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Heavy metal deposition through rainfall in Chinese natural terrestrial ecosystems: Evidences from national-scale network monitoring

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HIGHLIGHTS

- Investigating heavy metal deposition through rainfall in Chinese natural ecosystem.
- Precipitation, vehicles number, energy consumption affect heavy metal deposition.
- Wet heavy metals deposition was positive correlated with soil metals contents.
- Increasing heavy metals deposition have adverse effects on natural ecosystem.

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ABSTRACT

Industrialization and urbanization have led to increasingly serious levels of atmospheric heavy metal pollution, which is one of the main sources of heavy metals to terrestrial ecosystems. Therefore, it is essential to quantify atmospheric fluxes and explore their potential effects on natural ecosystems and human welfare. We monitored water-soluble heavy metals (lead (Pb), cadmium (Cd), and chromium (Cr)) in rainfalls on a monthly basis in 2013 and 2014, at 31 field stations located in typical natural Chinese ecosystems. The average soluble Pb, Cd, and Cr deposition was 1.90 ± 1.54, 0.28 ± 0.25, and 0.96 ± 0.48 mg m^{-2} yr^{-1}, respectively, with a large variation among the different sites. Generally, the atmospheric deposition of soluble Pb, Cd, and Cr was higher in the southwest, central, south, and north China than in the northwest and northeast China, Inner Mongolia, and Qinghai-Tibet. As expected, the atmospheric heavy soluble metal deposition fluxes were significantly correlated with the number of vehicles ($Ps < 0.1$). The wet deposition of soluble Pb and Cr was positively correlated with oil and coal consumption, unlike Cd deposition. Moreover, soluble Pb and Cd in atmospheric wet deposition were positively correlated with the contents of Pb and Cd in soil at different regions. In this study, atmospheric heavy metal deposition through rainfall in typical natural ecosystems in China is assessed at the national scale, alerting potential ecological hazards resulting from an increasing atmospheric heavy metal deposition and providing a basis for future studies.

1. Introduction

Atmospheric wet deposition is commonly considered as the most effective approach to remove various pollutants from the atmosphere and is one of the main sources of toxic heavy metal input to natural terrestrial ecosystems (Al-Khashman et al., 2013; Pan and Wang, 2015). In the past decades, anthropogenic activities have significantly altered airborne heavy metals through global population growth and industrialization (Bacardit and Camarero, 2009; Lei et al., 2011). Atmospheric heavy metals mainly originate from artificial sources, e.g., smelting, fossil fuel combustion, and waste incineration, with a relatively minor contribution from natural sources, e.g., soil dust and volcanic activity (Bacardit and Camarero, 2009; Cheng and Hu, 2010). Most atmospheric heavy metals

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eventually deposit on the surface through dry and wet deposition. Some heavy metals, such as lead (Pb), cadmium (Cd), chromium (Cr), mercury (Hg), and arsenic (As) are poisonous for plants, animals, and humans, by altering their metabolism, inhibiting growth, and decreasing the production (Das et al., 1997; Nagajyoti et al., 2010; Singh et al., 2013). Despite current international efforts to effectively decrease the increasing ratios of atmospheric pollution, most natural terrestrial ecosystems are still considered at risk because of the long-term high-intensity atmospheric heavy metal deposition and pollution (Shanker et al., 2005; Bacardit and Camarero, 2009; Luo et al., 2013; Bian et al., 2015).

Although some studies have investigated atmospheric heavy metal deposition rates at a local scale and for small regions (Azimi et al., 2005; Sakata et al., 2008; Sharma et al., 2008; Kara et al., 2014; Pan and Wang, 2015), no results have been reported at regional or national scales. Furthermore, the atmospheric deposition of heavy metals is expected to be higher in urban and industrial areas than in remote natural ecosystems owing to the limited critical radius of atmospheric transport and the reduced emissions from anthropogenic activities. Unfortunately, most observation sites in previous studies were located in urban and industrial areas, such that their results cannot be used to estimate the heavy metal deposition and evaluate the impacts of heavy metal deposition on natural ecosystems or remote areas (Golomb et al., 1997; Hu and Balasubramanian, 2003; Sakata et al., 2008; Kim et al., 2012). It is therefore important to better quantity the pollution status resultant from atmospheric heavy metals in natural ecosystems and delineate future environmental protection policies.

Soluble fractions of deposited heavy metals are an important part of wet deposition, accounting for 37–100% of the total forms (Cizmecioglu and Muezzinoglu, 2008), and it is also believed that a greater proportion of water-soluble metals likely originate from anthropogenic sources (Voutsa and Samara, 2002; Heal et al., 2005). Moreover, heavy metals are bioavailable and poisonous only in their soluble form. In this study, 31 field ecological stations from the Chinese Ecosystem Research Network (CERN) (Fu et al., 2010), which was initially established for monitoring N deposition (Zhu et al., 2015), were further selected to assess the atmospheric deposition of heavy metals (Pb, Cd, and Cr) in their water-soluble form during rainfall (wet deposition) on a monthly basis by network monitoring in 2013 and 2014 (Fig. 1). To our knowledge, this study is the first attempt to evaluate the atmospheric heavy metals deposition flux through rainfall at the national scale considering Chinese terrestrial ecosystems. The main goals of this study were to 1) quantify the atmospheric heavy metal deposition through rainfall in Chinese natural ecosystems, 2) demonstrate the main factors influencing the wet deposition of atmospheric heavy metals, and 3) explore the relationship between atmospheric heavy metal deposition and soil metal content in China.

2. Methods

2.1. Site description

Thirty-one field ecological stations from the CERN were selected to monitor the atmospheric heavy metal deposition through rainfall (Table S1, Fig. 1). The stations were located in typical natural Chinese ecosystems, including forests, grasslands, deserts, lakes, marshes, and karst ecosystems, covering 20 Chinese provinces and eight ecological regions according to climate and vegetation (Fig. 1).

2.2. Sampling and analysis

According to the long-term monitoring guide from the CERN, rainwater (snow) was collected in plastic buckets installed 1.5 m above the ground at the onset of a rain (or snow) event. Samples were only collected over the duration of rainfall, and included rained out soluble and insoluble particulates. In detail, the samples were collected from 3 to 5 rainfall events per month in 2013–2014 by manual collection. After each rainfall event, the samples were stored in polyethylene plastic bottles under −20 °C, and at the end of the month these subsamples were evenly mixed on an equal-volume-per-collection basis to obtain one mixed sample for each month. All plastic buckets and polyethylene plastic bottles were cleaned with distilled water three times and finally dried prior to use.

In general, there are three types of pretreatments for heavy metals in rainfall. The first one is to measure the heavy metal concentration after filtration, where the determined heavy metal concentration represents the water-soluble fraction (Cong et al., 2015). The second is to acidify the samples without filtration and then determine the heavy metal concentration to represent the concentration of acid-soluble fractions (Sakata and Asakura, 2009). The third is to use the acid digested method for the unfiltered precipitation and then determine the total heavy metal in rainfall (Cizmecioglu and Muezzinoglu, 2008; Pan and Wang, 2015). In this paper, we only measured water-soluble fractions of heavy metals in rainfall in the laboratory. These samples were filtered by gravity through a 0.45 μm membrane filter to remove the particulates, and then the concentration of soluble Pb, Cd, and Cr were measured using an inductively coupled plasma optical emission spectrometer (ICP–OES) (Optima 5300DV, PerkinElmer, America). Duplicate blanks and standard reference materials (Chinese National Standards GB/T 23942-2009) were used to assure data quality. All blanks were analyzed in the same manner as field samples, and all procedures were applied for the blank samples. The R^2 of calibration curves for all heavy metals were ≥0.999. The elements were not detected in blanks according to instrumental detected limits (1 ppb).

2.3. Calculation and analysis

The fluxes of atmospheric heavy soluble metal deposition through rainfall (or wet deposition) were calculated as:

$$D = \sum_{i=1}^{n} C_i \times P_i \quad (1)$$

where D (mg m^{-2}) is the annual deposition flux of a specific heavy metal (i.e., Pb, Cd, or Cr), C_i is the monthly rainfall concentration of a specific heavy metal (mg L^{-1}), P_i is the monthly precipitation (mm), and n is the number of months.

Then, the atmospheric wet deposition fluxes of the heavy soluble metals for the eight regions were averaged for the observation sites in the specific regions. Similarly, we obtained the atmospheric heavy soluble metal deposition for the 20 provinces. Linear and curvilinear regressions were used to evaluate the relationships between the atmospheric heavy soluble metal deposition and the mean annual precipitation, number of vehicles, oil consumption, and coal consumption. The datasets for the number of vehicles, oil consumption, and coal consumption were obtained from the National Bureau of Statistics of China (Table S2). Data of heavy metal concentration in soil for different provinces of China were obtained from Chen et al. (2015), who obtained these values through a national soil heavy metal pollution survey. In their study, more than 38,000 topsoil samples were collected during April 2005 to December 2013 within the territory of the People's Republic of China (excluding the Hong Kong, Macao, and Taiwan). They used a standard method to analyze soil samples, and calculated metal