ELSEVIER

Atmospheric deposition of polycyclic aromatic hydrocarbons on the Lake Balaton, Hungary

Eszter Bodnár, József Hlavay*

Department of Earth and Environmental Sciences, University of Veszprém, 8201 Veszprém, P.O. Box 158, Hungary

Abstract

The concentration of polycyclic aromatic hydrocarbons (PAHs) in atmospheric precipitation and aerosol samples was monitored on the Lake Balaton to examine the seasonal variations and depositions. Samples were collected at Tihany located on the north part of the Lake Balaton between April 2002 and April 2003. Aerosol particles were sampled on quartz fiber filters using low volume sampler (1.2 m^3/h). For the determination of the size distribution of PAHs, aerosol was collected on aluminium foils by an eight-stage Berner-type low-pressure impactor (31.2 m^3/h, cutoff diameters: 0.0625–8 μm). The dry deposition velocities on water surface as a function of the particle diameter were estimated. The collection of rain and snow samples was performed by an automatic wet-only sampler. The seasonal mean concentration of the ΣPAHs in precipitation was found as 149, 96, 586, and 1136 ng/l in spring, summer, autumn, and winter, respectively. In the atmospheric aerosol samples, the seasonal mean concentration of the ΣPAHs varied from 3.2, 1.7, 6.2, and 31 ng/m^3 in spring, summer, autumn, and winter, respectively. It was found that PAHs generally showed the maximum concentration in the 0.25- to 1.0-μm size range in every season. Wet (280 μg/m^2×year) and dry (70 μg/m^2×year) deposition rates were calculated, and pollution loading of PAHs from the atmosphere to the Lake Balaton was obtained as 170 kg/year of wet and 40 kg/year of dry deposition.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Polycyclic aromatic hydrocarbons (PAHs); Precipitation; Atmospheric aerosol; Dry and wet deposition; Particle size distribution

1. Introduction

The environmental analysis of polycyclic aromatic hydrocarbons (PAHs) is of importance since decades due to their toxic and carcinogenic properties and their quite long lifetime in the environment. PAHs are produced mainly by incomplete combustion of organic matter. Major sources include emissions from fossil fuel combustion, forest fires, industrial fumes, oil spills, and road construction materials. The distribution of individual PAH compounds is characteristic on a given source. Because of the stability of the fused aromatic rings, they can be widely dispersed by atmospheric transport, and PAHs can act as tracers for sources. As semivolatile organic compounds, PAHs are transported in the atmosphere as gas and/or particulate phases and scavenged according to various processes: (i) wet deposition, where gas and particle phase PAHs are incorporated into cloud droplets (in-cloud scavenging) and removed by rain and snow (below-cloud scavenging), (ii) dry deposition, which results from the direct impaction of particle phase PAHs; (iii) air–water exchange, they might be adsorbed when facing large aquatic systems.

The wet deposition rate of PAHs can be directly calculated from the concentration of pollutants in precipitation. The estimation of the dry deposition rate is more complicated. However, examples can be found on the direct measurement of dry deposition of pollutants on different surfaces [1–5], while it is more general to calculate it from the concentration of PAHs in aerosol samples and the dry deposition velocity [6–11]. The estimation of dry deposition velocities demands a quite deliberate task, because it is influenced by many factors, such as the size of the particles associated with PAHs, the characteristic and state of the depositional surface, the conditions of the atmosphere (temperature, wind speed, stability, relative humidity), and they may vary by orders of magnitude. Horstmann and McLachan [12] found the particle-phase mean dry deposition velocities of 6 PAH compounds as 0.73 cm/s on

deciduous forest and 0.050 cm/s on coniferous forest, but several authors calculated with a 0.34 cm/s value [6,8–11]. It is known that dry deposition velocity is greatly dependent upon the particle size of aerosol. Dry deposition of coarse particles (>1 μm) in the gravitational space takes place by sedimentation, and the velocity increases by the particle size with the Stokes law. In the accumulation mode (0.1–1 μm), the dry deposition of aerosol particles goes for a minimum value because neither sedimentation nor diffusion is efficient. In the nucleation mode (<0.1 μm), dry deposition velocity increases again with decreasing particle size due to the Brownian movement. Earlier, it was found that the main fraction of PAH compounds was bound to aerosol particles <1 μm [13,14]; however, some authors found that significant amount of PAHs could be associated to the particles in the larger size range too [5].

Recently, a monitoring system set up around the Lake Balaton was developed, and the transport of PAHs between the atmosphere and hydrosphere has been estimated. In this work, the concentration of 13 EPA priority PAHs was determined in precipitation and aerosol samples collected at Tihany site. Using a cascade impactor, the size distribution of particle phase PAHs in eight fractions was also determined, and the atmospheric wet and dry deposition rates were calculated.

2. Experimental

2.1. Sampling and sample preparation

Atmospheric samples (aerosol and precipitation) were collected at Tihany located on the north part of the Lake Balaton. The sampling site was built up on a hill separated from a busy road of the village about 200 m. The surrounding areas of this summer resort village (<1500 inhabitants) are free from industrial activity. The main local sources of anthropogenic air pollution 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 taken on quartz fiber filters (Watman QM-A) of 4.7-cm diameter using low volume sampler (1.2 m^3/h). 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, aerosol was also collected on aluminium foils by an eight-stage Berner-type low-pressure impactor (31.2 m^3/h, cutoff diameters: 0.0625–8 μm) for 168 h in Tihany. The aluminium foils were equilibrated in a humidity-controlled atmosphere 24 h before and after sampling and weighed to obtain the total suspended particle (TSP) concentration. The collection of rain and snow samples was performed by an automatic wet-only sampler with a cross-sectional area of 452 cm^2. The precipitation was collected into a glass beaker through a glass funnel.

All the sample preparations were carried out as published earlier [15]. QM-A filters containing aerosol phase PAHs were extracted in acetone (Super Purity Solvent, Romil, England) in an ultrasonic bath, the extracts were then cleaned using octadecyl–silica solid-phase extraction cartridges (Bakerbond, J.T. Baker, USA). Aluminium foils (Berner-impactor) were extracted in dichloromethane (Super Purity Solvent, Romil), the extracts were purified on octadecyl–silica solid-phase extraction cartridge, and the solvent was changed to methanol (Super Purity Solvent, Romil) [16]. Preconcentration of PAHs in precipitation samples was performed by solid-phase extraction cartridge (Bakerbond, J.T. Baker) filled with 500 mg cyclohexyl packing using propane-2-ol (Super Purity Solvent, Romil; sample/propan-2-ol, 4:1 v/v%) as organic modifier and dichloromethane followed by methanol as eluent [17,18].

2.2. Analysis of PAH compounds

Separation and quantification of the 13 PAH compounds as fluorene (Flu), phenanthrene (Phen), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), benz(a)anthracene (B(a)ant), chrysene (Chry), benzo(b)fluoranthene (B(b)fluo), benzo(k)fluoranthene (B(k)fluo), benzo(a)pyrene (B(a)pyr), dibenz(ah)anthracene (Dib.ant), benzo(ghi)perylene (B.per), indeno(123-cd)pyrene (Ind)) were carried out by HPLC method with fluorescence detection [16]. For analysis of PAHs, HPLC purity acetonitrile (Romil) and water (Milli-Q water purification system, Waters, Milford) were applied. Eluent was composed as follows: linear gradient from 40 v/v% acetonitrile in water to 100% acetonitrile in 20 min, then 100% acetonitrile for 15 min with a flow rate of 1 ml/min. Separation was performed on a LiChrospher PAH, 250×4 mm, 5 μm polymeric type C$_{18}$ packing column. Waters HPLC system equipped with a Rheodyne 7125 injector (sample volume 20 μl) and Waters 470 programmable fluorescence detector were used for detection. Data acquisition and processing were carried out by Maxima 820 chromatography software. Standards as PAH mixture of 610-M (Merck) were used. Blanks were carried out without PAH compounds, and concentrations were found under the limit of detection (LoD). Recovery of PAHs ranged from 64% (Flu) to 94% (Ind) in the case of aerosol samples and from 43% (Flu) to 87% (Chry) for precipitation samples [16]. The values were adjusted accordingly. No certified reference materials were available on PAH of aerosol samples. Recently, the efficiency of the sonication of the aerosol samples was investigated using different extraction parameters, and the volume of extracting solvents and the number and duration of extraction were optimized for the estimation of the accuracy [15]. Different factors affecting the recovery of PAHs from precipitation, such as the conditioning of the SPE cartridge, the addition of organic modifiers to the sample, the flow-rate of the sample loaded on the cartridge with different organic