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Heavy metals in river surface sediments affected with multiple pollution sources, South China: Distribution, enrichment and source apportionment

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ABSTRACT

Understanding sources and fate of heavy metals in river basin is crucial for assessing risks associated with human and ecosystem exposure. To provide basic information for agriculture and industry transferring in future, environmental development planning and decision-making, and drinking water source protecting associated with human health in the region, compound heavy metal pollution in the Maba River, South China, was investigated to evaluate spatial distribution and pollution levels using geo-accumulation index (I_{geo}). In addition, heavy metal concentrations in sediments were measured and compared with sediment quality guidelines (SQGs). The main contamination sources of heavy metals and the concrete contribution were identified and calculated using multivariate statistical analysis (MSA) and factor analysis-multiple linear regression (FA-MLR) methods. The results showed that the heavy metals exposed in sediments of the Maba River largely due to anthropogenic sources, such as smelting and mining. The heavy metal concentrations found in surface sediments were significantly higher than the local background values, especially in the mixed region. The migration and transformation process of river metals was mainly affected by hydraulic conditions and sediment characteristics. The I_{geo} and SQGs produced similar levels of heavy metals pollution in sediments, thereby confirming each other's results, indicating that the Maba River is heavily contaminated, and As, Hg, Pb, Zn, Cd and Cu were likely to effect on the aquatic ecosystem. Based on MSA and FA-MLR, the results showed that about 87% of Cu came from the mine tailing wastewater runoff, 77%, 66% and 72% of Tl, Hg and Cd respectively originated from the smelting wastewater discharge. Results of this study will be useful in assessing and managing regional point source pollution. Further investigation on fate and toxicity of heavy metals associated with human health risks is needed in future studies.

1. Introduction

Rivers perform a suite of ecological functions such as water transport, aquaculture, agricultural irrigation, domestic water and tourism. Based on different scientific and policy objectives, various ecological functions of rivers have been studied and evaluated, including hydrology (Ikem and Adisa, 2011; Jacobson and Jacobson, 2013), water quality (Ocampo-Duque et al., 2013; Zhang et al., 2012a), sediment quality (Nilin et al., 2013; Yang et al., 2012), vegetation composition (Cui et al., 2013) and animal population dynamics (Ayllón et al., 2012; Ryu et al., 2011). Among these factors, sediment quality has generated substantial concern because it is not only essential for acting as a reservoir of pollutants, but also directly interacts with other factors across multiple spatial and temporal scales (Bartoli et al., 2012; Erftemeijer et al., 2012; Fu et al., 2014). For example, industrial material and process, mineral type (Ji et al., 2013; Reglero et al., 2009; Resongles et al., 2014; Zhang et al., 2011), land use (Kuusisto-Hjort and Hjort, 2013; Zhou et al., 2012), hydrological connection, water quality, aquatic animal population (Fu et al., 2013) and vegetation characteristic have been demonstrated to be related to sediment quality. Thus, sediment quality serves as an important indicator for characterizing the effects of pollution sources and human activities (Wang et al., 2014; Xu et al., 2014), and furthermore, to direct pollution repair of the watershed and policy and management of the surrounding industries (Jacobson and Jacobson, 2013; Selin et al., 2010). Particular sediment quality parameters are selected as indicators of specific anthropogenic activities, such as toxic organic matters, heavy metals, microbial population, salinity, total organic carbon (TOC) and sediment components (Erftemeijer et al., 2012). In most cases, heavy metals are significant parameters due to its toxicity, bioaccumulation and persistence in the natural environment.

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Heavy metals may be geologically from geological weathering, industrial, mining, atmospheric precipitation, transport, agricultural and urban activities (Guerra-García and García-Gómez, 2005; Ouyang et al., 2006). Significant quantities of heavy metals are discharged into aquatic environment and accumulated in sediments, which might (1) directly pollute the raw water, resulting in sublethal effects or death in local fish populations and accumulate in crops through irrigation (Pekey et al., 2004); (2) release to the water through sediment resuspension, adsorption or desorption reactions, reduction or oxidation reactions and the degradation of organisms (Dong et al., 2012; Feng et al., 2007; Zhao et al., 2013). Such processes enhance the dissolved concentration of metals in the environment and threaten the ecosystem and human health.

Rivers also play an important role in the acceptance and transport of pollutants, because on the one hand they act receiving waters of point source (industrial, mining) and non-point source (city lives, agriculture, atmospheric precipitation) pollutants, on the other hand they are sources of great river or sea. Rivers usually include some streams originated from spring water runoff, land surface flow, industrial and agricultural drainage and are characterized by their small area, specific pollutants and sediment composition, and multiple pollution sources. In China, there are a large number of these types of rivers. The Maba River found throughout the Qujiang region of Shaoguan City, Southern China, is a typical representative because there are mining and smelting industrial zone upstream and it also covers the living area and farm belt and flows into the Beijiang River, which is a main drinking water source of Guangdong Province. In recent years, the Maba River has suffered significant heavy metals pollution due to the increasing industrialization and mining activities, which causes Beijiang River water quality decline, such as, the Beijiang River has broken out Cd and Tl pollution many times in last decades (Song et al., 2011). Base on the unique benefits for both local residents' health and drinking water quality, more attentions should be paid for such rivers for evaluating pollution level and controlling the discharge of point pollution sources.

Research on heavy metal pollution in sediments of such rivers has been limited due to without exactly background values and historical record of hydrological characteristic information. In order to simplify the analysis process, these rivers are generally considered to have little or no connection with biological process and mineralization, and the heavy metal distribution are primary dependent on precipitation, adsorption, desorption and runoff (Feng et al., 2007; Ikem and Adisa, 2011; Rowe, 2014). Moreover, the local soil background values are used to evaluate heavy metal enrichment (Song et al., 2014; Zahra et al., 2014). Furthermore, these rivers hold the most obvious characteristics of regional and the sediment quality may therefore respond to pollution source in the surrounding environment.

The field study is to address the identified research gaps that will provide valuable information of the spatial distribution, pollution level and source apportionment of selected heavy metals. Objectives are: (1) to quantify and reveal the spatial distribution of heavy metals (Pb, As, Cd, Zn, Cr, Mn, Ni, Cu, Tl, Hg) in surface sediments of the Maba River; (2) to assess the heavy metal enrichment by using the geo-accumulation index (I_{geo}); (3) to evaluate the potential ecological risk and toxicity of sediment-bound heavy metals considering ecological risk indices and Sediment Quality Guidelines (SQGs); and (4) to identify the possible sources with multivariate statistical analyses (MSA) and their concrete contribution by using factor analysis-multiple linear regression (FA-MLR).

2. Materials and methods

2.1. Study area and sampling sites

River study sites were uniform distributed throughout the Qujiang Living area, Shaoguan City, Southern China, across Nanhua, Maba and Baisha towns, the target river mainly originates from a limestone area, thus the pH of river water are always above 7 except the tributary stream affected by AMD (Fig. 1, Table S4). This region is located at the base of the Dabaoshan Mountains and smelting industry park of Shaoguan City, and is a headwater tributary of the Beijiang River. The water and sediment quality of the upper portion river may influence the middle and lower reaches where there are large urban populations. Increasing development pressure of iron and steel enterprise and mining since 2000 associated with the region's location upstream of the big city (Guangzhou), large amount of wastewater, and gradually saturated of pollutants in the accepted water necessitate timely assessment of the Maba river in this region. While there is a paucity of data regarding heavy metal distribution, pollution level and source apportionment of the river in this region.

The primary source of water input for the Maba River in the study area includes two tributaries, the Meihua River and Nanhua River, the former is originated from a reservoir and through the smelting park with smelting wastewater into it, and the latter forms by two streams, are Caoxi Stream and Zuanxi Stream, respectively. The Zuanxi Stream is originated from spring water and soil surface runoff, while the Caoxi Stream comes from a mine tailing water from the Dabaoshan mine (about 4.35 km from the source), around both are villages and farmlands. After the confluence of two tributaries, the Maba River is becoming more wider and deeper, while the water flow velocity decreases, thus forms an area defined as the mixed region, which looks like an activity reservoir (Table S1). Therefore, the potential sources of heavy metals in the Maba River are geological weathering, smelting, mining, atmospheric precipitation, agricultural and urban activities, and the sediment properties are mainly determinate by the composition, including soil types and pollutant species.

There were 16 river sampling sites in this study, labeled different letters and ordinal numbers 1 to 16 for the whole watershed area (Fig. 1). Site K1 is located in the non-pollution region with high terrain for a control point and three sites (I2–I4) are located in the smelting-affected area, with I3 is located close to the only outlet of smelting wastewater. V5 was collected from Zuanxi Stream under a bridge, while T6 was collected from Caoxi Stream. Three sites (S7-S9) are situated in the living area with high lined embankment and six sites (M10-M15) are located in the downstream of the living area, with the trunk stream (M10-M13) is named the mixed region, M13 is located in the junction region between the Beijiang River and the Maba River, while M14 in the upriver, and M15 in the downriver. Site B16 is situated on upstream of the Maba River as a control point too. Considering the different characteristics of origin and convergence, the sampling sites were grouped separated from the letters.

2.2. Sampling and pre-treatment

Surface sediment samples were collected at every three months intervals (four seasons) between March 2013 and January 2014 with assuming that the sediment quality is stable in each season. The samples collected from each site consisted of 4/5 composite samples. Composite surface sediments (0–20 cm) were collected using a cylindrical sediment core sampler with inner diameter of 6 cm and length of 100 cm. After sampling, the sediment samples were sealed in clean polyethylene bags, placed in a cooler at 4 °C, and transported to laboratory immediately for further analysis.

Pretreatment process refers to turn the sediments into the samples for detecting by the steps drying, grinding, sieving and digesting. The details conclude that sediment samples were air dried, then, stones and plant fragments were removed through a 2 mm sieve, after that the samples were grinded and finally passed through a 0.15 μm sieve, then the residue stored in unpolluted glass bottles. Weighed 0.20 g sediment samples and digested in microwave digestion tank with 6.5 ml HNO_3, 2.6 ml HF (5:2) mixture in a microwave oven (MARSX-press, CEM). After microwave digestion for 30 min, the liquid samples were collected and removed the excess acid by heating in electric hot plate.

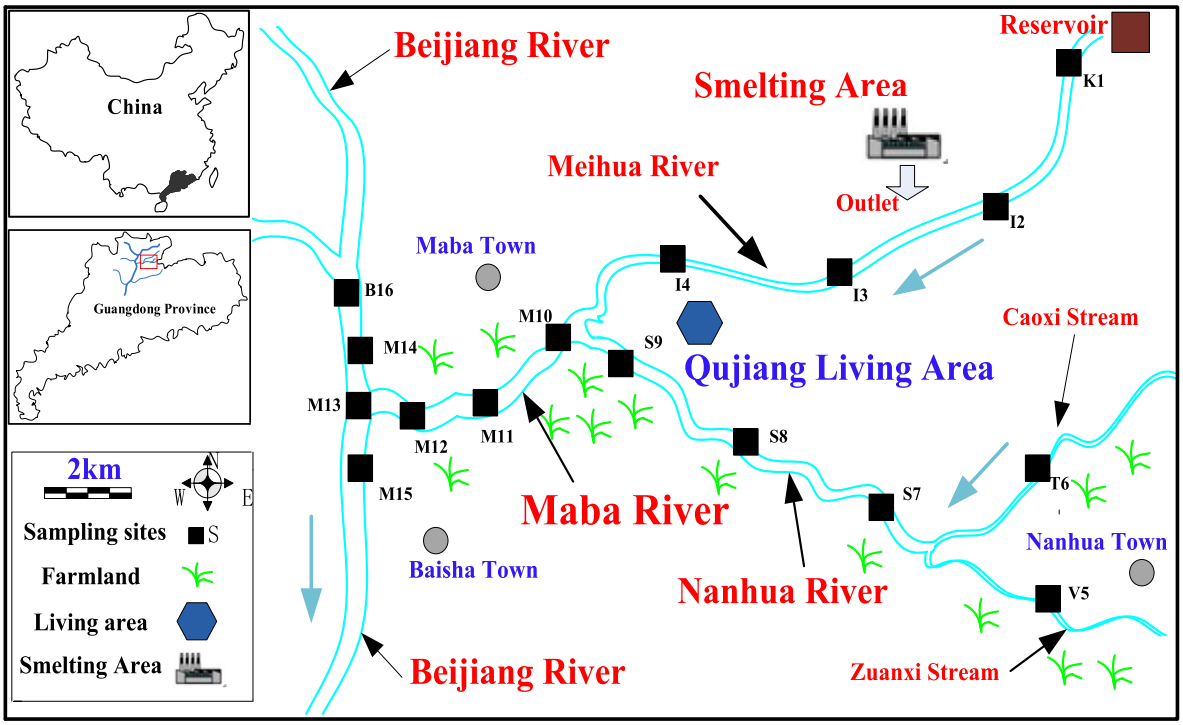

Fig. 1. Location of the study area and sampling sites along with the Maba River, Guangdong Province, China.

Then adjusted the nearly solid state samples to a suitable volume (50 ml) by using double deionized water and filtered with membrane (0.45 μm) for detecting (Liao et al., 2016).

2.3. Analytical methods

The sediment particle size fractions were separated into three grain sizes of <60, 60–250, and >250 μm using a series of sieves (Li et al., 2015). The soil pH was measured using a mixture with the 1: 2.5 soil-to-water ratio stirred with a clean glass rod for 30 min, after which pH values were measured using a pH-meter (Ahmed et al., 2012). Weighed 2 g sediment samples, then injected 20 mL 1.5 mol/L HCl for acidification treatment for the purpose to remove inorganic carbon, the acidification time was 0.5 h, after drying at 60 °C, the TOC of the bulk samples were measured using a Vario EL-III CHN analyzer with the combustion temperature at 960 °C (Yang et al., 2012). The heavy metal concentrations were detected by atomic absorption method, and chose different detectors according to the nature and content of selected heavy metals. The sediment samples were analyzed for Pb, Zn, Cr, Mn, Ni, and Cu by a flame absorption spectrometry (FAAS) equipped with deuterium background correction (AA-6300C, Shimadzu). And then Cd and Tl were measured by using a graphite furnace atomic absorption spectrometry (GFAAS) with Zeeman background correction (GFA-EX7i, Shimadzu). Arsenic and Hg were measured by cold vapor atomic absorption spectrometry (**CVAAS**) (Liao et al., 2016). Results of triplicate analyses revealed good reproducibility of the equipment, the total standard deviations of all analyzed samples ranged from 0.0182 to 4.235 (example analysis in Table S2).

2.4. Quality control

The analytical data quality was guaranteed through the implementation of laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with standards, analysis of reagent blanks and standard reference material GBW07436. Analytical blanks and standard reference material were run in the same way as samples, and heavy metal concentrations were determined using standard solutions prepared in the same acid matrix. Sediment reference material was used ($N = 3$) to ensure the validation of data and the accuracy and precision of analytical method (Table S3). The recoveries were 80.90 ~ 114.4% for all metals regarding their certified/noncertified values (Table S3). Total heavy metal concentrations were expressed in mg/kg dry sediments, and the results were expressed in average values. All the reagents used were of supra quality and of analytical grade. All solutions were prepared by using ultra pure water. All plastic, quartz and glassware were soaked in HNO_3 (10%) for at least 24 h and rinsed repeatedly with ultra pure water.

2.5. Contamination assessment

The degree of metal contamination in sediment was assessed by the geo-accumulation index (I_{geo}) which was originally introduced by Müller (1969). The I_{geo} value was defined by the following equation:

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

where C_n represents the measured concentration of metal (n) in samples (mg/kg), B_n represents the geochemical background value of metal (n) (mg/kg). Factor 1.5 is used to account the possible variation in the background values. In this study, B_n values are the soil background values of Guangdong Province. The I_{geo} consists of seven classes, where: Class 0 ($I_{geo} \le 0$), uncontaminated; Class 1 ($0 < I_{geo} < 1$), uncontaminated to moderately contaminated; Class 2 ($1 < I_{geo} < 2$), moderately contaminated; Class 3 ($2 < I_{geo} < 3$), moderately to heavily contaminated; Class 4 ($3 < I_{geo} < 4$), heavily contaminated; Class 5 ($4 < I_{geo} < 5$), heavily to extremely contaminated; Class 6 ($I_{geo} \ge 5$), extremely contaminated (Nilin et al., 2013).

2.6. Sediment quality guidelines

The sediment quality guidelines (SQGs), which have been developed from biological toxicity test of benthic environment, are used to evaluate adverse biological effects of sedimentary contaminations in

the study region. Two sets of sediment quality guidelines such as threshold effects level (TEL) and probable effects level (PEL), or effects range low (ERL) and effects range medium (ERM) are proposed to determine whether the metals in sediments pose a threat to aquatic ecosystem (Long et al., 1998; MacDonald et al., 2000). In this study, we applied both sets of SQGs to assess the potential adverse biological effects.

Due to the SQGs used above only taking into account individual metal, the mean effect range-median quotient (mERM-Q) is adopted for assessing the potential effects of multiple heavy metal contaminations in sediments (Long et al., 2006). The calculated equation are as follows:

$$mERM{-}Q = \left(\sum_{i=1}^{n} ERM{-}Q_i\right)/n \quad (2)$$

$$ERM{-}Q_i = C_i/ERM_i \quad (3)$$

where C_i represents the total concentration of selected metal i, ERM_i represents the corresponding ERM value of selected metal i, and n represents the number of selected metals. The mERM-Q is classified into four levels: mERM-Q < 0.1, 9% probability of toxicity; 0.1–0.5, 21% probability of toxicity; 0.5–1.5, 49% probability of toxicity; and >1.5, 76% probability of toxicity (Hu et al., 2013b; Long et al., 2006).

2.7. Statistical analyses

In order to decipher the interrelationship among heavy metals or sampling sites, Pearson's correlation matrix (PCM), hierarchical cluster analysis (HCA) and principal component analysis (PCA) are performed with a statistical software SPSS17.0. PCM is used to identify the relationship among the metals and confirm the results of multivariate analysis (Tahri et al., 2005). HCA is used to identify spatial variability between the sites based on physicochemical parameters or heavy metals enrichment level based on concentrations, Euclidean distance is used as dissimilarity matrix, and Ward's method is used as a linkage method (Zahra et al., 2014). PCA is used to ascertain contamination sources (natural and anthropogenic), whereby a complex data set is simplified by creating several new variables or factors, each representing a cluster of interrelated variables within the dataset (Varol, 2011).

Although PCM, HCA and PCA were applied to the data set provide qualitative information about sources of metal contaminants, it is not adequate for supplying quantitative information regarding the contributions of each source type. To overcome this problem, the multiple regression method is applied to the data set for further analysis, which is mainly applied on the analysis of river water and atmospheric environment quality currently (Karami et al., 2012; Pekey et al., 2004; Thurston and Spengler, 1985; Zhou et al., 2007). In this study, factor analysis-multiple linear regression (FA-MLR) is used to quantify the contributions of each source to sediment of the Maba River (Atgin et al., 2000; Brady et al., 2014). The accuracy of the FA-MLR exercise can be tested by calculating "observed to predicted" ratios (Thurston and Spengler, 1985). Details of FA-MLR method can be found in previous studies (Guo et al., 2004; Pekey et al., 2004; Thurston and Spengler, 1985).

3. Results and discussion

3.1. Sediment quality

Location and description of sampling sites along the Maba River and the composition and characteristics of sediments are presented in Table S1. The sediments were mainly composed of fine grained (clays and silts) in the mixed region (M10-M13) and Nanhua River (S7–S9), while very fine to medium sands were observed in the Meihua Rive, Zuanxi Stream and Caoxi Stream. The studied sediments were neutral and weak alkaline due to the mean pH ranging from 6.97 to 8.05, the biggest pH value was found at site I3, which might be caused by alkaline coking wastewater (pH > 9) (Ou et al., 2014). The TOC (% C) was ranged from 0.21 to 6.58 for all sediment samples, similar to the pH, the higher TOC values were found downstream of the outlet of the smelting discharge. Zhang et al. (2012b, 2012c) reported that the coking wastewater contains lots of organic matters (such as PAHs) and the TOC values were significant high. Due to such environmental conditions, presumably, the high heavy metal concentrations can be enriched in sediments by adsorption, complexation and precipitation, especially in the mixed region.

The on-way distribution of target metals in surface sediments from the Maba River is shown in Fig. 2. Obviously, except Cu, Tl and Hg, the highest concentrations of the other metals were observed in the mixed region. Chromium and Ni had a similar spatial distribution pattern, the highest concentrations were 65.34 and 41.45 mg/kg respectively at site M12, which were comparable with the soil background (B.G) values (50.53 and 14.40 mg/kg) of Guangdong Province (Ye et al., 2012), and site I3 and T6 had lower Cr and Ni concentrations by comparing with site K1 and B16, indicating that these two metals presumably mainly originate from the geological weathering due to no massive enrichment. Thallium and Hg had the highest concentrations at site I4 where the smelting wastewater had discharged into the Maba River, the values reach to 8.51 and 5.54 mg/kg respectively, indicating that smelting is a seriously point source of these two metals. The results were numerically consistent with previous studies, where showed that Tl is produced by environmental contamination as a byproduct of smelting, and Hg is produced from the coal combustion (Resongles et al., 2014; Scala and Clack, 2008). Copper had high concentration at site T6 in Nanhua River (520.1 mg/kg) and the highest concentration at S9 (857.3 mg/kg), indicating that wastewater containing with copper was discharged into the river, inferring that the mine tailing water from Dabaoshan contains high concentration of Cu (Lin et al., 2007). High Pb, As, Cd, Zn and Mn concentrations were observed in both tributaries, indicating that these five elements mainly come from smelting and mine tailing. In the downstream of the confluence of Meihua River and Nanhua River, Pb, As, Cd, Zn, and Mn had the highest concentrations at site M12 with values of 1671, 1103, 45.67, 3523 and 2458 mg/kg, respectively. Compared with the B.G values, the heavy metal concentrations except Cr and Ni in the mixed region were far higher (Ye et al., 2012), especially Cd and As exceeded >480 and 120 times, respectively. Moreover, frequent monitoring and additional health risk assessments are necessary for metal levels above the upper limits in the future.

Metals in sediments from the Maba River were compared with the other studies. Zinc had the highest mean values in the study area for all sampling sites, it could reach 1133 mg/kg, following by Mn, Pb, Cu, As, Cr, Ni, Cd and Tl, while Hg had the lowest mean concentration, which was 2.28 mg/kg. The mean concentration of Cd (14.61 mg/kg) in the Maba River was similar to the findings in the Xiangjiang River (14.97 mg/kg) (Sun et al., 2011), which was caused by mining activities in Hunan Province, China, but much higher than other domestic rivers (e.g. Yangtze River, Pearl River) with the range of 0.09 to 2.93 mg/kg (Fu et al., 2013; Yang et al., 2009; Ye et al., 2012). The mean concentrations of Pb, As, Zn, Cu and Hg in this study were about 10 to 20 times higher than those in most domestic rivers (Hu et al., 2013a; Zeng et al., 2013). Manganese concentration (1075 mg/kg) in sediments was comparable to the concentration in Xiangjiang River (Sun et al., 2011), but was about 3 times of the Huanghe River (Hu et al., 2015; Qiao et al., 2013). The mean concentration of Tl was 10 times higher than the local soil B.G value, and was about 3 times of the Pearl River (Ye et al., 2012). The critical comparison results between the Beijiang River and the mixed region of the Maba River showed that the concentrations of Pb, As, Cd, Zn and Cu were >20 times higher, especially Cd exceeded 40 times, Tl and Hg were about 10 times higher. The results indicates that the Maba River can surely bring high concentrations of heavy

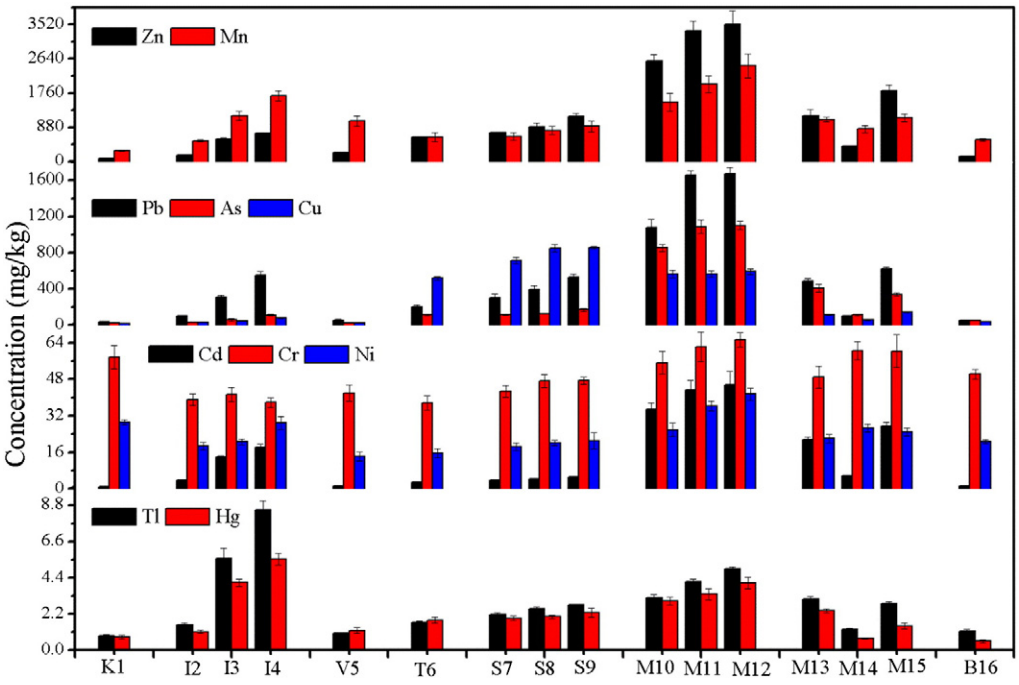

Fig. 2. Heavy metal concentrations in surface sediments along with the sampling sites from the Maba River (Mean ± S.D.), Guangdong Province, South China.

metals to the receiving water Beijiang River annually, becomes a hidden problem of water quality.

The concentrations of heavy metals along the river gradually increased in each group (I2–I4, S7–S9 and M10–M12), and then accumulated in the mixed region. Factors influencing the migration of heavy metals in sediments may be river width and depth, water flow velocity, sediment composition, pH and TOC, and so on. The correlation analysis was carried out between the distribution of heavy metal concentrations and the influence factors, then the combinations of the high correlation coefficients ($r > 0.65$, $p < 0.01$) were selected for linear fitting, the results are shown in Fig. 3. Linear relationship between Tl, Hg and TOC values were observed, because these metals and high concentrations of organic matters are discharged from the smelting wastewater at the same time, presumably, the co-adsorption and precipitation or complexation might

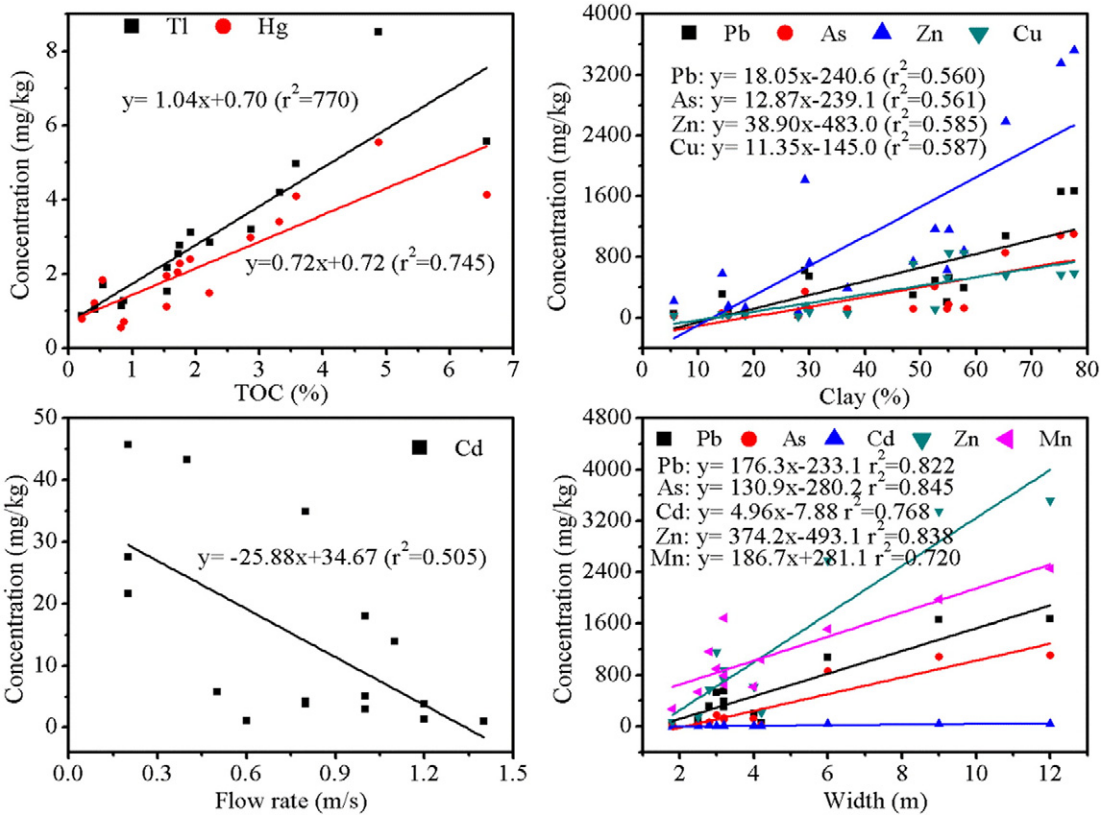

Fig. 3. The linear relationship between the concentration distribution of heavy metals and the environmental conditions or sediment characteristics of the Maba River ($r > 0.65$, $p < 0.01$).

occur (Bartoli et al., 2012; Fu et al., 2014). Cadmium is a water migration element, in addition to CdS, other Cd compounds are soluble in water, and easy to be absorbed by suspended solids and sediments (Odor et al., 1998; Tassi et al., 2014). Obviously, the concentrations of Cd in sediments decreased with the increasing of flow velocity, and positively correlated with river width. Commonly, river width increases, the corresponding water velocity decreases, thus the water pollutants have a longer dwelling time. Also, the clay content in sediments increases with the extension of hydraulic retention time. As shown in Fig. 3, the concentrations of Pb, As, Zn and Mn displayed correlation with river width, moreover, the concentrations of Pb, As, Zn and Cu in sediments were correlated with clay content. The results are in accordance with previous studies, where reported that >90% of the contaminants in aqueous are adsorbed and accumulated in sediments by Clay and silt (Fu et al., 2014). In a word, in addition to the intense influence of point sources, the river characteristics, such as width, depth, flow rate, clay content, also have effects on the distribution of heavy metals, however, the factor related to these river characteristics is residence time.

3.2. Contamination assessment

Contamination assessment is used to further explain the pollution level by the enrichment of high concentrations of heavy metals in sediments in the study area basic on selecting appropriate background values. Here, the I_{geo} was applied. As shown in Fig. 4, the I_{geo} values showed the decreasing order Cd > Hg > As > Zn > Cu > Pb > Tl > Mn > Ni > Cr. All Cr I_{geo} values were lower than 0, and Ni I_{geo} values were lower than 1, indicating uncontaminated status for Cr and uncontaminated to moderately contaminated status for Ni in sediments of the study area (Nilin et al., 2013). Cadmium had the highest I_{geo} value (8.34) of all target metals, and also had the highest mean I_{geo} value (5.70), indicating extremely contaminated status for Cd in the study area. Moreover, the range of I_{geo} values for Pb, As, Zn, Mn, Cu, Tl and Hg were −0.56 to 4.96, 0.66 to 6.36, 0.09 to 5.62, −0.61 to 2.55, −0.58 to 5.01, 0.06 to 3.37 and 2.23 to 5.56, indicated moderately contaminated to extremely contaminated (Hu et al., 2013b). Due to the influence of point sources, the range of I_{geo} values of site I4 and T6 were −1.00 to 6.99 and −1.01 to 4.42, indicating uncontaminated to heavily contaminated. The mixed region, where great quantities of heavy metals were observed, the highest I_{geo} value was obtained at site M12 with the range from −0.21 to 8.33, the mean I_{geo} values was 4.07, indicating extremely contaminated of this region. Furthermore, the range of I_{geo} values of site M15 were −0.33 to 7.61, indicating that the heavy metals in the Maba River will consistently enter into the Beijiang River, which causes seriously heavy metal pollution to the downstream population by endangering the water quality of drinking water.

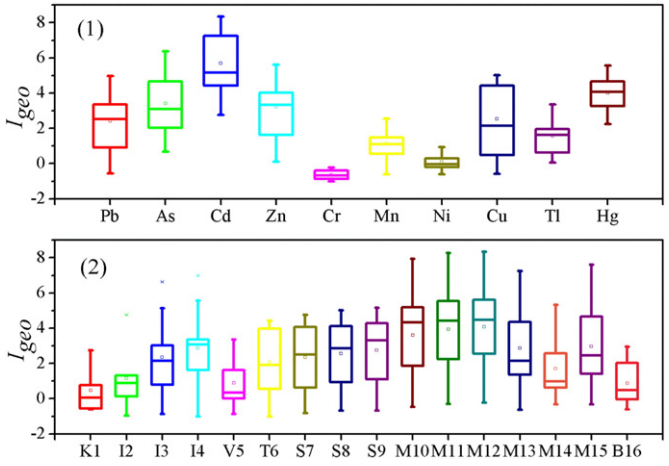

Fig. 4. The spatial variations of geo-accumulation index (I_{geo}) of selected heavy metals and sampling sites in surface sediments of the Maba River, Guangdong Province, China. The boxes represent 25th and 75th percentiles, three horizontal bars represent 5th, 50th, and 95th percentiles, and the asterisks stand for outliers.

3.3. Application of sediment quality guidelines

The monitoring and assessing results indicated that the metals observed in sediments were seriously accumulated in the study area, which could cause potential toxicity to aquatic ecosystems. To confirm the existence of toxicity and evaluate the adverse biological effects of sedimentary contaminations, two sets of sediment quality guidelines were applied. Low values of the TEL and ERL shows a minimal adverse biological impact, while the PEL and ERM represent a frequent adverse biological effect (Long et al., 1998; MacDonald et al., 2000). The results of comparisons between SQGs and metal concentrations are presented in Table 1.

When compared to the TEL-PEL SQGs, Cr and Ni were between TEL and PEL in 100% and 81.25% of samples, respectively, indicating that these two metals may occasionally be associated with adverse biological effects. However, Pb, As, Zn, Cd, Cu and Hg were higher than PEL in 81.25, 100, 75, 81.25, 43.75 and 100% of samples, respectively, indicating that the concentrations of these metals are likely to result in frequent occurrence of harmful effects on sediment-dwelling organisms (Long et al., 2006). However, when compared with the ERL-ERM SQGs, 100% of samples for Cr and 87.5% of samples for Ni were below the ERL. With respect to Pb, As, Cd, Zn, Cu and Hg, 68.75, 68.75, 43.75, 81.25, 43.75 and 68.75% of samples were above ERM, respectively, indicating that Cr and Ni were minor effects to the sediment organisms, the harmful effects of Pb, As, Cd, Zn, Cu and Hg in sediments of the Maba River would occasionally occur, As and Zn were the most frequently, followed by Pb, Hg, Cd and Cu.

In order to combine metal-specific SQGs values and to determine the possible biological effect of compound metals, the mERM-Qs for measured heavy metals (except Mn and Tl, no giving values) were calculated according to the formula (3) and (4) (MacDonald et al., 2000). The spatial distribution of multi-metal toxicity risk potential of the Maba River presented in Fig. 5 showed that all the mERM-Qs were higher than 0.1, with the highest ecotoxicological potential (6.69) located in the mixed region of the Maba River. The mERM-Q values of sites K1, V5 and B16 fell in the range between 0.1 and 0.5, indicating that the combination of metals might have 21% probability of being toxicity. The sites I2, S7, S8 and M14 fell in the range of 0.5–1.5, and the remaining sites were higher than 1.5, indicating that the combination of metals might have 46% and 76% respectively probability of being toxicity. Overall, the compound metals in sediments of the Maba River are doubtless to cause biological toxicity.

3.4. Identification of pollution sources

Previous studies have indicated heavy metals in sediments originate from different geological weathering and anthropogenic sources. In order to obtain an overview of heavy metals behaviors and possible metal sources in the study area, multivariate statistical analyses (PCM, HCA and PCA) were carried out.

PCM was applied to measure the degree of correlation among heavy metals and to provide insight information regarding possible metal sources, a significant positive correlation existed among the metals studied in sediments of the Maba River (Table 2). Here, Pb, As, Cd, Zn and Mn concentrations were significantly correlated with each other ($r > 0.82$, $p < 0.01$), indicating that these five elements have similar anthropogenic sources (Varol, 2011). Significant correlation between Tl and Hg ($r = 0.96$, $p < 0.01$) indicated that these two elements were derived from the discharge of smelting. Moreover, Tl and Hg also showed slightly correlation with Pb, Cd and Mn. Copper did not show significant correlation with other target metals, indicating that Cu came from another point source which might be mine tailing due to

Table 1
Comparison between heavy metal concentrations (mg/kg) in the Maba River and sediment quality guidelines (SQGs) with percentage of samples in each guideline.

Sediment quality guidelines (SQGs)/(effect)	Metal concentrations (mg/kg)							
	Pb	As	Cd	Zn	Cr	Ni	Cu	Hg
TEL	35	5.9	0.596	123	37.3	18	35.7	0.174
PEL	91.3	17	3.53	315	90	36	197	0.486
ERL	35	33	5	120	80	30	70	0.15
ERM	110	85	9	270	145	50	390	1.3
Compared with TEL and PEL	% of sample in each guideline							
< TEL	0%	0%	0%	6.25%	0%	6.25%	18.75%	0%
≥ TEL < PEL	18.75%	0%	25%	12.5%	100%	81.25%	37.5%	0%
≥ PEL	81.25%	100%	75%	81.25%	0%	12.5%	43.75%	100%
Compared with ERL and ERM	% of sample in each guideline							
<ERL	0%	12.5%	43.75%	6.25%	100%	87.5%	37.5%	0%
≥ERL < ERM	31.25%	18.75%	12.5%	12.5%	0%	12.5%	18.75%	31.25%
≥ERM	68.75%	68.75%	43.75%	81.25%	0%	0%	43.75%	68.75%

TEL: threshold effect level, dry weight.
PEL: probable effect level, dry weight.
ERL: effects range low, dry weight.
ERM: effects range median, dry weight.
Mn and Tl have no SQGs values.

high concentration was observed at site T6 in the Caoxi Stream, which originated from Dabaoshan (Lin et al., 2007). Undoubtedly, it can infer that Pb, As, Cd, Zn and Mn mainly originated from both anthropogenic activities. Cr and Ni existed significant correlation ($r = 0.858$, $p < 0.01$) and showed no significant correlations with Tl, Hg and Cu, indicating that Cr and Ni do not have common anthropogenic sources with above elements.

HCA was applied to river sediment quality data set to group the similar selected heavy metals and sampling sites of the Maba River. The analyzed parameters HCA rendered a dendrogram (Fig. 6(a)) where all ten metals in the study area were grouped into two statistically significant clusters. Cluster 1 included (Tl, Hg, Cd), (Ni, Cr) and (Pb, As, Cu) were identified as low to moderate concentrations' elements (Rodrigues et al., 2013). Although Tl, Hg and Cd revealed severe enrichment by comparing with of soil B.G values, the total concentrations of them were lower than 50 mg/kg, which were comparable with Ni and Cr. Lead, As and Cu derived from anthropogenic sources, mainly including wastewater discharges from smelting and mine tailing, were moderate concentrations with the highest value lower than 1700 mg/kg. Cluster 2 contained Zn and Mn derived from both smelting and mining, represented high concentration elements.

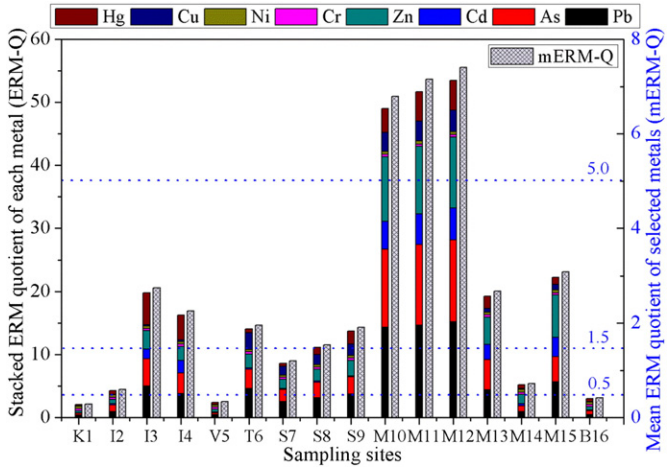

Fig. 5. Effects rang median quotient (ERM-Q) and mean effects rang median quotient (mERM-Q) of selected heavy metals in surface sediments of the Maba River, Guangdong Province, China.

Similarly, spatial HCA rendered a dendrogram (Fig. 6(b)) where all 16 sampling sites along the Maba River were grouped into three statistically significant clusters. Cluster 1 (I2, B16, K1, V5 and M14) and (I3, T6, S7, S8 and S9) sites were located in low or low to moderate pollution regions, which mainly affected by geological weathering as well as anthropogenic origins. Cluster 2 (M13, M15 and I4) sites were in a moderate to high pollution region (Chai et al., 2015). Cluster 3 (M10, M11 and M12) sites were in a high pollution region, due to receiving metallic wastewater discharges from smelting and mine tailing, and the heavy metal concentrations were magnified due to the adsorption or complexation of sediments.

Principal component analysis (PCA) was performed on normalized data to compare compositional pattern between sediment samples and to identify influencing factors. The corresponding eigenvalue, principal components (PCs), variable loadings and the explained variance of selected metals in sediments are presented in Table S5. The result of PCA revealed that the three PCs with eigenvalues >1 that explained about 94.47% of total variance in the sediment quality data set, which indicated that the different sources or controlling factors for heavy metals in surface sediments of the Maba River. The principal component analysis loading plots of the first three PCs presented in Fig. 7 showed that these elements could be classified into Group 1 (Tl and Hg), Group 2 (Cd, Mn, As, Pb and Zn), Group 3 (Cr and Ni) and Group 4 (Cu), PC coefficients having a correlation >0.70 were considered significant (Chai et al., 2015; Maanan et al., 2015). The classification results consistent with the results of PCA.

The first principal component (PC1), with high loadings (>0.70) of Pb, As, Cd, Zn and Mn explained 65.87% of the total variance suggested that these metals in the study area were mainly derived from common compound anthropogenic sources, (smelting and mining). The distribution patterns of these metals may depend on the contribution of pollution sources, river environmental conditions and the adsorption of sediments (Bartoli et al., 2012; Erftemeijer et al., 2012). The second principal components (PC2) accounting for 17.83% of total variance corrected with Tl, Hg, Cr and Ni (loading > 0.70), in which the PC values of Cr and Ni were negative, indicating that Tl and Hg originate from different types of sources with comparing Cr and Ni. Considering their relatively high I_{geo} values on sites I3 and I4, indicating that Tl and Hg were mainly discharged from the smelting. The third principal components (PC3) accounting for 10.76% of total variance corrected with Cu (loading > 0.70), indicating that Cu originates from a different anthropogenic source (Chai et al., 2015). With the loading weight 0.895 of Cu on PC2, and its relatively high CF was observed on site T6, indicating that Cu mainly comes from the mine tailing of Dabaoshan which is a copper

Table 2
Pearson correlation matrix for selected heavy metals in surface sediments of the Maba River, Guangdong Province, China.

	Pb	As	Cd	Zn	Cr	Mn	Ni	Cu	Tl	Hg
Pb	1.000									
As	0.964[a]	1.000								
Cd	0.942[a]	0.938[a]	1.000							
Zn	0.983[a]	0.974[a]	0.944[a]	1.000						
Cr	0.577[b]	0.660[a]	0.603[b]	0.635[a]	1.000					
Mn	0.894[a]	0.829[a]	0.895[a]	0.849[a]	0.415	1.000				
Ni	0.587[b]	0.661[a]	0.678[a]	0.638[a]	0.858[a]	0.638[a]	1.000			
Cu	0.470	0.595[b]	0.215	0.589[b]	0.095	0.227	0.107	1.000		
Tl	0.505[b]	0.330	0.544[b]	0.398	-0.088	0.707[a]	0.464	0.054	1.000	
Hg	0.605[b]	0.447	0.601[b]	0.503[b]	-0.090	0.767[a]	0.469	0.207	0.964[a]	1.000

[a] Significant correlation at the 0.01 level.
[b] Significant correlation at the 0.05 level.

mine in North Guangdong Province and is mining for nearly 30 years (Lin et al., 2007). Therefore, the PC2 may represent the anthropogenic factor of point source to the metal contaminations.

3.5. Factor analysis-multiple linear regression (FA-MLR)

Based on the qualitative information analyzed by multivariate statistical analyses about sources of heavy metals in surface sediments of the Maba River, FA-MLR method was applied to quantify the contributions of each source in the mixed region. The varimax rotated factor analysis results are presented in Table S6 with probable source types. According to Table S1 and Fig. 1, regardless of mineralization and desorption effect of heavy metals in sediments, hypothesizes that heavy metal sources contains smelting, mining, geological weathering (background concentration) and others (including atmospheric precipitation, agricultural wastewater and sewage). The eigenvalue was set to 1.0 as a threshold in order to limit the number of extracted factors, and factor loadings equal to or >0.3 were considered as significant and were presented (Pekey et al., 2004). Four factors were obtained which explained about 98.37% of the total variance, with the first factor accounting for 52.05%, the second factor for 25.98%, the third factor for 11.61% and the fourth factor for 8.73%. The first factor has high loadings of Pb, As, Cd, Zn, Tl, Hg and Cd, all these elements in this factor are likely to originate from smelting. The second factor contains Pb, As, Cd, Zn, Mn and Cu, indicating that these metals come from the mining. The third factor displays high loadings of Cr and Ni. The two elements often found in crustal components, therefore, are identified as mainly originating from geological weathering (Guo et al., 2004). The fourth factor is characterized by high loadings of Cr, Ni and Hg. Commonly, geological weathering, atmospheric precipitation, agricultural wastewater and sewage contains high level of heavy metals, however, the contents of metals in these sources are much lower than in activities sources.

The source contribution (in percent) to each metal and observed to predicted ratios (O/P) are calculated, the percent contribution of each source of the observed heavy metal concentrations are presented in Fig. 8. Generally, the O/*P* values of the elements varied between 1.12

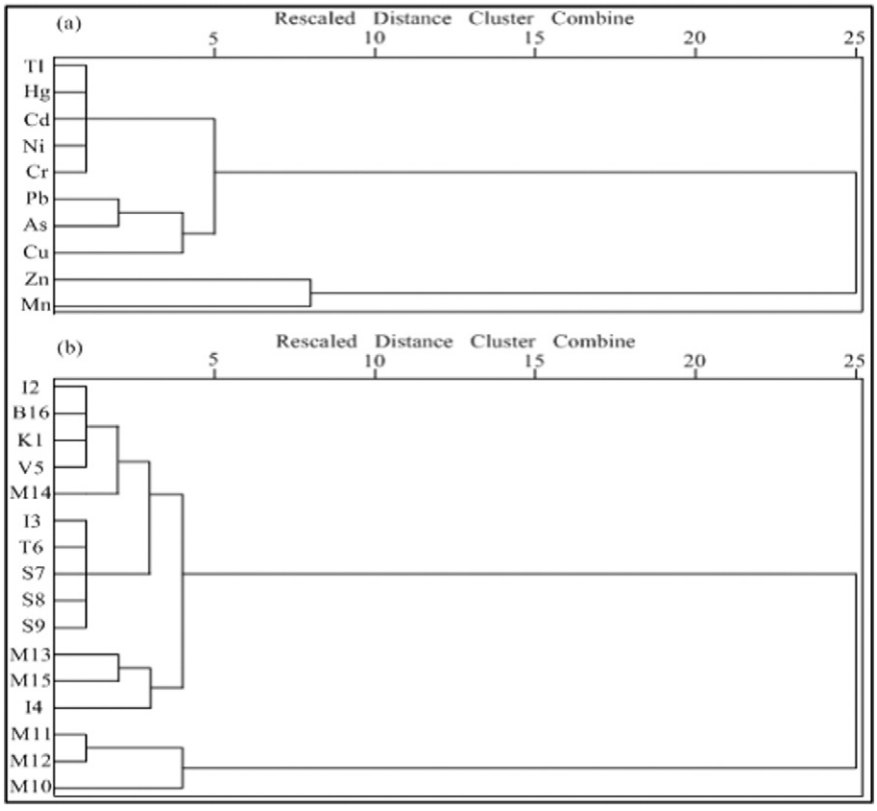

Fig. 6. Hierarchical clustering analysis among selected heavy metals and sampling sites in surface sediments of the Maba River, Guangdong Province, China, distance metrics are based on the Euclidean distance single linkage method (nearest neighbor).

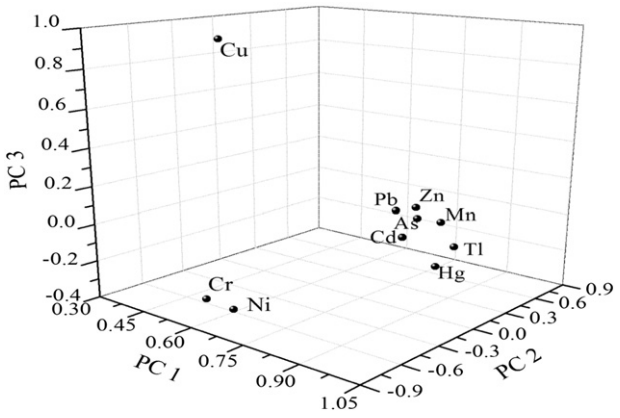

Fig. 7. The principal component analysis loading plot of selected heavy metals in surface sediments of the Maba River, Guangdong Province, China.

(Cu) and 0.88 (Cr), indicated that these elements are predicted with an uncertainty of better than 15%. Chromium and Ni with moderate R^2 values ($0.70 < R^2 < 0.80$) indicated that the FA-MLR method can't efficiently explain the contributions. However, the rest of target metals had higher R^2 values and were extremely close to the original communality values. Moreover, 87% of Cu came from the runoff of the mine tailing, while 77%, 66% and 72% of Tl, Hg and Cd, respectively originated from the discharges of smelting. Copper, As, Zn and Mn mainly contributed by source 1 and source 2, while both 80% of Cr and Ni came from the geological weathering (source 3). Source 4 contains atmospheric precipitation, agricultural wastewater and sewage, the error of the result also contributes heavy metals to the environment, but the contents are relatively low. Furthermore, the prediction errors are slightly larger, because that the contribution analysis of non-point sources is more difficulty. The percent of Hg contributing by source 4 (20%) were higher than others, following by Mn, Zn, As and Pb. The result was consistent with previous study, where reported that the concentrations of Hg, As and Pb in the atmospheric of smelting area are significant high, because these metals are relatively easy to volatilize, especially for Hg (Cai et al., 2012; Driscoll et al., 2013). Therefore, the FA-MLR method can further accurately assess the contribution of each heavy metal by various sources. When the compound percent contributions of identified sources were used to calculate metal concentrations, the estimated concentrations were observed to be similar to the measured values.

4. Conclusion

Useful tools and methods, such as geo-accumulation index (I_{geo}), sediment quality guidelines (SQGs), multivariate statistical analyses (MSA) and factor analysis-multiple linear regression (FA-MLR) were employed to evaluate sediment quality and identify the potential pollution sources and the concrete contribution in Maba River, South China. The field study showed that Pb, As, Cd, Zn, Mn, Cu, Tl and Hg in sediments of the Maba River were obviously contaminated, especially Cd and As exceeded >480 and 120 times respectively by comparing with the soil background values, while no significant Cr and Ni pollution were observed in the area. The concentrations of heavy metals along the tributary gradually increased except Cr, and then accumulated in the mixed region. The migration process is mainly affected by hydraulic conditions (flow rate, river width) and sediment characteristics (TOC, clay). The highest values of I_{geo} were found in the mixed region near the entrance of the Beijiang River, then the concentrations followed the decreasing order Cd > Hg > As > Zn > Pb > Tl > Mn > Ni > Cr, indicating that this region accumulates a huge amount of metallic pollution due to the convergence of all kinds of wastewater. The significantly high concentrations of As, Pb, Cd, Zn, Cu and Hg in sediments were found in the mixed region by comparing with SQGs, indicating that the target metals are likely to result in harmful effects, and the risk are expected to occur frequently on aquatic organisms. Results of PCM, HCA and PCA identified that the loading of Cr and Ni were mainly related to geological weathering, whereas Pb, As, Cd, Zn, Mn, Cu, Tl and Hg were mainly from the anthropogenic sources, such as smelting and mine tailing. Further analysis with FA-MLR showed that about 87% of Cu comes from the runoff of mine tailing, while 77%, 66% and 72% of Tl, Hg and Cd respectively from the discharges of smelting. The uncertainties between the computational predicted concentrations and the actual detected concentrations were lower than 15%. Based on the field investigation and data analysis, the Maba River takes shape a seriously compound heavy metals pollution, implying that the effective management and repair technology are urgently needed, for protecting the local ecological environment and drinking water source.

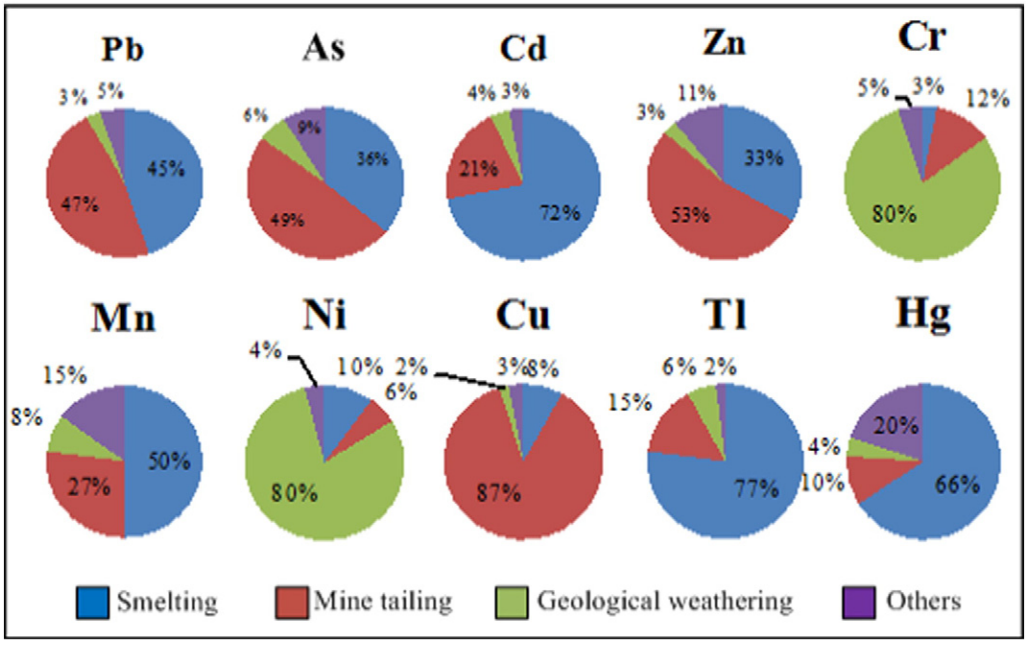

Fig. 8. Percent apportionment of the possible source types based on the observed heavy metal concentrations (mean values).

Conflict of interest

The authors declare that there is no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gexplo.2016.08.013.

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