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Analysis of metal(loid)s contamination and their continuous input in soils around a zinc smelter: Development of methodology and a case study in South Korea☆

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ABSTRACT

Soil contamination due to atmospheric deposition of metals originating from smelters is a global environmental problem. A common problem associated with this contamination is the discrimination between anthropic and natural contributions to soil metal concentrations: In this context, we investigated the characteristics of soil contamination in the surrounding area of a world class smelter. We attempted to combine several approaches in order to identify sources of metals in soils and to examine contamination characteristics, such as pollution level, range, and spatial distribution. Soil samples were collected at 100 sites during a field survey and total concentrations of As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn were analyzed. We conducted a multivariate statistical analysis, and also examined the spatial distribution by 1) identifying the horizontal variation of metals according to particular wind directions and distance from the smelter and 2) drawing a distribution map by means of a GIS tool. As, Cd, Cu, Hg, Pb, and Zn in the soil were found to originate from smelter emissions, and As also originated from other sources such as abandoned mines and waste landfill. Among anthropogenic metals, the horizontal distribution of Cd, Hg, Pb, and Zn according to the downwind direction and distance from the smelter showed a typical feature of atmospheric deposition (regression model: $y = y_0 + \alpha e^{-\beta x}$). Lithogenic Fe was used as an indicator, and it revealed the continuous input and accumulation of these four elements in the surrounding soils. Our approach was effective in clearly identifying the sources of metals and analyzing their contamination characteristics. We believe this study will provide useful information to future studies on soil pollution by metals around smelters.

1. Introduction

A major anthropogenic source of trace metal pollution in the environment is the smelting of nonferrous metals (Li et al., 2011; Shen et al., 2017; Zhan et al., 2014). Ample evidence shows that atmospheric deposition of smelter emissions causes soil contamination (Tembo et al., 2006; Svendsen et al., 2007; Šajn et al., 2013; Zhan et al., 2014; Ghayoraneh and Qishlaqi, 2017; Shen et al., 2017), and high concentrations of metal(loid)s such as Cd, Cu, Hg, Pb, Zn, and As have been found in soils around smelters in various countries (Borgna et al., 2009; Stafilov et al., 2010; Li et al., 2011; Liu et al., 2013; Šajn et al., 2013) often at concentrations that are well above regulatory limits and therefore should in principle require some form of remediation.

It is generally not too difficult, via transect- or systematic

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sampling studies, to determine the concentration of metal(loid)s in soils at various distances from a given smelter facility, and to identify the region where this concentration pauses (eco)toxicological risks. Once the extent of this contaminated region is known, one can design an appropriate remediation strategy. This process has been carried out by various groups of researchers in different parts of the world, and in particular by Hong et al. (2009) a few years back for the Seokpo zinc smelter located in Bonghwa County, Gyeongbuk Province (South Korea). In the vicinity of the smelter, these authors focused on Cd and Zn pollution in the predominantly agricultural land; where nearby residents grow vegetables and fruit trees, to satisfy local consumption.

Once a strategy for remediation has been clearly identified, it would seem straightforward for local or government officials to turn to polluters to pay for clean-up costs. However, experience has shown time and again that it is relatively easy for those responsible for the pollution to deflect the charges by claiming that metal(loid) concentrations that are above regulatory standards in soils near smelter sites are due to natural background metal(loid)s concentrations in soils being high, not to actual pollution. Unfortunately, a clear methodology to assess the true extent of metal(loid)s pollution around smelter sites appears to be lacking at this point, making it very difficult for decision-makers to move forward.

In this context, a key objective of the research described in the present article was to return to the Seokpo zinc smelter site already analyzed by Hong et al. (2009), and to devise a method to tease apart metal(loid) pollution from background levels in soils in the vicinity of the smelter. To achieve this objective, several approaches were combined. The concentrations of metals in the soil were surveyed extensively through site investigation. Then, we conducted a multivariate statistical analysis and examined the spatial distribution by identifying the horizontal variation of metals according to particular wind directions and distance from the smelter and drawing a distribution map by means of a GIS tool.

2. Materials and methods

2.1. Site description

Located in the village of Seokpo, in Bonghwa County, Gyeongbuk Province, Republic of Korea (Fig. 1), the Seokpo zinc smelter started operation in 1970 and is now one of the largest Zn producers in Asia. The annual production capacities of the smelter for zinc (zinc slab), sulfuric acid, copper sulfate, silver (by-product of smelting zinc ores), and indium are 350,000, 600,000, 1,500, 28,000, and 30 tons, respectively, according to its official website (www.ypzinc.co.kr).

The study site is within a radius of approximately 5 km from the smelter (Fig. 1). It mostly comprises forests (72.33 km^2), upland fields (2.60 km^2), rivers and lakes (1.68 km^2), transportation routes (0.57 km^2), residential areas (0.39 km^2), and industrial areas (0.37 km^2). About 66.2% of the total unforested land (except for rivers and lakes) is used for agriculture (upland fields).

The study site experiences a temperate monsoon climate with an annual mean temperature of 12.9 °C, and extreme maximum and minimum temperatures of 34.1 °C and −9.5 °C, respectively (KOSIS, 2015). The annual mean precipitation is 1196 mm, and the temporal distribution of precipitation throughout the year is highly heterogeneous. More than 78% of the total annual precipitations fall from June to October (KOSIS, 2015). In dry winter seasons, winds from the northwesterly quadrant are predominant, whereas hot and humid summers are dominated by southeasterly winds (KMA, 2016).

2.2. Soil sampling

An extensive investigation of soil metal(loid) contents was carried out in May 2016. As shown in Fig. 1, surface soil samples were collected at depths of 0–20 cm from 100 sampling points in agricultural fields. However, sampling points 9, 39, 68, 79, 82, and 96 were not under agricultural land but comprised other forms of land use such as parking lots, playgrounds (for schools), and miscellaneous land. The location of each sampling site is provided in Supplementary Table S1. The sampling locations can be broadly divided into three regions A, B, and C. Under the assumption that the smelter occupied the central point and there was a prevailing wind direction, Site B is located between approximately 0.5 and 1.0 km from the smelter, vertically to the prevailing wind direction. Sites A and C are located between approximately 1.0 and 5.6 km in the upwind and downwind directions, respectively.

At each sampling site, five samples of surface soils were collected in a zig-zag pattern and mixed thoroughly to obtain a representative composite sample in accordance with the standard Korean method (KMoE, 2013). The soil samples were collected using a stainless steel hand auger and stored in pre-labeled polyethylene zip bags. Appropriate care was taken at the sampling sites to avoid collection of any obvious contaminants, as well as plant leaves, gravel, and other debris.

2.3. Chemical analysis and mechanical properties

All soil samples were sent for analysis to a nationally accredited professional analysis institute (NAPAI) (Analysis & Certification Division, Foundation of Agri. Tech. Commercialization & Transfer, South Korea) related to soil pollution. The NAPAI's official website can be accessed at http://www.fact.or.kr.

Chemical and mechanical properties of all soil samples were analyzed following standard procedures. The pH value was determined on a 1:5 (V/V) soil:distilled water suspension by the Korean standard method (KMoE, 2013). The mechanical properties of soils were determined by the internationally recognized pipette method. Particle size fractions were defined as sand (0.05–2.00 mm), silt (0.002–0.05 mm) and clay (<0.002 mm) and the granulometry of the soil was categorized according to the USDA soil texture classification. *Aqua regia* digestion (3:1, v/v, $HCl + HNO_3$) was conducted to determine the total concentrations of As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, and Zn in the soil (<0.15 mm) using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES; Optima 8300DV, Perkin Elmer, USA) in accordance with the Korean standard method (KMoE, 2013).

2.4. Statistical analysis

Statistical analyses were conducted using SPSS 20.0 (IBM, USA) and the graphs were prepared in SigmaPlot 12.0 (Systat Software, Inc., USA). The statistical distribution of data was checked with the Kolmogorov–Smirnov test for normality with a mean confidence interval of 95%. The relationships between pairs of metal(loid)s were evaluated using Spearman's rank correlation coefficient as a non-parametric measure, with statistical significance set *a priori* at $p < 0.01$. Inter-element relationships provide information on metal sources and their pathways (Manta et al., 2002; Rodríguez et al., 2008). The non-parametric correlation coefficient is a common parameter used to quantify the relation between pairs of variables when the presumption of normality is not warranted (Škrbić and Đurišić-Mladenović, 2010).

Multivariate statistical analysis is effective at distinguishing natural sources and anthropogenic inputs of metal(loid)s in soil pollution surveys (Dragović et al., 2008; Szolnoki et al., 2013).