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Material transport between the atmosphere and sediment of the Lake Balaton

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Abstract

A monitoring system was developed to gain information on the present level of pollutants in the Lake Balaton, Hungary. Determination of 13 polycyclic aromatic hydrocarbons (PAHs) and inorganic pollutants (mostly toxic metals) in aerosol, precipitation and sediment samples was carried out. The aim of collecting aerosol and precipitate samples in the same site at the same period was to determine the distribution of elements in two depositions. For the fractionation by particle size, aerosols were sampled by a cascade impactor. A simple three-stage sequential leaching procedure was applied to establish the distribution of metals among environmentally mobile, bound to carbonates and oxides, and environmentally immobile, (bound to silicates) fractions in aerosols. Sediment samples were collected from 17 different sites inside of the lake and 10 sites at harbors at 30–70 cm in depth. Core samples were cut to 10-cm pieces, dried at room temperature, and finally passed through a 63-μm sieve. Total concentrations of elements were determined by atomic absorption spectrometry (AAS) after an acidic digestion. The concentrations of PAHs were determined by HPLC method with fluorescence detection.

In aerosol samples collected from September 6, 2002 to January 26, 2003, concentration of Cd was <0.1 $\mu g/m^3$, and the majority of Cd has been found in the mobile fraction. Cadmium was associated to particles between 0.25 and 2 μm indicating the anthropogenic origin. Similar distribution of Pb was obtained in all seasons, and the highest concentration of Pb was found as 8.6 ng/m^3 in particle size of 0.7 and 1.4 μm. Results of total concentration of elements of bottom sediments of the Lake Balaton and harbors were compared to Interim Sediment Quality Guideline (ISQG) values and the Probable Effect Level (PEL) values. Data showed that the average concentrations of elements were usually less than those of ISQGs and other background data for soils and geochemical values. The sediment is not polluted and its disposal is feasible. There is no direct correlation between the concentration of elements deposited onto the surface of the lake from dry and wet deposition and the upper part of the sediment. So, from the budget of the deposition, the concentration of elements in the upper layer of the sediment cannot be predicted.

Seasonal changes of the concentration of PAHs in aerosol was observed, samples collected at winter contained the highest values. In December–January 2002/2003, the wet deposition was found as 64 $\mu g/m^2$ period. Among the individual compounds, the wet deposition rate of phenantrane, fluoranthene and pyrene was dominant, while for dry deposition, these compounds were fluoranthene and pyrene. The concentrations of ΣPAHs found for all sites and depth of sediment samples ranged from 11 to 1734 μg/kg dry weight with an average of 132 μg/kg. These values represent a quite low pollution level compared to other sediment with anthropogenic influence. Based on the results, it can be definitely confirmed that the chemical quality of the water and sediment of the Lake Balaton is satisfactory.

Keywords: Polycyclic aromatic hydrocarbons (PAHs); Metals; Precipitation; Atmospheric aerosol; Dry and wet deposition; Sediment

1. Introduction

Lake Balaton is the largest lake of Central Europe with a surface of about 600 km^2 and an average depth of 3.25 m. The shallow lake is one of the most valuable and important recreation zones. Monitoring of the lake concerning the determination of organic and inorganic pollutants is fundamental to the solution of environmental problems. Sediments are basic components of the lake, as they provide foodstuffs for living organisms and serve as sinks for harmful chemical species. It is necessary to know the mechanisms of transport of trace pollutants in lakes to understand their chemical cycles in nature.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants of environmental concern, by-products from

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the incomplete combustion of fossil fuels and wood. Residential heating, coke production, incineration and internal combustion engine are major sources of PAHs. Since the compounds adsorbed on the particles may remain in the atmosphere for several days, PAHs can be used as tracers of anthropogenic activity. For evaluation of the transport processes, the source of the pollutants deposited into the Lake Balaton is of importance. Most of the pollutants are being transferred into the aquatic ecosystem, and for the complete picture, the investigation of atmospheric aerosols is also of great significance. The wet deposition rate of PAHs can be calculated from the concentration of pollutants in precipitation. More complicated to ascertain the dry deposition rate, since along with the concentration of PAHs in aerosol, distribution of PAHs in different particle size and the dry deposition velocity on the water surface have to be also determined. PAH compounds deposited from the atmosphere in the natural waters can be accumulated in the upper part of sediments due to its low volatility. From the sediment, either they can be removed by the uptake of plants or microorganism, or they can penetrate into the deeper part of sediments. It is already proved that several species of algae and microorganism are able to decompose the PAHs, primarily the small molecular weight compounds, from the top layer of the sediment [1]. For the interpretation of the transport processes and sources, the knowledge of the individual distribution of PAHs is of importance, since a given source usually contains a characteristic pollution fingerprints. If similar distributions are found in the different receptor points, the contribution of a single source can be similar among the points. On the other hand, the different distribution indicates different sources, as well as decomposition and other processes can be taken place. Previous studies showed that slight amount of PAHs deposited into the Lake Balaton by atmospheric deposition: 40 kg/year with dry deposition and 170 kg/year with wet deposition [2]. Black River, OH USA, was contaminated with PAHs from coke ovens and five cores were analyzed for 18 PAHs [3]. The total PAH concentrations of cores ranged between 250 and 0.1 mg/kg. Chemical Mass Balance (CMB) modeling of PAH sources showed that the coke oven contribution was minimal (20–30%).

In a dated sediment core of the Huzenbachersee (Black Forest, Germany), the chemical speciation of several metals (Mg, Ca, Al, Fe, Mn, Cu, Pb, Cr, Zn and Cd) was evaluated applying sequential chemical extraction [4]. In the sediment core, two distinct periods of increased amounts of Pb, Zn, Cd and Fe were found indicating the industrialization period. Chromium, Mn, Ni, V and U have been determined in inter-tidal sediments collected from locations along the Cumbrian coast [5]. Elevated levels of Cr (39.5±0.9 mg/kg), V (33.0±0.6 mg/kg) and U (39.0±1.2 Bq/kg) were observed at Whitehaven, whilst concentrations of Mn were highest in samples from more northerly locations. The Cr contamination might be also arisen from chemical manufacturing, whereas the V was thought to originate from oil spillage. The sediment–water system can be divided in three parts: the oxic layer, the anoxic layer and the oxic–anoxic interface [6]. Data show that trace metals like Cu, Zn and Cd occur as sulphides in marine and estuarine anoxic sediments. Calculations prove that organic complex forming is unlikely and the dominant species are sulphide and bisulphide complexes. The oxic–anoxic interface plays the major role in the potential flux of trace metals from the sediments; however, this interface is not well studied. Precipitate and aerosol samples were collected in the same site at the same period inside and around the Lake Balaton to determine the distribution of elements in two depositions [7]. Calculations were affected by the dry deposition velocities and some emission sources along with the air trajectory. The comparison of dry and wet depositions showed that the ratio of D_{dryt}/D_{wet} was significant, in particular, for Fe, Al, and Cu, indicating that the dry deposition played an important role [7].

In our work, a monitoring system was developed to gain information on PAH and metal pollutants in aerosol and sediment samples. A fractionation of elements in aerosol samples by particle size and chemical bonding was carried out. The three-stage sequential leaching procedure was applied to establish the distribution of metals in atmospheric aerosol. Determination of PAHs from aerosol and sediment samples was carried out by HPLC method and the size distribution of aerosol was also investigated.

2. Experimental

2.1. Sampling and sample preparation

Aerosol and precipitation samples were collected at three sites located around the Lake Balaton: Keszthely (A1), Tihany (A2) and Siófok (A3) (Fig. 1). The surrounding areas of these summer resort towns are free from industrial activity. The main local sources of anthropogenic air pollutions are traffic (in summer) and residential heating (in winter). Due to the continental climate of Hungary, the temperature is between −10 and 30 °C. Aerosol samples were collected from April 2002 to April 2003, on quartz fiber filters (Whatman QM-A) of 4.7 cm diameter for PAH analysis and on Teflon filters of 5 cm diameter (pore size 0.45 μm) for elemental analysis, using low volume sampler (1.2 m^3/h). The samplers were operated simultaneously for 46 or 72 h and half-monthly samples were analyzed together. For the determination of the size distribution of PAHs and elements, aerosol was also collected on aluminium and cellophane foils, respectively, by an eight-stage Berner-type low-pressure impactor (31.2 m^3/h, cut-off diameters: 0.0625–8 μm) continuously in Tihany. Each filter was placed in a clean Petri-dish during transport and storage. The aluminium foils were equilibrated in a humidity-controlled atmosphere for 24 h before and after sampling and weighed to obtain the Total Suspended Particle (TSP)