Concentrations of Heavy Metals in Six Municipal Sludges from Guangzhou and Their Potential Ecological Risk Assessment for Agricultural Land Use

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Abstract

Six kinds of municipal sludge samples were collected from wastewater treatment plants (WWTPs) from Guangzhou in southern China. Total concentration of Cu, Pb, Zn, Cr, Ni, Cd, and Mn in the sludge was determined, and used obtained values to appraise the degree of agricultural land pollution on the base of four pollution indixes. Results showed that the concentrations of the heavy metals Cu (4.567 mg/kg), Mn (1.844 mg/kg), Ni (148 mg/kg), Cr (121 mg/kg), and Cd (5.99 mg/kg) in S1 sludge were higher than that of the other sludges. In six sludge samples the concentrations of Mn, Zn, and Cu were highest, followed by Ni, Pb, and Cr. Cd had the lowest concentration. All 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 (GB18918-2002). The geoaccumulation index (I_{geo}) assessment results indicate that there are serious risks in agricultural utilization for the existing Cu and Zn in these six kinds of sludges, especially the I_{geo}, which was 6.53 for Cu, 3.21 for Mn, 2.78 for Cd in the S1 sludge. The results of *RI* showed that sludge had high potential ecological risks, especially caused by Cd, which should give rise to widespread concerns. The potential ecological risk index (*RI*) of heavy metals in six sludge samples was ranked in the order of S1>S2>S4>S3>S5>S6.

Keywords: municipal sludge, heavy metal, geoaccumulation index (I_{geo}), potential ecological risk index (*RI*)

Introduction

The increasing numbers of plants for the treatment of wastewater have brought about an increase in the genera-

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tion of sewage sludge [1]. Large volumes of sludge need to be disposed of or treated in some manner. One way of sludge disposal is its application on land, and this has become common practice [2]. The application of sewage sludge on agricultural soils has been widespread in many countries around the world and this has been shown to

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

Name of WWTP	No.	Treatment scale (m³/d)	Population equivalents	Treatment process	Disposal and use of sludge	Proportion[a]
KFQ	S1	$3.0×10^4$	$6.0×10^4$	Activated sludge	Landfill	70%
DTS	S2	$60.66×10^4$	$142.7×10^4$	Activated sludge	Sanitary landfill	40%
LJ	S3	$40.0×10^4$	$134.3×10^4$	Anaeroxic-Anoxic-Oxic (A²/O)	Building materials	<5%
LD	S4	$103.67×10^4$	$225.8×10^4$	Alternating activated sludge	Building materials	<5%
ZZ	S5	/	/	A²/O – Aeration ditch	Sanitary landfill	100%
ZQ	S6	$4.0×10^4$	$18.6×10^4$	Microporous aeration – Carrousel 2000 oxidation ditch process	Building materials	<5%

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

improve soil properties and increase plant productivity [3]. In the European community, over 30% of sewage sludge has been used as fertilizer in agriculture.

Agricultural land application appears to be a logical and reasonable way of treating sewage sludge, since it may improve many soil properties, such as pH and contents of organic matter and nutrients [4-6]. In Belgium, 57% of the sludge is applied to land. In France, 60% of the sewage sludge is used for land application [7]. Sewage sludge is effective as a fertilizer, increases dry matter yield of many crops [8], and can also improve soil physical properties such as porosity, aggregate stability, bulk density, and water retention and movement [9]. Although dewatered sewage sludge contains valuable nutrients such as nitrogen, phosphorus, organic matters, and essential trace elements, it also contains various toxins, especially heavy metals, which cause harm to the soil-plant system and further might pose a serious risk to human health [10, 11]. The advantages and disadvantages caused by land application of sewage sludge have attracted the attention of environmental authorities, the public, and scientists [12].

According to statistics data of the Ministry of Construction of the People's Republic of China, the number of wastewater treatment plants was 427 in 2000 and increased rapidly to 708 in 2005. Therefore, the volumes of sewage sludge increased correspondingly, and now up to $1.0×10^8$ t of sewage sludge is produced annually. There has been an increasing tendency in recent years to use sewage sludge as fertilizers in agriculture. The agricultural areas of land application of sewage sludge, usually in the suburbs of cities, involves nearly all the main food crops and vegetables in China such as rice, wheat, corn, millet, soybean, rye, taro, Chinese cabbage, cucumber, tomato, lettuce, hot pepper, cauliflower, and cabbage [13, 14].

Guangzhou, with a population of above 10 million, is one of the largest industrial centers and fastest expanding cities in China. Its overall economic power is the third among all China's cities and just after Shanghai and Beijing, contributing to 1/10 of China's gross domestic product (excluding Hong Kong). It was expected that, by 2020, the volume of waste water in the center district of Guangzhou city will reach $4.30×10^6$ m³/d [15], and the sludge produced will be $1.29~2.15×10^4$ m³/d (98% mois-

ture), calculated by the method that the amount of sludge production is 0.3%~0.5% of the volume of waste water. Therefore, how to dispose of and use this large amount of sludge safely and economically will be a common environmental problem to be concerned.

Recently, environmental awareness has been intensified, and the utilization and treatment of sewage sludge has become a major environmental concern throughout China. Therefore, it is necessary to monitor and evaluate the environmental quality of heavy metals before using the sludge in agricultural applications. A variety of evaluation methods for heavy metals were proposed from different perspectives, in which the mostly used methods are enrichment factor (EF) [16], the geoaccumulation index (I_{geo}) [17], pollution load index [18], the potential ecological risk index (RI) [19], excess after regression analysis [20], fuzzy subset theory [21], face graph [22], comprehensive pollution index [23], Nemerow comprehensive index (P_n) [24], and secondary phase enrichment factor [25]. These methods represent the internationally advanced level in the evaluation of heavy metals in soil and sediment, but the potential ecological risk assessments on heavy metals in sludge during agricultural usage are much less studied. At the same time, the risk assessment of heavy metals would provide a certain theory support for risk management of sludge.

The main objectives of this study were to:
(1) Investigate the concentration and distribution of relatively hazardous elements (Mn, Cr, Pb, Cu, Ni, Cd, and Zn)
(2) Assess the potential ecological risk of elements in sludge based on geo-accumulation index (I_{geo}) and the potential ecological risk index (RI)
(3) Predicate the potential risk for agriculture, and provide evidence on the feasibility of sludge reuse for agronomic application.

Materials and Methods

Sampling and Pre-Treatment

Dewatered sludge samples were obtained from four WWTPs at Guangzhou (S1, S2, S3, and S4). The combined total volume of effluent in these four WWTPs accounts for

Table 2. Physico-chemical properties of sludges from the selected municipal and industrial wastewater treatment plants.

	Moisture content (%)	pH	Organic carbon (%)	Total N (%)	Total P (%)	Ca (%)	Mg (%)	Na (%)	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

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, the other two sludge types, including those from the papermaking mill in Guangzhou (S5) and the domestic WWTP (S6) from Zhaoqing adjacent to Guangzhou, were also collected separately. The locations of sample points are shown in Fig. 1. Samples were collected from the terminal conveyor belts of four WWTPs on the same day. Each sludge sample was collected four times during a sampling time that lasted for 2 hours and at intervals of 0.5 h. The samples were air-dried at room temperature, ground, and homogenized in an agate mortar, sieved (mesh pore size: 0.14 mm), and then stored in jars at room temperature.

Physico-Chemical Analysis of the Sludge

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 [26, 27]. Stated briefly, pH of sludge was measured in a preparation made up by a 1:5 ratio of sludge and water suspensions. The organic matter content of the sludge samples was determined by ashing at 500ºC for 3 hours. The TN was measured by the Kjeldhal method. The contents of total Na, Ca, Mg, Fe, P, and K were determined by atomic absorption spectrometry (AAS, Z-2000, Hitachi). All values obtained for these physicochemical properties are listed in Table 2.

Determination of the Total Heavy Metal Concentration

A subsample of 1.00 g of dry sludge (<63 μm) was weighed directly in a dried, cleaned PTFE digestion vessel and 10 mL of HF (40% v/v), 15 mL of HNO$_3$ (65% v/v),
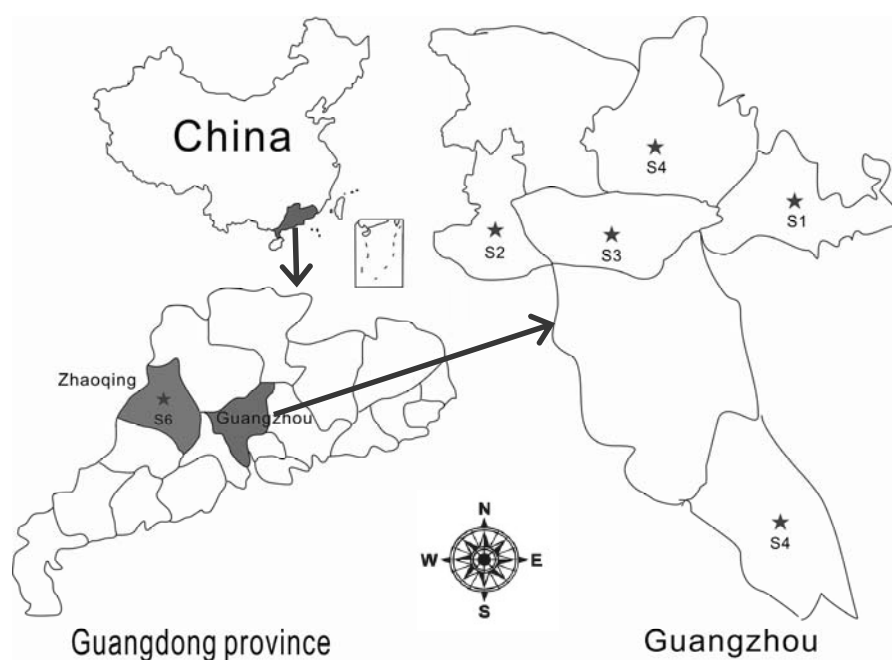

Fig. 1. Sketch map showing the sampling sites.

Table 3. Pollution grades of geo-accumulation index of the metals.

I_{geo} class	I_{geo} value	Grades of quality
0	$I_{geo} \leq 0$	Uncontaminated
1	$0 < I_{geo} \leq 1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} \leq 2$	Moderately contaminated
3	$2 < I_{geo} \leq 3$	Moderately to heavily contaminated
4	$3 < I_{geo} \leq 4$	Heavily contaminated
5	$4 < I_{geo} \leq 5$	Heavily to extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

and 1 mL of $HClO_4$ (60% v/v) were added. Afterward, the digestion vessel was placed in the chamber of the microwave system. The digestion conditions were optimized using different times and powers in the microwave system. The maximum recoveries were obtained at a power of 60% (400 W) for 25 min [28]. After digestion, the sample solution was allowed to air-cool and then 4.00 g of boric acid were added. The solution was filtered through a Whatman No. 42 filter paper and quantitatively transferred to a 50 mL calibrated flask and diluted with deionized water.

Potential Ecological Risk Assessment Methodology

The geoaccumulation index (I_{geo}) has been used since the late 1960s, and has been widely employed in European trace metal studies. Originally used for bottom sediments [29], it has been successfully applied to the measurement of soil contamination [30]. The I_{geo} enables the assessment of contamination by comparing current and pre-industrial concentrations, although it is not always easy to reach pre-industrial sediment layers. Pollution levels of toxic metals in sewage sludge for agricultural land use could be defined as the following equation:

$$I_{geo} = \log_2 \frac{C_n}{1.5 B_n} \qquad (1)$$

...where: C_n – the measured content of the metal n in sewage sludge, mg/kg; B_n – the background or pristine value of the heavy metal, mg/kg. In this study, the back-

ground value of individual metal is the mean value in soil of the Pearl River Delta in Table 5. The constant factor 1.5 is introduced to analyze natural fluctuations in the contents of a given substance in the environment and very small anthropogenic influences [31]. Müller [32] proposed seven classes of the geo-accumulation index, as shown in Table 3.

The assessment of ecological risks of toxic metals in sewage sludge was carried out using the potential ecological risk index (RI) proposed by Hakanson [33]. RI method covers a variety of researching domains, i.e. biological toxicology, environmental chemistry as well as ecology, and could evaluate ecological risks caused by toxic metals comprehensively. The calculating methods of RI are listed below.

$$C_f^i = \frac{C_n^i}{C_0^i} \qquad (2)$$

$$E_r^i = T_r^i \times C_f^i \qquad (3)$$

$$RI = \sum_{i=1}^{n} E_r^i \qquad (4)$$

...where: C_f^i is the single metal pollution index; C_n^i is the concentration of heavy metal in samples, mg/kg; C_0^i is the reference value for the heavy metal, mg/kg. (In this study, the background value of individual metal is the mean in soil of the Pearl River Delta in Table 5); E_r^i is the monomial potential ecological risk factor; T_r^i is the metal toxic response factor, according to Hakanson [33], the values for each element are in the order of Zn=1 < Cr=2 < Cu=Ni =Pb=5< As=10 < Cd=30 < Hg=40; RI-the potential ecological risk caused by overall contamination.

Hakanson [33] defined five categories of E_r^i and four categories of RI, as shown in Table 4. RI is the comprehensive potential ecological index, which is the sum of E_r^i. It represents the sensitivity of the biological community to the toxic substance and illustrates the potential ecological risk caused by the overall contamination [34, 35].

Results and Discussion

Physicochemical Properties of Sludge from Select Wastewater Treatment 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

Table 4. Indices and grades of potential ecological risk of toxic metals contamination.

E_r^i value	E_r^i/Risk grades	RI value	RI/Risk grades
$E_r^i < 40$	Low potential ecological risk	RI<150	Low potential ecological risk
$40 \leq E_r^i < 80$	Moderate potential ecological risk	$150 \leq RI < 300$	Moderate potential ecological risk
$80 \leq E_r^i < 160$	Considerable potential ecological risk	$300 \leq RI < 600$	Considerable potential ecological risk
$160 \leq E_r^i < 320$	High potential ecological risk	$RI \geq 600$	Significantly high potential ecological risk
$E_r^i \geq 320$	Extremely high potential ecological risk		

Table 5. Total contents of Cu, Pb, Ni, Mn, Cr, Zn, and Cd in sludge samples collected from select wastewater treatment plants, and the control standards for pollutants in sludges for agricultural use of China and other countries (mg/kg dry matter).

	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	-
Mean in China[b]	533	115	79.1	397[c]	222	1270	7.18
Mean in soil of the Pearl River Delta[d]	33	40	21.2	[e]/	71.4	84.7	0.58
Murcia, Spain[f]	204	58	17	/	38	487	1.10
Dom ažale, Slovenia[g]	433	126	621	/	856	2032	2.78
Control standards for pollutants in sludges for agriculture use (Threshold values)							
China pH<6.5[h]	800	300	100	/	600	2000	5
China pH≥6.5[h]	1500	1000	200	/	1000	3000	20
America[f]	1500	300	420	/	1200	2800	10
Canada[f]	500	200	100	/	1000	2000	10
EU pH>7[i]	1750	1200	400	/	1500	4000	40
EU pH<7[i]	1000	750	300	/	1000	2500	20

[a]Below the detection limits; [b]According to Ma et al. [45]; [c]According to McGrath et al. [46]; [d]According to Wong et al. [47]; [e]Have no statistical data; [f]According to Fuentes et al. [44]; [g]According to Ščančar et al. [43]; [h]From China's" Control Standards for Pollutants in Sludges for agriculture use (GB 18918-2002)" [48]; [i]From from the threshold values of heavy metals established in Directive 86/278/EEC as function of soil pH

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 g/kg to 40 g/kg OM, 1.0 g/kg to 2.0 g/kg total N, 0.44 g/kg to 0.85 g/kg total P, and approximately 16 g/kg total K [36]. All the parameters closely reflect those found in the bibliography for sludge of similar characteristics, some of which has been used for soil improvement [37-41]. 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.

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 5. Generally, the sludge samples shown in Table 5 had higher concentrations of Cu and Zn but relatively lower concentrations of Cr, Ni, and Pb.

Similar results on the differences in the concentrations of heavy metals have been reported by Alvarez et al. [42] and 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 that in Murcia, Spain [44]. However, the amount 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 that reported by Domažale, Slovenia [43]. The concentrations of heavy metals in sludge from S1 and S2 were significantly higher (P<0.05) than that 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 Domžale (Slovenia) [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 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 do 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.

Table 6. Geoaccumulation index of heavy metals in sludge samples and their grading of potential pollution levels.

No.	Cu		Pb		Ni		Mn		Cr		Zn		Cd	
	I_{geo}	$R*$	I_{geo}	R	I_{geo}	R	I_{geo}	R	I_{geo}	R	I_{geo}	R	I_{geo}	R
S1	6.53	6	0.44	1	2.22	3	3.21	4	0.18	1	2.63	3	2.78	3
S2	2.47	3	0.79	1	2.05	3	2.54	3	-0.30	0	2.96	3	2.36	3
S3	1.94	2	0.46	1	1.22	2	0.11	1	-1.11	0	2.84	3	1.81	2
S4	1.56	2	0.22	1	1.29	2	0.99	1	-1.05	0	2.26	3	2.10	3
S5	1.82	2	-	-	1.70	2	-0.30	0	-2.46	0	2.50	3	1.30	2
S6	0.91	1	-1.79	0	0.68	1	2.29	3	-2.79	0	2.00	2	-	-

*R – rank of I_{geo} classification

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 content were the second highest, whereas Pb and Cr content were relatively lower. These results concur with the findings of Ma et al. [45]. Comparing 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 (Domžale and Murcia) [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) [48] is listed in Table 5. A comparison of metal concentrations in sludge with the permissible values indicated that the concentrations of Cu and Cd in S1, 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 S3, S4, and S6 samples 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 (GB18918-2002) [48]. Moreover, except Pb concentrations in S5 and S6, and Cr in S3, S4, S5, and S6, the concentrations of other metals listed in Table 5 were higher than those reported in the crop soil background data for Guangzhou. Therefore, sludge

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 [49] and chemical remediation [50]. Soil contamination, especially with heavy metals, is a serious problem in China. For example, concentrations of heavy metals in 36,000 ha sampled from 300,000 ha of basic agricultural protected cropland [51] 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.

Potential Risk Assessment of Heavy Metals in Municipal Sludge

Contamination Degree Based on I_{geo}

To make sure that the application of I_{geo} can obtain the environmental information of heavy metal pollution in the sludge for agricultural purposes, it was assumed that the range of agricultural utilization of the sludge was the Pearl River Delta region, which was in conformity with the requirements for selection of geochemical background values of heavy metals [52]. The I_{geo} of heavy metals in sludge and classification of the degree of pollution were obtained by Formula (1) and shown in Table 6.

According to the I_{geo} values listed in Table 6, it can be seen that the content of Cu and Mn in S1 sludge were far more than the average background value of crop soil of the Peal River Delta and the pollution levels were the extreme strong pollution and strong pollution, respectively. Zn and Ni reached the level of moderate pollution, but Pb and Cr were uncontaminated. The results of I_{geo} show that the risks of heavy metals in S1 sludge are in the decreasing order of Cu>Mn>Cd>Zn>Ni>Pb>Cr. In S2 sludge, Zn and Mn were the main pollution elements, reaching to the level of moderate pollution and the level between moderate and strong pollution, respectively. Moreover, Cu and Ni reached the level of moderate pollution, but Pb and Cr was almost null pollution. In S2 sample, it could be concluded that the contamination degree of heavy metals was ranked in the order of Zn>Mn>Cu>Cd>Ni>Pb>Cr. Comparing S1 sludge with S2 sludge, it was found that the reason for the high degree

Table 7. Potential ecological risk assessment results of toxic metals in sludges.

No.	E_r^i							RI	Grades*
	Cu	Pb	Ni	Mn	Cr	Zn	Cd		
S1	691.97	10.15	34.91	13.92	3.39	9.27	309.83	1073	Very high risk
S2	41.52	13.00	31.13	8.69	2.44	11.65	231.72	340	Considerable risk
S3	28.79	10.30	17.45	1.62	1.39	10.73	157.76	228	Moderate risk
S4	22.12	8.74	18.40	2.97	1.45	7.19	192.41	253	Moderate risk
S5	26.52	/	24.29	1.22	0.54	8.47	110.69	171	Moderate risk
S6	14.09	2.18	12.03	7.32	0.43	6.01	/	42	Low risk

*Grades – grades of potential ecological risk of the environment

of pollution in the former was that it is located in the industrial development zone and thus the proportion of industrial sewage entering water was higher than the latter. Due to the robust development of the electronics industry, part of Mn and Ni industrial sewage increased greatly and accumulated in sludge. Combined with the results of I_{geo} assessment, it can be concluded that there are serious risks in agricultural utilization for the existing Cu and Zn in these six kinds of sludge samples, which needs more strict control on the emission of Cu, Mn, Ni and other metals in industrial wastewater.

Potential Ecological Risk Assessment Based on RI

Hakanson [33] suggested that the potential ecological risk index is mainly related to the concentration, type, quantity, toxicity, and sensitivity of metal pollutants, etc. The relationship between the degree of pollution and the risk coefficient (E_r^i), as well as the potential ecological risk index (*RI*), was summarized in Table 4. According to Hakanson's methodology, a metal toxic coefficient should include information on both sides: metals harmful to the human body and aquatic ecosystems. Therefore, the "principle of abundance" and "release effect" should be discussed. At the same time, the heavy metals in sludge harm the environment through the two principles: "principle of abundance" and "release effect" during agricultural use, which meets several necessary prerequisites in the ecological evaluation system based on the abundance of elements and the principle of release. The toxic coefficients (T_r^i) selected in this paper were: T_r^i (Mn)= T_r^i (Zn)=1, T_r^i (Cr)=2, T_r^i (Pb)= T_r^i (Ni)= T_r^i (Cu)=5, T_r^i (Cd)=30, respectively [33]. The results of pollution evaluation of heavy metals in sewage sludge can be seen in Table 7.

The potential ecological risk assessment results of toxic metals in six sludges were summarized in Table 7. For the monomial potential ecological risk, E_r^i values for Cu in S1 sludge was above 320, which indicated that Cu denoted extremely high risk to the environment. E_r^i values for Pb, Cr, Ni, Mn, and Zn in six sludges were below 40, indicating low risk. On the whole, the risk indices (E_r^i) in S1 were ranked in the following order: Cu>Cd>Ni>Mn>Pb>Zn>Cr, while the metals in the S2 sludge varied in the order of Cd>Cu>Ni>Pb>Zn>Mn>Cr. Except S6, all the E_r^i values for Cd in other five sludges were more than 110, indicating that Cd posed more risks to the local ecosystem than the other heavy metals except Cu in S1. The very high risk to environments posed by Cd should give rise to widespread concerns. Consequently, it can be concluded that the main ecological risk element in S1 is Cu and Cd, and in S2, S3, S4, and S5 is Cd, which should be conducted during the pretreatment before the sludge was used in agriculture, such as the bioleaching technology with low costs, good leaching effects, and simple operations [53].

In order to quantify the overall potential ecological risk of observed metals in sludge, *RI* was calculated as the sum of all seven risk factors. Descriptive statistics of *RI* were shown in Table 7. *RI* in the six sludge samples ranged from 42 to 1,073, with an average of 351. It is clear that the grade of potential ecological risk of S1 is very high, and S2 was considerable ecological risk, S3, S3, and S4 sludge have moderate ecological risk, while S6 has low risk. It could be concluded that the potential ecological risks (*RI*) of heavy metals in six sludge samples were ranked in the order of S1>S2>S4>S3>S5>S6.

RI could characterize the sensitivity of the local ecosystem to the toxic metals and represent ecological risk resulting from overall contamination. From Table 5, it was shown that element of Cd accounted for most of the total risks, and the percentages arranged from 28.8% to 76.05% with a mean of 61.4%. Cu ranked second among the metals contributing to the total risk, and the average was 24.52%, which was followed by 11.7% (Ni), 5.18% (Zn), 3.98% (Mn), 3.59% (Pb), and 0.59% (Cr). The most toxic metals, i.e. Cd, contributed more than 60% of the total potential ecological risk in S2, S3, S4, and S5. It could be concluded that the high ecological risk was primarily dominated by metals of Cd in S2, S3, S4, and S5, and Cu in S1. In the whole, Cu and Cd were the dominant risk elements in the S1, and Cd was the dominant risk element in the S2, S3, S4, and S5.

The evaluation targets in soil and river sediments are Cu, Pb, Zn, Cr, Ni, Mn, which were the same as those in control projects of heavy metals in sludge during agricultural applications. In order to explain the applicability of I_{geo} and *RI* in ecological risk evaluation of heavy metals in

Table 8. The range and the corresponding pollution degree of C_f^i and P_n.

Range of C_f^i	C_f^i/Degree of pollution	Range of P_n	P_n/Domain of pollution
$C_f^i < 1$	Low contamination factor	$P_n \leq 0.7$	Safety domain
$1 \leq C_f^i < 3$	Moderate contamination factor	$0.7 < P_n \leq 1.0$	Precaution domain
$3 \leq C_f^i < 6$	Considerable contamination factor	$1.0 < P_n \leq 2.0$	Slightly polluted domain
$C_f^i \geq 6$	Very high contamination factor	$2.0 < P_n \leq 3.0$	Moderately polluted domain
		$P_n > 3.0$	Seriously polluted domain

Table 9. C_f^i and P_n assessment results of toxic metals in sludges.

No.	C_f^i							P_n
	Cu	Pb	Ni	Mn	Cr	Zn	Cd	
S1	138.39	2.03	6.98	13.92	1.69	9.27	10.33	99.58
S2	8.30	2.60	6.23	8.69	1.22	11.65	7.72	7.73
S3	5.76	2.06	3.49	1.62	0.69	10.73	5.26	8.16
S4	4.42	1.75	3.68	2.97	0.73	7.19	6.41	5.78
S5	5.30	/	4.86	1.22	0.27	8.47	3.69	6.45
S6	2.82	0.44	2.41	7.32	0.22	6.01	/	5.53

sludge, the contamination factor (C_f^i) [54] and Nemerow's synthetical pollution index (P_n) [24] are also applied to evaluate the pollution of heavy metals in sludge.

The C_f^i of each heavy metal was defined as the ratio of its concentration to the background value of the corresponding metal using the following equation:

$$C_f^i = \frac{C_n^i}{C_0^i} \qquad (5)$$

...where, C_n^i is the mean content of metals from sludge, and C_0^i is the pre-industrial concentration of individual metal.

Nemerow's synthetic pollution index was applied to assess soil environmental quality in a previous study [24]. In the present study, this method was utilized for the degree of soil environmental pollution and integrative assessment of soil environmental quality for the sludge application in agricultural land use. The pollution index (P_n) was defined as the following equation:

$$P_n = \sqrt{\frac{(MaxP_i^2 + \bar{P}_i)^2}{2}} \qquad (6)$$

$$P_i = \frac{C_i}{S_i} \qquad (7)$$

...where P_n is Nemerow's synthetic pollution index, P_i is the pollution index of the ith heavy metal, C_i is the measured concentration of the ith heavy metal, S_i is the required standard of the ith heavy metal, and P_i and $MaxP_i$ are the average and the maximum value of the pollution indices of all heavy metals respectively.

In this study, the background value of individual metal in sediments from the Pearl River Delta is applied as the pre-industrial concentration of C_0^i and S_i. The background value of individual metal is the mean in soil of the Pearl River Delta in Table 5. The classification criteria of C_f^i and P_n are presented in Table 8. The C_f^i and P_n assessment results are shown in Table 9.

From the results of C_f^i evaluation, Zn was considerable contamination. However, ecological risk caused by Zn was low. The P_n values of six sludges were more than 3 and the domain of pollution for all the sludges were seriously polluted domain, which were not consistent to the RI evaluation. From the results of geo-accumulation evaluation, Cd was mainly in the moderate to heavily contaminated degree. However, ecological risk caused by Cd was considerable or high due to its high toxicity. On the other hand, Pb, Zn, and Mn accumulated significantly in the sludge, but their ecological risks were relatively low. Thus it can be seen that the I_{geo}, C_f^i, and P_n methods were mainly focused on the accumulation levels of individual metal without regard to the toxic response factor. Potential ecological risk index (RI) could describe both ecological risk caused by single pollutant and overall risk or contamination from varied pollutants. When the environmental quality was evaluated, four assessment methods should be comprehensively considered in order to get the more comprehensive and accurate assessment results.

Conclusions

Municipal sludge had high organic carbon, and was rich in such nutrients as N and P, showing potential for use in nutrient modification. The total concentrations of Cu in S1, Ni in S1, S2 and S5, and Cd in S5 exceeded the allowable values for agriculture land use. 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). This result showed promise with respect to agricultural applications for S3, S4, and S6. However, the total contents of heavy metals in S1, S2, and S5 were high, and treatment by remediation is necessary before application in agriculture.

Combined with the results of I_{geo} assessment, it can be concluded that there are serious risks in agricultural utilization for the existing Cu and Zn in these six kinds of sludge, which need more strict control on the emissions of Cu, Mn, Ni and other metals in industrial wastewater. Except for S6, all the E_r^i values for Cd in the other five sludge samples were more than 110, indicating that Cd posed more risks to the local ecosystem than the other heavy metals except Cu in S1. The potential ecological risks (RI) of heavy metals in six sludges were ranked in the order S1>S2>S4> S3>S5>S6.

Comparing the risk values of the heavy metals based on different methods, the main reason for the disagreements may be that the assessment methods of I_{geo}, C_f^i, and P_n ignore the toxic response factors of the different heavy metals. RI considers both the total concentration and toxic response factors of the heavy metals. The different assessment methods should be thoroughly considered for the sludges used for agricultural purposes to obtain more comprehensive and accurate assessment results.

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