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Identification of anthropogenic inputs of trace metals in lake sediments using geochemical baseline and Pb isotopic composition

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ABSTRACT

Source identification of trace metals in the water environment is important in understanding its environmental behavior and in the prevention and remediation of further pollution. Here, the regional geochemical baseline (RGB) and Pb isotopic ratios are combined to decipher the anthropogenic contribution rate, main anthropogenic source, and transport pathway of trace metals in sediments collected from the largest freshwater lake in northern China, Baiyangdian (BYD) Lake. The established RGB values of Cr, Ni, Cu, Zn, Cd, and Pb were 63.0, 27.8, 24.7, 46.1, 0.18, and 22.0 mg/kg, respectively, which were slightly different from the regional soil background values. Based on the RGB and actual concentrations of trace metals in the lake sediments, the calculated average anthropogenic contribution were lower than 20% except for Cd. Compared with the other trace metals, Cd was the element most impacted by anthropogenic input, which was mainly caused by the point source pollution in some sites. The risk assessment (geo-accumulation index and potential ecological risk) using the RGB as the regional background values showed that BYD sediments were uncontaminated by the trace metals, and at low ecological risk from the trace metals. The results of these two risk assessments further validated the assessment of the anthropogenic contribution by the RGB. In addition, Pb isotopic ratios result showed that coal combustion was the main potential source of anthropogenic Pb in the BYD sediments and atmospheric deposition was the main transport pathway. This study tried to combine the geochemical baseline and Pb isotopic composition to identify the anthropogenic input of trace metals in the sediments. It will provide a new insight into assessing the anthropogenic contributions, identifying the main anthropogenic sources, and transport pathways of trace metals in water environment.

1. Introduction

Lakes are important freshwater resources on Earth and play important roles in water conservation, flood control, regional climate regulation, and landscape amenity (Hansen, 2012; Thevenon et al., 2013). However, due to anthropogenic activities, trace metals enter into the water ecosystem through atmospheric deposition, sewage, and wastewater discharge (Bindler et al., 2011; Rajeshkumar et al., 2018; Yang et al., 2014). More than 90% of trace metals are deposited in the sediments and become a potential source of metals in aquatic environments (Beutel et al., 2008; Rajeshkumar et al., 2018). Therefore, the risk assessment and source identification of trace metals in the water environment is necessary to evaluate the extent of trace metal pollution and identify the pathways by which metals enter into the environment (Miller et al., 2014; Yang et al., 2014).

Traditional pollution risks are assessed using index assessment methods (single factor contaminant index, geo-accumulation index (I_{geo}), and enrichment factor (EF), etc.) (Jafarabadi et al., 2017; Sharifinia et al., 2017; Xu et al., 2017). The risk assessment result varies with the background. In fact, the regional background depends on local geochemical properties (Jiang et al., 2013). However, regional natural background neglects natural variation in trace metal contents (Covelli and Fontolan, 1997; Daskalakis and O'Connor, 1995). Moreover, a "natural background" that strictly refers to the pristine geochemical composition does not actually exist (Karim et al., 2015). The geochemical baseline is defined as the natural level of the trace metals on the Earth's surface that has not been influenced by human activities (Tian et al., 2017). Moreover, the geochemical baseline can distinguish the natural and anthropogenic concentrations (Matschullat et al., 2000; Teng et al., 2009; Zhang et al., 2014; Karim et al., 2015). In recent years, the geochemical baseline has been applied as the reference background in the risk assessment (Karim et al., 2015; Tian et al., 2017).

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Source identification is a common issue in the investigation and mitigation of metal pollution. The traditional approach relies on the statistics of large sample databases to determine the source of pollutants (Facchinelli et al., 2001). However, the method requires large databases and sophisticated statistics. Stable isotopes, which can be considered as the “signature” of elements, provide an advanced method for tracking the source of trace metals in sediments (Cheng and Hu, 2010). Lead isotope ratios have been increasingly applied to yield information on geochemical origins, to establish the principal sources of anthropogenic Pb, and to identify the pathways by which lead enters into the environment (Fernandez et al., 2008; Han et al., 2015, 2017; Miller et al., 2014).

Baiyangdian (BYD) Lake is the largest freshwater lake in northern China and is heavily impacted by human activity. BYD Lake is adjacent to the Xiongan New Area, which is intended to provide the non-capital function of a development hub for Beijing. BYD Lake is viewed as the “kidney of northern China”. Due to the rapid development of industry and agriculture, various ecological and environmental problems have emerged in the 1990s, such as declining biodiversity (Xu et al., 1998), eutrophication (Chen et al., 2008), water quality deterioration (Liu et al., 2010), metal and organic pollution (Gao et al., 2013; Guo et al., 2011; Zhang and Liu, 2014). However, the effect of anthropogenic activities on trace metal pollution in the BYD Lake is still unclear.

In this study, the objectives were to: (1) summarize the temporal-spatial variation and historic trends in trace metal pollution in the BYD sediments that were collected in 2004–2010; (2) establish the regional geochemical baseline (RGB), and then use RGB to quantitatively determine the anthropogenic input of trace metals, and evaluate the risk from the trace metals applying I_{geo} and potential ecological risk (RI); and (3) identify the origin of the anthropogenic input and transport pathways using Pb isotopic ratios.

2. Materials and methods

2.1. Description of study area

BYD Lake is located in the central, northern China, with an area of 366 km^2 (38°43′–39°02′ N, 115°45′–116°07′ E). The total surface area of the BYD basin is 31,199 km^2 (Bai et al., 2010). The BYD Lake enjoys a continental monsoons climate and its average annual precipitation is 556 mm (Yang and Mao, 2011). The average annual air temperature varies from about 7.5 ℃ (high altitude part) to about 12.7 ℃ (low altitude part). In the recent 50 years, the water depth has varied in the range of 5.2–9.26 m. The lake is considered as drying when the water depth is lower than 5.5 m. The water in BYD Lake is mainly derived by water diversion from other reservoirs, such as the Wangkuai Reservoir, Angezhuang Reservoir and Xidayang Reservoir.

2.2. Sample collection and processing

Thirty-nine surface sediment samples were collected during October 2010 in BYD Lake (Fig. 1). The surface sediment samples were collected with a grab sampler, and were taken back to the laboratory. The sediments were frozen and lyophilized at −80 °C, ground in an agate mortar and passed through a 100 mesh nylon sieve to ensure homogeneity.

2.3. Trace metal analysis

An aliquot of 40 mg of each sediment sample was digested using concentrated HNO_3, H_2O_2, and HF. The detailed procedure is described in the supplementary material. The metals in the digested sediment samples were analyzed using an Elan DRC-e inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer, USA). Quality control was checked using certified reference materials (GSS-9, GBW07423), produced by the Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences. Analytical reagent blanks were prepared with each batch of digestions and then analyzed for the same elements. The average recoveries of the different metals were in the range of 82.0–95.8% (Table S1).

2.4. Pb isotopic ratios measurement

The Pb isotopes were separated using the micro columns of anion exchange resins in the Dowex-I (200–400 mesh) (Sigma-Aldrich, USA), with HBr and HCl was used as the eluents. The Pb isotopic compositions were determined using the Elan DRC-e ICP-MS (PerkinElmer, USA). The ICP-MS parameters for detection were showed in the supplementary materials. All sediment samples were considered for Pb isotopic ratio analysis. The average values of the standard NIST SRM-981 were $^{206}Pb/^{207}Pb = 1.094 \pm 0.001$ and $^{208}Pb/^{207}Pb = 2.370 \pm 0.032$ (N = 20), respectively, which are close to the certified standard values (1.093 and 2.370, respectively). The analytical uncertainties, at two-fold standard deviations (SD) for Pb isotopic ratios were generally lower than 0.5%.

2.5. Regional geochemical baseline calculation

The RGB values of the trace metals in the sediments were calculated by normalization. In the literature, some conservative elements, such as Al, Li, Cs, Sc, V, Fe, have been employed as the reference elements (Lin et al., 2012). Sc has also been applied as the reference element when investigating the background of metals in soils (GNBVS, 1980). In this study, Sc was an inert element with a low variable coefficient (0.17), which is not subject to environmental influence, and hence, Sc was selected as the reference element. The equations of linear regression between the metals and Sc were established. The following equation describes the baseline model:

$$C_m = a\, C_{Sc} + b \tag{1}$$

where C_m and C_{Sc} are the concentrations of the metals and Sc, respectively; a and b are regression constants. In Eq.(1), the natural sediment can be defined by the 95% confidence interval, where the points falling within the intervals are characterized as representing natural sediments (Teng et al., 2009). Therefore, the data points falling outside of the 95% confidence bands were removed during calculation of the RGB. Then, the baseline of a metal is obtained by the following equation:

$$B_m = a\, \overline{C}_{Sc} + b \tag{2}$$

where B_m is the baseline of the metal m, and $\overline{C}_{Sc}$ Sc is the mean concentration of Sc in the study area.

2.6. Pollution risk assessment

2.6.1. Geo-accumulation index (I_{geo})

I_{geo} was applied to assess the degree of metal contamination and accumulation (Müller, 1969), and was calculated using the following equation:

$$I_{geo} = \log_2\left(\frac{C_i}{1.5B_i}\right) \tag{3}$$

where C_i is the metal concentration in the sediment; B_i is the background value and 1.5 is the background matrix correction factor. Based on the I_{geo} values, pollution can be classified into seven classes: uncontaminated, uncontaminated to moderately, moderately, moderately to strongly, strongly, strongly to extremely, and extremely contaminated when the I_{geo} is < 0, 0–1, 1–2, 2–3, 3–4, 4–5, and > 5.

2.6.2. Potential ecological risk index (RI)

RI is introduced to assess the degree of ecological risk from trace metals in sediments. RI is calculated using the following equation: