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Evaluating the suitability of different environmental samples for tracing atmospheric pollution in industrial areas☆

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ABSTRACT

Samples of lichens, snow and particulate matter (PM_{10}, 24 h) are used for the source identification of air pollution in the heavily industrialized region of Ostrava, Upper Silesia, Czech Republic. An integrated approach that uses different environmental samples for metal concentration and Pb isotope analyses was applied. The broad range of isotope ratios in the samples indicates a combination of different pollution sources, the strongest among them being the metallurgical industry, bituminous coal combustion and traffic. Snow samples are proven as the most relevant indicator for tracing metal(loid)s and recent local contamination in the atmosphere. Lichens can be successfully used as tracers of the long-term activity of local and remote sources of contamination. The combination of PM_{10} with snow can provide very useful information for evaluation of current pollution sources.

1. Introduction

Air pollution and the atmospheric deposition of metals onto natural environments has attracted increasing interest in the past decades (Hernandez et al., 2003; Walker et al., 2003; Zhang and Liu, 2004; Aubert et al., 2006). The deposition of metals is considered a major environmental problem because metals are known to have a significant effect on ecosystems (Bargagli et al., 2002; Agnan et al., 2013) and human health (Pacyna et al., 2009). Compared to other types of environmental pollutants, metals are particularly dangerous because of their ubiquity and persistence (Luo et al., 2015).

One of the most important pollutant carriers in the atmosphere is particulate matter (PM). Particulate matter comes primarily from anthropogenic sources, such as coal-based power generation and industrial activities (e.g., heat generation, iron industry, coal coking, smelting), traffic and re-suspension processes from urban surfaces (Konieczyński et al., 2012). Three types of PM sources can be defined: i) long-distance sources (e.g., particles transported by wind); ii) short-distance sources (e.g., re-suspension of road-deposited sediments); and iii) traffic related sources and other general sources with low influence (Tippayawong et al., 2006). Although efforts have been made to lower industrial emissions, this problem persists with small combustion utilities, e.g., domestic sources. These sources are important, especially during winter, because different fuels are used and are hard to control (Konieczyński et al., 2012). Particulate matter has become an important subject of studies with the urban air quality being of special interest. Some studies (Grynkiewicz Bylina et al., 2005; Wróbel et al., 2000) indicated elevated concentrations of PM_{10} and $PM_{2.5}$ because of the growing amount of traffic, which has had a significant effect on the emission of particulate matter since the 1990s (Zajusz-Zubek et al., 2015).

The main forms of wet atmospheric deposition are vertical deposition (rain and snow) and horizontal deposition (fog and ice accretions) (Voldrichova et al., 2014). Snow is considered to be an ideal medium to monitor the deposition of pollutants from the atmosphere (Cereceda-Balic et al., 2012). Snow sampling allows the geochemical scanning of large areas and provides information regarding current air pollution, while the re-suspension of earlier

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pollution load has no effect because of snow coverage on all surfaces (Gregurek et al., 1998). A relatively high accumulation rate for snow favours investigations of pollutant sources during winter with snow episodes (Rosman et al., 2000). Atmospheric deposition events can be easily sampled (Cereceda-Balic et al., 2012) compared to direct deposition monitoring (Gregurek et al., 1998). The deposition time can be defined from meteorological data (Kuoppamäki et al., 2014). Generally, snowflakes accumulate more inorganic pollutants from the atmosphere than raindrops because of their larger surface area and slower deposition (Cereceda-Balic et al., 2012).

Epiphytic lichens present another suitable sampling strategy for monitoring the atmospheric deposition of metals because they have no roots or well-developed cuticles, which allows them to absorb moisture and nutrients exclusively from the atmosphere (Simonetti et al., 2003). Lichens accumulate soluble elements and insoluble metal-rich particulates largely through (Wolterbeek, 2002) intercellular accumulation and the entrapment of metal particles (Szczepaniak and Biziuk, 2003). Since the 1960s, lichens have been widely used as biomonitors of atmospheric pollution (Conti and Cecchetii, 2001 and references therein) because of their simplicity, cost efficiency, and ability to monitor large areas at any time of the year, which allows spatial and temporal evaluation of the accumulation of pollutants in the environment (Dorrul Demiray et al., 2012). For example, Simonetti et al. (2003) studied the isotope compositions of Pb in epiphytic lichens (*Usnea* and *Bryoria* spp.) in North America and proved that lichens can be effectively used as tracers of atmospheric pollution even at a regional scale. Similar studies were also performed in the Czech Republic. Sucharová et al. (2014) measured the Pb concentrations and Pb isotope compositions in moss samples from sites all across the Czech Republic. The authors demonstrated that the concentration of Pb in moss over the past fifteen years has been decreasing. Nevertheless, 90% of the Czech Republic is still affected by 435 $\mu g\ m^{-2}\ year^{-1}$ of atmospheric deposition of airborne Pb. Sucharová et al. (2014) also examined the surroundings of Ostrava, one of the most polluted areas in the EU. Many studies addressed the advantages of lichens and/or mosses for biomonitoring. Bargagli et al. (2002) found mosses to accumulate higher concentrations of lithophile elements (Al, Cr, Fe, Mn, Ni, and Ti) and atmophile elements (Hg, Cd, Pb, Cu, V, and Zn) in lichen. According to Reimann et al. (1999), lichens reflect the precipitation chemistry only to a limited degree for Ag, Al, As, Bi, Co, Cr, Cu, Fe, (Hg), Mg, Mo, Ni, Pb, (S), V, and Zn. However, inputs either via rain or snow for many elements seems to play an important role in determining the composition of lichen. Mosses reflect the precipitation chemistry for Ag, Al, As, B, Bi, Cd, Co, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Rb, (S), Sr, and V. In general, moss reflects rain chemistry rather than snow.

Stable Pb isotopes are a powerful fingerprinting tool for tracing pollution sources in the environment. This method is based on the fact that natural sources (background Pb derived from weathering bedrocks) and anthropogenic sources have different Pb isotope compositions. Each Pb source has its own distinct isotope composition, so distinguishing individual sources of Pb in an environmental sample is possible (Gregurek et al., 1998; Komárek et al., 2008). The main drawbacks of using Pb isotopes for tracing arise when the sources isotopically overlap or are not well defined. In this case, using only one type of environmental sample to trace anthropogenic inputs may be challenging and inefficient, and different samples are often necessary for source apportionment studies (Sen et al., 2016). Lichens, snow and PM_{10} are subjected to the same sources of anthropogenic pollution and thus should display similar Pb isotope signatures. Because the combination of these samples provides information on airborne pollution in general, investigating the content of metal(loid)s and Pb isotope composition provides a more holistic view on urban pollution (LeGalley et al., 2013). While many authors have focused on analyses of one type of sample (*lichens*: Riga-Karandinos and Karandinos, 1998; Jeran et al., 2002; Simonetti et al., 2003; *snow:* Gregurek et al., 1998; Kuoppamäki et al., 2014; Wang et al., 2015; *PM:* Sharma et al., 2014; Zajusz-Zubek et al., 2015; Padoan et al., 2016) or different types of samples (e.g., Bargagli et al., 2002; Walker et al., 2003; Le Roux et al., 2005; Cloquet et al., 2006; Aubert et al., 2006; Salo et al., 2012; LeGalley et al., 2013), only a few studies have investigated the suitability of different environmental samples for analyses of atmospheric pollution and identified the associated downsides (e.g., Bergamaschi et al., 2002; Dmuchowski et al., 2011).

The main aim of this study is to i) evaluate the suitability of environmental samples (snow, lichens, and PM_{10}) for tracing atmospheric pollution; ii) confirm applicability of samples in different conditions (long-term and short-term pollution, local and distant sources) in highly industrialized areas with many overlapping sources by using concentration and Pb isotope analyses as fingerprints of contamination sources.

2. Material and methods

2.1. Study area

The study area is located in the Moravia–Silesian Region in the Northeast Czech Republic. The landscape forms a valley that is known as the Moravian Gate, which leads from the southwest to the northeast and into the Silesian region of Poland (Fig. 1). Air typically flows through the valley, predominantly from the southwest. This area is considered to be one of the regions with the worst air quality in the EU (Horálek et al., 2007). Anthropogenic pollution in this area mainly results from the heavy steel and coal industries but also from the dense transport infrastructure in the region (Mikuška et al., 2015). During winter, the air quality is highly influenced by emissions from local combustion sources (heating). The city of Ostrava is known for its long mining and smelting history. Black coal mines in the area originate from the 19th century, and three areas currently have a total of 8 active mines and 63 closed mines. The maximum coal production occurred in the 1980s, with a production of approximately 25×10^6 tons of coal (Novák et al., 2003). Additionally, several stationary industrial sources of pollutants (e.g., metals, particulate matter, nitrogen oxides, sulphur dioxide, and benzo(a)pyrene) exist directly in the city or in the close vicinity. The mixing of emissions from multiple sources and the complex atmospheric chemistry and transport patterns means that tracing and quantifying the emissions from different sources by studying the deposition of metal(loid)s in the environment highly challenging.

2.2. Sampling and sample preparation

Sampling sites can be divided into three different transects both in the city of Ostrava and its surroundings. The sites were chosen according to the predominant wind direction and positioned with respect to the main industries in the region. (Fig. 1). Sampling on each site was performed during two sampling campaigns. The first occurred in February 2015, when snowpacks, lichens and PM_{10} filters were collected. The second was performed in June 2015, when a second set of PM_{10} filters was sampled. Snow samples were collected in duplicates from intact snow into 2-L acid-cleaned PET containers avoiding the upper layer which may be affected by dry deposition. The total depth of the snow was between 20 and 40 cm, and the distance between samples at each site was 30–50 m. The duplicates were mixed after melting and acidified by concentrated