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# Contamination, toxicity and speciation of heavy metals in an industrialized urban river: Implications for the dispersal of heavy metals

Qihang Wu [a,b,c], Haichao Zhou [c], Nora F.Y. Tam [c], Yu Tian [c], Yang Tan [c], Song Zhou [d], Qing Li [d], Yongheng Chen [a,b,*], Jonathan Y.S. Leung [e,**]

[a] Collaborative Innovation Center of Water Quality Safety and Protection in Pearl River Delta, Guangzhou University, Guangzhou 510006, China
[b] Key Laboratory of Water Quality Safety and Protection in Pearl River Delta (Ministry of Education), Guangzhou University, Guangzhou 510006, China
[c] Department of Biology and Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China
[d] School of Civil Engineering, Guangzhou University, Guangzhou 510006, China
[e] School of Biological Sciences, The University of Adelaide, Adelaide, South Australia, Australia

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ABSTRACT

Urban rivers are often utilized by the local residents as water source, but they can be polluted by heavy metals due to industrialization. Here, the concentrations, toxicity, speciation and vertical profiles of heavy metals in sediment were examined to evaluate their impact, dispersal and temporal variation in Dongbao River. Results showed that the sediment in the industrialized areas was seriously contaminated with Cr, Cu and Ni which posed acute toxicity. Heavy metals, except Cr and Pb, were mainly associated with non-residual fractions, indicating their high mobility and bioavailability. The non-industrialized areas were also seriously contaminated, suggesting the dispersal of heavy metals along the river. The surface sediment could be more contaminated than the deep sediment, indicating the recent pollution events. Overall, when the point sources are not properly regulated, intense industrialization can cause both serious contamination and dispersal of heavy metals, which have far-reaching consequences in public health and environment.



## 1. Introduction

Despite the advance in sewage treatment technologies, water pollution caused by sewage discharge has still been a serious problem in many developing countries due to the high operating cost of sewage treatment facilities as well as lack of effective management and enforcement (e.g. Singh et al., 2002; Ikenaka et al., 2010; Louhi et al., 2012; Chen et al., 2015). Therefore, regular monitoring is indispensable to evaluate the impact of pollutants on public health and environment. Among various pollutants, heavy metals are of special concern because of their toxicity, persistence and bioavailability (Montouris et al., 2002). In the aquatic environment, heavy metals can readily accumulate in sediment through adsorption, and thus sediment *per se* is a good monitoring tool for heavy metals (Soares et al., 1999). Nevertheless, solely measuring the total concentration of heavy metals in sediment is still insufficient to accurately evaluate their impact because they can be released from the sediment to the water column upon disturbance or alteration in the physico-chemical conditions (de Miguel et al., 2005). The remobilized heavy metals are subsequently dispersed by water current and potentially contaminate the pristine areas, such as estuaries and wetlands (Williams et al., 1994; Li et al., 2007; Bai et al., 2011; Wu et al., 2016). In addition, the mobility, toxicity and bioavailability of heavy metals depend on the physico-chemical form rather than total concentration (Tack and Verloo, 1995). As such, studying the speciation of heavy metals is crucial to fathom their behavior and biological risk in sediment.

Compared to other developing countries, China suffers the most from water pollution due to rapid economic growth and intense industrialization. In particular, the Pearl River Delta is one of the most urbanized and industrialized regions, accounting for more than 10% of the National Gross Domestic Product (National Bureau of Statistics of China, http://data.stats.gov.cn). The intense industrialization inevitably leads to heavy metal pollution in this region primarily due to sewage discharge from the factories (e.g. metal and electronics industries) (Cheung et al., 2003; Liu et al., 2011; Ye et al., 2012; Wu et al., 2014). To date, heavy metal pollution in the Pearl River Estuary has been well-studied (Wang et al., 2013), while substantially overlooked is heavy metal pollution in urban rivers. As the Pearl River Estuary is connected to numerous urban rivers, studying heavy metal pollution in these urban rivers can provide vital information for identifying the pollution sources in this region. More importantly, as urban rivers are often utilized, either purposely or accidentally, by local residents as

* Correspondence to: Y. Chen, Collaborative Innovation Center of Water Quality Safety and Protection in Pearl River Delta, Guangzhou University, Guangzhou 510006, China.
** Corresponding author.
*E-mail addresses:* chenyongheng2008@163.com (Y. Chen), jonathan_0919@hotmail.com (J.Y.S. Leung).

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water source, noxious effects on human health could be incurred due to heavy metal pollution (e.g. Singh et al., 2002; Islam et al., 2015). Furthermore, physico-chemical properties and hydrological conditions in riverine sediment are more prone to drastic changes than those in marine sediment owing to human disturbance; therefore, the impact of remobilization and dispersal of heavy metals cannot be overlooked.

Here, we chose Dongbao River in Shenzhen (commonly known as Maozhou River or Black River by the local residents) as the model site to illustrate the impact and dispersal of heavy metals. From the early 1980s to 1990s, Shenzhen was urbanized and industrialized rapidly, and has become the first Special Economic Zone in China. Industrialization is extremely intense in the catchment area of Dongbao River, where more than 7000 factories from metal and electronics industries can be found. As most of the factories are primitive and the sewage is discharged without proper treatment, Dongbao River is regarded as one of the most polluted urban rivers in China. To mitigate this problem, the Shenzhen government has amended the regulations and made more inspections in recent years, but the effectiveness of these measures remains unknown. In the present study, the concentrations and speciation of heavy metals in the surface sediment along the river were determined to elucidate their toxicity, biological risk and dispersal. Their correlation with sediment properties, including pH, total organic matter and particle size was also studied. Furthermore, the vertical profiles of heavy metals were examined to estimate the effectiveness of the mitigation measures taken by the Shenzhen government. The findings are not only vital for protecting public health and environment in this region, but also valuable to understand the impact and behavior of heavy metals due to intense industrialization.

## 2. Materials and methods

### 2.1. Study site and sampling method

Dongbao River (22°46′N, 113°47′E), which is connected to the Pearl River Estuary, was selected as the study site. Based on our observation, factories mainly from metal and electronics industries were ubiquitous on both flanks of the river. The water in the river was dark and stinky, and the flow rate was low. Sewage discharged from the drainage pipes was commonly observed. Sampling was conducted in December 2013 during low tide. A total of seven sampling points along the river were chosen: (1–4) Points A–D located in the industrialized area; (5) confluence; (6) outlet where a mangrove is found; (7) mudflat located at the lower intertidal of the mangrove (Fig. 1). At each sampling point, three random replicates of surface sediment (ca. 8 cm from the top) were collected by a spade. To study the vertical profile, three random replicates of core sediment were collected by a PVC core sampler (10 cm in diameter × 48 cm deep) at Point A, Point C, confluence and outlet. The sediment sample in each core was cut into six layers from the top at 8 cm depth interval by a PVC knife.

### 2.2. Analyses of sediment properties and heavy metals

The sediment samples were freeze-dried, ground into powder and passed through a 2 mm sieve, after measuring the particle size using a particle size analyzer (S3500, Microtrac, USA). For pH, the sediment sample was mixed with deionized water (1:5, w/v), followed by measuring the pH of the mixture using a pH meter (pH 3000, STEP Systems, Germany). Total organic matter (TOM) was determined by mass loss upon ignition at 550 °C for 6 h. To extract heavy metals, ca. 0.3 g sediment was digested by a mixture of concentrated hydrochloric acid and nitric acid (3:1, v/v) using automatic digestion block (ST40, Beijing Polytech Instrument Ltd., China). The concentrations of heavy metals in the extract, including chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), were determined by inductively coupled plasma-optima emission spectrometry (Optima 5300DV, Perkin-Elmer Instruments, USA), while cadmium (Cd) by atomic absorption spectrometer (AAnalyst 800, Perkin-Elmer Instruments, USA). To estimate the accuracy of this method, a certified reference material from the State Oceanic Administration of China (GBW 07334) was used for recovery test. The recoveries for all heavy metals ranged from 89.6 to 98.5% (RSD: 5.65–8.53%).

### 2.3. Sequential extraction of heavy metals

The method proposed by Rauret et al. (1999) with minor modifications was applied for the three-step sequential extraction of heavy metals, which is summarized as follows:

(1) Acid soluble fraction: Approximately 0.5 g freeze-dried sediment was transferred into a 50 ml polyethylene centrifuge tube, followed by adding 20 ml 0.11 M acetic acid for extraction. The mixture was then sonicated for 30 min.
(2) Reducible fraction: Heavy metals in the residue after the first step were extracted by 20 ml 0.5 M hydroxylamine hydrochloride, followed by 30 min sonication.
(3) Oxidizable fraction: The residue after the second step was digested by 5 ml 30% hydrogen peroxide (pH 2.2) at room temperature for 1 h. The centrifuge tube was stoppered and shaken occasionally. Then, another 5 ml 30% hydrogen peroxide was added to the centrifuge tube which was then heated up to 85 °C with occasional shaking for 1 h. After cooling at room temperature, heavy metals in the residue were extracted by 25 ml 1.0 M ammonium acetate (pH 2.0), followed by 30 min sonication.
(4) Residual fraction: Heavy metal concentrations in the residue after the third step were measured using the method described in Section 2.2.
Between each extraction step, the supernatant used for heavy metal analysis was separated from the solid residue by centrifugation at 3500 rpm for 15 min. The residue was then rinsed with 10 ml deionized water twice and shaken for 15 min, followed by centrifugation at 3500 rpm for 15 min so that the supernatant was discarded.

### 2.4. Statistical analyses

Toxic unit (TU), defined as the ratio of heavy metal concentration to probable effects level (PEL), was calculated to evaluate the toxicity of each heavy metal (Pedersen et al., 1998). The potential acute toxicity of heavy metals was estimated by the sum of individual TU. Permutational analysis of variance (PERMANOVA), followed by a pairwise test, was applied to determine the spatial variation in sediment properties and heavy metals using software PRIMER 6.0 with PERMANOVA + add-on. Pearson correlation analysis was applied to correlate heavy metals with sediment properties using software SPSS 20.0 for Windows.

## 3. Results

### 3.1. Sediment properties and concentrations of heavy metals

The pH of sediment ranged from 6.90 to 7.40, except Point A (5.97) and Point B (6.16) at which the sediment was slightly acidic (Table 1). Total organic matter was generally low at all sampling points, ranging from 0.87% to 1.87%. Significantly higher TOM was found at Points A, B and C than that at other sampling points. The sediment was generally sandy in the region, except Point D at which the sediment was relatively silty.

Compared to the guideline values in China (GB 18668-2002), heavy metal pollution was very severe in Dongbao River (Table 2). At all sampling points, the concentration of Cd (0.61–1.33 mg $kg^{-1}$) exceeded the Grade I guideline value which aims to protect mariculture and marine protected areas. The concentrations of Cr (350–