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Historical trends of anthropogenic metals in Eastern Tibetan Plateau as reconstructed from alpine lake sediments over the last century

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HIGHLIGHTS

- Alpine lake sediments in the Eastern Tibetan Plateau reflected regional anthropogenic metal emissions.
- Anthropogenic metals appeared around 1950, significantly increased in the 1980s, and peaked in the mid-1990s.
- Over 80% of Cd, Pb and Zn were quantified from anthropogenic emissions in atmospheric deposition since the mid-1990s.
- Regional anthropogenic emissions are expected to continue for Cd and Zn, but decrease for Pb.

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ABSTRACT

Reconstructing trace metal historical trends are essential for better understanding anthropogenic impact on remote alpine ecosystems. We present results from an alpine lake sediment from the Eastern Tibetan Plateau to decipher the accumulation history of cadmium (Cd), lead (Pb) and zinc (Zn) over last century, from the preindustrial to the modern period. Cd, Pb and Zn in the sediment of Caohaizi Lake clearly suffered from atmospheric deposition, and the mining and smelting were regarded as the main anthropogenic sources. Since the mid-1990s, over 80% of trace metals were quantified from anthropogenic emissions. The temporal trends of anthropogenic metal fluxes showed that the contamination history of Pb was earlier than that of Cd and Zn, which was in agreement with the regional Pb emission history, but lagged behind the Pb decline in Europe and North America. The fluxes of anthropogenic Cd and Zn were relatively constant until the 1980s, increased sharply between the 1980s and the mid-1990s, and then kept the high values. The anthropogenic fluxes of Pb showed a marked rise around 1950, and increased sharply in the 1980s. In the mid-1990s, this flux reached the peak, and then decreased gradually. The Pb deposition flux at present in comparison with other lake records in the areas of Tibetan Plateau further demonstrated that trace metals in the Caohaizi Lake region were probably from Southwest China and South Asia. Economic development in these regions still puts pressure on the remote alpine ecosystems, and thus the impact of trace metals merits more attention.

1. Introduction

As potent toxic elements that can be bioaccumulated in food webs, the transport and fate of trace metals, such as cadmium (Cd), lead (Pb), and zinc (Zn), are a critical contamination issue for terrestrial and aquatic systems. The majority of trace metals in the atmosphere is apt to deposit to remote alpine ecosystems through dry and/or wet deposition. This has been reported worldwide by investigating the environmental archives like soils (Bacardit and Camarero, 2010b; Bing et al., 2014), sediments (Thevenon et al., 2011b; Bacardit et al., 2012), mosses (Gerdol and Bragazza, 2006; Shotyk et al., 2015), lichens (Loppi, 2014), snow (Veysseyre et al., 2001; Bacardit and Camarero, 2010a) and peat bogs (Novák et al., 2003; Martínez Cortizas et al., 2012). In general, however, temporal trends for trace metal deposition are rare, especially for the remote high mountain systems where instrumental records of

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atmospheric metal deposition are sparse.

Trace metals entering aquatic ecosystems through runoff or atmospheric deposition accumulate eventually in sediments. Thus, lacustrine sediments, recording and preserving the history of trace metal accumulation, are most valuable archives of the catchment area and the atmosphere over time (Heim and Schwarzbauer, 2013). Remote mountain lakes are relatively isolated from anthropogenic impact, which provide signals of atmospherically transported pollutants. Furthermore, lake sediments in high altitude document data reflecting the temporal changes of the contamination sources and of variations in the transport path regimes (Garçon et al., 2012). Therefore, high-altitude lake sediments are essentially important for alpine ecosystems to quantify metal fluxes from anthropogenic emissions.

In order to identify anthropogenic versus natural origins of trace metals in sediments, the isotopic signature of Pb has been used due to its particular property of being present in the environment; that is, the variations of Pb isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb) vary depending on its sources (Bindler et al., 2008; Bacardit et al., 2012). Thus, the contamination history of Pb has been paid much more attention compared with other contaminated metals in sediments. Another approach that is to calculate metal enrichment relative to certain conservative element (e.g., enrichment factor) is frequently used to distinguish metal sources in sediments. However, this method is only effective if the anthropogenic sources of trace metals are well-defined (Reimann and de Caritat, 2005), since natural processes may affect element fractionations from the original source (Reimann and Caritat, 2000). The Pb deposits are commonly associated with other trace metals like Cd and Zn, and this may result in similar sources of these metals in the environment. Therefore, the multiple methods including Pb isotopes, enrichment factors and statistical analysis will obtain more correct information on the sources of trace metals in sediments.

Gongga Mountain (29°20′–30°20′N, 101°30′–102°15′E, summit: 7556 m a.s.l. (above sea level)) is the highest mountain on the eastern edge of Tibetan Plateau. The eastern slope of Mt. Gongga is characterized by a high mountain and a deep valley (1100–7556 m a.s.l.), a transitional seasonal climate and typical pristine forests. Recently, many researchers have found evidences of atmospheric metal depositions in this remote high mountain. Yang et al. (2009) analyzed the element composition of $PM_{2.5}$ and PM_{10} at the elevation of 1600 m a.s.l. on the eastern slope of Mt. Gongga, and concluded that several trace metals (e.g., Zn and Pb) were sourced from long-distance atmospheric transport. Wu et al. (2011) found the Cd accumulation in the surface soils of the eastern slope of Mt. Gongga from atmospheric deposition. In addition, our recent studies showed that Pb and Zn in the soils and mosses on the eastern slope of Mt. Gongga were also affected by atmospheric deposition, whereas copper (Cu) was not the case (Bing et al., 2014). However, to our knowledge, there is no research on the deposition fluxes or rates of these atmospheric sourced metals on the Mt. Gongga.

Here, we present the observations on the temporal changes of trace metals (Cd, Pb and Zn) from atmospheric deposition in a small mountain lake (Caohaizi Lake), which is the only lake formed since the last glacial period on the eastern slope of Mt. Gongga. The objectives of the presented study are to (1) reconstruct historical trends of trace metals in atmospheric deposition, (2) quantitatively distinguish anthropogenic contribution to these metals, and (3) evaluate the deposition fluxes of atmospheric sourced metals. For these purposes, other elements (Al, Ca, Cu, Fe, K, Li, Mg, Mn, Na, Sr and Ti) in the sediment were also measured to bolster the analysis.

2. Materials and methods

2.1. Study area

Caohaizi Lake, formed since the last glacial period (Zhong et al., 2002), lies on the eastern slope of Mt. Gongga (Fig. 1). The lake lies at an altitude of approximately 2780 m a.s.l. with a very small area of <1.0 km^2 and an average depth of 1.4 m. There is no inflow and outflow, and thus the water balance of Caohaizi Lake is controlled by precipitation and evaporation on the lake surface. The lake is surrounded mostly by glacial deposits and slope wash from granite and metamorphic rocks containing a large amount of mica (Wu et al., 2013b).

The eastern slope of Mt. Gongga is mainly influenced from the Asian monsoons from southerly and southeasterly air mass (Fig. 1). According to the data from the Alpine Ecosystem Observation and Experiment Station of Gongga Mountain, CAS, on the eastern slope of Mt. Gongga (101°59′54″E, 29°34′34″N, 2948 m a.s.l.), the mean annual temperature is 4.2 °C and the mean annual precipitation is 1947 mm, mainly in the summer season (Wu et al., 2013a).

2.2. Field sampling

Two sediment cores (38 cm and 42 cm) were collected using the gravity corer (the diameter of 6 cm) in March 2012. The sampling site was selected in the center area of the lake in order to avoid marked human disturbance (Fig. 1). The shorter core was used to obtain information of the sediment chronology, and the longer one was to analyze elemental concentrations. The sediments were sliced in the field and stored in plastic bags. The upper 20 cm in the shorter core were sampled at intervals of 0.5 cm, whereas the intervals of the rest were enlarged to 1.0 cm. For the longer core, the intervals were 1.0 cm. Samples for the geochemical analysis were air-dried at normal temperature in the laboratory before analysis.

2.3. Laboratory analysis

The sediment chronology was constructed by measuring radionuclides (^{210}Pb and ^{137}Cs). ^{137}Cs, ^{210}Pb and ^{226}Ra activities were detected using an Ortec HPGe GWL series well-type coaxial low background intrinsic germanium detector after the samples were dried in low temperature (<40 °C) and weighted. The excessive ^{210}Pb ($^{210}Pb_{exc}$) in each sample was obtained by subtracting the activity of ^{226}Ra from the total activity of ^{210}Pb.

The sediment samples for element analysis were digested with HCl–HNO_3–HF–$HClO_4$. The concentrations of major elements (Al, Ca, Fe, K, Mg, Mn, Na, Sr and Ti) were analyzed using an American Leeman Labs Profile inductively coupled plasma-atomic emission spectrometer (ICP-AES), and the concentrations of trace metals (Li, Cu, Cd, Pb and Zn) were determined by inductively coupled plasma mass spectroscopy (ICP-MS). Standard solution SPEX™ from United States was used as the standard. Quality control was assured by the analysis of duplicate samples, blanks and reference materials (GSD-9 and GSD-11, Chinese geological reference materials). According to the measurement of the repeated samples and reference materials, the relative standard deviation (RSD) was below 3% for ICP-AES analysis and below 5% for ICP-MS analysis, respectively. The recovery of the reference materials was 92–108% for ICP-AES analysis and 90–110% for ICP-MS analysis, respectively.

Lead isotopes (^{206}Pb, ^{207}Pb and ^{208}Pb) of the samples after the corresponding digestion described above were measured by ICP-MS (Agilent 7700x). An international standard reference material (SRM981-NIST, United States) was used for instrument calibration and standard material (GBW04426, China) for the analytical control. The maximum deviations of both ^{208}Pb/^{206}Pb and ^{207}Pb/^{206}Pb