Water solubility of phosphorus in animal manure compost

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Abstract
The characterization of phosphorus (P) in animal manure compost (AMC) is important to estimate both the risk of P loss from agricultural land and the availability for crops. In this study, 16 AMCs (4 cattle manure composts, 5 swine manure composts, 5 layer manure composts and 2 broiler litter composts) were extracted by large amounts of water for many hours (sequential water extraction). The dissolution patterns of P and some cations were described using two kinetic models and the maximum amount of water soluble P (P_0) was determined statistically. The P_0 values were corresponded to the sum of WEP and $NaHCO_3$ extractable P by modified Hedley method, indicating $NaHCO_3$ extractable P fraction is soluble to water and available for crops. The P_0 values were positively (r=0.854, p<0.001) correlated with Mg_0, and negatively (r=-0.492, p<0.05) correlated with water soluble Ca. The result suggests that the amount of labile P in AMC is controlled by Mg and/or Ca concentrations.

Key Words
Animal manure compost, Phosphorus, Magnesium, MAP, Sequential water extraction.

Introduction
Animal manure compost (AMC) contains significant amounts of phosphorus (P) that can be utilized for crop production. However, P accumulation in soil by excessive AMC application can increase potential risk of P loss via overland flow and/or subsurface drainage (Sims *et al.* 1998). It is very important to determine the solubility of P in AMC to provide adequate amount of available P for crops and minimize the risk of P loss. The measurements of water extractable phosphorus (WEP) in manure and AMC have been conducted, especially, to estimate P loss risk from agricultural lands which received manure and AMC application. The method of WEP extraction adopted by most references is the one which the manure (dry weight equivalent) to water ratio is 1:200 (Sharpley and Moyer 2000; Kleinman *et al.* 2002). However, Toor *et al.* (2006) observed an increase in concentration of WEP in dairy feces with increase in manure to water ratio from 1:200 to 1:400. The result indicates that more stable P (P extracted by $NaHCO_3$, NaOH and HCl) can be extracted by water if manure to water ratio is so large. The objectives of this study are 1) to determine the potential water solubility of inorganic P in AMC, and 2) to estimate phosphate compounds in AMC which are readily soluble and available for crops using sequential water extraction method.

Methods
Sampling of AMCs
16 AMCs (4 cattle manure composts (CMC1-4), 5 swine manure composts (SMC1-5), 5 layer manure composts (LMC1-5), and 2 broiler litter composts (BLC1, 2)) collected from several prefectures in Japan were used to examine P solubilities. The composition of minerals in more 10 SMC samples was determined using X-ray diffractometer.

Extraction methods
A 0.15g sample of air-dried AMC was sequentially extracted by 30ml deionized water (1: 200), 0.5M $NaHCO_3$ (pH=8.5), 0.1M NaOH, and 1M HCl using the Frossard *et al.*(1994) method, modified as suggested for soils by Hedley *et al*. (1982). Sequential water extraction was conducted to determine the P dissolution rates and the maximum amounts of WEP. AMCs were sequentially extracted using 3.5L/g of water for 20hr maintaining an AMC to water ratio of 1:200 using a stirred, flow-through reaction vessel.

Equations
In sequential water extraction experiment, the relationship between water volume flowed (L/g) and the amounts of cumulative extracted elements (P, Ca, Mg and K) was described using two simple kinetic models as examined by Pierre *et al*. (2005). When taking it as an example of P, the cumulative extracted P for a first-order reaction kinetic is obtained like below:

$P(t) = P_0 [1-\exp(-t/\tau 1)]$ [1]

"t", "P (t)", "P_0" and "τ1" is water volume flowed (L/g), cumulative extracted P at t (mmol/g), the initial P in the WEP pool (mmol/g) and a characteristic number, respectively. For second-order kinetic, the cumulative extracted P is shown like below:

$P(t) = P_0 t / (t+\tau 2)$ [2]

"τ2" is a characteristic number for the second-order kinetic reaction. P in eq.[1] and eq.[2] can be replaced with Ca, Mg and K. All analysis and modelings were conducted using JMP4.0.5.J (SAS Institute, 2001).

Results

Solubility of P in AMC

Total P concentration of SMC (36.0 mg P/g) was greatest, followed by LMC (28.9 mg P/g), BLC (16.8 mg P/g), and CMC (12.4 mg P/g). The significant difference was seen between SMC and CMC (table 1). Most of P in CMC, SMC, and LMC was inorganic P (Sum of each P fractions) with small amount of residual P. The percentages of inorganic P in CMC, SMC, and LMC were 89%, 93%, and 77%, respectively. Some of LMC (LMC4 and LMC5) and BLC contained more residual P (5.8 to 8.9 mgP/g, >25% of total P) than the others. Most of residual P was thought to be organic P form.

Table 1. Phosphorus fractionation of AMC by sequential chemical extract.

Livestock	n	Concentration of P in each fractions (mgP/g)					
		Total	H_2O	$NaHCO_3$	NaOH	HCl	Residual
Cattle	4	12.4 b	4.5 b	4.3 ab	0.4 a	1.8 b	1.4 c
Swine	5	36.0 a	9.6 a	7.3 a	1.4 a	15.4 a	2.3 bc
Layer	5	28.9 ab	5.9 b	3.0 ab	0.4 a	13.9 a	5.8 ab
Broiler	2	16.8 ab	3.3 b	0.9 b	0.2 a	6.0 b	6.4 a

Values followed by the same letter are not significantly different using Tukey's HSD (p<0.05).

Sequential water extraction

The relationships between water volume flowed and cumulative extracted P is shown in Figure 1. The P dissolution patterns of all of AMCs were fitted to first-(I) or second-(II) order kinetic model.

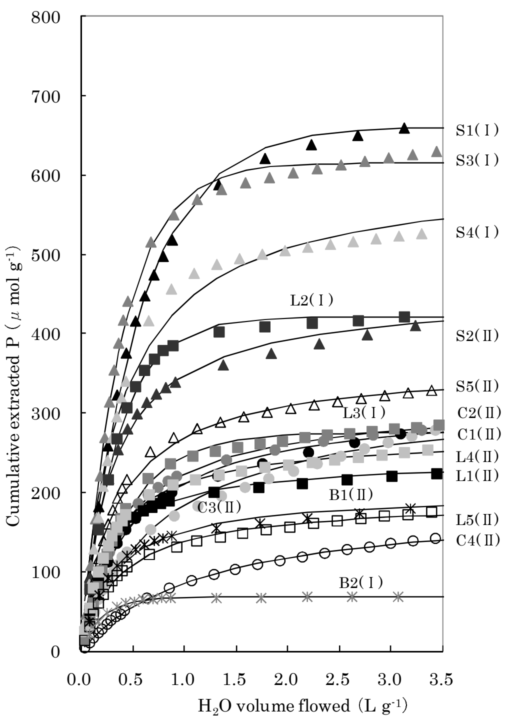

Figure 1. The dissolution pattern of P by sequential water extraction. C: CMC, S: SMC, L: LMC B: BLC, I: First-order kinetic model, II: Second-order kinetic model. The curves in the figure are regression curves.

Sequential water extraction

Figure 2 shows the relationship between P_0 and WEP or WEP+NaHCO3 P. As Pierre (2005) indicated, WEP was well correlated with P_0 (r=0.920, p<0.001). However, slope of liner regression was 0.53, indicating

WEP by sequential chemical fractionation method (materials to water ratio of 1: 200) cannot evaluate all of P which has potential solubility to water. The underestimate of soluble P may occur if WEP extraction at low material/water ratio (1: 10, 1: 100, or 1: 200) is applied to estimate the P availability of AMCs for crops or the risk of P loss to environment. In the other hand, the sum of WEP and $NaHCO_3$-P was almost corresponded with P_0, indicating $NaHCO_3$-P can be dissolved in water and available for crops.

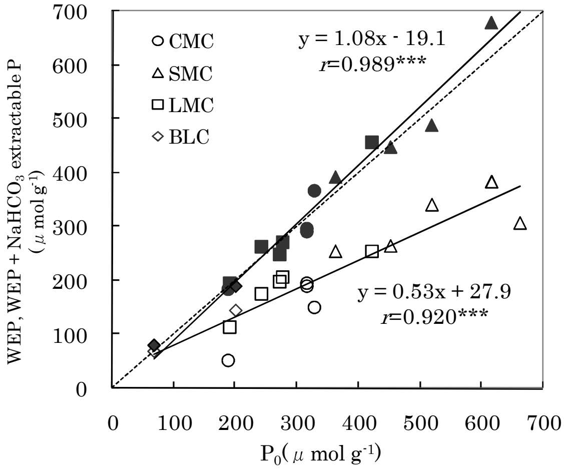

Figure 2. The relationships between P_0 values and WEP (white symbols) or WEP+$NaHCO_3$ extractable P (black symbols). Dashed line indicates the 1:1 relation.

The estimation of WEP compounds

There was strong, positive (r=0.854, p<0.001) correlation between Mg_0 and P_0. The results indicate that the amount of labile P in AMCs is controlled by magnesium solubility. In the other hand, Ca solubility was negatively correlated with P_0 (Figure 3).

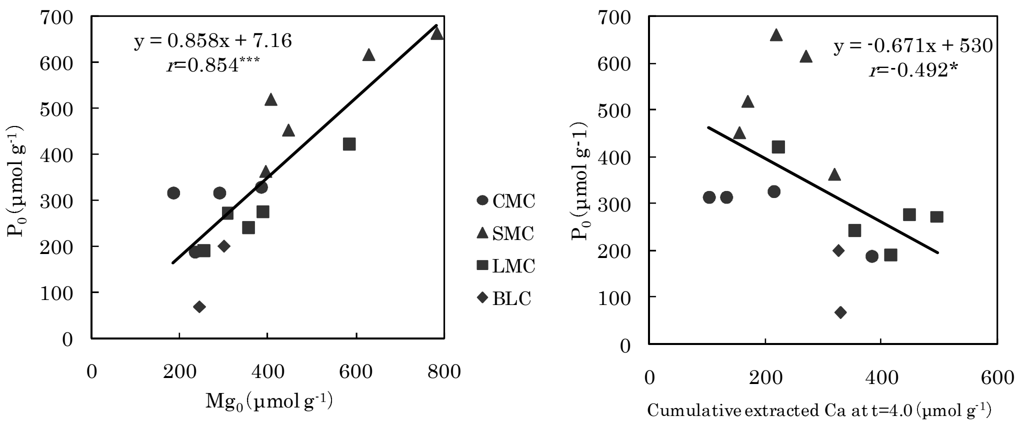

Figure 3. The relationship between P_0 and Mg_0 or Cumulative extracted Ca at t=4.0 (Ca(4.0)).

P compounds in SMC

Figure 4 shows X-ray diffraction pattern of SMC before and after water extraction. The result indicates WEP compound in SMC was magnesium ammonium phosphate (MAP).

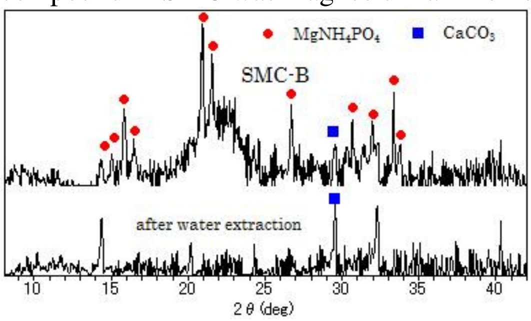

Figure 4. Changes of X-ray diffraction pattern of a SMC after water extraction.

Conclusion

This study was conducted to clarify the potential water solubility of P in AMCs and estimate phosphate compounds which are labile and available for crops. The value of P_0 which was readily dissolved, was greatest in SMC, followed by LMC, CMC, and BLC. The P_0 values were greater than WEP by sequential chemical fractionation (material to water ratio of 1: 200), and corresponded to the sum of WEP and $NaHCO_3$-P, indicating $NaHCO_3$-P can be dissolved to water and available for crops. There was positive, significant correlation between Mg_0 and P_0 (r=0.854, p<0.001). It was implicated that most of labile P in manure compost were magnesium phosphates which are soluble in water. X-ray diffraction pattern indicated magnesium phosphate in SMC was MAP. To understand more details of solubility and availability of P in manure composts, rainfall experiment or cultivation test is needed.

References

Frossard E, Tekely P, Grimal JY (1994) Characterization of phosphate species in urban sewage sludges by high-resolution solid-state ^{31}P-NMR. *European Journal of Soil Science* **45,** 403-408.

Hedley MJ, Stewart JWB, Chauhan BS (1982) Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Science Society of America Journal* **46,** 970-976.

Kleinman PJA, Sharpley AN, Wolf AM, Beegle DB, Moor PA (2002) Measuring water extractable phosphorus in manure. *Soil Science Society of America Journal* **66,** 2009-2015.

Pierre GM, Walter MT, Steenhuis TS (2005) Simple models for phosphorus loss from manure during rainfall. *Journal of environmental Quality* **34,** 872-876.

Sharpley AN, Moyer B (2000) Phosphorus forms in manure and compost and their release during simulated rainfall. *Journal of environmental Quality* **29,** 1462-1469.

Sims JT, Simard RR, Joern BC (1998) Phosphorus loss in agricultural drainage: Historical perspective and current research. *Journal of environmental Quality* **27,** 277-293.

Toor GS, Hunger S, Peak JD, Sims JT, Spark DL (2006) Advances in the characterization of phosphorus in organic wastes: environmental and agronomic applications. *Advances in Agronomy* **89,** 1-72.

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