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Distribution of extractable fractions of heavy metals in sludge during the wastewater treatment process

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Abstract

Sludge samples were collected from different treatment steps of Gaobeidian wastewater treatment plant (WWTP) of Beijing City, PR China, to investigate the distributions of total and chemical fractions of Fe, Mn, Ni, Cu, Zn, Cr, Pb, and Mo in different sludges. The highest total concentrations were found for Fe, Mn, Pb, and Mo in digested sludge (DS), Ni and Cr in thickened sludge (TS), Zn in dewatering sludge (DWS), and Cu in active sludge (AS). The lowest concentrations were observed in AS, except for Cu in TS. Significant differences of total metal concentration were observed between AS and TS (or DS), suggesting that sludge thickening and digesting treatments significantly influenced the total metal concentrations. Fe, Cu, Ni, Cr, Mo, and Pb distributed principally in the residual fraction in all sludges, while Zn and Mn presented in a highly available fraction. For same metal in different sludges, the portion of easily mobile fraction decreased significantly along the wastewater treatment process, and metals in AS presented in the highest available fraction. Organic matter contents, TN, and TP of sludges exhibited a significant positive correlation with the concentrations of exchangeable and reducible fraction of Pb, Mo, Cr, Cu, and Fe, while sludge pH demonstrated significant negative correlations with the concentrations of these metals.

Keywords: Sewage sludge; Heavy metals; Total concentration; Fraction; Wastewater treatment plant

1. Introduction

Conventional active sludge treatment process has been widely employed to treat a wide range of wastewaters. Different kinds of active sludge treatment processes for municipal sewage were originally designed for removing organic matter and other nutrient elements (e.g., nitrogen and phosphorus) [1]. However, metals in wastewaters can also be effectively removed, which is regarded as an additional benefit. The mechanism of the metal removal during wastewater treatment has also been widely reported in previous literatures [2–5]. As a result of rapid economy growth in China, the rapid increasing construction of a large number of new wastewater treatment plants is expected to yield four million tonnes of dry sludge in coming years [6]. Therefore, the disposal of the sludge generated from urban wastewater treatment is becoming a crucial environmental problem [7,8].

One of the most attractive potential sludge disposal methods is agronomic application due to their potential values of organic matter, N, P, and other plant nutrients [8,9]. However, possible barriers on agricultural application of sewage sludge are worth of further investigations [10]. One of major restrictive factors for agronomic application of sewage sludges is heavy metals retained in sewage sludge from the influent wastewater during wastewater bio-treatment process. These metals are non-biodegradable and pose eco-toxicity in environment [11]. Consequently, the studies on heavy metal concentrations in sewage sludge and their bioavailability received a great scientific attention in recent decades.

At present, it is widely accepted that the determination of total heavy metal contents in sewage sludge do not provide sufficient information of its potential hazardous effects on environment because the mobility and eco-toxicity of heavy metals depend strongly on their specific chemical forms or bindings [8,12]. Various extraction schemes, both single and sequential extraction procedure, have been developed and applied to evaluate the environmental impact of heavy metals in soils, sediments, and sewage sludges [13–15]. The application of these techniques

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was recently reviewed by Kot and Namieśnik [16]. Among those sequential extraction techniques, the BCR program (developed by the Community Bureau of Reference in 1987) is widely used and is harmonized methodology for determining chemical fraction of metals in soils, sediments and sewage sludge [7,15,17,18].

The total contents of Fe, Mn, Cu, Zn, Ni, Cr, Pb, and Mo in sewage sludge samples collected from each treatment step of the Gaobeidian wastewater treatment plant (WWTP) of Beijing, PR China, were determined, and the chemical fractions of these metals were also investigated by using the BCR sequential extraction procedure. The aim of the present work was to investigate distribution of total metal contents and their chemical fractions in the sludge of different treatment steps in the WWTP system. The information can be used to assess the potential mobility or bioavailability of these metals, and provide evidence on the suitability and feasibility of the sewage disposal for agronomic application.

2. Material and methods

2.1. Sampling and pre-treatment

Located in the southeast of Beijing City, the capital of China, the Gaobeidian wastewater treatment plant (Gaobeidian WWTP) is the largest WWTP in China. Using conventional active sludge process as the bio-treatment technology, everyday this plant treats 1,000,000 m^3 wastewater from both domestic and industrial sources, which is common in most municipal activated sludge systems. Five sampling stages were selected from the whole process, and these stages are primary sludge (PS), active sludge (AS), thickened sludge (TS), digested sludge (DS), and dewatering sludge (DWS). Sludge samples were collected three times in a month, and the digested and the dewatering sludge were collected 24 days later in accordance with the digested treatment period of this WWTP. Three individual samples of same sludge were homogenized to provide a compound sludge sample. The treatment process diagram of Gaobeidian WWTP and the sampling points are shown in Fig. 1.

Samples of sewage sludge were air-dried at room temperature, grounded and homogenized using an agate mortar. The samples were then passed through a 1-mm nylon sieve, and kept in polyethylene bags for measurement.

2.2. Determination of physicochemical properties and total metal contents

Physicochemical properties of the sludge samples were determined as follows: sludge pH and electric conductivity (EC) were measured on sludge extract at a sludge/deionized water ratio of 1:10 (w/v) by a digital pH meter and an electric conductivity meter. Sludge organic matter content was determined by loss on ignition (LOI) at 450 °C for 3 h. Total nitrogen (TN) was extracted by Kjeldhal digestion, and determined in the form of NH_4–N by the Indophenol Blue method [19]. Total contents of phosphorus (TP) were digested together with total metal contents first, and then determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Prodigy, Leeman LABS, USA).

To determined metal concentrations in sludge samples, 0.1 g of each powdered sample was wet-digested with 15 ml concentrated HNO_3–$HClO_4$ (3:1) acid mixture in a 25-ml Teflon PFA (perfluoroalkoxy) vial. After 3 ml HF acid was added, the mixtures were then heated until a clear solution was formed, and continued to near dryness. The cooled residue was dissolved in 5 ml 10% HNO_3, and the solution was diluted to 25 ml with deionized water for measurements [20].

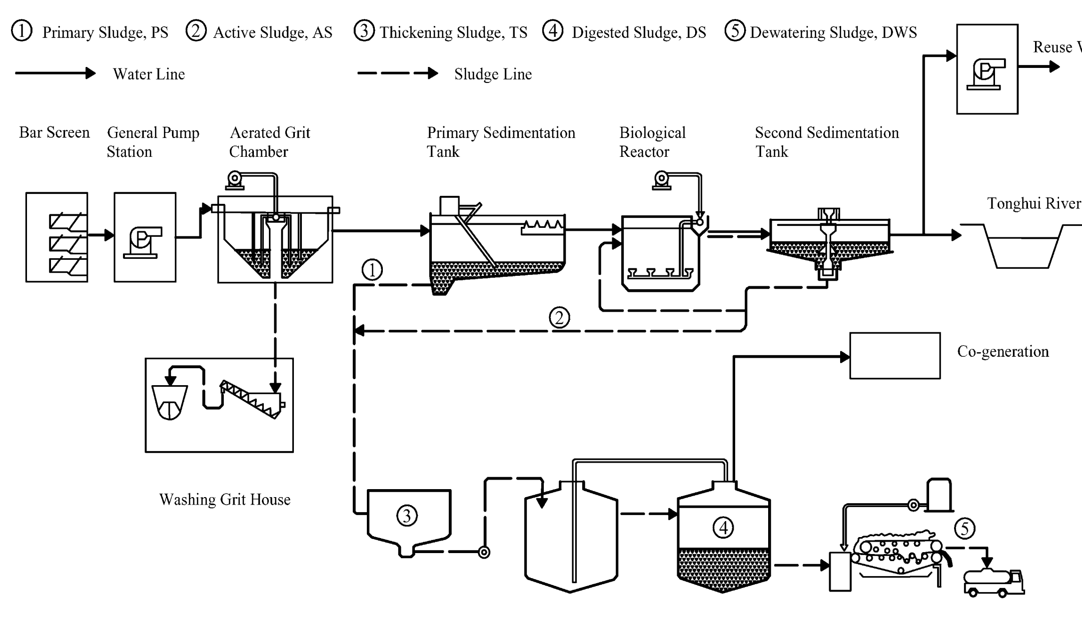


Fig. 1. Schematic diagram of Gaobeidian wastewater treatment plant and sampling points.

2.3. Extraction procedures for sludge samples

The BCR's sequential extraction procedure described as Ure et al. [15] was employed in extract metal fractions in the sludge. For practical reasons, both sample amount and extractant volume were reduced by one-half to keep the weight per volume ratio same as in the original BCR extraction scheme. The extraction procedure was described as following:

Exchangeable/acid soluble fraction (*F1*): Twenty milliliters acetic acid (0.11 mol l^{-1}) was added in a 50 ml polypropylene centrifuge tube containing 0.5000 ± 0.0001 g of powdered sludge sample. The tubes were shaken for 16 h at ambient temperature (20 ± 1 °C) on an end-over mechanical shaker operating at 40 rpm. The extract was separated from the solid residue by centrifugation (4000 rpm), transferred into a polyethylene container, and stored at −4 °C until analysis.
Reducible fraction (*F2*): The residue from the step above was shaken with 20 ml hydroxylamine hydrochloride (0.1 mol l^{-1}, acidified to pH 2 with nitric acid). The extraction procedure was same as in the F1.
Oxidizable fraction (*F3*): To residue from F2, 20 ml hydrogen peroxide (30%, acidified to pH 2 with nitric acid) was carefully added, and, after digestion, the extraction was continued in 25 ml ammonium acetate (1 mol l^{-1}, acidified to pH 2 with nitric acid). The extraction procedure was followed as described in F1.
Residual fraction (*F4*): The residue from F3 was digested using the method described for the digestion of total metal contents.

A blank was also run at the same time. All glassware and plastic containers were previously soaked in Suprapure nitric acid (Merck) overnight, and rinsed with deionized water. The concentrations of Fe, Mn, Ni, Zn, Cu, Cr, Pb, and Mo in different fractions, and the total concentrations of these metals in sludge were determined by ICP-AES.

3. Results and discussion

3.1. Physicochemical properties of the sludge

Table 1 shows the physicochemical properties of the sludge from Gaobeidian WWTP system. The pH of the sludge samples ranged from 6.96 (active sludge, AS) to 7.63 (digested sludge, DS). The electrical conductivity (EC) values ranged from 1069 μS cm^{-1} (active sludge, AS) to 1896 μS cm^{-1} (dewatered sludge, DWS), with a mean value of 1446.8 μS cm^{-1}.

Organic matter contents (LOI) varied greatly among different sludge samples collected from different treatment steps in Gaobeidian WWTP. The highest organic matter content was found in the active sludge (AS, 73.0%), which might be attributed to the fact that active sludge was mainly composed by biomass. In general, the primary sludge is characterized mostly by the suspending materials in the influent wastewater. In this study, organic matter contents of the primary sludge (44.4%) in this plant were lower than that of active sludge, but higher than the other sludge samples, indicating a high organic matter content of input wastewater. Thicken sludge showed moderate organic matter content (39.6%). The lowest organic matter contents were found in the digested sludge (37.9%) and dewatering sludge (37.2%) possibly because of decomposition of organic matters into inorganic matter during the anaerobic digested treatment process.

The active sludge samples exhibited the highest total nitrogen (TN) (5.83%) and total phosphorus (TP) (17.96 g kg^{-1}). Considering that the highest organic matter contents presented in active sludges, the high TN and TP could be attributed to the assimilation of nutrients by the biomass in the active sludges. The lowest TN was found in digested sludge (2.37%) and dewatering sludge (2.36%), which was in agreement with the content of organic matter. The mean values of TN for the primary sludge and thickened sludge were 3.43 and 2.89%, respectively. For TP, the mean values in primary, thickened, digested, and dewatered sludges were 14.77, 14.11, 14.98, and 15.14 g kg^{-1}, respectively. These values fall in the range of those reported in literatures [7,8].

On average, soils in China contain 10–40 g kg^{-1} organic matter, 1.0–2.0 g kg^{-1} total N, and 0.44–0.85 g kg^{-1} total P [21]. Comparing the averages in soils, sewage sludge has considerable more nutrient elements than soils, highlighting the potential agronomic benefits of sewage sludge.

Table 1
Physicochemical properties of sludge samples from Gaobeidian WWTP system (in dry matter)

	TP (g kg^{-1})	TN (%)	LOI (%)	EC (μS cm^{-1})	pH 1:10 (w/v)
PS	14.77	3.43	44.4	1502	7.39
AS	17.96	5.83	73.0	1069	6.96
TS	14.11	2.89	39.6	1506	7.52
DS	14.98	2.37	37.9	1353.5	7.63
DWS	15.14	2.36	37.2	1896	7.58

PS, primary sludge; AS, active sludge; TS, thickening sludge; DS, digested sludge; DWS, dewatering sludge.

3.2. Total concentrations of metals in sludge

Total concentrations of Fe, Mn, Pb, Ni, Cu, Zn, Cr, and Mo in sludge samples were shown in Table 2. Fe was the most abun-

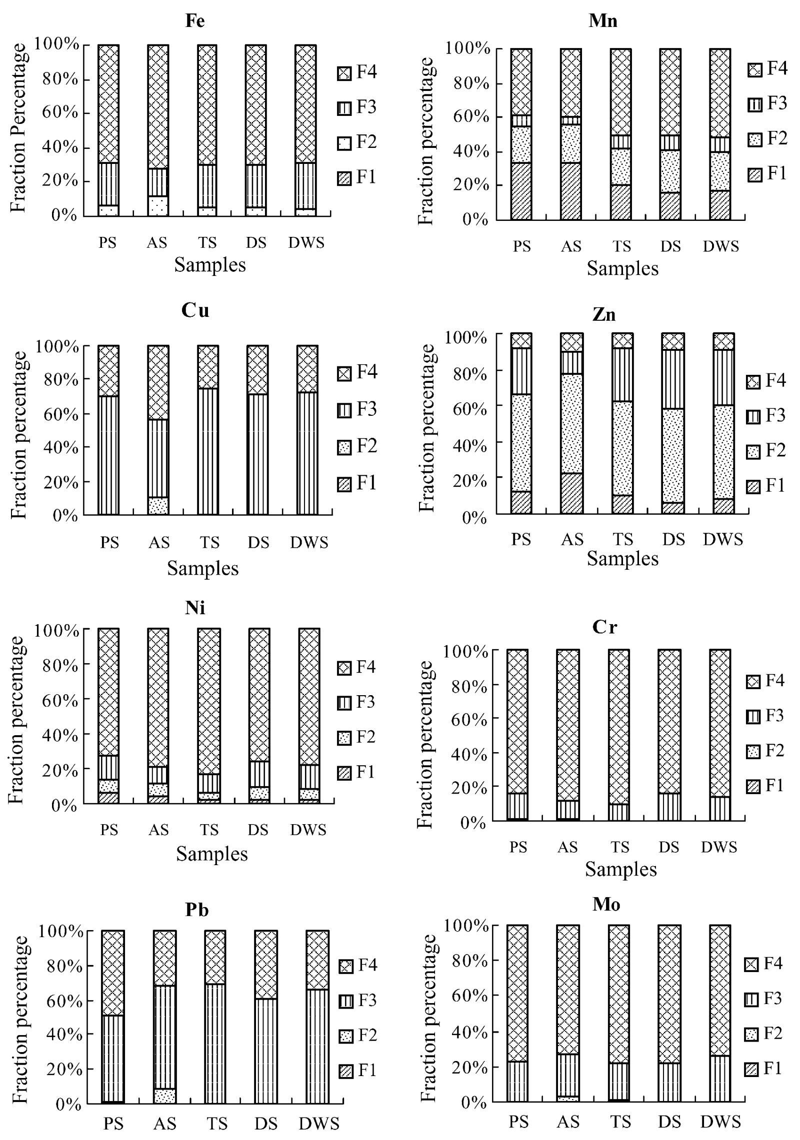
Table 2
Total metal contents in Gaobeidian WWTP system (mg kg^{-1}, in dry matter)

Samples	Fe	Mn	Cu	Ni	Zn	Pb	Cr	Mo
PS	16980.0	243.0	58.0	52.6	710.9	35.3	64.7	29.9
AS	12457.6	214.5	67.5	49.9	595.6	28.1	60.0	18.6
TS	16995.7	240.3	55.2	99.2	678.6	33.1	124.7	33.8
DS	18236.5	260.5	58.7	55.3	736.3	41.1	75.0	35.7
DWS	18208.2	257.6	59.6	69.8	746.5	40.2	91.0	32.2
pH < 6.5[a]	/[b]	/	800	100	2000	300	600	/
pH ≥ 6.5[a]	/	/	1500	200	3000	1000	1000	/

[a] From "Discharge standard of pollutants for municipal wastewater treatment plant", PR China (GB 18918-2002).
[b] "/" shows no limited values in GB 18918–2002.

dant metal (12457.6–18236.5 mg kg^{-1}, in dry matter), while Mo exhibited the lowest abundance (18.6–35.7 mg kg^{-1}) in all sludge samples. The total concentrations of other metals ranged from 214.5 to 260.5 mg kg^{-1} for Mn, 55.2 to 67.5 mg kg^{-1} for Cu, 49.9 to 99.2 mg kg^{-1} for Ni, 595.6 to 746.5 mg kg^{-1} for Zn, 28.1 to 41.1 mg kg^{-1} for Pb, and 60.0 to 124.7 mg kg^{-1} for Cr. Compared to the data published in previous literature [22], our results were consistent with the ranges of metal concentrations in sewage sludge in China. According to the maximum allowed values enacted by Chinese legislation, none of the metal concentrations exceeded the maximum allowed values of the discharge standard of pollutants for municipal wastewater treatment plant (GB 18918-2002).

Digested sludge (DS) had the highest concentrations of Fe, Mn, Pb, and Mo, thickened sludge (TS) contained the highest concentrations of Ni and Cr, and Zn and Cu, was, respectively, high in dewatering sludge and active sludge. The lowest metal concentration was in AS, with an exception for Cu in thickened sludge. As metal concentrations in PS reflected the condition of influent wastewater, the distribution of metals in primary sludge (PS) can be an important factor in understanding the transformation of metals in the wastewater treatment processes. The distributions of Mo, Pb, Fe, Mn, and Zn exhibited a similar order of AS < TS < DS < DWS. For Ni and Cr, the distribution order was AS < DS < DWS < TS, while the order was TS < DS < DWS < AS for Cu. Little difference for all metal concentrations between DS and DWS confirmed that dewatering treatment of digested sludge did not affect the total metals concentrations. However, significant difference was found between AS and TS (or DS), suggesting that sludge thickening and digesting treatments significantly influence the total metal concentrations.



F1: Exchangeable fraction; F2: Reducible fraction; F3: Oxidizable-fraction; F4: Residual fraction

Fig. 2. The percentage distribution of each metal fraction in sludge samples.

3.3. Distribution of metal chemical fraction in different sludge samples

Fig. 2 presents the extractable fraction of metals in sludge in a percentage of the summation of the four fractions, which is reasonably similar to the total contents obtained from the original samples with HNO_3–$HClO_4$–HF digestion. The recovery rate was 85–110% in most cases, and this recovery rate was in agreement with those published data for the same extraction scheme [8,23].

The distribution of the metal fractions varied from one metal to another. For Fe in all sludges, the predominant fraction was the residual fraction (68.95–72.4% of the total), followed by the oxidizable fraction (16.0–26.3%), a result consistent with the findings by Fuentes et al. [8]. Similar to previous publications [7,8], the residual fraction was the predominant fraction for Cr (84.4–90% of the total) and Mo (72.8–78.6% of the total) in all sludge samples. However, Álvarez et al. described the oxidizable fraction as the predominant fraction for Cr [24]. This difference might be because of the properties of the sludges, particularly the sulfur contents, as Cr sulfide represents part of oxidizable fraction in sludges. Likewise, Ni distributed mainly in the residual fraction (72.7–83.5% of the total Ni) in all sludges as described by Fuentes et al. [8]. However, the sum of the first two fractions (exchangeable and reducible fraction) in the present work was 6.5–14.1% of the total Ni, significantly lower than the data obtained by Fuentes et al. (20–40%). For Cu and Pb, the predominant fraction was the oxidizable fraction, which contains 46.5–72.7% of the total Cu, and 50.5–68.8% of the total Pb. This result was similar to those published in literature [8,9].

The residual fraction was the highest portion of the four fractions for Mn in all sludges, but the fraction distribution of Mn differed among different sludges. For PS and AS, the distribution order of Mn percentages in different fractions was F4 > F1 > F2 > F3, while the order for TS, DS and DWS was F4 > F2 > F1 > F3. Different fraction distribution orders of Mn were also observed in different sludges by Solís et al. [7] and Álvarez et al. [24].

In all the sludge samples, Zn was principally distributed in the reducible fraction, followed by the oxidizable fraction. As mentioned in previous literatures [8,9], the sum of the first two fractions (F1 + F2) accounted for 58.5–77.5% of the total Zn, indicating its relatively high mobility and bioavailability.

According to the original scheme of BCR's sequential extraction program, the exchangeable/acid soluble fraction (F1) represented metals in ionic form or bound to carbonates. The reducible fraction (F2) represented metals bound to amorphous iron and manganese oxides and hydroxides. The oxidizable fraction (F3) represented the portion of metal bound to organic matter and sulphides. And the residual fraction (F4) represented the portion of metals bound to silicate lattice or crystalline iron and manganese oxides [15,18]. The exchangeable fraction (F1) and the reducible fraction (F2) were summed up under the label of easily mobile and available fraction (F_{1+2}), and the oxidizable fraction (F3) was pooled together the residual fraction (F4) as an immobile and less-available fraction (F_{3+4}). To explore the variation of chemical fractions during the wastewater treatment process more effectively, the results of BCR's sequential extraction procedure of this study were grouped into two classes (F_{1+2} and F_{3+4}), and re-arranged in Table 3.

Table 3 shows that active sludge (AS) had the highest percentage of the mobile and available fraction for most metals, similar to the results in previous literatures [24,25]. Active sludge was formed mostly by microorganism floc, and possessed greater surface area than other sludges. The large surface area of AS was favored by metal ions to form loose bindings on sludge floces. These loosely bound metals could be released into water fairly easily, and therefore they were recognized as the easily mobilized metals. Additionally, the physicochemical properties of sludge might also play an important role for the distribution of metal fractions [26]. Table 4 presented the correlations between sludge physicochemical properties and the concentration of easily mobile fraction (F_{1+2}) of metals in sludge. Significant correlations were found between organic matter contents and TN ($R = 0.991$, $p < 0.01$), and TP ($R = 0.934$, $p < 0.05$), suggesting that the sludges, except for PS, were mainly composed by microorganism floces. Significant positive correlations were also found between the organic matter contents and the concentrations of Pb, Mo, Cr, Cu, and Fe in exchangeable and reducible fraction (F_{1+2}), with correlation coefficients as $R = 0.997$, 0.923, 0.983, 0.952, and 0.979, respectively, $p < 0.05$. And similar significant positive correlations were also observed between easily mobile fraction of metals and TN, and TP of sludges. Considering the above discussion for the highest easily mobile fraction of metals in AS, the positive correlations might be attributed to the composition of sludge [3]. Significant negative correlations were found between sludge pH values and the concentrations of easily mobile and available fraction (F_{1+2}) of metals in sludges, with correlation coefficients of $R = -0.969$, -0.906, -0.983, -0.940, and -0.977 for Pb, Mo, Cr, Cu, and Fe, respectively,

Table 3
Percentage of extractable fraction obtained by application of the BCR's procedure

	Fe		Mn		Cu		Zn		Ni		Pb		Cr		Mo	
	F_{1+2}	F_{3+4}	F_{1+2}	F_{3+4}	F_{1+2}	F_{3+4}	F_{1+2}	F_{3+4}	F_{1+2}	F_{3+4}	F_{1+2}	F_{3+4}	F_{1+2}	F_{3+4}	F_{1+2}	F_{3+4}
PS	6.7	93.3	54.7	45.3	0.0	100.0	66.6	33.4	14.1	85.9	0.7	99.3	0.6	99.4	0.0	100.0
AS	11.5	88.5	56.1	43.9	9.8	90.2	77.5	22.5	11.6	88.4	8.6	91.4	1.1	98.9	3.3	96.7
TS	4.9	95.1	42.2	57.8	0.0	100.0	62.5	37.5	6.5	93.5	0.0	100.0	0.1	99.9	0.6	99.4
DS	4.9	95.1	41.1	58.9	0.0	100.0	58.6	41.4	9.4	90.6	0.0	100.0	0.2	99.8	0.0	100.0
DWS	4.6	95.4	39.8	60.2	0.0	100.0	59.8	40.2	8.6	91.4	0.0	100.0	0.2	99.8	0.1	99.9

F_{1+2}, the sum of percentage in F1 and F2; F_{3+4}, the sum of percentage in F3 and F4.

Table 4
Correlation between physicochemical properties and the easily mobile fraction (F_{1+2}) of metals in sludges

Physicochemical properties	Easily mobile fraction of metals[a]								Physicochemical properties		
	Fe	Cu	Mo	Cr	Pb	Ni	Zn	Mn	LOI	pH	TN
LOI	0.978**	0.983**	0.939*	0.980**	0.996**	0.737	0.716	0.801	1		
pH	−0.979**	−0.943*	−0.908*	−0.985**	−0.972**	−0.823	−0.752	−0.858	−0.986**	1	
TN	0.979**	0.952*	0.923*	0.983**	0.977**	0.798	0.747	0.849	0.991**	−0.997**	1
TP	0.906*	0.965**	0.862	0.902*	0.960**	0.574	0.617	0.647	0.934*	−0.881*	0.882*

[a] The total concentrations of exchangeable/acid soluble fraction and reducible fraction of metals in sludge.
* Correlation is significant at the 0.05 level (two-tailed).
** Correlation is significant at the 0.01 level (two-tailed).

indicating that the stability of metals increased with the increasing sludge pH values [26]. Consequently, organic matter contents and pH values of active sludge might have significantly influenced the metal distribution in fractions in these sludges.

Table 3 shows an evident that the percentage of exchangeable and reducible fraction (F_{1+2}) in total decreased significantly along the wastewater treatment steps, suggesting an enhancement in stability of metals in sludges along the wastewater treatment process. Many previous studies focused on the variation of metal chemical fractions during sludge digestion or compost process [24,27,28]. In present work, however, the changes in metal stability during thickening process appeared to be more significant than that of during sludge digesting and dewatering treatments. The percentage of easily mobile and bioavailable fraction (F_{1+2}) decreased significantly after the sludge thickening treatment (Table 3), while there was no significant difference of fraction distribution for same metal among the three types of treated sludges (thickened sludge, digested sludge, and dewatering sludge). This suggested that thickening treatment of sludge significantly influenced the distribution of chemical speciation of heavy metals in sludge. Considering the influences of sludge thickening treatment on the physicochemical properties (including TN, TP, and LOI) (Table 1) and total concentrations of heavy metals in sludges (Table 2), the thickening treatment of sludge might play an important role for these variations. The possible mechanism of the influences of the thickening treatment on the distribution of extractable fraction of metal in sludge would be further studied in the nearly future.

4. Conclusions

The distribution of heavy metals in sewage sludge is an important factor because it is closely related to metal mobility and bioavailability. Total concentrations and chemical fraction distributions of metals in sludges collected from different treatment steps of Gaobeidian WWTP were determined and compared in the present study. The determination of total metal concentrations digested with HNO_3–HF–$HClO_4$ in sludge samples showed that the highest concentrations were found for Fe, Mn, Pb, and Mo in digested sludge (DS), Ni and Cr in thickened sludge (TS), Zn in dewatering sludge (DWS), and Cu in active sludge (AS). However, the lowest concentrations were mostly observed in AS, with an exception for Cu in TS. Significant differences of total metal concentration were observed between AS and TS (or DS) suggested that sludge thickening and digesting treatments significantly influenced the total metal concentrations. And none of the concentrations recorded exceeded the restricted values of the discharge standard of pollutants for municipal wastewater treatment plant (GB 18918-2002, China). The results of the sequential extraction by BCR three-step procedure indicated that Fe, Cu, Ni, Cr, Mo, and Pb in all sludge samples distributed principally in the residual fraction, while Zn and Mn appeared to be highly mobile and available. For same metal in different sludges, there are significant variations in fraction distribution between raw sludge (primary sludge and active sludge) and treated sludge (thickened sludge, digested sludge, and dewatering sludge), and the significant variations of metal fraction distribution occurred during sludge thickening treatment, suggesting that the sludge thickening treatment also influenced the distribution of extractable fraction of metal in sludge. Analysis of correlations between physicochemical properties of sludge and metal fraction distributed in different sludges showed that sludge organic matter contents exhibited a significant positive correlation with the concentrations of exchangeable and reducible fractions of Pb, Mo, Cr, Cu, and Fe, with the correlation coefficients as $R = 0.997$, 0.923, 0.983, 0.952, and 0.979, respectively, $p < 0.05$. Similar positive correlations were also observed between easily mobile fraction (F_{1+2}) of metals and the concentrations of TN and TP in sludge. However, sludge pH values presented significant negative correlations with the concentrations of these metals ($R = -0.969$, -0.906, -0.983, -0.940, and -0.977 for Pb, Mo, Cr, Cu, and Fe, respectively, $p < 0.05$). This confirmed that the organic matter contents and sludge pH might have significantly affected the distribution of metal fraction in sludge.

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