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Atmospheric metal pollution records in the Kovářská Bog (Czech Republic) as an indicator of anthropogenic activities over the last three millennia

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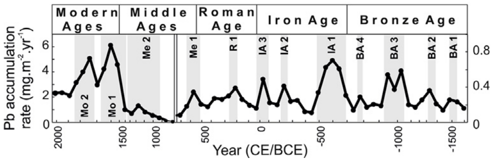
HIGHLIGHTS

- Pb, Cu, As, Ag are useful elements for the reconstruction of atmospheric pollution.
- Metallurgy activities were indicated during Bronze and Iron Ages.
- The onset of intense mining was documented in the late 12th and 15th centuries.
- The last boom of mining in the Ore Mts was detected between 1700 CE and 1830 CE.
- Present-day Pb and As fluxes did not reach such high values compare to previous periods.

GRAPHICAL ABSTRACT



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ABSTRACT

Three peat cores were extracted from the Kovářská Bog in the central Ore Mountains to study anthropogenic pollution generated by mining and metallurgy. The core profiles were ^{14}C dated, and concentrations of selected elements were determined by ICP MS and HG-AAS. Principal component analysis indicated that Pb, Cu, As and Ag may be useful elements for the reconstruction of historical atmospheric pollution. Total and anthropogenic accumulation rates (ARs) of Pb, Cu and As estimated for the last ca. 3500 years showed similar chronologies, and revealed twelve periods of elevated ARs of Pb, As and Cu related to possible mining and metallurgic activities. In total, four periods of elevated ARs of Pb, Cu and As were detected during the Middle and Late Bronze Ages, including a distinct Late Bronze Age pollution event between 1030 BCE and 910 BCE. The Iron Age included three episodes of increased ARs of Pb and As; the first and the most distinctive episode, recorded between 730 and 440 BCE, was simultaneous with the Bylany culture during the Hallstatt Period. The Roman Age was characterized by one pollution event, two events were detected in the Middle Ages, and the last two during the modern period. Enhanced element ARs in the late 12th and 15th centuries clearly documented the onset of two periods of intense mining in the Ore Mountains. Metal ARs culminated in ca. 1600 CE, and subsequently decreased after the beginning of the Thirty Years' War. The last boom of mining between 1700 CE and 1830 CE represented the last period of important metallurgical operations. Late Medieval and modern period metal ARs are in good agreement with written documents. Earlier pollution peaks suggest that local metal production could have a much longer tradition than commonly believed; however, archaeological or written evidence is scarce or lacking.

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1. Introduction

The history of metal mining extends back over the last five millennia (Martínez Cortizas et al., 2016). Metallurgical processes are accompanied by the release of pollution into the atmosphere, and metal-enriched dust and gases are then deposited back to the surrounding environment and recorded in geochemical archives. Rain-fed (i.e. ombrotrophic) peatlands supplied solely from atmospheric deposition are one of the most important continental geochemical archives (Shotyk, 1996). Accumulated organic matter is able to bind metals and metalloids, and if they are not subsequently subjected to post-depositional mobility, peat records enable reconstructions of historical atmospheric pollution over several millennia (e.g. Shotyk, 1996; Shotyk et al., 2002). This approach has been frequently applied in many studies across Europe. Some of these peat record studies focused on reconstructions of historical mining in the vicinity of large ore deposits, for example Sn and Cu deposits in Devon and Cornwall, SW England, UK (Meharg et al., 2012), Pb, Cu, Zn deposits in mid-Wales, UK (Mighall and Chambers, 1993; Mighall et al., 2002a,b; Mighall et al., 2009), Northern Pennine orefield, Leadhills and Wanlockhead in Scotland, UK (Küttner et al., 2014; Mighall et al., 2004; Mighall et al., 2014), Pb, Ag, Cu and Fe deposits in the Vosges Mountains, France (Forel et al., 2010), a medieval site of Pb-Ag metallurgical activities in the Mont-Lozère Massif, France (Baron et al., 2006; Jouffroy-Bapicot et al., 2006), mining activities focused on Au, Pb, Zn, Cu, Ag, Fe and especially Sn deposits in the Iberian Peninsula (e.g. Martínez Cortizas et al., 2002; Pontevedra-Pombal et al., 2013), and Ag, Pb, Zn and Cu deposits in the Harz Mountains, Germany (e.g. Kempter and Frenzel, 2000). In general, these studies have compared metal deposition patterns with known written documents and archaeological evidence of past mining. Most of them have succeeded in extending previous knowledge about mining and smelting at individual sites, or have even detected early mining activities where other evidence was missing (e.g. Forel et al., 2010; Mighall et al., 2009; Mighall et al., 2014). Geochemical analyses of peat cores are sometimes supplemented by pollen and charcoal abundances to evaluate interactions between human activities and the environment (e.g. Mighall and Chambers, 1993; Mighall et al., 2004; Mighall et al., 2017).

In the Czech Republic, bogs have frequently been studied to assess atmospheric pollution over the past 100–200 years and to trace pollution sources (e.g. Mihaljevič et al., 2006; Novák et al., 2003; Vile et al., 2000). Insight into the deeper history of Pb atmospheric deposition was provided by Veron et al. (2014), who analyzed a Holocene-long peat core from the Boží Dar Bog, in the Ore Mountains; however, the temporal resolution of the core was insufficient to document anthropogenic pollution in more detail.

The Ore Mountains, situated on the Czech-German border (Erzgebirge in Germany and Krušné hory in the Czech Republic), are remarkable for their wealth of mineral deposits. They surround NW Bohemia, which has been exposed to continual human activities since the Middle Paleolithic. Despite the long-lasting human presence in this region, the first evidence of settlement in the Ore Mts. is dated to the High Middle Ages (Jančárek, 1971; Wagenbreth and Wächtler, 2013). The harsh climate and short growing season were not favorable for settlement, but prospecting, mining and ore processing activities likely proceeded a long time before, similar to mining activities in the Hartz Mountains (Kempter and Frenzel, 2000 and references therein). The earlier presence of humans in the Ore Mountains is supported by ancient trade routes passing through this mountain range, as well as by archaeological Bronze Age findings dated to the Knovíz culture, such as a foundry site in Místo near Hasištejn Castle, bronze daggers from Černovice near Chomutov and Podhůří near Jirkov, and a bronze sword from Výsluní (Sonnenberg; Blažek and Meduna, 1995). Ore mining and smelting in the mountain area has been archaeologically evidenced since the High Middle Ages (Jančárek, 1971; Wagenbreth and Wächtler, 2013). However, abundantly documented prehistoric settlement, findings of casting devices, and the presence of plentiful metalliferous artifacts in the foothills may indicate ancient demands for local ore sources. Possible ore mining and processing is further supported by an abundance of both Cu and Sn deposits located close to archaeologically documented settlements, especially in the Bohemian part of the Ore Mountains. The lack of archaeological knowledge of the oldest mining could be due to the evidence being erased or destroyed by later activities. According to written sources, a period of intense mining started in the 12th century with a maximum in 16th century, and continued into the 20th century. The total production of the main commodities of the Ore Mts. during the mining history is estimated as 10,000 t of Ag, 300,000 t of Sn, 300,000 t of Pb, 25,000 t of Cu, 150,000 t of Zn, 130,000 t of U and 2,000,000 t of Fe (Wasternack et al., 1997).

We analyzed three geochemical peat profiles from the Kovářská Bog (KOV) in the Ore Mountains with the aim to i) determine the trophic status throughout the peat profile, ii) assess the post-depositional mobility of selected elements, iii) reconstruct historical anthropogenic activities based on geochemical records of immobile metals/metalloids and pollen abundances with respect to local archaeological findings, and iv) compare the results to nearby European sites.

2. Materials and methods

2.1. Site description and sampling

The study site Kovářská (50°26′32 N, 13°4′39 E, 870 m a.s.l.) is an ombrotrophic mire, situated in the Ore Mountains, Czech Republic, on gneiss bedrock (Fig. 1). The bog area is 45 ha, and maximum peat depth is 6.9 m. Mean annual temperature is 5.0 °C, and mean annual precipitation is 924 mm. The bog vegetation is dominated by *Sphagnum*, *Eriophorum vaginatum*, and *Pinus mugo* ssp. *rotundata*.

Three peat cores were collected in lawn microhabitats using a 0.5 m long, 5 cm wide Russian corer, with a maximum distance between the cores of 5 m. The first peat core (KV1) was drilled to the bottom of the bog to the depth of 6.5 m in June 2013. In October 2013, second (KV3) and third (KV4) cores were drilled to the depth of 3 m. All cores were wrapped in plastic, then aluminum foil and stored at 4 °C until analyses.

2.2. Geochemical analyses

Peat cores were sliced into 5-cm sections, dried at 40 °C, milled in an agate mortar and homogenized. The following three different methods of digestion were used to prepare samples for analyses of selected elements.

2.2.1. Digestion for As, Ag and Bi analyses

1 g of the milled peat sample was put into a 50 ml graduated flask with 10 ml of a 1:1 mixture of water and concentrated HCl and HNO_3 (mixed at a 9:1 ratio). Then, the content of the flask was boiled for 10 min, cooled, and diluted to the mark with deionized water.

Digestion efficiency for all elements was 90%, assessed by internal standard Metranal 31 (Analytika) for Bi and As and by international JG 3 standard for Ag.

2.2.2. Digestion for Cu analyses

3 ml of HF (Lach-Ner, 40%) was added to 1 g of milled peat. In the next step, 10 ml of HF (Lach-Ner, 37%) and 1 ml of $HClO_4$ (Lach-Ner, 70%) were added, carefully mixed and moved to a laminar flow-box. The sample was then heated on a hotplate, and after the first white fumes of $HClO_4$ were given off, the solution was mixed with an additional 5 ml of HF (Lach-Ner, 40%) and evaporated. The residue was dissolved with 1 ml of $HClO_4$ and 5 ml of H_3BO_4 (saturated solution) and warmed again until white fumes of HCl appeared. Then, the sample was cooled in the water bath, 5 ml of HCl and 20 ml of deionized water were added and left on a plate until clarification of the solution.