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Effect of depositional regimes on polycyclic aromatic hydrocarbons in Lake Bled (NW Slovenia) sediments

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) were measured in sediment cores from two contrasting depositional regimes in urban Lake Bled (NW Slovenia). The concentration of PAH in surface sediments, mostly derived from combustion, was higher in Zaka Bay where bottom waters are permanently oxic, than in the western basin where bottom waters oscillate between suboxic and anoxic (1930 vs. 1150 ng PAH g^{-1} dry weight (dw), respectively). This pattern is the reverse of what might be expected if PAH were to preferentially degrade under oxic conditions. Two PAH from non-combustion sources, perylene and retene, are also present in the sediments. Post-depositional diagenetic formation of perylene appeared to occur only in anoxic sediments. Differences in the source of sedimentary organic matter (autochthonous vs. allochthonous) is probably not a major factor in perylene formation, since the two locations have markedly different sources of organic matter but quite similar concentrations of perylene in deeper sediments, ranging from 250 to 350 ng g^{-1} dw. Thus, redox conditions may play a role in perylene generation. On the other hand, redox conditions in general can not be the only or even the major factor affecting the fate of sedimentary PAH since uniform compositions and depth distributions for pyrolytic PAH were observed in both cores, in spite of the two locations differ in redox, mixing and biota conditions. Thus, degradative loss of PAH is unlikely in Lake Bled sediments.

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) belong to the group of Persistent Organic Pollutants (POP). PAH are hydrophobic compounds typically containing from two to six fused benzene rings. Their production is mainly associated with high-temperature pyrolysis of fossil or biomass fuels and low-temperature catagenesis. Several PAH are also formed from biogenic precursors during early diagenesis (Wakeham et al., 1980; Meyers, 2003). Most PAH are relatively recalcitrant and persist in the environment. Because they are semi-volatile, there is continual transfer between the atmosphere and the Earth's surface. Consequently, PAH are found in all compartments of the environment (i.e., atmosphere, waters, sediments, soils, biota) in urban and remote settings (e.g., Fernandez et al., 2000; Wakeham et al., 2004, and references therein). Some PAH are toxic, carcinogenic and/or mutagenic and because of this potential human health impact are included on the US EPA Priority Pollutant List, resulting in increased environmental attention in recent years.

Several biological, chemical and physical factors influence PAH behavior and fate in the environment. PAH concentrations may be attenuated by biodegradation and chemical oxidation in sediments where biological or physical mixing exist (e.g., Arzayus et al., 2002; Quantin et al., 2005), although association of PAH with sedimentary mineral and organic matrices may reduce the extent of degradation (Gustafsson and Gschwend, 1997). Microbial degradation is now considered as one of the more important processes leading to the decrease of PAH concentrations in sediments. Whereas it had previously been thought that PAH were degraded only under aerobic conditions, studies have now confirmed anaerobic degradation as well, potentially mediated by denitrifying and sulfate reducing bacteria (Coates et al., 1997; Arzayus et al., 2002).

The aim of the paper is to investigate the behavior and fate of PAH in lacustrine sediments characterized by contrasting redox conditions. Thus, two sediment cores from Lake Bled (Slovenia) were studied, one representing oscillating but predominantly suboxic/anoxic conditions and the other deposited under permanently oxic conditions. Concentrations of parent and alkylated PAH were measured. Diagenetic formation of perylene and retene was studied in detail, and several combustion-derived PAH isomer ratios were calculated to assess the effect of depositional regimes on PAH distributions. Overall, depth distributions of PAH in Lake Bled provide a means of evaluating the effects of redox that could reflect a potential for biodegradation and/or chemical oxidation of PAH.

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These issues are particularly relevant for transport and fate of PAH, ecotoxicological and health impact and bioremediation strategies.

2. Materials and methods

2.1. Site description and sampling

Lake Bled (46° 22′ 30″ N, 14° 07′ 30″ E) is an urban glacial subalpine lake situated at an elevation of 475 m above sea level (NW Slovenia, Fig. 1). The lake has a surface area of 1.47 km^2 and can be divided into two basins that are separated by an island; a deeper western basin (depth of 30 m), and a 24 m deep eastern basin. A shallow embayment in the western basin (Zaka Bay) is approximately 15 m deep. Lake Bled has two surface inflows (Misca and Solznik Creeks) and one outflow (Jezernica Creek).

A modified Kajak–Brinkhurst gravity corer equipped with a 70 × 6 cm plexiglass tube was used to collect sediments. Two cores were collected in 2000 and represent distinct depositional regimes. The western basin sediments are deposited under oscillating oxic/suboxic/anoxic bottom water conditions (Cermelj et al., 1996; Muri and Wakeham, 2006), while Zaka Bay sediments are deposited under permanently oxic bottom waters (Ogrinc et al., 2002; Muri and Wakeham, 2006). Sediments were extruded in the field and cut into 1-cm slices. All utensils and glassware were pre-rinsed with distilled water and organic solvents to prevent contamination. Core sections were stored in glass jars, freeze-dried, homogenized and stored frozen until further analyses.

2.2. Analyses

Fourteen parent (non-alkylated) PAH [i.e., phenanthrene + anthracene (Ph + An), fluoranthene (Fl), pyrene (Py), benz[*a*]anthracene (BaA), chrysene + triphenylene (Ch + Tr), retene (Re), benzofluoranthenes [b and k isomers] (BF), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), perylene (Per), indeno[1,2,3-*cd*]pyrene (IndP), benzo[*g,h,i*]perylene (BghiPer), dibenzanthracenes (DiBAn), and coronene (Cor)] and methyl- and dimethyl-phenanthrenes were measured in the sediments as described by Muri et al. (2003). Briefly, dry sediment samples were spiked with deuterated PAH (phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) and Soxhlet extracted with dichloromethane. Extracts were then rotary evaporated, solvent-exchanged to hexane and fractionated on 5% deactivated silica. Following elution of aliphatic hydrocarbons with hexane, PAH were eluted using additional hexane and hexane/toluene (3:1). PAH were analyzed with a gas chromatograph coupled to a mass spectrometer. A DB-5 column (30 m, 0.25 mm i.d., 0.25 μm film thickness) was used for compound separation with helium as carrier gas. Selected ion monitoring (SIM) mode with an ionization energy of 70 eV was used for PAH determination. PAH identification and quantification was based on the *m/z* peaks corresponding to the molecular weights of the individual PAH. To support the quality of the data, several QA/QC procedures were performed. Procedural blanks were performed with each set of six samples. Blanks contained negligible or undetectable concentrations of individual PAH. Precision of the method was also assessed. Real sample replicate analyzes yielded relative standard deviations of up to 10%. Concentrations of PAH were calculated relative to the deuterated surrogates. The concentrations were thus corrected for recovery.

For organic carbon (OC) analyses, HCl (1 M) was added to dry sediment samples until effervescence ceased. OC concentrations were then determined with a CHN elemental analyzer (Carlo Erba EA 1108) at a combustion temperature of 1020 °C. Blank samples and standard samples with known elemental composition were used for QA/QC. Precision of the method, based on replicate analyzes of real samples, was from 3% to 5%.

The sediments were dated radiometrically. Details on the analytical procedure can be found in Muri et al. (2002). Briefly, a γ-ray spectrometer equipped with a high purity Ge well-type detector was used to measure the ^{210}Pb and ^{137}Cs activities in each sediment slice. Sedimentation rates were obtained on the basis of unsupported ^{210}Pb activity levels using the constant rate of supply (CRS) model. The dating was additionally confirmed by ^{137}Cs. The Zaka Bay core was, while the western basin core was not age-dated in this study. In the former core, sediments >8 cm depth yielded an average sedimentation rate of 4.5 mm yr^{-1} (Jeran, Z., Personal communication), while for the latter an average sedimentation rate of 2.4 mm yr^{-1}, determined by Cermelj et al. (1996), was used for age assessment.

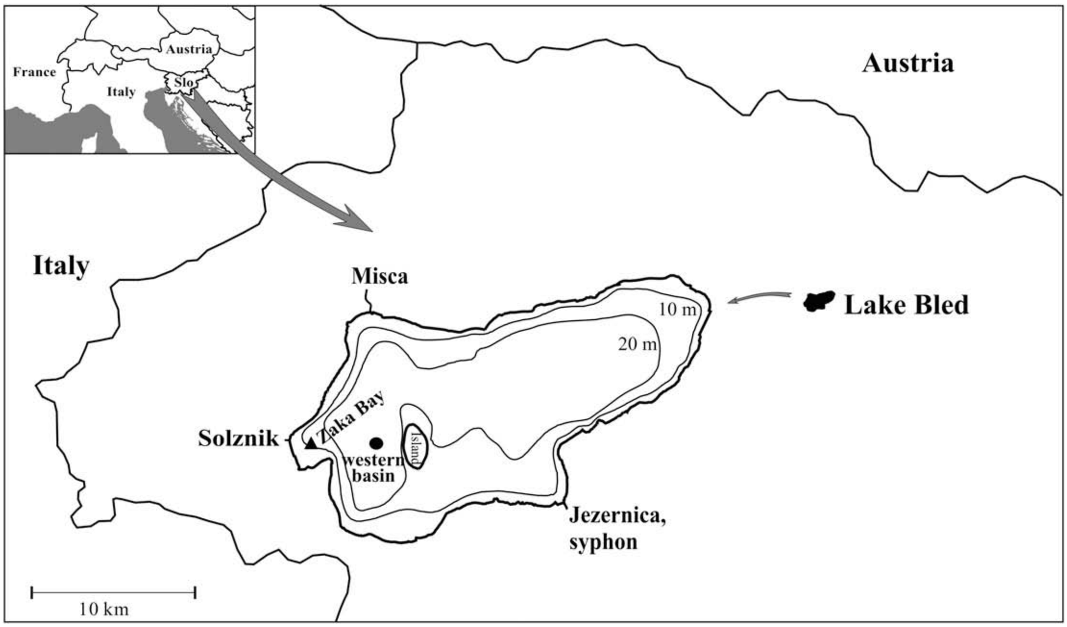

Fig. 1. Environmental setting of Lake Bled and location of the sampling points (the western basin [circle] – oscillating redox conditions; Zaka Bay [triangle] – oxic conditions).