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Short communication

Total concentrations and fractions of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge from municipal and industrial wastewater treatment plants

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Abstract

Heavy metals are one of the important factors that affect the final disposal of sewage sludge. In this paper, the metal mobility and bioavailability of heavy metals in sewage sludge were studied by using Community Bureau of Reference (BCR) sequential extraction procedure to get more information for the reasonable disposal of sludge. Sewage sludge was collected from five municipal wastewater treatment plants and three industrial wastewater treatment plants. The sludge was examined for and the total concentrations and different chemical fractions of Cd, Cr, Pb, Cu, Ni and Zn. The total metal concentrations of heavy metals in sludge varied greatly. The contents of Zn and Cu were the highest, followed by then Cr, Ni and Pb and the content of Cd was the least. There was no significant difference in total metal concentration between municipal and industrial wastewater treatment plants. Fractions extracted by the BCR sequential procedure were acid soluble/exchangeable, reducible and oxidizable fraction. Sludge pH was found to have profound effect on the chemical fractions of heavy metals. Acidic sludges (Xiamen and Jinlin Petrochemical Group Co., wastewater treatment plant) had higher proportion of the acid soluble/exchangeable fractions than in neutral sludge. In neutral sludges, Pb and Cr were principally distributed in between the oxidizable fraction and the residual fraction; Cu was in the oxidizable fraction; Cd mainly in the residual fraction in municipal wastewater treatment plants and had high percentage of acid soluble/exchangeable and reducible fractions in industrial wastewater treatment plants; Ni and Zn had higher percentage in the acid soluble/exchangeable and the oxidizable fraction.

Keywords: Sewage sludge; Sequential extraction; Fraction; Heavy metals; Wastewater treatment plant

1. Introduction

Sewage sludge contains many organic contaminants (such as PCBs and PAHs), heavy metals and pathogens. Non-hazardous treatments of sewage sludges can degrade parts of the organic pollutants, effectively kill some pathogens, but heavy metals present in sludge cannot be removed by common treatment technologies such as composting, aerobic or anaerobic digestion [1,2]. So the sludge disposal may result in secondary environmental pollution if treated improperly. Among the different ways of sewage sludge disposal, land application is low cost and high effective and has been used widely [3–5]. However, application of sewage sludge may result in heavy metal accumulation in cultivated soils. This fact has received more and more concern in recent years [6–10]. Detailed information on heavy metals present in sewage is necessary before their land application. The threshold values of toxic limits heavy metals in sludge have been set in many countries for their safe disposal to agricultural fields and to reduce their potential risk hazard on agricultural ecological system. Some studies have shown that the available fraction of heavy metals mainly decided the mobility, bioavailability or phytotoxicity of heavy metals in soils [11]. Therefore, the quantification of different chemical fractions of heavy metals in sewage is necessary for information on metal mobility, as well as on their bioavailability or phyto-toxicity.

On the other hand, the source of heavy metals in wastewater, whether domestic or industrial, also has profound effects on the total content as well as chemical fractions of heavy

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metals in sludge. For example, industrial effluents are the predominant source of Cd, Hg, Cr and Ni, while Cu and Zn are mainly of domestic origin, and the major source of Pb may be both surface runoff and domestic wastewater [2]. In China, mainly the domestic wastewater and partly industrial wastewater and surface runoff are used in municipal wastewater treatment plants. Wastewater treatment plants are run by the large scale corporations to treat their effluents before their ultimate discharge into environment. So there might be some differences in total content and chemical fractions of heavy metals in selective sewage sludge samples.

In the present paper, sewage sludge collected from five municipal wastewater treatment plants and three industrial wastewater treatment plants of petrochemical, brew and paper industry was examined for the total concentrations of Cd, Cr, Pb, Cu, Ni and Zn and chemical fractions of heavy metals to get a preliminary assessment for the land application of sewage sludge.

2. Materials and methods

2.1. Collection of sewage sludge samples

Wet anaerobic sludge samples were obtained from selective wastewater treatment plants listed in Table 1. The samples were air-dried, passed through a sieve having openings of 2 mm diameter and stored in dry glass bottles at room temperature. Sludge pH was measured in 1:2.5 sludge and water suspensions. Organic carbon of the sludge samples was determined by ashing at 360 °C for 2 h. Cation exchange capacity (CEC) values were determined following the procedure outlined by Grauer (1992) [12]. Total contents of phosphorus (P) and potassium (K) were determined by ICP-MS (POEMS II, TJA). Some properties of sludges from the selective wastewater plants are presented in Table 2.

2.2. The sequential extraction test and determination of heavy metals

Sequential extraction was performed using the three-step procedure recommended by Community Bureau of Reference (BCR, now Measuring and Testing Programme), in which metals are divided into acid soluble/exchangeable (*F*1), reducible-fraction (*F*2) and oxidizable-fraction (*F*3) [10,11].

Table 1
Sewage sludge collected from selective municipal and industrial wastewater treatment plants

Name and address of wastewater treatment plant	Sample no.	Source of wastewater
Gaobeidian, Beijin	S1	Domestic and industrial
Second wastewater plant of Jinan, Jinan	S2	Domestic and industrial
Taian, Tanan	S3	Domestic and industrial
Suojincun, Nanjing	S4	Domestic and industrial
Xiamen, Xiamen	S5	Domestic and industrial
Jinlin Petrochemical Group Co., Nanjing	S6	Industrial
Jianglin Beer Co. Ltd., Nanjing	S7	Industrial
Jinyinxing Paper Industry Co. Ltd., Nanjing	S8	Industrial

Step one: A half-gram aliquot of sludge was taken in a 50 mL polypropylene centrifuge tube and 20 mL volume of acetic acid (0.11 mol L^{-1}) was added to it. The contents were shaken for 16 h (overnight) at ambient temperature (20 °C) on an end-over-end mechanical shaker operating at 40 rpm. The extract was separated from the solid residue by centrifugation (4000 rpm), decanted into a polyethylene container and stored at 4 °C untill analysis.

Step two: The residue from Step one was slurried with a portion of a 20 mL volume of 0.1 mol L^{-1} hydroxylammonium chloride (adjusted to pH 2 with nitric acid). The extraction procedure described above was followed.

Step three: The residue from Step one was dispersed in 5 mL volume of hydrogen peroxide (8.8 mol L^{-1}) and digested at room temperature for 1 h with occasional shaking. A second 5-mL aliquot of hydrogen peroxide was continued by heating the tube to 85 °C in a water bath for 1 h. The contents were evaporated to a small volume (1–2 mL). Twenty-five milliliter of ammonium acetate (1.0 mol L^{-1}, adjusted to pH 2 with nitric acid) was added to the cool and moist residue, shaken, centrifuged and the extract separated as described for Step one.

Step four: One milliliter each of HNO_3, $HClO_4$ and HF were added to 0.1 g dry sludge samples taken in

Table 2
Physicochemical properties of sludge from the selective municipal and industrial wastewater plants

	pH	CEC (cmol kg^{-1})	Organic carbon (%)	Total N (%)	Total P (g kg^{-1})	Total K (g kg^{-1})
S1	6.8	89.6	46.8	2.6	6.5	5.8
S2	6.7	72.0	25.9	1.9	8.0	12.6
S3	6.4	63.6	39.2	2.0	17.4	7.5
S4	7.4	52.2	42.5	2.6	12.1	8.2
S5	4.4	21.5	25.0	1.6	10.3	12.6
S6	5.9	17.6	56.0	2.5	10.2	6.1
S7	7.7	54.4	26.2	1.9	19.3	3.3
S8	7.4	47.0	44.1	0.4	0.8	2.0
Mean ± S.D.	6.6 ± 1.1	52.2 ± 24.2	38.2 ± 11.4	1.9 ± 0.7	10.6 ± 5.9	7.3 ± 3.9

poly(tetrafluoroethylene) beakers. The contents were heated on a hot plate and evaporated to near dryness. After cooling, the residues were dissolved in 1% HNO_3. The resultant solutions were subsequently used to determine the heavy metals.

A blank was also run at the same time and no detectable contamination was found when aliquots of the sequential extraction reagents were processed and analyzed with the samples. The concentrations of Cd, Cr, Pb, Cu, Ni and Zn in different fractions and the resultant solutions of Step four were determined by ICP-MS (POEMS II, TJA).

2.3. Calculation and statistical analysis

The summation of three fractions was subtracted from the total content to get the content of the residual fraction. All statistical analyses were carried out on the Statistical Package for Social Science (SPSS).

3. Results and discussion

3.1. Physicochemical properties of sludge from selective wastewater plants

The data contained in Table 2 show that the properties of sludge from selective wastewater plants varied widely. The ranges were from 250 to 560 kg^{-1} for organic carbon, 4 to 26 kg^{-1} for total N, 0.8 to 19.3 g kg^{-1} for total P and 2.0 to 12.6 g kg^{-1} for total K. Their contents are similar to or above them in farmyard manure. In China, the mean contents of soil were 10–40 g kg^{-1} for organic matter, 1.0–2.0 g kg^{-1} for total N, 0.44 to 0.85 g kg^{-1} for total P and about 16 g kg^{-1} for total K, respectively [13]. Comparing the contents of sludge with those of soils, the former had higher contents of organic carbon, total N and total P, but lower content of the total K. A survey in 2000 showed that 70–80% of the total cultivated land was lack of enough nutrients and insufficient application of organic fertilizer and excessive utilization of chemical fertilizers had caused the deterioration of farmland quality, the cultivated horizon became thinner and water retention ability decreased [14]. The pH value of sewage sludge varies from 4.4 to 7.7. The CEC values varied from 17.6 to 89.6 cmol kg^{-1}. This sewage sludge has a good manure value.

3.2. Total content of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge

The total contents of Cd, Cr, Pb, Cu, Ni and Zn in sludge presented in Table 3 showed a wide variation of the concentration of heavy metals. In general, these sludge samples had higher contents of Cu and Zn but relatively lower contents of Cr, Ni, Pb and Cd. Similar wide variation in the concentration ranges of heavy metals have been reported by Álvarez et al. [15] and Ščančar et al. [16]. However, the total concentration of Cr, Ni and Pb in sludges reported by Ščančar et al. and for Cr and Pb observed by Álvarez et al. were much higher than the results of present investigation. On the other hand, the concentrations of Zn and Cu noted in this investigation were higher than the results of these workers. Statistical analysis showed that there was no significant difference in total concentration of metals between municipal and industrial wastewater treatment plants. It appears that if the discharged standard of industrial wastewater of China were enforced strictly, the metal content in sludge could be effectively reduced. The source of municipal wastewater treatment plants includes industrial effluents, domestic wastewater and surface runoff, so the control of heavy metals in wastewater source of municipal wastewater treatment plants was harder than that of industrial wastewater treatment plants.

"Discharge standards of pollutants for municipal wastewater treatment plant (GB 18918-2002)" was issued in 2002 and enforced in 2003 in China [17]. A comparison of metal concentrations in sludge with their permissible values, the concentrations of Cr, Ni and Cu in S3 and Cd and Zn in S5 were beyond the permitted values restricting their use in agriculture. Metal concentrations in other six sludge samples were below the permitted values so these could be safely used in agriculture. Soil contamination due to heavy metals was a serious problem in China, for example, concentrations of heavy metals in 36,000 ha sampled from 300,000 ha ba-

Table 3
Total contents of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge collected from selective wastewater treatment plants, and their permitted values in the discharge standards of China (mg kg^{-1}-dry weight)

	Cd	Cr	Pb	Ni	Zn	Cu
S1	2.82	61.56	13.58	22.65	1095.34	267.69
S2	3.22	141.37	27.90	45.13	846.54	282.45
S3	3.05	1844.22	16.26	233.82	1594.97	2051.26
S4	3.82	82.72	15.87	36.02	1261.24	245.70
S5	112.03	108.54	93.73	59.76	6718.87	581.60
S6	6.97	102.04	14.10	93.42	1629.89	472.31
S7	2.99	108.46	19.11	34.89	564.24	120.31
S8	0.90	88.90	26.98	15.80	327.03	169.73
Mean ± S.D.	17.0 ± 38.4	317.23 ± 317.2	28.4 ± 27.0	67.7 ± 71.3	1754.8 ± 2057.8	523.9 ± 635.7
China[a] (soil pH < 6.5)	5	600	300	100	2000	800
China (soil pH ≥ 6.5)	20	1000	1000	200	3000	1500

[a] From "Discharge standards of pollutants for municipal wastewater treatment plant (GB 18918-2002)".

sic agricultural protecting cropland in 2000 were found to be beyond the permissible limit values of state standards for cropland [14]. A strict enforcement of state standards should be observed to limit the indiscriminate application of sludge in cropland.

3.3. Extractable contents of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge

Different chemical fractions of heavy metals represented as percent of their total concentrations in sludge shown in Fig. 1 revealed that the distribution of the metal fractions varied widely for different metals. The percentage of *F*1 fraction of almost all metals in S5 and S6 was higher than other sludge samples owing to the acidic nature of these two sludge samples. Merrington et al. stressed the importance of pH on the availability of metals in sludge [18]. The content of *F*1 fraction of Cr in S1, S2, S4 and S7 and of Pb in S1, S2, S4, S7 and S8 were below the detection limit of ICP-MS, therefore, these were not taken into consideration during statistical analysis and not shown in Fig. 1. Chromium, Cu and Pb were found to be principally distributed in the *F*3 and residual fractions in all sludge samples. Nickel had higher percentage of *F*1 (5.6–46.7%) but lower percentage of *F*2 fraction (1.6–11.4%). The percentage of *F*1, *F*2 and *F*3 for Zn was all above 10%. Cadmium was principally distributed in the *F*3 and residual fractions in S1 and S4, and in *F*1 and *F*2 fraction in S5, S6, S7 and S8. Among different chemical fractions of heavy metals in sludge, *F*1 fraction (water soluble, exchangeable, and bound to carbonate forms) represented a form of high mobility and potential bioavailiability. The percentage of *F*1 for Cd in S6, S7 and S8 was much higher in

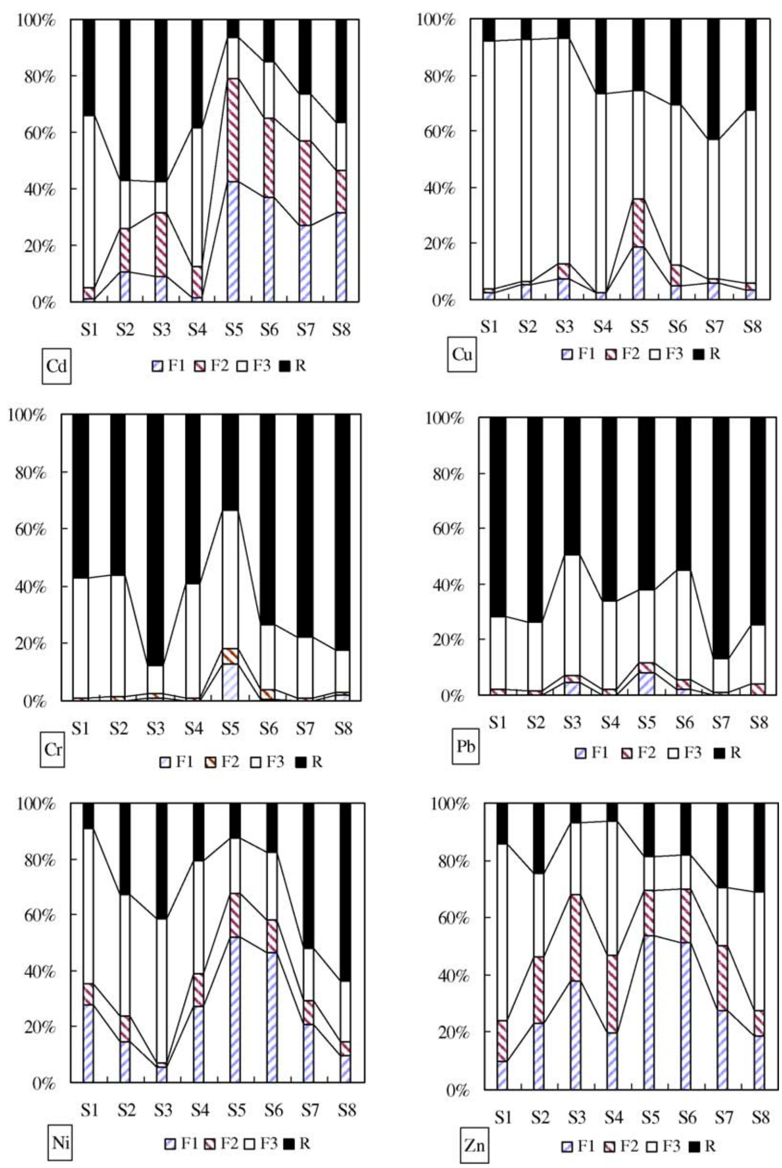

Fig. 1. The percentage of each fraction of heavy metals in sludge extracted by the BCR sequential extraction procedure.

S1, S2, S3 and S4 (except S5 influenced by pH). This showed that the mobility and bioavailability of Cd in sludge from industrial wastewater treatment plants were much higher than from municipal wastewater treatment plants. Because the permitted value of Cd in the discharge standard was very below (Table 3), the higher percentage of *F*1 fraction of Cd in acidic sludge from municipal wastewater treatment plant and sludge from industrial wastewater treatment plants may cause potential phyto-toxicity after agricultural application. There is no significant difference in the percentage of *F*1 for other metals. The percentage of *F*1 for Ni and Zn ranged from 9.6 to 51.1 and 10.0 to 51.1, respectively. So the mobility and bioavailability of Ni and Zn in sludge was higher as compared to other heavy metals. These results are in corroboration to the findings of Šèanèar et al. [16]. Attention should be, therefore, paid to the mobility of Ni and Zn in sludges from municipal treatment plants and Cd in sludges from industrial wastewater treatment plants after their application.

4. Conclusions

Sewage sludge collected from eight sewage treatment plants has high organic carbon, and is rich in nutrient like N and P, so they can be used as good organic fertilizers. But the impact caused by heavy metals after their agricultural application of sludge should be assessed. Total concentration of Cr, Ni and Cu in S3 and Cd and Zn in S5 exceeded the permitted values of GB 18918-2002, so S3 and S5 cannot be used in agriculture due to high metal concentration. Total metal concentrations in sludge from three industrial wastewater treatment plants failed to show any significant difference against those from municipal wastewater treatment plants. Extractable fractions of different heavy metals varied greatly. In acidic sludge (S5 and S6), the percentage of *F*1 fraction of most heavy metals was higher than that in neutral sludge. In neutral sludge, Pb and Cr were principally distributed in the oxidizable and residual fractions. Cu was mainly in the oxidizable fraction. Cadmium was principally in the residual fraction in municipal wastewater treatment plant sludge while in industrial wastewater treatment plant sludge high percentage of acid soluble/exchangeable and reducible fractions was noted. Nickel and Zn had higher percentage in the acid soluble/exchangeable and the oxidizable fractions. In China, a statewide survey for compilation of data on the production of sludge, their heavy metal composition and speciation should be carried out for their environmentally safe disposal.

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