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Application of PAH concentration profiles in lake sediments as indicators for smelting activity

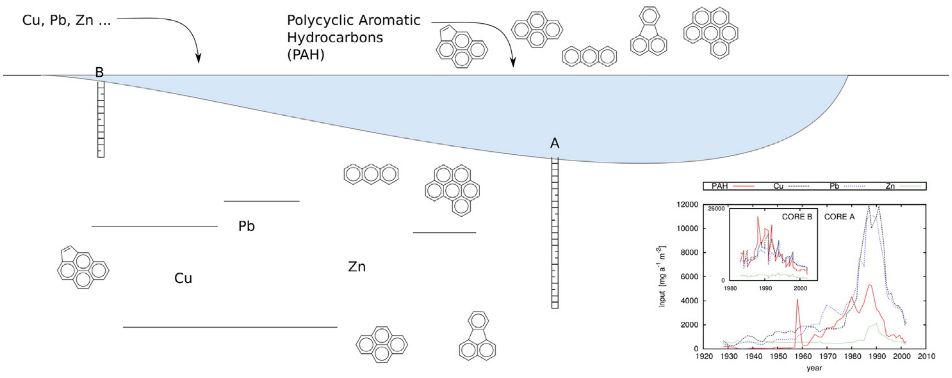
Wiebke Warner [a,*], Hans Ruppert [b], Tobias Licha [a]

[a] Geoscience Centre, Department of Applied Geology, Hydrochemistry Group, University of Göttingen, Goldschmidtstr. 3, 37077 Göttingen, Germany
[b] Geoscience Centre, Department of Sedimentology and Environmental Geology, University of Göttingen, Goldschmidtstr. 3, 37077 Göttingen, Germany

HIGHLIGHTS

- Lake sediments can function as environmental archives.
- PAHs are good selective and sensitive indicators for smelting.
- Diagnostic ratios for PAHs based on partition coefficients are suggested.

GRAPHICAL ABSTRACT



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ABSTRACT

The ability of lake sediment cores to store long-term anthropogenic pollution establishes them as natural archives. In this study, we focus on the influence of copper shale mining and smelting in the Mansfeld area of Germany, using the depth profiles of two sediment cores from Lake Süßer See. The sediment cores provide a detailed chronological deposition history of polycyclic aromatic hydrocarbons (PAHs) and heavy metals in the studied area. Theisen sludge, a fine-grained residue from copper shale smelting, reaches the lake via deflation by wind or through riverine input; it is assumed to be the main source of pollution. To achieve the comparability of absolute contaminant concentrations, we calculated the influx of contaminants based on the sedimentation rate. Compared to the natural background concentrations, PAHs are significantly more enriched than heavy metals. They are therefore more sensitive and selective for source apportionment. We suggest two diagnostic ratios of PAHs to distinguish between Theisen sludge and its leachate: the ratio fluoranthene to pyrene ~2 and the ratio of PAH with $\log K_{OW} < 5.7$ to PAH with a $\log K_{OW} > 5.7$ converging to an even lower value than 2.3 (the characteristic of Theisen sludge) to identify the particulate input in lake environments.

1. Introduction

Policyclic aromatic hydrocarbons (PAHs) and heavy metals are ubiquitous environmental toxics (Sverdrup et al., 2002). Haykiri-Acma et al. (2011), Erlenkeuser et al. (1974) and Bertine and Goldberg (1971) proposed that increasing coal/lignite combustion, and the resulting fly ash, will increase the mobilization of heavy metals. PAHs are the most stable form of hydrocarbons due to their low hydrogen to carbon ratio (Manahan, 2010). They are typically of anthropogenic origin, formed during the incomplete combustion of mobile, domestic, industrial and fossil energy sources (Ravindra et al., 2008). Natural sources of PAHs,

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* Corresponding author.
E-mail address: wwarner@geo.uni-goettingen.de (W. Warner).

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such as volcanic eruptions or non-anthropogenic wildfires, are difficult to quantify (Wild and Jones, 1995). Low molecular weight PAHs undergo a worldwide atmospheric dispersion, while PAHs with higher molecular weight are mainly associated with particulate matter (Subramanyam et al., 1994). Very low biodegradation of PAHs under nutrient-low and anoxic conditions was observed, especially for those with high molecular weight (Breedveld and Sparrevik, 2000).

Due to their persistence (Schneider et al., 2001) and low mobility (Malawska et al., 2006), PAHs have been used as environmental archives (Thuens et al., 2013). With their high temporal resolution, sediment cores can be successfully utilized for the reconstruction of historical PAH deposition (Simcik et al., 1996; Hites et al., 1980). The sediment cores of lakes not only show atmospheric contamination, but also the contamination history of the catchment area; even single fire events can be detected (Denis et al., 2012). Therefore, in the last two decades the PAH distribution in sediment cores from rivers, lakes and estuary/marine profiles have been increasingly studied. In order to predict the historical atmospheric input of PAHs and to quantify a specific source, such as the PAH content in fly ash particles, PAH studies are typically conducted on sediment cores taken from lakes in remote areas with low anthropogenic influence (Denis et al., 2012; Rose and Rippey, 2002). Few studies have investigated sediment cores taken from lakes that are supplemented by rivers with several anthropogenic sources of input (Vrana et al., 2001). Studies which compare PAH data to heavy metals on lake sediments are rare (Müller et al., 1977). Exact source apportionment of PAHs is difficult, but the application of diagnostic ratios is a common method and can be usefully applied (Ravindra et al., 2006a, 2006b; Oda et al., 2001; Grimmer et al., 1981). The majority of studies on the distribution patterns of PAHs deal with their occurrence in the atmosphere in order to predict air quality and health risks in metropolitan areas (Dvorská et al., 2012; Zhang and Tao, 2009; Menichini, 1992).

In order to exploit PAHs and extend their applicability in environmental archives, we investigated sediment cores from Lake Süßer See in the Mansfeld area (Germany), which was influenced by centuries of copper shale mining and smelting. Due to the fact that both PAHs and heavy metals were emitted in high amounts from different sources, this site is ideal for deriving diagnostic ratios as indicators and for comparing the enrichment factors of PAHs relative to heavy metals. Additionally this study aims to check the sensitivity of PAH enrichment relative to metals and organic matter.

2. Materials and methods

2.1. Description of sampling site

Lake Süßer See, with a surface area of 2.68 km^2 and a catchment area of 160 km^2, is located 30 km west of Halle (Germany) within the Mansfeld geosyncline, an outcrop of copper shale (Becker et al., 2001), see Fig. 1. The River Böse Sieben and some smaller spring streams contribute to the Lake's inflow. Mining and smelting are registered for 800 years in the Mansfeld area (Hartwig et al., 1999). Nearby smelting sites, Helbra and Eisleben, were opened in 1880 and reached their maximum production in the first quarter of the 1980s (Schreck, 1996). Since the installation of gas washing technology in 1910, Theisen sludge, a fine grained contaminant loaded residue from copper shale mining, was produced and deposited in a few open dumps. They were sealed in 1992 with geopolymers. Altogether approximately 220,000 t of Theisen sludge were deposited in the Mansfeld area. The Sludge reached Lake Süßer See via the riverine system of Böse Sieben or via atmospheric input. The Mansfeld area is one of the driest regions in Germany. It has a precipitation rate of 490 mm per year, with heavy rain events in summer (averaged 60 mm in June, www.dwd.de). From 1949 to 1990, during former GDR, extensive lignite combustion should be considered as an important atmospheric input factor of PAHs and heavy metals (Thuß et al., 1995).

The remains of mining and smelting were deposited in more than ten previously open dumps in Helbra and Eisleben. Contaminants from these remains could reach Lake Süßer See via deflation by wind of dried Theisen sludge, erosion of the fine-grained sediments during heavy rain events, or leaching of contaminants from Theisen sludge. The contaminants then undergo dispersion in both ground and surface water. Especially during times when extensive mining and smelting were taking place, the dumps released Theisen sludge into surface waters. Heavy metals, transported as ions, are weakly bonded to the solid phase (Concas et al., 2006). PAHs, particularly those with a high molecular weight, are bonded to the particles (Readman et al., 1984). Nowadays, approximately 30,000 t of metalliferous sediments are spread over the catchment area of the River Glume, which discharges into the River Böse Sieben and enters Lake Süßer See (Lorenz, 1993).

2.2. Sampling

Core A was taken from the center of Lake Süßer See, while core B was collected from the litoral zone close to the main contributor River Böse Sieben, see Fig. 1. Core samples were taken in June 2013 using blank free tools and were stored in an oxygen-free environment at 4 °C. The extraction was carried out within four weeks. One half of each core was used for multi-element analysis and the other half for PAH analysis.

2.3. Chemicals

For ICP-OES analysis subboiled hydrofluoric acid (40%) (p.a. quality), nitric acid (65%), hydrochloric acid (37%), sodium hydroxide (for sodium hydroxide solution) and sodium sulfate were purchased from Merck (Darmstadt, Germany) and hydrochloric acid (70%) from Carl Roth (Karlsruhe, Germany). For sulphur and carbon analysis, tungsten and iron from Eltra (Haan, Germany) were used. As an internal standard for organic analysis a mixture of acenaphthene D10, benzo(*g*,*h*,*i*)-perylene D12, chrysene D12, naphthalene D8, perylene D10, phenanthrene D10 and pyrene D10 was purchased from Dr. Ehrenstorfer (Augsburg, Germany) (concentration 15 ng μL^{-1}). Isohexane was purchased from Fischer Scientific (Schwerte, Germany) and ultrapure water was obtained from a combined water purification system consisting of Elix 5 and Milli-Q Gradient A10, both from Merck Millipore (Schwalbach, Germany).

2.4. Sample preparation and analysis

Sediment cores were divided into 2 cm segments. For zinc, lead and copper analysis, samples were dried at 105 °C until a constant weight was reached. Digestion of samples was carried out as follows: 200 mg of homogenized dried sample were weighed into teflon vessels and treated with a mixture of 3 mL hydrofluoric acid, 3 mL perchloric acid, and 2 mL nitric acid at 150 °C for 15 h under pressure. During the following vaporization phase, vessels were heated at 180 °C for 10 h. The residue was dissolved in a dilute mixture of nitric and hydrochloric acid and further treated at 150 °C for 3 h in sealed teflon vessels. For more detail see Ruppert et al. (2013).

For PAH analysis, 500–1000 mg of a wet sample were used. Its water was captured using sodium sulfate in order to avoid incompatibility with the extraction solvent. The samples were transferred into teflon vessels, 5 μL internal standard and 3 mL isohexane added. The vessels were closed tightly and heated in a CEM Mars Express microwave at 1600 W (10 min preheating to 130 °C, 20 min extracting at 130 °C). The microwave extraction was repeated three times. The extracts were then combined and stored at −18 °C until analysis.

Element analysis for zinc, lead and copper was carried out on the digested sample by using ICP-OES Fissions Maxim I 109 ARL. All results were drift and blank corrected. Sulphur and carbon analysis was performed on an Eltra Metalyt CS 100 RF by adding elementary tungsten and iron to 20–100 mg of each sample and heating it to 1400 °C. PAHs