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# Anthropogenic impact on diffuse trace metal accumulation in river sediments from agricultural reclamation areas with geochemical and isotopic approaches

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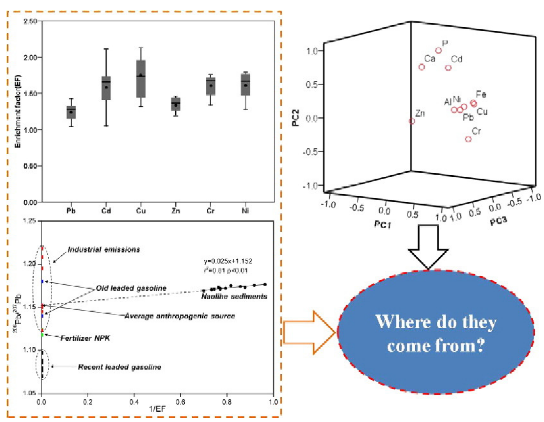
## HIGHLIGHTS

- Trace metals have accumulated in the Naolihe sediments.
- Natural weathering was still a major contributor to metal accumulation.
- Anthropogenic Pb, Cu, Cr and Ni mostly came from atmospheric deposition.
- Local fertilizer application was the main anthropogenic source of Cd.

## GRAPHICAL ABSTRACT

The trace metal accumulation was mainly ascribed to natural weathering processes, but anthropogenic contribution could represent up to 40.09% of total sediment content. Anthropogenic Pb, Cu, Cr and Ni mostly came from atmospheric deposition, while fertilizer application was the main anthropogenic source of Cd.

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## ABSTRACT

A better understanding of anthropogenic impact can help assess the diffuse trace metal accumulation in the agricultural environment. In this study, both river sediments and background soils were collected from a case study area in Northeast China and analyzed for total concentrations of six trace metals, four major elements and three lead isotopes. Results showed that Pb, Cd, Cu, Zn, Cr and Ni have accumulated in the river sediments after about 40 years of agricultural development, with average concentrations 1.23–1.71 times higher than local soil background values. Among them Ni, Cr and Cu were of special concern and they may pose adverse biological effects. By calculating enrichment factor (EF), it was found that the trace metal accumulation was still mainly ascribed to natural weathering processes, but anthropogenic contribution could represent up to 40.09% of total sediment content. For Pb, geochemical and isotopic approaches gave very similar anthropogenic contributions. Principal component analysis (PCA) further suggested that the anthropogenic Pb, Cu, Cr and Ni inputs were mostly related to the regional atmospheric deposition of industrial emissions and gasoline combustion, which had a strong

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affinity for iron oxides in the sediments. Concerning Cd, however, it mainly originated from local fertilizer applications and was controlled by sediment carbonates.



## 1. Introduction

The rapid industrialization, urbanization and agricultural intensification are impacting the biogeochemical cycle of many elements (Marx et al., 2010). One of the most significant impacts is from the emission of hazardous trace metals into soils, which has caused serious pollution accidents and aroused strong public concerns in recent years (Alvarez-Ayuso et al., 2012; Niu et al., 2013). Although they are naturally occurring elements, the trace metals originating from anthropogenic sources are considered to be weakly stable and easier to transfer from soils to other environmental components (Ghrefat et al., 2012). Consequently, from an environmental safety and health perspective, the key question is to what extent anthropogenic activities have actually elevated trace metal concentrations in soils.

Agriculture is a potential pathway of diffuse trace metal pollution in soils and from soils to surface waters (Bur et al., 2009). In order to effectively reduce the trace metal concentration of agricultural soils, a quantitative inventory of trace metal inputs has been developed in many countries, which provides valuable information on the contribution of various anthropogenic sources (Belon et al., 2012; Luo et al., 2009; Nicholson et al., 2003). However, it is necessary to note that these inventories were usually conducted on a national scale, according to published data on the trace metal contents of source materials and estimated quantities applied to agricultural land. Consequently, there will be uncertainty when they are used on a scale of small or specific regions due to the spatial heterogeneity in trace metal sources. For example, sewage irrigation is generally considered as an important source of trace metal pollution in Chinese agricultural soils (Cheng, 2003), but indeed it seldom becomes the main source in water-rich regions.

The experimental data obtained from river sediments are useful for regional monitoring purpose, which can also help to indicate the diffuse trace metal pollution (Jiao et al., 2014a). This is especially true for agricultural reclamation areas, where soil erosion is serious and the composition of river sediments can be considered on average as representative of trace metals in soils they originate from (Bur et al., 2009). Consequently, these sediments represent an important reservoir of diffuse trace metals from both natural and anthropogenic sources. Different methods such as PCA, EF and lead isotopes have been widely used in the river sediment analysis to identify trace metal sources and to apportion natural vs. anthropogenic contributions (Sakan et al., 2009; Sun et al., 2011).

The Sanjiang Plain is an important agricultural area in Northeast China. Trace metal contamination of soil was rarely reported in this remote location. However, the region has gained attention after several decades of intensive agricultural reclamation (Shan et al., 2013). To ensure continuous high productivity, chemical fertilizers were generally applied at very high rates in this region. Our previous studies indicated that local fertilizer application and regional atmospheric deposition were possible anthropogenic metal sources for the soils (Jiao et al., 2014b, 2014c). However, the relative contribution of these pollution sources remains unclear. A better understanding anthropogenic pollution sources can help assess the impact of long-term fertilizer application on diffuse trace metal accumulation in the agricultural environment, which could be well achieved by river sediment analysis.

Therefore, our main objectives with this study were: (1) to assess the accumulation and associated environmental risk of Pb, Cd, Cu, Zn, Cr and Ni in river sediments from a typical agricultural watershed; and (2) to identify the major anthropogenic origin and possible behavior of these metals.

## 2. Materials and methods

### 2.1. Study area description

The Naolihe watershed in the central part of Sanjiang Plain was selected as a case study area, which has a total area of 24,863 $km^2$ (Fig. 1). As it benefits from rich soil nutrients and water resources, the major part of this watershed has been devoted to agricultural activities since the 1970s. Rice and maize are the two main types of crops being grown in paddy land and upland. There are no major mining or other industrial point sources in this watershed. Precipitation, surface and groundwater supply all irrigation water. This watershed has a typical continental monsoon climate with the average annual temperature and rainfall of 1.91 °C and 600 mm, respectively (Ouyang et al., 2014). The hydrological regime of rivers is mainly seasonal, with a low water period from November to March and high water flows between May and September. The watershed average elevation is 60 m, which generally decreases from south to north and from west to east.

### 2.2. Sampling procedure and pretreatment

In July 2013, a total of 12 sediment samples were collected from the Naoli River and its main tributaries (Fig. 1). At each sampling site, 3 sediment cores were obtained by using a plastic tube of 4 cm in diameter and 60 cm in length and they were removed from the upper 5 cm to mix into one composite sample. In order to obtain local geochemical backgrounds, 8 soil samples were also collected from selected reference sites (Fig. 1). These reference sites were all located in natural forested and grassed areas, where the soils have only been slightly impacted by human activities, especially the extensive application of chemical fertilizers. At each reference site, 3 sub-samples were taken at a minimum of 30 cm depth to avoid surface contamination and they were fully mixed to get a composite soil sample. Upon arrival in the laboratory, all of the samples were air dried at room temperature and ground with pestle and mortar until they passed a 0.149 mm nylon sieve. The sediment samples were further sieved to obtain the $< 63$ μm fractions, which are known to be metal-enriched.

### 2.3. Trace and major elements analysis

For analysis of the total phosphorus (TP), Pb, Cd, Cu, Zn, Cr, Ni, Fe, Al and Ca concentrations, the dry samples were digested by $HNO_3$–HF–$HClO_4$ mixture in a microwave system at 160 °C for 6 h. The solution of the digested samples was then analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The analytical data quality was assessed by using simultaneously the reference material GBW-07402. Good agreements were obtained between the measured and the certified values, with the recoveries ranging from 96.74 to 105.22%. In addition, a sequential extraction scheme developed by the Community Bureau of Reference (BCR) was applied to determine the concentrations of Fe and Al associated to different soil fractions. This BCR method is described in detail elsewhere (Rauret et al., 1999), which separates a metal into acid-soluble (exchangeable and carbonate-bound metals), reducible (Fe/Mn oxide-bound metals), oxidizable (organic matter/sulfide-bound metals), and residual (silicate-bound metals) fractions. The overall recovery rates, calculated by comparing the cumulative concentrations of different fractions with the concentration of bulk sample, varied between 95.66 and 102.81%.