andrès *et al*. (2007) also observed increased mortality after sludge amendment, which may be due to high tropical precipitation immediately after plantation.

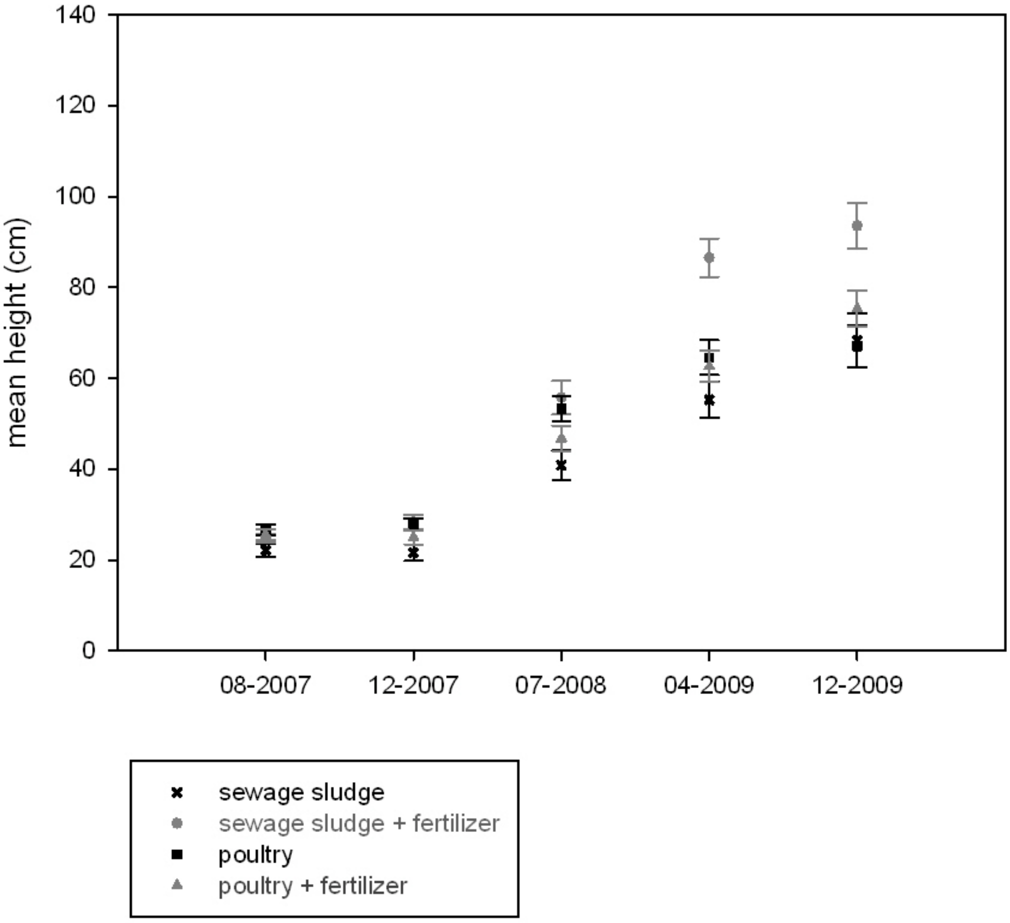


Figure 2. mean height of *Carpolepis* in amended plot with (+F) and without fertiliser.

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Characteristics of the soils of Toruń cemeteries

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Abstract
Necrosols are defined as soils resulting from excavations for graves. Soils of graveyards occur throughout the world. Cemeteries could be found in every town or city and in most villages. There was just only one published paper representing a genetic approach to investigation of necrosols (Sobocka 2004). Sobocka (2003) has defined a new anthropogenic soil type, included in the latest proposal of the anthropogenic soil classification. Necrosols are defined as soils formed by special human activity in cemeteries and burial grounds with specific soil horizons sequence, specific physical, chemical and biological properties. Aims of this paper are to investigate morphological, chemical and physical properties of necrosols in Toruń. This is part of a larger studies on urban soils of Toruń town in Northern Poland.

Key Words
Technosols, Necrosols, cemeteries.

Introduction
Necrosols are defined as soils resulting from excavations for graves. Soils of graveyards occur throughout the world. Cemeteries could be found in every town or city and in most villages. In central Europe, the post-mortem changes in human corpses usually take place in the earth. Ideally, decomposition leads to the entire skeletalisation of corpses, which is usually achieved within the regular resting time: 15–25 years (Fiedler and Graw 2003) Soil researches on cemeteries are very rare. First scientific researches dealing with necrosols were published in Czechoslovakia by Smolik (1957) and Svec and Hlina (1978). For the first time Necrosols was included in classification of urban soils in system proposed by Burghardt (1994). Also in Russia there was elaborated Systematics for urban surface formations (Stroganova *et al.* 1998; Gerasimova, Stroganova and Prokofieva 2003). In this system necrosols are defined as urban soils, depending on depth of burial and age of cemetery. In Poland the problem of graveyard soils was mentioned only in one paper (Bednarek *et al.* 2004).
There was just only one published paper representing genetic approach to investigation of necrosols (Sobocka 2004). Sobocka (2003) has defined a new anthropogenic soil type, included in the latest proposal of the anthropogenic soil classification. Necrosols are defined as soils formed by special human activity in cemeteries and burial grounds with specific soil horizon sequences, specific physical, chemical and biological properties.
Aims of his paper are to investigate morphological, chemical and physical properties and compare them with reference soils located on the verge of cemeteries, which were not disturbed by burial.

Methods
Six soil profiles located on cemeteries of Toruń were described and analyzed in 2006:
- 2 profiles was located in Central Communal Cemetery established in 1975;
- 2 profiles was located in St. George cemetery existing since 1811;
- 2 profiles was located in St. Jacob the Apostle Parish cemetery established in 1817.

In each cemetery there was located 2 soil pits – one in grave and reference one, out of the grave area, near the fence. Soil samples were submitted to standard physical and chemical analyses: relative moisture content [%]; Bulk density (g cm^{-3}); hygroscopic moisture [%]; Soil colour according to Munsell; texture (by Bouyoucose method modified by Casagrande and Prószyński; pH in water and in 1M KCl (1 : 2.5); $CaCO_3$ by Scheibler method; organic carbon (OC) by Tyurin method); total nitrogen by Kjeldahl method; total phosphorus by Bleck method, modified by Gebhardt; NA and K by ES method, Ca and Mg by AAS method (Bednarek *et al*. 2004).

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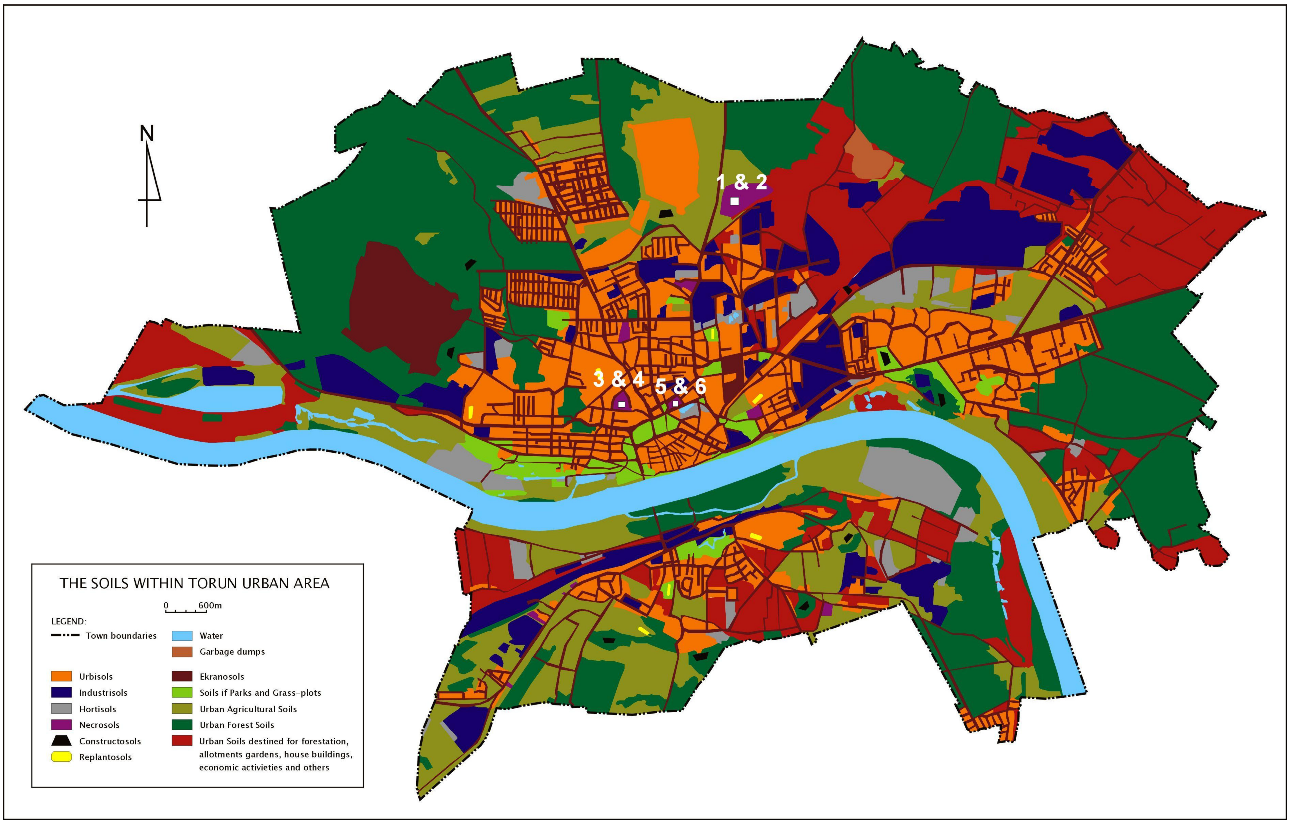

Figure 1. The map of soils within Toruń Urban Area with localization of soils profiles (reproduced from Bednarek, Charzynski, Zawadzka (2003); modified).

Results

Sand is dominant texture fraction in all horizons and layers of investigated soils (83-98%), silt fraction is from 1 to 8% and The fraction of clay had the lowest percentage share (0-4%). Investigated necrosols are well aerated and characterized by high permeability but low water-holding capacity and low soil absorbing capacity. Such soils are suitable for cemeteries because of relatively short time of complete human body decomposition (20 years).
The main features of morphology of necrosols are (Gerasimova *et al.* 2003*)* are: absence of natural horizons, presence of urban layers with sharp transitions and presence of anthroskeleton (e.g. fragments of bricks, glass, nails). This was also observed in soils of Torun cemeteries.

Samples taken from St. George cemetery and St. Jacob the Apostle Parish cemetery, two oldest ones in town consisted large quantities of human-made materials and artifacts. Example of sorts of artifacts found in profile 3 and 6 are shown in Table 1 and on Figures 2 and 3. Distribution of the bulk density values was different from the natural soils, where is usually rising with depth. In profiles 1 and 3 highest values of bulk density can be found in uppermost horizons/layers. In profiles 2 and 4 the lowest values of bulk density was noted in C horizons.

In all investigated soils OC content was rather low (0.17 – 1.62%). The pH values in most soils were neutral or slightly alkaline, which can be connected with some amounts of $CaCO_3$ to be found in most of the profiles (No 2, 3, 4 and 5). Only one soil profile (1) was characterized by acidic reaction. It was the soil in nearly natural state (Brunic Arenosol according to WRB 2006) located in youngest of the cemeteries, earlier used for military purposes. Background value for total phosphorus in sandy soils in central Poland is about 250 mg/kg. In investigated soils it had usually higher values, especially in urban layers (up to 524 mg/kg) and layers enriched in organic matter (up to 580 mg/kg). The highest value of P (984 mg/kg) can be found in A horizon of profile 3. This soil used to be a garden soil and organic fertilizers could be the source of phosphorus in that case.

Table 1. Sort of artefacts in skeleton in profile 3 (St. George cemetery).

Horizon/layer	Sort of artefacts	%
W1	gravel	37
	loam	31
	concrete and bricks	13
	cinder	9
	metals	7.5
	ceramics	1.3
	plastic	0.5
	bones	0.1
A	concrete and bricks	72
	gravel	25
	cinder	2
	glass	0.8
	charcoals	0.6
	bones	0.2
AC	gravel	81
	charcoals	14
	bones	4.3
	plastic	1

Table 2. Selected chemical properties.

Horizon	Depth (cm)	Bulk density (g/cm^3)	Hygro-scopic water (%)	OC (%)	N (%)	C/N	P (mg/kg)	$CaCO_3$ (%)	pH	
									H_2O	KCl
Profile 1										
A	0-4		0.59	0.80	0.056	14	307	-	5.3	4.4
Ap	4-25	1.60	0.51	0.51	0.030	17	245	-	4.8	4.4
A2	25-30	1.55	0.42	0.36	0.020	18	267	-	4.9	4.5
Bv	30-62	1.52	0.44	-	-	-	156	-	4.8	4.6
C	62-(118)	1.54	0.11	-	-	-	87	-	5.0	5.0
Profile 2										
WA	0-11	1.57	0.83	0.98	0.070	14	382	0.3	8.1	7.6
W	11-15	1.57	0.22	-	-	-	121	-	7.9	7.0
A	15-36	1.63	0.53	0.50	0.035	14	347	-	7.6	6.6
B	36-60	1.67	0.32	-	-	-	137	-	7.4	6.1
C	>60	1.51	0.14	-	-	-	80	-	7.2	6.0
Profile 3										
W1	0-14	1.62	0.29	0.34	0.021	16	339	0.4	8.1	7.8
A	20-50	1.19	1.17	1.62	0.124	13	984	0.4	7.6	7.1
AC	50-70	1.48	0.24	0.17	0.014	12	247	0.3	7.9	7.5
C	70-(160)	1.57	0.14	-	-	-	186	0.2	7.6	7.0
Profile 4										
An	0-53	1.46	0.61	0.69	0.049	14	472	0.5	8.1	7.6
AC	53-65	1.66	0.20	-	-	-	126	0.4	8.6	8.3
C	65-(110)	1.60	0.13	-	-	-	115	0.2	8.0	7.3
C (inclusion)	65-(110)	1.52	0.40	0.50	0.035	14	292	0.4	7.8	7.4
Profile 5										
A	0-20	1.35	0.70	0.84	0.060	14	468	0.8	7.7	7.4
W1	20-33	1.33	0.63	0.62	0.051	12	524	1.0	7.7	7.3
W2	33-70	1.38	0.63	0.43	0.039	11	361	0.9	7.9	7.4
W3	70-87	1.47	0.50	0.44	0.040	11	390	1.0	8.0	7.5
W4	87-(110)	1.54	0.58	0.47	0.044	11	372	0.7	7.9	7.3
Profile 6										
A	0-60	1.38	0.64	0.93	0.068	14	580	-	7.2	6.8
AC	60-85	1.49	0.53	0.78	0.053	15	372	-	7.1	6.5
C	90-(100)	1.49	0.44	0.48	0.038	13	352	-	7.3	6.7

Figure 2. Artefacts from profile 6 – bones and clothing pieces (nylon stockings).

Figure 3. Layer with coffin remnants in profile 6.

Conclusion

Cemeteries soils are characterized by very variable morphological, physical and chemical properties, which depend on age of cemetery and former land use (settlement areas, gardens, garbage dumps, industrial plants). Specific features of necrosols are:

- presence of mixed and disturbed horizons;
- presence of large quantities of artefacts;
- raised amount of OC in lower layers as a effect of body decomposition;
- raised amount of phosphorus in comparison with background values;
- higher pH values

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Effect of covering with natural topsoil as a reclamation measure on mining dumpsites

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Abstract
Soil reclamation after open-cast brown coal mining is a way of landscape restoration. Covering of the dumpsite earth with natural topsoil (topsoiling) is a common reclamation practice. We compared soil characteristics between areas with natural topsoil cover and without this cover on two different dumpsites. It was shown that natural topsoil cover increased organic carbon content and humus quality of the soil and slightly increased the content of available phosphorus that is generally deficient in the dumpsite soils of the region. In contrast, contents of available calcium and magnesium were lower on the covered sites; however, the supply of these nutrients is still very good. Natural topsoil cover also decreased the content of clay. However, the total and capillary porosity decreased. The effect of topsoil cover on soil pH was not consistent between the two sites under study. The effect of topsoil cover on soil heterogeneity was also assessed using geostatistics. In conclusion, the natural topsoil cover can generally improve the starting quality of the developing soil.

Key Words
Soil reclamation; mining dumpsites; basic characteristics; topsoil cover; spatial heterogeneity; geostatistics.

Introduction
Large-scale open-cast mining of brown coal is a commonly used method of mining. It leads to formation of permanent dumps of sterile rock. An effort is concentrated on landscape reclamation and revitalisation of these sites in the northern parts of the Czech Republic. In order to make either agricultural or forest exploitation possible, it is necessary to reclaim the dumpsite earths. They are usually sterile rocks, often very clayey, with no or very low organic matter content and sometimes also with unfavourable soil reaction. One reclamation measure consists in covering soil with natural topsoil (Bell 2001; Borůvka and Kozák 2001). It should increase organic matter content and improve nutrients status. Physical properties, particularly soil structure, are often improved (Valla *et al.* 2000). Moreover, topsoiling should increase biodiversity of the newly created soils (DePuit 1984; Schladweiler *et al.* 2005).

The spatial heterogeneity of those anthropogenic soils is usually high, as the deposited material is very heterogeneous, including sterile rock with variable composition and from different depths, remains of brown coal carbon, and possibly added material rich in organic matter. This variability did not develop naturally as a result of pedogenic processes and natural spatial distribution, as it is the case in natural soils, but it is the result of human activities (Borůvka and Kozák 2001; Rohošková *et al.* 2006). The time of the development of reclaimed dumpsite soils is too short for the factors to manifest fully (Sencindiver and Ammons 2000). Nevertheless, temporal changes of reclaimed soils even at the initial stages of their development are very important (e.g. Šourková *et al.* 2005).

The aim of this study is to evaluate the effect of natural topsoil cover on soil properties of two dumpsites in Northern Bohemia and to assess the heterogeneity of the reclaimed soils.

Methods
Studied areas and sampling
Two dumpsites of the Severočeské doly, a.s., mining company were selected: Libouš and Pokrok. Both are formed by clays. Soil samples were collected on both areas using a sampling scheme shown on Figure 1. 45 soil samples were collected on each site from the depths of 0 to 20 cm. The sampling scheme was placed on each dumpsite on the border between areas with and without topsoil cover so that approximately half of the sampling points were located on the area with natural topsoil cover, half of the points were on the area without the cover.

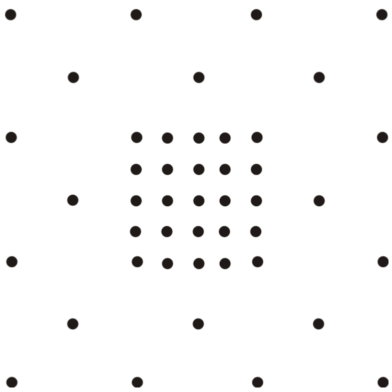

Figure 1. Sampling scheme applied on both dumpsites. The size of the big square was 90x90 m at the Libouš dumpsite and 120x120 m at the Pokrok dumpsite.

Soil analyses
Selected basic soil characteristics were determined by commonly used methods. Exchangeable soil pH (pH_{KCl}) was measured potentiometrically in 0.2M KCl extract (1:2.5; w:v; Zbíral 2002). Oxidisable (mainly organic) carbon content (C_{ox}) was determined oxidimetrically by a modified Tyurin method (Pospíšil 1964). Humus quality was assessed by the ratio of absorbances of sodium pyrophosphate soil extract (1:20; w:v) at the wavelengths of 400 and 600 nm (A_{400}/A_{600}; Pospíšil 1981). Content of carbonates was determined volumetrically after reaction with 10% HCl. Particle size distribution was determined by the areometric method. Available nutrients (Ca_{av}, Mg_{av}, K_{av}, P_{av}) were determined in Mehlich 3 solution (Zbíral 1996). Physical properties (bulk density – □$_d$, total porosity, capillary porosity) were determined using a common procedure on undisturbed soil samples collected into physical cylinders.

Data treatment
Data were statistically processed using Statgraphics Centurion XV software (StatPoint, Inc.). Spatial variability was described using GS+ geostatistical software (Robertson 2000) and ArcMap v. 9.2 (ESRI Inc.).

Results and discussion
Comparison between areas with topsoil cover and without this cover is shown in Table 1.

Table 1. Effect of natural topsoil cover on chemical and physical properties of reclaimed dumpsite soils of the Pokrok and Libouš dumpsites: mean values and t-test results (t and P values). Differences at P ≤ 0.05 are put in bold.

Characteristic	Pokrok dumpsite				Libouš dumpsite			
	Without cover	With cover	t-value	P	Without cover	With cover	t-value	P
C_{ox} (%)	0.312	1.827	**-12.79**	**< 0.001**	0.721	1.263	**-6.503**	**< 0.001**
A_{400}/A_{600}	4.18	3.76	**3.767**	**0.001**	4.909	3.917	**7.957**	**< 0.001**
pH_{H2O}	6.83	6.17	**4.094**	**< 0.001**	6.365	7.167	**-4.781**	**< 0.001**
pH_{KCl}	6.38	5.88	**3.148**	**0.003**	5.969	6.663	**-4.062**	**< 0.001**
Carbonates (%wt.)	0.042	0.045	-0.130	0.897	0.048	0.078	-0.434	0.666
Ca_{av} (mg/kg)	3744.4	3424.8	1.337	0.187	3851.3	5239.4	**-3.462**	**0.001**
Mg_{av} (mg/kg)	1345.3	534.3	**10.15**	**< 0.001**	1658.3	1336.2	**4.532**	**< 0.001**
K_{av} (mg/kg)	411.0	286.0	**7.838**	**< 0.001**	442.2	253.3	**9.785**	**< 0.001**
P_{av} (mg/kg)	12.19	27.52	**-4.998**	**< 0.001**	13.72	15.01	-0.290	0.774
Clay (%wt.)	56.70	31.17	**11.88**	**< 0.001**	49.46	44.01	1.354	0.183
Silt (%wt.)	34.56	37.00	-1.884	0.066	36.05	35.12	0.397	0.693
Sand (%wt.)	8.74	31.83	**-15.64**	**< 0.001**	14.49	20.87	-1.882	0.067
□$_d$ (g/cm^3)	1.295	1.327	-0.559	0.579	1.15	1.30	**3.922**	**< 0.001**
Porosity (%vol.)	49.40	46.15	**2.096**	**0.041**	55.06	49.07	**3.922**	**< 0.001**
Capillary porosity (%vol.)	44.85	35.27	**7.500**	**< 0.001**	45.30	40.08	**4.000**	**< 0.001**

On both dumpsites, covering with natural topsoil increased the content of oxidisable carbon and improved organic matter quality indicated by lower A_{400}/A_{600} ratio. It shows that the organic matter from natural topsoil is more mature and humified than the organic matter of dumpsite earths. Moreover, a part of the oxidisable carbon in the uncovered dumpsite earths can be coal waste rather than soil organic carbon (Bořůvka *et al*. 1998). The effect of topsoil cover on soil pH was not consistent between the two dumpsites under study; both pHs were lower in covered soils on the Pokrok dumpsite compared to the soils without topsoil cover, while the opposite was true for the Libouš dumpsite. Nevertheless, all pH values are quite favourable, ranging around neutral values, probably thanks to the carbonate content in all soils.

Topsoiling slightly increases the content of available phosphorus that is generally deficient in the dumpsite soils of the region. In contrast, the contents of available calcium, magnesium, and potassium were lower on the covered sites; however, the supply was still very good in soils of both areas.

Natural topsoil cover also decreased the content of clay, particularly at the Pokrok dumpsite. Content of sand was increased correspondingly, which could lead to better physical properties as the dumpsite earths of the area are generally very clayey. However, the bulk density (ρ_d) increased and total and capillary porosity rather decreased by topsoiling, probably due to the machinery traffic. Nevertheless, the proportion of coarser pores increased on the cover areas, which is a positive sign implicating better aeration and easier infiltration and water transport in the soils with natural topsoil cover.

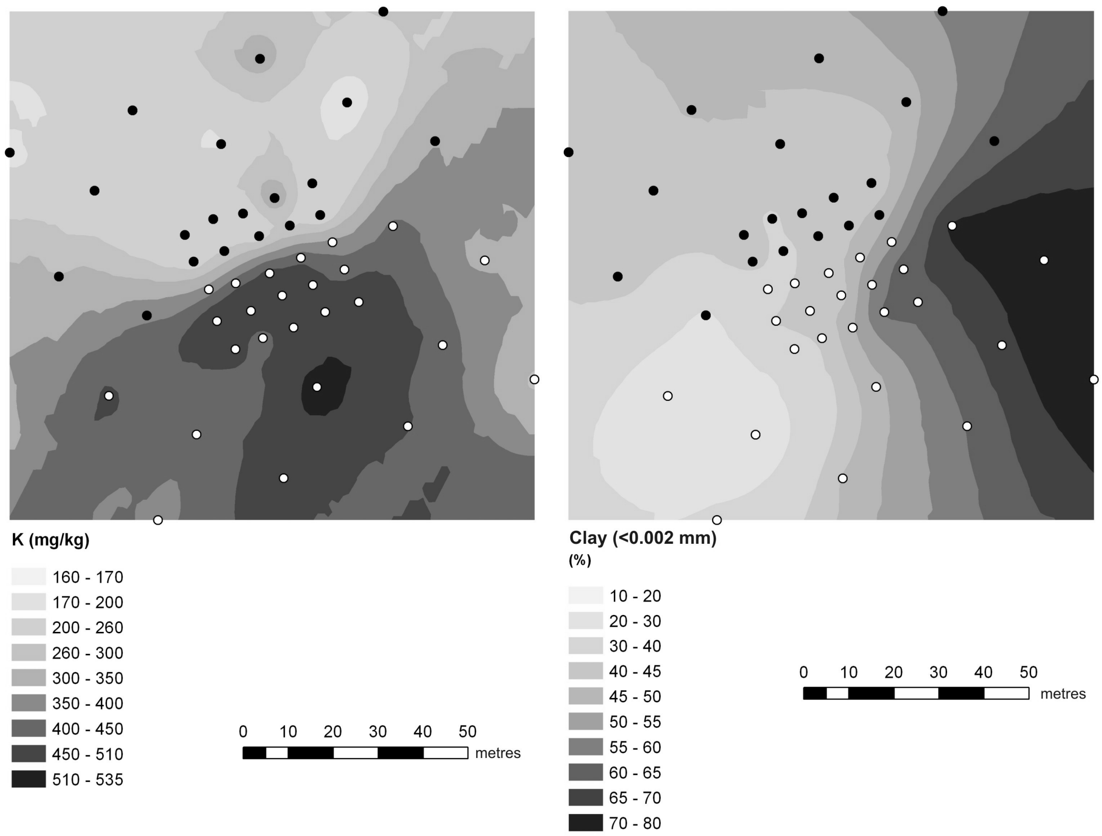

Figure 2. Example of spatial distribution of soil properties: content of available K (left) and content of clay (right) on the Libouš dumpsite study area. White points indicate sampling points without natural topsoil cover, black points those with topsoil cover.

Spatial distribution was assessed by means of geostatistics. Variogram parameters differed between the areas with and without topsoil cover; however, there was not a consistent difference (data not shown). Kriging maps showed spatial distribution and the effect of topsoil cover on the spatial distribution of soil properties. For some soil properties there is a clear shift between the areas with and without cover, as for example in case of available K content in the Libouš dumpsite (Figure 2, left). In contrast, there are characteristics that do not show a clear effect of topsoil cover on their spatial distribution, as for example clay content in the Libouš dumpsite (Figure 2, right).

Conclusion

The natural topsoil cover can generally improve the starting quality of the developing soil. It can facilitate further soil forming process, as well as the exploitation of the soils particularly for agricultural use. Spatial variation and distribution of soil properties is also influenced by the way of reclamation.

Acknowledgement

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Fertility status of soils developed on an inactive mine tailings deposition area in Papua

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Abstract
Tailings are the residue of mined material after separation of metals such as copper, gold and silver elements. Separation of minerals involves crushing of the host material to fine particles and separation of the metals by flotation or other techniques. The total amount of tailings produced by PTFI from their Grasberg mine is about 230,000 tons/day. These tailings are deposited in a lowland area and are confined by two levees. There are two types of plant growth on inactive tailings according to land use (natural succession area or reclaimed agricultural area). This study of soil fertility on the mine tailings was required to contribute to information on the management of tailings. Representative sampling locations were chosen based on soil texture. Soil (0 - ≤ 50 cm depth) was subjected to laboratory analysis. Total soil N is very low (< 0.02%), CEC low to medium (≤ 20 me/100g), and organic C ranges from 0.1 - 2%. pH is 7 - 8 resulting in the low availability of some nutrients, but values of extractable Cu may be high (≥ 300 mg/kg). Nutrient elements are more abundant in soils on fine textured tailings.

Key Words
Fertility, soil development, tailing ModADA.

Introduction
Tailings are the portion of the original mineral-bearing rock left after extraction of copper, gold and silver minerals. The separation of these minerals involves crushing and grinding the rock into a fine sandy material and separation of ore minerals by a flotation technique. This process is done at Mile-74, where the tailings are deposited into the Aghwagon river located at an altitude of 2,800 m asl and tailings flow gravitationally to the lowlands, where they are deposited in the Modified Ajkwa Depositional Area (ModADA), in Mimika, Papua. According to PTFI (2000; 2003; 2006; 2007), tailings are deposited at the rate of about 230,000 tons/day. The main sulfide minerals of the ore are chalcopyrite, covellite, bornite, and digenite (PTFI 1997) and some of these minerals are present in the tailings which are treated with lime to combat the acid sulfate reaction. The tailings in ModADA are deficient in some macro nutrients, while base cations and some micro nutrients are abundant. Deposition of tailings in ModADA will take place until the year 2040. A study of the soil fertility of tailings is required in order to determine the ability of vegetation to grow on the inactive tailings area. Amelioration requirements for a considerable area of tailings that will require revegetation need to be determined to optimise land use. The objectives of this research were: 1) to study vegetation cover and soil characteristics on inactive tailings in ModADA; 2) to identify the capacity of the tailings areas to support agricultural crops and natural reforestation based on soil properties.

Methods
Study area
The research was done on tailings ModADA in Timika, Papua (Figure 1). The tailings area is located in the lowlands of Timika and has a high rainfall from 3,500 - 4,000 mm/year, temperature from 25- 27 ^{o}C, and humidity > 90%. On the west side of the west levee of the tailings deposition area, there are about 1500 ha of the tailings that are inactive (8 - 20 years). There are two approaches adopted by PTFI to rehabilitate the tailings area, these are: 1) enable the natural succession of local vegetation to develop, and 2) develop the deposit area with agriculture, forest plants, and animal livestock. The first area with a natural succession has a depth to ground water < 50 cm, and is known as the Succession Area. The second area is used both for agriculture and forestry with a depth to ground water ≥ 100 cm, and is known as the Reclamation Area.
The representative location for soil sampling was chosen based on differences in existing vegetation and particle size distribution (coarse - medium - fine) of tailings from north to south on the inactive tailing area, ModADA.

Plant identification for the natural succession and reclamation areas
Plant species were identified for the natural succession and reclaimed areas from Mile 24-28 covering a transect from south to north. Transects were established and plant species were identified by standard methods (LIPI 2004). The vegetation in the reclaimed area was not identified by transects but by observation during soil sampling. The data collected were used to study the distribution of each plant species and to identify plant species suitable for use in the tailings area.

Soil sampling
Soil samples from the reclaimed and natural succession sites from each distinct layer to a depth of 50 cm, were taken for analysis of pH, organic C, base cations, CEC, macro and micro nutrients, and texture.

Results
Vegetation in the inactive tailings area, ModADA
1. Succession area
Vegetation in the natural succession area was predominantly *Phragmites karka* (seedling) with an importance value > 80%, followed by *Ficus adenosperma, Ficus armiti, Nauclea papuana, Glochidion macrophila, Macaranga aleoritoides* (level trees); *Adina nerifolia, Pandanus* sp., *Casuarina equistifolia, Glochidion macrophila, Camnosperma berpetiolata, Ficus damaropsis,* and *Sterculia* sp. (young trees). *Phragmites karka* is the dominant species in the natural succession area. *P.karka* is a robust, erect, perennial grass (reed) up to 4 m tall with an extensive, creeping, branching rhizome or stolon up to 20 m long. It spreads by its creeping rhizomes (underground) or stolon (above ground) (PROSEA 2003) and grows in standing water and is tolerant to flooding. The ability of *P.karka* to dominate the inactive tailings deposition area creates a better soil microclimate and rapidly increases soil organic carbon compared to the other vegetation. Most successions contain a number of stages that can be recognized by the collection of species that dominate at that point in the succession. Succession stages are closely tied to the tolerance of plant species for soil conditions. Succession stops when species composition no longer changes with time, and this community is said to be a climax community. Climax represents a relatively stable plant community which has a dominant plant population suited to the environment. Stages of succession in general are as follows: Grasses-Forbs → Shrub-Seedlings → Sapling-Pole → Young → Mature → Climax (Martin and Gower 1996). A general succession of plant species based on the research work in the ModADA is illustrated in Figure 2.

2. Reclamation area
Reclamation activities since 2000/2001 have been implemented by planting with various native forest and agricultural plants. Native plants including *Metroxylon sago*, *Pometia pinata*, and *Casuarina equisetifolia* show good plant growth comparable to growth on adjacent non-tailings soil. Most of the reclamation area is dominated by *C.equisetifolia* which also occurs in the natural succession area. *Calopogonium muconoides* occurs in this area and is well adapted as a cover crop in the reclamation area. The South to North (Mile 26-28) area is planted in blocks with the followed of species 1). *C .equisetifolia*, *Metroxylon sago*, with *C.muconoides* as cover crop; 2). *Pometia pinata*, *C.equisetifolia*, with *Paraserianthes falcataria* as a border plant and *C.muconoides* as a cover crop; 3). Alley Cropping (*Paraserianthes falcataria, Leucaena leucocephala*, *Gliricidae sapium*, *Caliandra surinamensis*, *Sesbania grandifolia)*, *C.equisetifolia*, *Coconut nucifera*; 4). *Pennisetum purpuphoides*, *C.equisetifolia*; 5). *C.equisetifolia, C.muconoides*; and 6). *C.equisetifolia, C.muconoides, P.karka, Dryapteris* sp. Although the tailing area on the north side is dominated by sandy materials, crops grow and adapt readily to the soil material. Based on Management Report and Environmental Monitoring of PTFI (2004) using routine monitoring of the growth of crops in the reclamation area occupied by *P.pinata* and Alley Cropping, the rate of growth increased each month.

Soil fertility of the reclaimed area
The land cover in the Double Levee ModADA area is mostly natural vegetation, and species depend on soil characteristics. So far, the soils developed on the tailings in these areas are still relatively young and consequently their structure ranges from loose to massive reflecting the presence of predominantly sandy to silty materials, and a low content of OM (< 1%). Only one area with particle size of silty coarse sand has an OM > 1% in the surface soil. The pH ranged from neutral to alkaline. Only a few samples had an acid pH for the surface soil. All of the soil samples with a sand texture have a range of pH from 7-8 in each layer. Whereas, soils with a texture of loamy coarse and silty coarse sand have a tendency to be acid in the surface soil and alkaline in the subsoil.

Soil pH affects the solubility and availability of most nutrients. The availability to plants of most metals decreases with increasing pH. Values of CEC were < 10 cmol/kg and OM ≤ 1%. Most CEC values are very low except for several surface soils. Total N is very low (< 0.02 %) in the reclaimed area with sandy soils. Total N tends to increase (≥ 1%) for the surface soil on both loamy coarse sand and silty coarse sand in the reclamation area. To increase the fertility of tailings soils, an application of OM would be beneficial with the goal of increasing CEC, organic C, and N. Observations of the macro- and micronutrient contents including metals in the reclaimed area indicate that N, K, and organic C contents tend to be low. Available micronutrient contents (Fe, Mn, Cu, Zn) tend to be high contents of other nutrient elements, relatively low to very low. The concentration of available Cu ranges from 100 to ≥ 300 mg/kg and varies between layers. The higher available Cu in sandy soils is caused by the low pH due to the impact of oxidation of sulfides and the high OM content especially for the horizon surface. Available Fe, Mn, Zn levels are lower than Cu. Tisdale *et al*. (2005) show that the availability of micro nutrients is usually low on soils of alkaline pH.

Soil fertility in the natural succession area

The average OM value of surface soil increases from north (maximum sand) to south (maximum silt) i.e.: 0.21, 2.29, and 2.32 % respectively. Organic C is most abundant in this area as a result of of *P. karka* biomass accumulation. It is evident that formation of an OM layer on the tailings via natural plant growth takes a long time (Jacob and Otte 2004). The increase in OM has an effect on available Cu because of the low pH. Cu tends to increase because of the oxidation of sulfide minerals due to the root of *P. karka* providing O_2 to submerged subsoil. Available Cu has a tendency to increase to a very high concentration (≥ 500 mg/kg) in each layer of the loamy coarse sand. Total S increases in sub soil horizons > 1% for both silty coarse sand and loamy coarse sand. Wang *et al.* (2006) show that fine particles with a high specific area increase adsorption of nutrients and metals. Acosta *et al.* (2009) also noted the tendency of metals to accumulate on fine particles.

Micro elements in plants

Plants utilise nutrients for their development if the nutrient is in available form in soil solution. Commonly the availability of a nutrient in soil is indicated by the plant nutrient status. The analysis of As, Cu, Hg, Pb, and Zn in the plants indicated that metal uptake from the tailings materials is minimal and levels of metals in the plants are below the maximum values stipulated in the National Food and Drug Administration Decree No.03725/B/SK/ B/VII/SK. Microelements such as Cu can be easily changed in solubility due to reaction with inorganic or organic materials with their solubility varying with pH (Pais and Jones 1997). Although the concentration of some micronutrients in tailings soils is relatively high the alkaline pH has limited metal uptake by the plants.

Conclusion

Clearly many plant species have the ability to grow and adapt to the soil conditions in the tailings area of ModADA. Characteristics of tailings are not optimum for growing plants, because of deficiencies of N, low organic C, high base cations (Ca, Mg) and available metals (Cu, Fe), and CEC values are low. pH values of the tailing soils are maintained at neutral to alkaline values by liming to limit metals uptake by plants.

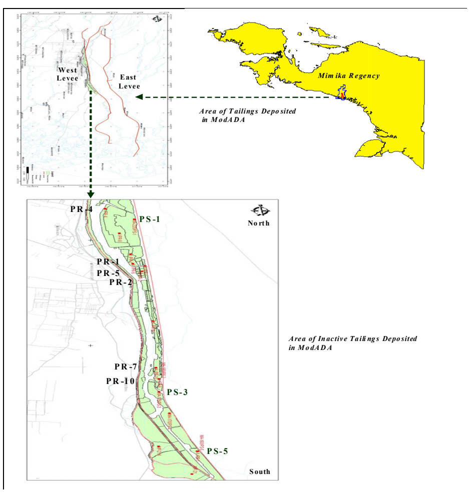

Figure 1. Area of Inactive Tailings in ModADA.

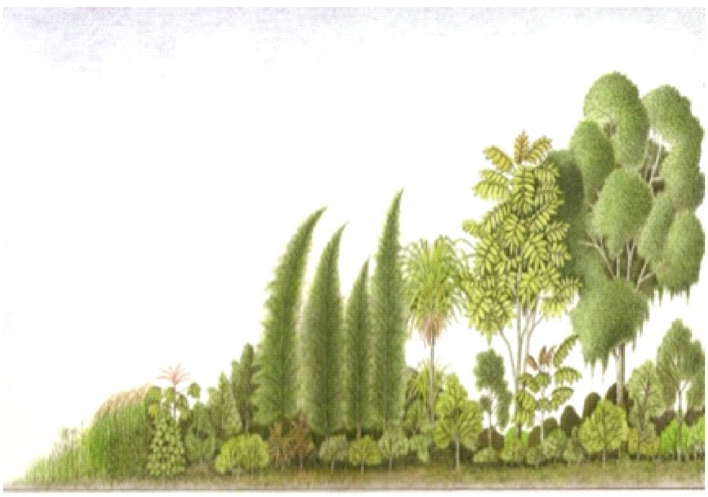

Figure 2. Pattern of Plant Succession on Tailings Deposition Areas, ModADA.

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Geochemistry of artifactual coarse fragment types from selected New York City soils

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Abstract
The coarse fragment (>2mm) content in six substratum horizons from two anthropogenic soil profiles in New York City was divided into natural rock fragments and human-made artifacts, and the latter sorted into types. The four most common types, asphalt, brick, concrete, and slag, were analyzed for several trace metals, as well as carbon, nitrogen, and sulfur. Asphalt fragments were relatively high in mercury and lead, while slag fragments were high in copper, lead, and zinc. To determine if any of the artifacts could be used as an indicator of the degree of soil contamination, the trace metal content in the fine earth fraction from each of the horizons was compared with the amount of each artifact present. Although the metal content of brick fragments was relatively low, the amount of brick present had highest correlation with fine earth trace metal content. High levels of carbon in asphalt and slag fragments indicate that the >2mm fraction can make a significant contribution of to the total carbon content in anthropogenic soils.

Key Words
Artifacts, technosols, urban soils, trace metals.

Introduction

The amount and type of coarse fragments are commonly described in soils but relatively few analyses have been conducted. Ugolini et al (1996) recognized the contribution of the soil skeleton, or coarse fragments, to the physical and chemical properties of soils. In a follow up report, Corti *et al.* (1998) proposed a classification system based on the degree of fragment alteration. Artifacts, or coarse fragments of human origin, are common in human altered soils, and can constitute a significant proportion of the soil. In WRB classification, soils with 20 percent or more (by volume, by weighted average) artifacts in the upper 100 cm of soil are placed in the *Technosol* Reference Soil Group; 10 percent or more merit a *Technic* intergrade qualifier. Classification of anthropogenic soils in the USDA-NRCS New York City Soil Survey separates those soils with less than 10 percent artifacts (clean fill) from those with greater than 10 percent. However, there has been little in the way of research on the direct effects of artifacts on soil properties. El Khalil *et al.* (2008) pointed out the contribution of the artifactual coarse fragments to the water soluble fraction of metals in some Moroccan soils.

Methods

Artifacts were selected from substratum horizons in two anthropogenic soil profiles in New York City, both located in city parks, in formerly wet areas covered (for at least 50 years) with tens of feet of artifact-laden fill materials. Samples 1 through 4 were taken from an Ebbets (Coarse-loamy, mixed, active, mesic Typic Eutrudepts) sandy loam in Kissena Corridor Park, Queens. Samples 5 and 6 were taken from a Laguardia (Loamy-skeletal, mixed, active, nonacid, mesic Typic Udorthents) sandy loam in Soundview Park, Bronx. Both soils had the weighted average of greater than 10 percent artifacts by volume (in the particle size control section) that is used to differentiate artifactual from "clean" soils in the New York City Soil Survey. However, only the Laguardia pedon met the 20 percent criteria for classification as a Technosol in WRB. The weighted average artifact content in the top 100cm for the Ebbets soil was 16 percent.

Two pedons were sampled by horizon and macromorphology described (Schoeneberger *et al.* 2002). Bulk samples were air-dried and sieved to <2-mm. The >2mm fraction was sieved and sorted into rock fragments and human-made artifacts. The latter were further separated into types, with four main groups: asphalt, brick, concrete, and coal slag. Laboratory analyses followed by codes were performed according to Burt (2004). Total C, N, and S was determined by dry combustion (6A2f) and calcium carbonate equivalent (CCE) by use of an electronic manometer to quantify gas evolution following acid contact in a closed vessel (6E1g). Total analysis of the <2-mm fraction and the artifact samples were determined by microwave digestion in concentrated HF, HNO3, and HCl, with determination of elements by ICP spectroscopy (4H1b).

Results

Table 1 shows the depth in the soil profile, and the composition, by weight, of the six horizons. Substratum horizons were selected since a thin layer of cleaner, better quality topsoil for successful plant growth is commonly placed over the chunkier artifact-laden material in parkland. The artifact proportion of these horizons varies from 2.5 to 80.7 percent. In Table 2, the breakdown by artifact type, concrete makes up the largest proportion of artifacts overall, and slag the least.

Table 1. Depth (cm), fine earth, artifact, and rock fragment content (% weight), soil horizons.

Horizon	Depth	Fine earth	Artifacts	Rock frags
1	31-53	66.6	17.8	15.6
2	53-69	91.0	2.5	6.5
3	69-90	23.5	73.0	3.5
4	90-112	43.2	49.2	7.6
5	23-37	65.3	24.9	9.8
6	61-102	17.6	80.7	1.7

Table 2. Artifact type content (% weight), soil horizons.

Horizon	Asphalt	Brick	Concrete	Slag
1	1.9	0.5	12.2	0.5
2	1.2	0.1	0.6	0.1
3	0.7	0.1	71.3	0.3
4	6.1	0	39.2	2.9
5	4.4	10.2	5.7	1.6
6	1.2	14.9	57.3	1.3

The trace element content of the fine earth fraction in each of the six horizons is given in Table 3, along with the New York State Department of Environmental Conservation Soil Cleanup Objectives for unrestricted use. The fine earth values in each of the horizons exceed the Objectives for at least one element, lead. Values in horizons 4, 5, and 6 exceed the Objectives for all four metals.

Table 3. Trace element content (mg/kg), soil horizons, with NYS Soil Cleanup Objectives, unrestricted use.

Horizon	Cu	Hg	Pb	Zn
1	22	.07	73	69
2	22	.14	132	65
3	48	.19	202	124
4	89	.42	248	195
5	60	.33	311	312
6	102	.44	1162	742
NYS DEC SCO	50	.18	63	109

Table 4 lists the mean and coefficient of variation for the trace element content of the four artifact types. Asphalt is relatively high in mercury, with an average value almost twice the soil Cleanup Objective. Slag has the highest copper and zinc contents, which exceed the Objectives by nearly two and more than six times, respectively. However, the variability in zinc was particularly high for slag, with values ranging from 17 to 3919 mg/kg.

Table 4. Trace element content (mg/kg), mean and (CV) values, artifact types.

	Cu	Hg	Pb	Zn
Asphalt	59 (.65)	.35 (.97)	111 (.53)	84 (.52)
Brick	25 (.39)	.04 (.38)	73 (.49)	126 (.80)
Concrete	29 (.32)	.07 (.65)	88 (.73)	110 (.73)
Slag	97 (1.28)	.13 (.48)	112 (.67)	653 (2.21)

Table 5 lists the correlation coefficients between artifact content and the fine earth trace metal content. This was an attempt to determine if the presence of any of the artifacts could be used as an indication of the degree of metal contamination of the soil. The amount of brick present generally has the best correlation with the four metals, especially lead and zinc, even though its content of these elements is relatively low. This may be due to the close association of brick with related construction debris, possibly finer sized, i.e., paints, metals, treated woods, which serve as a source of these elements. Asphalt or concrete, on the other hand, may come from street demolition.

Total artifact content also correlated quite well with fine earth trace metal content. The amount of slag present correlated best with fine earth copper content. Slag fragments had the highest copper contents of the artifact types.

Table 5. Correlation coefficients (r), artifact content & fine earth trace metal content.

n=6	Cu	Hg	Pb	Zn
asphalt	.400	.521	.179	-.052
brick	.615	.625	.866[b]	.906[c]
concrete	.557	.385	.462	.394
slag	.747[a]	.802[a]	.217	.316
total artifacts	.736[a]	.584	.662	.626

a= significant at .90 level; b=significant at .95 level; c=significant at .98 level

Table 6 lists the carbon, nitrogen, and sulfur contents of asphalt and slag. The high carbon content of asphalt fragments, and to a lesser degree slag, can be a significant addition to the total carbon content of the soil. Much of this addition, particularly in the case of slag, can be in the form of highly reactive and recalcitrant black carbon. The small amount of asphalt and slag fragments in the horizons 1 through 4 raised the carbon level in the top meter of the Ebbets soil from 14 to 16 kg C/m^2. Both the asphalt and slag are characterized by high C:N values, and comparatively high amounts of sulfur.

Table 6. Total C, N, and S (%), Mean and (CV) values, artifact types.

	C	N	S
asphalt	31.2 (.42)	0.3 (.53)	1.3 (1.95)
slag	4.4 (.49)	0.05 (.67)	0.1 (.93)

Conclusion

Chemical analyses of artifactual coarse fragments from New York City soils concur that this fraction contributes to the trace metal content of anthropogenic soils. Compared to New York State cleanup objectives, asphalt fragments were high in mercury and lead, while slag fragments were high in copper, lead, and zinc. The amount of brick present seemed to serve as the best indicator of trace metal content in these soils. High levels of carbon in asphalt and slag fragments indicate that the >2mm fraction can make a significant contribution of to the total carbon content in anthropogenic soils.

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Hydrodynamic characterization of BOF slags through numerical inversion of an evaporation experiment and through water infiltration experiments: a comparison.

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Abstract
Newer urban soils, frequently composed of several types of anthropogenic materials, may contain Basic Oxygen Furnace (BOF) slag, which is a steel industry byproduct. An understanding of the flow and solute transfer processes through urban soils requires a hydraulic characterization of these materials. This article is aimed at characterizing unsaturated hydraulic properties of the BOF slag with the evaporation experiment through parameter estimation method, and comparing the results with the values obtained from the field through water infiltration experiments using the adapted Beerkan Estimation of Soil Transfer Parameters method (Yilmaz *et al*. 2010). The results indicate a creation of a crusted layer at the surface of the column which avoids the characterization, for initial non crusted material. The parameter estimation technique using the experimental data gives acceptable values in agreement with the field data at one year. Such result is discussed in regard to the evolution of the material through carbonatation.

Key words
Soil characterization, unsaturated properties, Evaporation Method, BEST Method.

Introduction
Soils in urban areas are frequently composed of several types of anthropogenic materials whose hydraulic parameters are unknown. For instance, BOF slags that are byproducts of the steel industry are planned to be used as alternative materials in road and civil engineering, despite the fact that little is known in regard to their hydraulic properties. Only a few previous studies have focused on modelling flow through BOF slag (Chaurand *et al.* 2007; Yilmaz *et al.* 2009). Yet, the knowledge of their hydrodynamic properties is required to understand the effect on flows in the works and urban soils where they are found. Moreover, such knowledge is required to understand the pollutant release and transfer processes since flow patterns determine the release and transfer of solutes.

As means of hydraulic characterization, water infiltration experiments are quite common for the hydraulic characterization at the field scale. At the laboratory scale, the use of the evaporation method through analysis of experimental pressure heads at different heights in a vertical column has become widespread in obtaining such properties (Wind 1968; Tamari *et al.* 1993; Simunek *et al.* 1998). Among the various types of analysis of experimental data, the parameter estimation method (Kool *et al.* 1987) involves the coupling of a numerical model for variably saturated water flow with parameter optimization and this can estimate soil properties accurately (Santini *et al.* 1995; Simunek *et al.* 1998).

The present paper is intended (1) to provide a complete characterization of the unsaturated properties of the studied BOF slag using the parameter estimation technique through the Hydrus 1-D software and (2) to compare them with the results from water infiltration experiments performed at a test site and spanned along several dates, and analyzed through an adapted Beerkan Estimation of Soil Transfer Parameters (BEST) method (Yilmaz *et al.* 2010).

Materials and methods
The size fraction of the materials studied was 0 to 6 mm. Chemical properties were characterized by high calcium, iron and silicon contents. The BOF slag targeted in this study was cured for three years in an open area under conditions of atmospheric weathering.

The material was packed into a 17 cm high and a 10 cm in diameter column, placed on a monitored balance. Three tensiometers (T5, Ums Gmbh, Münich, Germany), with cups of 7 cm long and 0.5 cm in diameter were horizontally inserted into drill holes in the material core at 3, 6 and 9 cm from the sample surface.

The specific density ρ_s and the dry bulk density ρ_b of the BOF slag were respectively about 2.97 and 1.84 g/cm^3, leading to a porosity of 38 %. The volumetric saturated water content θ_s was equalized to the porosity. The system was saturated with water during a sufficient time to reach hydraulic equilibrium. A fan was used to ensure a potential evaporation rate of 0.8 cm/d. The measurement of the mass was performed by weighing with mass balance every hour and the measurements of pressure heads each five minutes. Initial pressure heads of -14 cm for the tensiometer at 3 cm was measured. The experiment was performed till the water pressure heads reach the limiting value of -750 cm. The experiment lasted eight days. At the end, the material was extracted from the columns and dried for the determination of the water content profile with 6 points.

Modelling was performed using HYDRUS 1D code that resolves the Richards' equation. The unsaturated soil hydraulic properties are described by the following expression (Van Genuchten 1980), in junction with Mualem capillary model (Mualem 1976):

$$\frac{\theta-\theta_r}{\theta_s-\theta_r}=\left(1+\left|\frac{h}{h_g}\right|^n\right)^{-m} \quad (1)$$

$$K(\theta)=K_S\left(\frac{\theta-\theta_r}{\theta_s-\theta_r}\right)^{0.5}\left[1-\left(1-\left(\frac{\theta-\theta_r}{\theta_s-\theta_r}\right)^{1/m}\right)^m\right]^2 \quad (2)$$

where n, $m(=1-1/n)$ are the hydraulic shape parameters, and h_g, θ_s, θ_r and K_s the hydraulic scale parameters. h_g is the scale parameter for water pressure head, and K_s is the saturated hydraulic conductivity. The value of θ_r was assumed to be close to zero, as is typically considered for coarse materials (Haverkamp *et al.* 2006).

The evaporation setup was simulated through a 17 cm length mesh with 0.1 cm length elements. Observation points were introduced at the tensiometer depths. The initial conditions corresponded to pressure equilibrium with -17 cm at the surface and 0 cm water pressure head at the bottom. The boundary conditions correspond to no flux at the bottom and a potential evaporation rate of 0.03 cm/h at the surface. The hydrodynamic parameters were estimated through the HYDRUS 1D inverse procedure. The data to be fitted correspond to the evolution of the pressure heads at the observation points and the total water loss at the end of the experiment. The additional hydraulic parameters to be fitted were the parameter n, the scale parameter for water pressure (h_g) and the saturated hydraulic conductivity (K_s).

Results and discussion

The soil hydraulic parameters were estimated from the evaporation experiment using a parameter inversion technique. For this purpose, we used the tensiometer readings as a function of time and the final water contents. As described before, mass measurements were used to calculate the evaporation rate at the top of the column for upper boundary condition. All data were introduced in Hydrus 1D. The tensiometers response and the numerically fitted *h(t)* function are shown in Figure 1.

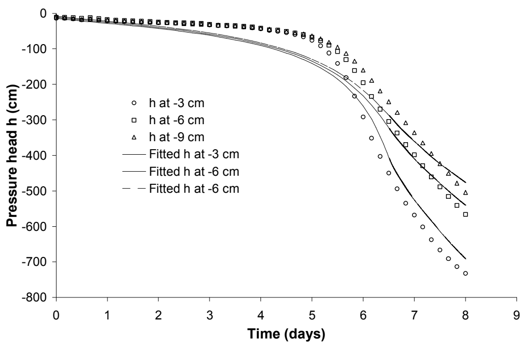

Figure 1. Experimental and numerical pressure head h (cm) in function of time (days).

The experiment was stopped after 8 days after the first tensiometer reached a value of -750 cm. The fitting of numerical data with experimental points can be considered correct. Moreover, the inverse procedure provided accurate values with the following values: estimated value for the scale parameter h_g of -33 cm with a confidence interval width of 6%, an estimated value for the saturated hydraulic conductivity *Ks* of 547 cm/d with a confidence interval width 50%, and an estimated value for n of 1.64 with a confidence interval width of 6%.

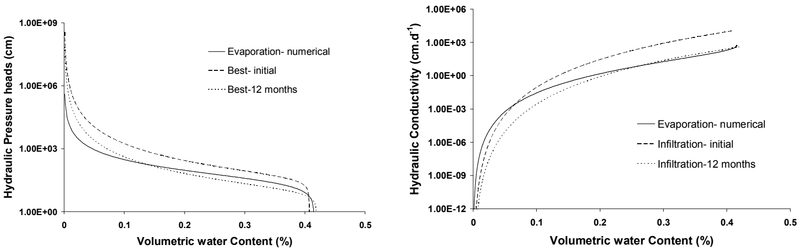

Figure 2. Water retention and hydraulic conductivity curves compared with curves from inverse analysis of infiltration experiments in the coarse zone of the experimental site

The field experiments were performed on an experimental embankment, built with the studied BOF slag. During the setup of the site, two zones appeared, a zone with fine materials (bulk density: 1.95 g/cm^3) and another zone with coarse materials (bulk density: 1.72 g/cm^3). Infiltration experiments were done immediately after the construction of the embankment was completed and then one year after. During this experiment, we found that the hydraulic properties of the BOF slag changed after 12 months due to the atmospheric events causing a carbonatation reaction at the surface of the slag material. These changes are assumed to be due to the clogging of pores through the formation of a coating of carbonates around the grains (Yilmaz *et al.* 2010). The water retention curves $h(\theta)$ and hydraulic conductivity curves $K(\theta)$ are illustrated in (Figure 2) in comparison with the hydraulic properties from the water infiltration experiments related to the coarse zone (Yilmaz *et al*. 2010).

As regards the Figure 2, the water retention curves from field experiments after 12 months and from evaporation experiments resemble. The hydraulic conductivity curve of the evaporation experiment is characterized by a similar tendency with the infiltration inversion of 12 months. During the evaporation experiments, it was noticed that a crusted zone formed at surface after a few days (coating of grains by carbonates). This may explain such agreement. In fact, the time required for the evaporation experiment is sufficient to crust the material by carbonatation. The evaporation experiment seems to be inappropriate to characterize a non crusted BOF slag.

However, as the crust occurred on the top of the column, in order to characterize the non crusted material below; the inverse modelling approach should be integrated with a double layer material. If the implementation of the two materials for the inversion of evaporation based experiment data could have been performed, this could have resulted in the following problems: (1) the increase in the number of parameters to be estimated and (2) the unknown variables such as the thickness of the crust versus time. These results point to the need for methods that may implement the evolution of the material with time and the need to adapt the base evaporation method to such material.

Conclusions
We characterized the hydrodynamic properties of the BOF slag using the parameter estimation technique through an evaporation experiment. During the evaporation experiment and due to a formation of a layer of crusted material, the inversion of the evaporation data by the parameter estimation technique gives similar results to the field infiltrations experiments after one year. In order to characterize the non crusted zone, a double layer material approach should be used; however, this would result in the need to estimate more parameters and difficulties to provide accurate values. The evaporation method for the material as BOF slag needs to be adapted, the evolution in time of the initial material has to be implemented in the parameter estimation technique. These aspects will be the subject of further research.

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Magnetic response of heavy metals pollution in urban soils: magnetic proxy parameters as an indicator of heavy metals pollution

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Abstract
Magnetic and chemical analyses were performed on urban soils collected from Lishui city, China, to evaluate the potential of magnetic measurements as an indicator of heavy metals pollution in urban soils. Magnetic susceptibility (χlf), saturation isothermal remanent magnetization (SIRM) and concentration of metals (Cd, Cu, Pb and Zn) were measured on samples of urban soils. Concentration-dependent magnetic parameters (χlf and SIRM) are significantly positively correlated to the concentration of heavy metals (Cr, Ni, Cu, Zn, Cd and Pb), but not correlated with V, Co and As. The χlf and SIRM also have strong linear correlation with integrated pollution index (IPI), indicating that χ and SIRM can be used as effective proxy indicators for the pollution degree of heavy metals in urban soils. Magnetite was identified as the possible dominant magnetic carrier using temperature-dependent measurements of saturation magnetization (Ms-T curve). The results proved the applicability of magnetic method in detecting heavy metals pollution in urban soils.

Key Words
Urban soil, heavy metal, magnetic susceptibility, saturation isothermal remanent magnetization.

Introduction
Soil contamination is considered as one of the main threats to the environmental quality and the health of people. Accelerated industrialization and urbanization has resulted in an increased pollution of soil, water and a growing risk for heavy metal uptake by human. Urban soils are the "recipients" of various pollutants and the heavy metal concentration in soils is frequently reported as an indicator of urban environmental quality (Wong *et al*. 2006). Therefore, it is important to understand the content, distribution, mobility and possible sources of heavy metals in urban soils. Recently, the rapid, non-destructive and inexpensive magnetic measurements have increasingly been used as complementary methods to help characterise urban soil pollution. It has been accepted as a rapid mapping tool and proxy indicator of heavy metal pollution in soils and sediments. The concept of magnetic measurement is based on the assumption that magnetic particles and pollutants are produced together during anthropogenic activities, such as industrial and traffic processes. For example, many studies have indicated that there is a good relationship between heavy metals and magnetic parameters in soils (Blaha *et al*. 2008; Chaparro *et al*. 2008; El-hasan 2008; Lu *et al*. 2006, 2007; Spiteri *et al*. 2005; Yang *et al*. 2007). Their close relationship has been proven by combined analyses of chemical composition and magnetic parameters of soils. The strong positive correlation between magnetic parameters and heavy metal contents has been observed in urban soils (e.g. Lu *et al*. 2006, 2007; Yang *et al*. 2007). Although many studies on magnetic proxy of heavy metal concentrations have been carried out in developed countries and big industrial cities in China, only limited data is available on magnetic monitoring of heavy metals in middle and small cities of rapidly developing regions. Therefore, this work aims to apply the environmental magnetism approach to examine the magnetic properties of urban soils, to help assess heavy metal pollution, and to establish links between the enhanced concentrations of magnetic particles and heavy metals.

Methods
Soils
The studied area Lishui city (the geographical position being N28°25-28′ and E119°53′-58′), situated in Zhejiang Province, China, is a small but rapidly growing green city without significant industrial activity. Traffic emissions and anthropogenic activities may be the main source of urban pollution governing the accumulation of heavy metal in soils. Soil parent materials in this urban area are mainly Quaternary alluvial deposits with low magnetic mineral content. A total of 126 topsoil samples were collected from the city planning area of Lishui, which includes all high density inhabited and commercial centre of city, but also extends to new developing industrial parks and un-urbanized areas around the city. The top 10 cm layer of the soil was taken with a stainless steel spade and stored in a plastic bag. At each sampling site, 5-6 subsamples of topsoil were taken and then mixed thoroughly to obtain a bulk sample to get a representative

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sample. Samples were air-dried, ground, passed through a nylon sieve of a 100 mesh, and stored. Additionally, the outcropping rock and parent material samples were collected in order to estimate the geological background on the magnetic parameters in urban soils.

Methods

Magnetic susceptibility of urban soils was measured using a Bartington MS2 magnetic susceptibility meter linked to a MS2B dual frequency sensor (470 and 4700 Hz). Frequency dependent susceptibility (χfd) was calculated as a percentage of [(χlf-χhf)/χlf×100]. Isothermal remanent magnetization (IRM) was performed using a Molspin pulse magnetizer and measured on a Molspin spinner magnetometer (Molspin Ltd.). The IRM acquired at 1T was referred to as the saturation IRM (SIRM). Using an IRM acquired with a back field of 100mT, the S_{-100mT} ratio was calculated as follows: $S_{-100mT} = IRM_{-100mT}/SIRM$. High-temperature saturation magnetization (Ms-T) curves for representative soil samples were undertaken in air on a Vibrating Field Transition Balance (VFTB, N. Petersen, Munich). Approximately 1.0 g of each sample was digested by the *aqua regia* in a microwave oven (Mars-5, CEM Company, USA). After digestion, the solution was filtered and diluted with deionised water to get 50 ml of solution. Concentrations of Cr, V, Co, Ni, Cu, Zn, As, Cd, and Pb were analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Accuracy of analyses was checked using standard and duplicate samples. Data statistical analysis was made with the EXCEL software.

Results

Magnetic parameters and heavy metal contents of urban soils

Magnetic susceptibility (χlf) and saturation isothermal remanent magnetization (SIRM) from urban soils of Lishui city are shown in Table 1. The χlf and SIRM of bedrocks and parent materials (geological background) show low mean values of less than 32×10^{-8} m^3/kg and 26.0×10^{-4} Am^2/kg, respectively, reflecting a rather insignificant geological background effect. Urban soils yield relatively high mean χlf values of 95.5×10^{-8} m^3/kg, ranging from 9.8×10^{-8} to 503×10^{-8} m^3/kg. The elevated χlf and SIRM values in the urban soils indicate that the anthropogenic inputs contain a higher portion of magnetic material than the lithogenic/pedogenic background. SIRM shows a good linear correlation with χlf (r^2=0.94, p<0.01) (Figure 1), suggesting that the two parameters can be assumed as representative of the amount of ferrimagnetic particles in the urban soils and equally suited for the magnetic proxy.

Table 1. Statistical summary of magnetic parameters in urban soil samples in Lishui city, China

	χlf (10^{-8} m^3/kg)	χfd (%)	IRM_{20mT} (10^{-4} A m^2/kg)	SIRM (10^{-4} A m^2/kg)	S_{-100mT} (%)
Min	9.8	0.00	6.1	954.4	15.2
Max	503.9	11.11	3182.0	28517.5	100.0
Mean	95.5	3.42	603.9	7078.4	84.6
SD	64.1	2.49	449.9	4678.8	12.4
Median	67.6	2.70	379.9	4832.3	89.2
Skewness	1.84	0.60	2.04	1.77	-1.93

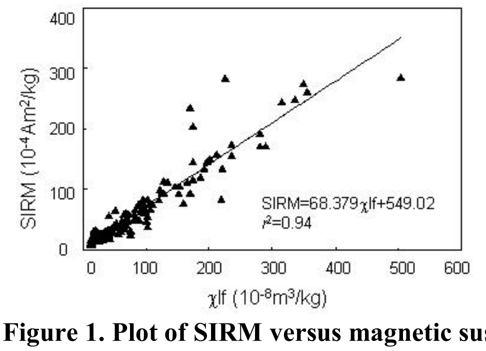

Figure 1. Plot of SIRM versus magnetic susceptibility (χlf) for urban soils

The concentration of heavy metals in urban soils is shown in Table 2. Results show the contents of Cd, Cu, Pb, and Zn are higher than the background concentration (BC) of soils in the Zhejiang Province (ZPSSO 1994), indicating that these urban soils have been strongly polluted with Cd, Cu, Pb, and Zn. This is considered to be the result of a gradual accumulation from automobile exhausts and other anthropogenic pollution sources over time. Compared to average concentrations in urban soils of other larger cities in China, especially large and/or old industrialized cities (e.g. Lu *et al*. 2006, 2007; Yang *et al*. 2007), the Cr, Cu and Ni concentrations in urban soils samples of Lishui city are much lower (Table 2). On the other hand, Ni does not present evident enrichment with respect to background values.

To assess the soil pollution level, a pollution index (PI) of each metal and an integrated pollution index (IPI) of the seven metals were calculated. The PI was defined as the ratio of the heavy metal concentration in the study to the background concentration of the corresponding metal in the studied area. The IPI of the seven metals was defined as the mean value of the metal'PI, which is an indicator of the heavy metal contamination. The mean IP of Cd, Cu, Pb, and Zn were 4.3, 2.2, 2.7, and 3.3, respectively, indicating the presence of metal pollution in soils. By contrast, Cr, Ni and As show low contamination with mean PI of 1.06, 0.71, and 1.28, respectively, indicating that there was no obvious pollution of these heavy metals in these urban soils. The IPI of soils varied from 0.76 to 5.51 with an average of 1.92 (Table 2).

Table 2 Statistical summary of heavy metal concentrations (mg/kg) in urban topsoil samples in Lishui city, China (n=126)

	Cr	V	Co	Ni	Cu	Zn	As	Cd	Pb	IPI
Min	9.41	17.95	2.17	3.70	4.72	60.04	0.93	0.05	29.18	0.76
Max	105.10	177.26	34.00	50.21	140.83	873.53	36.45	3.19	166.93	5.51
Mean	34.54	42.55	6.35	14.33	35.80	192.38	8.81	0.53	63.15	1.92
SD	10.64	10.81	1.78	4.92	14.57	86.91	3.53	0.37	15.38	0.93
Median	32.36	39.08	5.99	12.74	30.92	157.00	7.60	0.34	58.73	1.66
Skewness	2.08	3.94	5.02	2.16	2.24	2.89	2.51	2.41	1.89	2.02
BC	36.73	-	-	22.31	17.76	69.00	6.45	0.167	25.61	

Correlation between magnetic parameters and heavy metal contents in urban soils

Table 3 lists the linear correlation coefficients between the concentration of heavy metals and magnetic parameters in urban soils. The correlation matrix indicates that the concentration-dependent magnetic parameters (χlf, IRM$_{20mT}$, and SIRM) all have a strong linear correlation with heavy metal concentrations except for V, Co and As (Table 3). The highest coefficients are found for Zn (0.703) and Cd (0.687). Of the three concentration-dependent magnetic parameters, χ is the best indicator of heavy metal pollution. Significant correlations between magnetic parameters (χlf and SIRM) and PLI can be clearly seen from the scatter plots shown in Figure 2. The results indicate the existence of positive relationship between heavy metal contamination and magnetic enhancement in urban soils. The fact that content of heavy metals associated closely with magnetic parameters suggested that magnetic measurements can be used a proxy indicator of heavy metals pollution in urban soils.

Table 3 Correlation coefficients of magnetic parameters and heavy metal concentrations in urban soil samples in Lishui city, China (n=126)

	Cr	V	Co	Ni	Cu	Zn	As	Cd	Pb
χlf	**0.461**	0.014	0.040	**0.493**	**0.542**	**0.703**	0.017	**0.687**	**0.526**
IRM$_{20mT}$	**0.406**	0.014	0.040	**0.422**	**0.455**	**0.586**	0.022	**0.631**	**0.414**
SIRM	**0.417**	0.064	0.082	**0.440**	**0.467**	**0.603**	0.010	**0.691**	**0.431**
χfd	-0.185	0.082	0.052	0.044	0.053	-0.117	0.165	-0.156	0.088
SIRM/χ	-0.095	**0.539**	**0.358**	0.022	-0.124	-0.218	-0.142	**-0.243**	**-0.236**
S$_{-100mT}$	0.165	0.030	0.069	0.124	0.022	0.081	0.010	0.166	0.081

Correlations in bold are significant at p<0.01.

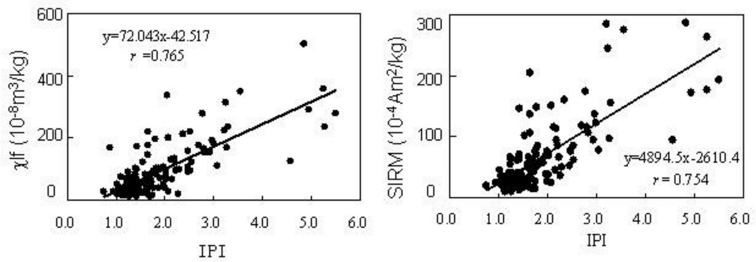

Figure 2. Correlation between the integrated pollution index (IPI) and magnetic parameters (magnetic susceptibility and SIRM). The correlation analysis was carried out after eliminating two outlier samples.

Identification of magnetic particle source in urban soils
High-temperature magnetization (Ms-T) curve showing that magnetization varies with temperature are useful for the identification of magnetic mineralogy. Figure 3 illustrates the temperature-dependent magnetization variations of representative sample. The Ms-T curve show a major decrease in magnetization at about 580°C, the Curie temperature of magnetite, suggesting that magnetite is the dominant magnetic carrier. In addition, the increase of magnetization at 410°C could be due to the presence of a small amount of pyrite, which is transformed into magnetite. However, the transform is much weaker than the phase transition at 580°C (magnetite), revealing that magnetite is the dominant magnetic carrier. Upon cooling, a sharp increase was initiated at around 580°C, indicating the presence of magnetite.

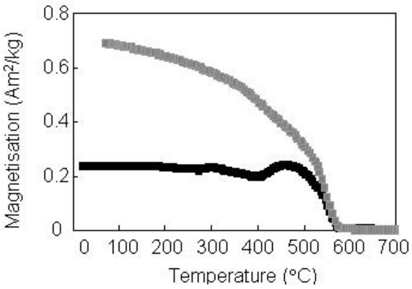

Figure 3. High-temperature magnetization (Ms-T curve) of representative urban soil sample. Solid and dashed lines represent heating and cooling runs, respectively. The applied field is 355 mT.

Conclusion
Magnetic measurements and heavy metal analyses performed on urban soils from a rapidly growing small city showed significantly elevated concentrations of magnetism and heavy metals. Concentration-related magnetic parameters have significant linear correlation with the concentration of Cr, Ni, Cu, Zn, Cd and Pb. The magnetic susceptibility and SIRM of urban soils also significantly correlates with PLI, their correlation coefficients are 0.765 and 0.754, respectively. High-temperature magnetization variation of urban soil indicates that the predominant magnetic carrier in urban topsoils is magnetite. The elevated magnetism and heavy metal concentration of urban soils are attributed to traffic emissions and anthropogenic activities. These results suggested that magnetic parameters can serve as an effective surrogate indicator for heavy metal pollution in these urban soils.

Acknowledgments
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Municipal composts improve landscape plant establishment in compacted soil

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Abstract
Urban landscape soils are often compacted by construction activities, thereby restricting plant establishment. Common approaches to improve plant establishment on compacted soils are to till soil before plant installation, to apply compost, or to choose plants that can tolerate drought. This research was undertaken to evaluate the relative importance of remedial practices (tillage, compost application, and plant selection) on survival and growth of landscape plants in compacted, non-irrigated soil in a mediterranean climate (western Oregon, USA). In 2008, moist silt loam soil was compacted with a vibrating roller, followed by application of compost, tillage, and plant installation. Planting holes (25 cm deep x 15 cm diameter) for installation of transplants from 3.8-L pots were drilled into compacted soil using a power auger. We report soil and plant data for 2009. Pre-plant compost application increased plant growth and quality of both standard and drought-tolerant landscape plants. The first-year plant growth response to compost was the same for compost left on the soil surface or compost incorporated via roto-tilling. Apparently, enough compost fell into the planting holes on the "no till" plots to stimulate plant establishment. Biosolids compost provided more plant-available nitrogen than yard debris compost, but compost effects on plant growth and quality were similar for most plant varieties. Groundcover plants grew more with the biosolids compost than with the yard debris compost. We conclude that compost application is beneficial for plant establishment for all landscape species tested, and that it is not essential to incorporate the compost into soil before planting.

Key Words
Compost, compacted soil, urban, landscape.

Introduction
Research objectives are to:

1. Evaluate the relative importance of remedial practices (tillage, compost application, and plant selection) on survival and growth of landscape plants in compacted non-irrigated soil
2. Determine whether it is essential to incorporate compost by tillage before installing plants

Methods
Experimental design
Randomized complete block (3 x 2 x 2 factorial) with 4 replications:

- 3 pre-plant compost treatments (biosolids compost, yard debris compost, no compost)
- 2 pre-plant tillage treatments (tilled, not tilled),
- 2 groups of landscape plants (4 species of typical landscape plants, 4 species of landscape plants that are considered drought tolerant)

Site preparation
Location: Oregon State University North Willamette Experiment Station, Aurora, Oregon USA (http://oregonstate.edu/dept/NWREC). Prior to planting, Willamette silt loam soil (Fine-silty, mixed, superactive, mesic Pachic Ultic Argixerolls) was prepared by compacting moist (20 g H_2O/kg) soil with a tandem vibrating roller (Figure 1a). Surface bulk density (0-10 cm) of the compacted soil as determined by coring was 1.5 g/cm^3. Compost (220 dry Mg/ha; approx. 7-8 cm depth; Table 1) was applied after soil compaction, and was either incorporated by rototilling to 10-15 cm depth, or was left on the soil surface (Figure 1b). Planting holes (25 cm deep x 15 cm diameter) for installation of transplants from 3.8-L pots were drilled into compacted soil using a power auger (Figure 1c). After plant installation all plots were mulched with 7-cm of fine Douglar fir (*Pseudotsuga menziesii*) bark (Figure 1d).

Transplanting
Landscape plants were transplanted from 3.8 L (1-gal) pots in Sept, 2008. Two groups of plants were included in the trial. We installed 4 cultivars considered standard landscape plants for our area (*Nandina domestica* 'Compacta', *Vinca major* 'Bowles', *Viburnum davidii*, *Berberis thunbergii* 'Crimson Pygmy'), and 4 cultivars considered more drought-tolerant (*Rosmarinus officinalis* 'Blue Spires', *Cistus* 'Bicolor Pink', *Ceanothus gloriosus*, *Caryopteris x clandonensis* 'First Choice').

Measurements
Soil compaction was determined using a recording penetrometer in fully moist soil (rainy season; Jan 2010). Soil was sampled for nitrate-N analysis in October 2009, approximately 13 months after plant installation. Five soil cores were collected from each plot with a push probe after scraping away mulch and compost from the soil surface. We measured aboveground plant dry weight for 4 plant varieties in October 2009. Plants were removed at ground level then dried at 60^{o}C for 96 h. We also collected data on visual appearance (plant quality) of all plant varieties on a 1 to 5 scale.

Table 1. Nutrient analysis of composts.

Compost Analysis	Unit	Biosolids compost	Yard debris compost
NH_4-N	mg/kg	2100	57
Total N	g/kg	18	14
Organic C	g/kg	420	260
Ash	g/kg	168	499
C:N		23	19
P	mg/kg	9700	2600
K	mg/kg	1500	7100
pH		7.7	7.0
EC (1:5)	mS/cm	1.6	0.9
Stability	mg CO_2-C/g OM/day	1.0 (very stable)	2.9 (stable)

Compost analysis by Soil Control Lab, Watsonville, CA, USA using standard methods (U.S. Composting Council 2004).

Figure 1. Field trial installation, Sept 2008. Soil compaction with vibrating roller (a), tillage treatment (b), plant installation with power auger in no-till treatment (c), all plots planted and mulched with Douglas-fir bark (d).

Results
Soil
Tillage and compost application did not result in large differences in soil compaction as measured by the penetrometer (Figure 2). Penetrometer resistance readings reached approximately 2000 kPa at a depth of 25 cm for no-compost and compost treatments. The compaction applied with the vibrating roller during site preparation increased penetrometer resistance at 25 to 45 cm depth. Although compost did not have a large effect on penetrometer resistance (0-25 cm depth), compost application did increase water infiltration rate (data not shown).

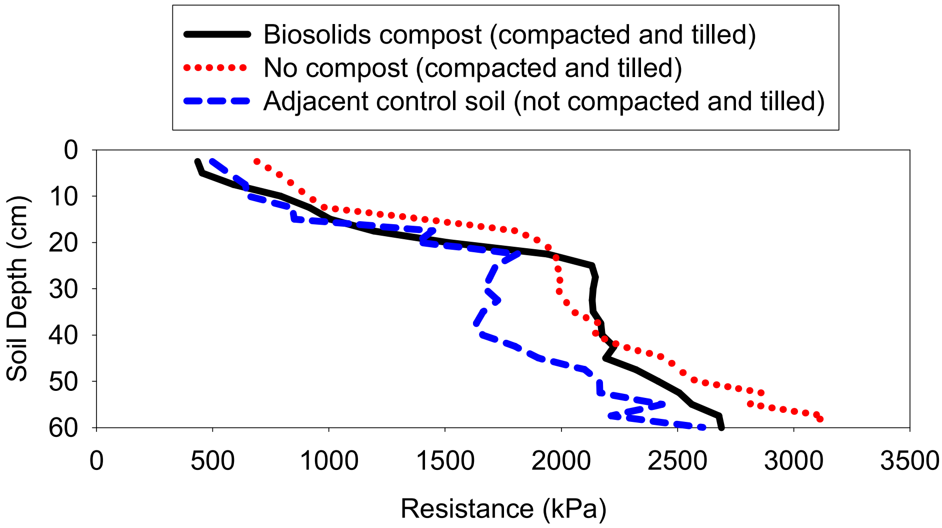

Figure 2. Soil resistance (kPa) as measured by recording penetrometer at 16 months after plant installation.

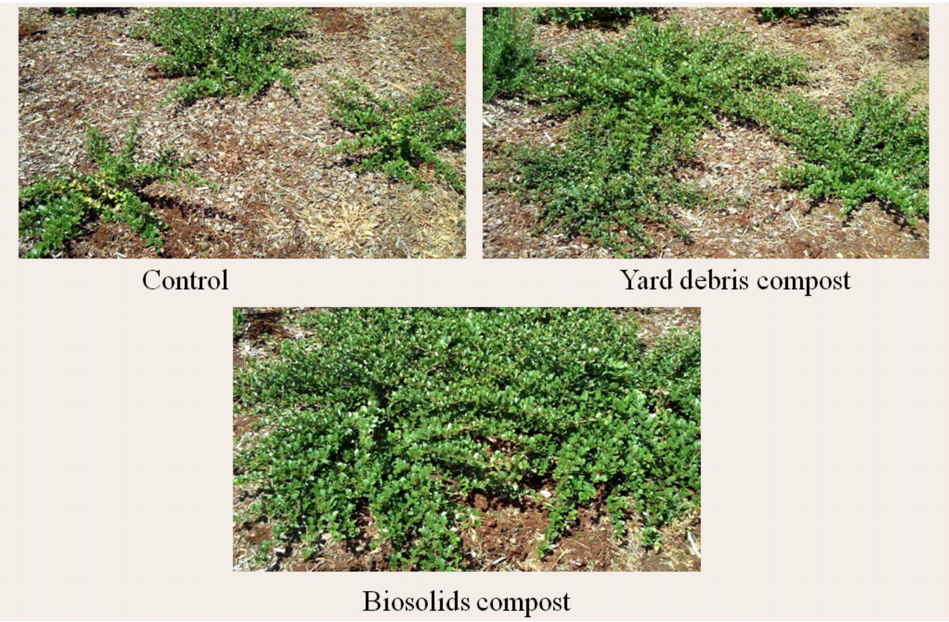

Figure 3. *Ceanothus gloriosus* ground cover plants in July, 2009. Soil amendment treatments (preplant, Sept 2008): control (no compost), yard debris compost or biosolids compost.

Plant Response

In 2009, the pre-plant compost application increased plant growth (Table 2) and quality (data not shown). Across all plant varieties, the first-year plant growth response to compost (plant growth, plant quality, or plant dry weight) was similar for compost left on the soil surface or compost incorporated via retotalling. Plant dry weight was greater with biosolids compost than for yard debris compost for two groundcover plant species (*Vinca major* and *Ceanothus gloriosus*; Table 2).

Table 2. Effect of soil amendment on plant dry weight (October, 2009; 13 months after plant installation).

Soil amendment	*Caryopteris x clandonensis*	*Ceanothus gloriosus*	*Nandina domestica*	*Vinca major*
		g dry wt/plant		
Biosolids compost	315	782	111	120
Yard Debris compost	230	661	106	97
No compost	183	342	63	75
Contrasts		P value		
Compost vs. no compost	0.06	<0.0001	<0.0001	<0.0001
Biosolids compost vs. yard debris compost	0.12	0.06	0.67	0.01

Biosolids compost provided more plant-available nitrogen than the yard debris compost (Tables 1 and 3). *Ceanothus* groundcover color and spread was greater was greater with the biosolids compost (Figure 3). Groundcovers likely benefit from greater nutrient availability at the soil surface, because of a shallow rooting pattern.

Table 3. Soil nitrate-N (0-20 cm) under surface mulch layer.

Soil Amendment	Tillage	Soil NO_3-N
		mg/kg
Biosolids compost	No till	43
	Till	44
Yard debris compost	No till	12
	Till	12
No compost	No till	8
	Till	8

Soil samples collected Oct, 2009, 13 months after plant installation.

Conclusion

Pre-plant compost application increased plant growth and quality of both standard and drought-tolerant landscape plants. The first-year plant growth response to compost was the same for compost left on the soil surface or compost incorporated via roto-tilling. Apparently, enough compost fell into the planting holes on the "no till" plots to stimulate plant establishment. Biosolids compost provided more plant-available nitrogen than yard debris compost, but effects on plant growth and quality were similar for most plant varieties. Groundcover plants grew more with the biosolids compost than with the yard debris compost. We conclude that compost application is beneficial for plant establishment for all landscape species tested, and that it is not essential to incorporate the compost into soil before planting.

Acknowlegement

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Restoration of soil function requires plants, arbuscular mycorrhizal fungi and organic matter

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Abstract
Insufficient topsoil often limits the establishment of native plants during restoration of mine sites. We address this problem by developing a suitable "capping topsoil" from coal mine overburden (spoil) for use at an open cut coal mine in Hunter Valley, NSW, Australia. The hierarchical model of aggregation served as the basis for the experiment. Plants with or without arbuscular mycorrhizal (AM) fungi were grown in 0, 6, 12 or 18% w/w of compost in spoil and placed in elongated tubes. Non-mycorrhizal plants in 18% compost amended spoil maximised water retention. Below 18% compost the presence of mycorrhizal fungi on roots of plants led to maximum water retention. A plateau in water retention was reached with the addition of between 6 and 12% compost in the mycorrhizal treatments, which is equivalent to 1.75 – 3.5% organic carbon in soil. Plants, AM fungi and organic matter were required to convert a massive mine spoil to a suitable "capping topsoil".

Key Words
Volumetric water content, matric potential (Ψ_m), soil water curves.

Introduction
Extraction of subsurface materials to access mineral seams is a consequence of open cut mining. In Australia, these subsurface materials (overburden or spoil) require rehabilitation and restoration to varying degrees under the terms of the mining licence. The need for rehabilitation of these materials provides us with the opportunity to test many concepts of soil biology. Re-establishing native Australian plants directly into subsurface materials is rarely successful (Roe 1997). Spoil is often massive, lacking in organic carbon and soil microbiota, it can be saline, have adverse pH or be contaminated with metals (Dragovich and Patterson 1995). Spoil has poor water-holding capacity, few available minerals for plant growth and little resilience and resistance to perturbations (Fityus *et al.* 2008).

Ideally when rehabilitating spoil, fresh or stored topsoil from the A horizon is used to cap these subsurface materials (Harris *et al.* 1996). Sufficient topsoil for capping is rarely available through a combination of previous land use, erosion, contamination with weed seed and mixing of topsoil with subsoil. A supplementary source of topsoil, or a method to generate topsoil from existing materials would reduce the need to plant into bare spoil. The very attributes that make spoil a poor growing medium may be advantageous as the relatively inert and sterile properties of spoil can be exploited by utilising it as a parent material for development of a suitable "capping topsoil".

Topsoil has a number of important attributes: organic matter and organic carbon contribute to good structure, enabling penetration by plant roots, minerals are available for plant growth, soil microbes and saprotrophic fungi contribute to nutrient cycling and arbuscular mycorrhizal (AM) fungi support diverse plant communities and contribute to soil aggregation (Tisdall and Oades 1982; van der Heiden 2002). Aggregation in topsoil arises as a consequence of the combined effect of fine roots, hyphae of mycorrhizal fungi and microbial mucilages that interact with the physical and chemical properties of soil in a hierarchical manner (model of Oades 1984; Tisdall 1991, 1994; Tisdall and Oades 1982). The model may be utilised to form the basis for constructing topsoil through addition of each of the proposed constituents required for aggregate formation. Changes in aggregation can then be inferred by quantifying soil water holding characteristics.

The aim of the work presented here was to test and quantify the contribution of the organic matter and mycorrhizal fungi to aggregation in mine spoil. It is part of a larger body of work examining the development of a "capping topsoil" from mine spoil.

Methods

Compost (0, 6, 12 or 18% w/w) derived from bulk household and industrial garbage via the Bedminster process was mixed with spoil from a coal mine in the Hunter Valley, NSW, Australia and placed in elongated pots (final concentration 0, 1.7, 3.5, 5.2% organic carbon). The pots could be opened lengthwise to allow harvest of an intact core. Seedlings of *Dodonaea viscosa, Acacia decora* and *Lolium perenne* with or without eight different AM fungi were then transplanted into the amended spoil. Non-mycorrhizal plants were supplemented with phosphorous to give equal biomass within treatments. After six months in controlled growth conditions plants were harvested and soil water characteristics measured. Soil water characteristic curves were plotted from soil saturation to 1000 cmH_2O (98kPa) for each of the treatments. Soil aggregate stability by wet sieving and distribution of organic carbon in soil fractions were also determined but data are not presented here.

Results

Addition of organic matter alone decreased the bulk density of the soil in all treatments (data not shown) and increased the capacity to store water at any given matric potential (Ψ_m) at the 6 and 12% compost amendments (Figure 1A - C). Within a given compost treatment addition of non-mycorrhizal plants further increased water retention (Figure 1A – D) over compost alone. Addition of mycorrhizal plants maximised water retention at Ψ_m >50cmH_2O for the 0, 6 and 12% amendments (Figure 1A – D). Additions of compost beyond 12% did not increase water holding capacity of the soil under mycorrhizal plants. While addition of 18% compost conferred no additional water holding capacity for the compost alone and mycorrhizal plant treatments over the 12% amendments (Figure 1C – D), maximum water retention was found after adding 18% compost to the non-mycorrhizal plant treatment (Figure 1D).

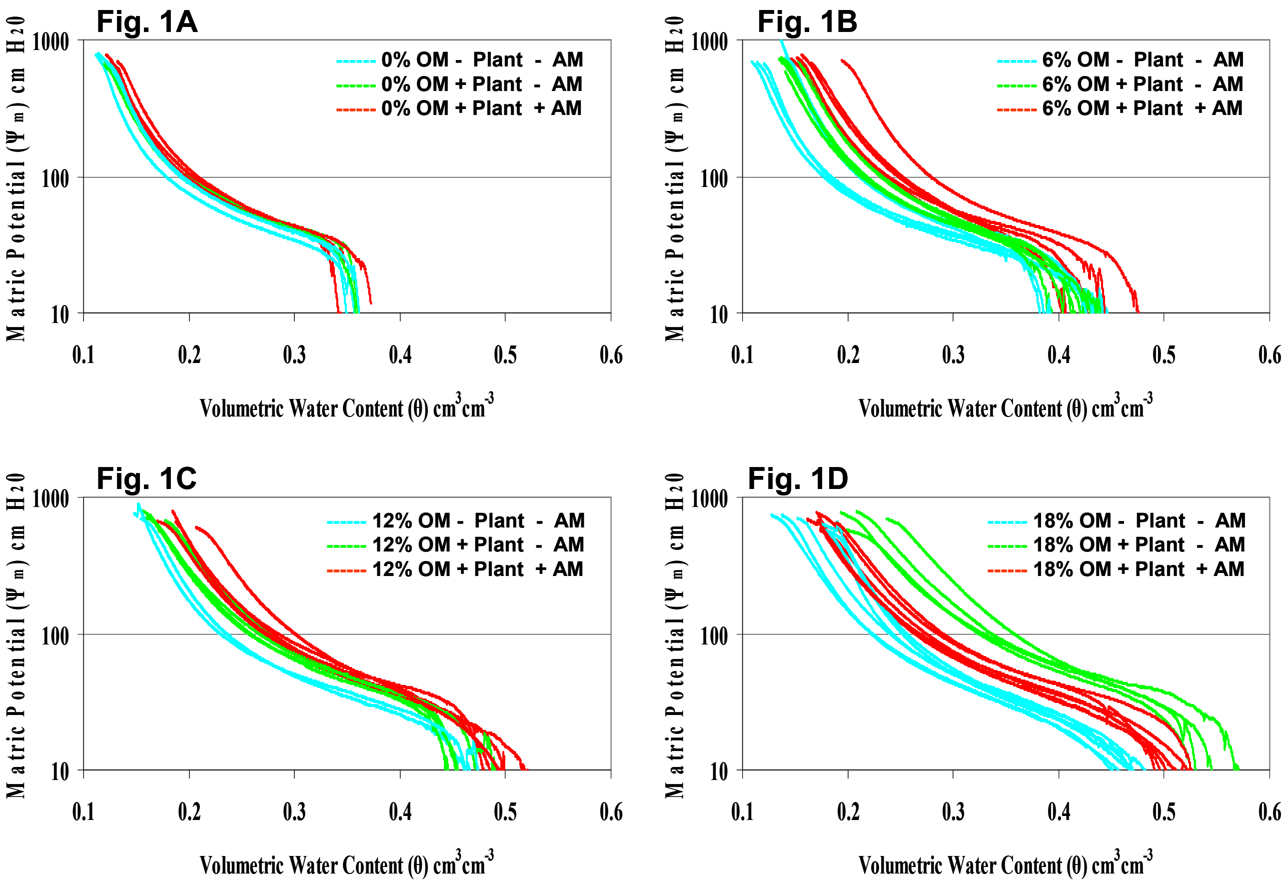

Figure 1. A - D Soil water characteristic curves 0, 6, 12, 18% organic matter (OM) [0, 1.7, 3.5, 5.2% organic carbon].

Discussion

Addition of organic matter, roots of plants and AM fungi each contributed to the development of the water holding characteristics of the spoil compost mix. The data from this experiment supported the view that the addition of organic matter decreases the bulk density of soil, and increases the quantity of water that is potentially held by the soil, regardless of the presence of plants. While addition of 18% compost maximised water retention, addition of compost alone is insufficient for forming a "capping topsoil" from mine spoil. Compost degrades over time, therefore a continuing carbon input to the soil is needed to sustain the carbon content. Additionally, the development of an interconnected pore structure, through the rearranging and enmeshing effect of root and AM fungal hyphae would provide a more attenuated pattern of water infiltration and extraction for plants (Auge *et al.* 2001; Tisdall and Oades 1982).

The addition of non-mycorrhizal plants to the compost amended spoil increased the water holding capacity beyond that of compost alone. The fine roots of plants (0.2 – 1 mm dia.) contribute to aggregation of soil (Miller and Jastrow 1990). Non-mycorrhizal roots may also contribute root exudates which determine the community structure of saprotrophic microbiota in the rhizosphere (Marschner and Baumann 2003) possibly increasing adhesion between soil particles (Tisdall and Oades 1982). Below 18% compost the presence of mycorrhizal fungi on roots of plants led to maximum water retention in amended mine spoil. A plateau in water retention appeared to have been reached with the addition of between 6 and 12% compost, which is equivalent to 1.75 – 3.5% organic carbon in soil. The data from this experiment provides further evidence for the contribution of AM fungi to the creation of soil structure and greatly expands existing knowledge on their influence of soil water characteristics (Auge *et al.* 2001). The complete mechanism is unclear but is likely to include the development of macro-aggregates following enmeshment of micro-aggregates. The hyphae will also express exudates, adding to the energy supporting the microbial community.

A self-sustaining soil would meet the desired characteristics of a "capping topsoil". Soil structure will be maintained beyond the six months of this experiment if plants and mycorrhizal fungi continue growth and development, as is likely in the field. Active growth of both will contribute to deposition of organic exudates and debris. Mine spoil clearly requires initial addition of organic matter if formation of a "capping topsoil" suitable to support native plant growth is the goal of restoration. In the field the addition of 18% compost to spoil is impractical for economic reasons. Below 18% compost the presence of mycorrhizal fungi on roots of plants led to maximum water retention in amended mine spoil, and we suggest that for field applications, planting mycorrhizal seedlings in 6 – 12% compost in spoil is a practical approach. The locally supported content of organic carbon in restored field soils is uncertain at this time. However long-term field studies at the mine site indicate carbon storage in restored spoil of between 2 and 3% (Nussbaumer and Cole unpublished data) which is the addition of between 6 and 12% compost. These analyses will be tested in the field.

Several questions remain: while we deliberately introduced AM fungi to the amended spoil, many other microbes would have colonised the soil mixtures. The identification and contribution made by each of these and other groups of microbes requires further examination. At the very least, saprotrophic microbes will contribute to the turnover of organic matter (Holland and Coleman 1987) and possibly to the development of micro-aggregates through the exudation of mucilage. The role of microbial mucilage in soil aggregation is poorly understood. Interactions between saprotrophic and symbiotic microbes are also complex and careful examination is required to determine their degree of contribution and the importance of their interactions. In addition, whether complex AM fungal communities support complex plant communities on the capping topsoil requires more careful exploration (van der Heiden 2002). Planting alone in mine spoil frequently fails to provide satisfactory vegetation (Carter and Ungar 2002). Addition of mycorrhizal plants alone did not improve the establishment of a capping topsoil nor did the addition of compost without plants. The development of realistic microbially complex capping topsoil clearly requires addition of organic matter, plants and their attendant AM fungi.

Conclusion

Successful rehabilitation and restoration of mine sites is limited by insufficient topsoil. The hierarchical theory of aggregation served as a useful tool for examining the development of structure in a massive mine spoil. Addition of organic matter, plants and their AM fungi resulted in the development of a "capping topsoil" within six months as indicated by soil water characteristics.

Acknowledgements

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Soil composition in slots between pavement plates of side walks and adjacent lawns of a residential and heavy industry area

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Abstract
In a heavy industrial area the top soil composition of lawns was compared with soil in slots between plates of side walks adjacent to lawns. The sand fill in the slots comprises soil material with a particle size that is finer than medium sand and also includes higher organic matter content. Compared to the lawn soils there was a strong accumulation of organic matter, silt and heavy metals in the top layer (0-0.2 cm) of soils in the slot fills. All materials and compounds decreased in the slots with depth. Different pattern of decrease occurred for mineral particles, organic carbon, iron, specific magnetic susceptibility, manganese, lead, zinc and cadmium. The origin of soil materials in the slots between plates of side walks was discussed.

Key Words
Pavement plates, soil neighbourhood, particle sorting, heavy metal content, mechanical filter function.

Introduction
Dominant topics of urban soil research have been brown fields and leisure park areas. Many of the other urban soil uses have not or seldom been areas of investigation. Among them are side walks. The importance of soil in the slots between cobbles and concrete plates is that they are for many people the daily, and often the only soil contact. Wenikajtys and Burghardt (2002) presented results of differentiation of compounds of soils in the slots with depth. Nehls *et al.* (2008) concentrated their work on slot filling from black carbon content and properties. There is a lack on soil dust research in urban areas. However, several authors (e.g. Hoeke and Burghardt 2002; Hoeke 2003) have investigated the processes and amount of soil dust release and transport, and showed the great importance of dust for urban soil formation in the Ruhr area, Germany.
The results from Wenikajtys and Burghardt (2002) indicate that in the composition of dust of sidewalks not only streets but also open soil parcels are involved due to their close proximity. Important contributions are likely to be from industrial dust deposition in some areas.

Material and methods
The study areas were two locations in the heavy industry city of Duisburg, Ruhr area, Germany. The first location was a low block residential area, constructed in 1962 on arable land about 1 km north of iron works with manganese breaking plant and pig iron foundry, both closed in 1985, and 500 m north of a motorway. The following three sidewalks were investigated along: (i) a main street (site 1) with low traffic, (ii) a side street (site 2), and (iii) a service road (site 3). Sites 1 and 2 had trees along the street. Site 3 was located nearer to former industrial plants than site 1 and 2. At site 3 the adjacent houses were about 5 m away. The distance of houses was much further for sites 1 and 2. The age of the pavement of all three sites was about 40 years at the time of sampling. The second location (site 4) was situated along a small green area in front of a close apartment building row and opposite a large iron foundry and steel plant complex at the conjunction of a main street with higher traffic and a side street. Currently much green is located around the area, which was lacking before. The age of the side walk plates is uncertain. Aerial photos showed no change to buildings for at least 80 years. All soils of site 1 - 4 were from fills of construction rubble covered by soil material. The width of the slots was about 4 mm. Samples were taken from top soils of the lawn adjacent to the side walk and from the slots between concrete plates of side walks. Analytical standard methods were used for particle size distribution, heavy metal extraction with aqua regia and determination with ICP. C and N were analysed by combustion at 1100°C and measured with a gas analyser (Analysator Euro EA). The specific magnetic susceptibility was analysed with a Forgenta Magnetic Analyzer (FMA 5000).

Results and discussion
The slots between the pavement plates were filled by construction with coarse sand and medium sand. The sand bed underneath the plates was often hardened by lime. The composition of the slot fillings from sand limited the size of particles, which could intrude into the sand. Large particles were separated and remain on the side walks. The sand filling entered fine and finest sand, silt and clay. Their content decreased with depth

(Figure 1). The amount of penetrated soils into the slots was calculated by assuming the occurrence of original sand in 2-5 cm depth of the slots. Location 1 to three showed an accumulation of up to additional 60%, location 4 of up to 160% soil (Figure 2). That means the originally loose sand filling had become dense with time. All grain sizes occurred. Main particle size fraction was silt which accumulated in all depth. At site 4 dominated coarse silt.

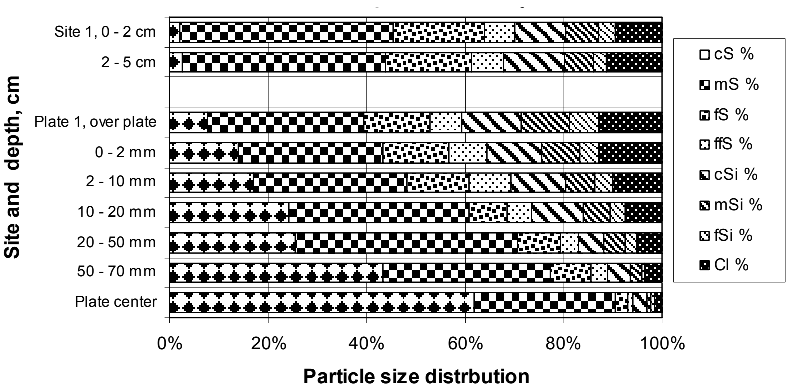

Figure 1. Particle size distribution with depth of top soil of lawn of site 1, and of slots between plates of the adjacent side walk.

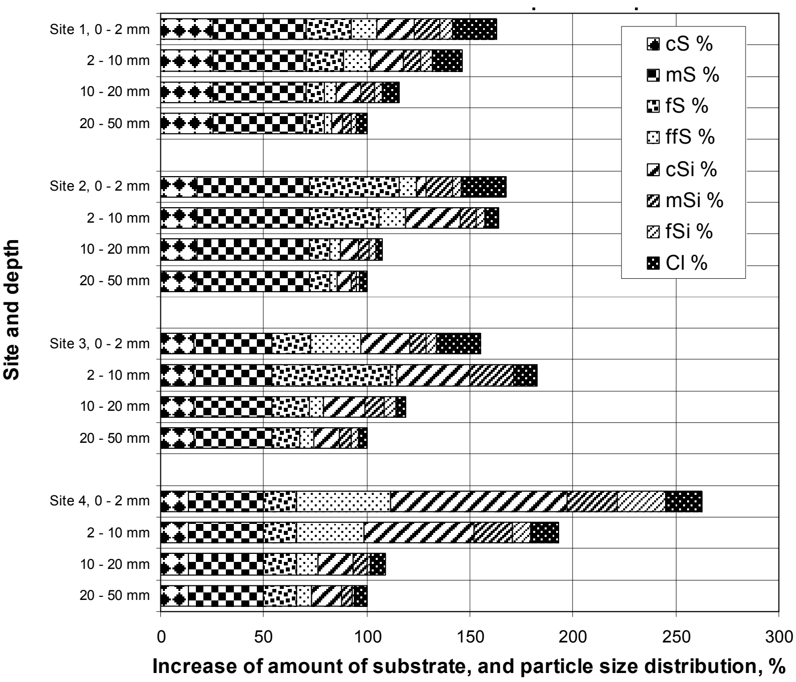

Figure 2. Change of grain size distribution with depth by dust intrusion into the sand fill of slots between pavement plates.

The C content (Figure 3a) from organic matter and black carbon was in the soils of the lawns and in the slots high. At site 4 it was much higher than in the others. In the slots the C content decreased with depth. This is not so pronounced for site 3 and 4. The N content (Figure 3b) shows similar results. But for site 4 it was lower. C/N ratio (Figure 3c) was for all soil samples from lawns and from slots in the range of about 15 or less which is typical for natural soils. There is no indication of noticeable accumulation of black carbon. This was also found for the top layer of slot filled site 4 with C/N ratio of 22. Underneath the top layer the C/N ratio increased to values above 50 to 80. Coal has C/N ratios of about 28 to 35. That means that the C/N ratio of site 4 indicates the occurrence of black carbon in the soil of slot fill. The soils were strongly contaminated by heavy metals (Figure 4). The origin of pollution is likely to be from industry, traffic in the streets and domestic heating. Some sources will be represented by individual metals. For heavy industry areas this will be iron and for some places also manganese. Lead will be more typical for traffic sources. Zinc and cadmium will be common for all sources. All top soils of the lawn had as expected high iron contents.. The iron content increased from site 1 to 3. Site 4 was similar to site 1. The slots of the pavement had a strong iron accumulation in the top layer, which is about 2 fold of the soils, and for site 4 about 4 fold. Sites 1, 2 and 4 showed the same trend in decrease for iron as occurred for organic carbon. For site 3 another distribution pattern with depth occurred. The iron content increased until the depth of 2 cm. The contents clearly show the influence of the local iron industry.The distribution pattern for iron is similar to specific magnetic susceptibility. For site 4, the pattern of values from the top soil of the lawn and of the pavement slots was with 7 times higher than for iron. The manganese concentrations were higher than for most natural soils. The soils of the lawn had contents from 1 to 6 g/kg, the lowest values at site 4 and the highest at site 3. The contents show a clear influence from a local iron industry. The manganese content of the slots was 3 to 5 times higher. The distribution with depth pattern differed from that of iron. Beside site 4 the manganese content increased. One explanation will be reduction processes during water logging in the sand of pavement plates. Manganese will be more soluble and washed into deeper sand layers near the surface.

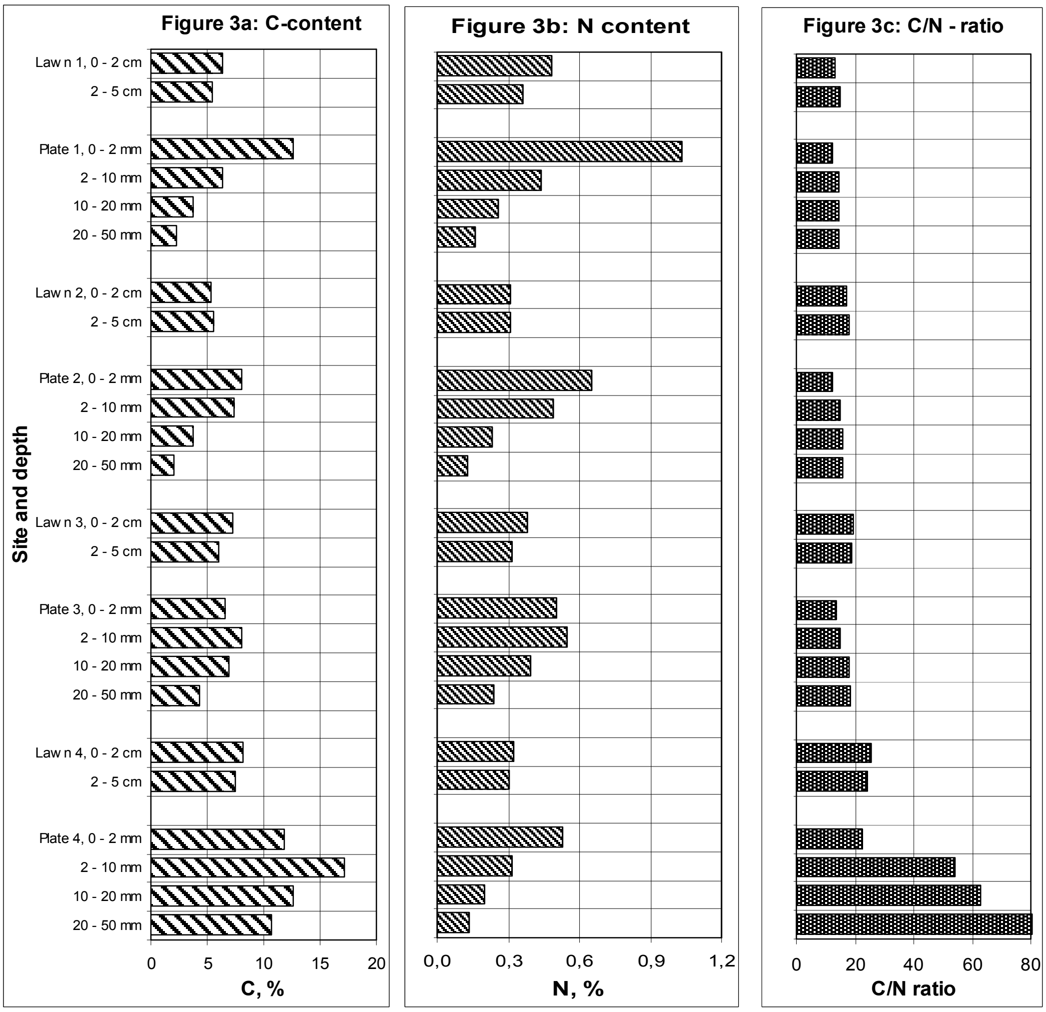

Figure 3. (a) C content, (b) N content and (c) C/N ratio from organic matter and black carbon.

Lead content was high in the soils of the lawn. It increased from site 1 to site 3. It was comparable low at site 4. This was not expected. Site 3 had as service road the lowest traffic and site 4 the highest one. Probably its origin is not only from traffic but also from industrial or domestic heating sources of the houses near by. The lead content was in the top layer of slots only slightly higher than in the soils of the lawn. Only for site 2 occurred a strong increase of about the 2 to 3 fold. For site 1 to 3 the highest lead accumulation occurred over all three top layers. Site 4 showed the decrease with depth. The elevated zinc content of the lawn was for all 4 sites with about 400 – 600 mg/kg nearly the same.

The accumulation in the top layer of slots was about 2 to 3 fold of the content of soils of the lawn. There were only low differences between the sites. The distribution pattern of zinc with depth in the slots was similar to iron. The contents decreased from top to the depth. Only site 3 showed the deviation in his pattern as described already for lead and iron. The soils of the lawn showed elevated cadmium contents between 1.3 and 3.1 mg/kg. The highest values occurred in site 3. The cadmium concentration increased in the slots up to 5 mg/kg. The distribution pattern with depth of the slots was similar of that of zinc and iron.

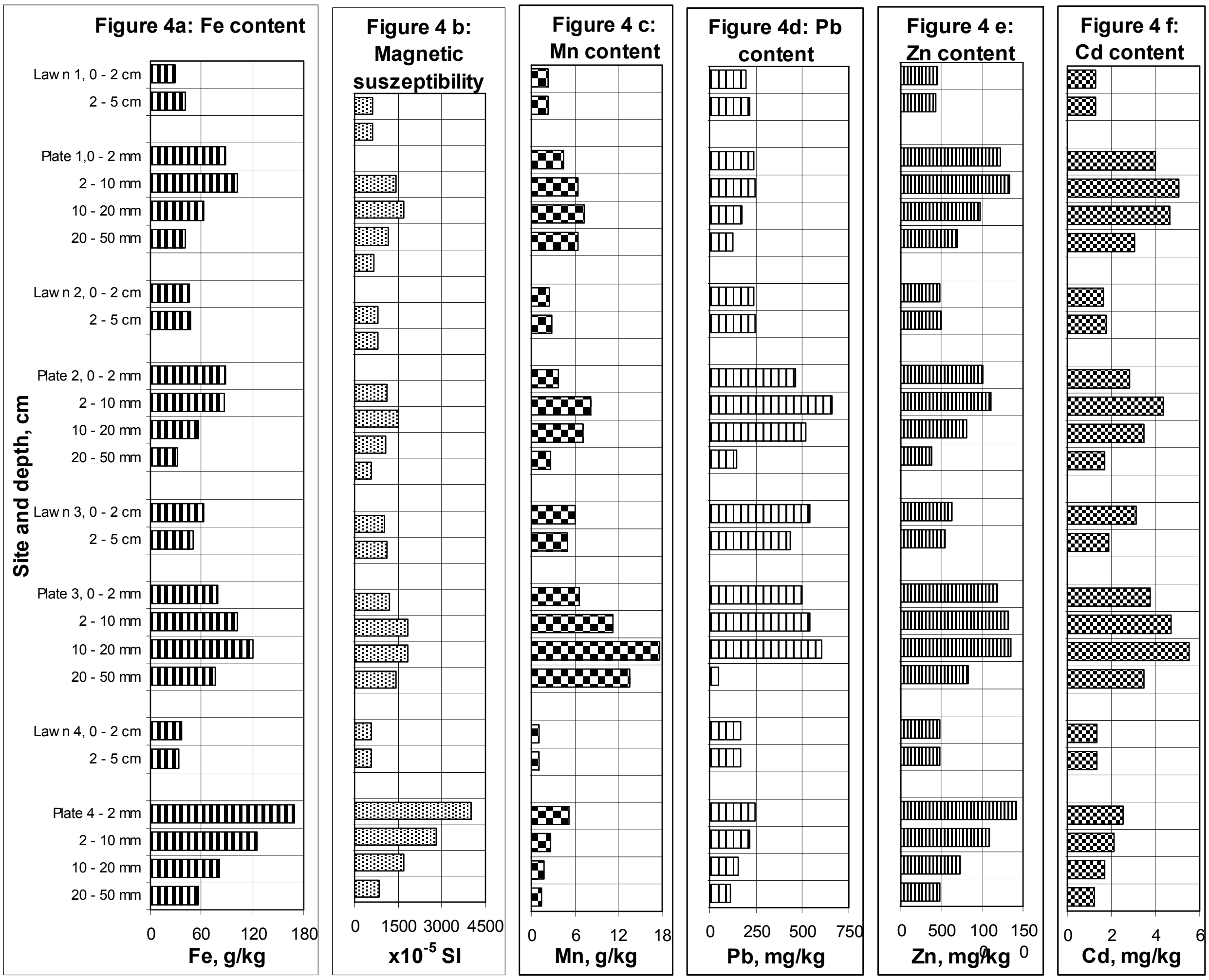

Figure 4. (a) Fe content, (b) magnetic susceptibility, (c) Mn content, (d) Pb content, (e) Zn content and (f) Cd content.

Conclusion

The soils in the slots of pavement of side walks are distinctly higher in polluted materials than in the soils of adjacent lawns. One reason will be the separation of the sand fraction by the mechanical filter effect of the sand filling of the pavement slots. Thus fine soil particles of fine sand and finer will be accumulated in the fill of slots. There is no clear indication that there is much dust deposed directly from street and from traffic. The C/N ratio shows that the material found on side walks is more related to the organic matter of adjacent soils. The black carbon deposition from industry and traffic seems to be to low to be distinct indicated by C/N ratio. The effect of the two different heavy industry sites is clearly recognized by the strong increase in heavy metal contents specific for each of the areas. However, the deposited amount of industrial dust seems to be low compared to the amount of soil material deposed on walk ways.

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Soil factors affecting vegetation establishment after sand mining on North Stradbroke Island

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Abstract
A study was undertaken to investigate causes for poor native vegetation establishment and erosion in rehabilitated sand dunes following sand mining at North Stradbroke Island, Australia. The problem was mainly associated with the use of topsoil from old rehabilitated sites from earlier mining ventures (designated as pre-mined topsoil) as opposed to using topsoil from unmined native areas (designated as unmined topsoil). The approach was to characterise the soil properties pertinent to soil erosion and measured poor plant growth from two rehabilitated areas of similar age but using the different topsoils, pre-mined and unmined. Results indicated that the greatest soil physical difference between the topsoil areas was the severity and frequency of water repellency (ratings 6-severe and 5- moderate to severe) that occurred in the pre-mined topsoil. Ca and Mg contents were also lower in the pre-mined topsoil area compared to that of the unmined topsoil, as was the lower Ca:Al ratio (<1), indicating a possible impact of poor cation balance on vegetation growth. Despite differences in surface stability and vegetation growth, soil carbon was not a differentiating factor between the unmined and pre-mined topsoil areas.

Key Words
Mined land rehabilitation, water repellency, Ca:Al ratio, dune rehabilitation.

Introduction
A requirement of sand mining operations on North Stradbroke Island is to produce a landform similar to pre-mining and to establish vegetation communities on post-mine dunes constructed from mined residues or tailings. During rehabilitation, reconstructed sand dunes are first overlain with a layer (0.2-0.3 m) of topsoil that had been removed from unmined areas ahead of the mine path. Following this, a sorghum (*Sorghum bicolour*) cover crop is sown along with a mixture of native seeds and blended fertilizer. Once seeded the soil surface is sprayed with Terolas®, an aqueous bituminous emulsion at a rate of 1.8 L/m^2. Terolas® is used for two reasons: (i) to produce surface stability against wind and water erosion, and (ii) to maintain soil moisture for germination and establishment. Problems of poor native vegetation establishment and high incidence of gully erosion have occurred at certain revegetated sites. These sites were associated with the use of topsoil collected from areas that had been rehabilitated in the late 1970s to early 1980s and are currently re-mined (designated as pre-mined topsoil), as opposed to topsoil from unmined native areas (designated as unmined topsoil) which is the case in newly mined areas. The aim of this study was therefore, to characterise the soils in the rehabilitation areas, and to compare the soil physical and chemical properties pertinent to soil erosion and poor plant growth from rehabilitation areas of similar age but using the two types of topsoil.

Site location and climate
The study was conducted at a mine site situated ~ 2.5 to 5.5 km south of the township of Point Lookout (27° 26' S, 153° 32' E) on North Stradbroke Island (NSI), 40 km east of Brisbane in Moreton Bay. Rainfall is summer-dominant (mean monthly precipitation ranging from ~ 10 - 370 mm) with short intense rain events, particularly associated with summer storms. Evaporation exceeds rainfall (almost double the rainfall), and mean annual daily temperature ranges from 15 to 25^{o}C. Natural landform at NSI mainly consists of dune sands of different ages with low inherent fertility (but sufficient to support a range of eucalyptus-dominated communities), wallum vegetation (coastal vegetation on sandy acidic soils) and dystrophic (poorly nourished) lakes with peaty brown, acidic water. Soils can be excessively dry in young dunes and permanently waterlogged in swamps and wetlands. The most common natural soil type is the Podosol (Isbell 2002) with deep yellow or pale brown siliceous sandy subsoils containing iron and aluminium compounds. The source of soil nutrients are a small quantity of weatherable minerals in the sand and salt from sea spray (Pillai-McGarry and Mulligan 2008). The study mine site was operational from 1966 for a period of 20 years and mining recommenced at the site in early 2000.

Methods

Fifteen trenches (1m x 2m x 1.5 m deep) were mechanically dug in two areas that were rehabilitated in 2006 and managed in a similar manner. Nine of the trenches (T1 to T9) were located in the area where pre-mined topsoil was used (designated as Block A) and six (T10 to T16) in the area where unmined (native) topsoil was used (designated as Block B).

Field sampling and measurements

At each trench, the following field measurements and observations were undertaken:
(i) Site and soil description- visual estimates of vegetation type and percent cover, slope and aspect and basic soil description (McDonald *et al.* 1990) to 1 m depth of a freshly exposed vertical face; (ii) three replicated soil samples were collected at 0.05 m intervals to 0.2 m, at 0.1 m intervals to 0.4 m and 0.2 m intervals to 1 m depth, transported to the laboratory, air-dried and prepared for analysis by passing through a 2 mm sieve; (iii) four replicated cores for bulk density determination (70 mm dia. x 60 mm or 20 mm long) were vertically inserted at each of 0 m, 0.03 m, 0.06 m, 0.15 m, 0.3 m, 0.5 m, and 0.7 m depths using hand pressure applied to a flat stainless steel plate, placed on top of the core, the core with soil was excavated with a knife, soil oven-dried (105^{o}C) in the laboratory and bulk density calculated using core volume; (iv) water repellency of the surface soil was tested and rated using the water drop penetration test (WDPT) (NSW Department of Sustainable Natural Resources 2005) by placing a droplet of de-ionised water, using a 10 mL syringe, onto the soil surface bounded by a steel ring (70 mm dia. x 20 mm long) inserted into the surface, and time for penetration recorded. Five replicated readings were made so that a range of penetration times were obtained.

Laboratory analyses

The aim of the laboratory analyses was to provide a comparison of soil fertility from the different rehabilitation sites for use as a possible indicator for plant growth differences. All chemical analyses except for total carbon were carried out on the <2 mm fraction of the soil. Unless otherwise stated, all analytical procedures were as outlined by Rayment and Higginson (1992). Measurements made were: (i) $pH_{1:5\ water}$ using a TPS pH meter following end–over- end shaking for 1 h, (ii) total C and N of ground soil passed through a 0.5 mm sieve, by combustion using an Elementar Vario Macro CHNS Analyser; (iii) exchangeable basic cations and Al, Fe and Mn were measured using an ICP-AES (SPECTROFLAME MODULA E) after a 16 h extraction with unbuffered 0.01 M silver-thiourea (1:50 soil:solution ratio).

Water repellency test

To standardise soils, the WDPT was also conducted in the laboratory on air-dry samples. Soil subsamples were placed in cylindrical containers (0.02 m dia. x 0.15 m deep) and repellency rating was measured on replicated samples.

Results

The most striking differences in visual features between Blocks A and B were the greater density and diversity of above-ground native vegetation and the low weed population in Block B compared to Block A. The mean live vegetation groundcover was lower for Block A (32.2%; range: 5-50%) compared to Block B (45%; range: 10-80%). A typical profile of the reconstructed soil (Plate 1) indicated an abrupt transition between a generally hardsetting topsoil and a less cohesive subsoil (tailings) with minimal evidence of a transition zone despite two years of formation.

Plate 1. Typical profile of a two-year old reconstructed and rehabilitated sand dune. The topsoil exhibited a hard-setting zone below 0.05m depth and above the subsoil (tailings). Hard-setting refers to the strength of a soil tested under a specified moisture condition (moist and/or dry). In this profile the soil was hard below 0.05m, but the subsoil crumbled.

Topsoil depth varied spatially (0.16 to 0.39 m) across the study area. In Block A, rooting depth was mainly confined to the topsoil (mean depth was 0.22 m), whereas in Block B it extended into the subsoil (mean depth 0.36 m). A common feature noted while soil sampling, particularly in Block A, was the extensive lateral growth of thick (>50 mm dia.) roots in the 0-0.15 m depth (mainly associated with adjacent plants of *A.concurrens*) while finer roots were found at deeper depths where conditions were generally moister.

Although the topsoil was less dense to ~0.35 m (related to where the subsoil commenced) in Block B, there was no significant difference in bulk density for comparable depths between Blocks (Figure 1). The gradual increase in bulk density below the 0.1m depth was associated with the hard-setting layer and a decrease in rooting density and porosity in this layer. The lower bulk density in Block B may be associated with the better plant establishment and root growth contributing to improved porosity.

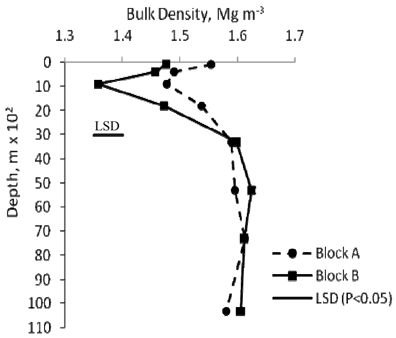

Figure 1. Mean dry bulk density profile of the soils in Blocks A (●) and B (■). LSD ($P<0.05$) compares means at any given depth.

Field testing for water repellency gave similar results to those from laboratory testing presented in Figure 2, and variability between laboratory replicates was close to zero. Repellency was particularly severe in Block A with soils from over 65% of the trenches in Block B having ratings of severe (6) or moderate to severe (5) repellency on the soil surface. Water repellency also extended to depths below the immediate surface.

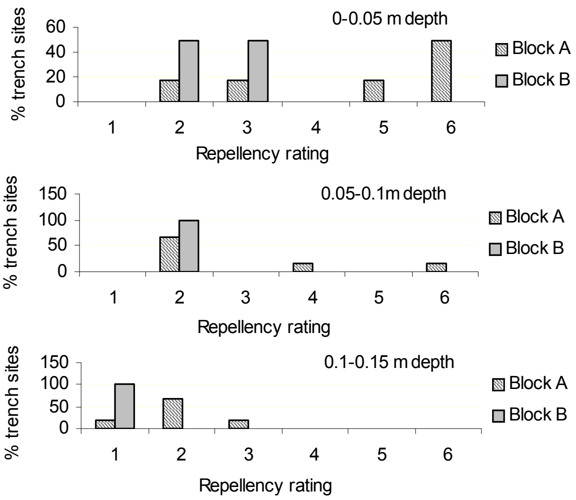

Figure 2. Water repellency ratings of soils tested under standard air-dry conditions in the laboratory 1 = not significant, 2 = very low, 3 = low, 4 = moderate, 5 = moderate to severe and 6 = severe.

Visual evidence of poor water infiltration caused by water repellency was recorded in the field (Plate 2) where uneven vertical infiltration of water, following an overnight rain event of 108 mm, occurred through root channels and other macro-pores (e.g. rotting plant material, faunal channels) resulting in patchy wetting of the soil.

Plate 2. Water repellency: irregular wetting in the vertical soil profile in Block B after overnight rainfall of 108 mm

The greatest difference in soil chemical properties between Blocks (Table 1) was in exchangeable Ca and Mg contents with more than double the amount of Ca and nearly double of Mg in Block B compared to Block A. The Ca:Al ratios in Block A was >1 in the topsoil compared to Block B where ratios were > 1. Surprisingly, % total C was low for all soils (<1%) with no difference between Blocks, possibly indicating low carbon accumulation in early years of rehabilitation.

Table 1. Means of selected soil chemical properties of the soils in Blocks A and B at six depths. Means with similar lettered superscript are not significant at P<0.05, for any given property.

Soil depth (m)	pH	Total C (%)	Exchangeable cations ($cmol_c$/kg)		Al ($cmol_c$/kg)	Ca:Al
			Ca	Mg		
Block A						
0-0.05	5.4^{a}	0.4^{a}	0.05^{a}	0.03^{a}	0.08^{a}	0.6
0.05-0.1	5.2^{ab}	0.4^{a}	0.08^{abc}	0.06^{b}	0.17^{b}	0.5
0.1-0.15	5.1^{b}	0.5^{a}	0.07^{ab}	0.05^{ab}	0.22^{c}	0.3
0.15-0.2	5.1^{b}	0.4^{a}	0.08^{abc}	0.04^{ab}	0.23^{c}	0.3
0.2 – 0.3	5.1^{b}	0.5^{a}	0.14^{c}	0.06^{b}	0.24^{c}	0.6
0.3-0.4	5.3^{ab}	-	0.12^{bc}	0.05^{ab}	0.05^{a}	2.4
Block B						
0-0.05	5.6^{a}	0.6^{a}	0.24^{d}	0.08^{c}	0.08^{a}	3
0.05-0.1	5.5^{a}	0.6^{a}	0.26^{d}	0.1^{c}	0.12^{a}	2.2
0.1-0.15	5.5^{a}	0.5^{a}	0.31^{e}	0.11^{c}	0.15^{b}	2.1
0.15-0.2	5.5^{a}	0.5^{a}	0.28^{de}	0.08^{c}	0.16^{b}	1.8
0.2 – 0.3	5.6^{a}	0.4^{a}	0.24^{d}	0.07^{bc}	0.13	1.8
0.3-0.4	5.6^{a}	-	0.1^{b}	0.02^{a}	0.06^{a}	1.7

Conclusion

Firstly, the greater incidence and severity of water repellency in Block A topsoil compared to Block B may have contributed to poor emergence and low surface stability in this area. Poor water infiltration and patchy soil wetting can affect germination and emergence particularly of small-seeded species and thereby hinder vegetation establishment. In addition when short intense storms typical of Queensland summers occur, rainfall concentration on the soil surface can create localised channels on sloping land leading to gully erosion once the non-cohesive subsoil is exposed. In this study, water repellency was not associated with differences in total C content, suggesting that water repellency may be attributed to differences in the nature of C in the topsoils of each Block associated with past vegetation history. The contributing factor to repellency in the topsoils is currently being further investigated. Secondly, lower levels of basic cations associated with greater aluminium content in the Block B soil may suggest a cation imbalance which may have impacted on plant growth. The Ca:Al ratio is considered to be a useful indicator for plant growth (Vanguelova 2007; Poschenrieder *et al.* 2008) in sandy soils, as Ca deficiency can occur by nutrient exclusion if exchangeable Al is significantly large. The effect of nutrient imbalance alone and in combination with water repellency in these soils is a focus of current studies. Based on the present study, rehabilitation strategies on mined sand dunes similar to the study site, should consider: (i) the application of an appropriate soil wetting agent at planting to overcome site water repellency and, (ii) a site specific fertilizer plan taking into account the soil nutrient imbalance.

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Soil-like conditions can be achieved inorganically in alkaline bauxite residue

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Abstract
Achieving a stable cover of vegetation on alkaline bauxite residue is challenging because alkalinity, sodicity, salinity and nutrient deficiency inhibit plant establishment. When the residue sand fraction is used as the growing medium there are additional problems of nutrient loss by leaching and poor water retention. Organic amendments or topsoil are consequently thought widely to be valuable for rehabilitation. Recognising the importance of organic matter for developing soil and achieving a stable ecosystem, we conducted a glasshouse experiment with kikuyu grass (*Pennisetum clandestinum*) to test the feasibility of generating organic matter *in situ* with water, nutrients and sunlight using inorganically amended residue sand. The amendment of the sand consisted of adding 4 % gypsum and 5 % carbonated (CO_2-sparged) red mud together with 150 mg/kg P as phosphoric acid and a range of macro- and micronutrients. Grass was grown by planting discs of turf in 64 pots (90 x 500 mm pipes fitted for leachate collection) each containing 2.9 kg of amended residue which had been leached with about 25mm of water.

Experimental treatments consisted of 16 treatment combinations of 4 leaching frequencies and 4 rates of N application as solutions of ammonium sulfate applied every 4 days and containing maintenance levels of K and Mg. After 3 months, leachate pH had declined from 8.5 to 7.7. Leaching every 4 days for 3 weeks reduced electrical conductivity (EC) of leachate to < 5dS/m and used 1-2 pore volumes (100-200 mm) of water. Maximum dry matter production (roots and shoots) was about 35 g/pot after 3 months. This equates to about 50 Mg/ha. Growth response to N was linear up to the highest N rate of 6470 kg/ha ammonium sulfate. The results suggest that use of a non-invasive, sodium-tolerant grass such as kikuyu, besides providing a protective cover, has considerable potential for generating organic matter and accelerating soil development during restoration of bauxite residue.

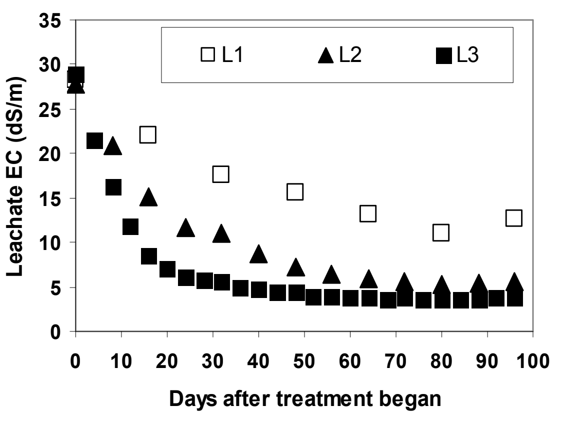
Key Words
Bauxite residue, alkalinity, salinity, kikuyu grass, carbon sequestration, gypsum

Introduction
The residue (about 70 million tonnes a^{-1} globally) from digesting bauxite with NaOH for alumina production is caustic and requires considerable amelioration before it will support plant growth. The commonest ameliorant is gypsum which serves as a sink for both soluble and hydrolysable alkalinity through calcite precipitation. This occurs slowly in the presence of atmospheric CO_2 but can be hastened through prior carbonation. At Alcoa of Australia's Western Australia refineries, bauxite-processing residue sand (> 150 µm) is separated and used in constructing outer embankments of residue storage areas, which are subsequently rehabilitated as part of progressive closure. Recent research suggests that mixing a small amount of mud with residue sand might overcome problems of poor retention of water and nutrients which affect vegetation growing on sand, and that excessive alkalinity might be avoided when carbonated mud is used for this purpose.

Methods of field-scale rehabilitation may employ organic amendments such as sewage sludge, compost or woody mulch to improve physical, chemical and microbial properties. It has been suggested that minimising the immobilisation, leaching or volatilization of plant nutrients such as P, N, Mg and some trace elements, by supplying them in slowly biomineralisable form, might be an important advantage of organic ameliorants even though inorganic fertilizers may be cheaper (Eastham *et al.* 2006). The objective of this study was to find out whether, and at what rate, vigorous plant growth could be achieved in residue that has been amended inorganically, the idea being to generate organic matter for soil development without having to import organic amendments or soil materials. Axiomatically, any process that produces organic matter instead of consuming it must achieve a better score for environmental effectiveness, especially if it is cheaper and creates a protective soil cover that subsequently can be managed through succession towards a planned ecosystem.

Methods and materials
The experiment was conducted in a glasshouse using kikuyu grass (*Pennisetum clandestinum*, var. Village Green) in 64 pots filled with residue sand (uncarbonated) from the Kwinana alumina refinery after being amended with the following additions: 5 % carbonated mud (added as a slurry), 4 % gypsum ($CaSO_4.2H_2O$), and 150 mg/kg P (applied as dilute phosphoric acid). Two handfuls of garden soil were added to achieve microbial inoculation prior to final blending. Each pot consisted of a 500 mm length of 90 mm diameter plastic piping fitted with a base perforated with ten 3mm holes, and was filled to 10cm from the top with 2.9 kg of amended residue. The following elements (mg/kg) were then added in a 100ml mixed solution applied to each pot: 50 N as KNO_3 plus 30 N as $(NH_4)_2$ SO_4, 40 Mg as $MgSO_4$, 150 K as KNO_3, 1 B as H_3BO_3, 0.1 Mo as $(NH_4)_6Mo_7O_{24}$, 2 Zn and 1 Cu as sulfates, and 50 Mn as $MnCl_2$. Pots were fitted with a plastic leachate collection bag at the base and mounted on flower pots for stability. A disc of established kikuyu grass, cut by hammering a sharpened piece of the piping through a slab of commercial turf, was placed firmly on the surface of residue in each pot. The pots were lightly watered daily for three weeks in the glasshouse to produce a uniform growth of grass (about 5 cm) which was removed by clipping flush with the top of the pots prior to commencing treatments. These consisted, in 4 replications, of 16 combinations of (a) four leaching frequencies, whereby 200 ml water was either not applied (L0) or applied every 16, 8 or 4 days (L1, L2 and L3,respectively), after watering to field capacity (which was done every 4 days by weighing) and (b) four levels of nitrogen applied every 4 days as 10 ml of solution supplying 0, 3, 6, or 12 mg/kg N as ammonium sulfate (N0, N1, N2 and N3, respectively) and incorporating in the same solution a maintenance application of 16 mg/kg K as KCl and 3 mg/kg Mg as $MgSO_4$. (The molar ratio N:K:Mg in the N3 treatment was thus 0.86:0.41:0.13). Every 4 days prior to irrigation the pots were weighed, and the volume, pH and electrical conductivity (EC) of leachates were measured prior to storage at 4 ^{0}C. Three harvests of grass were cut (1 per month) and the dry mass (60^{0}C) recorded. Columns of residue with roots were extruded from the pots and sectioned into 4 equal parts after slicing away the original turf with stems and stolons. A sub-sample of each section was retained for analysis and the roots were separated by washing on a screen and drying at 60^{0}C.

Results
Before the first application of treatments the pots had been pre-leached and an average of 0.09 ± 0.01 pore volumes of leachate was collected from each pot with an average EC of 78 dS/m and pH of 8.5. A second leaching was applied to the pots after planting and produced the same quantity of leachate with an average EC of 33 dS/m and pH of 8.4. The EC and pH of leachates collected after treatments had commenced are shown in Figure 1.



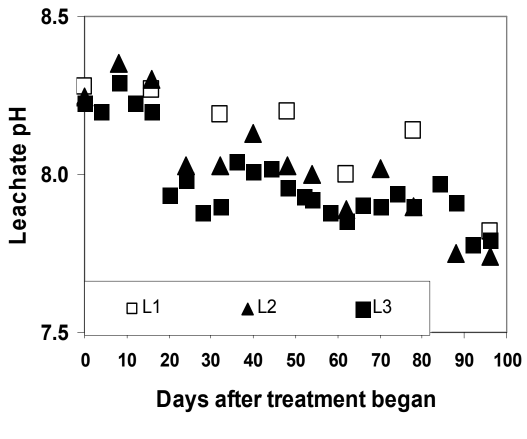


Figure 3. Decline in EC and pH during the course of the experiment after treatments commenced, as a function of leaching frequency (L1: leaching every 16th day; L2: every 8th day; L3: every 4th day).

Leaching frequency affected the rate of decline in leachate EC more clearly than that of leachate pH. The EC decline can be seen (Figure 2) to have conformed approximately to a single pattern when plotted against water applied, and even more so when plotted in relation to volume of leachate collected.

The final cumulative mean yield of shoots (4 replications; 3 clippings) and other plant parts (3 replications) is shown in Figure 3. Positive interaction between leaching and nitrogen level was evident in yields of foliage but not stems, stolons and roots. The first of the 3 clippings showed this interactive tendency more strongly (data not shown), probably because of the larger salinity differences between leaching treatments during the first month.

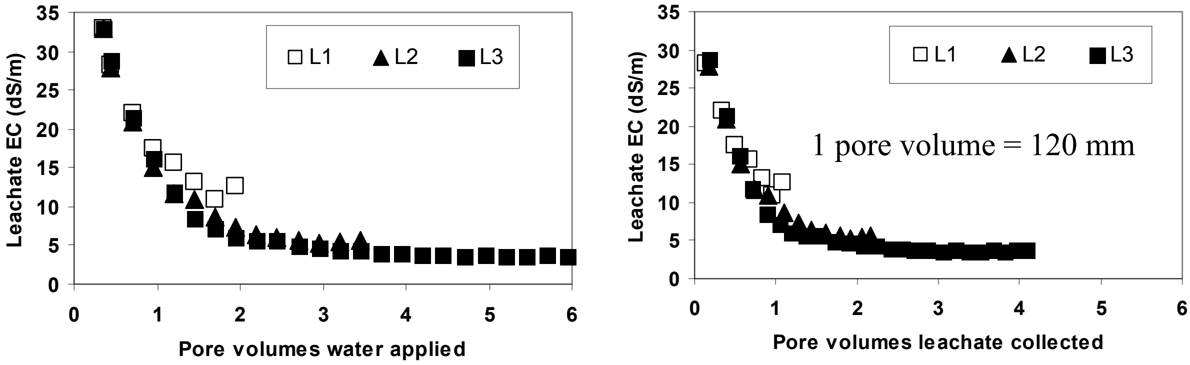


Figure 2. Leachate EC relative to applied water and leachate volume, as a function of leaching treatment.

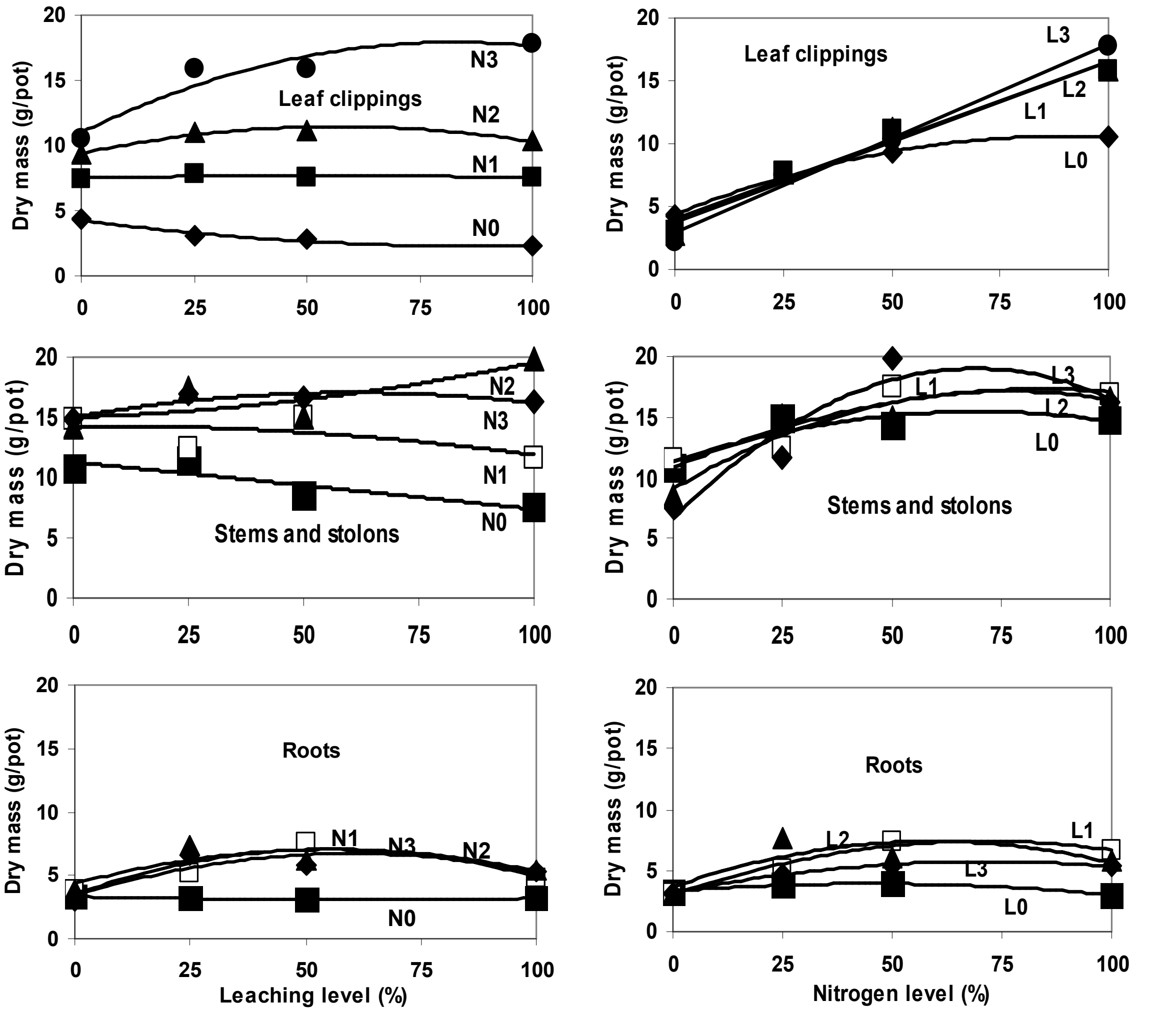


Figure 3. Yield of kikuyu grass leaves, stems and roots plotted relative to leaching (L) and nitrogen (N) levels. (The L or N levels indicated as 0, 1, 2 and 3 are equivalent to relative levels of 0, 25, 50 and 100 %, respectively).

Discussion and conclusions

Analysis of initial leachate from the pots indicated that a tolerable solution pH (~8.5) was achieved with the combined addition of carbonated mud and gypsum but that salinity was severe. X-ray diffraction of salt from dried leachate indicated thenardite (Na_2SO_4). Figure 2 suggests that between 1 and 2 pore volumes of leachate (about 100-200 mm water) removes most of the salt from the 40-cm root zone. This is efficient compared with field observations and is probably due to the uniformity of gypsum reaction. Leaf dry mass in the first month was 1.8 in L0N3 and 4.8 g/pot in the L3N3 treatment, confirming the value of early leaching. The response to N was also large: L3N0 had a corresponding yield of only 1.1 g/pot. After 3 months, N level had induced no effect on pH which varied between 7.6 and 7.9 in leachate and residue. The latter at the top of the pots effervesced with HCl, confirming persistence of carbonate buffering. Further analysis of solids and leachates including total acidity will be needed to quantify nitrification effects. The response to N (Figure 3) was linear up to the highest rate (N3), equal to 1360 kg/ha N or 6470 kg/ha ammonium sulfate. Dry biomass at highest yield levels was about 35g/pot after discounting initial turf mass (~5g). This translates to roughly 50 Mg ha^{-1} in 3 months. About 1/5th of this took the form of roots which extended throughout the volume of all pots. Although direct extrapolation to field conditions is not warranted the results clearly demonstrate substantial C sequestration potential and that alkaline bauxite residue can become a highly productive medium for plant growth with a suitable combination of water and conventional fertilizer salts.

The treatments that collectively produced these results included the following: (a) addition of gypsum, without which sodic and alkaline conditions would remain prohibitive (Woodard *et al.* 2008); gypsum provides Ca for calcite as a sink for alkalinity, thus promoting the dissolution of sodalite; (b) irrigation, to maximize growth response to nutrients and remove excess salts; (c) use of a vigorous strain of sodium-tolerant grass (Mills *et al.* 2004); (d) use of carbonated mud (Khaitan *et al.* 2009) to ameliorate the uncarbonated sand; (e) a generous basal application of macro- and micronutrients; (f) large nitrogen applications as ammonium sulfate in solution every four days, with simultaneous maintenance applications of K and Mg to compensate for leaching losses and possible fixation (e.g. Mg in struvite and K in sodalite or dawsonite); (g) a relatively warm temperature regime (between 15 and 30^{o}C). Many of these treatments were designed to deal with side-effects associated with alkalinity and mineralogy of the bauxite residue. The next step would be to work backwards with subtractive treatments to find out the extent to which each of these factors is limiting. The present results suggest that the expense of organic amendments or imported topsoil (Wehr *et al.* 2006) could be obviated if the residue itself is turned into a suitable growth medium. Intensive propagation of a pasture such as kikuyu (especially a male-sterile strain with limited invasive capacity) could provide a stable cover as a prelude to introducing native plant species for establishing ecosystems similar to Jarrah forest or Banksia woodland. Kikuyu is readily killed with glyphosate. Rapid neutralisation of alkalinity and build-up of organic matter to create soil-like conditions might boost confidence in the rehabilitation process prior closure. Disposal of leached sodium sulfate seems to be the most limiting requirement for success on a field scale and getting it done early makes sense. This applies to whatever revegetation strategy is adopted.

Acknowledgements
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Specifics of urban soils (Technosols) survey and mapping

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Abstract

Systems of soil survey, sampling and mapping e.g. for planning and zoning processes are complicated by ongoing consumption of urban soils; by sealing or building activities regardless the soil functions in urban landscape. For the case study of Bratislava city there are presented some peculiarities of survey and mapping processes. Also some obstacles met in this process are listed. The strategy of soil mapping is based on demands of soil quality according to site use of various groups of urban population. Proper methodology includes: recognition of urban ecosystems respecting demands of the urban population on soil quality; selection of representative soil profiles, soil description field book: urban pedon or polypedon description and classification, mapping: use of so-called pedo-urban complexes; sampling and analyses of surface or subsurface soil contamination on risk elements. To delineate soil complexes in urban areas there is a need for GIS based soil data. As a base for urban area delimitation and digitalization aerially scanned orthophoto maps at the scale 1:5,000 and digitized in ArcMap (ESRI inc.) were used. Outputs of the soil survey and mapping could provide many maps: e.g. soil map (at the scale 1:25 000), map of soil texture, map of parent materials (incl. anthropogenic) and many derived map compilations to be used for urban planning aims.

Key Words

Urban soil, Technosol, urban pedon, pedo-urban complex, soil sealing

Introduction

In most cities there are available data concerning soils and their various properties. Also methodological approaches which include urban soil survey; sampling and soil properties evaluation for urban planning and zoning processes have been revealed over the world, like TUSEC-IP (Lehmann *et al*. 2005), and other publications on urban soil assessment in landscape (Craul 1992, 1999, Vrscaj *et al*. 2008). Most of these approaches try to assess urban soils from the viewpoint of different soil functions. In cities we have areas like historical centers, industrial plants, urban greens and parks, playgrounds and schoolyards, residential areas, recreation areas, abandoned brownfields, etc. Survey and mapping of urban soils (mainly Technosols) is a very complicated and complex task. Human activities have played an overwhelming role in the distribution of soil or parent materials with different pedogenetic processes. Urban soil spatial variability represents a great deal of their complexity. Therefore understanding and knowledge of pedogenesis cannot be applicable to the whole urban landscape. Generally soils in cities are completely stripped and stockpiled or backfilled around the construction objects. Most commonly occurring soil group are Technosols (WRB 2006). In the paper there is described some new principles of urban soil survey and mapping methodology regarding numerous soil functions in an urban landscape. Also some obstacles referring to urban soil (Technosol) diagnostics and classification or soil sealing covers affecting the mapping process have been taken into consideration.

Methods

To achieve given aims the traditional pedo-geographical methodology of soil unit survey and mapping was recognized, verified by application using aerial orthophoto-maps and GIS tools. Methodology was completed by new ideas of urban areas mapping with knowledge about soil functions in urban landscape. General strategy includes pedogenesis of soils predominantly occurring in cities, mainly Technosols, classification procedure related to the Slovak Morphogenetic Soil Classification system (Collective 2000) what is the role of anthropogenic (human-transported) material and its properties by specific terminology concept (urban pedon, pedo-urban complex) was introduced into the urban soil mapping strategy. Also the problem of soil sealing is mentioned as one of the great factors in urban soil survey and mapping.

Results

Soil genesis of Technosols

Genesis of soil occurring in urbanized areas differs from soils situated in natural landscape. Soil genesis is conditioned by several factors:

– Parent material – soil properties are attributable to their origin (prevailingly from techogenic or semi-technogenic substrata); and to the manner of their disturbance rather than natural pedogenetic processes.
– Youth (initial soils) – the time period is to short for diagnostic horizons formation (Burghardt 2001)
– Mostly extreme physical and chemical properties not common in natural landscapes.
– Mostly excess contents of dust (PM_{10}), risk elements (contaminants) and pathogenic organisms
– Presence of artifacts (WRB 2006).

A lack of detailed urban soils classification in recognized in Slovakia. Taxonomic classification has progressed very slowly and has not gained widespread acceptance. If the urban soil is not readily classified mapping is not facilitated.

Soils found in cities

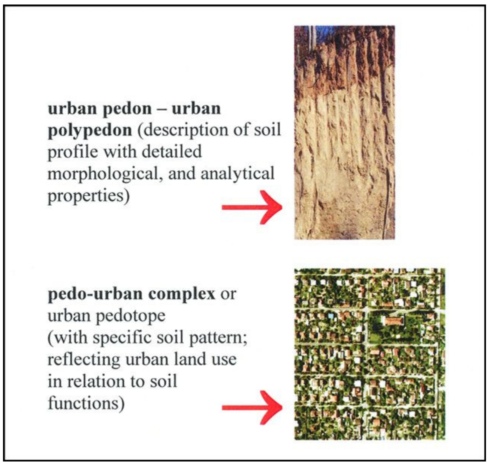
There are various soil types, a great variety with strong heterogeneity in the vertical direction (e.g. through soil profile) or horizontal direction (spatial differentiation). The variety of soil can be divided: (i) natural soils, (ii) man-influenced soils, (iii) man-changed soils; and (iv) man-made soils (artificial) soils.
In cities of Slovakia there are mapped mainly two groups of anthropogenic soils: Kultizems´s soil group at which diagnostic principles is profound "in situ" transformation or perturbation of top horizon by deep tillage, trenching, deep cultivation, fertilizer application, etc. They have many features similar to Anthrosols (WRB 2006) but they are not defined by the same way. Anthrozem soil group is most similar to Technosols (WRB 2006). They are man-made soils developed from human-transported material. This "ex situ" material is most important for diagnostics and is divided into three subgroups: with natural origin, with semi-natural origin; and with technogenic material (Sobocká el al 2000). Not all Anthrozems meet diagnostics of Technosols however the rule of 20 percent and more of artifacts in the upper 100 cm from soil surface is kept.

Urban soil survey and mapping

The complexity of soil units in the urban landscape is so great that single mapping units could not be used, however each recognizable urban soil unit is important for interpretation because it contains capabilities for soil function implementation.
Two-levels of urban soil survey and mapping is considered in Figure 1

1) urban pedon, urban polypedon (description and classification of soil profile according to morphological, physical-chemical and analytical properties
2) pedo-urban complex or urban pedotope (with specification of the urban pattern reflecting urban land use in relation to soil functions).

Figure 1. Levels of urban soil survey and mapping



The system is complicated by ongoing land consumption and by sealing regardless to soil functions respecting. Two levels of terms have to be distinguished: soil sealing as impervious cover of soil surface by asphalt, concrete, roads, etc.; and land consumption as land use change for buildings, construction activities with possible open green areas maintenance. Predominantly soil sealing has strong impacts on soils, their properties and consequently on inner-city green areas reduction.

Strategy of soil survey and mapping

The strategy of soil survey, mapping sampling and assessment of urban soil was demonstrated in a case study of Bratislava city (Sobocká 2007). It consists of:

1) recognition of pedo-urban complexes (land use) respecting the demand of urban population on soil quality
2) selection of representative soil profiles (e.g. industrial sites, commercial-housing areas, residential sites, traffic infrastructure, green zones, parks, recreation sites, child playing grounds, cemeteries etc.
3) soil description field handbook (urban pedon or polypedon)
4) sampling and analyses for analysis of risk elements (heavy metals, organic pollutants)
5) mapping of soil units: using pedo-urban complexes delineation and digitalization of aerially scanned ortho-photomaps in the scale 1:5,000; GIS tools use (ArcMap, ESRI, inc.)
6) soil map compilation (in the scale 1:25,000 and other derived maps for various aims compilation (Figure 2 and 3).

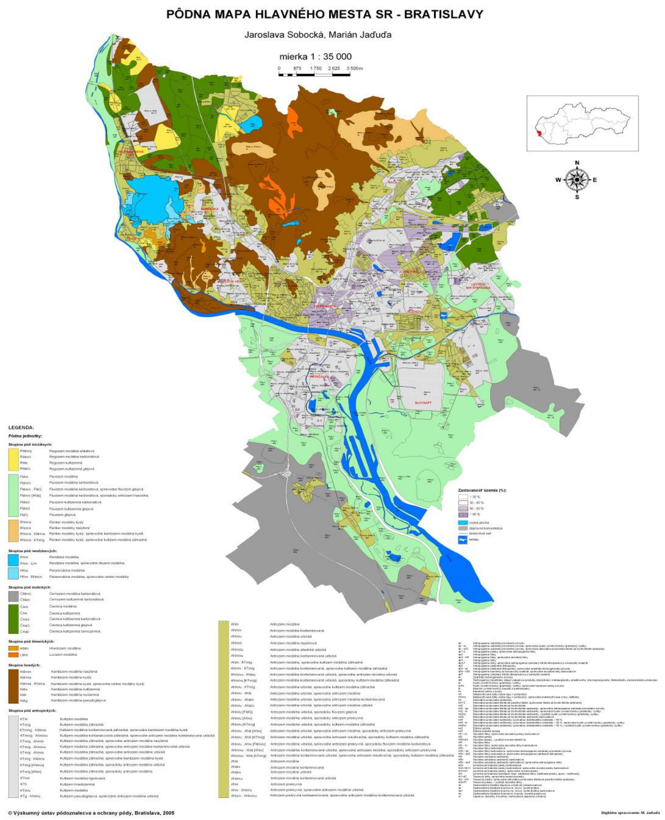


Figure 2. Soil map of Bratislava city at the scale 1:25 000

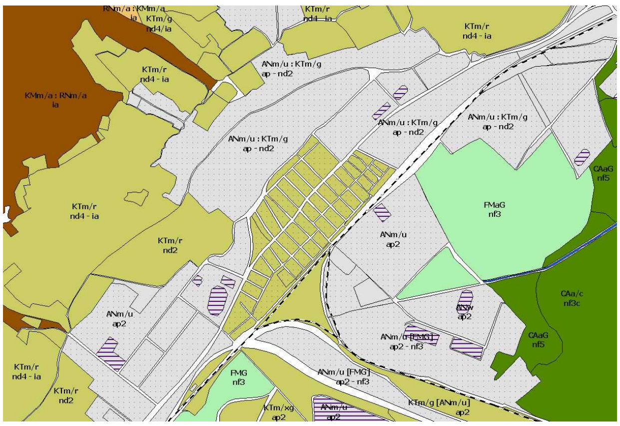


Figure 3. Detail of the soil map of Bratislava city

What are main obstacles in urban soil survey and mapping?
There are several problems:

- to identify and classify soil units with anthropic features
- to identify and classify variability of anthropogenic (technogenic) material
- to measure analytical data for noxious compounds
- to measure soil sealing using appropriate methods
- to identify auxiliary data incl. urban site history knowledge
- to use strong digging technology in urban soil pits and be aware of tubes, cables and other subsurface elements
- to respect private owners in cities at soil pits.

Conclusions

For urban planners and designers there is a urgent need to create a Manual for urban soil description, classification and assessment as helpful guidelines can be included and to enable awareness of soil in urban planning processes. Also urban survey can indicate new soil types which can enlarge the current soil classification system.

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Study on some components of urban forest ecosystems with respect to recreation

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Abstract
Studies were carried out on the components of ecosystems in the region of the north-eastern parts of Lyulin Mountain in the green zone of Sofia-Pernik agglomeration (Bulgaria). Three plots in the most visited areas were investigated. Soil morphology, mechanical composition, water regime, humus substances, soil acidity and CEC of *Cambisols* were studied. The presence of exchangeable Al in surface soil layers which have formed by the suspected destruction and dissolution of layer silicate minerals. The high content of "aggressive" fulvic acids confirmed that the upper organic soil horizons are more vulnerable to stronger pollution. The concentrations of Cu and Pb were higher compared with other relatively non-polluted territories nearby, while other pollutants Zn, Cd and Pb were in lower concentrations. The natural regeneration in *Fagus sylvatica* L. pure or mixed forests was observed. The bio-groups have good structure with beech as a dominant tree species. The results showed an influence of urban pollution on forest vegetation. The Factor of Accumulation (FA) was estimated for the main tree species and the trees were arranged according to their preferences to element' accumulation.

Key Words
Parks, cambisol soil types, vegetation, anthropogenic effects.

Introduction
Recreation areas have a long-term effect on soils and total ecosystems and studies in these zones are of a great importance. The "compaction" effect is a direct result of recreation areas and could be expressed in: a) direct mechanical changes in soils and b) damages in physical and chemical soil properties in the upper soil horizons (Brown *et al.* 1977). The level of soil compaction is related to decreases in soil moisture in surface horizons and the low percent of porosity, which promotes poor physical properties and changes textural fraction ratio. The level of compaction is also related to the decrease in exchangeable Ca and Mg and in other cases Al. Moreover, recreation areas are also influenced by understory vegetation and the processes of natural regeneration, which is related to the development of poor productivity in surface soil horizons (Stoyanova and Grozeva 1995). The aim of this study was to investigate both soil characteristics and natural regeneration in urban forest ecosystems in proximity to Sofia region with respect to recreation areas.

Materials and methods
We have analyzed the components of ecosystems in the region of the north-eastern parts of Lyulin Mountain, situated in the green zone of Sofia-Pernik agglomeration (Bulgaria). The experiment was performed between 1996 and 1998. The characteristics of the chosen three experimental plots are presented in Table 1. Morphological characteristics were described at the macromorphological level, which includes parameters such as colour and structure. This information established soil types to be *Cambisols* (FAO 1998; Table 1).

Table 1. Soil characteristics of the plots.

Plot	*Cambisols* (FAO,1998)	Dominant tree species	Origin, age	Exposition; part of the slope; slope	Altitude (m)
Manastira	*Eutric Cambisols*	*Fagus sylvatica* L.	Natural, 100 years	E; central part of the slope; 15-18°	850
Hizhata	*Eutric Cambisols*	*Fagus sylvatica* L.	Natural, 40 years	E; low part of the slope; 10-12°	920
Poljanite	*Modic Cambisols*	Herbaceous; single trees of *Fagus sylvatica* (and other tree species)	Natural, 30-60 years	Upper part of the slope; 3°	940

The soil morphology, mechanical composition, water regime, humus substances, soil acidity, CEC and heavy metals content of soils were characterized. Natural regeneration was measured by application of dendro-biometrical studies and the impact of recreation areas was determined using the database from national statistics annuals.

The sampling of soils was completed for one representative soil profile per plot and the following characteristics were determined according to standardized methods (Donov *et al.* 1974): *Bulk density* – method of Katchinski; *Texture* – pipette method with HCl; *Soil acidity* – in distilled water - with pH-meter "Pracitronic, MV 88"; *Soil organic matter (SOM)* [%] – ISO 10694; *Total nitrogen* [%] – Kjeldhal; *Exchangeable K* – method UNEP – UN / EC 910651 by AAS Perkin Elmer 370 A; *Heavy metals* - AAS Perkin Elmer 370 A and *CEC* – Ganev and Arsova method (Ganev and Arsova 1980). The Factor of Accumulation (FA) was estimated as a ratio between the content of the element in the leaves a.d.m. (mg/kg) and the content of the element in the rooting zone (mg/kg).

Results and discussions

From Figure 1, which presents the average soil moisture regime, we established that the dry period is during August and the water deficiency is higher in open plot (i.e. Poljanite).

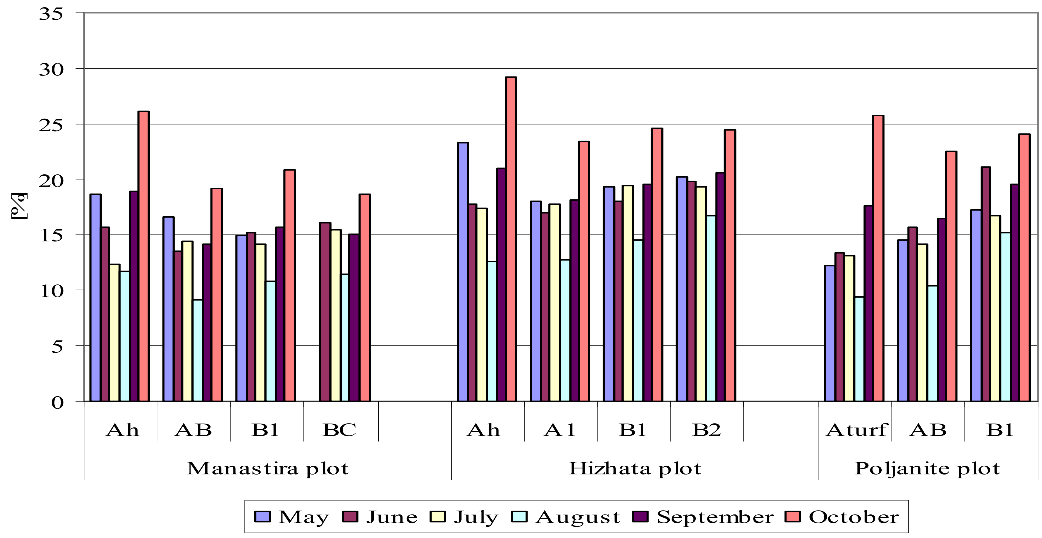

Figure 1. Soil moisture seasonal dynamic in studied experimental plots estimated with mean values.

Table 2. Physical characteristics of *Cambisols* from Lyulin Mountain.

Object,depth (cm)	Bulk density (g/cm^3)	Texture fractions (%)			Porosity (%)	Relative density	Hygroscopic moisture (%)	Moisture of permanent fade (%)
		clay	sand	<0.001 mm				
				Manastira plot				
Ah 0-6	0.96	41.02	58.98	5.33	58	2.28	2.51	4.36
AB 6-24	1.05	49.08	50.92	10.63	57	2.46	2.19	3.93
B_1 24-63	1.17	73.99	26.01	10.89	53	2.49	2.75	4.80
BC 63-80	-	16.46	83.54	2.06	-	2.45	2.84	5.41
				Hizhata plot				
Ah 0-4	1.10	70.25	29.75	4.85	54	2.40	3.26	5.98
A_1 4-19	1.06	45.31	54.69	8.55	64	2.43	2.97	5.52
B_1 19-47	1.34	54.17	45.83	2.92	46	2.47	4.18	7.96
B_2 47-80	1.39	12.40	87.60	1.03	42	2.38	3.30	7.02
				Poljanite plot				
A_{turf} 0-12	1.08	33.51	66.49	4.71	56	2.48	4.73	7.62
AB 12-29	0.97	49.64	50.36	7.03	58	2.33	3.41	6.22
B_1 29-70	1.14	16.46	83.54	2.16	55	2.51	2.90	6.50

The brown forest soils in the region are strongly influenced by the products of both broadleaved vegetation and other factors of soil formation. Results obtained for soil physical characteristics of studied plots are presented in Table 2 and show the bulk density varied from 0.96 to 1.39, which is a prerequisite for good soil aeration. The relative density varies around 2.5 and the ratio between organic and mineral parts of the soils is also good. The porosity stays near to 50 % in the different soil horizons. The textural composition the soils are sandy loams (SL). Only in the first experimental plot – Manastira – was there sufficient clay accumulation in the B-horizon and this could be explained with leaching at plot level.
The results of chemical analysis of some soil characteristics are presented (Table 3).

Table 3. Chemical characteristics of soils from the studied experimental plots.

Plot/horizon	SOM (%)	Total N (%)	pH (H_2O)	CEC (meq/100g)	Exchangeable ions (meq/100g)			Heavy metals (mg/1000g)					
					Al	Ca	Mg	Mn	Fe	Cu	Zn	Pb	Cd
					Manastira plot								
Ah	5.4	0.15	5.3	30.1	0.3	19.1	3.5	115	1665	5.7	14.2	3.9	-
AB	3.44	0.09	5.3	24.9	0.6	8.1	11.8	105	1662	5.9	19.8	4.3	-
B_1	0.64	0.07	5.4	32.9	0.2	21.6	7.5	90	1687	9.9	13.6	2.2	-
BC	-	0.06	5.5	37.5	0.3	21.6	10.8	98	1687	9.3	11.4	1.6	0.2
					Hizhata plot								
Ah	9.67	0.15	4.9	40.2	3.1	23.2	4.1	88	1687	9.5	9.8	2.3	0.2
A_1	3.87	0.11	4.9	40.8	3.4	19.3	7.9	108	1707	9.8	11.4	2.3	0.2
B_1	1.46	0.07	6.1	50.9	0.0	25.2	17.9	135	1740	13.2	17.1	0.1	0.2
B_2	-	0.06	6.7	51.4	0.0	26.0	17.6	110	1742	14.5	19.1	1.	0.2
					Poljanite plot								
A_{turf}	4.49	0.11	6.1	51.4	0.0	41.3	2.2	125	1725	14.3	11.1	1.6	-
AB	3.44	0.18	6.0	44.1	0.0	29.2	7.8	130	1697	9.8	18.2	2.4	-
B_1	2.83	0.12	5.7	41.1	0.2	23.8	11.5	125	1685	10.3	18.4	1.8	-

The SOM is higher in the plots with good developed forest vegetation (Manastira and Hizhata plots). The profile distribution of soil organic substances is different for forests plots and the open plot. In the Poljanite plot the decrease in SOM in depth is relative uniformity. Soil nitrogen concentration is between 0.06 and 0.18 % and the trends in soil profiles are similar to carbon contents. Available nitrogen content depends on soil acidity. In the studied soils the pH is acid in the upper soil horizons of forested areas and low acidity in the open plot and as a whole these soils have poor nitrogen regimes. Results show the presence of intense ions-exchangeable processes in soils – CEC is between 25 and 50 meq/100g. The exchangeable Al only exists in surface layers of the Hizhata plot where acidic conditions may lead to layer silicate destruction and an increase in relatively low levels of exchangeable Al concentration. According to colloidal reactivity these soils could be ordered as follows: Manastira plot – mean colloidal, Poljanite plot – strong colloidal and Hizhata plots- very strong colloidal. According to the data the surface soil horizons are vulnerable to stronger pollution and other negative anthropogenic influences. The heavy metal content confirms this assertion. The soils from Manastira plot with pH = 5.3 are endangered by the accumulation of Zn and Pb. This is also observed in soils from the Poljanite plot where the pH = 5.7 and there is a potential danger from Cu and Zn pollution. The probability of heavy metal pollution is low in the Hizhata plot by reason of higher pH values (6.1 and 6.7 for deeper soil horizons respectively). Comparative analyses with the database from relatively non-polluted regions nearby show that the content of Cu and Pb is higher in Lyulin Mountain.
The other part of our studies was related to processes associated with the natural regeneration in the recreation areas. The natural regeneration of forests of *Fagus sylvatica* L. was also determined. The observations showed that the bio-groups have good structure with beech-tree as dominant species (Figure 2).

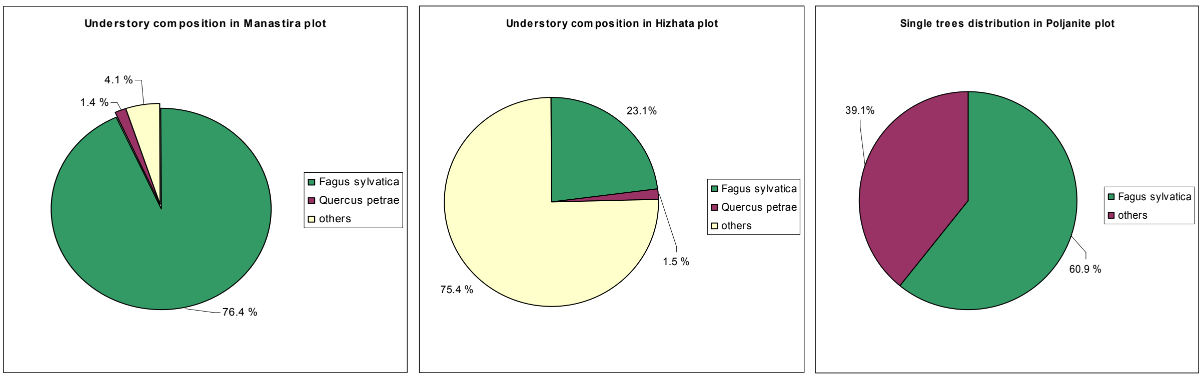

Figure 2. Natural regeneration in bio-groups of experimental plots.

The chemical analyses of the assimilation organs of trees present the influence of urban pollution on forest vegetation. The Factor of accumulation (FA) was estimated for the main tree species and trees were arranged according to their preferences to element' accumulation as follows: *Fagus sylvatica* L.: Mn > Zn > Cu > Pb > Fe; *Quercus petrae* Liebl. : Mn > Zn > Pb > Cu > Fe; *Acer pseudoplatanus* L.: Zn > Pb > Cu > Mn > Fe; *Tilia cordata* Mill.: Pb > Zn > Cu > Mn > Fe; *Acer platanoides* L.: Zn > Mn > Pb > Cu > Fe; *Crataegus monogyna* Jacq.: Zn > Pb > Cu > Mn > Fe.

Concentrations of heavy metals in assimilation organs of trees are not an immediate threat both to the vegetation and to those who use this park of the green system of the capital city as a place for recreation. The status of forest ecosystems in Lyulin Mountain is good and ensures appropriate conditions for short and durable recreation.

Conclusion

The direct impact from recreation activities was established in the Hizhata plot where in surface soil horizons the bulk density is higher and there is an increased presence of exchangeable Al. The surface soil horizons in studied plots are susceptible to increased soil pollution. Soils with low pH values are endangered by heavy metal pollution, especially from Zn and Pb. The process of natural regeneration is good and this contributes the development of improved recreation areas. The biometrical analyses show that the bio-groups have good structure with diversity of tree species in good health. As a whole the beech-trees dominates in the understory vegetation. The increase in heavy metals content in tree leaves confirms the sanitary and esthetic functions of the forests and the necessity to instigate prevention measures and monitoring of forest ecosystems in recreation zones. At present the status of forest ecosystems in Lyulin Mountain ensures appropriate conditions for short and durable recreation.

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The BIOTECHNOSOL project: biological dynamics and functioning of a constructed Technosol at the field scale

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Abstract
Within the French National programme GESSOL and the GISFI consortium, the BIOTECHNOSOL project has been carried out. The purpose of the project aims to acquire information about the biodiversity of constructed Technosols that are used to restore brownfields. Results indicate an increase of biodiversity in the system within the two first study years.

Key Words
Technosols, soil biota, Brownfields.

Introduction

Technosols (USS Working Group WRB 2006) are soils, whose properties and pedogenesis are dominated by artificial or transported materials. In the case of industrial brownfield management, constructed Technosols can be used intentionally to reclaim ecosystem. These Technosols can be constituted from artificial materials, usually considered as wastes. Sponsored by the French National Soil Programme GESSOL, and within the GISFI (Groupement d'Intérêt Scientifique sur les Friches Industrielles), a consortium of soil biologists has been constituted to study a model Technosol ecosystem at the field scale. The main question of the project focuses on the capacity of the Technosols to allow essential functions of a natural soil, particularly vegetation development, which means restoration of physical and chemical fertility. Our hypothesis is that soil organisms, by their diversity and functional complementarities, are essential actors in the system for the main physical (aggregation, bioturbation) and chemical (Carbon and Nitrogen cycles) processes. In this context, our objective is to assess the colonisation dynamic of the Technosol by soil biota and their impact on several functions.

Material and methods

The Technosol is composed of a layer of green-waste compost (CDV) on the surface, a layer of a mixture of clean-up industrial soil and papermill sludge (50/50) (TIT/SPP) and a final layer of papermill sludge (SPP) (Figure 1). Two kinds of Technosol profiles are studied, differing by their water retention: the « éponge végétale » profile maintains water for vegetation, while the "confinement" profile limits water transfers to the substrate. The pedogenesis of these Technosols has been studied for several years demonstrating their capacity to perform basic soil functions (Séré, Schwartz *et al.* 2008). For that purpose a field of more than 1 ha, using this Technosol, has been established in October 2007, on a derelict Brownfield in the Lorraine Region. The working group is constituted of soil ecologist specialists of various biota (Bacteria and Mycorhiza, nematodes, microarthropods, macroarthropods and earthworms), agronomists, and soil bio-physicians. Sampling has occurred each year at spring time since 2008 (Figure 2).

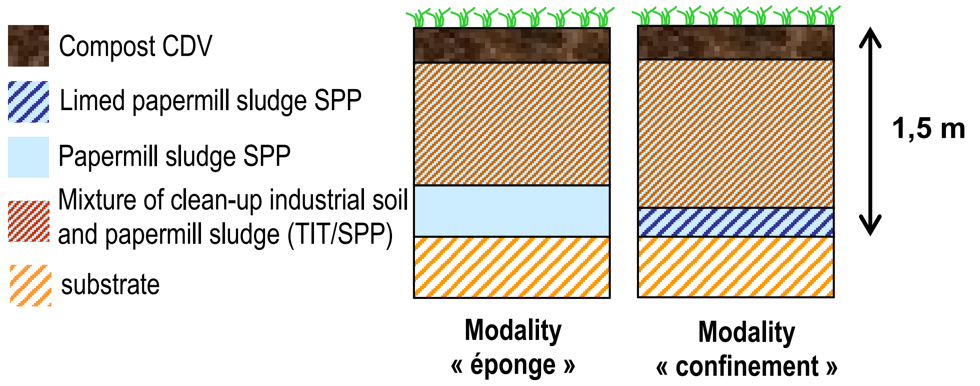

Figure 1. profiles of the constructed Technosols.

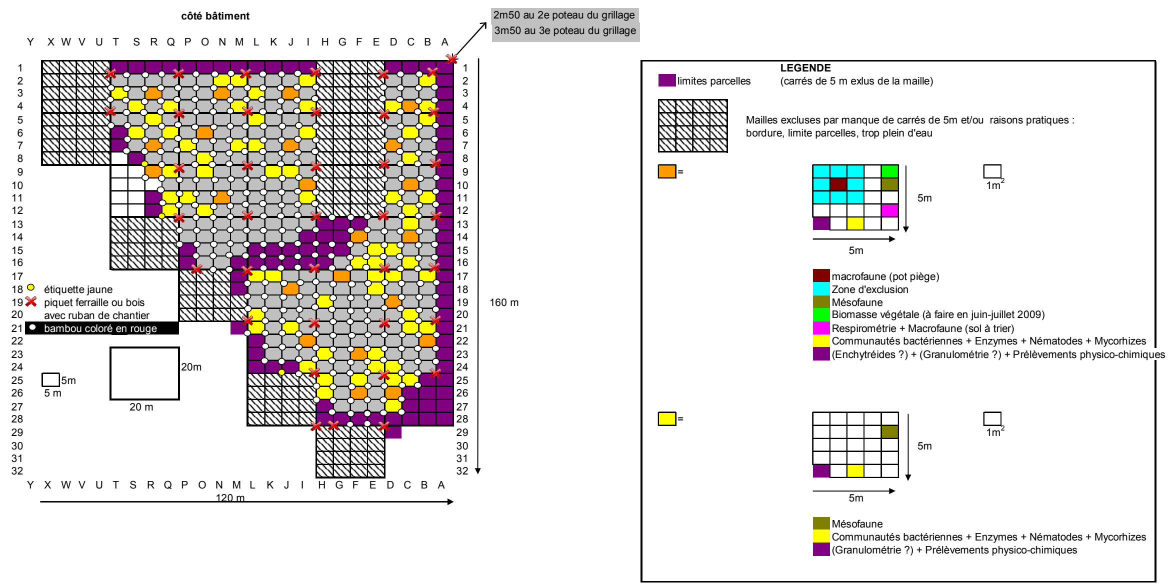

Figure 2. Schema of the sampling grid and sampling strategy on the field.

Table 1. list of the Collembola species sampled on the Technosol in 2008.

Species	Geotropism	Ecology
Cryptopygus thermophilus	Hemiedaphic	Compost
Hypogastrura manubrialis	Hemiedaphic	Compost
Proisotoma minuta	Hemiedaphic	Compost/pionner
Sminthurinus elegans	Hemiedaphic	Low vegetation
Isotoma viridis	Epiedaphic	Ubiquist
Parisotoma notabilis	Hemiedaphic	Ubiquist
Sphaeridia pumilis	Hemiedaphic	Ubiquist

Results

The first results (2008 and 2009 sampling) indicate that the system is typical of pioneer ecosystems, with the presence of bacterivorous nematodes and absence of macrofauna. Initial Collembola communities are largely influenced by the initial materials (particularly composts) and the borders of the field (Table 1), showing a centripetal colonisation during the first 2 years. However, an increase of species richness, particularly concerning nematodes, is observed between 2008 and 2009. Furthermore some significant differences appear between the two profiles, especially concerning plant species richness and soil respirometry.

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The feasibility of phytoremediation combined with bioethanol feedstock production on diesel-contaminated soil

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Abstract
The purpose of this study was to identify plant species capable of cleaning up diesel-contaminated soil and then to convert their biomass to bioethanol. Five selected plant species (*Catalpa ovata, Lolium perenne, Pinus densiflora, Populus tomentiglandulosa,* and *Thuja orientalis*) were cultured on an 8,000 mg/kg area of diesel-contaminated soil to assess their remediation properties. Lignocellulosic composition, concentration of reducing sugars, and saccharification yields were analyzed. In 120 days, diesel concentration in the planted soil, with fertilizer, was significantly decreased. However, no phytoremediation activity of plant species on diesel degradation was observed over the fertilization effect. Diesel contaminated soil resulted in reduced plant biomass of most tested plants. However, biomass of *P. densiflora* was not significantly decreased in the diesel contamination plot. The reducing sugar concentration ranged from 60.5 to 83.6 mg/g, depending on the tested plant species. The highest saccharification yield was obtained with *P. densiflora*.

Key Words
Bioethanol feedstock, diesel-contaminated soil, lignocellulose, phytoremediation, TPH.

Introduction
As a result of human economic and industrial activity, massive amounts of soil and water have been contaminated with oil and petrochemical products. Total petroleum hydrocarbon (TPH) contamination is recognized as a serious threat to environmental ecosystems. TPHs are a complex mixture of chemical substances such as alkanes, aromatics and asphaltene fractions (Admon *et al.* 2001) and are very toxic to living organisms. Phytoremediation has been proposed as a cost effective, non-intrusive, and environmentally friendly technology for the restoration of soils contaminated with TPH. Furthermore, biomass generated during phytoremediation can be used for production of bioenergy such as bioethanol. Bioethanol is a non-polluting alternative fuel derived from renewable sources of plant biomass. In this study, five plants were assessed in a greenhouse experiment in terms of their effectiveness in phytoremediation and to optimize the possibility of bioethanol production the resulting plant biomass.

Materials and methods
Preparation of the experimental soil
Sandy loam soil was collected from 5 to 10 cm depth. Collected soil had the following characteristics: pH = 5.65, EC = 0.03 dS/m, NO_3^--N = 8.66 mg/kg, NH_4^+-N = 1.9 mg/kg, P = 8.51 mg/kg, organic matter = 0.8%, CEC = 1.9 $cmol_c$/kg. The initial concentration of diesel in the experimental soil was set at 8,000 mg/kg. To ensure soil/diesel mixture homogeneity, multiple soil TPH analyses were carried out.

Plant materials and growing conditions
Five selected plants (*Catalpa ovata, Lolium perenne, Pinus densiflora, Poplar tomentiglandulosa,* and *Thuja orientalis*) were tested in a greenhouse for 120 days. These plant species were selected based on a previous study. The pots had an inside diameter of 23cm and a height of 25cm and were filled with 6 kg of diesel contaminated soil. Each pot also contained 5g of commercial compound fertilizer (NPK 21-17-17). Seedlings of the selected plant species were transplanted into the pots at one plant per pot. In the case of *L. perenne*, 50 seeds were sowed per pot. Control pots contained no plants, only contaminated soil with a) fertilizer application (5 g NPK 21-17-17) or b) no fertilizer application. Soil moisture was maintained at field capacity during the experiment. Each experiment was replicated three times.

Sampling and analysis
Three soil samples were collected with a soil auger from each pot at 0, 30, 75, and 120 days and deposited into amber glass jars at for analysis. Diesel levels in the experimental soils were determined by measuring TPH by GC-MS. Plant materials were harvested at 120 days after the start of the experiments, and dried at 75°C for 3 days. Shoot and root biomass was determined on a dry weight basis.

Lignocellulosic content of plant raw materials
The cellulose, xylan and lignin content of the biomass was determined by a two step H_2SO_4 hydrolysis method. Each sample (300 mg) of dried biomass was hydrolyzed in 3 mL of 72% (w/w) H_2SO_4 at 30°C for 1 hour. The mixture was diluted by adding 84 mL of distilled water, and further hydrolyzed at 121°C for 1 hour. The hydrolysis solution was filtered through preweighed filtering crucibles. The crucibles and insoluble lignin residue were dried at 105°C for 4 hours, and then burnt into ash in a muffle furnace at 575°C for 24 hours. Recorded weights of the residue and crucible before and after burning were used to calculate the concentration of insoluble lignin, according to the method from Sluiter *et al* (2004). The filtrate was captured to analyze the concentration of soluble lignin, glucose, and xylose. The concentration of soluble lignin in the hydrolysis liquor was calculated from the absorbance value of the sample at 320 nm (Sluiter *et al.* 2004). Glucose and xylose were analyzed using an HPLC instrument equipped with an ELSD detector. Sugars were separated on a Shodex Sugar SP0810 column at 30°C with 70% acetonitrile as an eluent, at a flow rate of 0.5 mL/min.

Saccharification experiment using cellulase
A hydrolysis mixture consisting of 0.2% biomass, 40 FPU cellulase (Celluclast 1.5L, Novozyme) per gram substrate, and 10 mL of sodium acetate buffer (pH 5.0) was incubated at 37°C in a rotary shaker at 150 rpm. Samples were taken from the reaction mixture at different time intervals and heated to 100°C immediately to denature the enzyme. Samples were cooled and then centrifuged for 10 min at 8000 rpm. Reducing sugars in the supernatant were determined using the 3, 5-dinitrosalicylic acid (DNS) method. Saccharification yield was calculated from the following equation: % Saccharification = reducing sugars × 0.9 × 100/carbohydrates in substrate. Cellulase activity was determined by the filter paper unit (FPU) method (Wood and Bhat 1988). (One FPU is defined as the amount of enzyme that releases 1 μmol of glucose equivalent from Whatman No.1 filter paper per minute.)

Results
At 120 days after the start of the experiment, the initial 8,000 mg·/kg diesel concentration had decreased to a range of 659.3 to 1,240.5 mg·/kg in the planted pots with the fertilization treatment, whereas a diesel concentration of 2,946.7 mg·/kg remained in the unplanted control pot without fertilizer application (Figure 1). In the control pots, decomposition of diesel was most marked with NPK fertilizer. When the NPK fertilization was used in the diesel contaminated pots, diesel levels were dramatically decreased regardless of the presence of plants. Much research has also reported that fertilizer application can positively influence diesel degradation by enhancing plant growth and microbial degradation (Merkl *et al.* 2005; Pichtel and Liskanen 2001).

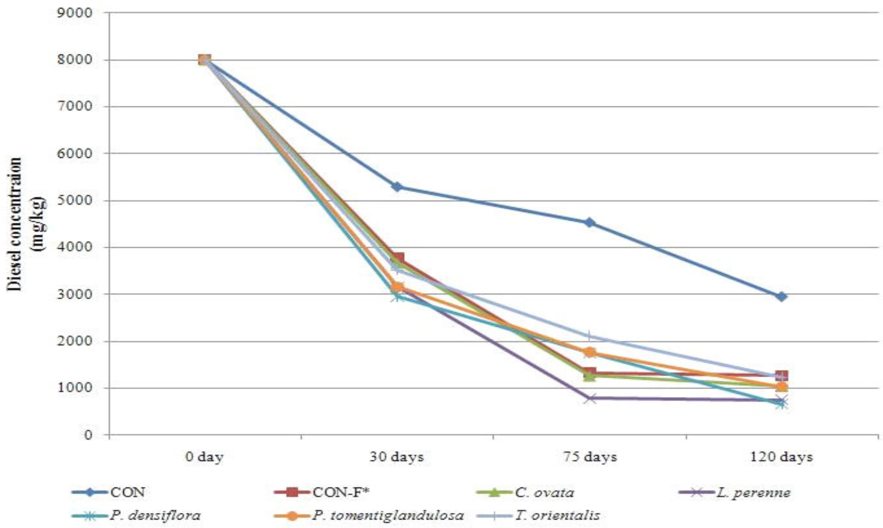

Figure 1. Effectiveness of TPH removal by two unplanted control pots and planted pots. Data were generated from TPH analysis of the soil samples collected after 120 days of phytoremediation.
*** Means unvegetated plot with fertilizer application.**

Plants do not normally grow in the harsh physical and chemical conditions, such as severely contaminated area (White *et al.* 2003). In this study, the changes in plant biomass depended on the plant species growing in the diesel-contaminated soil (Table 1). Most of tested plants were damaged by growth in 8,000 mg/kg diesel contaminated pots. In 120days, *L. perenne* had significantly lower shoot and root biomass in the diesel contaminated soil. In the case of *C. ovata* and *P. tomentiglandulosa*, shoot biomass in the diesel contaminated plot was not significantly decreased, but root biomass was severely decreased compared with uncontaminated plot. *P. densiflora* appeared to have a good tolerance of diesel contaminants, because the biomass of this plant was not significantly affected compared with the uncontaminated plot.

Table 1. Influence of diesel concentration on shoot and root biomass following a 120-day greenhouse study.

Plant species	Diesel concentration (mg/kg)	Parameters (g/pot)	
		Shoot biomass	Root biomass
C. ovata	0	32.29 ± 8.22	27.55 ± 13.4
	8,000	29.10 ± 7.54	7.05 ± 3.12
L. perenne	0	23.46 ± 2.69	19.55 ± 5.73
	8,000	8.21 ± 1.26	7.78 ± 2.24
P. densiflora	0	17.09 ± 5.23	5.23 ± 0.47
	8,000	16.06 ± 6.58	8.12 ± 0.12
P. tomentiglandulosa	0	30.61 ± 2.60	8.84 ± 0.07
	8,000	25.00 ± 1.98	4.78 ± 0.51
T. orientalis	0	7.84 ± 2.10	3.57 ± 1.55
	8,000	4.72 ± 1.53	2.98 ± 0.71

The biological process for converting the lignocellulose to bioethanol is an attractive technique to utilize its energy. The lignocellulosic composition varied among the plant species chosen for this study (Table 2). In all of the woody species, lignin was the major component, followed by cellulose and hemicellulose. However, in *L. perenne*, a kind of grass, there was a higher fraction of hemicellulose than in the woody species. *P. tomentiglandulosa* and *T. orientalis* had the highest content of cellulose.

Table 2. Lignocellulosic composition of the plant materials.

Plant species	Lignocellulose (g/100g)	Cellulose (g/100g)	Hemicellulose (g/100g)	Lignin (g/100g)
C. ovata	90.5	26.6	6.2	57.7
L. perenne	84.9	16.6	29.3	39.0
P. densiflora	88.4	33.0	7.2	48.2
P. tomentiglandulosa	83.8	37.2	3.0	43.6
T. orientalis	88.3	37.2	8.3	42.8

The reducing sugar concentrations and saccharification yields following hydrolysis of plant materials are given in Table 3. The lowest saccharification yield and reducing sugar concentration were obtained from *L. perenne* (7.56%). This may be due to its low content of cellulose. The highest saccharification yield was achieved for *P. densiflora* (10.4%). Although the cellulose contents of *P. tomentiglandulosa* and *T. orientalis* were higher than that of *P. densiflora*, the saccharification yield obtained for these were lower than that obtained for *P. densiflora*. This was probably due to the rigid structure of the lignin, which protects cellulose and hemicellulose against enzymatic hydrolysis (Béguin and Aubert 1994; Krisztina *et al.* 2009).

Table 3. Reducing sugar concentration and saccharification yield following the hydrolysis of plant materials.

Plant species	Reducing sugar (mg/g-substrate)	Saccharification yield (%)
C. ovata	78.1	9.76
L. perenne	60.5	7.56
P. densiflora	83.6	10.4
P. tomentiglandulosa	62.1	7.76
T. orientalis	71.5	8.94

Conclusion

The present study demonstrated that the combination of an adequate nutrient amendment, such as NPK fertilization, and the selection of highly tolerant plant species are key factors in successful phytoremediation. The efficiency of removing diesel in vegetated treatments with fertilization was as high as 85% while that in the corresponding unplanted control without fertilization was only 63%. The efficiency of remediation in diesel contaminated soil was not significantly different between planted pots and unplanted pots when fertilizer was applied to diesel contaminated soil. This effect was considerable given the small pot volume and nutrient competition with microbials. The plants tested in this study were able to grow in 8,000 mg/kg diesel contaminated soil, but experienced seriously reduced shoot and/or root biomass, with the exception of *P. densiflora.* The reducing sugar concentrations and saccharification yields to produce bioethanol were varied among the plant materials. The highest saccharification yield was obtained on *P. densiflora*. This study is currently being expanded to field scale studies in order to assess phytoremediation of diesel contaminated areas and to optimize saccharification processes using plant biomass generated under these conditions.

Acknowledgement
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The potential value of biosolids for revegetation at landfill sites

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Abstract
Landfill soils or Technosols are challenging environments on which vegetation is grown. In this paper, the usefulness of biosolid application to improve plant growth is investigated. The capping material over the landfill site, situated in South Australia, Australia, possessed high clay content, low organic carbon and poor soil structure. The application of biosolids enhanced growth of sunflower dramatically. Heavy metal enrichment in soils and translocation to sunflower shoots were limited. Biosolid application to the landfill cover material shows considerable promise in the revegetation of landfill sites.

Key Words
Technosols, revegetation, biosolid, heavy metals, bioavailability.

Introduction
Globally, disposal of waste to landfill remains the most common method of waste management. Up to 95% of generated refuse is placed in landfill, both worldwide and in Australia. Landfills are often found within urban areas as a result of urban expansion. With the large demand for space within expanding urban areas, there is a push to increase the beneficial use of brownfield areas. Landfill sites are unlikely to be suitable for redevelopment for most land use purposes in urban areas. Landfill of municipal wastes is typically achieved by adding a clay liner over the waste with low hydraulic conductivity to reduce water flow through the waste and limit contamination of the surrounding environment. Most landfill liners, however, inevitably crack and deteriorate allowing water seepage into the landfill. An alternative landfill "lining," often known as *Phytocapping,* shows promise in minimizing cracking and effective water interception through evapotranspiration. Soil materials or Technosols (IUSS 2007) on top of the clay liners themselves are not good environments for plant growth. They may be contaminated by a range of chemicals, be low in nutrients and have poor physical characteristics for plant growth. Selection of appropriate plant species and amendments to improve the growing conditions of the substrate is essential to advancing this promising capping technique. In this study, the effect of biosolid application rates was investigated on Sunflower and Giant Reed *in situ*. The aim of this study was to test the hypothesis that plant growth at the Coleman Rd landfill site would be enhanced by biosolid application.

Methodology
A landfill site (~17 Ha) located at Coleman road in South Australia owned and operated by Salisbury City Council was used in the field study. Basic soil properties before amendment with Biosolids are shown in Table 1. Typical properties of the biosolids are presented in Table 2. The soils on top of the clay liner are classified as a Technosol (IUSS 2007) or as Anthroposol in the Australian classification system (Isbell 1996). Soils in the top 60cm depth show very high clay content, high pH (8.6-8.7), high effective cation exchange capacity (ECEC) (21.0 - 471.1 cmol/kg) and high electrical conductivity (313-426 µS/cm). The site shows low levels of organic carbon (0.8-1 % OM). Soils were tilled manually to form farrows.

Table 1. Soil properties from Coleman Rd landfill site for the 0-20 and 20-40 cm depths.

	pH(1:5) water	EC (µS/cm)	OM (%)	%Clay	ECEC (cmol/kg)	SAR
0-20cm	8.6	313	1.1	64.8	41.1	8.3
20-40cm	8.7	426	0.8	64.3	21.0	3.2

Table 2. Typical Biosolid characteristics used in field trial.

	pH(1:5) water	EC (µS/cm)	OM (%)	N (%)	P	K	Cu	Zn	Cd	Pb
					mg/kg					
Biosolid	6.64	8680	43.4	0.84	800.0	2285	444.4	766.6	7.620	96.88

The experimental layout consists of three levels of biosolid application as main treatments and 3 plant species as subplots. To separate plots (50 m^2) soils were amended with biosolids from Bolivar Treatment Plant at rates of 0, 25 and 50 tonnes/ha (dry-weight). Biosolids were mixed approximately to the top 0.2 m of the soil. Biosolids were added 20/11/08. Within each main plot, Sunflower (*Helianthus annas*) seeds were sown on 09/02/09. Giant Reed (*Arundo donax*) was planted on 20/12/08. Plants were watered once per week using drip irrigation.

Results

A significant level of heterogeneity in soil texture existed laterally within and between each experimental plot. Soil sampling showed that the clay liner was approximately 50-60cm from the soil surface. Reducing conditions commonly existed from 30-40 cm depth to the clay liner. The black appearance of soil at 50-60 cm and smell suggested the formation of sulfidic material. Visual assessment of plant growth showed a dramatic improvement in the performance of sunflower due to biosolids (Plate 1). Sunflower heights in the control ranged from 30 cm to approximately 1m. By comparison, a large proportion of sunflower plants ranged in height from 1 -1.5 m. In both biosolid treated plots germination of sunflower was good. Germination in the control plot by contrast was poor and delayed. Biosolid application was shown to significantly increase sunflower growth from the control (Figure 1), although different application rates did not significantly affect yield. Despite excellent growth at 50 t/ha, few plant roots ventured below a depth of 30 cm. Sunflower roots usually formed a small cup-shaped root zone with little vertical expansion. The lack of root growth down profile may be due to the lack of aeration and poor soil structure with increasing depth. *A. Donax* appeared to have performed better in the 50 t/ha biosolid treatment. However, the overall performance was modest with poor establishment in all plots.

Sunflower 50 t/ha 09/05/09 Sunflower control 09/05/09

Plate 1. Performance of sunflower in 50 t/ha and control plots at Coleman Rd.

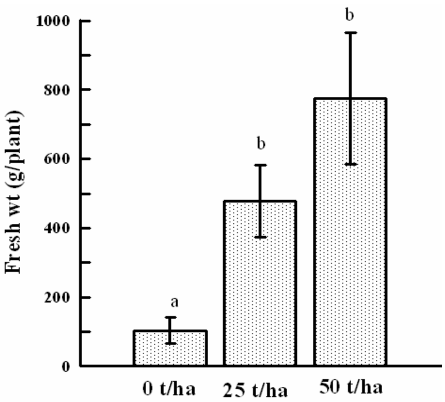

Figure 1. Effect of biosolid application on sunflower growth in the landfill field trial. Different letters indicate a significant difference (α=0.05).

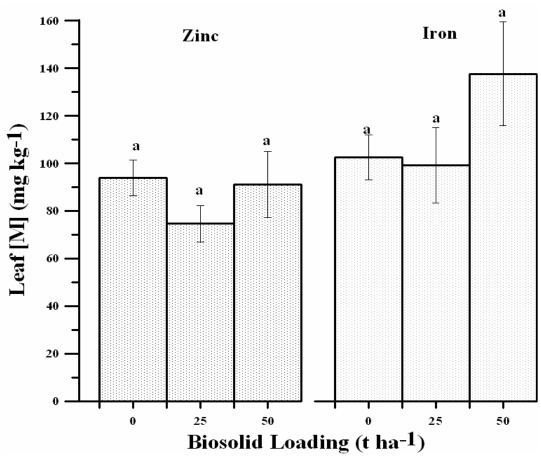

Figure 2. An example of metal concentrations in leaves of sunflower grown at Coleman Rd. Different letters indicate a significant difference (α=0.05).

Total extractable concentrations of Cu, Zn, Ni, Cd, As and Pb concentrations in soil were low for all treatments (< 30 mg/kg or < 0.5 mg/kg). Furthermore, no significant differences between treatments were observed (P=0.05). Similarly, NH_4NO_3 extractable contents, which are often used as a chemical indicator of plant available metals, were very low for divalent metals. The low plant available metal contents in these soils may partly be due to the high pH of these soils. The non-significant differences observed in total and plant available concentrations in biosolid amended soils were reflected in shoot concentrations in sunflower. With biosolids containing relatively low heavy metal concentrations, biosolid application to Technosols at landfill sites shows promise for re-vegetation and reuse of these areas.

Conclusions

The capping material over the Coleman Rd landfill possessed high clay content, low organic carbon and poor soil structure. The application of biosolids appeared to enhance germination and growth of sunflower. Heavy metal enrichment in soils and translocation to sunflower shoots were limited. Biosolid application to the landfill cover material shows considerable promise in the revegetation of landfill covers.

Acknowledgements

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The relevance of soils within the concept of the Astysphere

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Abstract
No geological exogenic force has altered the earth's surface during the last centuries in such an extent as human activity. Urban systems become main regulators for fluxes of many chemical elements on a global scale due to ongoing industrial and economic development and population increase. Additionally, urban systems are constantly expanding. For natural history, urbanisation is a new phenomenon never existed in previous geological eras. Because of the tremendous global impact of urban systems, a new geoscientific sphere is developing: the Astysphere (Norra 2009). This sphere comprises the parts of the earth influenced by urban systems. Geoscientifically, urban areas correspond to sediment formations. Within the Astysphere, soils are important as sinks and sources for pollutants and various materials, as foundation for construction activities, for water storage and local urban climate and as living space for numerous organisms. Urban soils are globally linked by substance fluxes between urban systems. Since construction materials, living conditions, traffic and industrial processes become fairly similar in the world wide urban systems, also urban soils increasingly become similar on a global scale, a process called convergence in ecology. The concept of the Astysphere grasps urban soils as entity of the globally interlinked urban systems.

Key Words
Soil, Astysphere, urban systems, Technosol, soil pollution.

Introduction
Unquestionably, volcanoes, earth quakes, wind, rain, plant and animal life enormously contribute to form the earth's face by abrupt impacts or permanent ongoing processes of lower intensity. But are they the main forces forming the present earth's face? During the last centuries no geological exogenic forces have changed the earth's surface as mankind has done. Humans have altered the morphology and element balances of the earth by establishing agrosystems first and urban systems later. Currently, urban systems happen to become the main regulators for fluxes of many elements on a global scale due to ongoing industrial and economic development and a growing number of inhabitants. Additionally, urban systems are constantly expanding and cover more and more former natural and agricultural areas. For nature, urban systems are new phenomena, which never existed in previous geological eras. The spread of urban systems over the globe is highlighted in Figure 1.

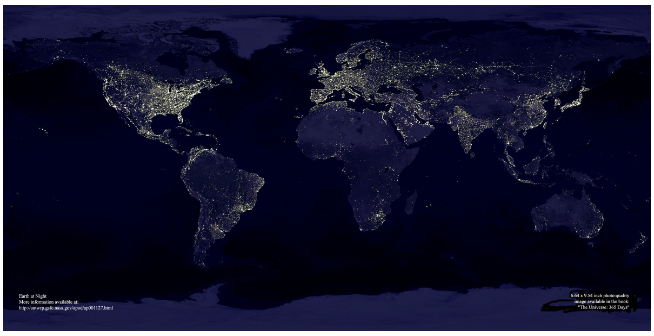

Figure 1. The lights indicated urban settlements.

For 2008 it was estimated that about 50% of the world population live in urban areas. It is estimated that in 2050 around 70% of the world population will live in urban areas (United Nations 2008). That means, till 2050 the number of urban population doubles and equates to the today's world population. Concurrently, the urban area is constantly growing. The global extension of urban areas is under discussion. In 2000, 0.3% of the total land area of countries was urbanized. It is expected that cities grow 2.5 times in area by 2030 or will cover 1.1% of the total countries area (Angel *et al.* 2005). Other calculations from Salvatore *et al*. (2005) claim that already in 2000 up to 2.7% of the total land area was urbanized. The portion of areas developed for traffic and settlement purposes is higher in developed countries. In Germany, already 12.5% of the total area is used for traffic and settlements and every day more than 120 ha are added. Furthermore, ongoing urbanization causes the sprawl of more or less dense urban systems over the globe.

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Urban systems are globally cross linked to each other by fluxes of energy, information and matter. Urban processes do not only affect urban systems within their specific borders but also remote areas by pollution via the air path or by mining activities and even tourists. Thus, a new sphere develops that changes the world's shape, the Astysphere. This Astysphere is a new approach to integrate urban systems into the geoscientific concept of spheres and an initial point for the understanding of urbanization of the earth as natural process (Norra 2009).

Walter Suess presented 1875 the concept of geoscientific spheres. He distinguished spheres, such as the lithosphere and the atmosphere to promote a comprehensive understanding of the system earth. Since then, based on the works of geochemists like Clark, Goldschmidt and Vernadsky, this idea became a dominating concept for the understanding of the distribution of chemical elements in the system earth. Later, due to the importance of human beings on global element fluxes, the terms technosphere and anthroposphere (Bacchini and Brunner 1991) were introduced. Nevertheless, in face of the ongoing urbanization of the earth, this concept is not any more precise enough to develop a comprehensive understanding of global element fluxes. Thus, it seems appropriate to classify the anthroposphere into an agriculturally and an urban dominated sphere. According to the greek terms agros (αγροζ) for agriculture and asty (αστυ) for city or town in opposite to the surrounding farmland, the anthroposphere comprises an agrosphere (Krishna 2003) and an astysphere. The agrosphere corresponds to the rural and agrarian environment, and the astysphere represents the urban environment. Both spheres are intensively connected due to former and recent agricultural activities on urban land and vice versa. Figure 2 displays the position of the astysphere within the earth's spherical system in a simplified sketch. The Astysphere comprises also parts of other spheres such as the atmosphere, hydrosphere and the pedosphere and is always part of the biosphere. Within the Astysphere, soils are important sinks for elements and materials and show specific development properties.

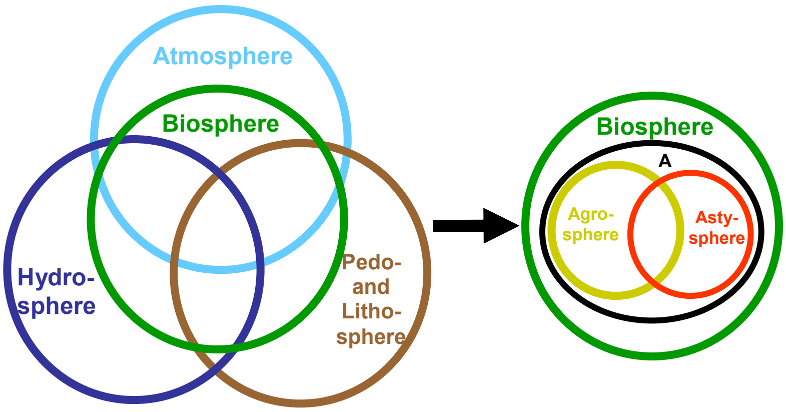

Figure 2. The position of the astysphere within the earth's spherical system. A.: Anthroposphere

Methods

Urban soil investigations can be classified into two different types. One is focused on soil properties of specific soil profiles to investigate the soil development or contamination at specific locations. Soil pits are dug out and soil horizons are differentiated and analyzed. Those soil profiles can be classified according to soil classification systems such as the WRB or of Germany (AK Stadtböden der Deutschen Bodenkundlichen Gesellschaft 1997). The soil profiles can be connected to specific urban land use types and urban soil maps can be generated. The other type of urban soil investigations considers the urban wide pollution of soils by specific land uses that happen for a large part via the atmospheric pathway. Maps of urban soil pollution are produced by interpolation routines. Both methods highlight the global connection of urban soils as part of the Astysphere.

Results and discussion

Figure 3 shows an example of a soil profile in Qingdao, China, investigated in 2004. This figure highlights the sedimentation of anthropogenic materials in urban systems. Urban soils can contain slags, ashes, waste, building rubble, tar, sludge, etc. and mixtures of those materials. Furthermore, these artificial materials can be mixed with natural substances. This process of waste and material disposal in urban systems corresponds to the geological process of sedimentation (Taylor 2007).

Figure 3. Technosol over capped Cambisol in the Old City of Qingdao. 87 cm of new material accumulated since the first construction development (indicated by the white band that is a lime terrace) took place during the German occupation about 100 years ago.

A comprehensive set of urban soil profile investigations were compiled by Lehmann and Stahr (2007). Typical soil profiles can serve as standard soils for specific urban land use types. In that manner, urban soil maps can be generated as presented by Grenzius and Blume (1983) for Berlin or by Holland (1996) for Stuttgart. Those maps especially consider subsurface processes and the fact that urban soils are part of the more or less human controlled urban development process. With respect to the urban wide pollution of soils by specific land uses that happens for a large part via the atmospheric pathway maps of urban soil pollution were produced by interpolation routines. They show the urban footprint of the urban wide pollution as is demonstrated for Karlsruhe (Figure 4). Similar investigation have been carried out in various cities all over the world, e.g.: Rhichmond Upon Thames, UK: Kelly *et al*. 1996; Osnabrück, Germany: Bloemen *et al*. 1998; Tallinn, Estland: Bityukova *et al*. 2000, Palermo, Italy: Manta *et al*. 2002; Sevilla, Spain: Madrid *et al*. 2004, Shenyang, China: Wang *et al*. 2006, Damascus, Syria: Möller *et al*. 2005 and Glebe, Australia: Markus and McBratney 1996. By these studies, it becomes obvious that the process of soil pollution by and in urban systems is a globally occurring and systematic process. The global urbanization process makes sure that more and more soil is affected and converted to urban soil.

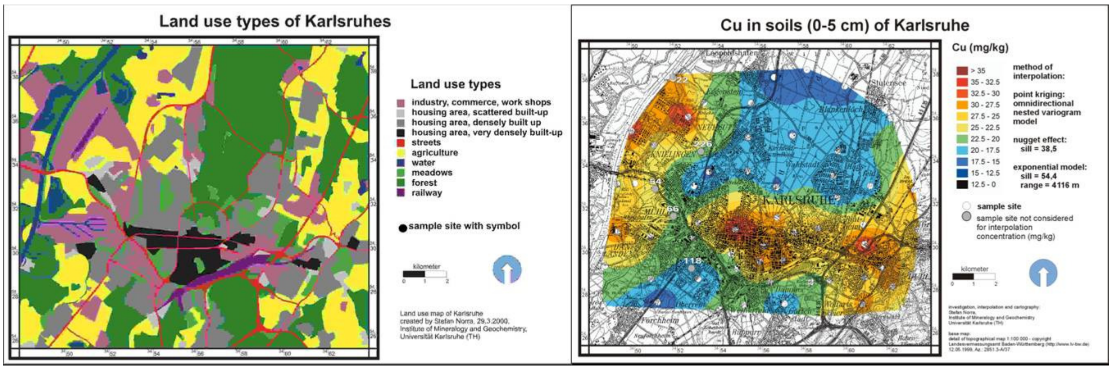

Figure 4. Distribution of land use types and Cu concentration in the upper 5 cm of soils of Karlsruhe, Germany. Highest Cu concentrations match primarily to industrial and inner urban areas. (Norra 2001)

The pedosphere within the astysphere

The pedosphere is one of the main compartments of the astysphere. Here, in urban soils, anthropogenically steered sedimentation processes occur. Urban soils act as sinks for technological materials and anthropogenic emitted pollutants all over the world. Since materials, which are deposited in urban systems are fairly similar in different parts of the world (construction materials, organic waste, household waste, industrial waste such as slags and sludges, technological products such as glass and plastics, etc.) the urbanization process compensates natural differences of soils caused by climate or parent rock. Such a process is called convergence in ecology.

One typical process all over the world is e.g. the input of alkaline materials (lime, mortar, concrete) generally resulting in neutral to basic urban soil reactions. Further processes are the input of heavy metals via the atmospheric path way. Therefore, globally, urban soils contain higher concentrations of those elements as do unaffected soils. Furthermore, those elements occur in ratios not abundant in non-urban soils. Due to worldwide transport activities between urban systems, urban soils contain information from distant other urban and non-urban systems. Those information is contained in materials that could be residues of Brazilian or Australian coal in German soils, African banana peel in European road side soils, abrasion particles from trolley systems of South American copper, packaging material wastes from all over the world, wood, paper, steel, alloys, etc.. However, until now, far too little emphasis has put on fundamental research of urban soils that mainly occur in newspapers and in research projects in cases of highly toxic but locally limited cases of soil contamination. Soil development processes in urban systems are far too little understood as well as their sink properties. Similarities and differences between urban soils from different regions should be investigated with more effort, since although the materials deposited in urban areas are often comparable, but development processes urban soils undergo might be different in varying climates. Form the viewpoint of the concept of the Astysphere, the extension of urban soils will increase in future. Those soils will be affected by pollution and deposition of various materials with rates not comprehensively known yet. However, recent urban soils will form a globally distributed rock unit of varying extension in geological future.

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The spatial distribution and sources of metals in urban soils of Guangzhou, China

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Abstract
Heavy metals in urban soils are of great environmental concern because of their potential long-term effects on human health. To evaluate soil environmental quality, a total of 426 surface soil samples (0-10cm depth) were collected from different administrative districts of Guangzhou, the largest and developed city in South China. GIS-based geostatistical technique and multivariate statistics were applied to generate metal spatial distribution maps, and to identify metals influenced by anthropogenic activities. Kriging interpolation of spatial data proved to be a powerful tool in identifying the contamination hotspots and possible sources of heavy metals. Hotspot areas of metal contamination were mainly concentrated in the western and southern parts, and closely related to industrial and long-term domestic activities. Principal component analysis (PCA) results suggested the following trends: (i) Fe, Ni and Mn are predominantly derived from natural sources; (ii) As, Cu, Hg, Pb and Zn from anthropogenic sources; and (iii) Cd from both sources.

Key words
Urban geochemistry; Soil survey; Heavy metals; Kriging interpolation map; GIS; Multivariate statistics.

Introduction
In densely populated urban areas, good quality of urban soil is essential to the health of urban inhabitants. Evaluating the environmental impact of contaminants in soils must start with a robust determination of their concentration and spatial distribution. This is especially important in urban areas with soils comprising complex heterogeneous properties and spatial patterns. A number of studies have indicated urban soils are more contaminated than rural soils due to extensive impact from anthropogenic activities. Understanding spatial distribution and sources of metals in surface soils is necessary to implement mitigation strategies to reduce concentrations, minimize human exposure and protect populations at risk. The use of GIS-based geo-statistical techniques to describe the spatial distribution of heavy metals in urban soils has been demonstrated previously (e.g. Davis *et al.* 2009; Lee *et al.* 2006; Zhang 2006). Multivariate analysis (principal component analysis -PCA) provides fingerprints for identifying the origin of soil pollution, and has been widely used to assist the interpretation of environmental data and to distinguish between natural and anthropogenic inputs (Manta 2002). The purposes of this study were: (1) to determine concentrations of metals (As, Cd, Cu, Fe, Hg, Mn, Ni, Pb, Zn), including variability and spatial distribution patterns by using GIS-based geostatistical techniques in the surface soils in Guangzhou; (2) to undertake a multivariate statistical approach (PCA) for data interpretation to identify possible sources for these metals.

Materials and Methods
Soil sampling and analysis
Guangzhou, the capital city of Guangdong province, is located in South China. More details were described in Lu *et al.* (2007). A total of 426 sampling sites were selected in different areas of Guangzhou, including Tianhe, Yuexiu, Liwan, Baiyun and Haizhu administrative districts (Figure 1). Composite soil samples collected at a depth of 0–10cm were obtained by mixing subsamples from five random points within 2 m^2 in each sampling site.
Bulk soil samples were air dried and hand crushed to pass through a 2-mm nylon sieve. Sub-samples were then ground with an agate grinder to go through a 0.15-mm nylon sieve.
Soil pH values were measured in a 1:2.5 (w/v) ratio of soil to deionised water (w/v). Soil organic matter (SOM) was determined by a wet oxidation method. Soil Cu, Fe, Mn, Ni, Pb and Zn were measured by using flame atomic absorption spectrometry (FAAS)

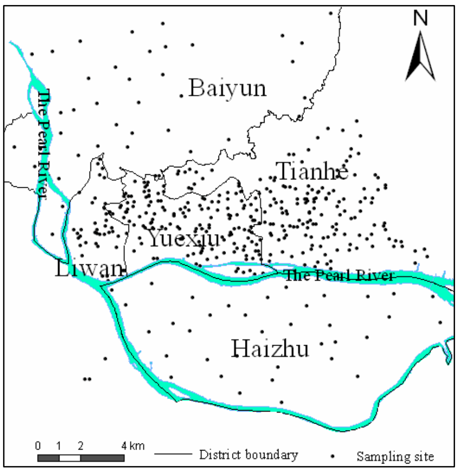

Figure 1. Location map of soil sampling sites in Guangzhou

(Hitachi Z-5300), and Cd by using a graphite furnace AAS (Hitachi Z-5700) after digestion with a mixture of HNO_3, HF and $HClO_4$. Soil As was measured by hydride generation atomic fluorescence spectrometry (HG-AFS 230, Beijing) after digestion with HCl and HNO_3. Soil Hg was measured by cold vapour atomic absorption (F732-V, Shanghai) after digestion with a mixture of H_2SO_4, HNO_3 and $KMnO_4$.

Data analysis and mapping

Basic statistics of the raw data and multivariate analysis (PCA) were performed using Minitab® v.14. The geostatistical analysis was carried out using GS+® v7.0. Based on the fitted semivariogram models, the ordinary Kriging provided by ArcGIS® v9.0 was used to map the spatial distribution of metal concentrations.

Results and Discussions

Descriptive statistical and correlation analysis

A descriptive summary of soil pH, organic matter and metal concentrations in urban soils is provided in Table 1. Acid soils (pH<6.5) accounted for about 28.4% of the soils, neutral (pH 6.5-7.5) and alkaline soils (pH>7.5) accounted for 44.4 and 27.2% respectively. This indicated that the pH for urban soils in Guangzhou has a tendency to be much higher than natural soils, which are dominated by being acidic or strongly acidic (GDSGSO 1993). Soil organic matter varied significantly among urban soils ranging from 2.56 to 199mg/kg.

The distribution of metal concentrations was skewed by a small number of large values. The extent of skewness, shown by difference (expressed as a percentage of median values), was the greatest for Hg (79%) and least for Fe (3%). Similar trends were obtained by examining the ranges of concentration values for each metal. Proportionately (the maximum values as a multiple of the minimum values) Hg (1223) had the largest range, and Fe (10) had the smallest range. The mean concentration of As, Fe and Ni was lower, whereas Cd, Cu, Hg, Mn, Pb and Zn were higher, than soil background values in Guangzhou.

Table 1. Descriptive statistics of soil properties and metal contents in urban soils (n=426).

Parameter	Min	Max	Median	Mean	Std..Dev.	Skewness	Kurtosis	Soil Background Value in Guangzhou
pH	2.55	9.33	7.12	6.86	0.99	-1.23	1.80	-
SOM g/kg	2.56	199	21.8	25.4	18.9	3.58	23.5	-
As mg/kg	1.4	144	14.1	17.4	15.0	4.17	25.9	17.4
Cd mg/kg	0.03	2.41	0.23	0.32	0.29	3.27	15.2	0.083
Cu mg/kg	5.0	417	25.3	35.8	41.4	5.34	37.1	13.6
Fe g/kg	6.1	61.8	27.0	27.9	7.87	0.56	0.61	29.0
Hg mg/kg	0.01	12.2	0.34	0.61	1.00	5.53	47.2	0.157
Mn mg/kg	21.2	1286	185	218	136	2.18	10.4	158.6
Ni mg/kg	2.5	77.6	16.2	18.7	10.3	2.03	6.92	22.03
Pb mg/kg	18.5	4903	63.8	87.6	238	19.5	395	42.88
Zn mg/kg	10.1	1795	78.8	107	116	8.18	108	58.1

Table 2. Pearson correlation coefficients among metals in urban soils and soil properties (n=426).

	SOM	pH	As	Cd	Cu	Fe	Hg	Mn	Ni	Pb	Zn
SOM	1	-0.083	0.327**	0.427**	0.456**	0.081	0.354**	0.182**	0.371**	0.154**	0.398**
pH		1	-0.154**	0.032	-0.004	-0.058	-0.051	0.085	-0.013	0.012	0.064
As			1	0.237**	0.143**	0.203**	0.190**	0.107*	0.286**	0.061	0.134**
Cd				1	0.530**	0.258**	0.192**	0.401**	0.607**	0.256**	0.603**
Cu					1	0.156**	0.218**	0.233**	0.471**	0.321**	0.616**
Fe						1	0.009	0.315**	0.499**	0.260**	0.223**
Hg							1	0.074	0.173**	0.064	0.160**
Mn								1	0.485**	0.236**	0.348**
Ni									1	0.117*	0.344**
Pb										1	0.763**
Zn											1

**. Correlation is significant at the 0.01 level (2-tailed). *. Correlation is significant at the 0.05 level (2-tailed).

Pearson correlation coefficients among metals and soil properties were listed in Table 2. Soil As concentration was negatively correlated with pH, implying that as pH increases, arsenic mobility increases. Therefore, arsenic would have a short residence time in these soils and tend to move downwards as pH increases. Concentrations of all analyzed metals except for Fe were positively correlated with soil organic matter, suggesting an important retention of metals by soil organic matter or metal input to the soil through various organic matter materials. Cd, Cu, Pb and Zn were closely related ($P<0.01$), and Pb showed poorer correlations with As and Hg, which might suggest their common or different origins.

Spatial distribution pattern of metals

Since the probability distributions of the As, Cd, Cu, Hg, Pb, and Zn concentration data were heavily skewed (Table 1), the Box-Cox transformation was used to make the data more normal and less skewness prior to geostatistical analyses, and all metals mentioned above passed the normality at the level of 0.05. Experimental semivariograms suggested that the theoretical Gaussian model was in reasonable agreement with the data for soil As, Cu, Pb and Zn, whereas Hg and Cd data were best fitted to the Spherical and Exponential model respectively. The ordinary Kriging interpolation was used to generate the filled contour maps (Figure 2). Similar spatial distribution of Cu, Zn, Cd, and Pb were found in the geochemical maps, and As and Hg showed similarity. This provided a spatial refinement and reconfirmation of the results in the statistical analysis, in which strong associations were found among Cu, Zn Pb and Cd, and between As and Hg (Table 2). The contour maps displayed several critical concentration 'hotspots' for each of the metals investigated. In general, the higher concentrations of metals (hotspots) were located in Liwan, Yuexiu and Haizhu districts.

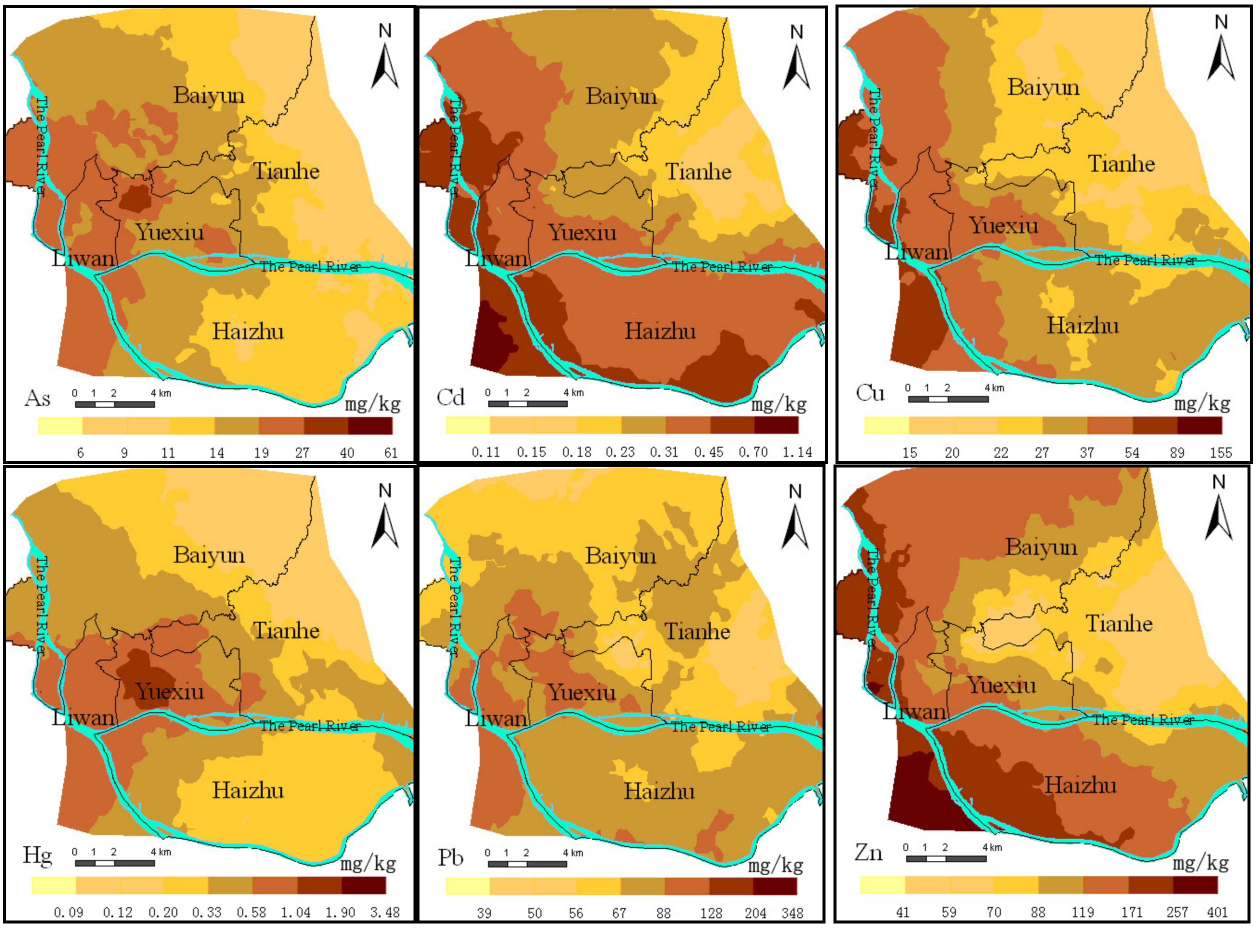

Figure 2. Distribution maps of As, Cd, Cu, Hg, Pb, and Zn concentrations in urban soils.

Metal distribution was closely related with industrial activities and city history. For example, several factories were located in the Liwan district such as a power plant, cement factory, casting factory and smelting plant. Similarly, in the Haizhu district a chemical plant, battery factory and toy factory existed. Waste emission from factories has led to elevated metal (Cu, Cd, Pb and Zn) concentration in soils. In the Yuexiu district, the old city centre has more than a 2000-year history of domestic activities such as coal burning, which has resulted in As and Hg accumulations in soils. Furthermore, some urban parks were formerly a rubbish dumping site for both municipal and industrial wastes. The data presented here established a baseline for future monitoring and management of these metals in urban soils.

Principal components analysis (PCA)

The results of PCA for metal contents indicated that the "eigenvalues" of the three extracted components are greater than one, both before and after the matrix rotation. As a consequence, metals could be grouped into a three-component model, which accounted for about 66% of all data variation. Spatial representation of the three rotated components is shown in Figure 3. The first principal component (PC1), explains 26.03% of the total variation, which exhibited a high positive factor loading on Cu, Zn, Pb and Cd. The second principal component (PC2) explains 23.39% of the total variation, and exhibited a high positive factor loading on Ni, Fe Mn and Cd. The third principal component (PC3) shows a high positive factor loading on Hg and As. For the first and third group metals, they illustrated an obvious accumulation according to their soil background values (Table 1), and previous investigations indicated they were strongly related to the impact of urbanization and industrialization. They probably mainly originated from anthropogenic origins, including industrial, road traffic and domestic emission.

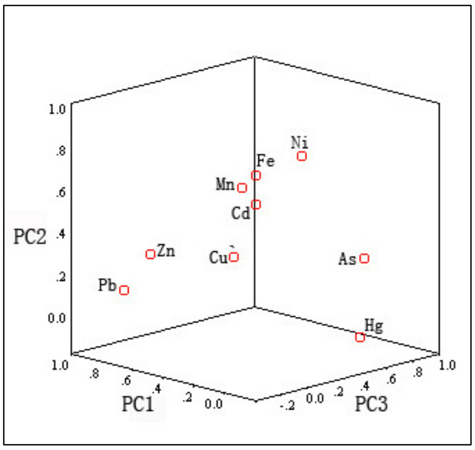

Figure 3. Principal component analysis loading plot for the three rotated components.

The second group consisted of Fe, Ni, and Mn whose concentrations were dominated by the mineralogy of soil parent material. This may be explained by the mean Fe and Ni concentrations measured in these soils, which did not exceed soil background values and Fe had a normal distribution with skewness of 0.61 (Table 1). Similar results can be found in other studies (Lee *et al.* 2006; Zhang 2006).

Cd had a high loading for both PC1 and PC2, which indicates that it possibly has both natural and anthropogenic sources.

Conclusion

The urban soils in Guangzhou showed a wide range in metal concentrations. Additional information from the data set was extracted by GIS-based geostatistics and PCA. The spatial distribution maps of As, Cd, Cu, Hg, Pb, and Zn concentrations, which was generated using Kriging interpolation, displayed several hotspots of heavy metal pollution in Liwan, Yuexiu and Haizhu administrative districts. PCA suggested that Fe, Ni and Mn are predominantly derived from natural sources; As, Cu, Hg, Pb and Zn from anthropogenic sources; and Cd from both sources.

Furthermore, this work also highlights the need for: (i) further studies in assessing both the human and ecosystem risks associated with urban contaminated soils, (ii) establishing Chinese soil guideline values for urban environments, and (iii) undertaking remediation measures for contaminated urban soils.

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Vertical distributions of magnetic susceptibility of the urban soil profiles in shanghai and their environmental implications

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Abstract

Magnetic susceptibility (χ_{lf}) and heavy metal contents in six soil profiles in one agricultural and two industrial areas in Baoshan District, Shanghai, were studied. The results showed that χ_{lf} of the two soil profiles in the Luodian agricultural area ranges from 12.6-54.6×10^{-8} m^3/kg, with a mean of 24.1×10^{-8} m^3/kg, and is higher at the surface (0-30 cm) but rapidly decreases and tends to be stable below a depth of 30 cm. χ_{lf} of soil profiles in the Shidongkou industrial area ranges from 23.2-158×10^{-8} m^3/kg, with the mean of 56.5×10^{-8} m^3/kg; that in the Wusong industrial area from 20.3-471×10^{-8} m^3/kg, with the mean of 102.2×10^{-8} m^3/kg. χ_{lf} in the two industrial areas reaches the highest in topsoils (0-5 cm) but fluctuates with increasing depth. The vertical distribution trends of χ_{lf} in all profiles are similar to those of heavy metal contents. Moreover, the χ_{lf} values of all the profiles are positively correlated with heavy metal contents. However, the correlation coefficients between χ_{lf} and heavy metals in the industrial areas are much higher. This suggests that the magnetic signals in urban/industrial soils in Shanghai can indicate the presence and trends in heavy metal pollution effectively.

Key Words

Urban/industrial soils, magnetic susceptibility (χ_{lf}), heavy metals, Shanghai.

Introduction

Magnetic aerosols emitted from industries and vehicles are efficient absorbers and carriers of pollutants, such as heavy metals or organic pollutants, due to their large surface area (Hunt *et al*. 1984). When they deposit on the ground, both magnetic signals and pollutant loads in the soil will simultaneously be elevated. Many previous studies (Hay *et al.* 1997; Strzyszcz and Magiera 1998; Durza *et al.* 1999) reported that there are significant correlations between χ_{lf} and heavy metal contents in soils. Therefore, χ_{lf} (or magnetic remenance) can indicate and delineate increases and potential decreases of soil pollution in regions (Hay *et al.* 1997; Hoffmann *et al.* 1999). Magnetic parameters of soil can also be used to discriminate different pollution sources (Lecoanet *et al.* 2003). In recent years, magnetic measurements of soil pollution also attracts much interest in China (Lu *et al.* 2001; Li *et al.* 2006; Lu and Bai 2006; Hu *et al.* 2007). However, most of these studies focus attention to topsoils, rather than whole soil profiles. For this reason, further studies on vertical variations of χ_{lf} in urban soil profiles will be conducive to identifying and predicting sources of magnetic particles and the history of urban pollution. In this investigation, six soil profiles located in an agricultural area at Luodian Town and two industrial areas at Shidongkou and Wusong in Baoshan District were studied with the objectives for revealing vertical distributions of χ_{lf} in the urban soil profiles in Shanghai and their environmental implications.

Methods

The terrestrial part of Shanghai is situated in the Yangtze Delta. The soil in Shanghai is mainly derived from the tidal sediments of the Yangtze River Estuary and classified as Entisols because of its young age and initial development. Baoshan district, situated at the northern part of Shanghai, is a well-known industrial area, where many large metallurgical and power plants are located, such as the Baoshan Steel Company. The industry and rapid urbanization in Baoshan district has exerted an adverse impact on soil environments (Hu *et al.* 2004). In spite of this, a certain amount of agricultural land, mainly cultivating rice and vegetables, is still left in the northwestern part of the district. In this investigation, six soil profiles were selected, two located in the Luodian agricultural area and two in Shidongkou and two in Wusong industrial areas. The profiles are coded as L1, L2, S1, S2, W1 and W2, respectively. Soil profiles were sampled at intervals of 5 cm in the topsoils (0-10 cm), and 10 cm at depth. Soil samples were air-dried, ground and passed through a 2 mm sieve after discarding gravel and crop residues, and through a 0.149 mm sieve for chemical analyses. About 10 g soil samples (<2 mm) were used to determine mass magnetic susceptibility at low frequency (0.47 kHz) (χ_{lf}) and high frequency (4.7 kHz) (χ_{hf}) using a Bartington magnetic susceptibility meter model

MS2 (Hu *et al.* 2007). Soil samples (<0.149 mm) were digested with the mixed acids (HNO_3+HF+$HClO_4$) and dissolved by 2% HNO_3 solution. The concentrations of heavy metals (Cu, Zn, Pb, Cd, Co, Ni, Mn and Fe) in the solution were determined by ICP-AES.

Results

The χ_{lf} values of the L1 and L2 profiles at the Luodian agricultural area are similar, with the maxima of 45.2×10^{-8} m^3/kg and 54.6×10^{-8} m^3/kg, respectively, the same minima of 12.6×10^{-8} m^3/kg and the mean of 21.9×10^{-8} m^3/kg and 26.2×10^{-8} m^3/kg, respectively. The χ_{lf} of the profiles is higher at the soil surface (0-30 cm) and reaches maxima at 5 cm in depth, but rapidly decreases and tends to be weak and stable below 30 cm depth (Figure 1). The profiles show a gleyed steel-gray colour because of the influence of a high groundwater table. The weak magnetism of the soils beneath the depth of 30 cm may be attributed to reducing conditions and dissolution of magnetic minerals under the anaerobic conditions.

The χ_{lf} values of the S1 and S2 profiles at the Shidongkou industrial area are also similar, with a maximum of 154×10^{-8} m^3/kg and 158×10^{-8} m^3/kg, a minimum of 29.3×10^{-8} m^3/kg and 23.2×10^{-8} m^3/kg and mean of 63.5×10^{-8} m^3/kg and 49.5×10^{-8} m^3/kg, respectively. The χ_{lf} of profiles reaches the highest value at the surface (0-5 cm), which is likely to be attributed to deposition of magnetic aerosols emitted from power and metallurgical plants in the area. The χ_{lf} of S1 tends to be stable beneath a depth of 40 cm, with a mean of 40.0×10^{-8} m^3/kg; that of S2, however, fluctuates and shows a maximum at a depth of 60 cm (Figure 1), which may be related to the anthropogenic disturbance of soil profiles.

The χ_{lf} values of W1 and W2 profiles at the Wusong industrial area are different, with a maximum of 471×10^{-8} m^3/kg and 172×10^{-8} m^3/kg, a minimum of 48.6×10^{-8} m^3/kg and 20.3×10^{-8} m^3/kg and a mean of 169×10^{-8} m^3/kg and 45.4×10^{-8} m^3/kg, respectively. The χ_{lf} curves of the profiles are also different in pattern: The χ_{lf} of the whole W1 is high and particularly enhanced at 0-20 cm and 50-70 cm sections, with a maximum at 60 cm in depth (Figure 1). The χ_{lf} of W2 is significantly enhanced at 0-10 cm, but decreases and maintains stable below a depth of 10 cm. The Wusong industrial area was established in the 1950s, where many metallurgical plants are located (Hu *et al.* 2004). As previously studied (Hu *et al.* 2007), the magnetic enhancement of the topsoils is mainly attributed to atmospheric deposition of anthropogenic magnetic particles from industrial or vehicular emissions. The χ_{lf} fluctuations in profiles may be caused by the anthropogenic disturbance, or historical pollution.

Table 1 Correlation coefficients (r) between χ_{lf} and heavy metal contents in the soil profiles in Baoshan, Shanghai

	Profiles	Cr	Cu	Pb	Zn	Cd	Ni	Co	Mn	Fe
χ_{lf}	L1+L2 (n=26)	0.678(**)	0.880(**)	0.796(**)	0.487(*)	0.299	0.665(**)	0.453(*)	-0.477(*)	0.530(**)
	S1+S2 (n=26)	0.351	0.651(**)	0.857(**)	0.778(**)	0.806(**)	0.485(*)	-0.045	0.474(*)	0.573(**)
	W1+W2 (n=18)	0.942(**)	0.961(**)	0.955(**)	0.736(**)	0.232	0.599(**)	-0.355	0.882(**)	0.654(**)

Note: "*" means the correlation significant at $P< 0.05$ level; "**" means the correlation significant at $P< 0.01$ level.

The vertical variations of χ_{lf} of L1 and L2 are comparable to those of heavy metal accumulations: Both are high at the 0-30 cm section but rapidly decrease and tend to be stable below 30 cm in depth (Figure 1). Statistical analyses indicates that χ_{lf} is significantly positively correlated with concentrations of Cr, Cu, Pb, Zn, Ni, Co and Fe, respectively (Table 1). The agricultural area has few highly polluted industries and is far away from traffic hubs but is located on the leeward side of the Shidongkou Industrial area and may accept a small amount of magnetic aerosols from the industries far away, which explains the magnetic enhancement of topsoils and the significant correlations between χ_{lf} and heavy metals in the area.

The χ_{lf} curves of S1 and S2 are also comparable to concentrations of heavy metals. Especially in the S2 profile, both show maxima at a depth of 60 cm (Figure 1). The χ_{lf} of S1 and S2 is significantly positively correlated with Cd, Cu, Pb, Zn, Ni, Mn and Fe concentrations, respectively (Table 1). The χ_{lf} curves of W1 and W2 are also similar to those of heavy metal concentrations except for Co (Figure 1). Both reach maxima in topsoils (0-5 cm). Especially in the W1 profile, both show peaks in the 60-70 cm section. The χ_{lf} of W1 and W2 is significantly positively correlated with Cr, Cu, Pb, Zn, Ni, Mn and Fe concentrations, respectively (Table 1) – displaying highest correlation coefficients. Especially, those between χ_{lf} and Cr, Cu and Pb concentrations reach more than 0.94 (Table 1).

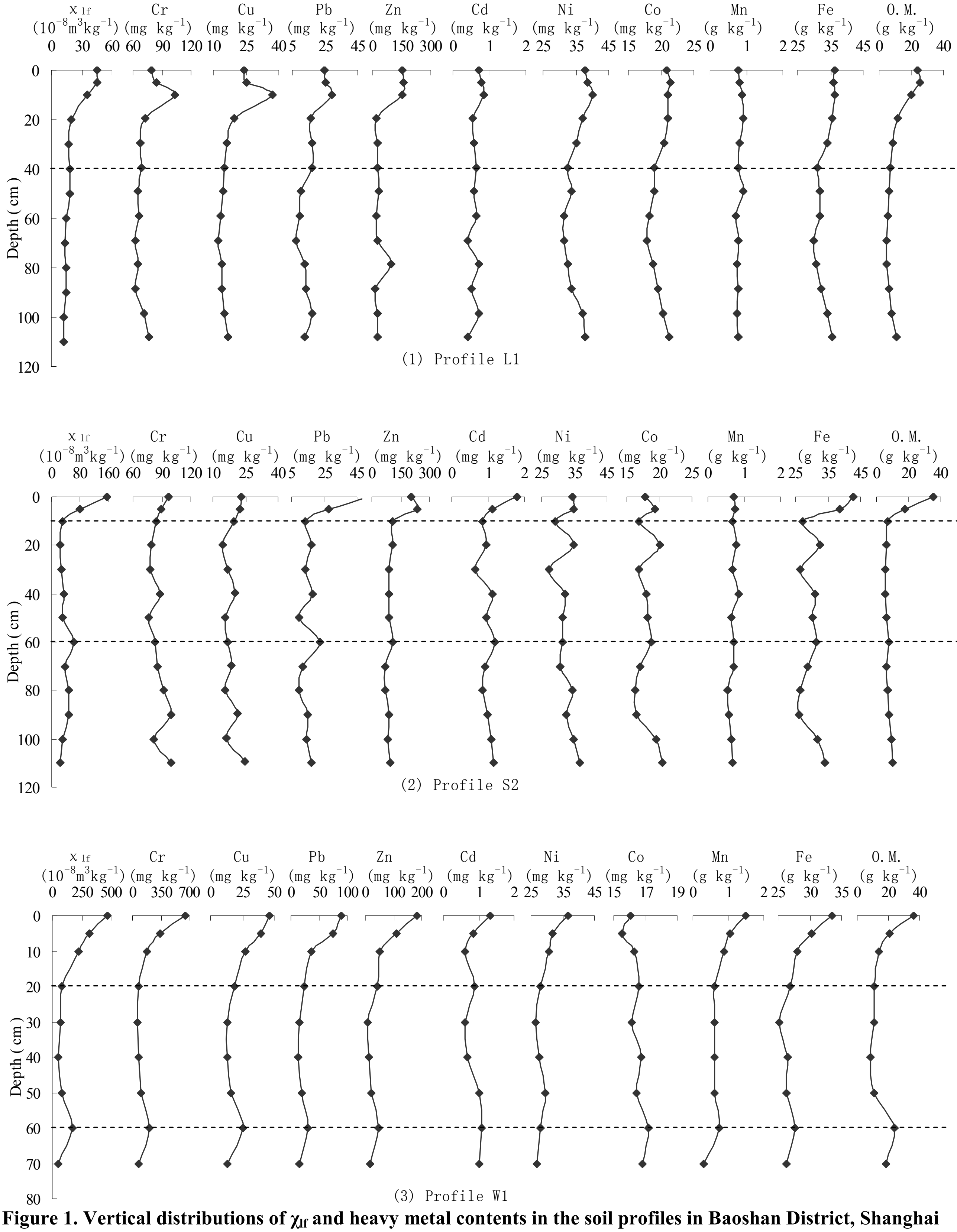

Figure 1. Vertical distributions of χ_{lf} and heavy metal contents in the soil profiles in Baoshan District, Shanghai

Conclusion

The χ_{lf} of soils in industrial areas much higher than in the agricultural area, which is in agreement with previous studies (Hu *et al.* 2007). Moreover, the soil χ_{lf} in the older industrial area of Wusong is significantly higher than that of the new one of Shidongkou. Soil profiles in the agricultural area are mostly natural and undisturbed, with χ_{lf} being higher at the topsoils and becoming weak and stable at depth. The χ_{lf} curves of soil profiles in the industrial areas mostly reach maxima in the topsoils and show fluctuations at depth, which may be caused by anthropogenic disturbance. The soil χ_{lf} in the three areas is mostly significantly positively correlated with heavy metal concentrations. However, the correlation coefficients between them in the industrial areas are much higher, which suggests that the χ_{lf} in the urban/industrial soils in Shanghai can indicate heavy metal pollution more effectively.

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Wastewater treatment processes and mechanisms of organic matter, phosphorus, and nitrogen removal in a multi-soil-layering system

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Abstract
The treatment processes inside a Multi-Soil-Layering system (MSL) were investigated by using a laboratory-scale system, which was set up in a D10×W50×H23-73cm acrylic box enclosing “soil mixture blocks” alternating with permeable zeolite layers. Six MSL systems consisted of 1~6 layers of soil mixture layers were constructed. For the study of the treatment processes inside the system, wastewater, with mean concentrations (mg/L) of BOD: 28.1, COD: 65.7, T-N: 9.8, T-P: 1.0, was introduced into the system at a loading rate of 1000 L/m^2/day. In the both of BOD and COD, the concentrations in soil mixture layers (SML) were lower than those in permeable layers between SML (PLb). As the flow rate in SML decreased and the rate in PLb increased, the concentrations in the PLb increased in each system. Phosphorus concentration was lower in the SML than in the PLb, probably because P was adsorbed mainly by soil and mixed iron particles. Therefore, phosphorus removal efficiency was strongly influenced by the flow rate in SML. The ammonia adsorption and nitrification were almost completed up to 3rd layer in this study. However, the removal of nitrogen did not so much proceed below 4th layer because of low denitrification efficiency.

Key Words
Multi-Soil-Layering system, processes of wastewater treatment, organic matter removal, nitrogen removal, phosphorus removal, soil-based wastewater treatment system.

Introduction
The physical, chemical, and biological properties of soil have been used for wastewater treatment systems all over the world for a long time. To bring out the water purifying function of soil as much as possible, the author’s group has been addressed the study of Multi-Soil-Layering (MSL) system. The MSL system consists of soil units (soil mixture layers : SML) arranged in a brick-like pattern surrounded by layers of zeolite or alternating particles of homogeneous sizes (permeable layers : PL) that allow a high hydraulic loading rate (HLR). The MSL system is effective for the prevention of clogging and shortcuts which are the main constraints in the conventional soil-based wastewater treatment systems (Masunaga *et al*. 2003, Sato *et al*. 2002, 2005, Wakatsuki *et al*. 1993). Although a large number of basic and applied researches have been investigated, it has not been clear the processes of wastewater treatment in the MSL system. So far, some settings such as the number of layers and the apparatus size and height have been established empirically. In this research, six laboratory-scale MSL systems consisted of SML of 1~6 layers were made for the purpose to evaluate the treatment processes. In addition, treated water from SML and PLb at the bottom of each system was separately collected. We attempted to reveal the wastewater treatment mechanisms in SML and PLb of each layer by the analysis of both the quantities and qualities in treated water.

Materials and methods
Appearance of the MSL systems in the present study
Figure 1 shows the structure of the laboratory-scale MSL system used in this study. For the MSL system, an acrylic box D10 × W50 × H23-73cm in size, forming an alternate brick layer-like pattern with zeolite and SML, was used. Six MSL systems consisted of SML of 1~6 layers were constructed. To collect the outflow water from SML and PLb separately, plastic divider plates were installed at the bottom part of the systems as shown in Figure 1. A 1.2cm diameter hole was made at the bottom of each partition part and a vinyl tube was attached to each hole. The SML consisted of volcanic ash soil (rich in organic materials classified as Andisol), saw dust, approximately 1mm diameter granular iron, and charcoal in ratios of 70, 10, 10, and 10%, respectively, on a dry weight basis. The bulk density of SML was 0.84g/ml. The void spaces (PL) between each block and block sides were filled with zeolite 3-5mm in diameter. In Addition, to measure

oxidation-reduction potential inside the system, the ten platinum electrodes were installed from the side in system No.VI, as shown in Figure 1.

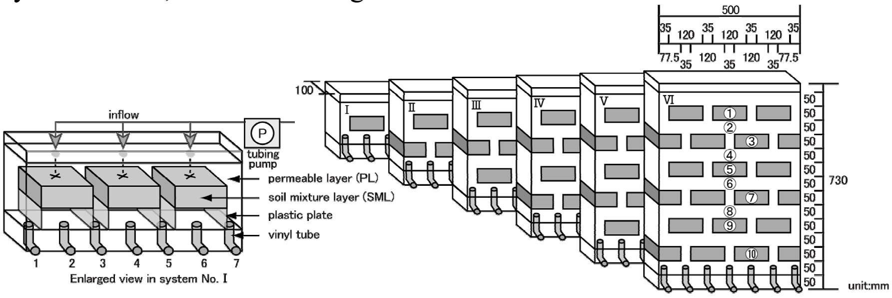

Figure 1. Structure of Multi-Soil-Layering (MSL) system for studies on characterization of treatment processes inside system. Numbers in system No.VI show setting places of Eh electrode.

Evaluation of wastewater treatment processes in respective layers of the system
Domestic wastewater from a nearby community disposal plant was diluted three times with well water and introduced into these systems for evaluation of wastewater treatment processes. Average characteristics of the diluted wastewater were as follows: pH 7.71, SS 14.9 mg/L, BOD 28.1 mg/L, COD 65.7 mg/L, T-N 9.8 mg/L and T-P 1.0 mg/L. HLR was set at 1000 L/m^2/d. The inflow water was divided into three points by using peristaltic pump. The three points were positioned right above centers of three SML in top layer of the systems, as shown Figure 1.This experiment was started on Aug 12, 2005 and was terminated on Dec. 22, 2005 (132th d). The outflow water was collected from each vinyl tube and sampled five times on Aug. 15 (3rd d), Aug. 30 (18th d), Sep. 29 (48th d), Nov. 9 (89th d), and Dec. 7 (117th d) during the experiment of wastewater treatment. Wastewater and outflow water (treated water) were analyzed for the following: BOD, COD, NH_4-N, NO_3-N, NO_2-N, T-N, PO_4-P and T-P.

Results and discussion

Characteristics of water movement inside systems
Figure 2 shows changes in proportion of water flow volume in SML of each system during wastewater treatment. In the system No.I, the proportion sharply decreased to approximately 30% on the 3rd d, and then gradually decreased with time. The decrease probably resulted from proliferation of microorganisms and overgrowth of biofilm in the SML. At the same time, the water which could not flow into SML flowed into PLb. Subsequently, the water probably flowed down into the SML of next layer in MSL systems with more than 2 layers. The facts indicated that the structure of MSL system made possible such high-speed treatment as the conventional soil-based water purification systems could not continue to treat for clogging. As the number of layers increased, it took a longer time before the proportion in SML started to decrease.

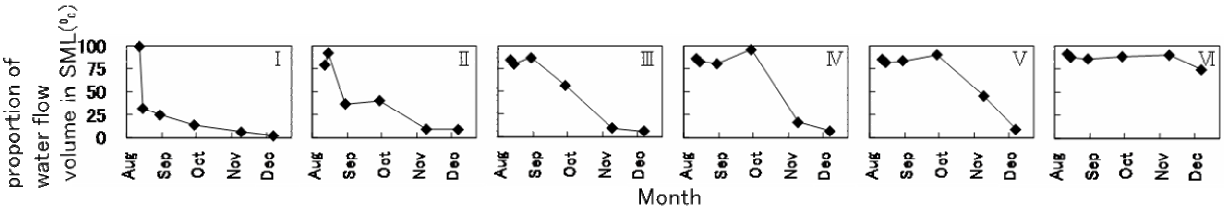

Figure 2. Changes in proportion of water flow volume in soil mixture layer (SML) of each system during wastewater treatment. The first value (0th day) in each graph shows the percentages when well water was flowed into the systems in HLR of 1000 L/m/d.

Processes of organic matter (BOD and COD) removal
In the SML, the concentrations of BOD were extremely low except the system No.I (Figure 3). In contrast, the COD in the SML decreased with the increase in the number of layers. In the both of BOD and COD, their concentrations in SML were lower than those in PLb. Additionally, as the flow rate in SML decreased and the rate in PLb increased, the BOD and COD in the PLb increased in each system (Figure 2, 3). These facts indicated that the efficiency of organic matter removal was higher in SML than in PLb, and the water permeability in SML was important for organic matter removal. COD was higher than BOD in each system. The results suggested the removal of COD needed more number of layers than that of BOD. This was because COD includes easily and slowly decomposable organic matter, whereas BOD represents easily decomposable organic matter.

Processes of phosphorus removal

The PO_4-P and T-P concentrations were lower in the SML and fluctuated less than that in the PLb (Figure 3). Previous studies suggested the phosphorus removal was mainly based on phosphorus adsorption on soil and metal irons added in the SML (Wakatsuki *et al*. 1993). Furthermore, the PO_4-P and T-P in PLb clearly increased with decrease in the flow rate in SML of each system. These results indicated the permeability of SML was also very important on phosphorus removal in MSL system. The concentrations in SML of system No.I-III were showing an upward tendency with time. This was probably because the adsorption of phosphorus on ferric hydroxides decreased and/or the adsorbed phosphorus leached from the SML due to establish an anaerobic condition in those SML.

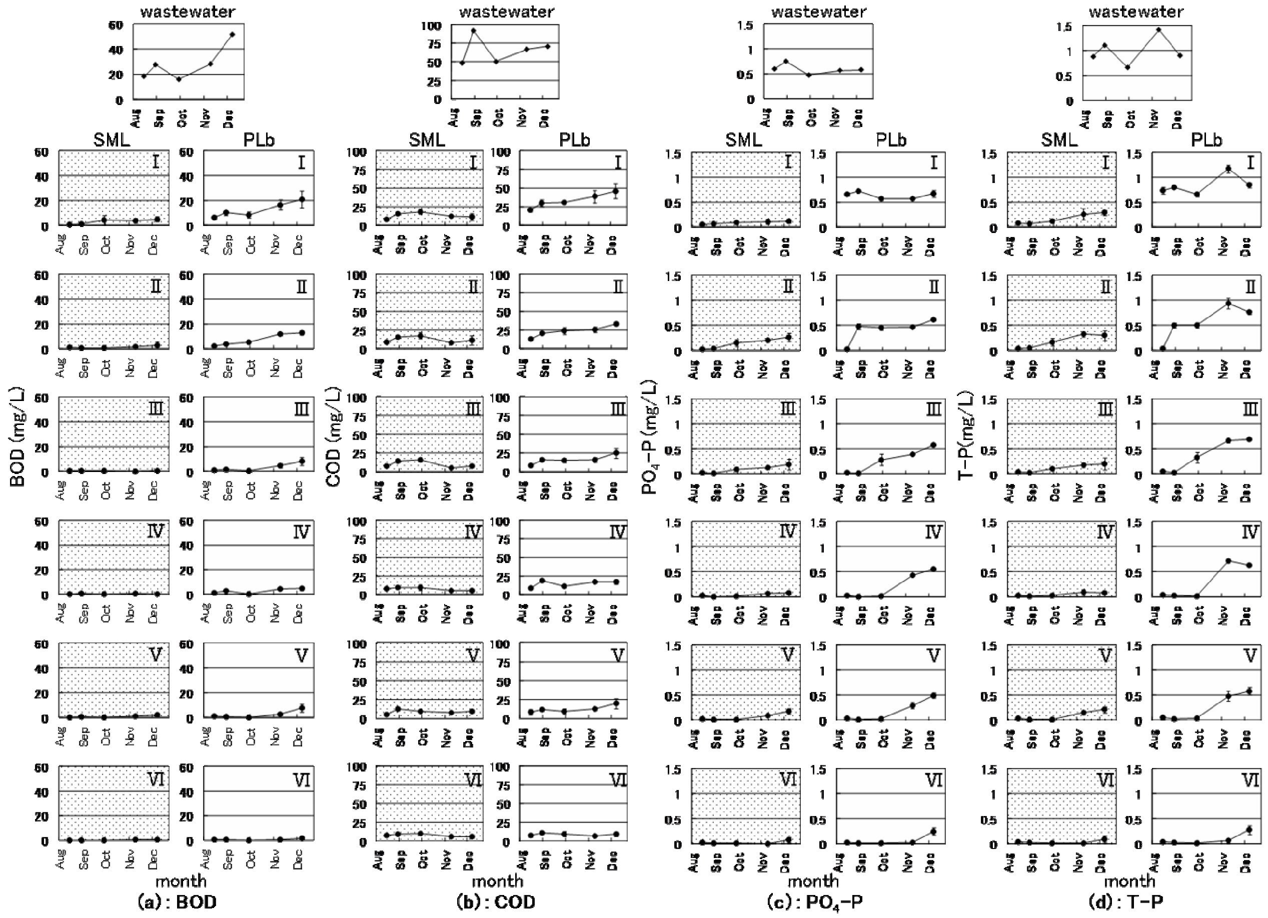

Figure 3. Changes in mean concentrations of (a)BOD, (b)COD, (c)PO_4-P and (d)T-P of the wastewater and treated water in each system. The error bars show the standard deviations. SML: Soil Mixture Layer, PLb: Permeable Layer between SML.

Processes of nitrogen removal

NH_4-N was significantly low in every SML and PLb of the systems with more than 3 layers (Figure 4), probably because NH_4-N adsorption on soil materials and zeolite took place and nitrification proceeded with time. The concentration showed an increasing trend with time in PLb of system No.I and II. It was because the contact efficiency of wastewater with the soil and zeolite decreased due to the increase in flow rate in PLb with time. The peaks of NO_2-N were observed in each part on 18th d (Figure 4). NO_3-N increased to 48th d from start of this experiment, followed by the trend of decreasing was observed except system No.II. This was because nitrification proceeded from the start and denitrification occurred later. In system No.I, reducing of nitrification probably also contributed to the decrease in NO_3-N after 48th d because NH_4-N also increased with time in the system. In system No.II, the decreasing of NO_3-N was not observed in SML. This was probably because NH_4-N which was not removed in first layer transformed to NO_3-N by nitrification in SML of second layer. Although the decreasing of NO_3-N by denitrification was observed in system No.III after 48th d, the difference of NO_3-N concentration among system No.IV-VI was small. Although decreasing of Eh with decrease in the water flow rate was observed in the SML of 1st - 3rd layer, Eh in SML of 4th - 6th layer and PLb of each part showed relatively high value (data not shown). In addition to that, BOD almost removed up to 3rd layer (Figure 3), and it was suggested that denitrification mainly occurred in SML of 1st to 3rd layer. The trend of T-N shows such behaviour as sum of concentrations of NH_4-N, NO_2-N and NO_3-N.

Figure 4. Changes in mean concentrations of (a) NH_4-N , (b) NO_2-N , (c) NO_3-N and (d)T-N of the wastewater and treated water in each system. The error bars show the standard deviations. SML: Soil Mixture Layer, PLb: Permeable Layer between SML.

Conclusion

In this study, the water flow rate in SML was an essential factor for removal of organic matter, phosphorus and ammonia. This result and previous studies suggested that selection of soil with proper particle size, mixing of high permeable materials with SML and setting of aeration regime were important to keep the proper flow rate in SML (Sato *et al*. 2002, 2005). Proper aeration has shown effective in the prevention of clogging. Additionally, the ammonia adsorption and nitrification were almost completed up to 3rd layer, and denitrification did not so much proceed after 4th layer. These results suggested that the aeration in upper parts of the system for nitrification and the extra addition of organic matter (especially high CN ratio materials) to SML in the lower parts for denitrification were effective for simultaneous removal of organic matter, phosphorus and nitrogen.

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Weathering trajectory of bauxite residue mud as predicted by high-temperature treatment

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Abstract
Weathering of parent materials, an essential part of soil formation, can be a slow process in the field being partially constrained by reaction kinetics. Increasing temperature and pressure can accelerate attainment of chemical equilibrium. This study used pressure vessels to elevate temperature and pressure in order to rapidly determine the likely weathering trajectory of bauxite residue mud. Supernatant pH, EC, and alkalinity decreased over time with pH decreasing by 2.5 units after two days' treatment at 235°C. This behaviour suggests that residue mud has the capacity to 'auto-attenuate' porewater alkalinity and salinity without applied treatments. In the treated mud, gibbsite and tricalcium aluminate concentrations decreased whereas boehmite, hematite, goethite, calcite, sodalite, and muscovite increased in concentration relative to anatase. Precipitated hematite was more aluminous than the original hematite present in residue mud. Besides implications for the potential recovery of additional alumina from bauxite residue, the results suggest that residue alkalinity could be 'auto-attenuated' over very long (geological) periods of time.

Key Words
Bauxite residue, environmental remediation, weathering, reaction kinetics, alkalinity, salinity.

Introduction
Bauxite residue is an alkaline, saline, sodic slurry discharged to deposit areas as a by-product of the Bayer process. Bauxite residue mud (BRM) refers to the solid fraction of the slurry consisting of particles <150 µm in diameter (minimum 50% w/w of total solids). Despite dewatering and rinsing of the slurry, BRM is approximately 48% w/w solids suspended in pH 13 liquor. Leachate from BRM deposits continues to be collected through purpose built drainage systems after closure of deposit areas and it can maintain a pH > 10.5 for 20 years or more. Residue mud presents a greater long-term management challenge than residue sand (particles >150 in diameter) as (a) it is produced in greater quantities than residue sand; (b) it drains more slowly than sand, (c) entrained liquor maintains a higher pH despite extended rainwater leaching due to resupply of alkalinity by dissolution of minerals associated with this particle size fraction, and (d) its fine (and usually waterlogged) pores limit the rate of atmospheric carbonation.

Practices for rehabilitation of BRM deposits should be designed to accelerate natural mechanisms of alkalinity and salinity attenuation such as precipitation, dissolution, and leaching. The weathering trajectory of BRM therefore needs to be identified. Weathering of parent materials, an essential part of soil formation, can be a slow process in the field, partially constrained by reaction kinetics. Increasing temperature and pressure can accelerate attainment of chemical equilibrium. This study used pressure vessels to elevate temperature and pressure in order to rapidly determine the likely weathering trajectory of BRM.

Methods
Uncarbonated BRM was supplied by Alcoa World Alumina Australia (Kwinana refinery, Western Australia). Five temperatures (100, 130, 165, 200, and 235°C) were employed in order to generate kinetic data and identify reaction products. Each Teflon lined pressure vessel contained 4 g of residue (60% solids content) and 5 mL of MilliQ water, which was then heated to temperature in a rotating oven for up to 900 hours. Treated slurries were separated into liquid and solid phases by centrifugation. Supernatants were immediately filtered (0.2 µm cellulose acetate, Advantec MFS) and analysed for pH, EC, and total alkalinity by titration. Subsamples were acidified and stored at 4°C prior to ICP-OES analysis (PerkinElmer Optima 5300DV) for Al, Ca, Fe, K, Na, Si, and Ti. Treated solids were shaken with acetone to remove entrained solution, centrifuged and then airdried. Dried solids from 100, 165 and 235°C treatments were ground in an agate mortar and pestle and packed into glass capillaries for XRD analysis at the Powder Diffraction beamline (10BM1) at the Australian Synchrotron.

Peak locations and areas of selected minerals were calculated from synchrotron XRD patterns using Traces (v6.7.20, GBC Scientific Equipment Pty. Ltd. 2006). Naturally occurring anatase in the BRM was used as an internal standard for the purpose of comparing peak areas between patterns. Aluminium substitution was estimated for goethite using the d-spacings of the (110) and (111) reflections and the equation of Schulze (1984) and for hematite, using the *a* dimension as determined by least-squares refinement of (012), (104), (110), (113), (024), (116), (214), and (300) spacings and the equation of Schwertmann *et al*. (1979). Kinetic data were extracted from mineral peak areas observed in synchrotron XRD patterns using an approach identical to that of Murray *et al*. (2009). Mineralogical composition data was sourced from Taylor and Pearson (2001) and solution chemistry was determined by analysis of supernatants detailed above.

Results

Supernatant chemistry

pH, EC, and alkalinity all decreased at 165, 200, and 235°C (Figure 3). This indicates that BRM has the capacity to 'auto-attenuate'; that is, to lower its porewater alkalinity and salinity. Electrical conductivity and alkalinity increased over time for the 100 and 130°C treatments; however, the 165, 200, and 235°C treatments showed an initial increase relative to values for the unheated control, followed by a decrease over time in EC and alkalinity. These results suggest that the reaction is initially dominated by dissolution of the solid phase in contact with added water, and thereafter reflects chemical reactions that consume soluble alkalinity.

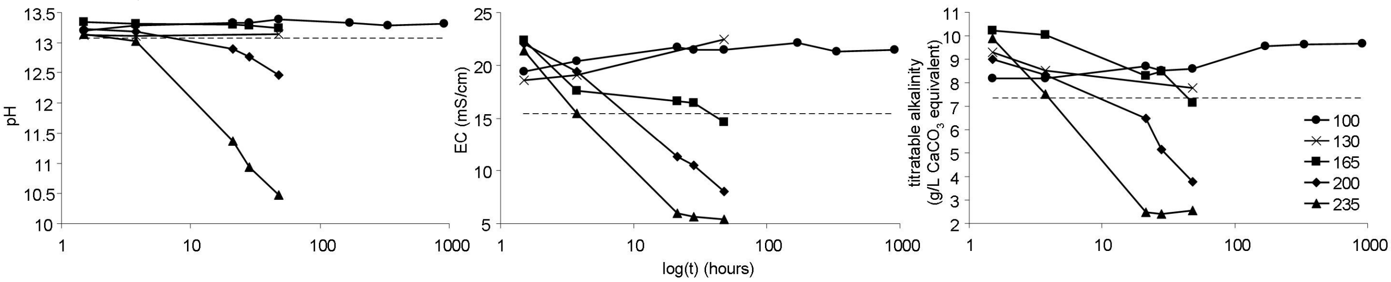

Figure 4. pH, EC and total alkalinity of supernatants from treated BRM. Dashed line indicates control values.

Solids mineralogy

Precipitation of iron and aluminium oxides, calcite, sodalite and muscovite are likely to be major mechanisms for lowering alkalinity and salinity in porewater, given the increase in XRD peak areas of these minerals compared to that of anatase (Table 1). Gibbsite dissolved and is likely to have been precipitated as boehmite. Tricalcium aluminate (TCA) dissolved more slowly than gibbsite and the Al and Ca supplied to solution are likely to have precipitated as boehmite and calcite, respectively. The hematite and goethite that precipitated during treatment appeared more aluminous than the original minerals in BRM, but remained within the ranges observed in other bauxite residue muds (4-12 mol% Al substitution in hematite and 17-35% mol% Al substitution in goethite) (Snars and Gilkes 2009).

Solution chemistry

ICP-OES analysis of supernatants after treatment showed net removal of Al, K, Na, and S from solution at temperatures ≥165°C (Figure 5). This agrees with observations of boehmite, sodalite, and muscovite precipitation. Iron concentrations in solution remained near or below the detection limit at all treatment temperatures except 235°C. Crystalline goethite and hematite may have formed from amorphous/nanocrystalline Fe oxides, which would account for little change of Fe in solution. Precipitation of Al-substituted Fe oxides also accounts for some removal of Al from solution. The assumption of anatase insolubility was supported by ICP-OES data, which indicated little Ti was released to solution except at 235°C. Titanium and iron were released simultaneously, which could indicate dissolution of a minor Fe-Ti phase. Ilmenite dissolution does not appear to account for this behaviour.

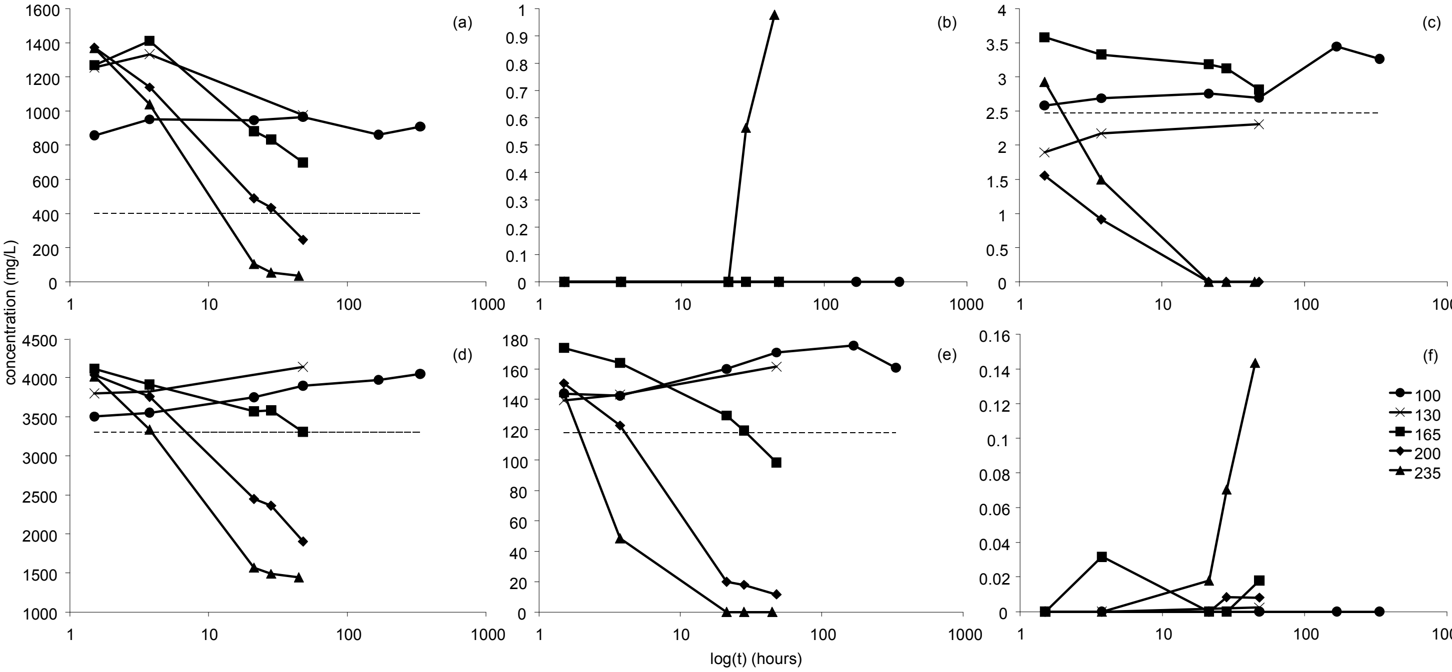

Figure 5. Concentrations of selected elements in treated supernatants, as determined by ICP-OES: (a) Al; (b) Fe; (c) K; (d) Na; (e) S; (f) Ti. Dashed lines indicate concentrations in control treatments. Where no dashed line is visible, concentrations in the control were below detection limits.

Table 1. Percentage change in mineral:anatase XRD reflection intensity ratio relative to untreated material. The ratio was calculated from primary peak areas of each mineral from synchrotron XRD patterns.

Temp (°C)	Time (hours)	Boehmite	Calcite	Gibbsite	Goethite	Hematite	Muscovite	Sodalite	TCA
100	1.5	82	30	54	47	15	16	47	41
100	21	102	43	47	48	29	25	62	24
100	48	153	44	46	52	30	44	64	-2
100	336	313	88	43	107	89	49	106	-2
165	1.5	300	53	-100	71	55	28	68	-14
165	21	468	95	-100	119	109	81	118	-100
165	48	584	106	-100	138	117	193	190	-100
235	1.5	348	85	-100	99	90	72	123	-35
235	3.8	526	88	-100	114	119	83	150	-100
235	21	587	94	-100	141	177	131	294	-100
235	48	643	111	-100	156	198	195	389	-100

Reaction kinetics

Sharp-Hancock analysis indicated that the plots of ln(-ln(1-a)) against ln(t) were well described by linear functions as r^2 values were generally >0.80, indicating that a single reaction mechanism likely dominated over the course of the reaction. This reaction mechanism may have been first-order surface controlled, because activation energies determined from Arrhenius plots ranged from 76 – 131 kJ/mol (Table 2), which is consistent with first-order surface controlled reaction kinetics. Reaction half-lives as predicted by the Avrami-Erofe'ev equation were predicted far more accurately by the first-order surface control model than for other models, for example three-dimensional (3D) diffusion control (Table 2). From the kinetic data presented in Table 2, it is possible to calculate the time required for reactions to proceed to a designated value of α at a designated temperature. This allows for extrapolation to field conditions, at an approximate temperature of 298K. Calcite, boehmite, goethite and hematite will reach half-completion within two centuries; however, muscovite and sodalite would take substantially longer to reach half-completion. This indicates that although 'auto-attenuation' of residues is possible, it will take millions of years to achieve chemical equilibrium in the field.

Table 2. Activation energies (E_a), frequency factors (A), and reaction rates (k) calculated from Arrhenius plots; reaction half-completion times ($t_{1/2}$) as calculated by interpolation of Sharp-Hancock lines of best fit to observed data (OB) and the Avrami-Erofe'ev equation predicted for first order surface control (FO) and 3D diffusion control (3D) (Francis *et al.* 1999) for mineral transformations in BRM.

		Calcite	Boehmite	Goethite	Hematite	Muscovite	Sodalite
Ea (kJ/mol)		100	88	76	76	94	131
ln A		18	13	10	8	13	21
$t_{(1/2)}$ at 508K (hours)	OB	0.00068	0.75	0.47	2.1	5.8	5.8
	FO	0.030	0.60	0.63	2.7	3.2	4.2
	3D	1.2	197	215	2738	3709	5879
$t_{(1/2)}$ at 298K (years)	FO	61	164	21	94	2396	1513193
log(k) (s^{-1})	508K	-2.2	-3.5	-3.5	-4.2	-4.2	-4.3
log(k) (s^{-1})	298K	-9.4	-9.9	-9.0	-9.6	-11	-14

Note: The rapid dissolution of gibbsite and TCA precluded calculation of reaction kinetics for these phases.

Conclusion

Rehabilitation of alkaline, saline bauxite residue mud is a growing concern for the alumina industry. This study has identified a possible weathering trajectory for BRM, involving precipitation of boehmite, calcite, goethite, hematite, muscovite and sodalite, and dissolution of gibbsite and TCA. Porewater became less alkaline and saline during treatment. Reaction kinetics calculations based on an assumption of anatase insolubility indicated that some of the transformations observed at 235°C could proceed to a significant extent within decades, but may only reach equilibrium on a geological time scale. Ideally, treatments applied to bauxite residue deposits should aim to accelerate mineral transformations observed in this study. Encouraging mineral precipitation by applying elements such as Ca and Si in a dissolved or soluble form could be one way of achieving rapid precipitation. Given the potential costs associated with ongoing, long-term residue management, consideration should also be given to the viability of a 'secondary digest' step in the Bayer process, involving heating residue from the standard Bayer process to accelerate the transformations observed in this experiment. The effect of treatments applied prior to deposition (such as carbonation and seawater neutralization) and post-deposition (such as applied irrigation and gypsum) on the weathering trajectory predicted by high temperature treatment should also be investigated.

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