Dynamic of lead speciation in sewage sludge composting

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Abstract A large-scale sewage sludge composting experiment was conducted to develop an understanding of changes that occur to Pb chemical speciation, distribution and bio-availability during the course of composting. The four-stage Tessier sequential extraction method was employed to investigate the dynamics of heavy metal Pb speciation (exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and sulphides, residual) during the course of sewage sludge composting. The concentrations of the total Pb and the five Pb fractions concentrations were increased during the whole stage of compost. However, the percentages of Pb distribution with respect to total Pb were changed in the following manner: exchangeable, bound to Fe-Mn oxides and bound to carbonates Pb with respect to total Pb were increased, while the percentages of bound to organic matter and sulphides, and residual Pb with respect to total Pb were decreased during composting. The data showed that the quantity of Pb in the less toxic portion, such as consisting of organic matter and sulphides bound and residual Pb, was increased, and that the contamination and bio-availability of heavy metal Pb in sewage sludge was reduced during the composting process.

Keywords Compost; heavy metal; Pb; sewage sludge; speciation

Introduction China produced $2.30 \times 10^9$ tons municipal wastewater by 2001 (Yu, 2003) which, if not collected and treated, can be a significant health and pollution hazard (Veeken and Hamelers, 2002). The requirements of China’s laws dealing with waste water quality has led to the construction of more than 400 wastewater treatment plants, with a total treatment capacity of $2.53 \times 10^7$ t/d (Chen et al., 2003). With the cities rapidly expanding in size, many more waste water treatment plants will be built to handle the increasing quantities of waste water. Around 0.02% (v/v) sludge is produced after sewage treatment. It is thus urgent and necessary to deal with the sewage sludge with the new central wastewater treatment plants founded. This will lead to additional environmental problems unless economical and safe techniques are available for the disposal or use of the sludge materials.

Landfill, incineration and land application are the three main ways to deal with the sewage sludge. Landfill can cause groundwater pollution due to leaching and it is difficult to find suitable sites, while incineration can cause air pollution and thus expensive off-gas treatment (Veeken and Hamelers, 1999). Compared to landfill and incineration, land application is a preferred and practical disposal method for sewage sludge in China. Sewage sludge can be applied to arable land to improve soil fertility and soil physical properties. Indeed, this practice is inexpensive and easy to carry out. Sewage sludge is used less and less as raw materials because it releases nitrogen and other elements which can reach underground water or kill plants and because of its bad odor (Korboulewsky et al., 2002). Therefore, sewage sludge undergoes a composting process in order to reduce its hazards. Heavy metals are potential contaminants in sewage sludge that may affect waste treatment and processing, and limit the use of these waste materials as soil amendments. However, most of the sewage sludge contains low levels of
pollutants and therefore meets the strict regulations of the countries concerned (Chen et al., 2003).

Bio-acidification of sewage sludge prior to land application can be used to dissolve and remove a significant fraction of the heavy metals content of the product. However, this process results in a significant loss of the nutrient value of the sewage sludge (Shanableh and Ginige, 1999). Present legislation in different countries limiting the use of sewage sludge in agriculture refers to the total amounts of heavy metals in those wastes and in soils, and recommends that soil pH is to be maintained at 6 or higher (Planquart et al., 1999). The degree of heavy metals hazard to environment is not only related to the total concentration of heavy metals in sewage sludge, but also to their chemical forms (Parkpain et al., 2000). The speciation of a heavy metal is very important for the land application of sewage sludge. Qiao and Ho (1996, 1998) found that the addition of red mud prior to composting not only reduced leachability and plant availability of heavy metals in the compost, but also significantly reduced the levels of metals extractable by acid digestion. Many scientists are addressed in studying the concentrations of heavy metals in the bioavailable portion of sewage sludge, and determining if the heavy metals concentrations are increased or not by composting. Nevertheless, most of them are ignorant of the quantity of variations in the bioavailable forms. There is a dearth of information in the literature regarding the quantity changes of Pb chemical fractions, one of the major concern elements in Chinese sewage sludge, during composting.

In this study, a large-scale composting experiment was conducted to develop an understanding of changes that occur to Pb chemical speciation during the course of composting. The study focused on the influence of composting on Pb chemical speciation, distribution and bioavailability in order to identify if composting can limit or enhance the contamination of Pb.

**Methods**

**Preparation of composting mass**

Dehydrated digested sewage sludge was collected from Beijing Beixiaohe Wastewater Treatment Plant. The moisture content of reactor decreased to about 60% through mixing with CTB bulking agent 1:1 (v/v) (Gao et al., 2002). The pile dimension was 2.5 m × 1.5 m × 1.4 m (length × width × height). The treatment process was controlled by a forced aeration static pile system (CTB Temperature Feedback Control System installed with the soft of compost) and was composted for 32 days. The temperature was automatically monitored with the control system every day. Figure 1 shows the variation of the pile temperature with composting time. The temperature of compost pile steadily increased in the first 6 days until it reached the high temperature stage (50°C). After that the temperature of the pile was

![Figure 1](https://iwaponline.com/wst/article-pdf/50/9/75/419776/75.pdf)
kept between 50°C and 60°C during the next 20 days. On day 26 aeration amount increased by the control system and the pile temperature quickly decreased to 34.6°C in 6 days.

Data collection and chemical analysis
Approximately 200 g of samples were taken from the pile on days 1, 3, 6, 10, 15, 20, 26 and 32 for chemical testing. The compost samples were extracted with purified water at a ratio of solid: water (w/v) of 1:10 by shaking in a bath for 1 h at 25°C. The suspensions were centrifuged at 10,000 rpm and the supernatants were filtered through 0.45-µm membrane filter papers. The following analyses were carried out on the water extracts: pH using a pH meter (REX PHSJ-4A, China); dissolved organic carbon (DOC) concentration was determined by Total Organic Carbon Analyzer (Apollo 9000, USA). The Tessier sequential extraction method used previously in soil science was applied to study metal fraction of the samples (Tessier et al., 1979; Flyhammar, 1998; Illera et al., 2000). The method yields five different solutions: F1, exchangeable (1 mol·l⁻¹ MgCl₂, pH 7); F2, bound to carbonates (1 mol·l⁻¹ NaOAc/HOAc, pH 5); F3, bound to Fe-Mn oxides (0.04 mol·l⁻¹ NH₂OH·HCl in 25% HOAc); F4, bound to organic matter and sulphides (0.02 mol·l⁻¹ HNO₃ in 30% H₂O₂, pH 2; 3.2 mol·l⁻¹ NH₄OAc in 20% HNO₃); and F5, residue fraction (digested with concentrated HNO₃+HClO₄). For total Pb analysis, samples were digested with concentrated HNO₃+HClO₄. The metals were determined with a graphite furnace (Analytik Jena AG, German). All measurements were conducted in triplicate for each sample, and the results are presented as the average of three replicates.

Results and discussion
**pH and DOC**
Figure 2 shows that the pH value of the compost decreased from 6.21 to 5.88 during the initial phase of temperature-increasing. From day 3, the pH value of the compost rose rapidly from approximately 5.88 to 6.53. The pH value was maintained between 6.5 and 6.7 during the high temperature stage until its increase on day 20. At the latter stage of the composting process, the value increased until the pH of the end product reached a maximum value (pH 7.5). Initially, the microorganisms reproduced very rapidly because they had a high abundance of easily-degradable organic matter. The microorganisms produced many organic acids (acetic acid, butyric acid, etc), and the pH value of the compost decreased slowly at the beginning of the temperature increasing stage due to the formation of organic matter (Li and Zhang, 2000). With volatilization of the organic acids which was caused by the pile temperature increase, the pH value of the compost increased from day 3 (Fang and Wong, 1999).

DOC decreased dramatically during the period of temperature-increasing stage and high temperature stage (Figure 3). This was due to microbial oxidation of the most labile forms
of carbon, causing part of the carbon to be given off as CO$_2$ (Garcia et al., 1995). The DOC did not vary much during the temperature-declining stage and remained stable at 5,000 mg.kg$^{-1}$. The composting process typically is divided into two phases: active and curing. The first is characterized by intense microbial activity leading to decomposition of most biodegradable material and organic residue stability. The second is characterized by the conversion of part of the remaining organic material into humic substances (Adani et al., 1997). The stabilization of DOC during the later period was due to the fact that the sewage sludge had already undergone metabolism during the former active stage. Bolton and Evans (1991) reported that dissolved organic matter in leaches of municipal materials is one of the important factors in relation to the solubilization. DOC has the ability to form stable, soluble complexes with heavy metals (Ashworth and Alloway, 2004). This is a potential risk to the environment if the compost is added to soil as soluble organo-metal complexes may be maintained in solution within the soil. The decrease of DOC can reduce the hazards of heavy metals.

**Total Pb concentration**

The direct measurement of Pb gave a recovery of 102%, while the recovery calculated from the sum of the metal fractions using Tessier’s method was only 82% (Ho and Qiao, 1998). The total concentrations of Pb variation with time are shown in Table 1 which was determined by direct measurement of the compost samples and by the sum of the metal fractions in the sequential extractions. The results show the total Pb concentration was steadily increased from 77.1 to 97.3 mg/kg, equivalent to 126.2% of the raw material value. Since the heavy metals are non-biodegradable, the percentage of inorganic matter in contrast to the gross matter tended to increase as the organic matter decomposed.

Composting is the result of the actions of a microbial community, which converts easily-

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**Table 1** Chemical speciation of Pb in sewage sludge during composting

<table>
<thead>
<tr>
<th>Day</th>
<th>F1 (mg/kg)</th>
<th>F2 (mg/kg)</th>
<th>F3 (mg/kg)</th>
<th>F4 (mg/kg)</th>
<th>F5 (mg/kg)</th>
<th>Total* (mg/kg)</th>
<th>Total (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.4</td>
<td>9.38</td>
<td>6.62</td>
<td>4.79</td>
<td>26.8</td>
<td>59.0</td>
<td>77.1</td>
</tr>
<tr>
<td>3</td>
<td>11.8</td>
<td>8.78</td>
<td>6.84</td>
<td>4.93</td>
<td>29.2</td>
<td>61.5</td>
<td>78.2</td>
</tr>
<tr>
<td>6</td>
<td>11.7</td>
<td>9.60</td>
<td>7.19</td>
<td>5.40</td>
<td>31.2</td>
<td>65.1</td>
<td>81.3</td>
</tr>
<tr>
<td>10</td>
<td>12.1</td>
<td>9.69</td>
<td>7.73</td>
<td>5.03</td>
<td>31.1</td>
<td>65.6</td>
<td>82.5</td>
</tr>
<tr>
<td>15</td>
<td>12.1</td>
<td>10.1</td>
<td>7.59</td>
<td>6.04</td>
<td>36.9</td>
<td>72.8</td>
<td>87.9</td>
</tr>
<tr>
<td>20</td>
<td>12.5</td>
<td>9.93</td>
<td>8.00</td>
<td>6.95</td>
<td>39.8</td>
<td>77.1</td>
<td>91.5</td>
</tr>
<tr>
<td>26</td>
<td>12.3</td>
<td>10.0</td>
<td>8.19</td>
<td>7.11</td>
<td>41.9</td>
<td>79.5</td>
<td>94.7</td>
</tr>
<tr>
<td>32</td>
<td>12.4</td>
<td>10.4</td>
<td>8.47</td>
<td>7.97</td>
<td>42.5</td>
<td>81.7</td>
<td>97.3</td>
</tr>
</tbody>
</table>

F1, exchangeable; F2, carbonates-bound; F3, Fe-Mn oxides-bound; F4, organic matter and sulphides-bound; F5, residual; Total*, total Pb concentration calculated from the sum of the metals in sequential extraction fractions; Total, total Pb concentration with direct measurement
degradable organic matter to more stable and humified forms, and to inorganic products under controlled conditions, giving off heat as a metabolic waste product (Reinikainen and Herranen, 2001). It can be concluded that the total concentration of Pb in sewage sludge increased due to a loss of compost weight during the composting and the trend is inevitable. The main task for scientists is to decrease the availability fraction to the stabilization state in order to decrease the bioavailability of the heavy metal.

Dynamic of Pb chemical speciation

The total concentration of a heavy metal is usually used for assessment of hazards of sewage sludge compost application to land. This may be appropriate for the estimation of long-term risks. But it presents some problems for the estimation of short and medium term risks because it cannot provide enough information on the potential mobility and bio-availability of the metals under field conditions. Sequential extraction can provide more information about the chemical speciation of a metal (Illera et al., 2000; Qiao et al., 2003).

Table 1 shows the concentration changes of Pb speciation during the composting process. It was determined that each speciation concentration of Pb was enhanced by composting as a whole. Exchangeable Pb tended to increase from 11.4 to 12.4 mg/kg during the whole composting, and the concentration in end product was 8.0% higher than that of the raw material. Influenced by the changing of pH value, the concentration of carbonates-bound Pb decreased during the initial stage of temperature increasing, but it began to increase slightly after that stage. Acidic environment enhances the mobility of metal in the environment. Metals bound to carbonates are very sensitive to pH changes and they are leached lowering the pH (Perez-Cid et al., 1999). Wong and Fang (2000) conducted experiments to reduce the bioavailability of heavy metals through raising the pH of the compost mass. Fe-Mn oxides-bound Pb increased from 6.62 to 8.47 mg/kg during the composting. Organic matter and sulphides-bound Pb rose from 4.79 to 7.97 mg/kg and was 66.4% higher than that in the raw sludge. The increase in the five fraction concentrations may be attributed to the weight losses of the materials during the composting process through mineralization of organic matter.

Percentage of Pb distribution with respect to total Pb

Using the concentrations of Pb chemical speciation divided by its total concentrations of Pb determined by the sum of the metal in sequential extraction fractions, we could determine the changing trend of the percentage of Pb distribution (Figure 4). In contrast to the changing trend of Pb speciation concentration, the percentage of Pb concentration in fractions with respect to total Pb exhibits a different changing trend. The percentage of the exchangeable Pb fraction decreased dramatically from 19.4% to 15.1%. As the most bioavailable and toxic form, its decrease can reduce its hazards to environment. At the end of the composting, the percentage of carbonates-bound Pb fraction decreased visibly from 15.9% to 12.7%. However, the percentage of the Fe-Mn oxides-bound fraction did not change distinctly. Compared to the other three fractions, the percentage of Pb bound to organic matter and sulphides and residue Pb demonstrated a different pattern of change. As the highest portion of total Pb, the residual Pb accounted for 45.4% of the total quantity in contrast to the composting end product 52.0%. The residue was always the major fraction of Pb during the composting stage.

The relationship between plant available metal and its exchangeable, carbonate and bound to oxides fractions is very close, the metal present in those fractions is considered to be the most available forms for plants. Pb bound to organic matter and residual is considered to be non-available forms for plants. From Figure 4(f), the quantity of the non-bioavailable forms decreased during the composting stage. Hsu and Lo (2001) concluded that metal distribution in different chemical fractions was generally independent of...
composting age and, thus, independent of respective total metal concentrations in the composts. Nevertheless Garcia et al. (1995) found co-compost of the sewage sludge with Cd, Cu, Zn and Ni, there is less risk of metals in the wastes being added to soils being used by plants. Although the total quantity of Pb did not change during the sewage sludge composting, the percentage of Pb fractions increased (or decreased) meaning the total quantity of some fractions of Pb increased (or decreased) relatively.

**Conclusions**

The pH value of the sewage sludge of compost increased and the DOC concentration decreased dramatically during composting. The concentrations of total Pb and exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and sulphides, residual fractions increased during the whole process of composting. Even though the concentration of the most toxic fraction of Pb in the sewage sludge compost was steady increased compared to the raw material concentration, the total amount of the exchangeable Pb was reduced during the composting process. The other two bioavailable fractions, carbonates bound and Fe-Mn oxides bound Pb, had a similar trend to the exchangeable Pb. The percentage of the less toxic portion, consisting of organic matter and sulphides-bound and residual Pb accounted to the total Pb decreased. The bioavailability of heavy metal Pb in sewage sludge was reduced by composting treatment.

**Figure 4** Percentage of Pb distribution with respect to total Pb varied with composting time (a): exchangeable; (b): carbonates-bound; (c): Fe-Mn oxides-bound; (d): organic matter and sulphides-bound; (e): residual; (f): (d)+(e); ** Significance at the $P \leq 0.01$ level ($n = 8$); * Significance at the $P \leq 0.05$ level ($n = 8$)
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References