

Sorption of Lead in Animal Manure Compost: Contributions of Inorganic and Organic Fractions

Masahiko Katoh · Wataru Kitahara · Takeshi Sato

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Abstract This study investigated lead (Pb) sorption by inorganic and acid-non-soluble organic fractions, which were physicochemically fractionated from cattle, swine, and poultry composts, to understand how Pb is immobilized by animal manure compost and to evaluate the contribution of each fraction in Pb immobilization. Pb was predominantly sorbed on humic acid in the acid-non-soluble organic fraction; on the other hand, Pb sorption by the inorganic fraction could be attributed to the precipitation of Pb compound minerals such as lead phosphate and lead sulfate. The amounts of Pb sorbed on the inorganic fraction were 4.1–8.1 times higher than that sorbed on the acid-non-soluble organic fraction. The amount of Pb sorbed on the inorganic fraction and acid-non-soluble organic fractions was 37–60 and 19–43 %, respectively, of the total Pb sorbed. The results of this study clearly show that the inorganic fraction in the composts effectively immobilizes Pb. Furthermore, the high content of the inorganic components, particularly phosphorus, is important in Pb immobilization.

Keywords Animal manure compost · Inorganic component · Lead immobilization · Organic component · Phosphorus

1 Introduction

Contamination by heavy metals, which are common in soil throughout the world, poses a potential risk to human and animal health as well as plant growth owing to their migration through the soil profile into groundwater and their uptake by root systems. To reduce the mobility and bioavailability of heavy metals in soil, various remediation techniques have been applied to contaminated soil.

Lead (Pb) contamination is an extensive problem all around the world, particularly in farmlands (Chen et al. 2006; de la Fuente et al. 2008; Madejón et al. 2006), mines (Alvarenga et al. 2009; Walker et al. 2003; Walker et al. 2004), shooting ranges (Cao et al. 2009; Honda et al. 2007), and industrial plants (Boisson et al. 1999; Chiu et al. 2009); Pb is one of the most harmful and common soil contaminants. Soil remediation techniques such as excavation and transportation to landfill sites and chemical soil washing are often applied to Pb-contaminated soil. However, immobilization, which can transform heavy metals into a chemically stable state, is a more appropriate approach for Pb contamination in soil from shooting ranges and mines, where contamination is more extensive and asset values are very low. Accordingly, immobilization has been investigated as a soil

M. Katoh (✉) · W. Kitahara · T. Sato
Department of Civil Engineering, Gifu University,
1-1 Yanagido, Gifu 501-1193, Japan
e-mail: mkatoh@gifu-u.ac.jp

Present Address:
W. Kitahara
In Situ Solutions Co., Ltd.,
2-5-2 Kandasudamachi, Chiyoda-ku, Tokyo 101-0041, Japan

remediation technique in shooting ranges and mine sites (Boisson et al. 1999; Cao et al. 2009; Chiu et al. 2009).

Organic waste materials are widely used as soil amendments because they have many rich nutrients that can be supplied to plant and soil biota. These materials are composed of organic and inorganic components. The organic component such as humic acid (Logan et al. 1997; Stevenson 1976) and inorganic component such as phosphorus (Zhang and Ryan 1998) are present in organic waste materials, and they both have a high affinity for Pb. Thus, organic waste materials can be used as Pb immobilization amendments. Alvarenga et al. (2008) and Brown et al. (2003) suggested that the addition of organic waste material into Pb-contaminated soil reduces Pb mobility and bioavailability. Moreover, its application appears to improve plant growth in the soil because of the reduction in Pb bioavailability (Farrell and Jones 2010). The improvement in plant growth by the addition of organic waste materials is expected to induce lower mobility of Pb in soils as compared with inorganic amendments because plant cover on the soil surface would reduce the level of surface runoff and water percolation through the soil profile (de la Fuente et al. 2008).

The degree to which the mobility and bioavailability of heavy metals is reduced by the application of organic waste materials depends on both the type of organic waste (Farrell et al. 2010; Narwal and Singh 1998; van Herwijnen et al. 2007) and heavy metal present (Karaca 2004). Moreover, the physicochemical characteristics of organic waste materials, such as quality (Clemente and Bernal 2006; Doelsch et al. 2010; Gardea-Torresdey et al. 1996) and quantity (Karaca 2004) of organic component, salt content (Basta et al. 2001; Farfel et al. 2005; Ruttens et al. 2006), degree of maturity (Clemente et al. 2006; Walker et al. 2003), and level of pH correction (Farrell and Jones 2010; Walker et al. 2004), are important factors affecting the immobilization of Pb in soil. For example, Clemente et al. (2006) and Walker et al. (2003) reported that the application of manure could reduce heavy metal bioavailability and increase the level of zinc (Zn) and Pb fixation compared with that of compost. In addition, increased soil pH due to the alkalinity of organic waste materials may promote the precipitation of Pb carbonate and/or hydroxide minerals, which is expected to reduce the Pb solubility in soil, particularly in acidic soil (Walker et al. 2004).

The effectiveness of Pb immobilization using organic waste materials has been thoroughly investigated, and the

characteristics of each organic waste material on immobilization have been also evaluated (Clemente and Bernal 2006; Farrell et al. 2010; Karaca 2004; Narwal and Singh 1998; van Herwijnen et al. 2007). Furthermore, the mechanism of immobilization has been discussed (Clemente et al. 2006; Walker et al. 2003). However, how organic waste materials react with Pb is not fully understood. Also, which components in organic waste materials sorb Pb is not understood quantitatively. In particular, the contribution of organic and inorganic components of organic waste materials to Pb immobilization and their sorption mechanisms have not been fully elucidated. Thus, it is necessary to understand the abovementioned factors. Understanding the mechanisms of Pb immobilization is important because although organic waste materials could have low cost and be reliable immobilization amendments, some of them may rather increase the solubility of heavy metals (van Herwijnen et al. 2007). Thus, from this perspective, a suitable physicochemical component of organic waste material should be identified to facilitate Pb immobilization.

The principal source of organic waste material in Japan is animal manure compost. However, little information is available on the effectiveness of animal manure composts for the immobilization of heavy metals and rehabilitation of organisms (Chen et al. 2010; Doelsch et al. 2010). Furthermore, few studies have investigated the effectiveness of different types of animal manure compost for the immobilization of heavy metals, particularly Pb (Sato et al. 2010).

We investigated Pb sorption on inorganic and acid-non-soluble organic fractions that were physicochemically fractionated from cattle, swine, and poultry composts. These materials are composts mainly used in Japan. We aimed (1) to understand the mechanisms and quantitatively evaluate the contribution of inorganic and acid-non-soluble organic fractions in animal manure compost in Pb sorption and (2) to identify the optimal chemical composition of animal manure compost for Pb immobilization.

2 Materials and Methods

2.1 Preparation of Animal Manure Compost and Fractions

Four commercial animal manure composts were used in this study: one cattle manure compost (Cattle), one

swine manure compost (Swine), and two poultry manure composts (Poultry 1 and Poultry 2). The compost samples were air dried, passed through a 0.425-mm sieve to get the same particle size, and subjected to chemical analysis. The air-dried compost samples were stored in a refrigerator at -25°C before they were analyzed.

The compost samples were combusted at 600°C for 2 h. The residue after combustion was collected, weighed, and used as the inorganic fraction (Inorg) in the animal manure compost sample. The compost samples were subjected to extraction with 1 M HCl (1:50 solid/liquid ratio) for 1 h to remove almost all inorganic and acid-soluble organic fractions in the animal manure compost (Frossard et al. 1994). After centrifugation at 5,000 rpm for 5 min, the residue was collected, washed three times using ultrapure water, freeze dried, and weighed. This fraction represented the acid-non-soluble organic fraction in the compost sample. To confirm the presence of inorganic components in the acid-non-soluble organic fraction, a sample was combusted at 600°C and the mineral composition of the residue of the acid-non-soluble organic fraction in the Cattle compost was determined using an X-ray diffractometer (XRD; Ultima IV Rigaku Co. Japan).

The weight ratios of each fraction were calculated on the basis of the weights of the compost samples and residues after combustion or extraction.

The pH values of the compost samples were measured in ultrapure water using a pH meter (MM-60R DKK-TOA Co. Japan). The water-soluble organic carbon (WSOC) and acid-soluble organic carbon (ASOC) contents of the compost sample were extracted using ultrapure water and 1 M HCl (1:10 compost/solution ratio), respectively. The extracted solutions were passed through a $0.45\text{-}\mu\text{m}$ filter and analyzed to determine the carbon concentration using a total organic carbon (TOC) analyzer (TOC-V_{WS} Shimadzu Co. Japan). The organic matter (OM) contents of the compost samples were determined by combustion at 600°C for 2 h. The total elemental [calcium (Ca), magnesium (Mg), potassium (K), iron (Fe), manganese (Mn), phosphorus (P), Pb, cadmium (Cd), copper (Cu), and Zn] contents of the compost sample and inorganic fraction were determined by acid digestion with HNO_3 and HCl using a microwave. The digested solutions were passed through the $0.45\text{-}\mu\text{m}$ filter and analyzed to determine the elemental concentrations by inductively coupled plasma optical emission spectrometry (ICP-OES; ULTIMA 2

HORIBA Ltd., Japan). The total carbon (C) and nitrogen (N) contents of the compost sample and acid-non-soluble organic fraction were determined using a nitrogen and carbon (NC) analyzer (MT-6 Yanaco New Science Inc., Japan). The mineralogical composition of the inorganic fraction was determined by XRD. The acid detergent fiber (ADF) content of the acid-non-soluble organic fraction was determined according to Method 973.18 of the Association of Official Analytical Chemists (AOAC) (AOAC 1997). The C content of ADF was determined using the NC analyzer, and the ADF-C content in the acid-non-soluble organic fraction was calculated. The C content of humic acid and fulvic acid was determined according to the method described as follows. Humic acid and fulvic acid in the acid-non-soluble organic fraction were extracted from the acid-non-soluble organic fraction using 0.5 M NaOH (1:15 solid/liquid ratio, 16 h). Humic acid was obtained by acidification (pH <2), centrifugation, filtration, and freeze drying. The C content of humic acid was determined using the NC analyzer. The C content of fulvic acid was determined by measuring the C concentration in the filtrate using the TOC analyzer.

2.2 Pb Sorption (pH 5) on Animal Manure Compost

To a 50-ml polypropylene tube with three replicates, 5 mM KNO_3 (20 ml) and a compost sample (0.1 g) were added. The pH was adjusted to 5 using 0.1 M HNO_3 . Subsequently, 5 mM KNO_3 (20 ml; pH 5), which included Pb as PbNO_3 at a concentration of $3,000\text{ mg l}^{-1}$, was added to the tube. Thus, the Pb concentration and solid/liquid ratio in the sorption experiment were $1,500\text{ mg l}^{-1}$ and 1:400, respectively.

In a preliminary test, the sorption isotherm of Pb by all compost samples fitted well to the Langmuir isotherm and the level of Pb sorbed reached equilibrium with the initial Pb concentration ($1,500\text{ mg l}^{-1}$) for all compost samples.

After shaking for 24 h and centrifugation at 8,900 rpm for 10 min, the suspension was passed through the $0.45\text{-}\mu\text{m}$ filter and analyzed to determine concentrations of Pb and dissolved organic carbon (DOC) by using the ICP and TOC analyzers, respectively. The tube without Pb was also prepared following the procedure described above, and the DOC concentration without Pb was determined. The Pb-sorbed residue was collected. The residue was washed three times

using ultrapure water, freeze-dried, and analyzed to determine the crystalline Pb structure by XRD.

2.3 Pb Sorption (pH 5) onto Each Fraction in Animal Manure Compost

The amount of Pb sorbed on each fraction was determined following the procedure described in Section 2.2, except for Pb concentration. The Pb sorption experiment for the inorganic and acid-non-soluble organic fractions was conducted at 2,000 and 500 mg l⁻¹, respectively. The preliminary test demonstrated that the amount of Pb sorbed on each fraction at each Pb concentration reached equilibrium.

After the experiment, the residue of the inorganic fraction was collected, washed three times using ultrapure water, freeze dried, and analyzed to determine the crystalline Pb structure by XRD.

The contribution of each fraction to the total amount of Pb sorbed on the compost sample was calculated from the amount of Pb sorbed on each fraction and the weight ratio in the compost sample.

2.4 Statistical Analyses

Statistical analyses were performed using JMP ver. 8.0.2 (SAS Institute Inc.). An analysis of variance was used to measure the amount of Pb sorbed on the compost sample and each fraction, as well as DOC dissolution from the compost sample. The differences between the mean values were determined using Tukey's honestly significant difference (HSD) test at the 95 % confidence level.

3 Results and Discussion

3.1 Characteristic of Animal Manure Composts

The chemical properties of an animal manure compost sample are shown in Table 1. The Cattle and Poultry 2 composts had a neutral pH at 6.9, whereas the Swine and Poultry 1 composts had an alkaline pH at 8.0 and 8.5, respectively. The WSOC and ASOC contents of each compost sample were almost the same. The WSOC and ASOC contents were the lowest in the Cattle compost (7.6 and 14 mg g⁻¹, respectively), second lowest in the Swine and Poultry 1 composts, and highest in the Poultry 2 compost (104 and 105 mg g⁻¹, respectively). The ratios of WSOC and ASOC contents to the total C

content in the Cattle compost were lower than those in the other compost samples at 1.8 and 3.3 %, respectively. The WSOC and ASOC appeared to be easily decomposable organic carbon, which would have a relatively small molecular weight and be soluble in water and acid. Thus, the Cattle compost probably had the highest degree of maturity in the compost samples because lower contents of these organic components have higher degree of maturity (García et al. 1991). The OM and total C contents showed the same trend; the OM and total C contents were the highest in the Cattle compost (850 and 418 mg g⁻¹, respectively), second highest in the Poultry 2 and Swine composts, and lowest in the Poultry 1 compost (701 and 313 mg g⁻¹, respectively).

The total Ca and P contents in the Swine, Poultry 1, and Poultry 2 composts were higher than those in the Cattle compost. This can be attributed to calcium phosphate included in the feed of swine and poultry. Moreover, in these three compost samples, the total P contents in the Swine and Poultry 1 composts were higher than that in the Poultry 2 compost. The total Pb, Cd, Cu, and Zn contents in all compost samples were negligible, except for the Zn content in the Swine compost, which was present in the feed. Thus, these elements should not be dissolved from the compost when the compost is used as an immobilization amendment in soil. The total Fe and Mn contents in the Cattle and Swine composts were lower than the total Ca, Mg, and P contents. The elemental composition in all compost samples used in this study had average values from domestic composts (Ito et al. 2010; Yamaguchi et al. 2000).

3.2 Characteristic of Inorganic and Acid-Non-Soluble Organic Fractions of Animal Manure Compost

The total elemental constituents of the inorganic fraction are shown in Table 2. All the inorganic fractions from the compost samples had high levels of total Ca, K, and P contents. The total Ca and P contents in the inorganic fraction of the Cattle, Swine, Poultry 1, and Poultry 2 composts were 114, 152, 188, and 215 mg g⁻¹ and 54, 131, 111, and 96 mg g⁻¹, respectively; the total P contents in the inorganic fraction increased in the following order: Swine > Poultry 1 > Poultry 2 > Cattle composts. The total Fe contents of the inorganic fractions from all compost samples were lower compared with the other elements, although all the inorganic fractions contained at least some small amount of Fe. Figure 1 shows the XRD profile of the inorganic fraction. The XRD

Table 1 Chemical properties of animal manure compost (air-dried weight)

Compost	pH	WSOC (mg g ⁻¹)	ASOC	OM	Total										WSOC/TC	ASOC/TC			
					C	N	Ca	Mg	K	Fe	Mn	P	Pb	Cd			Cu	Zn	
Cattle	6.9±0.0	7.6±2.2	14±1	850±18	418±1	15±1	18±11	2±0	11±10	3.1±0.4	N.D. ^c	7.4±0.7	N.D.	N.D.	N.D.	N.D.	N.D.	1.8	3.3
Swine	8.0±0.0	57±7	60±2	747±9	344±2	37±1	50±4	10±1	21±3	2.5±0.2	0.3±0.0	39±2	N.D.	N.D.	N.D.	N.D.	N.D.	0.5±0.3	17
Poultry 1	8.5±0.0	78±1	52±2	701±5	313±3	23±2	64±10	14±3	53±7	N.D.	N.D.	39±5	N.D.	N.D.	N.D.	N.D.	N.D.	25	17
Poultry 2	6.9±0.0	104±2	115±3	774±1	394±5	42±0	61±3	10±0	33±2	N.D.	N.D.	28±1	N.D.	N.D.	N.D.	N.D.	N.D.	26	29

WSOC water-soluble organic carbon, ASOC acid (1 M HCl)-soluble organic carbon, OM organic matter, WSOC/TC or ASOC/TC ratio of WSOC or ASOC to total carbon content, MD not detected (<0.02 µg g⁻¹)

analysis showed the presence of calcium phosphate minerals such as apatite in all inorganic fractions. The peaks of calcium phosphate minerals in the Cattle compost were weaker than those of the other minerals. The peaks of the compounds were stronger in the Swine and Poultry composts than in the Cattle compost. Furthermore, only calcium phosphate minerals were identified in the inorganic fraction of the Swine compost. In addition to calcium phosphate minerals, K salts were identified in the inorganic fraction of the Cattle, Poultry 1, and Poultry 2 composts, while the inorganic fraction of the Cattle compost also contained quartz.

The physicochemical properties of the inorganic fractions were probably different from those of the compost samples because the inorganic fraction was the residue after combustion. An increase in the crystalline form of apatite, which was one of the main components in the compost, was observed after combustion (Furuta et al. 1998), and its higher crystallinity would induce less Pb sorption (Hashimoto and Sato 2007). However, the amounts of Pb sorbed on the apatite before and after combustion for 2 h were 497 and 480 mg g⁻¹, respectively (Kato et al. 2012). The difference between the amounts of Pb sorbed before and after combustion corresponds to 3.4 % of that of Pb sorbed before combustion. Accordingly, the effect of combustion on Pb sorption should be relatively small.

The chemical properties of the acid-non-soluble organic fraction are shown in Table 3. The total C contents in the acid-non-soluble organic fraction of the Cattle, Swine, and Poultry 1 composts ranged from 452 to 475 mg g⁻¹, whereas that of the Poultry 2 compost was as high as 505 mg g⁻¹. The ADF-C content in the acid-non-soluble organic fraction was the highest in the Cattle compost at 344 mg g⁻¹ and second highest in the Poultry 1 compost. Therefore, the acid-non-soluble organic fraction of the Cattle compost had a relatively higher maturity compared with the other compost samples because the ADF content, which includes cellulose and lignin (Dong et al. 2013), is thought to be an indicator for compost maturity. The acid-non-soluble organic fraction of the Poultry 1 compost had a high humic acid C content, whereas that of the Swine and Poultry 2 composts had a high fulvic acid C content.

The acid-non-soluble organic fraction used herein was the residue of 1 M HCl extraction. It is known that 1 M HCl extraction can remove almost all phosphate species (Frossard et al. 1994), which are the most stable inorganic components in the compost. Hence, 1 M HCl extraction

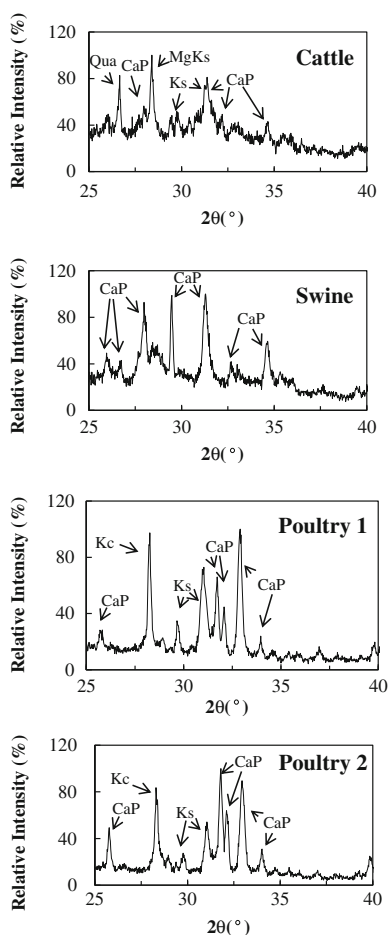
Table 2 Total elemental components in inorganic fraction of animal manure compost (air-dried weight)

Compost	Total				
	Ca (mg g ⁻¹)	Mg	K	Fe	P
Cattle	114±5	29±2	77±4	16±0	54±4
Swine	152±2	44±2	53±1	7±0	131±1
Poultry 1	188±3	48±2	170±4	4±0	111±4
Poultry 2	215±3	40±1	131±2	7±0	96±4

could remove almost inorganic components in the compost. However, to confirm that the entire acid-non-soluble fraction of the compost samples used herein

consisted of only organic components, the acid-non-soluble organic fraction was combusted. The results show that over 98 % of the acid-non-soluble organic fraction of the Swine, Poultry 1, and Poultry 2 composts was combusted (data not shown), indicating that almost all the acid-non-soluble organic fraction of these compost samples contained organic components. Ninety-five percent of the acid-non-soluble organic fraction of the Cattle compost was combusted. The XRD profile of the combusted residue of the acid-non-soluble organic fraction of the Cattle compost shows that quartz was only identified in the residue (data not shown). The amount of Pb sorbed on quartz is 3.9 mg g⁻¹ (Chiron et al. 2003). Hence, if the acid-non-soluble organic fraction of the Cattle compost included 5 % quartz, the amount of Pb sorbed would be estimated as 0.2 mg g⁻¹, suggesting that the contribution of the residue of the acid-non-soluble organic fraction to Pb sorption by the acid-non-soluble organic fraction was considerably small. These results demonstrate that the organic component of the acid-non-soluble organic fraction sorbed Pb. In the compost samples, 1 M HCl extraction might alter the chemical properties of the organic component in the compost samples. However, Pb would mainly sorb on the surface functional groups of organic components (Gardea-Torresdey et al. 1996), and their chemical property significantly depends on the solution pH. Hence, the effect of 1 M HCl extraction on Pb sorption should be relatively small because all Pb sorption experiments in this study were conducted under constant pH.

The weight ratios of each fraction are shown in Table 4. The ratios of the acid-non-soluble organic fraction were higher than those of the inorganic fraction in all compost samples. At 15 %, the ratio of the inorganic fraction of the Cattle compost was lower than that of the other composts. The ratio of the inorganic fraction of the Poultry 1 compost was 30 %, the highest among the compost samples. The ratios of the acid-non-soluble organic fraction of the Swine, Poultry 1, and Poultry 2



CaP: Calcium phosphate minerals ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$, $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_2\text{P}_2\text{O}_7$), Ks K_2SO_4 , MgKs $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$, Kc KCl , Qua quartz

Fig. 1 X-ray diffraction patterns of inorganic fraction of animal manure compost before Pb sorption. *CaP* calcium phosphate minerals ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$, $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_2\text{P}_2\text{O}_7$), *Ks* K_2SO_4 , *MgKs* $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$, *Kc* KCl , *Qua* quartz

Table 3 Chemical properties of acid-non-soluble organic fraction in animal manure compost (air-dried weight, milligrams per gram)

Characteristic	Cattle	Swine	Poultry 1	Poultry 2
Total C	452±5	461±2	475±1	505±0
ADF-C	344±7	126±3	196±1	132±1
Humic acid C	25±9	97±8	160±18	87±7
Fulvic acid C	52±6	136±15	72±7	117±13

ADF-C acid detergent fiber

composts ranged from 63 to 66 %, whereas that of the Cattle compost was 84 %. The high ratio of the acid-non-soluble organic fraction in the Cattle compost probably caused the overall high contents of C and OM. These results demonstrate that the weight ratios of the inorganic and acid-non-soluble organic fractions differed with the type of animal manure compost.

The unknown fraction was consistent with the fraction not recovered by the fractionation procedure used herein. The ratio of the unknown fraction of the Cattle compost was 1 %, clearly showing that almost all components of the compost were fractionated into either inorganic or acid-non-soluble organic fractions. In contrast, the ratios of the unknown fraction of the Swine, Poultry 1, and Poultry 2 composts were 9, 7, and 14 %, respectively, and were therefore not accounted for by the fractionation procedure. The acid-non-soluble organic fraction is the residue of 1 M HCl extraction, and some organic components in the compost can be extracted with 1 M HCl (Table 1). The ASOC components of the Cattle, Swine, Poultry 1, and Poultry 2 composts were 1.4, 6.0, 5.2, and 11.5 %, respectively, and these levels were very similar to the weight ratios of the unknown fraction. Thus, the unknown fraction probably consisted of the 1 M HCl extracted organic components.

Table 4 Inorganic and acid-non-soluble organic fractions to animal manure compost weight ratios

Compost	Inorganic ^a (%)	Acid-non-soluble organic ^b	Unknown ^c
Cattle	15±2	84±9	1
Swine	25±4	66±2	9
Poultry 1	30±1	63±4	7
Poultry 2	23±0	63±1	14

Weight ratio of each fraction to animal manure composts

^a Inorganic fraction

^b Acid-non-soluble organic fraction

^c 100 - (inorganic) - (acid-non-soluble organic)

3.3 Pb Sorption on Animal Manure Composts

Figure 2 shows the amount of Pb sorbed on the compost samples. The amounts of Pb sorbed on the Cattle and Poultry 2 composts were 160 and 218 mg g⁻¹, respectively, which were not significantly different. The amounts of Pb sorbed on the Poultry 1 and Swine composts were 294 and 407 mg g⁻¹, respectively; these two compost samples significantly sorbed more Pb than the Cattle and Poultry 2 composts. The highest level of Pb sorbed was found in the Poultry 1 compost. Figure 3 shows the amount of DOC before and after the sorption experiment. The level of DOC in the Cattle compost was the same before and after Pb sorption, whereas those of DOC in the Swine, Poultry 1, and Poultry 2 composts significantly reduced after Pb sorption. The reduction of DOC amount after Pb sorption could be attributed to the reaction of dissolved organic matter (DOM) with Pb ion, which would result in changing the DOM form into insoluble forms. The DOM from the compost contained humic and fulvic acids (Aoyama 1991, 1996). In addition, O'Dell et al. (2007) performed experiments to investigate the binding capacity of Cu and Zn to humic and fulvic acids in the compost and observed the precipitation of the metal-DOM complexes. Thus, herein, the precipitation of Pb and DOM by complexation possibly induced the reduction of DOC amounts after Pb sorption. Figure 4 shows the XRD profiles of the Pb-sorbed compost samples. No peaks were sharp, but the strongest peak existed at around 2θ=30° in all compost samples. These profiles suggest the precipitation of lead phosphate minerals such as pyromorphite by Pb sorption.

3.4 Pb Sorption by Inorganic and Acid-Non-Soluble Organic Fractions of Animal Manure Compost

The amount of Pb sorbed on the inorganic and acid-non-soluble organic fractions is shown in Fig. 5. The amounts of Pb sorbed on the inorganic fraction ranged

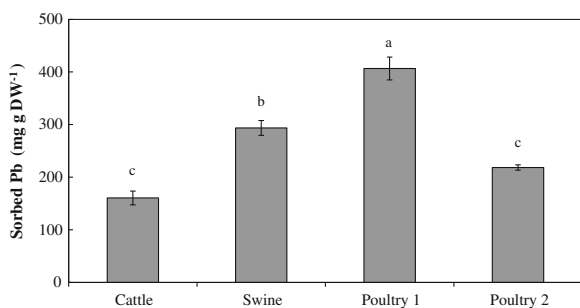


Fig. 2 Pb sorption on animal manure compost (pH 5). The bars indicate the standard error (SE). The different letters indicate significant differences at $P < 0.05$ on the basis of Tukey's HSD test

from 440 to 705 mg g⁻¹ and were 4.1–8.1 times higher than those sorbed on the acid-non-soluble organic fraction irrespective of the type of compost. Moreover, the differences in the amount of Pb sorbed on the acid-non-soluble organic fraction were smaller than those of the inorganic fraction. These results indicate that the inorganic fraction was able to sorb Pb more effectively than the acid-non-soluble organic fraction did, suggesting that compost containing considerable inorganic components can immobilize Pb in soil.

At 143 mg g⁻¹, the amount of Pb sorbed on the acid-non-soluble organic fraction of the Poultry 1 compost was higher than those of the other samples (81–84 mg g⁻¹) and was not related to the total C contents in the acid-non-soluble organic fraction. These results suggest that Pb was probably sorbed on the specific sites of the acid-non-soluble organic components. The Poultry 1 compost had the highest humic acid C contents. The application of humic acid to soil causes reduction in Pb solubility (Clemente and Bernal 2006). Furthermore, humic acid should sorb heavy metals from soil solution (Gardea-Torresdey et al. 1996). Therefore, the surface

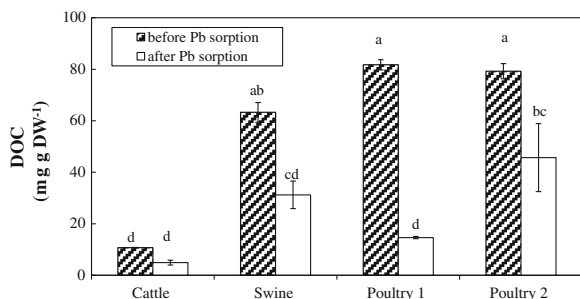


Fig. 3 Dissolved organic carbon (DOC) from animal manure compost before and after Pb sorption (pH 5). The bars indicate the SE. The different letters indicate significant differences at $P < 0.05$ on the basis of Tukey's HSD test

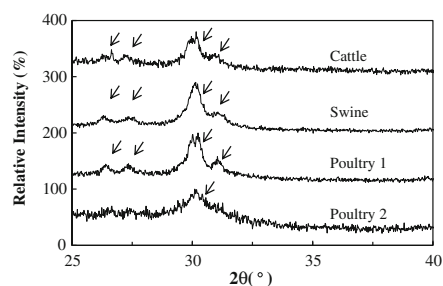


Fig. 4 X-ray diffraction patterns of Pb-sorbed animal manure compost. The arrows indicate the peaks of lead phosphate minerals such as pyromorphite

complexation of Pb with humic acid in the acid-non-soluble organic fraction probably caused the high Pb sorption in the Poultry 1 compost. The ADF includes cellulose and lignin (Dong et al. 2013), both of which are known to be heavy metal sorbers (Low et al. 2004). However, the level of Pb sorption by the acid-non-soluble organic fraction of the Cattle compost, which had lower humic acid C and higher ADF-C contents, was the same as those in the Swine and Poultry 2 composts. Hence, the contribution of cellulose and lignin to Pb sorption would be relatively low. From these results, Pb sorption in the acid-non-soluble organic fraction should occur predominantly by the reaction of Pb with humic acid. In addition, that the amount of Pb sorption by the acid-non-soluble organic fraction was noticeably low, and the differences in Pb sorption on the different types of compost were smaller than those by the inorganic fraction.

The amount of Pb sorbed on the inorganic fraction of the Swine compost was the highest at 705 mg g⁻¹, followed by the Poultry 1 compost (588 mg g⁻¹)

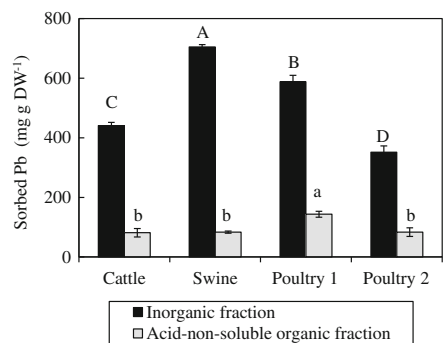
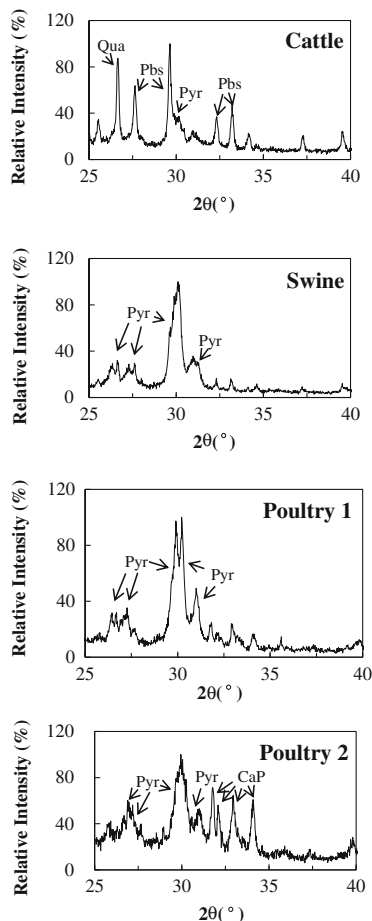


Fig. 5 Pb sorption on inorganic and acid-non-soluble organic fractions in animal manure compost (pH 5). The bars indicate the SE. The different letters in the same fraction indicate significant differences at $P < 0.05$ on the basis of Tukey's HSD test

(Fig. 5). The XRD profiles of the Pb-sorbed inorganic fraction showed the presence of only lead phosphate minerals such as pyromorphite in the Swine and Poultry 1 composts (Fig. 6). Moreover, as mentioned earlier, the XRD profiles of the Pb-sorbed compost sample suggest the precipitation of lead phosphate minerals (Fig. 4). The reaction of P with Pb induced the precipitation of pyromorphite (Cao et al. 2008), which has a very low solubility product ($\log K_{sp} = -25.05$) (Miretzky and Cirelli 2008). Therefore, the high amount of P in the inorganic fraction of the Swine and Poultry 1 composts might have caused the high level of Pb sorption. Many studies have reported that Pb solubility is decreased by



CaP: Calcium phosphate minerals ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$, $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_2\text{P}_2\text{O}_7$), Pyr: $\text{Pb}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$, Pbs: PbSO_4 , Qua: quartz

Fig. 6 X-ray diffraction patterns of inorganic fraction in animal manure compost after Pb sorption. CaP calcium phosphate minerals ($\text{Ca}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$, $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_2\text{P}_2\text{O}_7$), Pyr $\text{Pb}_5(\text{PO}_4)_3(\text{OH}, \text{F}, \text{Cl})$, Pbs PbSO_4 , Qua quartz

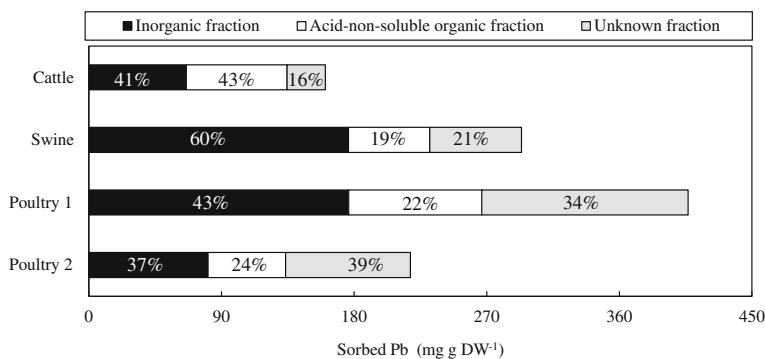
its reaction with P in composts; however, this study revealed that the reaction between Pb and P in the composts induced the precipitation of Pb phosphate minerals such as pyromorphite due to their crystal structure.

The inorganic fraction of the Cattle compost had a low P content as compared with that of the Poultry 2 compost (Table 2); however, it was able to sorb much more Pb. Lead phosphate minerals were identified in the Pb-sorbed inorganic fraction of both the Cattle and Poultry 2 composts. However, lead sulfate was also identified in the inorganic fraction of the Cattle compost, and this would be attributed to the reaction of Pb with sulfate because the inorganic fraction of the Cattle compost included potassium sulfate minerals before Pb sorption. However, only lead phosphate minerals were identified in the inorganic fraction of the Poultry 2 compost, although it also contained sulfate minerals. The precipitation of pyromorphite would only occur with the Poultry 2 compost, which had considerable P content, because the application of P amendment to lead sulfate in solution caused the precipitation of pyromorphite, which is more chemically stable (Cao et al. 2008). Pb sorption by Fe oxides in the inorganic fraction appeared to be another Pb sorption mechanism (Baghaie et al. 2011). They conducted a Pb sorption experiment using cattle manure compost with chemically removed Fe oxides, and they suggested that Fe oxides greatly affected Pb sorption on the compost sample. The inorganic fraction of the Cattle compost had the highest Fe contents, but the amount of Pb was lower than that sorbed on the Swine and Poultry 1 composts. This result strongly suggests that the contribution of Fe oxides in the compost sample to Pb sorption was smaller than that to the precipitation of Pb compound minerals; the presence of Fe oxides in the compost sample would not prevent the precipitation of Pb compound minerals.

3.5 Contribution of Inorganic and Acid-Non-Soluble Organic Fractions of Animal Manure Compost to Pb Sorption

Figure 7 shows the contribution of each fraction to the total amount of Pb sorbed calculated on the basis of the amount of Pb sorption (Fig. 5) and weight ratio (Table 4). The contributions of the inorganic fraction in the Cattle, Swine, Poultry 1, and Poultry 2 composts were 41, 60, 43, and 37 %, respectively, and were higher than the weight ratios of the inorganic fraction. This estimation

Fig. 7 Relative levels of Pb sorbed by inorganic, acid-non-soluble organic, and unknown fractions of animal manure composts. The values were calculated from the amount of Pb sorption (Fig. 4) and weight ratio (Table 2). The percentages indicate distribution ratio to Pb sorption on animal manure compost



suggests that in spite of their low content, the inorganic components in the compost were able to effectively sorb Pb despite the lower content of inorganic fraction. In contrast, the contributions of the acid-non-soluble organic fraction in the Cattle, Swine, Poultry 1, and Poultry 2 composts were 43, 19, 22, and 24 %, respectively. Thus, the effectiveness of Pb sorption by the acid-non-soluble organic fraction in the compost sample was lower than that of the inorganic fraction. Moreover, the relative effectiveness of the inorganic and acid-non-soluble organic fractions differed depending on the type of compost. The unknown fraction, which is consistent with the fraction not recovered by the inorganic and acid-non-soluble organic fractions, would contain 1 M HCl soluble organic component. Therefore, the relationship between the amount of reduction in the DOC before and after Pb sorption (Fig. 3) and the amount of Pb sorbed on the unknown fraction was investigated (Fig. 8); a strong positive correlation was found ($r^2 = 0.953^*$). This relationship clearly suggests that 1 M HCl soluble organic components in the compost were responsible for the sorption of Pb on the unknown

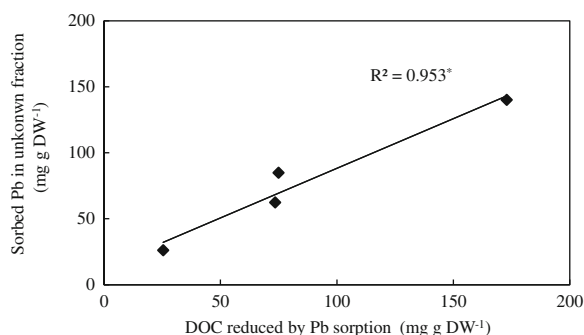


Fig. 8 Relationship between DOC reduced by Pb sorption and sorbed Pb in unknown fraction. Reduced DOC was calculated from Fig. 3, and differences of DOC were calculated before and after Pb sorption

fraction, as described in Section 3.2. The contributions of the unknown fraction in the Cattle, Swine, Poultry 1, and Poultry 2 composts were 16, 24, 34, and 39 %, respectively, and they were higher than those of the acid-non-soluble organic fraction in some compost samples. Accordingly, Pb sorption by 1 M HCl soluble organic components would be more effective for the acid-non-soluble organic fraction in compost. However, 1 M HCl soluble organic components would be readily decomposable (Paré et al. 1998). The compost with lower ASOC and WSOC contents (having a high degree of maturity as mentioned in Section 3.1) should be suitable as immobilization amendments because Pb-sorbed on decomposable organic components is likely to cause Pb dissolution with its decomposition when the compost is added to soil as an amendment.

The results show that the contribution of the inorganic and acid-non-soluble organic fractions differed depending on the types of compost. In addition, the effectiveness of the inorganic fraction to sorb Pb was considerably higher than that of the acid-non-soluble organic fraction. Therefore, the compost with high amount of inorganic component, particularly P, would be suitable as an immobilization amendment. Furthermore, the compost with a lower amount of water-soluble and acid-soluble organic components would also be suitable as a Pb immobilization amendment.

4 Conclusions

The fractionation procedure used recovered almost 100 % of cattle compost, whereas it did not recover all of the swine and poultry composts. The fraction not recovered consisted of a 1 M HCl soluble organic fraction. The differences in the amount of Pb sorbed on the acid-non-soluble organic fraction according to the type

of compost were substantially small. The amounts of Pb sorbed by the inorganic fraction were 4.1–8.1 times higher than those sorbed by the acid-non-soluble organic fraction. Pb sorbed on the inorganic fraction was positively attributed to the precipitation of Pb compound minerals such as lead phosphate and lead sulfate. Moreover, the high amounts of P in the inorganic fraction presumably caused higher amounts of Pb sorption. The amount of Pb sorbed by the inorganic fraction corresponded to 37–60 % of the total Pb sorbed, which was higher than that of the acid-non-soluble organic fraction (19–43 %). Furthermore, the unknown fraction, which consisted of 1 M HCl soluble organic components, appeared to have higher amounts of sorbed Pb than the acid-non-soluble organic fraction.

In conclusion, the relative amounts of Pb sorbed by the inorganic and acid-non-soluble organic fractions in the compost differed according to the type of animal manure. Based on the results, the compost with high inorganic fraction content, particularly P, and lower amount of acid-soluble organic fraction may be useful as a Pb immobilization amendment.

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