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Original Articles

Lead concentrations and stable lead isotope ratios in moss in Slovenia and Switzerland

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ABSTRACT

Using moss as a biomonitor is an established technique for monitoring atmospheric deposition of trace elements, including lead (Pb), a metal that is toxic for most organisms. Lead enters the environment during production and combustion processes and during the use of leaded gasoline. There are four stable isotopes of Pb, and the isotopic composition can be used to determine sources and pathways of atmospheric Pb pollution.

In this study we determined Pb concentrations and isotope ratios in moss (*Hypnum cupressiforme* and *Pleurozium schreberi*) collected from 1990 to 2015 in Switzerland and from 2006 to 2015 in Slovenia. We used microwave sample digestion and inductively coupled plasma mass spectrometry (ICP-MS) for Pb concentrations and multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) for Pb isotope ratio determination. The aim was to assess the change in atmospheric Pb deposition over time and the differences between and within the two countries. Additionally, we assessed the current Pb isotope ratios for both countries and evaluated the change over time in Switzerland.

The Pb concentration in moss decreased significantly over time in both countries. In 2015, at the end of the study period, concentrations were significantly higher in Slovenia compared to in Switzerland. Higher Pb concentrations in Slovenia may be related to the prolonged use of leaded gasoline or to the larger influence of industrial sources. Within Switzerland Pb concentrations differed significantly between regions. These differences are likely a consequence of different population densities and precipitation amounts. In Slovenia there were no significant differences between the regions, indicating that there are no large differences in Pb emissions.

The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ isotope ratios differed between Slovenia and Switzerland and between some regions within Switzerland. This finding shows that Slovenia and Switzerland, as well as the different regions within Switzerland, are influenced by different Pb sources. In Switzerland, $^{206}Pb/^{207}Pb$ increased and $^{208}Pb/^{206}Pb$ decreased over time and shifted away from the isotopic signature of leaded gasoline. Additionally, both isotope ratios became more homogeneous within Switzerland, which suggests that the sources of Pb became more similar. Overall, the Pb isotope ratios reflect the diminishing influence of leaded gasoline and indicate an increasing importance of industry, coal burning and natural bedrock as Pb sources.

1. Introduction

Lead (Pb) is a toxic heavy metal which enters the environment during production (e.g. mining and smelting) of Pb, combustion of coal and during the use of leaded gasoline (Komárek et al., 2008). The atmosphere is a major initial recipient of Pb emissions, from which it is – after a potential long-range transport – deposited into ecosystems. Plants take up lead from the soil as well as from aerosols and accumulate it in their tissues (Antosiewicz, 1992; Verma and Dubey, 2003). Eventually they show signs of chronic poisoning, such as reduced root growth (Breckle, 1999; Eun et al., 2000; Obroucheva et al., 1998) and inhibited enzyme activity (Hampp et al., 1973; Prasad and Prasad, 1987). The accumulation of lead in plants enables lead to enter the food chain, leading to the poisoning of both herbivores and carnivores.

Lead has a highly variable isotope composition and has four stable

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isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb (Komárek et al., 2008). ^{204}Pb is the only primordial stable isotope, whereas the others are formed through the radioactive decay of long-lived isotopes of U and Th into stable isotopes, i.e. ^{238}U to ^{206}Pb, ^{235}U to ^{207}Pb and ^{232}Th to ^{208}Pb (Komárek et al., 2008; Steinnes et al., 2005). The isotopic composition of lead is not affected by anthropogenic activity, such as smelting or refining (Bollhöfer and Rosman, 2001). Therefore, the isotopic ratio of Pb can be used to determine sources and pathways of atmospheric pollution of Pb (Bollhöfer and Rosman, 2001). The ^{206}Pb/^{207}Pb ratio has received the most attention in the literature because these two isotopes can be determined with the highest precision and because the isotope ratio varies in a specific way based on the radioactive decay of U and Th (Komárek et al., 2008). For further differentiation, ^{206}Pb/^{207}Pb is often compared to other isotope ratios, such as ^{208}Pb/^{206}Pb. In Europe the natural Pb isotope ratio is around 1.18–1.22 for ^{206}Pb/^{207}Pb (Krause et al., 1993) and around 2.08–2.02 for ^{208}Pb/^{206}Pb (Komárek et al., 2008).

Atmospheric deposition of Pb has occurred for several thousands of years. Since the onset of the Greek and Roman periods Pb isotope ratios, preserved in lake sediments and peat bogs cores, have been influenced by mining and smelting (de Vleeschouwer et al., 2007; Dunlap et al., 1999; Shotyk, 1998). Since the Middle Ages and the early Industrial Revolution (i.e. the middle of the 18th century), coal burning and combustion engines have been important sources of Pb pollution (Dunlap et al., 1999). Starting in the 1950s the use of leaded gasoline dominated Pb isotope ratios (Dunlap et al., 1999; Weiss et al., 1999), but its influence gradually declined after the phasing out of leaded gasoline beginning in the 1980s (Bollhöfer and Rosman, 2001).

Here we look at the development over time of Pb concentrations and isotope ratios in two European countries, Switzerland and Slovenia. In Switzerland Pb in gasoline was mostly imported from Australian and Canadian ores, with ^{206}Pb/^{207}Pb ratios between 1.04 and 1.10, which led to a decrease in ^{206}Pb/^{207}Pb ratios in deposited Pb during the 20th century (Agnan et al., 2015; Moor et al., 1996; Shotyk et al., 2002). For Slovenia we had no information about the source of Pb in gasoline. Switzerland is a Western European country with a prevalent Atlantic climate in the northern part (Jura, Plateau and Northern Alps), a Mediterranean-influenced climate in the Southern Alps and a rather dry climate in the Central Alps. The Alps comprise about 60% of the total area of the country. Slovenia is situated in Central to Eastern Europe and has a mainly continental to sub-Mediterranean climate. Four major European geographic regions meet in Slovenia: the Alps, the Dinarides, the Pannonian Plain and the Mediterranean.

Using moss as a biomonitor is an established technique for monitoring atmospheric deposition of trace elements. Carpet-forming moss species obtain most of their nutrients and other trace elements directly from precipitation and deposition of airborne particles (Rühling and Tyler, 1968). For Pb, the concentration measured in moss is closely related to the bulk deposition (Berg et al., 1995; Thöni and Seitler, 2004). Through an international cooperative programme under the UNECE Geneva Air Convention, moss has been used to evaluate atmospheric deposition in several European countries every five years since 1990 (Harmens et al., 2015a).

Here we determined Pb concentrations in moss collected from non-urban environments in Switzerland from 1990 to 2015 and in Slovenia from 2006 to 2015. For Slovenia, Pb concentrations of moss from urban forests in the municipality of Ljubljana were also investigated. The objectives of this study were to assess Pb concentrations in moss, infer changes in atmospheric Pb deposition over time, and determine differences between and within the two countries. Additionally, we assessed the Pb isotope ratios of mosses collected in 2015 for both countries and evaluated the change in isotope ratios from 1990 to 2015 in Switzerland. The aim was to determine possible sources of Pb contamination and the changes in these sources over time.

2. Methods

2.1. Moss species sampling and sample preparation

Sampling and preparation was done in accordance with the moss monitoring manual of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation, 2015). The methodology did not change significantly from 1990 to the present. Moss samples were gathered below the timber line in non-urban, open areas, e.g. forest clearings. Samples were taken at least 3 m away from the edge of the tree canopy in Switzerland but only at least 1 m away in Slovenia because of the absence of large forest clearings. An earlier study conducted in Slovenia showed that nitrogen concentrations are similar at 1 m and 3 m from the canopy (Skudnik et al., 2014), and we therefore assume that Pb values from the two distances are comparable as well. Following the moss monitoring manual, the sampling locations were at least 300 m away from main roads, villages and industries, except for the samples collected in Ljubljana urban forest (see Berisha et al., 2017 for details). Five subsamples were collected from each site. In the laboratory, the last 3 years of growth of the moss was selected, and an equal quantity (about 0.1 g) was taken from each subsample and combined to form a single sample representative of the site.

The moss species used in Switzerland were *Hypnum cupressiforme* Hedw. (Hc), which mainly occurs in the lowlands, and *Pleurozium schreberi* (Willd. Ex Brid) Mitt. (Ps), which occurs in the Alps. Samples were collected in 1990, 1995, 2000, 2005, 2010 and 2015. Moss samples from 72 or 73 Swiss sites were examined in each collection year, except in 1990 when samples were taken from only 69 sites. Sampling sites were evenly distributed over Switzerland across five biogeographic regions (Jura, Plateau, and Northern, Central and Southern Alps). These biogeographical regions are based on distribution patterns of flora and fauna, and they differ in population density as well as in geographical and meteorological properties such as geological history, elevation and precipitation (Fig. 1, adapted from Gutersohn, 1973). The Pb concentration in moss was measured for each site and sampling year. In 2015 lead isotope ratios were analysed separately for the samples from each site. As the isotope ratios had not been measured previously, the samples from 1990 to 2010 were prepared in 2015 by using archived moss samples that had been dried and stored at room temperature. To reach the amount of moss necessary for the analysis, the moss material was pooled by biogeographic region into five composite (mixed) samples before analysis.

In Slovenia Hc was collected at all sites. *Hypnum cupressiforme* is the most common species in Slovenia and is distributed across very different habitats and climatic regions: alpine in the north-west, continental in the centre, and sub-Mediterranean in the south-west (Kutnar and Martinčič, 2008). Moss samples for the determination of Pb concentrations were collected in 2006 (39 sites), 2010 (54 sites) and 2015 (56 sites). From 2006 the moss sampling sites were spatially connected to the ICP-Forests monitoring network (Level I and Level II; ICP Forests). Sampling locations were evenly distributed throughout the country on a regular 16 x 16 km grid, in 45 plots at forests sites representative of non-urban areas and in 10 plots at sites near ICP-Forests Level II plots (Fig. 1). For the isotope analysis 43 locations from the 2015 sampling event were included in the study. Additionally, we measured the Pb concentration and isotope ratios in samples from 25 sites that were collected in August 2013 within urban forests in the municipality of Ljubljana (Ljubljana urban forest; Fig. 1). For a detailed description of sampling methodology see Berisha et al. (2017).

2.2. Pb concentration and isotopes analysis

Swiss samples from 1990 to 2010 were analysed by several different