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Total concentrations and different fractions of heavy metals in sewage sludge from Guangzhou, China

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Abstract: Dewatered municipal sludge samples were collected from five municipal wastewater treatment plants (WWTPs) and one industrial WWTP in Guangzhou, China. A number of agricultural parameters and total metal concentrations in the sludge were determined. Metal speciation was also studied. The results showed that sewage sludge had high organic carbon, and was rich in such nutrients as N and P. The concentrations of Mn, Zn, and Cu were the highest, followed by Ni, Pb, and Cr, Cd had the lowest concentration. In addition, the concentrations of the aforementioned heavy metals in the sludge samples were higher than those recorded in the background data for crop soils. With the exception of Cu and Cd from site S1, and Ni from sites S1, S2, and S5, all other metal concentrations conformed to permissible levels prescribed by the national application standard of acid soil in China (GB 18918—2002). The results of the BCR sequential extraction showed that the concentrations of Mn and Zn were predominant in acid-soluble/exchangeable and reducible fractions. Cu was principally distributed in oxidizable and residual fractions, whereas Cr was present in oxidizable and residual fractions, Pb was found in the state of residual fractions, and the distribution of Ni and Cd did not show significant characteristics.

Key words: sewage sludge; heavy metals; metal fraction; sequential extraction; wastewater treatment plant (WWTP)

1 Introduction

Disposal alternatives for sewage sludge are applied to agriculture land or land not precluding use in agriculture, land filling, incineration or composting [1]. The application of municipal sludge to agricultural land is an attractive option for disposal because of the possibility of improving soil properties and increasing plant productivity with the recycling of valuable components including organic matter (OM), N, P, and other plant nutrients. In the European community, over 30% of sewage sludge is used as an agricultural fertilizer in agriculture. In UK for example, GOVE et al [2,3] reported on the increasing use of enhanced treated sewage sludge in agriculture. In Belgium, 57% of sludge is utilized for agriculture. In France, 60% of sewage sludge is used in land application [4].

A survey conducted in 2000 showed that 70% to 80% of total cultivated land lacked sufficient nutrients. Furthermore, the survey also revealed that the insufficient application of organic fertilizer and excessive utilization of chemical fertilizers resulted in the deterioration of farmland soil quality, reduction of the cultivation level, and decrease in the water-retention capability of the soil [5]. Therefore, sewage sludge has great potential in agricultural application. However, despite the fact that such application may benefit soil, concerns about possible environmental pollution hazards, such as unpleasant odor, water pollution, danger to livestock and other animals, and contamination by heavy metals, have to be considered [6−8]. Toxic metal mobility in sewage sludge-amended soil at neutral or slightly alkaline pH is relatively low. Soil acidification generally increases the solubility of heavy metals, consequently increasing availability for uptake by plants and/or transport to ground water [9]. Consumption of contaminated water by such plants may increase heavy metal contents in the food web [8,10,11]. Thus, heavy metal pollution has become the primary obstacle for the

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agricultural use of municipal sludge.

To evaluate the heavy metal burden in sewage sludge-amended soil [6,11,12], sediment [13] or sewage sludge [14] of the total metal concentrations was measured after digestion of samples with strong acids including HF treatment, or aqua regia extraction. Aqua regia extraction is a commonly used analytical procedure that is internationally standardized for sediment and sewage sludge analyses by DIN [15] and ISO [16]. In addition to total metal concentrations, the specific chemical forms of heavy metals and their modes of binding in soil are important determinants for estimating heavy metal mobility, bioavailability, and related eco-toxicity [17]. The specific chemical forms of heavy metals can be determined by selective sequential extraction analysis, which comprises several extraction steps based on the use of different chemical reagents and conditions [18]. Over the recent decades, a large variety of extraction schemes have been developed, and some have been widely used in the determination of the speciation of metals in soil and sludge [19−21]. However, these methods lack a standard analysis procedure and have a poor comparability that is strongly affected by the choice of extractants [22]. To harmonize and validate different fractionation schemes, the Bureau Communautaire de Reference (BCR, now the Measuring and Testing Programme) proposed the BCR three-step procedure [23,24]. This procedure compromises between analysis time and the amount of information obtained. In recent years, the BCR method has been used extensively for the study of heavy metals in soil and sludge [25−28].

Aside from the speciation of metals, local environmental characteristics also affect the estimation of metal mobility, bioavailability, and related ecotoxicity. Guangzhou is situated in the southern part of Guangdong Province, China. According to the Chinese soil classification system [29], the main soil type in the area is lateritic red soil. Guangdong Province, including Guangzhou and several other cities, is under severe H_2SO_4−HNO_3 type acid rain pollution, which results from industrial activities in the cities [30]. The evaluation of the biotoxicity of metals to the environment is essential in predicting changes in the metal behavior in response to these environmental conditions. Thus, the feasibility of the agricultural utilization of municipal sludge in the region primarily depends on two factors, namely, the speciation of heavy metals in sludge and the environmental characteristics of south China.

Guangzhou, with a population of over 10 million, is one of the largest industrial centers and among the fastest expanding cities in Guangdong Province. Guangzhou is ranked third in terms of overall economic power in all of China, next only to Shanghai and Beijing. The top two cities contribute one-tenth of China's gross domestic product (excluding Hong Kong). With the tremendous economic development in the past decades, industrial productivity and the utilization of natural resources have generated large amount of wastewater. The wastewater volume originating from the central district of Guangzhou is expected to reach 4.30×10^6 m^3/d by 2020 [31]. Proportionately, if sludge production is considered to be 0.3% to 0.5% of the volume of waste water, sludge production is expected to reach 1.29×10^4 t/d to 2.15×10^4 t/d (98% moisture content) by the same year. Therefore, the safe and economic disposal of such large amount of sludge in agricultural land may pose a huge challenge.

In this work, the agricultural significant parameters and total concentrations of the heavy metals (Cu, Pb, Zn, Cr, Ni, Cd and Mn) of the sludge from sewage treatment plants at Guangzhou were determined, and the speciation of each heavy metal was studied by BCR sequential extraction procedure. The bioavailability and eco-toxicity of heavy metals (Cu, Pb, Zn, Cr, Ni, Cd and Mn) were evaluated, which took into consideration both their speciation and local environmental characteristics, and the industrial layout was discussed preliminarily, based on the indication of the municipal sludge to the environment.

2 Experimental

2.1 Sampling and pre-treatment

Wet anerobic sludge samples were obtained from four wastewater treatment plants (WWTPs) at Guangzhou (S1, S2, S3 and S4) because the combined total volume of effluent in these four WWTPs accounts for more than 60% of the total wastewater volume originating from Guangzhou. Details of WWTPs are presented in Table 1. In order to obtain more information about other types of sludge in Guangdong more comprehensively, the other two sludge types, including that from the papermaking mill in Guangzhou (S5) and the domestic WWTP (S6) from Zhaoqing adjacent to Guangzhou, were also collected separately. Samples were collected from the terminal conveyor belts of four WWTP on the same day. Each sludge sample was collected four times during a sampling time that lasted for 2 h and at intervals of 0.5 h. The samples were air-dried at room temperature, ground, and homogenized in an agate mortar, sieved through a sieve (mesh pore size: 0.14 mm), and then stored in jars at room temperature.

2.2 Physico-chemical analysis

The significant agricultural parameters, such as moisture content, pH value, organic matter (OM), total nitrogen (TN), total phosphorus (TP), and the major

elements such as calcium (Ca), sodium (Na), potassium (K), magnesium (Mg), and iron (Fe) content, of sludge from the WWPT were determined using standard analytical methods [32,33]. All the values obtained for these physicochemical properties are listed in Table 2.

2.3 Sequential extraction test and determination of heavy metals

The total concentrations of Cr, Cu, Pb, Mn, Ni, and Zn in sewage sludge samples were determined by the modified sequential extraction described by QUEVAUVILLER et al [34]. Sequential extraction was performed by applying the three-step procedure defined by BCR. This method has been widely applied to investigating the distribution of element fractions in various samples, including in soil, sediment, sludge, etc [35,36]. During the extraction, metals were classified into acid-soluble/exchangeable fraction (F_1), reducible fraction (F_2), oxidizable fraction (F_3), and residual fraction (F_4). The detailed procedure is described as follows.

Step 1: Extraction of acid soluble/exchangeable fraction (F_1). Sludge sample (0.5 g) was introduced in a 50 mL polypropylene centrifuge tube containing 20 mL of acetic acid (0.1 mol/L) and then shaken for 16 h at room temperature. The solution and solid phases were separated by centrifugation at 4000 r/min for 20 min. Subsequently, the suspension was filtered through a 0.45 μm membrane filter and the solid residues were preserved for the subsequent extractions.

Step 2: Reducible fraction (F_2). The residues from Step 1 were shaken with a portion of 20 mL of 0.1 mol/L hydrox-ylammonium chloride (adjusted to pH 2 with nitric acid) for 16 h. The extraction procedure was the same as mentioned above.

Step 3: Oxidizable fraction (F_3). The residues from F_2 were dispersed in 5 mL of hydrogen peroxide (30%) and digested at room temperature for 1 h with occasional shaking. A second 5 mL aliquot of hydrogen peroxide was introduced into and digested at 85 °C (water bath) for 1 h. The contents were evaporated to a small volume (1−2 mL). 25 mL ammonium acetate (1.0 mol/L, adjusted to pH 2 with nitric acid) was added to the cool and moist residue. The sample was then shaken, centrifuged and the extract was separated as described in Step 1.

Step 4: Residual fraction (F_4). 5 mL HNO_3 was added to the residues from Step 3. The contents were heated on a hot plate and evaporated to almost dryness. After cooling, the residues were dissolved in 5% (v/v) 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 Zn, Cu, Pb, Mn, Ni, Cd and Cr in different fractions and the resultant solutions obtained in Step 4 were determined by

Table 1 Descriptive data of selected municipal and industrial wastewater treatment plants

Name of WWTP	No.	Treatment scale/($m^3 \cdot d^{-1}$)	Population equivalent	Disposal and usage of sludge	Proportion[a]
KFQ	S1	3.0×10^4	6.0×10^4	Landfill	70%
DTS	S2	60.66×10^4	142.7×10^4	Sanitary landfill	40%
LJ	S3	40.0×10^4	134.3×10^4	Building materials	<5%
LD	S4	103.67×10^4	225.8×10^4	Building materials	<5%
ZZ	S5	–	–	Sanitary landfill	100%
ZQ	S6	4.0×10^4	18.6×10^4	Building materials	<5%

Proportion[a]=The mass of industrial wastewater/Total mass effluents×100%

Table 2 Physico-chemical properties of sludge from selective municipal and industrial wastewater treatment plants

No.	Moisture content/%	pH	Organic carbon/%	Total N/%	Total P/%	*w*(Ca)/%	*w*(Mg)/%	*w*(Na)/%	*w*(Fe)/%	Total K/%
S1	83.2	7.85	32.2	3.11	2.04	3.71	0.15	5.32	1.53	1.08
S2	84.3	6.84	38.1	3.21	1.19	3.96	0.20	4.08	1.36	1.75
S3	80.0	6.35	35.2	3.72	3.62	2.82	0.17	6.42	1.44	1.77
S4	76.3	7.36	60.6	3.01	1.70	3.21	0.13	5.12	1.59	1.91
S5	76.2	7.45	62.1	1.25	1.87	12.95	0.33	5.13	0.26	0.67
S6	85.4	6.49	28.1	3.83	2.04	3.50	0.25	6.42	1.27	1.66
Mean	80.9	7.06	42.72	3.02	2.08	5.03	0.21	5.42	1.24	1.47

atomic AAS (Z−2000, Hitachi). Tests on each sample were conducted in triplicate, and the average value of results is reported here.

3 Results and discussion

3.1 Physicochemical properties of sludge from selected wastewater plants

Table 2 presents the properties of sludge obtained from WWTPs in Guangzhou. The moisture content of the dewatered sludge was approximately 80%, which is relatively high, with pH ranging from 6.35 to 7.85. The concentrations ranged from 281 g/kg to 606 g/kg for organic C, 12.5 g/kg to 38.3 g/kg for total N, 11.9 g/kg to 36.2 g/kg for total P, and 6.7 g/kg to 19.1 g/kg for total K. The aforementioned composition of dewatered sludge is similar to or higher than that reported for farmyard manure. In China, the mean composition of soil is: 10−40 g/kg OM, 1.0−2.0 g/kg total N, 0.44−0.85 g/kg total P, and approximately 16 g/kg total K [37]. All the parameters closely reflect those found in the bibliography for sludge of similar characteristics, some of which has been used for soil improvement [38−42]. Comparing the contents of sludge with those of soil, the former has higher organic C, total N, and total P but lower total K, suggesting high potential agricultural benefits for practical application.

3.2 Total concentrations of heavy metals in sewage sludge

Total Cu, Pb, Zn, Cr, Mn, Cd, and Ni contents, as well as the control standards for pollutants in sludge for agricultural use in China and other countries for municipal WWTP, are listed in Table 3. Generally, the sludge samples shown in Table 3 had higher concentrations of Cu and Zn but relatively low concentrations of Cr, Ni, and Pb. Similar results on the differences in the concentrations of heavy metals have been reported by ŠČANČAR et al [43]. In addition, the amounts of Cu in S1 and S2, Pb and Cr in six sludge sites except S5 and S6, Cd in six sludge sites except S6, and Ni and Zn in all the sludge sites were higher than those in Murcia, Spain [35]. However, the amounts of Pb, Ni, Cr, and Zn in six sludge sites, Cd in S4 to S6, and Cu in all sludge sites except S1 were lower than those reported by ŠČANČAR et al [43]. The concentrations of heavy metals in sludge from S1 and S2 were significantly higher (P<0.05) than those in other sampling sites because industrial wastewater constituted a large proportion of effluent in these two plants. Compared with the sludge in the study by ŠČANČAR et al [43], the concentrations of Cu, Pb, Ni, Cr, and Zn in S1 were approximately 22, 1.4, 8.7, 3.2, and 1.6 times, respectively. The higher concentrations may possibly be attributed to the fact that S1 is situated in a large

Table 3 Total contents of Cu, Pb, Ni, Mn, Cr, Zn and Cd in sewage sludge collected from selective wastewater treatment plants, and control standards for pollutants in sludges for agriculture use of China and other countries (mg/kg dry matter)

No.	Total content/(mg·kg^{-1})						
	Cu	Pb	Ni	Mn	Cr	Zn	Cd
S1	4567±143	81.2±2.8	148±6	1844±66	121±4	785±32	5.99±0.18
S2	274±6	104±4	132±6	1152±34	87±4	987±34	4.48±0.12
S3	190±4	82.4±2.7	74±1	214±10	49.6±1.9	909±28	3.05±0.13
S4	146±2	69.9±1.2	78±2	394±9	51.9±2.7	609±22	3.72±0.20
S5	175±3	–[a]	103±3	161±7	19.4±0.6	717±18	2.14±0.10
S6	93±1	17.4±1.1	51±1	970±30	15.5±0.4	509±20	–
[b]Mean in China	533	115	79.1	[c]397	222	1270	7.18
[d]Mean in soil of the Pearl River Delta	33	40	21.2	[e]/	71.4	84.7	0.58
[f]Murcia, Spain	204	58	17	/	38	487	1.10
[g]Dom ažale,Slovenia	433	126	621	/	856	2032	2.78
[h]China, pH<6.5	800	300	100	/	600	2000	5
[h]China, pH≥6.5	1500	1000	200	/	1000	3000	20
[f]American	1500	300	420	/	1200	2800	10
[f]Canada	500	200	100	/	1000	2000	10
[i]EU pH>7	1750	1200	400	/	1500	4000	40
[i]EU pH<7	1000	750	300	/	1000	2500	20

[a] Below the detection limits; [b] According to MA et al [44]; [c] According to McGRATH et al [45]; [d] According to WONG et al [46]; [e] Have no statistical data; [f] According to FUENTES et al [35]; [g] According to ŠČANČAR et al [43]; [h] From China's "Control Standards for Pollutants in Sludges for Agriculture Use (GB 18918—2002) [47]"; [i] From the threshold values of heavy metals established in Directive 86/278/EEC as function of soil pH.

industrial area in Guangzhou, where several chemical plants and electrical factories are located. The higher concentrations of heavy metals in sludge from S1 suggested that effluent from certain factories does not meet specified discharge standards. As a consequence, these pollutants settled and accumulated in the sludge and contributed to high heavy metal concentrations in the sewage sludge.

The amount of Zn was comparatively higher than that of other heavy metals. This finding may be attributed to the fact that almost all urban drainage pipes in China are made of galvanized material. Mn and Cu contents were the second highest, whereas Pb and Cr contents were relatively lower. These results concur with the findings of MA et al [44]. Compared the composition of Guangzhou sludge with the mean in China, the former exhibited lower concentrations for all heavy metals except for Cu in S1 and Ni in S1, S2, and S5. Compared with sludge from other cities [43], the concentrations of Cu, Zn, and Pb in S3, S4, S5, and S6 were relatively low. Based on Chinese mean levels, the concentrations of heavy metals in the aforementioned sites were similarly low. Statistical analysis showed no significant difference in the total concentrations of heavy metals in sludge between municipal and industrial WWTPs. If the discharge standards for industrial wastewater in China were enforced strictly, the metal concentrations in sludge could be reduced effectively. Wastewater sources for municipal WWTPs include industrial effluents, domestic wastewater, and surface runoff. Heavy metal control in the wastewater sources of municipal WWTPs is significantly harder than that of industrial WWTPs.

The maximum heavy metal content in sewage sludge permitted by China's control standards for pollutants in sludge for agricultural use (GB 18918—2002) [47] is listed in Table 3. A comparison of metal concentrations in sludge with the permissible values indicated that the concentrations of Cu in S1 and Ni in S1, S2, and S5 exceeded the permissible values, consequently restricting the use of sludge in agriculture. Sludge, especially from S1 and S2, is evidently unsuitable for agricultural use because of high Cu content in S1 and Ni content in S1 and S2. On the other hand, metal concentrations in the samples S3, S4, and S6 were less than the permissible values. Therefore, the sludge from these sites could be safely used in agriculture. At sites S1 and S2, the total Cu, Zn, Pb, Cr, Cd and Ni contents in sludge were found to exceed the discharge standards of pollutants for municipal WWTP (GB 18918—2002). Moreover, the concentrations of other elements were higher than those reported in the crop soil background data for Guangzhou, with the exception of Pb concentrations in S5 and S6, and Cr in S3 to S6. Therefore, sludges from S3, S4, and S6 can be used as good organic fertilizers, whereas those from S1 and S2 should not be used directly unless subjected to bioremediation [48] and chemical remediation [49]. Soil contamination, especially with heavy metals, is a serious problem in China. For example, concentrations of heavy metals in 3.6×10^7 m^2 sampled from 3.0×10^9 m^2 of basic agricultural protected cropland [5] in 2000 were found to exceed the permissible values specified in state standards for croplands. A strict enforcement of state-stipulated standards should be established to limit the indiscriminate use of sludge in croplands.

3.3 Speciation of heavy metals in municipal sludge

The bioavailability and ecotoxicity of metals primarily depend on their speciation in sludge (Table 4). Heavy metals distributed in the acid-soluble/exchangeable (F_1) and reducible fractions (F_2) can readily accumulate in plants or aquatic systems. Therefore, these fractions are identified as the directly impacting fractions. Guangzhou is located in a region prone to acid rain [30], and the red soil in this region has a high oxidizing property because of its acidity [29]. The oxidizable fraction (F_3) in an oxidizing state is easily mobilized and transformed into an F_1 or F_2 fraction. Therefore, potential ecotoxicity should not be ignored. Thus, F_3 can be identified as the potential toxicity fraction. The heavy metal bound to the residual fraction (F_4), which is "unreactive" and unaffected by environmental changes, is identified as the stable fraction.

Table 4 Relation among fraction of heavy metals, eco-toxicity and bioavailability

Fraction of heavy metals	Eco-toxicity	Bioavailability
Acid soluble/exchangeable fraction (F_1) and reducible fraction (F_2)	Direct toxicity	Direct effect faction
Oxidizable fraction (F_3)	Potential toxicity	Potential effect fraction
Residual fraction (F_4)	No toxicity	Stable fraction

Fractions of Cu, Zn, Pb, Mn, Ni, Cd, and Cr were determined by the BCR procedure in municipal sludge and represented as the percentage of total concentrations in sludge, as shown in Fig. 1. The statistically computed results of each heavy metal fraction in the sludge samples are listed in Table 5.

The distribution of the metallic fractions differs with the stabilization treatment used, although similarities exist in some cases (Fig. 1). One such case is Cu, which is primarily associated with the OM content. The Cu contents of F_1 and F_2 were low in all sludge

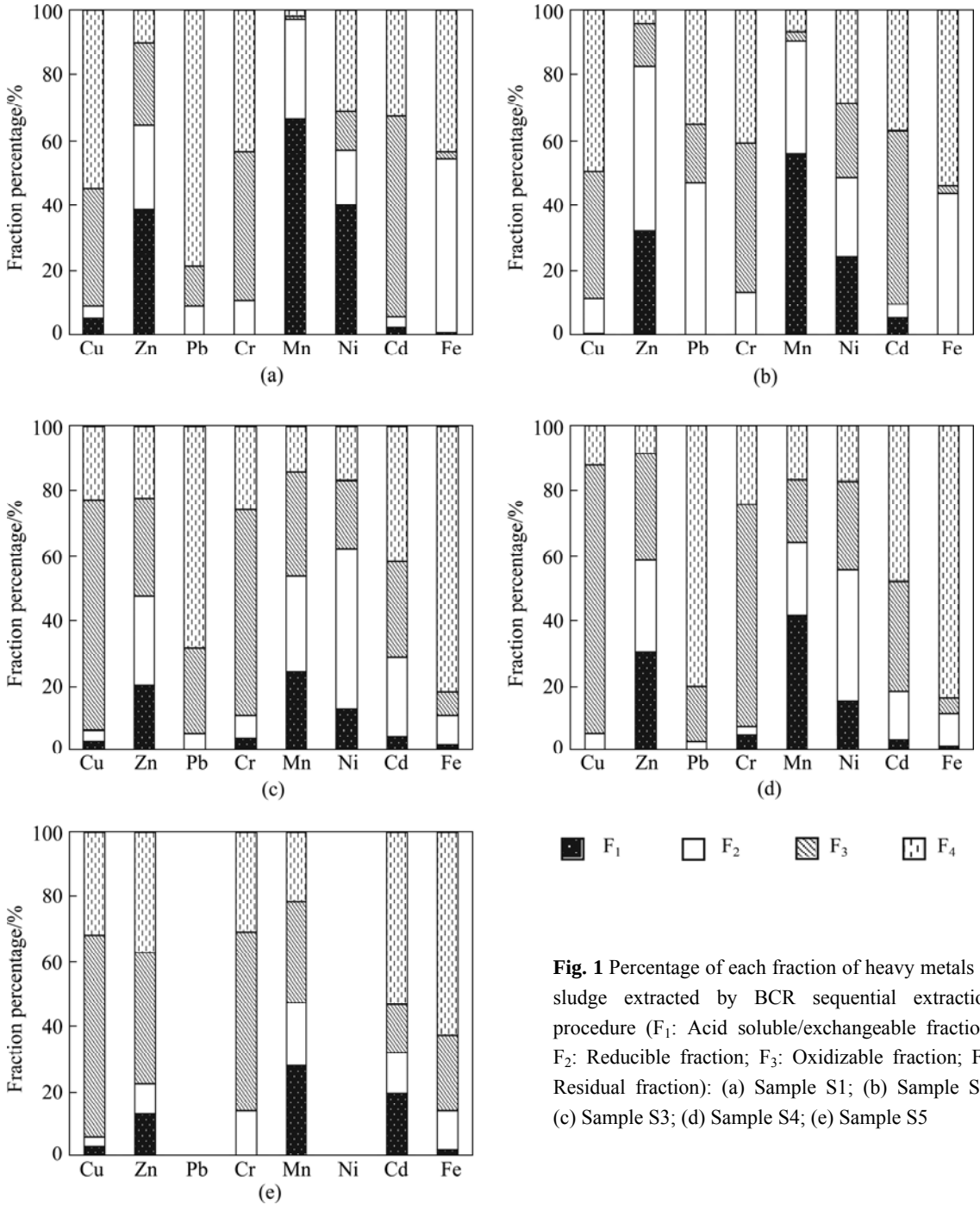

Fig. 1 Percentage of each fraction of heavy metals in sludge extracted by BCR sequential extraction procedure (F_1: Acid soluble/exchangeable fraction; F_2: Reducible fraction; F_3: Oxidizable fraction; F_4: Residual fraction): (a) Sample S1; (b) Sample S2; (c) Sample S3; (d) Sample S4; (e) Sample S5

samples. Cu content in the F_1 was especially low at less than 5% (except for S1), thus implying less direct toxicity to the environment. The greatest extraction percentage was obtained in F_3 and F_4 of all the sludge samples, which was expected given the affinity of OM and minerals for this type of element and the formation of stable complexes [43,50,51]. The sum of F_3 and F_4 accounted for 85% of total Cu in all the sludge samples, indicating that Cu is associated with strong organic ligands and probably occludes in such minerals as quartz and feldspars. However, the percentage of Cu associated with the OM fraction primarily depends on the quantity of Fe oxides in soil [52]. Additionally, the evaluation of the bioavailability of metals to the environment is essential in predicting changes in metal behavior in response to environmental conditions. Lateritic red soil, which is the predominant soil type in Guangdong Province, is rich in Fe oxides and Cu in F_3 and can be mobilized and available under oxidizing conditions. Therefore, the Cu in all sludge samples has a high potential for ecotoxicity and bioavailability to the soil of Guangdong, especially the S1 sludge.

Table 5 Statistical results[a] of each heavy metal fractions in samples (mg/kg)

Element	Fraction	Content of heavy metal				
		S1	S2	S3	S4	S5
Cu	F_1	231.0 ± 7.4	0.80±0.03	4.66±0.20	[b] –	5.22±0.27
	F_2	180.0 ± 7.5	28.60±0.82	6.74±0.23	7.32±0.38	4.40±0.27
	F_3	1607 ± 36	104.0±4.4	137.0±4.3	115.0±5.2	105.0±4.8
	F_4	2456 ± 78	131.0±4.3	43.70±2.28	16.60±0.58	53.50±2.02
Zn	F_1	332.0 ± 14.8	361.0±17.0	187.0±11.7	185.0±9.6	89.40±4.64
	F_2	223.0 ± 4.0	571.0±30.1	254.0±6.2	176.0±8.1	67.40±2.85
	F_3	220.0 ± 7.3	149.0±9.2	279.0±13.3	201.0±12.5	282.0±9.3
	F_4	85.00 ± 3.48	46.00±2.01	207.0±6.7	53.60±2.18	264.0±10.9
Pb	F_1	–	–	–	–	–
	F_2	7.72 ± 0.37	53.90±3.53	3.86±0.28	1.92±0.11	–
	F_3	10.90 ± 0.24	20.50±0.66	21.60±1.17	13.10±0.64	–
	F_4	69.80 ± 3.63	40.30±1.73	54.50±2.03	61.20±2.37	–
Cr	F_1	–	–	1.69±0.07	2.37±0.12	–
	F_2	14.50 ± 0.89	12.20±0.89	3.48±0.19	1.44±0.09	2.76±0.16
	F_3	59.40 ± 2.64	43.10±1.54	31.30±2.11	36.80±1.71	11.00±0.73
	F_4	57.00 ± 1.20	38.40±1.64	12.70±0.53	12.90±0.42	6.08±0.28
Mn	F_1	1190 ± 50	638.0±30.6	50.40±3.67	156.0±6.6	45.60±2.37
	F_2	543.0 ± 43.9	399.0±20.9	62.10±2.19	85.90±3.93	31.00±1.47
	F_3	20.30 ± 1.26	29.50±0.64	67.60±4.12	72.40±4.94	51.30±2.15
	F_4	33.50 ± 1.46	77.10±4.01	29.70±1.67	63.90±4.52	34.70±2.47
Ni	F_1	58.10 ± 3.02	30.60 ± 0.99	9.00±0.84	11.40±0.63	19.00±1.14
	F_2	24.60 ± 1.98	30.70 ± 1.89	36.00±2.21	30.10±1.56	12.30±0.39
	F_3	17.40 ± 0.57	29.40 ± 1.89	15.40±0.69	20.60±1.47	14.60±0.69
	F_4	45.30 ± 2.27	36.20 ± 2.70	12.10±0.69	12.80±0.62	51.90±2.27
Cd	F_1	0.14 ± 0.02	0.23 ± 0.04	0.15 ± 0.01	0.11 ± 0.02	–
	F_2	0.21 ± 0.02	0.20 ± 0.03	0.94 ± 0.03	0.50 ± 0.04	–
	F_3	3.79 ± 0.19	2.48 ± 0.08	1.27 ± 0.08	1.11 ± 0.07	–
	F_4	1.99± 0.07	1.71± 0.05	1.58± 0.07	1.59± 0.10	–

Results[a] are expressed as mean±SD (standard deviations); [b] –: indicated

Cr was principally distributed between F_3 and F_4 (F_3 and F_4 accounted for over 85% of Cr), as mentioned in Refs. [53−55]. For the more mineralized sludge, Cr was more likely to be found in F_3 than in F_4 because it probably forms sulfides with this type of sludge. For other sludge types, Cr was primarily associated with F_2. In F_2, Cr did not exceed 15% in all the sludge samples, and in *F*1, the contents of Cr in S1, S2, and S6 were all below detection limits. In F_1 fraction, the ratio of Cr in S3, S4, and S5 did not exceed 5%, indicating a low direct effect for the fractions.

Pb was primarily present in F_4 of S1 (approximately 85.90%), S3 (approximately 68.20%), and S4 (approximately 80.3%), with a lower percentage in S2 (approximately 38.75%), and was not detected in S5. However, in the S2 sample, F_2 was predominant, with Pb accounting for 51.83%. The results were in good agreement with the reports of other studies [52]. Pb can reportedly be immobilized by insoluble salts, such as phosphates [56]. The importance of soil OM in limiting Pb bioavailability has also been demonstrated [57]. The important role of Pb can explain its high concentration in F_3 of municipal sludge and can predict its low direct and potential bioavailability to the environment if the sludge is used for the organic modification of soil.

Zn showed the greatest degree of mobility based on the high proportion of metal extracted from F_1 (12.70% to 42.29%), F_2 (9.6% to 57.85%), and F_3 (15.10% to 40.20%). Zn thus appeared to have high bioavailability and potential ecotoxicity, a result that reflects the

findings of ALVAREZ et al [55]. However, Zn appeared to be preferentially bound to Fe oxides in soil [52], and HSEU [58] reported Zn to be associated with chemically reactive fractions (exchangeable and carbonate fractions) in native tropical soils, which have Zn concentrations of approximately 2% to 6%. A part of Zn can be occluded inside crystalline structures and not readily available for plant absorption. Therefore, the ecotoxicity of Zn in municipal sludge might have been overestimated in the soil in Guangdong, which is rich in Fe oxides.

Cd distribution in various fractions showed different patterns for each sewage sludge sample. The variable total Cd concentration was found in sludge from below the determination limits to 5.99 mg/kg, but in F_1 was relatively low in all the sludge samples. Approximately 63.32% of the total Cd content in S1 and 55.35% of total Cd content in S2 were extracted in the third step, indicating high bioavailability to the environment when soil conditions changed.

Ni was found in large quantities during the first extraction step. Quantities varied from 12.40% in S3 to 39.26% in S1. Ni was widely distributed in the four fractions. The sum of the first two fractions ranged from 31% of the sludge S5 to 62% of the sludge S3. In the sludge S5, Ni was mainly primarily with F_4 (approximately 53%). This high mobility of Ni was also found by FUENTES et al [35], WANG et al [59] and ŠČANČAR et al [43] in the speciation of heavy metals in different sludge samples.

Mn distribution in various fractions showed a number of different patterns for all samples. In the samples S1 and S2, Mn was found in large quantities during the first extraction step, accounting for 64.53% and 55.38%, respectively. However, lower percentages of Mn were found in the samples S3, S4, and S5. Over 40% of the total Mn was distributed in the fractions F_2 and F_3 in the sludge samples S3, S4, and S5, showing high bioavailability to the environment when soil conditions changed. Different fraction distribution orders of Mn were also observed in different sludge samples by SOLÍS et al [60] and ÁLVAREZ et al [55].

Notably, the distribution of heavy metal fractions varied widely for different metals, as shown in Fig. 1. Among all samples (including industrial and domestic sewage sludge) from S1 and S2, the active fractions (the sum of F_1, F_2, and F_3) of Zn and Mn had the highest concentrations and accounted for over 90%. In the sludge sample S5, pollution originated from the paper mill (industrial sewage sludge), with such heavy metals as Cu, Zn, Cr, and Mn, presents in a higher active fraction that constituted over 60% of pollutants. Cu, Zn, Mn, and Ni constituted over 70% of heavy metals in the sludge samples S3 and S4 (domestic sewage sludge). Therefore, the higher percentage of the active fraction in S1 and S2 from WWTPs comprising industrial wastewater may result in more serious potential phytotoxicity than the sludge samples S3, S4, and S5 when used for agricultural applications.

In the samples S1 and S2, heavy metals Zn, Mn, and Ni had a larger percentage (over 23%) in F_1, Cu and Cr existed predominantly in F_2 (over 35%), and Pb was associated with F_4 (over 68%). In the sludge samples from S3, S4, and S5, all metals, with the exception of Mn, existed primarily in F_3 and F_4, whereas the contribution of F_2 was small. In the samples S3, S4, and S5, Mn had a higher concentration in the fraction F_1 (water-soluble, exchangeable, and bound to carbonate forms) and represented high bioavailability. These results indicated that the mobility and potential bioavailability of Zn, Mn, and Ni in the samples S1 and S2 from industrial WWTPs were significantly higher than those in samples from municipal WWTPs.

Verification of the results of the BCR sequential extraction procedure was performed by comparing the sum of the four fractions (F_1, F_2, F_3, and F_4) with total concentrations of heavy metal from Table 3. The detailed calculations can be expressed as follows:

$$\text{Recovery}=\frac{F_1+F_2+F_3+F_4}{\text{Total concentration}}\times 100\% \quad (1)$$

The results are shown in Fig. 2. It is clearly apparent that the sum of four steps was in accordance with the total heavy metal concentrations with satisfactory recovery rating from 95% to 114%, which is very similar to that recorded in the bibliography for the same extraction scheme [53−55,61]. The results indicated that the modified BCR sequential extraction method used for detecting the speciation of Cu, Zn, Pb, Ni, Mn, Cd and Cr in different kind sludges is accurate and reliable.

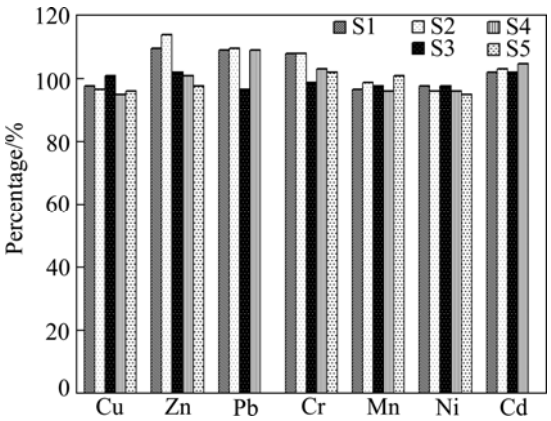

Fig. 2 Sum of percentage of each fraction

4 Conclusions

1) Municipal sludge collected from six sewage

treatment plants at Guangzhou, China had high organic carbon, and was rich in such nutrients as N and P. The analysis of the total contents of heavy metals in sludge showed that the total concentrations of Cu in S1, Ni in S1, S2, and S5, and Cd in S5 exceeded the allowable values. Only the heavy metals in samples S3 and S4 were below the permissible values in the national application standard of acid soil in China (GB18918—2002).

2) Under the Guangdong soil conditions, Cu, Zn, and Cr were primarily distributed in F_3, and Mn is primarily distributed in F_1, posing high potential ecotoxicity. However, the bioavailability of Zn might be overestimated for Guangdong soil. Pb was primarily found in F_4, showing low direct and potential ecotoxicity to the environment. Cd and Ni were distributed in various fractions and showed different patterns for each municipal sludge sample, highlighting the potential ecotoxicity in S1, S2, and S5.

3) Based on the indications exhibited by the composition of municipal sludge and permissible sewage discharge and from an environmental protection perspective, strict management and implementation of environmentally safe production policies are necessary to improve the environment surrounding the S1 WWTP area, where chemical plants are centralized.

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广州市不同来源污泥中重金属的含量和形态分布特征

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摘　要：采集了广州市 4 个不同来源污水处理厂及 1 个工业废水处理厂的脱水污泥，分析污泥的理化性质参数和重金属(Zn、Cu、Pb、Cr、Ni、Mn、Cd)的含量，重点利用 BCR 法研究不同污泥中重金属的赋存形态。结果表明，脱水污泥中有机质含量较高，并且富含 N 和 P 营养成分。污泥中重金属含量差别较大，其中 Mn、Zn、Cu 含量高，其次是 Ni、Pb、Cr，Cd 含量最低，但 5 个不同来源污泥中重金属的含量都高出广州市农田背景值。除了 S1 污水污泥中的 Cu、Cd 及 S1、S2、S5 污水污泥中的 Ni 外，其他污泥中重金属的含量都低于国家污泥农用控制标准(GB 18918—2002)。BCR 连续提取法表明，污泥中的 Mn 和 Zn 主要以酸可交换态及易还原态存在，Cu 和 Cr 主要以可氧化态和残渣态存在，Pb 大部分存在于残渣态，Ni 和 Cd 的形态分布没有明显特征。

关键词：城市污泥；重金属；金属形态；连续提取；污水处理厂

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