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Environmental impact

The safety of water supply has been attracted considerable concerns in the Pearl River Delta (PRD) area due to the severe pollution of water environment associated with rapid urbanization and industrialization. Migration and potential risk of heavy metals, as a kind of hazardous element, were assessed in Shima river, which is connected to Dongjiang River and may affect water supply for Hong Kong and Shenzhen. The findings of this research suggested that river water pollution could be attenuated by meteorological factor (heavy rainfall) or less release of heavy metals from the urban or industrial areas, while the secondary pollution of river water remain due to potential release of heavy metals from the aquifer (soil) along the river bank. Understanding the migration of heavy metals between river water and groundwater and the relative potential ecological risks are vital for implementation of pollution remediation and safety of water supply in the PRD area.

Distribution, migration and potential risk of heavy metals in the Shima River catchment area, South China

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Abstract The distribution, migration and potential risk of heavy metals in water and soil environments, related to city water supply, were investigated. Heavy metal concentrations in waters from the Shima River water ranged from not detected (n.d.) to 749 μg·L^{-1} for Mn, n.d. to 151 μg·L^{-1} for Ni, 7.00 to 494 μg·L^{-1} for Zn, n.d. to 93.0 μg·L^{-1} for Cu and n.d. to 9860 μg·L^{-1} for Fe, respectively. The highest concentration of heavy metals was found at an upstream site in February as the result of industrial effluent discharge. Groundwater (GW1–GW5) and soil (S1–S8) samples along the river bank showed similar levels of contamination due to a close hydraulic relationship and frequent exchange of water, probably resulting in migration of heavy metals from river water to the aquifer and accumulation at the interface. The mean concentrations of heavy metals in soil profiles were in the ranges 2.50–19.0 mg·kg^{-1} for As, 2.80–11.2 mg·kg^{-1} for Cd, 20.3—165 mg·kg^{-1} for Cr, 14.5–298 mg·kg^{-1} for Cu, 11.4–102 mg·kg^{-1} for Ni, 7.00–95.0 mg·kg^{-1} for Pb, 40.4–465 mg·kg^{-1} for Zn, 8.80×10^3–21.8×10^3 mg·kg^{-1} for Fe, and 62.2–430 mg·kg^{-1} for Mn, showing severe soil pollution by Cd. LUMISTox testing and the potential ecological risk index (*RI*) were used to assess the potential for adverse ecological effects caused by heavy metals in water and soil media. River water samples posed slight acute toxicity to *Vibrio fischeri* with luminescent inhibition rates (LIR) ranging from 24.6% to 38.4% in February. Elevated Zn and Cu significantly contributed to toxicity. However, groundwater did not exhibit any toxicity to *Vibrio fischeri*. The severity of the potential ecological risk for individual metals (E^i_r) decreased in the order Cd>Cu>Ni>As>Pb>Zn>Cr. *RI* values indicated that all soil samples in the study area posed a high level of ecological risk. Cd contributed significantly (95.5–98.9%) to potential ecological risk in soils.

Keywords: Shima River catchment; water pollution; soil quality; heavy metals; river-groundwater interaction; potential ecological risk;

Introduction

The Pearl River Delta (PRD) located in Guangdong Province in south China is one of the most developed areas of China. There are nine cities with a total area of 41700 km^2, including Guangzhou, Shenzhen, Zhuhai, Foshan, Huizhou, Zhaoqing, Jiangmen, Zhongshan and Dongguan.[1] Chinese reform, beginning in 1979, brought accessibility from the outside world and a time of rapid industrialization, urbanization and transition from traditional agriculture to industrial and technologically based agriculture.[2] The PRD area was significantly affected by economic expansion and heavy industry, resulting in one of the largest manufacturing locations in China. Some of the major manufacturing products include electronics, toys, dyes, clothing, leather, papers and petrochemicals, which discharge 3 ×10^9 tons of effluent annually, [1, 3] leading to the deterioration of water and soil quality over the past three decades in the PRD area.[1, 4]

Heavy metals are considered a ubiquitous substance and common pollutant in contaminated environments, arousing public interest due to their properties such as chemical stability,

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bio-accumulation, non-degradation and long-lasting harmful effects. [5-7] Vast preliminary research conducted on heavy metal pollution in river water, groundwater and soils [8-10] has included identification of sources, migration patterns and ecological effects. [11-14] Generally, heavy metals are derived from point sources, such as mining and smelting activities and industrial effluents, and non-point sources, such as indiscriminate use of heavy metal-containing fertilizers and pesticides in agricultural fields, as well as from the lithosphere. [8, 11] With respect to migration in a drainage basin, the study of movement of heavy metals driven by water cycling between or among environmental media has been the primary approach, and it has been found that metals can be transported by river water flow from upstream to downstream areas, into the aquifer along the river bank, by rainfall penetration from the surface to underground layers, or by groundwater flow from the aquifer back to river water at distant sites. [10] Atmospheric circulations is another migration pathway for heavy metals. [15-18] Different migration behaviors of heavy metals are closely associated with various environmental media; however, few studies regarding the exchange of heavy metals between different media have been reported. Winde *et al.* [19] reported that groundwater-stream interactions resulted in the migration of uranium in an aquifer and subsequent contamination of stream water. It was previously found that groundwater inputs of Cd and Zn contributed 43% and 28%, respectively, to the total annual Cd and Zn fluxes along 200 m of the Riou Mort River in 2004.[20] Hence, movement of heavy metals between river water and groundwater/aquifers along the river bank in a drainage basin is of great importance for understanding environmental behaviors and fate.

Excessive accumulation of heavy metals in a drainage basin can pose ecological risks [9, 21] and impose significant adverse effects on the surrounding ecological system. Furthermore, one pathway for toxicity in humans is from toxic effects in aquatic organisms in aquatic ecosystem-based food chains.[15] Effective tools for determining the ecological effects of heavy metal pollution are generally chemically and biologically based. Nevertheless, chemical-based models for assessing the potential risks caused by toxic substances in coastal sediment were integrated, [22] and the method was extended to the study of soil pollution. [23, 24] In the aquatic environment, organism toxicity testing is currently considered the most effective method for assessing water safety, as the aqueous medium may contain diverse, complex and variable contaminants. Integrated effects (e.g., antagonistic, additive and synergistic) of chemicals on the aquatic ecosystem may then be characterized directly. [25] It was found that interactive effects between copper and zinc and between lead and zinc on the bioluminescence of *V. fischeri* were synergistic, [26] indicating that toxicity tests may provide a direct quantitative measure of actual toxicity, adequately reflecting aquatic environmental conditions and supplementing the deficiencies in physicochemical assessments for establishing ecological risks. However, little information is available on the distribution, migration and toxic effects of heavy metals among different media resulting from river water-groundwater interaction in a catchment with extensive human activity, such as the PRD area.

The main objectives of the present study in the Shima River catchment are therefore 1) to investigate the temporal-spatial variation and sources of heavy metals in river water, groundwater and soil; 2) to analyze the migration of heavy metals via river water–groundwater interaction and calculate pertinent mass fluxes; 3) to assess the toxic effects of river water and groundwater using the LUMISTox® (*Vibrio fischeri*) system and identify potential toxins; and 4) to quantify soil pollution levels of heavy metals along the river bank along with the potential risks. Results may provide evidence for decision-making related to pollution control and protection of water and soil environments in the PRD water resource area.

Materials and methods

2.1 Study area

Shima River catchment, situated in Dongguan city, Guangdong province, south China (Figure 1), has a southern subtropical monsoon climate and experiences an annual mean precipitation of 1954 mm and mean temperature of 22.9℃. Typhoons are frequent in the study area in June, July, August, and September, and rainstorms occur regularly. Dongguan city is covered by unconsolidated Quaternary sediments with a clay soil thickness ranging from 0 to 18 m. The upstream area of the catchment is mainly underlain by Carbonatite, while the downstream area is dominated by hydatogenic rock and gritstone. The major soil types are lateritic red soil and calcareous yellow soil.

The Shima River (site R1–R6) with a length of 88 km and a catchment area of 1249 km^2, originates in Baoan county, a dense industrial area in Shenzhen City, and is the largest tributary of the Dongjiang River in Dongguan city. The Shima flows from south to north and discharges through an outlet located at Qiaotou (R6), and then joins the Dongjiang River near a water supply pumping station in a vital water resource area in the PRD, providing approximately 80% of Hong Kong's portable water through river extraction. Hence, the Shima River catchment is of strategic importance in protection of a safe water supply. In the dry season, the river water is obstructed by a rubber dam with a height and length of 3.25 m and 92 m, respectively, to avoid contamination of the inlet. The Tonghu River merges with the Shima River via an underground pipe between R6 and R7, then flows to the Xiaohai, Renhe, Hanxi Rivers and finally to the Dongguan Canal. River water, ultimately, flows into the Pearl River estuary through the town of Humen (R11). Four sluice gates within the Dongguan Canal - Xiakou (R8), Shigu (R9), Xinji Clough (R10) and the rubber dam (R6) - drain to the Dongjiang River (south main stream) during heavy rainfall.

2.2 Sample collection

River water (R1–R11) was collected by grab-sampling during three seasons, in February, June and November of 2012. Five piezometers (GW1–GW5) were constructed at varying distances from the river bank by hand drilling, and soil samples were collected at a depth 30 cm from the surface. The five piezometers (GW1–GW5) and two wells (GW6 and GW7) were sampled using a portable vacuum pump, with the well depth and water table measured in situ. Water and soil samples were collected in sterilized polyethylene bottles and plastic packets, respectively, and stored in a portable refrigeration unit. Water samples were transferred to refrigeration (4℃) under dark conditions in the laboratory, and soil samples were air-dried prior to analysis. Relevant data for the sampling sites are presented in Table 1 and Figure 1.

2.3 Physicochemical and biological analysis

2.3.1 Analysis of water samples

The electrical conductivity (EC), temperature (T), pH and dissolved oxygen concentration (DO) of water samples were measured in situ using a portable instrument (Horiba 3-in-1). Water samples were filtered through a polypropylene membrane with a diameter of 0.45 μm, 1 M HNO_3 was added to adjust the pH to 2, and the samples were then stored in a refrigerator at 4℃ until analysis. Trace metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were measured using inductively coupled plasma–atomic emission spectrometry (ICP–AES). The detection limits were 1 $\mu g \cdot L^{-1}$ for Cd, 5 $\mu g \cdot L^{-1}$ for Pb, Mn, Zn, Fe and 10 $\mu g \cdot L^{-1}$ for As, Ni, Cr and Cu.

2.3.2 Analysis of soil samples

Soil samples were ground using an agate mortar after air-drying at room temperature and removing coarse debris. Samples were then homogenized by straining through a 1-mm nylon sieve, and pH and EC were measured in a 1:2.5 (*w/v*) ratio of sub-soil to deionized water. A Malvern Mastersizer 2000 was used to analyze particle size. The dichromate oxidation method, as detailed by Nelson and Sommers, [27] was applied to determine soil organic matter content, and total soil phosphorus (P) was determined by wet oxidation in a mixture of concentrated perchloric and sulphuric acid. [28] Approximately 0.5 g each sub-sample was weighed and digested with 10 ml *aqua regia* (2.5 ml nitric acid and 7.5 ml hydrochloric acid) at 140-160℃ and heated on a hot plate. [29] 50 ml of 2% HNO_3 were then added to each mixture after cooling, followed by polypropylene membrane (0.45 μm) filtration of the supernatant for each sub-sample. Heavy metal (As, Cd, Cr, Cu, Ni, Pb, Zn, Mn, and Fe) concentrations were then measured using ICP-AES. The validity of the data were maintained by implementation of standard methods including calibration of a standard curve during ICP-AES measurement and application of standard operating procedures. Blanks, triplicates and recovery rates were applied for quality control of the heavy metal analysis. A standard solution of known metals was measured to calibrate the standard curve. Soil metal concentration data presented in this paper were corrected by subtracting the blank value. Detection limits were 0.1 $\mu g \cdot g^{-1}$ for Cd, 0.5 $\mu g \cdot g^{-1}$ for Pb, Mn, Zn, Fe, and 1 $\mu g \cdot g^{-1}$ for As, Ni, Cr and Cu, respectively. The standard deviation of each sample was within 10%, and the recovery rate fell in the range of 90–113% for all heavy metals.

2.3.3 Ecotoxicity assay

Luminescent bacterium *Vibrio fischeri* has been widely used as a sensitive, rapid and cost-efficient tool for monitoring toxicity in water quality studies. [30] The LUMISTox® measuring station using *Vibrio fischeri* was employed to assess the potential ecological risks of polluted water bodies in the study area, and the relative method is detailed in ISO-11348. [31] Briefly, the three analysis steps were as follows: first, water salinity was adjusted to 2% by mixing water samples (10 mL) and NaCl (0.2 g) in a centrifuge tube (15 mL); second, freeze-dried luminescent bacteria were reactivated by injection of a reconstitution solution (1 mL) and then warmed from -18 to 4℃ in a refrigeration unit. The luminescent bacteria suspension was diluted with 2% NaCl until the lowest emission intensity of 500 luminescent units (LU) was met, and then assayed after ~15 min. Finally, the ecotoxicity of the water samples was tested at a 1:1 (*v/v*) ratio of luminescent bacteria solution (0.5 mL) to sample (0.5 mL) in a cuvette at 15℃. The luminescence inhibition rate (LIR, %) of *Vibrio* *fischeri* was obtained after 15 and 30 min incubations. Toxicity classification was determined according to LIR percentage: no acute toxicity for a LIR<20 %, slight acute toxicity for 20% <LIR <50%, acute toxicity for 50% <LIR <100% and high acute toxicity for a LIR of 100%. [32] Each water sample was diluted with an equal amount of 2% NaCl to determine the dose-response relationship for calculation of EC_{20} or EC_{50}, i.e., the effective concentration (%) of water samples causing a 20 or 50% reduction in luminous intensity when the LIR of the sample exceeded 30 or 60%, respectively. Ecotoxicity assays were performed in quadruplicate, and test results were expressed as mean values with standard deviations.

2.3.4 Ecological risk assessment

Risk indices (*RI*) were adopted to characterize qualitatively and quantitatively the potential ecological risk of heavy metals in soils from the river bank: [22]

$$RI = \sum_{i=1}^{7} E_r^i = \sum_{i=1}^{7} T_r^i C_r^i = \sum_{i=1}^{7} T_r^i \left(\frac{C_s^i}{C_n^i}\right),$$

where *RI* is the sum of the individual potential ecological risks for all heavy metals evaluated, E_r^i is the *RI* of an individual heavy metal, T_r^i is the toxic-response factor, defined as 10, 2, 30, 5, 1, 5, and 5 for As, Cr, Cd, Cu, Zn, Pb, and Ni, respectively; [22, 24] C_s^i is the concentration of heavy metals in soil samples and C_n^i are reference values, in this case the environmental background values for soils in Guangdong province (Table 4). Table S1 shows the varied grade of potential ecological risk for heavy metals.

2.4 Monitoring of hydrological variation

Three conductivity, depth and temperature (CDT) sensors, calibrated prior to the monitoring process, were installed in river water and groundwater at sites R2, GW2 and GW3 to monitor changes in hydrological parameters. The monitoring program was started at 6:30 p.m. on 22 June 2012 and concluded at 2:30 p.m. on 24 June 2012 with data recorded at 10-min intervals. Groundwater table variations can reflect responses to fluctuations in river water levels, and the hydraulic gradient may be approximately determined using Darcy's Law. [33] The hydraulic gradient between the river and groundwater was calculated using the following equation:

$$\text{Gradient (\%)} = \frac{H_R - H_G}{L},$$

where H_R (cm) is the hydraulic potential of the river, H_G (cm) is the hydraulic potential of groundwater and *L* (cm) is the distance between the river and monitoring site of groundwater.

2.5 Data analysis

To describe differences in potential risk originating from water pollution during three typical periods and explain distributional variances in heavy metals at different soil sampling sites, one-way ANOVA with Duncan's test was applied to the LIR results from water samples. Significant differences were considered if $p<0.05$ or $p<0.01$. Hierarchical cluster analysis based on the farthest neighbor method with squared Euclidean distance and correlation analyses were used to identify the sources of heavy metal pollution in soils from the river bank. The Pearson coefficient was also adopted to assess the relationship between LIR and the sum of heavy metal (Cu, Fe, Mn, Ni and Zn) concentrations in water samples. Significant relativity was obtained if $p<0.05$ or $p<0.01$. Statistical analysis was completed using SPSS 16.0.

Results and discussion

3.1 Heavy metal concentrations in water bodies and river water–groundwater interactions

The results of physicochemical analysis are presented in Tables 2–3, and the detected values were compared with the Drinking Water Standards issued by the World Health Organization (WHO) [34] and the Ministry of Environmental Protection of China (MEP). [35]

3.1.1 River water

The water quality of samples R1–R11 was better in June than in February or November, probably due to dilution by tropical storm "Typhoon Talim", which generated a cumulative precipitation of 171 mm from 22-24 June, 2012. Monthly precipitation amounts descended in the order of June (256 mm)> November (168 mm)> February (51.2 mm). Acid-based properties of the river water remained stable, and the pH of samples in all three periods remained within the recommended range recommended by the MEP (6-9) and the WHO (6.8–8.5), [34, 35] except for R7 in June, during which an acidic pH was found in the Tonghu River. The dissolved oxygen (DO) threshold for protection of aquatic life recommended by Canadian Council of Ministers of the Environment (CCME) [36] is 5.5 $mg\cdot L^{-1}$, while that recommended by the MEP [34] is 6 $mg\cdot L^{-1}$. 84.8% of water samples were below or close to the threshold by CCME, [36] while no samples met the value recommended by the MEP. [34]

Metal concentrations in river water samples ranged from not detected (n.d.) to 749 $\mu g\cdot L^{-1}$ for Mn, n.d. to 151 $\mu g\cdot L^{-1}$ for Ni, 7.00 to 494 $\mu g\cdot L^{-1}$ for Zn, n.d. to 93 $\mu g\cdot L^{-1}$ for Cu and n.d. to 9860 $\mu g\cdot L^{-1}$ for Fe, as shown in Table 2, with As, Cd, Cr and Pb at levels below the detection limits. The highest concentration of heavy metals was detected at site R1 in February, suggesting abundant heavy metals originating from upstream locations, exclusively from discharge of industrial effluent in Baoan district, Shenzhen city. The relatively lower concentrations found at R7 compared with R6, particularly for Zn and Fe, may likely be attributed to dilution from the confluence of the Shima and Tonghu Rivers. A decreasing trend in metal concentrations from upstream to downstream was observed and may be attributed to the dilution of contaminants and deposition following adsorption of heavy metals onto suspended particles. [17, 37] Relatively lower metal concentrations were found in June and November (Table 2). Heavy metal concentrations in all water samples met the WHO and MEP standards for drinking-water quality, with the exception of Mn concentrations in November. Mn pollution remains an issue, as unsightly stains and a brown/black precipitate may result. [37] Comparable total heavy metal concentrations were observed at site R11 (Humen District) in June and November, despite heavy rainfall in June. In combination with the increasing trend from R8 to R11, it may be concluded that heavy metal release occurred in urban areas, especially Humen town. The temporal-spatial variation in heavy metal distributions demonstrated combined impacts from domestic wastewater, industrial effluents and meteorological factors.

3.1.2 Groundwater

Heavy metal concentrations in groundwater along the river bank (GW1–GW5) ranged from 14.0 to 800 μg·L^{-1} for Mn, n.d. to 91.3 μg·L^{-1} for Ni, n.d. to 196 μg·L^{-1} for Zn, n.d. to 36.0 μg·L^{-1} for Cu and n.d. to 686 μg·L^{-1} for Fe (Table 3). Metal concentrations (GW1–GW5) were comparable to or lower than those found in river water during the dry season (February) and may be attributable to an existing river water and groundwater hydraulic relationship along the river bank, allowing groundwater quality purification by the adsorption of heavy metals to soil particles. Mn concentrations in all groundwater samples (GW1–GW5) in February and November were higher than the value of 100 μg·L^{-1} recommended by the WHO [35] and MEP (Class I). [38] GW2 with a shallow groundwater depth of 108 cm displayed the highest concentrations of 64.0 μg·L^{-1} for Ni, 196 μg·L^{-1} for Zn and 36.0 μg·L^{-1} for Cu in June (Table 3), suggesting more concentrated metal sources exist at the aquifer/soil interface. As shown in Table 4 and S2, soils with the highest heavy metal concentrations and organic matter content at this site (S3) had greater potential to release metals into the aquifer due to the water induction of the unsaturated zone resulting from river water-groundwater interaction, leading to desorption of heavy metals from soils associated with reductive dissolution of iron and manganese oxides. [39]

GW6 and GW7 were collected from wells with depths of 431–451 and 431–451 cm, respectively, in Humen town. Water quality in GW6 and GW7 is not likely to be affected by river water pollution because of their distance (100 m and 120 m) from the river channel, and hence weakened hydraulic relationships between groundwater and river water. The EC and pH of GW7 were relatively stable compared to GW6 across the three seasons, as GW7 had a protective cover in place to ensure safe human consumption. The pH of waters from GW7 ranged from 4.86 to 5.40 (Table 3), illustrating acidification of the local unconfined aquifer. One contributing factor is likely to be acid precipitation and infiltration into the aquifer; acid precipitation from 2007 to 2012 in Dongguan City with intensified acid precipitation in 2007 and 2008 has been recorded in the Report on the State of Guangdong Provincial Environment. [40] Another factor may be the impact of pyrite oxidation. Forced oxidation of FeS_2 and FeS to H_2SO_4 under oxidizing conditions will generate H^+ ions and lower the pH of groundwater, a result supported by research conducted in Shenzhen city (near Dongguang city). [41] Fe concentrations in GW7 ranged from 1870–2560 μg·L^{-1} in different periods, exceeding Class V water quality standards [38] and rendering this water no longer suitable for human consumption. The higher Fe concentrations found in the aquifer are consistent with the effects of pyrite oxidation. Fe and Mn concentrations were lower in June than in February or November in GW6 compared with the sealed well (GW7), as a result of strong dilution by precipitation.

3.1.3 River water–groundwater interactions

River water and groundwater samples demonstrated similar concentrations of heavy metals during the dry season. Analysis of the hydraulic relationships between river water and groundwater was performed to understand the interaction process (Figure 2). A high correlation occurred in the hydraulic head time-series in river and groundwater, demonstrating a close hydraulic link between these two water bodies. Statistical time-series analysis yielded a significantly positive correlation ($p<0.01$) between water-level fluctuations in river water and groundwater, and strong linear regressions between R2 and GW2 (R=0.828) and between R2 and GW3 (R=0.776) were identified. The response time of groundwater lagged behind the river water by 30–70 min and 60–100 min when the monitoring distance was extended from 0.5 to 1.5 m from the river channel, showing that hydraulic effect reduced with increasing distance from the river bank.

The direction and velocity of water flow between river water and groundwater were controlled by the hydraulic gradient (Figure 3) and hydraulic conductivity of the aquifer at the river water-groundwater interface. A positive hydraulic gradient value (Period I and III) indicates that river water recharged into groundwater, and the reverse process (Period II and IV) occurred when the hydraulic gradient was negative, implying the possibility of water movement-driven heavy metal exchange between these two water bodies. However, metals would also accumulate by absorption (e.g., electrostatic force) and/or adsorption (e.g., deposition, precipitation and complexation) on soil particles once the metals accessed the soil porous medium. [8, 12]

3.2 Spatial distribution of soil heavy metals along the river bank

3.2.1 Soil properties and heavy metal content along the river bank

The soil properties (e.g., pH, EC, texture, organic matter and total P content) presented in Table S2 are key factors in controlling the spatial distribution of heavy metals. The EC and pH values of soils ranged from 4.98 to 131 ms·m^{-1} and from 6.14 to 7.46, respectively, with 69.2% of soil samples showing slight acidity. SOM (soil organic matter) and total P content were significantly higher ($p<0.01$) at midstream (S3, S4, S5 and S6) sites than at upstream or downstream sites along the river banks, likely as a result of fertilizer application at midstream sites where vegetation or crops have been cultivated over long periods. Soil particles with a diameter less than 63 μm were defined as the fine particle components (FPC) and were found in proportions ranging from 52.0–75.1 % with no significant differences among sampling sites.

Table 4 summarizes the measured concentrations of heavy metals in different soil profiles. Mean heavy metal concentrations were in the range 2.50–19.0 mg·kg^{-1} for As, 2.80–11.2 mg·kg^{-1} for Cd, 20.3—165 mg·kg^{-1} for Cr, 14.5–298 mg·kg^{-1} for Cu, 11.4–102 mg·kg^{-1} for Ni, 7.00–95.0 mg·kg^{-1} for Pb, 40.4–465 mg·kg^{-1} for Zn, 8.80×10^{3}–21.8×10^{3} mg·kg^{-1} for Fe, and 62.2–430 mg·kg^{-1} for Mn. Cr, Ni, and Pb concentrations in all soil samples were close to or below soil quality thresholds (SQTs, Class II). [42] In contrast, Cd, Cu and Zn levels exceeded the standard values at some sites. Nearly all heavy metal concentrations exceeded the soil background value for Guangdong Province with the exception of Fe, confirming heavy metal pollution in soil along the river banks. As SQTs were not developed to assess the potential ecological effect of heavy metals, [43] sediment quality guidelines (SQGs) were applied to assess the ecological risks caused by heavy metals. SQGs include two thresholds: the threshold effect level (TEL), below which adverse effects on aquatic ecosystems are not expected to occur and the probable effect level (PEL), above which adverse effects are expected to be observed. [44] The mean concentration of As was lower than the TEL, while mean concentrations of Cr, Ni, Pb, and Zn were between the TEL and PEL (Table 4 and Figure 4). Notably, 85% of samples exceeded the PEL for Cd, indicating potential ecological risks in the soil environment.

To provide a detailed assessment of soil pollution in the Shima River catchment, heavy metal concentrations in the study area were compared with those reported at other sites in China (Table 5). Soil As concentrations in Shima River catchment were comparable to those found in the Yangtze Delta, East China. [8] Similar mean values of Cr, Ni, and Pb were found in the Pearl River Delta as well as in other study areas (e.g. Liaoning province, Yangtze Delta and Yellow River).[43,47,49] However, average concentrations of Cu and Zn were significantly higher than those measured at all other sites. The most severe heavy metal pollution was found in Wenling city, PRD and Liaoning city with concentrations of 317 mg·kg^{-1} for Cr, 934 mg·kg^{-1} for Cu, 208 mg·kg^{-1} for Pb, and 2368 mg·kg^{-1} for Zn. [48,49] It is notable that the Cd concentration reported in the present study ranged from 2.00 to 11.2 mg·kg^{-1} with a mean value of 5.84 mg·kg^{-1}, 307-fold higher than that reported in the Yellow River area. [43] The highest concentration of Cd (11.2 mg·kg^{-1}) was comparable to that found in the Nanpan River (11.0 mg·kg^{-1}) near an industrial district. [50]

3.2.2 Distribution of soil heavy metals

As a whole, soil Cd, Cr, Cu, Ni, Pb, Zn, and Mn concentrations were higher at midstream sites than at upstream or downstream sites; this distributional pattern was similar to that of soil SOM and total P content (Table 4 and S2). Furthermore, significantly positive correlations among Cr, Cu, Ni, Pb, Zn and Mn concentrations and between SOM and total P content were identified (p<0.01) (Table 6). It is well known that SOM may act as a major sink for heavy metals including Cd, Cr, Cu, Ni, Pb and Zn due to a strong complexing capacity for metallic contaminants, [13] and that phosphate can reduce Cu, Pb or Zn mobility by ionic exchange and promote the accumulation of heavy metals in soil. [8] Soil As and Fe concentrations exhibited insignificant changes from upstream to downstream sites, and the former correlated with FPC (p<0.05), suggesting that fine particles may be a crucial factor in As distribution.

Distinct reductions in Cu, Ni, Zn and Mn concentrations from profile S3 to S5, as shown in Figure 4, were associated with river water—groundwater interactions, probably a result of transportation of heavy metals by river water into groundwater resulting in accumulation at closer sites (e.g. S3). Simultaneously, the hydraulic effect decreased with increasing distance from the river channel (Figure 2), allowing fewer metals to move further from the site. It was notable that soil Cd, Cr, Ni, Cu and Zn concentrations increased at a depth of 120 cm below the ground at sites S1, S3, S4, and S6, emphasizing the hydraulic relationship between polluted river water and groundwater as the groundwater table ranged from 108 to 150 cm (Table 1). An additional factor may be that the highest SOM and total P contents were found at these sites, with SOM measured as 1.77%, 4.34%, 3.07%, and 2.41% and total P as 1.78%, 2.38%, 2.63%, and 2.25% in S1, S3, S4 and S6 respectively. Decreasing Cr, Cu, Ni and Zn concentrations from top to bottom soil layers were found at S4 and S5, resulting mainly from reduced SOM and total P content.

3.2.3 Source identification of heavy metals

The hierarchical cluster analysis of soil heavy metals revealed three major clusters (Figure 5). Cd, Fe, and Pb were clustered as C1, while Cr, Ni, Cu, Zn, and Mn clustered as C2, and As occurred independently in C3. Although C1 incorporated Cd, Fe, and Pb, these metals likely originated from different sources, because Cd concentrations were 21.3–117-fold higher than the background value and showed insignificant differences across the study area, suggesting a non-point pollution source. The main source of soil Cd in Dongguan City is the application of agrochemicals (e.g., fertilizers and pesticides) in Dongguan city. [51] Mean concentrations of Pb (e.g., 60.0 and 60.8 $mg\cdot kg^{-1}$) exceeding the background value were higher at midstream sites (e.g. S5 and S6) near the roadside, and soil Pb generally stemmed from atmospheric deposition near roads with considerable traffic transportation or near factories. Thus the relative pollution approach for Pb in the PRD area proposed in previous studies was supported, [8, 51] implying that the source was likely terrestrial rather than polluted river water. For cluster C2, correlation analysis also showed a positive correlation ($p<0.01$) among Cr, Cu, Zn, Ni and Mn (Table 6), demonstrating an identical source. In addition, excess Pb, Cd, Zn, Cu, Ni, and Cr were recognized as typically anthropogenic as supported by Han, *et al*. [52]and Rodriguez Martin *et al*. [53] Fe and As concentrations might be geogenic, as their concentrations are close to background values, although they belong to different clusters. Clustered heavy metals probably imply identical sources of statistical similarity; however, a more accurate source identification of soil heavy metals should take the corresponding background and other reference values into consideration.

3.3 Potential risks of heavy metals in environmental media

3.3.1 Acute toxicity of water samples on *Vibrio fischeri*

LUMISTox® toxicity testing with *Vibrio fischeri* was employed to test the ecotoxicity of river water. A decreasing trend in the LIR of river water was consistent with that of heavy metal concentrations in February (Figure 6a and Table 2). The LIR of samples R1–R5, R9 and R10 exceeded the value of 20% which was considered to represent slight acute toxicity, with the most toxic water sample identified at site R1 with a LIR of 38.4%. The LIR of river water was significantly higher ($p<0.01$) in February than in June or November, except at site R7 and R11. A comparable toxic effect was found at R11, with LIR values of 16.8%, 15.6% and 20.1% in February, June and November, respectively. The LIR values of all water samples were higher in November than in June except for in R10. Heavier rainfall in June was the main factor reducing both contamination and LIR on *Vibrio fischeri*. Ecotoxicity of river water roughly followed a decreasing trend in the order of February>November>June.

No groundwater samples had significant toxicity on *Vibrio fischeri* over a 30-min exposure (Figure 6b), as relatively lower concentrations of heavy metals were observed. The LIR of groundwater samples was lower than 20 %; however, Hsieh *et al.* [54] found that the lowest observable effect concentration of Cu and Zn to *Vibrio fischeri* ranged from 6.78–13.6 $\mu g\cdot L^{-1}$ and 10.0–80.4 $\mu g\cdot L^{-1}$, respectively, after a 22-h incubation period. Cu and Zn could apparently exhibit chronic toxic effects to *Vibrio fischeri* even at low levels in groundwater samples (Table 3).

3.3.2 Preliminary identification of toxins in water samples

A significantly positive correlation ($p<0.01$) between the sum of heavy metal concentrations and LIR was identified for all water samples during the three periods (Figure 7), demonstrating an increase in LIR as metal concentrations increased. The EC_{50} of heavy metals to *Vibrio fischeri* have been reported to be 7440–8640 $\mu g\cdot L^{-1}$ for Mn, 22900 $\mu g\cdot L^{-1}$ for Fe, 104–576 $\mu g\cdot L^{-1}$ for Cu, 420–858 $\mu g\cdot L^{-1}$ for Zn and 1600–3640 $\mu g\cdot L^{-1}$ for Ni.[55-58] Sample R1 exhibited the most toxic effect to *Vibrio* *fischeri* having the highest concentration of Zn (494 μg·L^{-1}) and Cu (49.0 μg·L^{-1}) close to the ranges of the corresponding EC_{50} values, while Ni, Mn and Fe concentrations were significantly lower than the corresponding EC_{50} values. EC_{20} values of R1, R3, R4 and R5 decreased from 61.3%, 62.3%, 65.4% and 58.7% to 54.9%, 51.1%, 46.0% and 54.2%, respectively, for 15- and 30-min exposures (Table S3), suggesting that R1, R3, R4 and R5 would not exhibit acute toxicity once diluted 1.82-, 1.96-, 2.17- and 1.85-fold, respectively, after a 30-min exposure. This decreasing trend in EC_{20} was consistent with the toxic mechanism of heavy metals found by Petala *et al.* [59] It could therefore be concluded that Zn and Cu significantly contributed to ecotoxicity. River water (except R1, R3 and R11 in November) did not exhibit significant toxicity to *Vibrio fischeri* associated with the relatively lower concentrations of heavy metals in June and November. Slight acute toxicity of R1, R3 and R11 was partially attributed to interactive effects among different heavy metals. Tsiridis *et al.* [26] reported that interactive effects among Zn, Cu and Pb on *Vibrio fischeri* were synergistic even at low concentration combinations. The accurate identification of toxins requires further study as other explanations for toxic effects on *Vibrio fischeri* include undetected chemicals (e.g., PAHs, PCBs and DDT etc.), especially endocrine-disrupting chemicals, which have been found at elevated levels in the Shima River.[60]

3.3.3 Potential ecological risk of heavy metals in soil along the river bank

A potential ecological risk index was constructed in Håkanson [22] to determine the potential ecological risk posed by hazardous substances.[49] The calculated potential ecological risk of individual metals is summarized in Table S4. Based on the mean E^i_r of metals, the contamination caused by heavy metals decreased in the order: Cd>Cu>Ni>As>Pb>Zn>Cr. The E^i_r of Cd ranged from 894 to 3550, indicating a very high risk to the soil ecosystem, while Cu exhibited low or considerable risk; low risk was also presented by other metals. To quantify the overall potential ecological risk of heavy metals in soil, RI values are presented in Figure 8. Mean values at eight sites ranged from 1791 to 2293, suggesting that all soil samples in the study area pose a high level of ecological risk. It is notable that Cd contributed significantly (95.5%–98.9%) to the potential ecological risk index. According to other reports, [23, 49, 61] Cd is a hazardous element and contributes significantly to ecological toxicity. The similar result obtained in the present study highlights the potential ecological risk caused by Cd.

Conclusions

Industrialization, urbanization and human activities have significantly impacted water and soils in the Shima River catchment area. Severely polluted river water exhibiting high concentrations of heavy metals in the dry season has led to groundwater contamination and imposed significant threats on the drinking water resource area.

Observations of the interactions between river water and groundwater in June revealed heavy metal exchanges between the two water bodies. The long term of exchange of heavy metals has resulted in soil pollution along the river bank. In contrast, the polluted aquifer acts as a pollution source, triggering secondary river water pollution during interactions under conditions of heavy precipitation. Soil Cu, Zn, Ni and Mn originated mainly from polluted river water, and the concentrations of these metals decreased with increasing distance from the river bank. Pb presented an exception to this trend, and concentrations were varied based on a land-source origin rather than river water.

An ecotoxicity assessment concluded that water samples collected from some monitoring sections exerted slight acute toxicity to *Vibrio fischeri* in the dry and wet seasons, with Cu and Zn significantly contributing to ecotoxicity, and groundwater samples exhibiting no acute toxicity. According to the potential ecological risk index, high risk was identified at sites S3, S4, S5, and S6 with the highest contribution from Cd (95.5%–98.9%), strongly suggesting these soils were no longer suitable for agricultural production, and that soil remediation should be implemented immediately. Protection of water and soil resources necessitates agrochemical application control, reduction of industrial wastewater discharge into rivers and the establishment of additional sewage plants in the study area.

Acknowledgements

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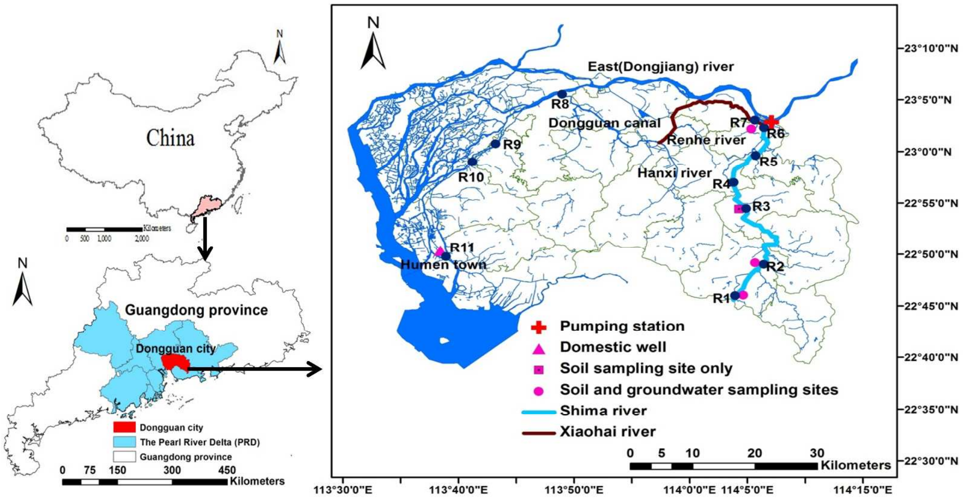

Fig. 1 Sampling sites and distribution of stream net in the study area.

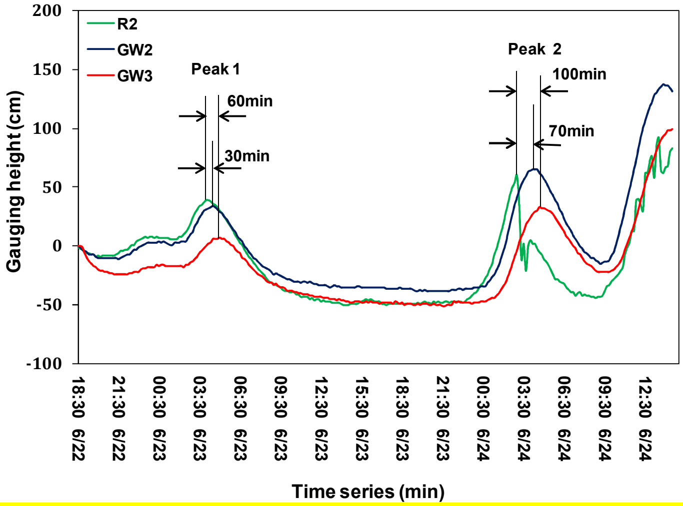

Fig. 2 Delay of groundwater response to river flow fluctuation in Shima river catchment.

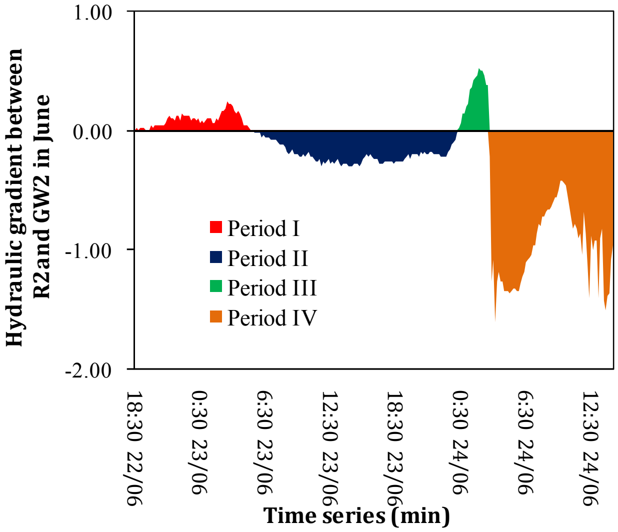

Fig. 3 Hydraulic gradient between river water and groundwater (GW2).

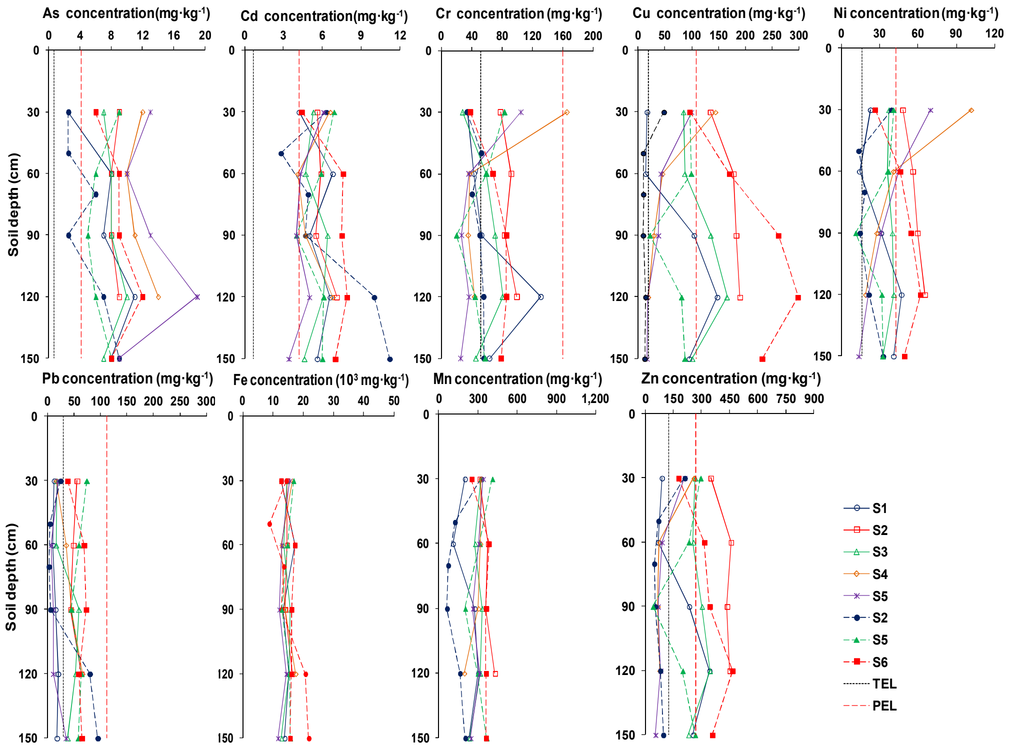

Fig. 4 Vertical distribution of heavy metals in five soil profiles (black dotted line shows the threshold effect level, TEL; red long dash line shows the probable effect level, PEL).

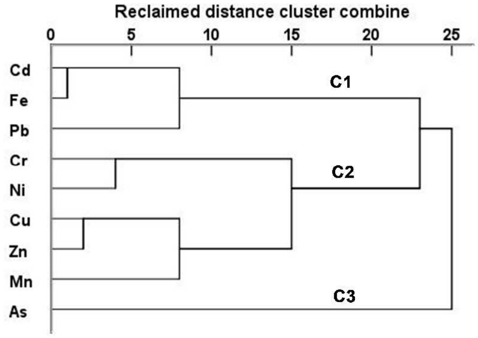

Fig. 5 Dendrogram of heavy metals in soil samples along the river bank.

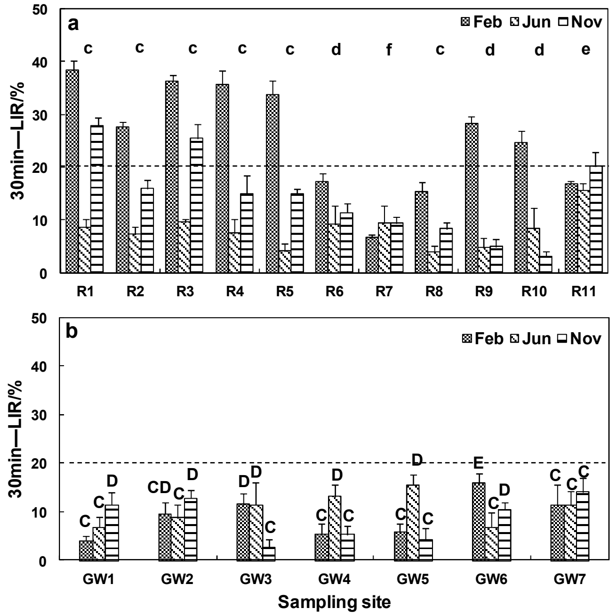

Fig. 6 LIR of water samples after a 30-min exposure in February, June and November (a, Temporal-spatial variation of LIR of river water samples; b, Temporal-spatial variation of LIR of groundwater samples; c, LIR exhibited significant differences at $p<0.01$ in the order February>November>June; d, LIR exhibited significant differences at $p<0.01$ in the order February>November and June, with no significant differences observed between November and June; e, LIR exhibited significant differences at $p<0.01$ in the order November>June, and no significant difference was observed between February and June; f, No significant difference was observed at $p<0.01$; CDE, significant differences of LIR in groundwater among different investigational periods at $p<0.01$).

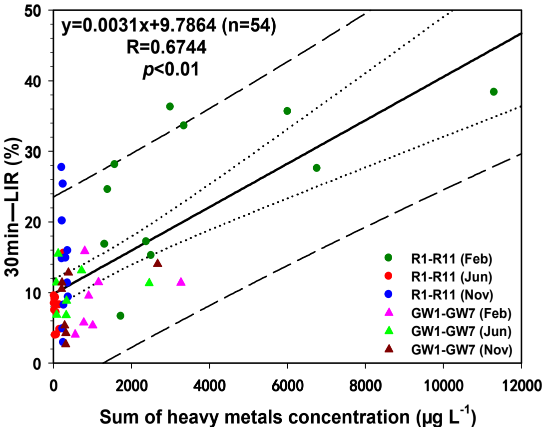

Fig. 7 Fitting relationship between LIR and sum of heavy metal concentrations (LIR, luminescent inhibition rate, %;).

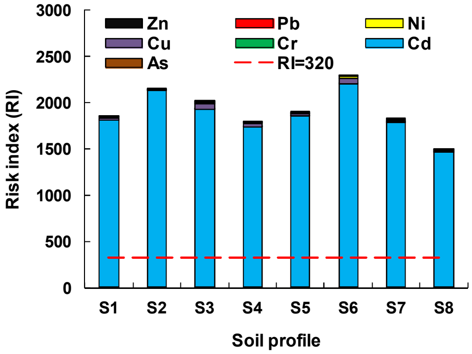

Fig. 8 Potential ecological risk of individual heavy metal and *RI* of soil profiles.

Table 1 Information on groundwater and soil sampling sites

Site	Distance from river bank (m)	Groundwater site[a]	Well depth (cm)	Water depth (cm)	Soil sampling site and depth (cm)	Land-use
R1	1.5	GW1[b]	150	112–150	S1(30, 60, 90, 120 and 150)	Uncultivated land
	6	—[d]	—	—	S2(30, 50,70, 90, 120 and 150)	
R2	0.5	GW2[b]	175	108–128	S3(30, 60, 90 and 120)	Farm land
	1.5	GW3[b]	150	130–150	S4(30, 60, 90, 120 and 150)	
	10	—	—	—	S5(30, 60, 90, 120 and 150)	
R3	5	—	—	—	S6(30, 60, 90, 120 and 150)	Farm land
R7	0.5	GW4[b]	150	118–138	S7(30, 60, 90 and 120)	Forest land
	1.5	GW5[b]	160	120–150	S8(30, 60, 90, 120 and 150)	
R11	100	GW6[c]	1705	431–451	—	Resident area
	120	GW7[c]	1449	422–457	—	

[a] unconfined aquifer, [b] newly built piezometer, [c] Domestic well, [d] data were unavailable

Table 2 Physicochemical parameters of river water samples

Site	pH	T	EC	DO	As	Cd	Cr	Pb	Mn	Ni	Zn	Cu	Fe
		℃	$m\cdot s^{-1}$	$mg\cdot L^{-1}$	$\mu g\cdot L^{-1}$								
February													
R1	7.46	21.0	73.3	1.12	n.d.	n.d.	n.d.	n.d.	748	151	494	49.0	9860
R2	7.26	19.1	31.3	5.60	n.d.	n.d.	n.d.	n.d.	84.0	30.0	85.0	18.0	6550
R3	7.48	22.4	61.2	2.50	n.d.	n.d.	n.d.	n.d.	420	52.0	116	25.0	2390
R4	7.37	21.9	59.1	2.48	n.d.	n.d.	n.d.	n.d.	749	61.0	119	28.0	5050
R5	7.35	22.1	57.8	1.55	n.d.	n.d.	n.d.	n.d.	443	80.0	104	24.0	2700
R6	7.15	21.1	57.2	0.34	n.d.	n.d.	n.d.	n.d.	436	130	247	93.0	1480
R7	7.24	18.4	55.9	1.08	n.d.	n.d.	n.d.	n.d.	394	95.0	88.0	39.0	1120
R8	7.33	17.2	55.3	1.81	n.d.	n.d.	n.d.	n.d.	315	71.0	94.0	39.0	2000
R9	7.41	18.7	53.3	4.60	n.d.	n.d.	n.d.	n.d.	298	72.0	113	n.d.	1100
R10	7.26	19.2	47.9	1.43	n.d.	n.d.	n.d.	n.d.	257	46.0	54.0	n.d.	1040
R11	7.21	20.1	51.9	3.48	n.d.	n.d.	n.d.	n.d.	236	42.0	120	n.d.	922
Mean	7.32	20.1	54.9	2.36	n.a.	n.a.	n.a.	n.a.	398	75.5	149	39.4	3110
Max	7.48	22.4	73.3	5.60	n.a.	n.a.	n.a.	n.a.	749	151	494	93.0	9860
Min	7.15	17.2	31.3	0.34	n.a.	n.a.	n.a.	n.a.	84.0	30.0	54.0	18.0	922
S.D.	0.11	1.71	10.1	1.61	n.a.	n.a.	n.a.	n.a.	203	37.3	124	23.9	2880
C.V. (%)	1.48	9.97	32.4	473	n.a.	n.a.	n.a.	n.a.	241	124	230	133	312
June													
R1	7.54	27.7	21.1	5.31	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12.0	n.d.	10.0
R2	7.48	27.0	50.3	5.75	n.d.	n.d.	n.d.	n.d.	24.0	22.0	24.0	n.d.	8.00
R3	7.41	27.2	26.1	5.58	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	24.0	n.d.	n.d.
R4	7.30	27.5	32.5	5.05	n.d.	n.d.	n.d.	n.d.	n.d.	13.0	21.0	n.d.	n.d.
R5	7.33	29.4	35.2	3.60	n.d.	n.d.	n.d.	n.d.	36.0	14.0	34.0	n.d.	n.d.
R6	7.23	28.3	28.3	3.41	n.d.	n.d.	n.d.	n.d.	n.d.	21.0	14.0	n.d.	n.d.
R7	6.29	28.6	22.1	3.29	n.d.	n.d.	n.d.	n.d.	12	22.0	22.0	n.d.	8.00
R8	6.93	27.9	23.5	2.46	n.d.	n.d.	n.d.	n.d.	13	15.0	11.0	n.d.	8.00
R9	7.10	28.1	28.8	1.88	n.d.	n.d.	n.d.	n.d.	125	14.0	16.0	n.d.	7.00
R10	7.03	28.2	26.8	2.14	n.d.	n.d.	n.d.	n.d.	126	13.0	14.0	n.d.	6.00
R11	7.29	27.6	34.0	2.05	n.d.	n.d.	n.d.	n.d.	160	n.d.	10.0	n.d.	10.0
Mean	7.18	28.0	29.9	3.68	n.a.	n.a.	n.a.	n.a.	70.9	16.8	18.36	n.a.	8.14
Max	7.54	29.4	50.3	5.75	n.a.	n.a.	n.a.	n.a.	160	22.0	34.0	n.a.	10.0
Min	6.29	27.0	21.1	1.88	n.a.	n.a.	n.a.	n.a.	12.0	13.0	10.0	n.a.	6.00
S.D.	0.35	0.68	8.22	1.50	n.a.	n.a.	n.a.	n.a.	63.4	4.13	7.32	n.a.	1.46
C.V. (%)	5.52	2.51	38.9	79.6	n.a.	n.a.	n.a.	n.a.	529	31.8	73.3	n.a.	24.4
November													
R1	7.23	27.1	59.5	3.68	n.d.	n.d.	n.d.	n.d.	127	58.0	21.0	n.d.	14.0
R2	7.4	26.4	56.9	1.41	n.d.	n.d.	n.d.	n.d.	268	55.0	13.0	n.d.	35.0
R3	7.04	24.4	52.5	2.04	n.d.	n.d.	n.d.	n.d.	168	51.0	12.0	n.d.	24.0
R4	7.12	23.9	55.2	3.02	n.d.	n.d.	n.d.	n.d.	146	40.0	12.0	n.d.	24.0
R5	7.11	23.5	51.9	4.54	n.d.	n.d.	n.d.	n.d.	239	45.0	16.0	n.d.	21.0
R6	7.07	24.1	49.8	4.03	n.d.	n.d.	n.d.	n.d.	303	42.0	11.0	n.d.	14.0
R7	7.04	23.9	23.8	4.15	n.d.	n.d.	n.d.	n.d.	322	42.0	10.0	n.d.	13.0
R8	7.35	23.5	45.9	3.38	n.d.	n.d.	n.d.	n.d.	199	43.0	15.0	n.d.	17.0
R9	7.37	23.5	45.9	4.03	n.d.	n.d.	n.d.	n.d.	183	41.0	9.00	n.d.	11.0
R10	7.23	23.5	44.5	3.03	n.d.	n.d.	n.d.	n.d.	196	42.0	7.00	n.d.	15.0
R11	7.20	23.7	48.2	2.18	n.d.	n.d.	n.d.	n.d.	177	28.0	10.0	n.d.	16.0
Mean	7.20	24.3	48.6	3.23	n.a.	n.a.	n.a.	n.a.	212	44.3	12.4	n.a.	18.6
Max	7.40	27.1	59.5	4.54	n.a.	n.a.	n.a.	n.a.	322	58.0	21.0	n.a.	35.0
Min	7.04	23.5	23.8	1.41	n.a.	n.a.	n.a.	n.a.	127	28.0	7.00	n.a.	11.0
S.D.	0.13	1.25	9.52	1.00	n.a.	n.a.	n.a.	n.a.	63.4	8.13	3.85	n.a.	6.98
C.V. (%)	1.88	5.30	40.0	70.9	n.a.	n.a.	n.a.	n.a.	50.0	29.0	55.1	n.a.	63.4
WHO[a]	6.5-8.5	n.i.	n.i.	n.i.	10	3	50	10	100	70	3000	1000	-
MEPC[b]	6-9	n.i.	n.i.	6	50	1	10	10	100	n.i.	50	10	300
MEPC[c]	6-9	n.i.	n.i.	2	100	10	100	100	n.i.	n.i.	2000	1000	n.i.

n.d.- not dected; n.i.-not issued; n.a.-not available; S.D. – standard deviation; C.V. – coefficient of variation.

a- Drinking water quality guideline of World Health Organization (WHO), 2011;

b and c- Environmental quality standard (Class I and V) for surface water of China, 2002;

Table 3 Physicochemical parameters of groundwater samples

Site	pH	T	EC	DO	As	Cd	Cr	Pb	Mn	Ni	Zn	Cu	Fe
		℃	m·s^{-1}	mg·L^{-1}	μg·L^{-1}								
February													
GW1	7.26	20.3	51.6	1.98	n.d.	n.d.	n.d.	n.d.	159	27.0	13.3	n.d	363
GW2	7.08	18.9	92.2	3.12	n.d.	n.d.	n.d.	n.d.	202	51.9	38.0	n.d	615
GW3	6.91	18.6	50.7	2.86	n.d.	n.d.	n.d.	n.d.	295	91.3	62.7	21.0	686
GW4	6.80	18.3	50.8	2.06	n.d.	n.d.	n.d.	n.d.	800	67.0	41.1	n.d	102
GW5	7.34	19.0	54.8	3.36	n.d.	n.d.	n.d.	n.d.	378	69.0	35.2	n.d	298
GW6	5.07	20.4	60.3	5.68	n.d.	n.d.	n.d.	n.d.	531	27.0	71.0	n.d	174
GW7	5.19	19.9	16.57	5.39	n.d.	n.d.	n.d.	n.d.	510	22.0	161	20.0	2560
Mean	6.52	19.3	53.9	3.49	n.a.	n.a.	n.a.	n.a.	411	50.7	60.3	20.5	685
Max	7.34	20.4	92.2	5.68	n.a.	n.a.	n.a.	n.a.	800	91.3	161	21.0	2560
Min	5.07	18.3	16.6	1.98	n.a.	n.a.	n.a.	n.a.	159	22.0	13.3	20.0	102
S.D.	0.97	0.85	22.1	1.49	n.a.	n.a.	n.a.	n.a.	223	26.5	48.3	0.71	854
C.V.(%)	19.1	4.62	133	75.1	n.a.	n.a.	n.a.	n.a.	140	120	363	3.54	837
June													
GW1	6.75	27.6	76.0	3.67	n.d.	n.d.	n.d.	n.d.	28.0	27.0	n.d.	n.d.	20.0
GW2	7.21	28.3	55.4	2.94	n.d.	n.d.	n.d.	n.d.	42.0	64.0	196	36.0	n.d.
GW3	7.16	27.9	70.5	3.06	n.d.	n.d.	n.d.	n.d.	14.0	18.0	37.0	10.0	n.d.
GW4	6.67	28.7	29.1	2.40	n.d.	n.d.	n.d.	n.d.	68.0	16.0	19.0	n.d.	6.00
GW5	6.29	28.3	22.1	2.13	n.d.	n.d.	n.d.	n.d.	50.0	24.0	34.0	n.d.	16.0
GW6	7.25	27.1	17.0	6.56	n.d.	n.d.	n.d.	n.d.	17.0	n.d.	8.00	n.d.	56.0
GW7	5.40	24.7	14.6	4.57	n.d.	n.d.	n.d.	n.d.	522	14.0	55.0	n.d.	1870
Mean	6.68	27.5	40.7	3.62	n.a.	n.a.	n.a.	n.a.	106	27.2	58.2	23.0	394
Max	7.25	28.7	76.0	6.56	n.a.	n.a.	n.a.	n.a.	522	64.0	196	36.0	1870
Min	5.40	24.7	14.6	2.13	n.a.	n.a.	n.a.	n.a.	14.0	14.0	8.00	10.0	6.00
S.D.	0.66	1.35	26.1	1.53	n.a.	n.a.	n.a.	n.a.	184	18.7	69.4	18.4	826
C.V.(%)	12.3	5.45	178	71.8	n.a.	n.a.	n.a.	n.a.	1318	134	868	184	13800
November													
GW1	6.46	28.6	66.7	6.99	n.d.	n.d.	n.d.	n.d.	206	n.d.	14.0	n.d.	n.d.
GW2	7.90	26.0	60.2	3.80	n.d.	n.d.	n.d.	n.d.	124	45.0	9.00	n.d.	208
GW3	7.60	25.6	49.0	2.59	n.d.	n.d.	n.d.	n.d.	168	n.d.	37.0	n.d.	113
GW4	7.61	25.2	30.7	6.80	n.d.	n.d.	n.d.	n.d.	200	43.0	29.0	n.d.	19.0
GW5	7.28	24.9	28.7	2.60	n.d.	n.d.	n.d.	n.d.	207	55.0	62.0	n.d.	n.d.
GW6	6.45	24.3	35.4	4.95	n.d.	n.d.	n.d.	n.d.	100	n.d.	11.0	n.d.	101
GW7	4.86	24.3	18.7	4.71	n.d.	n.d.	n.d.	n.d.	620	20.0	63.0	n.d.	1970
Mean	6.88	25.6	41.4	4.63	n.a.	n.a.	n.a.	n.a.	232	40.8	32.1	n.a.	482
Max	7.90	28.6	66.7	6.99	n.a.	n.a.	n.a.	n.a.	620	55.0	63.0	n.a.	1970
Min	4.86	24.3	18.7	2.59	n.a.	n.a.	n.a.	n.a.	100	20.0	9.0	n.a.	19.0
S.D.	1.06	1.48	17.7	1.80	n.a.	n.a.	n.a.	n.a.	176	14.8	23.1	n.a.	834
C.V.(%)	21.7	6.10	94.6	69.4	n.a.	n.a.	n.a.	n.a.	176	74.0	256	n.a.	4390
WHO[a]	6.5-8.5	n.i.	n.i.	n.i.	10	3	50	10	100	70.0	100	2000	300
MEP[b]	6-9	n.i	n.i	n.i	5	0.1	5	5	50	5	50.0	10.0	100
MEP[c]	<5.5 or >9	n.i	n.i	n.i	50	10	100	100	1000	100	5000	1500	1500

n.d.- not dected; n.i.-not issued; n.a.-not available; S.D. – standard deviation; C.V. – coefficient of variation.

a- Drinking water quality guideline of World Health Organization (WHO), 2011;

b and c- Quality standard for groundwater (Class I and V) of China, 1993;

Table 4 Statistical summary of heavy metal concentrations in different soil profiles along Shima River, background, TEL, and PEL values (mg·kg^{-1})

Site	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe (·10^3)	Mn
S1(*n*=5)	7.30a 2.50–11.0	5.60a 4.20–6.80	65.0a 34.8–131	76.0ab 14.5–148	31.3a 14.4–47.2	15.2A 10.0–20.0	197.8AB 68.8–343	14.5a 12.7–17.2	223ab 108–301
S2(*n*=6)	4.90a 2.50–9.00	6.70a 2.80–11.2	48.4a 34.1–56.1	17.6a 9.7–48.6	23.4a 13.7–39.3	35.7AB 3.00–95.0	93.1A 47.9–211	15.3a 8.80–21.8	157a 62.2–323
S3(*n*=4)	8.50a 8.00–9.00	6.03a 5.50–7.10	88.2a 77.9–99.4	172cd 135–190	57.4b 48.2–65.5	53.3AB 44.0–64.0	423C 349–457	15.0a 14.1–16.4	369c 312–430
S4(*n*=5)	8.00a 7.00–10.00	5.40a 4.60–6.40	56.9a 28.1–80.5	114.8bc 84.7–166	37.5ab 32.6–41.1	36.8AB 16.0–59.0	279BC 230–344	14.4a 12.8–15.7	296bc 235–330
S5(*n*=5)	6.80a 5.00–9.00	5.80a 4.00–6.90	53.0a 20.3–83.1	77.3ab 22.2–99.2	30.7a 11.4–40.9	60.0B 45.0–74.0	206AB 40.4–295	15.1a 12.8–16.8	318ab 201–409
S6(*n*=5)	8.80a 6.00–12.0	6.90a 4.40–7.90	71.3a 38.2–85.8	212d 96.6–298	47.8ab 26.5–62.0	60.8B 38.0–73.0	331BC 177–465	15.6a 12.7–17.2	343b 250–383
S7(*n*=4)	11.8a 10.0–14.0	5.55a 4.10–6.80	70.5a 35.5–165	59.6ab 19.0–144.2	47.4ab 19.1–102	40.8AB 17.0–66.0	119A 65.9–259	15.2a 12.8–17.5	284bc 194–322
S8(*n*=5)	12.8a 9.00–19.0	4.60a 3.40–6.40	45.9a 25.5–105	42.9a 16.8–99.9	36.0ab 13.9–69.7	16.8A 7.00–35.0	101A 54.6–210	13.3a 11.6–15.6	292bc 245–340
SQTs[a]	25.0	0.30	300	100	50.0	300	250	—	—
BVs[b]	13.52	0.094	56.53	17.65	17.8	35.87	49.71	24.2	279
TEL[c]	7.24	0.68	52.3	18.7	15.9	30.2	124	—	—
PEL[d]	41.6	4.21	160	108	42.8	112	271	—	—

Data expression: mean (minimum–maximum);

abc exhibited significant differences at $p<0.05$;

ABC exhibited significant differences at $p<0.01$;

a- Environmental quality standard for soil of China (6.5<pH<7.5), 1995;

b- Environmental background value for soil of Guangdong province, 1990;

c,d- (MacDonald, 1994; Esen et al., 2010)

Table 5 Comparison of heavy metal concentrations in soil between the Shima River catchment and other sites in China. Concentrations are reported in mg·kg^{-1} for all heavy metals

Region	As	Cd	Cr	Cu	Ni	Pb	Zn	Reference
Shima River, South China	8.44[a] 2.50–19.0[b]	5.84 2.00–11.2	61.2 20.3–165	93.5 9.70–298	37.9 11.4–102	39.44 3.00–95.0	213 40.4–465	Present study
Wanqingsha, Pearl River Estuary	N.A.	1.18–2.43	91.4–125	47.4–321	41.2–61.6	32.2–51.3	127–240	8
Pearl River Delta, South China	N.A.	0.58 n.d. –1.47	71.4 14.8–317	33.0 4.10–189	21.2 3.08–62.5	40.0 10.1–180	84.7 11.1–284	2
Xuzhou city, East China	N.A.	0.71 0.53–1.19	N.A.	68.0 56.0–110	N.A.	55.0 43.0–67.0	209 165–338	46
Yangtze Delta, East China	8.55 4.07–12.5	0.221 0.078–1.26	87.8 55.7–125	32.4 16.6–61.7	36.4 23.2–51.0	33.9 16.6–49.4	94.9 53.8–188	47
Wenling, East China	N.A.	0.316 0.080–5.29	N.A.	47.3 13.7–934	31.7 5.93–165	N.A.	131 68.7–650	48
Liaoning, Northeast China	N.A.	0.86 0.27–1.87	69.9 22.9–155	52.3 11.0–514	33.5 13.5–49.6	45.1 14.6–208	213 38.1–2368	49
Yellow River, Northwest China	N.A.	0.019 0.011–0.037	74.4 66.1–89.5	1.72 1.25–2.39	26.0 23.8–27.8	17.8 13.9–21.9	53.1 37.2–72.0	43
Nanpan River, Southwest China	N.A.	2.38 0.89–11.0	N.A.	40.2 22.1–68.4	N.A.	47.0 22.0–183	157 65.7–766	50

a average concentration of heavy metals
b range of heavy metals concentration
N.A. not available

Table 6 Correlation between heavy metal concentrations and soil properties

	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Mn
As	1								
Cd	0.186	1							
Cr	0.270	0.405*	1						
Cu	0.177	0.323*	**0.646****	1					
Ni	0.326*	0.316	**0.829****	**0.719****	1				
Pb	0.086	**0.696****	0.177	0.391*	0.162	1			
Zn	0.096	0.327*	**0.663****	**0.915****	**0.708****	0.375*	1		
Fe	0.281	**0.959****	0.343*	0.198	0.261	**0.682****	0.225	1	
Mn	0.375*	0.200	**0.443****	**0.697****	**0.688****	**0.417****	**0.739****	0.188	1
pH	-0.298	-0.175	-0.436**	-0.573**	-0.626**	-0.085	-0.478**	-0.107	-0.541**
EC	-0.173	0.106	0.281	0.368*	0.299	0.337*	0.601**	0.092	0.449**
FPC	**0.418****	0.063	0.312	0.206	0.270	0.122	0.226	0.081	0.296
SOM	0.052	0.090	**0.546****	**0.706****	**0.654****	0.228	**0.876****	0.068	**0.692****
Total P	0.057	0.304	**0.578****	**0.798****	**0.637****	**0.338***	**0.887****	0.232	**0.670****

* and ** represents significant correlation at the level of $p<0.05$ and $p<0.01$(two-tailed), respectively. FPC, fine particle component (<63μm)