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Distribution and source analysis of heavy metal pollutants in sediments of a rapid developing urban river system

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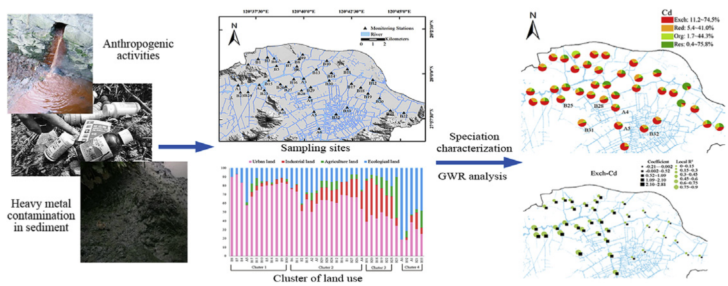
HIGHLIGHTS

- Sediments in Wenrui Tang River were seriously contaminated with heavy metals.
- Some heavy metals possibly derived from similar pollution source.
- Correlation of the heavy metal speciation with land use type was analyzed.
- GWR showed heavy metal pollution mainly associated with industrial activities.

GRAPHICAL ABSTRACT



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ABSTRACT

Heavy metal pollution of aquatic environments in rapidly developing industrial regions is of considerable global concern due to its potential to cause serious harm to aquatic ecosystems and human health. This study assessed heavy metal contamination of sediments in a highly industrialized urban watershed of eastern China containing several historically unregulated manufacturing enterprises. Total concentrations and solid-phase fractionation of Cu, Zn, Pb, Cr and Cd were investigated for 39 river sediments using multivariate statistical analysis and geographically weighted regression (GWR) methods to quantitatively examine the relationship between land use and heavy metal pollution at the watershed scale. Results showed distinct spatial patterns of heavy metal contamination within the watershed, such as higher concentrations of Zn, Pb and Cd in the southwest and higher Cu concentration in the east, indicating links to specific pollution sources within the watershed. Correlation and PCA analyses revealed that Zn, Pb and Cd were dominantly contributed by anthropogenic activities; Cu originated from both industrial and agricultural sources; and Cr has been altered by recent pollution control strategies. The GWR model indicated that several heavy metal fractions were strongly correlated with industrial land proportion and this correlation varied with the level of industrialization as demonstrated by variations in

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local GWR R^2 values. This study provides important information for assessing heavy metal contaminated areas, identifying heavy metal pollutant sources, and developing regional-scale remediation strategies.

1. Introduction

Heavy metal pollution in aquatic environments has the potential to cause serious aquatic ecosystem and human health impairments (Chowdhury et al., 2016). Metals dissolved in natural waters are easily absorbed by aquatic organisms and can rapidly bioaccumulate/biomagnify within the aquatic food web. Chronic metal exposure in aquatic ecosystems may adversely affect the activity, growth, metabolism, and reproduction of aquatic organisms (Wright and Welbourn, 2002). Long-term exposure to heavy metals by humans has been implicated in causing intellectual and developmental disabilities, behavioral problems, hearing loss, learning and attention problems, disruption of visual and motor function, and various cancers (Sarkar, 2009; Lanphear et al., 2005; Adams et al., 2014). A significant source of heavy metals in the human diet may originate from higher trophic level aquatic organisms (e.g., predatory fish) providing a linkage between aquatic food webs and human health. Further, interactions associated with chronic exposure to multiple heavy metals may induce more severe ecosystem and human health consequences than might be expected from low individual metal concentrations alone. Thus, it is important to fully assess the suite of heavy metals as well as their solid-phase fractionation to fully assess the toxicological risks associated with heavy metals in the environment.

The adverse impact of heavy metal pollution on aquatic ecosystems is especially severe in areas experiencing rapid urbanization and industrialization (Pan and Wang, 2012). Sediments can either release metals directly to the water column or serve as the source of metals for bioaccumulation/biomagnification in aquatic organisms, such as benthic fauna, shrimp and fish (Goretti et al., 2016). Anthropogenic activities are the primary contributor of heavy metal pollutants to sediments and soil (Wong et al., 2017) and therefore heavy metal pollution is strongly linked to land use (Li et al., 2017a, b). For example, heavy metals become enriched in paddy fields due to chemical fertilizers, animal wastes, atmospheric deposition and wastewater discharge (Chen et al., 2012; Li et al., 2017a, b). Pollutants discharged into receiving waters directly or carried by runoff will finally accumulate in aquatic sediments. Therefore, investigating the distribution and speciation of metals from contrasting land uses may provide unique chemical signatures in aquatic sediments that in turn provide a scientific basis to assess the pollutant source and their potential ecological and human health risks. The assessment of potential metal risks depends not only on total metal concentrations, but also on their chemical forms (i.e., speciation) influencing bioaccessibility and bioavailability (Simpson et al., 2012). For example, the exchangeable and weak acid extractable fractions are considered as the most mobile and bioavailable metal fractions (Tessier et al., 1979; Pueyo et al., 2008). Sediment characteristics (e.g., organic matter, redox status and pH) have a strong effect on distribution of metal fractions and their bioavailability, such as the positive correlation observed between organic matter and the oxidizable fraction of Cu and Pb in Tasik Chini, Malaysia (Ebrahimpour and Mushrifah, 2008). Thus, multi-step sequential extraction schemes have been used to estimate the bioavailability of metals in sediments and their potential risk to aquatic ecosystems and humans (Sakan et al., 2016).

Spatial analysis provides an advantage of understanding the variation of several impact factors on heavy metal pollution and generally involves the analysis of relationships among impact factors from a given geographic location. However, the relationship or structure of the variables will change within a watershed, the so called "spatial non-stationarity" condition (McMillen, 2004). Traditional regression models, such as ordinary least squares models (OLS model), assume a stable relationship between the independent and dependent variables throughout the study area, resulting in a uniform regression coefficient for the entire study region and failure to consider any variation of spatial characteristics (Williams et al., 2005).

Geographically weighted regression (GWR) was developed to overcome these disadvantages of traditional regression models. GWR is efficient for handling the spatial variation in the relationship between variables. In GWR models, the site location is considered in the regression equation to build the relationship between the independent and dependent variables when non-stationarity of spatial relationships exists (Fotheringham et al., 2002). This sssroach has been widely employed in water pollution management and aides in contamination prediction and risk assessment. For example, GWR was used for spatial prediction of trace metal concentrations in surface and ground waters based on spatial predictors in Pakistan, and the associated health risks of these waters were estimated according to the predicted spatial metal concentrations (Bhowmik et al., 2015). Similarly, Tu, 2013 demonstrated improvement of GWR models for predicting the influence of land use on water quality at the watershed scale in Northern Georgia compared to least squares regression. Additionally, Wu et al. (2016) applied GWR to identify the spatially varying relationship between land-use types and total heavy metal concentrations in sediment, but did not assess the relationship with heavy metal speciation. Thus, there is a research gap in studies using GWR methods to coupling land-use types with speciation of heavy metals in sediments, which is fundamental knowledge required for remediation and mitigation of heavy metal pollutants at the watershed scale. Therefore, this paper is novel in utilizing GWR to assess relationships between land-use types and heavy metal concentrations and their corresponding chemical fractionation, with the consideration of their spatial variation.

Given the importance of aquatic ecosystem protection and the negative impacts of heavy metal pollution on human health, new spatial analysis tools are highly warranted, especially in rapidly developing regions with a large number of industrial enterprises involving heavy metals. The main purposes of this study were to (i) assess heavy metal contamination of sediments in a highly polluted river systems affected by rapid industrialization, (ii) identify spatial distribution of total metal concentrations and solid-phase metal fractions at the watershed scale, and (iii) combine GWR with traditional multivariate statistical analysis to investigate variation in relationships between anthropogenic activities and heavy metals in river sediments. This study provides a framework for spatial assessment of metal pollution sources and information to guide remediation at the watershed scale. Further, this study highlights the power of incorporating GWR models in sediment pollution assessments and its potential for widespread use in studies of environmental pollution.