

Geochemical transfer of cadmium in river sediments near a lead-zinc smelter

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ARTICLE INFO

Keywords:

Cadmium pollution
North river
Sediment profile
Geochemical distribution
Pb–Zn smelter

ABSTRACT

Cadmium (Cd) is a highly toxic element and non-essential to human. Herein, the source and fate of Cd were examined in a typical sediment profile from the North River, South China, which was affected by the massive Pb–Zn smelting activities for decades. An exceptionally high enrichment of Cd, 107–441 mg/kg, was observed across the whole profile. Approximately 50–75% of Cd was retained in the weak acid soluble fraction. Risk assessment based on geoaccumulation index (I_{geo}), potential ecological risk index (E_{ri}^p), bioavailable metal index (BMI) and toxic risk index (TRI) further indicated an extremely strong degree of potential ecological pollution and high toxic risks. The mineralogical composition of particles from the sediment profile exhibited the presence of pyrite, magnetite, wurtzite and greenockite. This further confirmed that Cd was migrated from smelting slags to the North River basin and enriched in sediment profile. Sediment Cd speciation analysis also implied a possible transformation of Cd from metal oxides in smelting slags to adsorbed phases and carbonates, which enhances the bioavailability of Cd. The findings indicate proper countermeasures or remediation approaches should be promptly taken towards high ecological risks of Cd arising from the depth profile extending nearly 1 m, due to lead-zinc smelting related activities.

1. Introduction

Cadmium (Cd), an extremely toxic and carcinogenic metal, is regarded as a priority metal pollutant by the US EPA and included in the dangerous pollutants inventory by the European Union (USEPA, 2014; Khan et al., 2017; Liu et al., 2017; Holdaway and Wuyi, 2018). As a non-essential trace metal, human consumption of Cd-containing food and water even in low concentrations can cause chronic diseases. Long term exposure to Cd can lead to lung cancer, while toxicosis of high Cd induces nephropathy, bone damages and hematuria, such as “Itai-Itai” disease, which occurred in Japan in the 1960s (Jomova and Valko, 2011; Rodriguez-Barranco et al., 2014; Nishijo et al., 2017; Reyes-Hinojosa et al., 2019; Watanabe et al., 2020).

In natural environment, Cd as a trace metal, has low background concentrations in both the lithosphere and surface soils (0.20 and 0.53 mg/kg, respectively) (Liu et al., 2013, 2017). Mainly due to anthropogenic activities, elevated contents of Cd have been reported in numerous areas (Aleksander-Kwaterczak and Helios-Rybicka, 2008; Kubier et al., 2019; Li et al., 2019a, 2019b; Niu et al., 2020; Webb et al.,

2020). Large amounts of toxic metals have been discharged to the environment through industrial effluents and smelting slags, owing to rough smelting processes and inefficient recycling methods (Sobanska et al., 2016; Lan et al., 2019; Pang et al., 2019; Wang et al., 2019). Especially Cd in smelting slags can be re-migrated into the surface water or groundwater by weathering and rainfall flushing under natural conditions or human transportation, and finally enriched in the sediments (Sobanska et al., 2016; Wen et al., 2019; Yuan et al., 2019).

The North River, which is one of the three major tributaries of the Pearl River and serves as main water supply source of the northern Guangdong Province, has suffered from industrial effluents from a Zn–Pb smelter for a long time (Liu et al., 2016; Li et al., 2019b; Ye et al., 2019). Intensive smelting activities along the riverside have seriously increased the Cd concentrations in the nearby river system (Zhao et al., 2018b; Li et al., 2019b). Heavy metal concentrations in river water exceeding the background values were intermittently rising (Liu et al., 2018; Liu et al., 2020; Li et al., 2019b). Pertinent studies have investigated the distribution characteristics and migration behavior of Cd in river waters and surface sediments (Ciutat et al., 2007; Zhao et al.,

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2018c; Hua et al., 2019). However, few studies are available on Cd distribution in the sediment profiles in the North River.

The main objectives of this study therefore are (i) to understand the vertical distribution of concentration levels and species of Cd in North River sediment profile from a Pb–Zn smelter impacted area, (ii) to explore the transfer mechanism between different Cd species and migration behaviors, and (iii) to evaluate the environmental pollution risk. The findings of this work could be applied to the risk assessment of historical contamination at the local river catchments and provide reference to other Pb–Zn smelter impacted areas.

2. Materials and methods

2.1. Sampling site and sample collection

Flowing through several administrative regions including the Shaoguan city, the North River has a drainage basin of $5.20 \times 10^4 \text{ km}^2$ and is an important source of drinking water for 8 million residents in the Guangdong Province (He et al., 2017; Liu et al., 2018; Zhao et al., 2018c). Located in the upper reaches of the North River, the Shaoguan city has a large-scale traditional heavy industry. With the development of metal smelting, the North River has received large amounts of Cd-containing industrial effluents with metallurgical slags (Zhao et al., 2018a; Li et al., 2019b).

The collection of sediment samples in this study was carried out in winter 2014. As shown in Fig. 1, a sediment core was sampled in the

intersection of the river flowing through the smelter and the North River, ~500 m away from the Pb–Zn smelter. The Cd concentration in the river water near the sediment core was $1.96 \text{ } \mu\text{g/L}$. The sediment core was recovered using a 90-cm gravity corer and kept the original shape with minimum loss. The sediment profile was sliced at 3 cm intervals by a stainless-steel blade and packed in the plastic bags and stored at $4 \text{ } ^\circ\text{C}$ before measurements. A sediment sample from a pond far from the location of the sediment core was collected as the control sample to examine background metal concentrations. After drying at $50 \text{ } ^\circ\text{C}$, the constant-weight sediment samples were then hand-ground to powders ($< 200 \text{ } \mu\text{m}$) using an agate mortar and pestle set for further analysis.

2.2. Analytical methods

2.2.1. Digestion and sequential extraction

To determine the total contents of Cd (Cd_{Tot}), approximately 100 mg for each sediment samples were digested in the solutions with a mixture of HNO_3 , HF and HClO_4 at $150 \text{ } ^\circ\text{C}$. After digesting and evaporating to dryness, the samples were redissolved with 8 M HNO_3 and finally diluted with 8 mL deionized water. Metal concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a PerkinElmer ELAN 6000 instrument at standard operating conditions. The calibration standard solutions were prepared by diluting high-purity ICP multi-element standard solution VI (Merck, Darmstadt, Germany) with deionized water (Milli-Q Millipore,

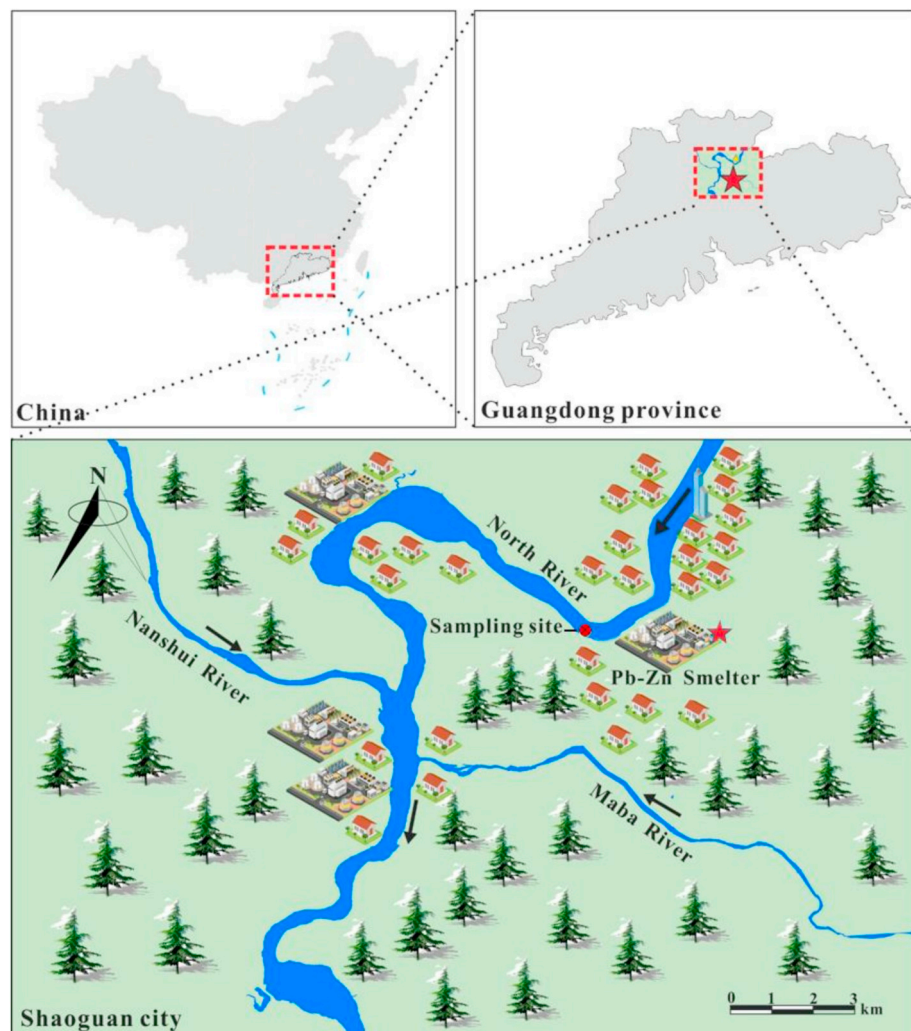


Fig. 1. Sketch map of the sampling sites near the potential source of lead-zinc smelter. (★ the Pb–Zn smelter; ● sediment core).

18.25 MΩ/cm). To verify the digestion procedure, a certified stream sediment reference material GBW 07311 (National Research Centre for Certified Reference Materials, Beijing, China) was simultaneously digested and analyzed. According to the standard sequential extraction procedure set up by Institute for Reference Materials and Measurement, Europe (IRMM), the speciation of Cd in the sediment was measured (Serife Tokalioğlu and Elçi, 1999; Liu et al., 2016; Liu et al., 2018; Alan and Kara, 2019). The procedure includes four main steps to distinguish fractions of Cd. The weak acid exchangeable fraction was determined using 0.11 mol/L CH₃COOH. The reducible fraction was determined using 0.50 mol/L NH₂OH·HCl. The oxidizable fraction was determined using 8.8 mol/L H₂O₂ and 1 mol/L CH₃COONH₄. The residual fraction was analyzed based on digestion of the residue using the same acids with the determination of Cd_{Tot}. Dissolved Cd concentrations in the digestions and extractions were determined by ICP-MS using a PerkinElmer ELAN 6000 instrument. Samples were determined three times and averaged. The relative standard deviation (RSD) between three runs was always better than 5%. The recoveries of Cd from the reference GBW 07311 were in the range of 95–105%.

2.2.2. Scanning Transmission Electron Microscopy

To characterize the mineralogical composition of sediments and smelting slags, representative samples from different layers of the sediment profile were determined for mineralogy and morphology by Scanning Transmission Electron Microscopy (STEM). The representative samples were dispersed in alcohol and then settled on a carbon-coated copper grid for measurement. The distribution of Cd and accompanying metals was determined using a JEOL JEM-2100 high-resolution transmission electron microscope operating at 200 kV. (Liu et al., 2019; Yin et al., 2019; Wang et al., 2020). Further, the representative particles were used to identify the specific minerals by high-resolution transmission electron microscopy (HRTEM) images in selected area.

2.3. Pollution assessment

The level of Cd contamination in the sediment was assessed based on various indexes, each of which can be categorized into different contamination classes (Table S1).

2.3.1. Enrichment factors (EFs) and geoaccumulation index

EFs is generally used to quantitatively assess the anthropogenic enrichment of trace metals. Herein, the enrichment factors (EFs) of Cd were calculated:

$$EF = \frac{(C_i/C_{ref})_{\text{sample}}}{(C_i/C_{ref})_{\text{background}}} \quad (1)$$

where C_i and C_{ref} are the concentrations of Cd and Aluminum (Al), respectively. Aluminum was used as the reference metal. The (C_i/C_{ref}) background ratio was calculated based on metal concentrations in the pond sediment (Sousa et al., 2019).

The geoaccumulation index (I_{geo}) set up by Müller (1981) was also calculated:

$$I_{geo} = \log_2 \frac{C_i}{1.5 \times C_b} \quad (2)$$

where C_i and C_b are the measured concentration of Cd and the geochemical background value of Cd, respectively (Ji et al., 2008; Wei et al., 2011). The Cd concentration in the pond sediment (0.210 mg/kg) was adopted as the background value in this study.

2.3.2. Comprehensive potential ecological risk index

To assess the potential pollution degree of Cd in the sediment, the Håkanson pollution assessment method based on Cd toxicity was applied (Håkanson, 1980). The potential ecological risk individual coefficient (E_r^i) was obtained by multiplying the toxicity coefficient factor with the degree of contamination:

$$E_r^i = T_r^i \times C_r^i = T_r^i \times \frac{C_{\text{surface}}^i}{C_n^i} \quad (3)$$

where T_r^i is toxicity response coefficient of Cd toxicity using standard heavy metal toxicity coefficient developed by Håkanson as reference (Gati et al., 2016; Zhao et al., 2018c); C_r^i is individual pollution coefficient; C_{surface}^i is the concentration of Cd in surface sediment; and C_n^i is the background concentration in the pond sediment.

2.3.3. Bioavailable metal index (BMI) and toxic risk index (TRI)

Sediment's toxicity is mainly attributed to the high concentration of bioavailable metal. The exchangeable and carbonate-bound fractions of Cd have relatively high toxicity and regarded as the major components of bioavailable fraction (Filgueiras et al., 2002; Li et al., 2019b). The bioavailability of trace metal was evaluated by the BMI:

$$BMI = \frac{C_F}{C_{B-F}} \quad (4)$$

where C_F and C_{B-F} are represented the total concentration of Cd in the exchangeable and carbonate fractions in the sediment profile and pond background sediment, respectively.

Toxic risk index, which takes both threshold effect concentration (TEC) and potential effect concentration (PEC) into consideration, was also calculated:

$$TRI = \sqrt{\frac{(C_S/C_{TEC})^2 + (C_S/C_{PEC})^2}{2}} \quad (5)$$

where C_S is the concentration of metal in the sediment while C_{TEC} and C_{PEC} are the TEC and PEC of metal (mg/kg), respectively. The TEC and PEC values of Cd 0.99 and 4.98, respectively are adopted.

3. Results and discussion

3.1. Total contents and vertical distribution of Cd in the sediment profile

Total contents of Cd (Cd_{Tot}) in the sediment profile from the Pb–Zn smelter impacted area ranged from 107 to 441 mg/kg, with an average of 196 mg/kg (Table S2 and Fig. 2). Cd_{Tot} in all these sediments significantly exceeded the content observed in the pond sediment which was 0.210 mg/kg (Table S2) and those in the sediments from the Pearl River and the Yangtze River which were 0.05 and 4.7 mg/kg, respectively (Zhao et al., 2018b; Li et al., 2019b). Cd_{Tot} in the sediments in this study were also higher than those in the sediment from Zambia Pb–Zn smelter (21.0 mg/kg) and Bukowno in Poland (26.1 mg/kg), and sediment from river near the Pb–Zn smelter in Taiwan (3.50 mg/kg) (James F. Verner et al., 1996; Li-jyur Tsai and Ho, 2007; Křibek et al., 2019). Cd_{Tot} was similar to that from other Pb–Zn smelter impacted areas, e.g., contaminated soils from Olkusz Pb–Zn smelter in Poland (153 mg/kg) and Czech Republic (316 mg/kg) (Ettler et al., 2006; Chrastný et al., 2015; Ettler, 2016; Ghayoraneh and Qishlaqi, 2017). The level of EF ranged from 320 to 1.282×10^3 , with an average value of 561 (Fig. 2b). The I_{geo} value for Cd ranged from 6.4 to 8.4, with an average of 7.2 (Fig. 6b). These results indicated that the sediments in this study were severely contaminated with Cd. The enrichment of Cd in the deep sediments indicated a long pollution history.

Based on the vertical distribution of Cd_{Tot} , there was no general

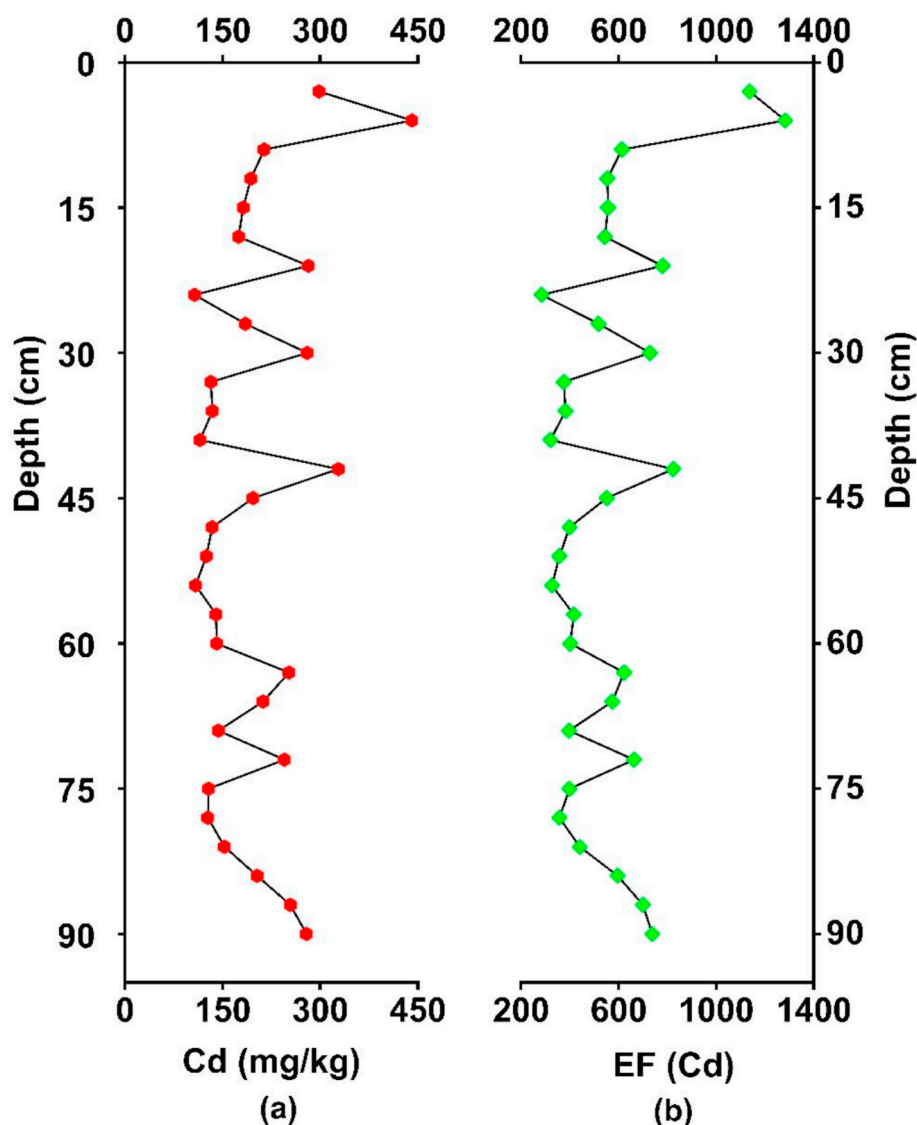


Fig. 2. Vertical distributions of Cd_{Tot} (a) and EF_S (b) in the sediment core.

trend along the sediment profile (Fig. 2). A fluctuation of Cd contents was observed in the surface layers (0–20 cm) and followed by a general increase with several fluctuations in sediment samples at depth, which suggested contamination episodes for Cd. Several reasons may explain the fluctuations of Cd contents in the sediment profile. Large quantities of smelting slags from the Pb–Zn smelter were dumped and exposed to weathering, which were migrated to the watercourse, after rainfall leaching. Over two million tons of effluents were reported to be discharged into the North River (Wang et al., 2013; Liu et al., 2019a). Due to the upgrading of industrial scale, the production of smelter greatly increased in 2006, accompanied with explosive waste emissions (Li et al., 2019b).

3.2. Mineralogical characteristics

Numerous Fe-, Zn-, Cu-, S- and Cd-bearing particles occurred as aggregates in the sediment (Fig. 3). The identified mineral phases in the sediment included pyrite (FeS_2) and magnetite (Fe_3O_4). The metals in the smelting slags often existed as metal sulfides such as pyrite (Sobanska et al., 2006, 2016). The smelting slags could also be easily

transported to the river under the rainwater washing, accompanying with transformation to metal oxides such as magnetite and then deposited in the sediment profile (Li et al., 2008; Ghayoraneh and Qishlaqi, 2017; Křibek et al., 2019; Liu et al., 2019a, Liu et al., 2019b).

High Cd, Zn, Pb and As concentrations were observed in the spherical particles from the sediment profile (Fig. 4). Such particles were mainly presented as $\sim 0.5 \mu m$ particles and observed in different depth (Figs. 3 and 4). From the result of EDS in the par from bottom of sediment profile, S and Zn were concentrated on prolate spheroid shaped particles, in which Cd was distributed with the same pattern. High-resolution transmission electron microscopy (HRTEM) and the Fourier transform (FFT) analysis further identified the presence of greenockite (CdS) and wurtzite (ZnS), based on the diffraction spots of (1 0 0) and (1 0 2) and diffraction spots of (01 8) and (1 0 6), respectively. Since the tetrahedron Cd is similar to Zn in covalent radius and crystal structure, both elements possess similar geochemical properties (Ye et al., 2010), and Cd often substitutes Zn in Pb–Zn ores (Ye et al., 2010; Chrastný et al., 2015). Under high temperature smelting process, the metals with low boiling points can be transformed into gaseous forms (Shen et al., 2017; Li et al., 2018; Lee et al., 2020). As a result, a majority of Cd and

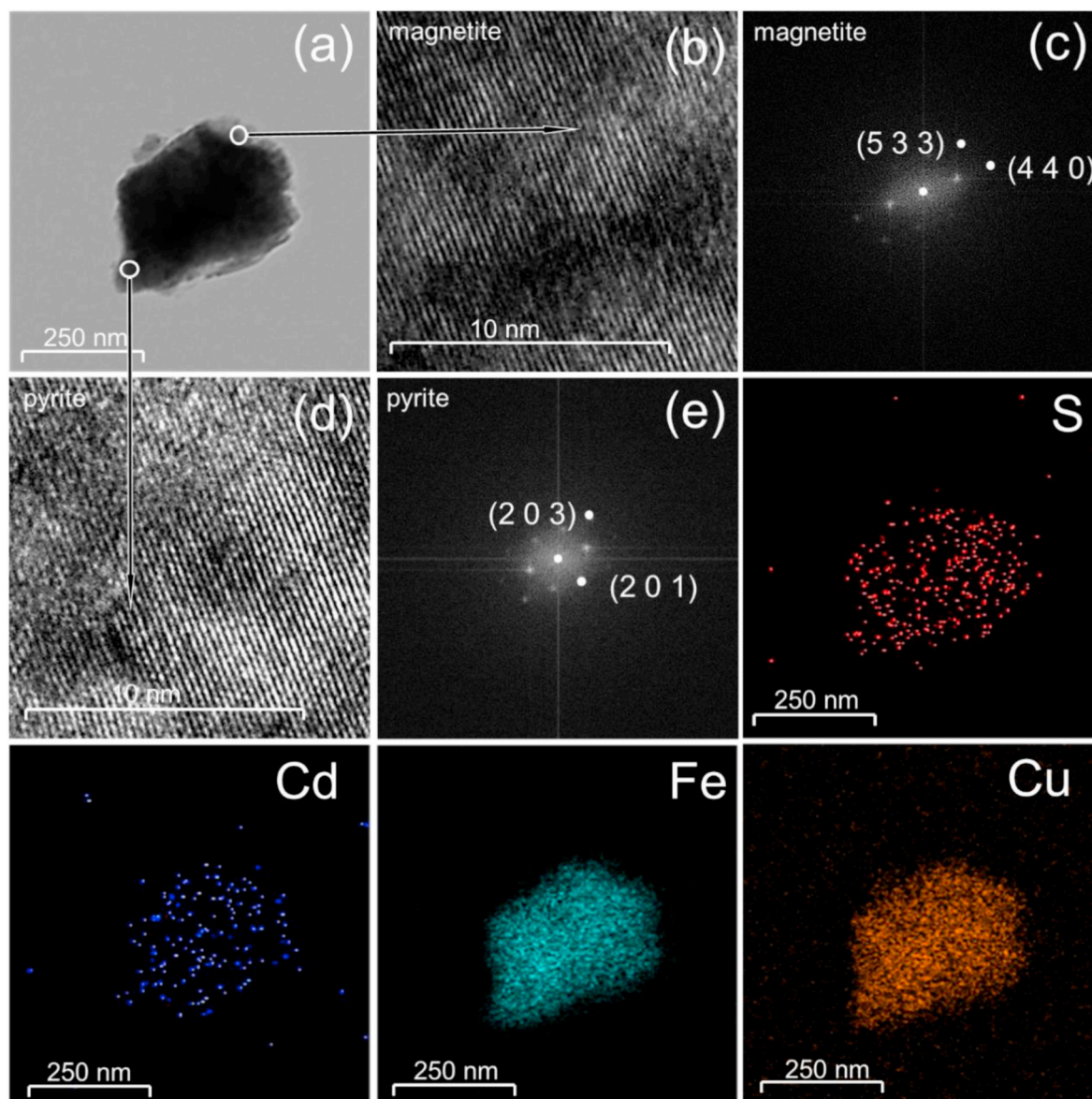


Fig. 3. Bright field TEM images of representative particle of surface sediment with respective SAED patterns shown below: (a) TEM image of particle from the surface sediment, (b) submicroscopic streaky structure of magnetite, (c) SAED patterns of magnetite, (d) submicroscopic streaky structure of pyrite and (e) SAED patterns of pyrite.

other volatile metals including Zn, Pb and As can be bound with fine particles, which eventually subside and deposit in the sediments (Muehe et al., 2013) (Khorasanipour and Esmailzadeh, 2016; Wojtkowska et al., 2016; Křibek et al., 2019). These results suggested that the Pb–Zn smelter played a crucial role in sediment heavy metal contamination.

3.3. Sediment Cd speciation

Based on results from sequential extraction (Fig. 5), approximately 60–80% of Cd retained in the weak-acid-exchangeable fraction (Cd_{Exc}) in the sediment at depth of 6–90 cm, while up to 25% of Cd_{Exc} occupied in topmost surface sediments (0–3 cm). The contents of Cd_{Exc} Ranged from 44.0 to 234.0 mg/kg in the whole depth profile. The Cd_{Exc} Fraction can represent adsorbed Cd by relatively weak electrostatic interaction and/or Cd coprecipitated with carbonates,

which easily release into the environment (Liu et al., 2016; Kubier et al., 2019; Liu et al., 2019a, Liu et al., 2019b; Yuan et al., 2019). The finding of high weak-acid exchangeable Cd fraction was consistent with other similar Pd–Zn smelting-affected areas, where Cd_{Exc} was higher than 40% (Aleksander-Kwaterczak and Helios-Rybicka, 2008; Álvarez-Ayuso et al., 2013; He et al., 2017; Lan et al., 2019; Li et al., 2019b). The smelting slags, which are generated by the Imperial sealed blast furnace smelting technology, are predominantly composed of metal oxides and silicates, followed by metal sulfides (Sobanska et al., 2016; Hussain Lahori et al., 2017; Xia et al., 2019). The transformation of Cd from smelting slags (mainly in metal oxides and silicates) to sediment (mainly in adsorbed and carbonate phases) may be explained by weathering effects (Sobanska et al., 2016; Křibek et al., 2019). Cadmium in smelting slags was mainly associated with Fe (hydr)oxides and a small amount of the sulfide phases, which would gradually be replaced by secondary Fe (hydr)oxides

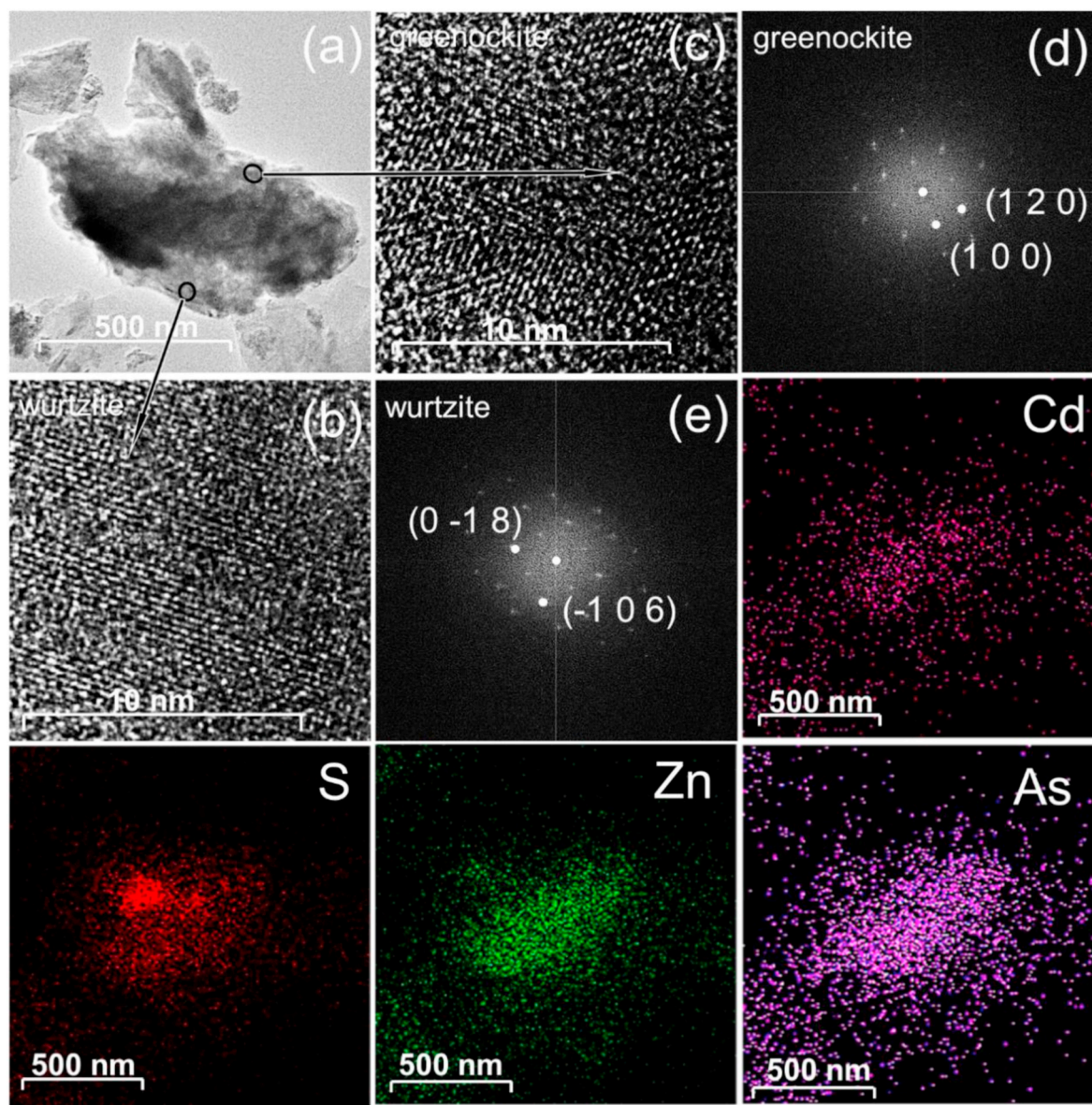


Fig. 4. Bright field TEM images of representative particle of middle sediment with respective SAED patterns shown below: (a) TEM image of particle from the middle sediment, (b) and (c) submicroscopic streaky structure of wurtzite and greenockite, respectively, (d) and (e) SAED patterns of wurtzite and greenockite, respectively.

through weathering before migration to sediments (Aleksander-Kwaterczak and Helios-Rybicka, 2008; Chrastný et al., 2015; Tyszka et al., 2018; Lan et al., 2019). The neutral to weakly acidic pH and high contents of organic matter in the surface sediment might have provided reducing conditions, which could lead to reductive transformation of Fe (hydr)oxides, thereby promoting transformation of Cd primarily associated with the Fe (hydr)oxides to the carbonates (Muehe et al., 2013).

The percentage of Cd in the reducible fraction varied from 10% to 35% (Fig. 5). The reducible fraction is the main Cd host in the slags before weathering (Liu et al., 2017, 2018; Li et al., 2019b;). Cd_{Red.} often has close association with Fe/Mn (hydro)oxides via coprecipitation and adsorption (Filgueiras et al., 2002). During its migration to rivers, Cd_{Red.} may be gradually weathered and transferred to Cd_{Exc.} (adsorbed and carbonate phases) and/or Cd_{Oxi.} (Muehe et al., 2013). Iron oxides play an essential role in immobilizing Cd in the reducible fraction and magnetite was found in the particle from the sediment

profile through STEM/EDS characterization (Fig. 3). Cd_{Red.} may be released to the waters upon reductive dissolution of Fe oxides in reducing conditions in sediment.

Cd_{Oxi.}, which mainly targeted sulfides, ranged from 2.0 to 92.0 mg/kg and the percentage of this fraction varied from 15% to 30%. The contents of Cd_{Oxi.} gradually decreased with depth in the sediment profile (Fig. 5a). High contents of organic matter in the surface sediment might have promoted Cd retention, which could explain accumulation of Cd_{Oxi.} in surface sediment, as compared with other depths (Vaněk et al., 2013; Kubier et al., 2019). Although the contents of Cd_{Red.} and Cd_{Oxi.} were lower than Cd_{Exc.}, they can release to the water especially in low pH or oxidized conditions (Wang et al., 2015; Saikia et al., 2018; Nasnodkar and Nayak, 2019).

Relatively low concentrations of Cd, 1.5–28.4 mg/kg, were founded in the residual fraction. It is presumably stable and hard to release to environment, having low risk for the environment (Filgueiras et al., 2002).

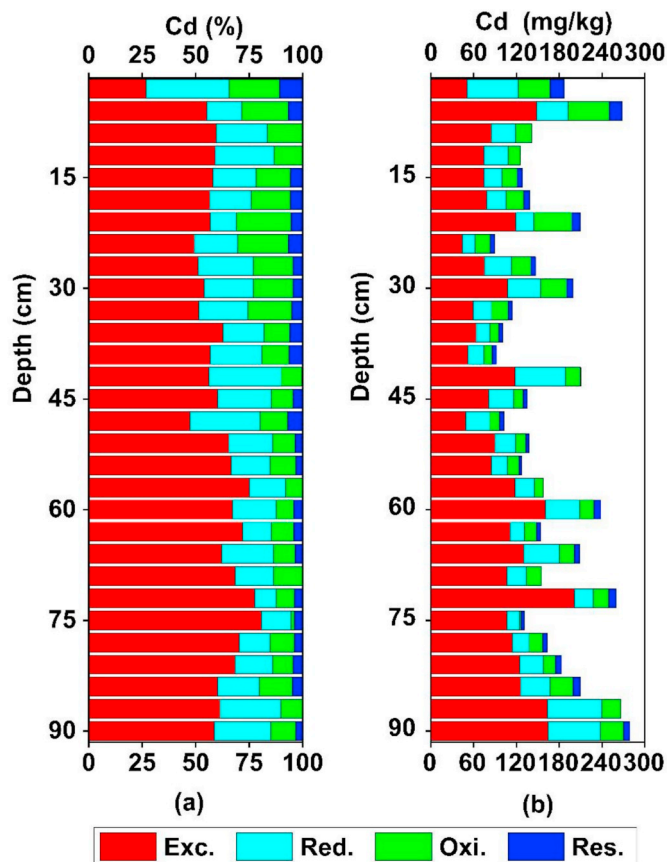


Fig. 5. Geochemical fractions of Cd in the sediment core: (a) percentages (b) contents (Exc.: weak-acid-exchangable fraction; Red.: reducible fraction; Oxi.: oxidization fraction; Res.: residual fraction). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

In summary, Cd was predominantly presented in the readily mobile fractions, which had relatively high bioavailability. Such portions of Cd were likely to be released into water again under certain circumstances and serve as a secondary contamination source.

3.4. Risk assessment

The E_r^i value of Cd varied with depth and ranged from 3921 to 15,940, which meant a very high risk in the depth profile (Fig. 6b). The TRI value ranged from 77 to 321, with the mean value of 143, indicating a very high toxic risk in the whole sediment profile (Fig. 7). For eliminating the influence of water flow disturbance in surface sediment, the 20–90 cm sediments were selected for Spearman correlation analysis. TRI and BMI showed a significant correlation of 0.628, agreeing with the above-mentioned highly bioavailable fractions of Cd. The TRI value in the surface sediment reached 321. Correspondingly, the BMI value in surface layer was also as high as 2471 (Fig. 7). Therefore, Cd in surface sediment have high toxicity and can potentially poison various water organisms through bioassimilation and bioaccumulation (Zhao et al., 2017). Such high TRI and BMI values in Pb–Zn smelter effected area in this study were also observed in other similar areas, for example, the bioavailable contents of Cd in soil from Pb–Zn smelter in Zambia reached 57–97% (Křibek et al., 2019). Hence, the Cd contaminants arising from non-ferrous metal smelting activities may be commonly characterized with conspicuous bioavailability, which tends to represent with higher toxicity and risk to ambient environment and living organisms.

In 2017, Guangdong Provincial Environmental Protection Agency initiated a very strict thallium-oriented pollution control regulation, i.e., regulating a threshold of 5 $\mu\text{g/L}$ for industrial wastewater discharge) throughout the province (GPEPA-GBQTS, 2017; Liu et al., 2019b), the consequent discharge of Cd was believed to be greatly mitigated as well since the thallium removal processes simultaneously decrease the concentration of Cd.

4. Conclusions

In this study, high enrichment of Cd was identified in the whole river sediment core retrieved from the lead-zinc smelter impacted area, exceeding the background value by three orders of magnitude. Extremely high content of Cd was observed in the surface sediments. Cd and other metals with low boiling points had similar distribution patterns in particles from electrical dusts produced from smelting process. Magnetite, pyrite, wurtzite and greenockite were observed at the different depths of the profile. As high as 25–80% of Cd was associated with the weak acid exchangeable fraction, having high risk to ambient environment and living organisms. The transformation of Cd between

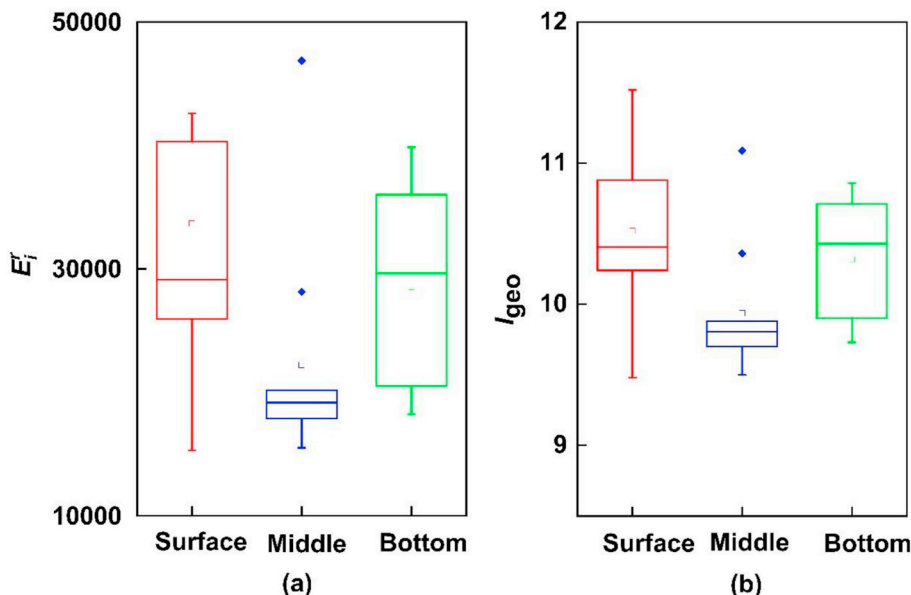


Fig. 6. Box plots of (a) potential ecological risk index (E_r^i) and (b) geoaccumulation indices (I_{geo}) for Cd at different depths of the sediment profile.

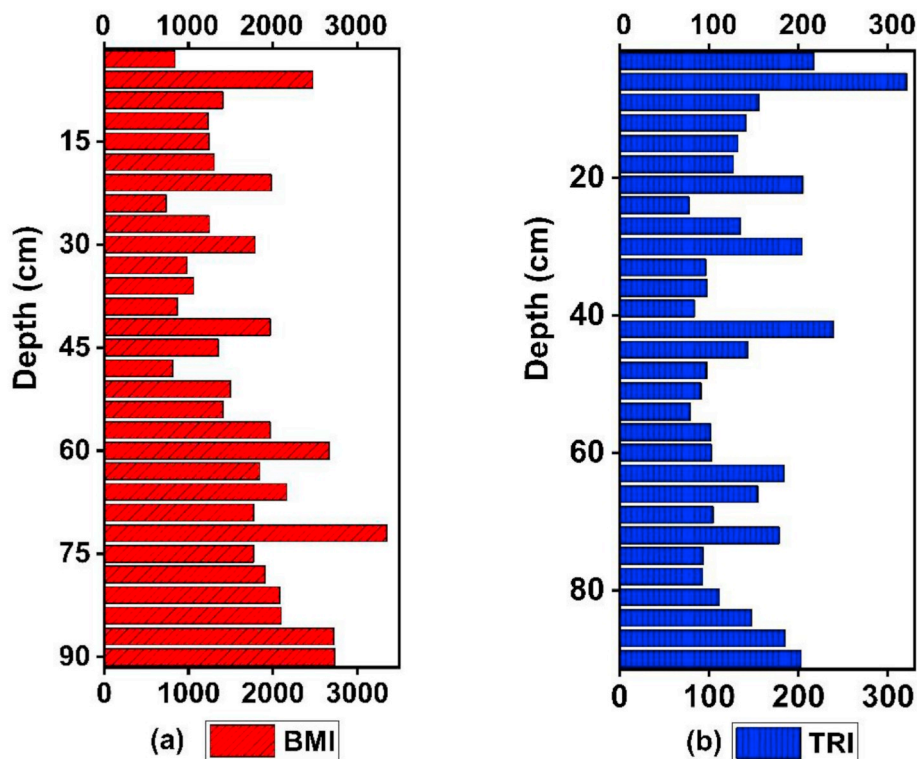


Fig. 7. The vertical distributions of (a) bioavailable metal index and (b) toxic risk.

smelting slags and sediments explained why Cd_{Exc} was the main fraction in the depth profile. All of these results confirmed that the Pb–Zn smelter was the pollution source to the North River. Environmental risk assessments by EF, E_r^i , I_{geo} , BMI and TRI further suggested that the North River sediments were extremely polluted by Cd. More attention and proper countermeasures are therefore needed to improve the environmental quality of the smelting affected area.

CRedit authorship contribution statement

Jin Wang: Writing - review & editing, Formal analysis, Project administration, Funding acquisition. **YanJun Jiang:** Writing - original draft, Data curation, Formal analysis. **Jing Sun:** Writing - review & editing. **Jingye She:** Writing - review & editing. **Meiling Yin:** Writing - review & editing. **Fa Fang:** Writing - review & editing. **Tangfu Xiao:** Writing - review & editing. **Gang Song:** Writing - review & editing. **Juan Liu:** Writing - review & editing, Project administration, Formal analysis, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was supported by the National Key Research & Development Program of China (2017YFD0800302), the Natural Science Foundation of China (Nos. 41873015, U1612442 and 41773011), the Guangdong Provincial Natural Science Foundation (2017A030313247) and the Research Fund Program of Guangdong Provincial Key Laboratory of Radionuclides Pollution Control and Resources (2017B030314182).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ecoenv.2020.110529>.

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