



# Passive sampling: An effective method for monitoring seasonal and spatial variability of dissolved hydrophobic organic contaminants and metals in the Danube river



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## ABSTRACT

Application of passive samplers is demonstrated for assessment of temporal and spatial trends of dissolved polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and priority metals in the middle stretch of the Danube river. Free dissolved concentrations of PAHs, measured using SPMD samplers, ranged from 5 to 72 ng L<sup>-1</sup>. Dissolved PCBs in water were very low and they ranged from 5 to 16 pg L<sup>-1</sup>. Concentration of mercury, cadmium, lead and nickel, measured using DGT samplers, were relatively constant along the monitored Danube stretch and in the range <0.1, <1–20, 18–74, and 173–544 ng L<sup>-1</sup>, respectively. Concentrations of PAHs decreased with increasing temperature, which reflects the seasonality in emissions to water. This has an implication for the design of future monitoring programs aimed at assessment of long term trends. For such analysis time series should be constructed of data from samples collected always in the same season of the year.

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## 1. Introduction

In December 2000 the European Union adopted the Water Framework Directive (WFD) to secure water resources for future generations (EU, 2000). In the implementation process of the WFD, all EU member states are required to perform trend monitoring on several pollutants priority substances in surface water that tend to accumulate in sediment and/or biota in surface water (EU, 2008). Long term measurements in water provide important information that can be used in evaluation of effects of accepted measures on lowering the emissions. Such a trend monitoring can be carried out in water, suspended particles and sediments as well as in biota. The decision, which matrix to survey is difficult especially for compounds present in water at very low concentrations, such as heavy metals and hydrophobic organic pollutants like polycyclic aromatic hydrocarbons (PAH) or polychlorinated biphenyls (PCBs). Among

other available monitoring methods passive sampling presents a promising approach because it provides sensitive and time integrative measurement of free dissolved concentrations of contaminants in water (Greenwood et al., 2007). Diffusion of organic pollutants from sampled media to the sampler is driven by the high affinity of analysed compounds to the sorbent material in the sampler. The concentration found in a passive sampler can be used for calculation of time weighted average (TWA) water concentration over extended periods of time. The major advantage of passive samplers over alternative matrices used for trend monitoring, e.g. sediments or biota, is that passive samplers constitute a well-defined sampling medium with a known uptake capacity. In contrast to results based on sediment or biota, passive sampling data require no corrections for organic carbon, lipid content or species to compare data on a temporal or spatial scale. Free dissolved concentration is a measure of organism exposure in water and passive sampling allows measurement even for compounds that cannot be measured in biota because of their excretion or metabolism by organisms. Furthermore, different sources of variance including analytical and environmental variance can be much better controlled, which in turn results in reduction of the required

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number of analysed samples to obtain results with comparable statistical power (Lohmann et al., 2012). Another advantage of use of passive samplers is the determination of free dissolved concentration in water, which is one of the important parameters for the assessment of pollutant bioavailability and fate in the aquatic environment. The freely dissolved concentration of contaminants in the water column is directly proportional to their fugacity in the water phase (Mayer et al., 2003). Pollution monitoring based on direct water measurement of dissolved concentrations of hydrophobic organic compounds by bottle sampling is not reliable, since the individual spot samples of water collected at the sampling sites reflect only the pollution situation at the moment of sampling. Measurement of truly dissolved concentration of these compounds in water cannot be easily achieved by conventional liquid/liquid or solid phase extraction techniques because of potential bias of these methods introduced by co-extraction of analytes bound to colloids present in water samples.

In this study, passive samplers were applied to characterize the temporal and spatial variability of dissolved heavy metals, PAHs and PCBs in the Danube river between the cities of Vienna and Bratislava (Fig. 1). This paper presents particular results of a larger study aimed at comparison of the most promising available monitoring methods (bottom sediments, suspended particulate samplers and passive samplers) for those pollutants (PAHs, selected heavy metals) to give a technical recommendation on how to perform a trend monitoring in the aquatic environment ([www.umweltbundesamt.at/umweltsituation/hestia\\_home](http://www.umweltbundesamt.at/umweltsituation/hestia_home)). This comparison will provide the basis for a technical recommendation on how to implement the WFD as well as for a future national and regional cooperation in monitoring and consistent evaluation of the quality of the water body.

## 2. Materials and methods

### 2.1. Chemicals

Organic solvents: acetone (Mikrochem, Slovakia), n-hexane SupraSolv (Merck, Germany), dichloromethane SupraSolv (Merck, Germany), hydrochloric acid 36%, p.a. (Merck, Germany), Triolein (Sigma Aldrich, Belgium), silicagel 60 (Merck, Germany). Gases for GC–MS/ECD equipment: nitrogen ECD and helium 6.0 (both Messer Tatragas, Slovakia). Etalons of 16 polycyclic aromatic hydrocarbons for calibration of equipment (PAH mix 9, 100  $\mu\text{g mL}^{-1}$  in cyclohexane), 6 polychlorinated biphenyls (10  $\mu\text{g mL}^{-1}$  in cyclohexane), perdeuterated polycyclic aromatic

hydrocarbons applied as performance reference compounds (D<sub>10</sub>-acenaphthene, D<sub>10</sub>-fluorene, D<sub>10</sub>-phenanthrene, D<sub>12</sub>-chrysene, D<sub>12</sub>-benzo(e)pyrene), surrogates (D<sub>8</sub>-naphthalene, D<sub>10</sub>-anthracene, D<sub>10</sub>-pyrene, D<sub>12</sub>-benzo(a)anthracene, D<sub>12</sub>-benzo(k)fluoranthene, D<sub>12</sub>-benzo(a)pyrene, D<sub>12</sub>-benzo(g,h,i)perylene), PCB30 and PCB185 were purchased from Dr. Ehrenstorfer, Germany. Terphenyl and PCB 121, the internal standards for instrumental analysis by GC/MS were purchased by Sigma–Aldrich, Germany. Physicochemical properties of analytes are given in Supplementary Information.

### 2.2. Passive samplers

#### 2.2.1. SPMDs

The SPMDs consisting of an LDPE membrane filled with 1 mL of triolein (95% purity), in nominal dimensions 2.54 × 91.4 cm (exposure surface area 460 cm<sup>2</sup>), wall thickness of 75–90  $\mu\text{m}$  were purchased from (Exposmeter, Sweden). Samplers contained 2  $\mu\text{g}$ /sampler of individual performance reference compounds (PRCs; D<sub>10</sub>-Acenaphthene, D<sub>10</sub>-Fluorene, D<sub>10</sub>-Phenanthrene, D<sub>12</sub>-Chrysene, D<sub>12</sub>-Benzo(e)pyrene). Before use they were stored in gas tight metal containers at –20 °C. The volume of sampler (triolein + membrane) is 4.95 mL.

#### 2.2.2. DGTs

DGT (diffusive gradients in thin film samplers) samplers were purchased by DGT Research Ltd, Lancaster, UK. Two versions of the sampler were applied: one for sampling mercury ions and another version for sampling heavy metals nickel, cadmium and lead. The sampler is composed of a plastic body, which contains a pre-filter with a surface area  $A = 3.14 \text{ cm}^2$ , diffusive hydrogel (0.8 mm thick) and adsorptive resin-gel (0.16 mL volume) layers.

### 2.3. Sampling sites

#### 2.3.1. Altenwörth an der Donau

Altenwörth on the Danube represents the location upstream of the Vienna area. The actual sampling site was located at the bridge on the left bank Danube river side arm in Altenwörth, approximately at the river kilometre (rkm) 1980, cca 55 km upstream Vienna agglomeration. This sampling site was not located directly in the main stream of the Danube, since the installation of the sampling equipment would have been logistically very difficult in the area of the adjacent Danube power plant. The sampled surface water is not affected by the backwater area of the Danube dam that is located downstream. The water level gradient at the bridge provides suitable conditions for operation of suspended sediment traps that were deployed simultaneously with passive samplers. The fast water current at the bridge enabled to achieve elevated sampling rates with SPMDs and thus to accumulate higher amounts of analytes.

#### 2.3.2. Langenzersdorf

The site Langenzersdorf is located at the weir 2 of the Marchfeld channel just upstream the main Vienna city agglomeration. The artificially constructed channel represents an important source of irrigation water for vegetable farmers of the Marchfeld area between the rivers March/Morava and the Danube. The site is located 1 km downstream the intake structure of Marchfeld channel from the left

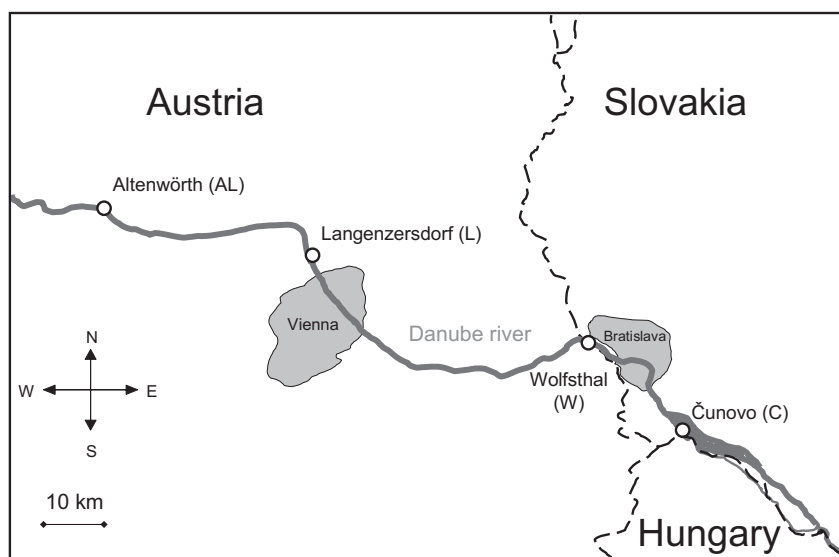


Fig. 1. Map of the sampling sites in the Danube river in Austria and Slovakia. Site symbols are given next to the site location names.

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