

Passive sampling: An effective method for monitoring seasonal and spatial variability of dissolved hydrophobic o...

Franko Humer, Robert Amdany


Environmental Pollution

Cite this paper

Downloaded from [Academia.edu](#) 

[Get the citation in MLA, APA, or Chicago styles](#)

Related papers

[Download a PDF Pack](#) of the best related papers 



[Passive sampling techniques for monitoring pollutants in water](#)

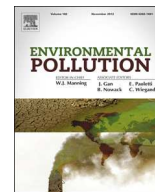
Branislav Vrana, Jesper Knutsson

[A New Simple Suspended-Load Sampler: Continuous Particulate Matter Collection from Rivers with Lo...](#)

Franko Humer

[Screening for Stockholm Convention persistent organic pollutants in the Bosna River \(Bosnia and Her...](#)

Sigurd Rognerud, Eirik Fjeld



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



Branislav Vrana^{a,b,*}, Veronika Klučárová^c, Eva Benická^c, Ninette Abou-Mrad^b, Robert Amdany^d, Soňa Horáková^a, Astrid Draxler^e, Franko Humer^e, Oliver Gans^e

^a Water Research Institute, Nabr. Arm. Gen. L. Svobodu 5, 812 49 Bratislava, Slovakia

^b Masaryk University, Faculty of Science, Research Centre for Toxic Compounds in the Environment RECETOX, Kamenice 753/5, 625 00 Brno, Czech Republic

^c Slovak University of Technology, Faculty of Chemical and Food Technology, Radlinského 9, 812 37 Bratislava, Slovakia

^d University of Witwatersrand, Department of Chemistry, P/Bag 3, Johannesburg, 2050, South Africa

^e Umweltbundesamt Environment Agency Austria, Spittelauer Lände 5, 1090 Vienna, Austria

ARTICLE INFO

Article history:

Received 11 March 2013

Received in revised form

11 July 2013

Accepted 23 August 2013

Keywords:

Danube

Free dissolved concentration

Persistent organic pollutants

Metals

Passive sampling

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⁻¹. Dissolved PCBs in water were very low and they ranged from 5 to 16 pg L⁻¹. 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⁻¹, 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.

© 2013 Elsevier Ltd. All rights reserved.

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

* Corresponding author.

E-mail addresses: branovrana@googlemail.com, vrana@recetox.muni.cz (B. Vrana).

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). 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 (D₁₀-acenaphthene, D₁₀-fluorene, D₁₀-phenanthrene, D₁₂-chrysene, D₁₂-benzo(e)pyrene), surrogates (D₈-naphthalene, D₁₀-anthracene, D₁₀-pyrene, D₁₂-benzo(a)anthracene, D₁₂-benzo(k)fluoranthene, D₁₂-benzo(a)pyrene, D₁₂-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 cm²), wall thickness of 75–90 μm were purchased from (Exposmeter, Sweden). Samplers contained 2 μg /sampler of individual performance reference compounds (PRCs; D₁₀-Acenaphthene, D₁₀-Fluorene, D₁₀-Phenanthrene, D₁₂-Chrysene, D₁₂-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

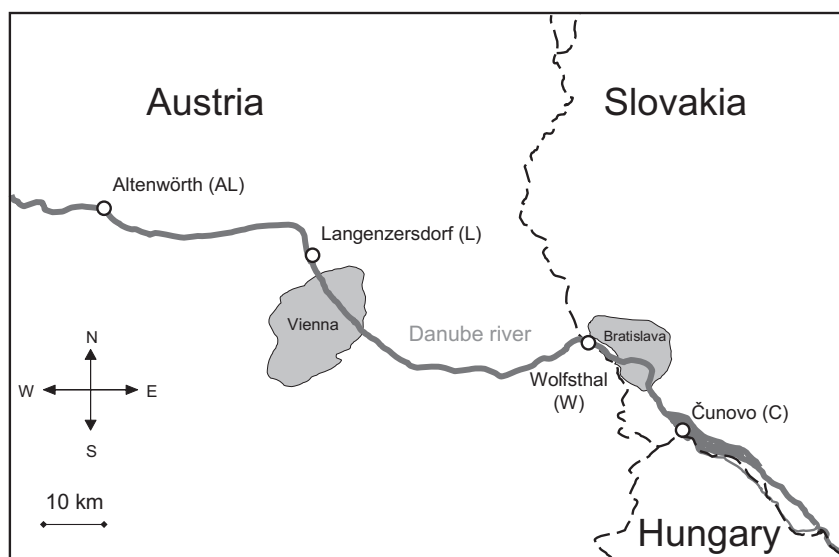


Fig. 1. Map of the sampling sites in the Danube river in Austria and Slovakia. Site symbols are given next to the site location names.

bank of the Danube at the rkm 1938. It is assumed that the flow velocity of Danube is slightly affected by the backwater of the Freudenu dam that is located 17 km downstream, but this should have only a minimum effect on water quality.

2.3.3. Wolfsthal

The sampling was performed at the Wolfsthal on-line monitoring station at Hainburg/Donau on the right Danube bank, approx. 15 km upstream Bratislava at the rkm 1879. The water from the Danube for passive sampler exposure was pumped into the monitoring station using submersible pumps operating at 1000–2000 L h⁻¹ that were installed in the main stream of Danube. During the sampling campaign performed in 2010, passive sampling was simultaneous with other alternative sampling methods including continuous collection of water samples and suspended particulate matter. For the purpose of this sampling campaign non-filtered water from the Danube was evenly distributed to particular sampling devices that included automatic water sampler, suspended particulate matter sampler and passive samplers, respectively. Data comparing various sampling techniques will be reported separately. The station facility was adapted to perform passive sampling as described in the sampling campaign description below.

2.3.4. Cunovo

The sampling site is located 15 km downstream the city of Bratislava at the rkm 1836 on the dam at the right bank in Cunovo. The Cunovo dam is a part of the Danube dam system Gabčíkovo and its basic function is to ensure the flow into the old Danube riverbed in the agreement between Slovakia and Hungary. The sampling was performed at the water intake object of the hydroelectric power plant in the Cunovo dam (http://www.gabcikovo.gov.sk/svdgn/stup_Cun.htm). In 2011, after nearly 20 years since the completion of the dam system, sediment dredging activities started in the reservoir Hrušov that is located just upstream the Cunovo dam. There are about 2 million cubic metres of sediment that must be removed in the coming years. These dredging activities can, potentially mobilize also pollutants that are assessed in the present study. During the sampling campaign the dredging project was performed at the right bank, and the flow of sampled water passed the area of dredging activities.

2.4. Sampling campaigns

2.4.1. 2010

In 2010 passive sampling was performed at a single monitoring site at the online monitoring station in Wolfsthal. Continuous sampling in 14-days passive sampler exposure periods started in July and ended in December 2010 with a single interruption from 14th September to 5th October for station maintenance. During each of the ten 14-day exposures three samplers of each type (SPMD, DGT) were deployed in parallel. For deployment samplers were mounted using a stainless steel wire holder inside a 1 m high glass cylinder with 5 cm inner diameter. The flow of Danube river water through the cylinder was kept constant at 140 L h⁻¹ for the entire 14-day exposure period. The dates of deployment periods are given in Table 1. In parallel with passive sampling, ten composite samples of whole water, representative for each of the 14-day sampler deployment period, were collected using an automatic water sampler installed in the monitoring station. Details are given in Supplementary Information. Concentrations of PAHs and heavy metals were determined in these composite samples.

2.4.2. 2011

The monitoring included 4 season sampling campaigns, in the months of February, April, July, and October 2011. The dates of deployment periods are given in Table 2. During each campaign 3 samplers in parallel were deployed at each site during 14 days cycles.

For deployment at the online monitoring station Wolfsthal samplers were mounted in a flow-through column as described for the 2010 campaign. At the

Table 1

Description of the sampling campaign at the site Wolfsthal in the Danube in 2010.

Exposure nr.	Exposure period		Exposure (days)	Water temperature (°C)	Mean discharge (m ³ s ⁻¹) ^b	SPMD-sampling rate R ₅ (Ld ⁻¹) ^a
	Start	End				
I	06.07.2010	20.07.2010	14	21	2176	16.4
II	20.07.2010	03.08.2010	14	20	2766	11.4
III	03.08.2010	17.08.2010	14	18	3371	6.0
IV	17.08.2010	31.08.2010	14	18	2417	6.6
V	31.08.2010	14.09.2010	14	15	2918	7.2
VI	05.10.2010	19.10.2010	14	12	1428	4.1
VII	19.10.2010	02.11.2010	14	10	1414	3.7
VIII	02.11.2010	16.11.2010	14	10	1364	3.4
IX	16.11.2010	30.11.2010	14	8	1469	3.7
X	30.11.2010	14.12.2010	14	4	1897	2.0

^a R₅ is the equivalent water volume extracted by SPMD per day for a compound with a medium molecular weight (Mw = 178; phenanthrene).

^b Calculated from volume discharge data available for the monitoring station in Bratislava.

Table 2

Description of sampling sites in the study area.

No.	Sampling site	Symbol	Water body	River kilometre	Longitude	Latitude
1.	Altenwörth	AL	Danube	1980	15°51'54"	48°22'44"
2.	Langenzersdorf	L	Danube	1938	16°21'22"	48°17'35"
3.	Wolfsthal	W	Danube	1879	16°59'15"	48°09'52"
4.	Čunovo	C	Danube	1836	17°13'29"	48°01'49"

remaining three sites samplers were placed into protective cage made of perforated stainless steel plate, preventing their mechanical damage and deployed in the river approximately 1 m below the water level with the help of ropes, buoys and anchors. After 14 days of exposure the samplers were collected, inspected for mechanical damage and the biofilm formation, photographed, transported to the laboratory in the protection package in a portable cool box. The prevention of contact of SPMDs with plastic materials and other potential sources of contamination were ensured. An additional field control sampler was exposed to air while samplers were being deployed and collected. The field control was processed as the deployed samplers and was used to measure contamination during transportation and handling. Three sampler fabrication controls were also analysed to determine contamination arising from the manufacturing process, sampler components, laboratory storage, processing and analytical procedures, but also to determine the initial concentration of PRCs in the SPMD samplers before exposure (Huckins et al., 2002; Booij et al., 2007). Several samplers were not retrieved due to loss of samplers during field exposure, namely by vandalism at site Langenzersdorf in April, and by sampler cage tear off at site Altenwörth in July. The SPMD samplers and their extracts were stored at separate place from chemicals, in a freezer under the temperature -20 °C. SPMD samplers were analyzed for hydrophobic organic pollutants PAHs and PCBs. DGT samplers were stored at 4 °C until processing and analysed for priority pollutant heavy metals nickel, cadmium, lead and mercury.

2.5. Sample extraction and analysis

2.5.1. SPMDs

SPMD samplers were cleaned from debris and mud and analytes were extracted two times 24 h by dialysis to hexane. Dialysates were further cleaned by gel permeation chromatography and silica gel or sulphuric acid modified silica gel for PAH and PCB analysis, respectively. The analysis of PAHs was performed using 6890N GC (Agilent, USA) equipped with a 30 m × 0.25 mm × 0.25 μm HP5-MS column (Agilent, USA) coupled to 5972 MS operated in electron impact ionization mode. PCB analysis was performed using GC-MS/MS 6890N GC (Agilent, USA) equipped with a 60 m × 0.25 mm × 0.25 μm DB5-MS column (Agilent J&W, USA) coupled to Quattro Micro GC MS MS (Waters, Micromass, UK) operated in EI+ ionization mode. Details of sample processing and instrumental analysis are given in Supplementary Information.

2.5.2. DGTs

Heavy metals accumulated in the DGT sampler adsorption resin were extracted with 1 mL of 1 mol L⁻¹ HNO₃ solution for 24 h. The determination of heavy metals nickel and lead in extracts was performed according to ISO 15586:2003, whereas cadmium was analysed according to DIN 38406/19. The analysis proceeded by atomic absorption spectrometry with graphite furnace (ET-AAS). Mercury analysis was performed by a microwave digestion with HNO₃ and H₂O₂ and an amalgam enrichment and reduction with sodium borohydride, followed by analysis of mercury by cold vapour atomic absorption spectrometry.

Table 3
Description of the sampling campaign in the Danube in 2011.

Campaign Nr. and sampling site	Exposure period		Exposure (days)	SPMD-sampling rate R_S (L d ⁻¹) ^a	Water temperature (°C)	Mean discharge (m ³ s ⁻¹) ^b
	Start	End				
I Al Altenwörth	16.02.	02.03.	14	15.8	4	1496
I L Langenzersdorf	16.02.	02.03.	14	11.5	3	
I W Wolfsthal	03.03.	17.03.	14	4.4	3	
I C Cunovo	03.03.	17.03.	14	12.9	3	1346
II Al Altenwörth	14.04.	28.04.	14	16.3	12	
II L Langenzersdorf	14.04.	28.04.	14	NA ^c	13	
II W Wolfsthal	14.04.	28.04.	14	4.14	13	
II C Cunovo	14.04.	28.04.	14	18.6	13	2063
III Al Altenwörth	22.06.	7.07.	14	NA ^c	19	
III L Langenzersdorf	22.06.	07.07.	14	20.9	19	
III Wolfsthal	22.06.	07.07.	14	12.0	19	
III C Cunovo	22.06.	07.07.	14	14.8	19	
IV Al Altenwörth	13.10.	27.10.	14	26.2	12	
IV L Langenzersdorf	13.10.	27.10.	14	17.6	11	
IV W Wolfsthal	13.10.	27.10.	14	3.4	11	
IV C Cunovo	13.10.	27.10.	14	19.7	11	

^a R_S is the equivalent water volume extracted by SPMD per day for a compound with a medium molecular weight (Mw = 178; phenanthrene).

^b Calculated from volume discharge data available for the monitoring station in Bratislava.

^c NA-not available because of SPMD sampler loss.

2.6. Calculation of dissolved water concentrations from passive sampler data

2.6.1. SPMDs

Dissolved water concentrations of target analytes were calculated from amounts accumulated in SPMDs as follows. Amounts of analytes absorbed by the samplers follow a first-order approach to equilibrium. Aqueous concentrations were calculated from the mass (N_S) absorbed by the SPMD, the in situ sampling rate of the compounds R_S and their sampler–water partition coefficients K_{SW} :

$$C_w = \frac{N_S}{V_S K_{SW} \left[1 - \exp\left(-\frac{R_S t}{K_{SW} V_S}\right) \right]} \quad (1)$$

where V_S is the volume of the SPMD (4.95 mL) and t is the sampler exposure time.

PRC dissipation also follows first-order kinetics. Sampling rates R_S were estimated from dissipation of PRCs from SPMDs during exposure using nonlinear least squares method by Booij and Smedes (2010), considering the fraction f of individual PRCs (D_{10} -acenaphthene, D_{10} -fluorene, D_{10} -phenanthrene and D_{10} -chrysene) that remain in the SPMD after the 14-day exposure as a continuous function of their K_{SW} , with R_S as an adjustable parameter.

$$f = \exp\left(-\frac{R_S t}{K_{SW} V_S}\right) \quad (2)$$

Here, $f = N_{PRC}/N_{0,PRC}$; $N_{0,PRC}$ = initial amount of the PRC at $t = 0$, N_{PRC} = amount of each PRC remaining after exposure, and t is exposure period (14 days). Assuming water boundary layer controlled uptake, R_S of individual target compounds in the higher hydrophobicity range was estimated by substituting Eq. (3) derived by Rusina et al. (2010) into Eq. (2).

$$R_S = FAM^{-0.47} \quad (3)$$

Here M is the molecular weight of the analyte, A is the surface area of SPMD (460 cm²). The factor F represents the effects of environmental conditions (temperature, flow, biofouling). It was obtained as an optimized value of adjustable parameter using nonlinear least squares method for estimating sampling rates (Booij and Smedes, 2010) after substitution of R_S in Eq. (2) by Eq. (3). The necessary K_{SW} values were interpolated from the empirical equation (Huckins et al., 2006)

$$\log K_{SW} = -0.1618(\log K_{OW})^2 + 2.321 \log K_{OW} - 2.61 \quad (4)$$

Booij et al. (2003a) observed that SPMD-water partition coefficients K_{SW} did not significantly change with temperature in the range from 2 °C to 30 °C, thus, for our calculations partition coefficients were not corrected for effect of temperature.

2.6.2. DGTs

Dissolved water concentrations C_{DGT} of metals were calculated from their masses accumulated in DGTs (N) according to Warnken et al. (2007).

$$C_{DGT} = \frac{N \Delta g}{D t A} \quad (5)$$

where Δg is the thickness of the diffusion gel layer, t is exposure time, A is the sampler surface area and D is the temperature dependent diffusion coefficient of a metal ion. Applied values of D were taken from the DGT manufacturer (www.

dgtresearch.com). It is assumed that mass transfer of metal species into DGT is controlled by diffusion in the gel layer. Thus, sampling by DGT should not be affected by the flow velocity/turbulence, as is the case for SPMDs.

2.7. Assessment of PAH patterns using principal component analysis

Principal component analysis (PCA) was used to compare the PAH levels and patterns in the dissolved phase, which was monitored at four sampling sites during four seasons in the 2011 sampling campaign. PCA analysis was based on absolute analyte concentrations and data were modelled according to the procedure described by Vrana et al. (2001).

3. Results and discussion

3.1. Aspects of sampling with SPMDs

The repeatability within three parallel determinations of PAH concentrations represented by mean relative standard deviation

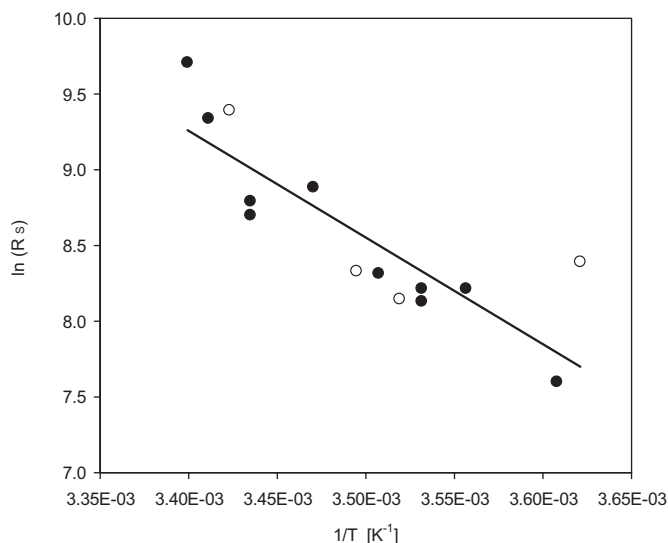


Fig. 2. Effect of water temperature on SPMD sampling rate of phenanthrene obtained during individual 14-day exposures at the site Wolfsthal in 2010 (black circles) and 2011 (white circles), respectively. The line represents linear regression of all SPMD sampling rates (expressed as natural logarithm; $\ln R_S$) vs. reciprocal of absolute temperature ($1/T$). The activation energy of mass transfer ΔE_a of 58 ± 10 kJ mol⁻¹ was calculated from the slope of the line multiplied by gas constant R according to Eq. (6).

was 24%, in that all the processes of analytical determination are included – sampling, extraction and determination by GC–MS. SPMD fabrication and field blanks contained concentrations of PAHs and PCBs that were below the instrumental limit of detection, with exception of naphthalene (up to 40 ng/SPMD). Blank subtraction for naphthalene in field exposed samplers was not done, because any naphthalene present in blanks dissipates from SPMDs

during exposure to level which is at equilibrium with water (Lohmann et al., 2012). Solvent blanks processed concurrently with samplers did not contain quantifiable amounts of target analytes. In some exposed samples compounds as benzo[b]fluorantene, benzo[k]fluorantene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, benzo[ghi]perylene were present at concentrations below limit of quantification. Those compounds are

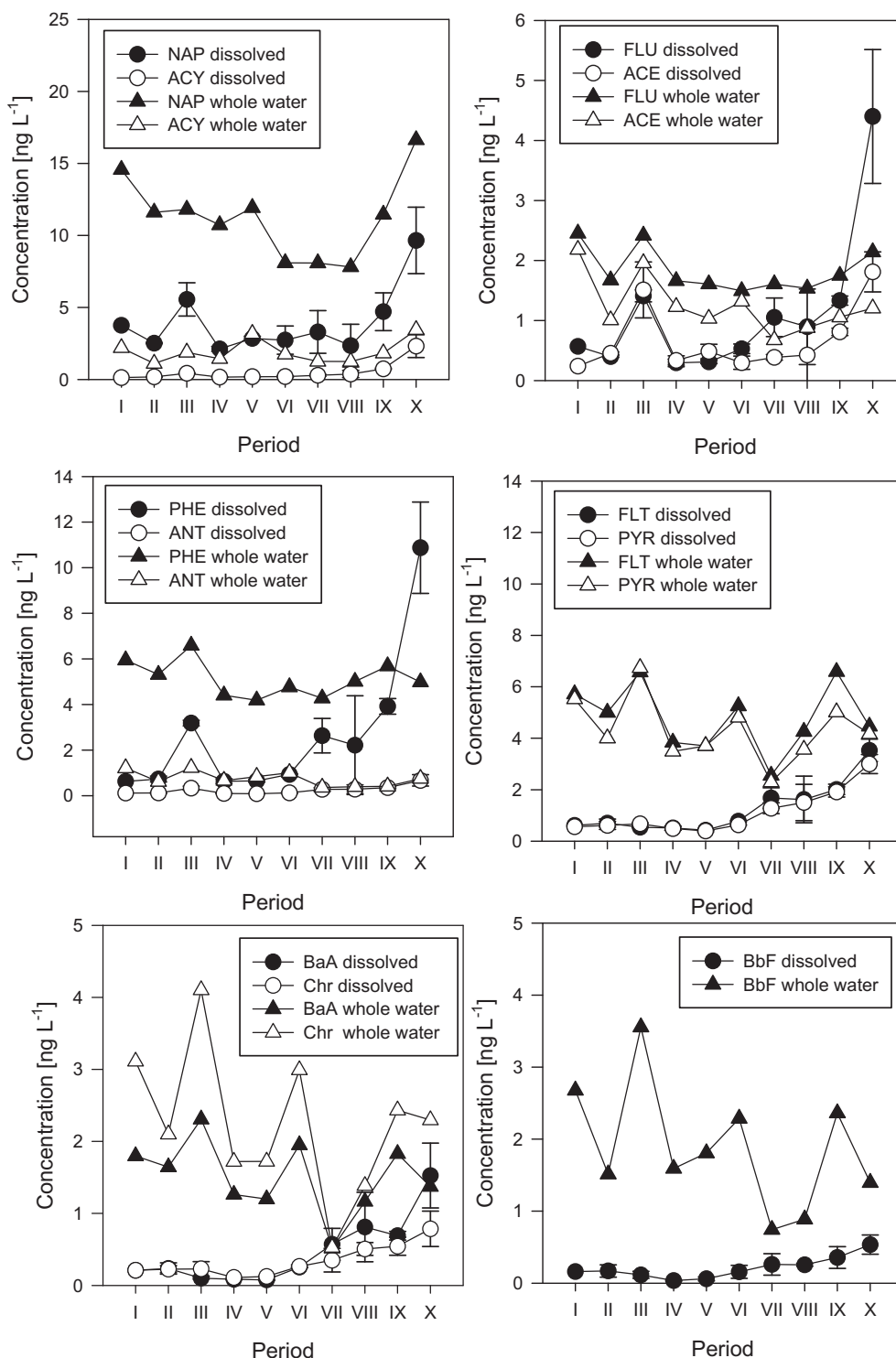


Fig. 3. Temporal variability of free dissolved (using SPMD) water and whole water (using continuous water sampler) PAH concentrations, at the online monitoring station in Wolfsthal in July–December 2010. Samplers were continuously exposed in 14-day deployment periods. Deployment and retrieval dates are reported in Table 1.

hydrophobic and predominantly partitioned to suspended particles and colloids in water and only a small fraction is present in the dissolved phase. For the calculation of the mean concentration of those compounds in water according to Eq. (1), the mass in sampler N_S was substituted by instrumental limit of quantification (LOQ). In such case the calculated water concentration of those compounds represents the highest possible concentration. Water concentrations estimated from LOQ for the above compounds were in range 0.01–0.29 ng L⁻¹. The highest LOQ values were calculated for the sampling site in Wolfsthal, because of low R_S values obtained at this site due to slow water motion inside the exposure tube. Where method LOQ was applied in mean value estimates, data in Figs. (4–5) are labelled with an asterisk. Detection limits in water can be significantly improved by a longer sampler exposure time or by exposure conditions, e.g. higher water turbulence. One option to increase sampling rates would be the use of samplers with a larger surface area, since the sampling rate is a product of mass transfer coefficient and sampler surface area. The 14-day exposure of samplers in this study was a result of a compromise to enable a direct comparison with other tested sampling methods (suspended particle traps and composite water samples).

The PRC-derived sampling rates R_S for phenanthrene from all field exposures are shown in Tables 1 and 3. R_S values for other compounds were derived using Eq. (3), which estimates a slight decrease in R_S with increasing molecular mass. Phenanthrene R_S values ranged from 2.0 L d⁻¹ at Wolfsthal in December 2010 to a maximum of 26.2 L d⁻¹ at Altenwörth in October 2011. In agreement with assumption of water boundary layer uptake different R_S values were obtained at different sites and during different seasons, which is related to differences in flow rates of water in the river and the position of sampler in the stream. Further relevant factors that affect mass transfer include the temperature and possibly the presence of biofouling and particle deposition on the surface of sampler. At the monitoring station Wolfsthal the sampler was placed in a glass tube, where the river water was pumped with lower flow velocity/turbulence than is in the river. This explains the generally lower sampling rates at this site. With exception of the sampling site Čunovo SPMD sampling rates increase with increasing temperature. The effect of temperature on passive sampling with SPMDs could be quantified at the site Wolfsthal (Fig. 2). Since the effect of flow velocity/turbulence on mass transfer into passive sampler at this site could be kept relatively constant, temperature was the only variable factor in exposures, when neglecting potential variable effects of biofouling

and suspended particulate matter concentrations on mass transfer. At other sites, such evaluation was not possible because flow conditions could not be controlled for caged samplers. The effect of temperature on R_S can be quantified in terms of activation energies (ΔE_a) for mass transfer, as modelled by the Arrhenius equation

$$R_S = R_{S\infty} \exp\left(-\frac{\Delta E_a}{RT}\right) \quad (6)$$

where $R_{S\infty}$ is the sampling rate at the hypothetical upper limit where temperature is infinite, R is the gas constant and T is the absolute temperature. Values of ΔE_a can be determined by plotting the natural logarithm of R_S ($\ln R_S$) vs. the reciprocal absolute temperature ($1/T$). The activation energy can then be calculated by multiplying the slope of the linear regression line with the gas constant. The calculated activation energy for phenanthrene in this study ΔE_a of 58 ± 10 kJ mol⁻¹ is in line with the average ΔE_a of 37 ± 21 kJ mol⁻¹ summarised for a broad range of studies by Huckins et al. (2006). This means that a temperature increase from 10 to 20 °C causes an increase in sampling rate by a factor about 2.3.

3.2. Temporal and spatial variability of PAHs in the Danube river

In 2010 temporal variability of PAH concentrations was investigated at a single sampling site in the Danube at Wolfsthal. Sum of concentrations of free dissolved PAHs determined from SPMDs deployed during the 2010 campaign were 5–39 ng L⁻¹. The SPMD data (Fig. 3) show that the freely dissolved concentrations of individual PAHs in the water column increase during the winter months. This may reflect the higher PAH emissions from pollution sources, mainly from burning of fossil fuels, in winter. The atmospheric deposition is one of the important transport processes, by which PAHs enter the water phase. The higher activity of emission sources in winter in combination with climatic conditions such as temperature inversion that limits the vertical dispersion and less intensive atmospheric reactions create favourable conditions for PAH deposition to water phase. Moreover, Henry's law constant increases with increasing temperature and thus, higher equilibrium concentrations in water are expected at lower temperatures even when atmospheric concentration remains constant (Staudinger and Roberts, 2001).

In addition to the general trend of concentration increase with decreasing water temperature, an increase of concentrations of

Table 4
Correlation of free dissolved (C_{free}) and whole water (C_{total}) concentrations of PAHs at the site Wolfsthal during the sampling campaign in 2010 with mean water temperature (T), suspended particulate matter content (SPM), and total organic carbon content (TOC).

Compound	Log K_{ow}	C_{total}				C_{free}			
		C_{free}	T	SPM	TOC	T	SPM	TOC	
Naphthalene	NAP	3.37	^a 0.70	0.03	0.28	0.34	-0.41	0.19	0.30
Acenaphthylene	ACE	4.00	^a 0.79	-0.31	0.28	0.15	-0.61	0.02	0.06
Acenaphthene	ACY	3.92	0.23	0.54	0.31	0.57	-0.33	0.38	0.57
Fluorene	FLU	4.18	0.37	0.27	0.28	0.57	-0.60	0.03	0.12
Phenanthrene	PHE	4.57	-0.01	0.29	0.17	0.55	^a -0.62	0.06	0.11
Anthracene	ANT	4.54	0.00	0.52	0.48	^a 0.65	-0.61	0.14	0.16
Pyrene	PYR	5.18	-0.11	0.31	0.31	^a 0.64	^a -0.68	0.01	-0.12
Fluoranthene	FLT	5.22	-0.15	0.19	0.10	0.42	^a -0.72	-0.09	-0.20
Chrysene	CHR	5.86	-0.14	0.34	0.33	^a 0.67	^a -0.69	-0.02	-0.14
Benzo[b]fluoranthene	BbF	5.90	-0.29	0.43	0.42	^a 0.67	^a -0.62	-0.01	-0.15
Benz[a]anthracene	BAA	5.91	-0.19	0.33	0.27	0.58	^a -0.75	-0.17	-0.24
Benzo[a]pyrene	BAP	6.04	-0.32	0.56	0.49	^a 0.75	^a -0.81	-0.20	-0.23
Benzo[ghi]perylene	BP	6.50	-0.53	^a 0.63	0.52	0.59	^a -0.77	-0.13	-0.20
Indeno[1,2,3-cd]pyrene	IP	6.50	0.36	0.08	0.37	0.47	^a -0.77	-0.13	-0.20
Dibenz[a,h]anthracene	DahA	6.75	-0.53	0.41	0.31	0.48	^a -0.77	-0.13	-0.20

^a Significant Pearson product moment correlation coefficients ($n = 10$, $p < 0.05$; non-directional t -test) and higher than 0.62.

Table 5
Dissolved concentrations (ng L⁻¹) of sum of PAHs, Cd, Ni and Pb measured in urban impacted European rivers.

River	PAHs	Cd	Ni	Pb	Reference
Danube	13–72	2–14	205–544	18–74	This study
Morava	25–203				Prokes et al., 2012
Marne		7–19			Thévenot et al., 1998
Seine		9–70			Thévenot et al., 1998
		11–67			Chiffolleau et al., 1999
	15–50	8–111	338–3760		Tusseau-Vuillemin et al., 2007
	3.5–106				Bourgeault and Gourlay-Francé, 2013
Thames			800		Neal et al., 2000
Rhône	55	11	423	76	Miege et al., 2012
Bosna	20–480				Harman et al., 2013
		1–24	218–2981	8–1000	Vrana et al., authors unpublished data

some lighter PAHs (naphthalene, acenaphthene, fluorene and phenanthrene) was observed during the third sampler exposure period (03.08. to 17.08. 2010). In August 2010, a local flood occurred at the Danube sampling profile in Wolfsthal and the elevated concentrations of dissolved compounds may be related to mobilization of these compounds during the event.

At the Wolfsthal site free dissolved concentrations of PAHs obtained with passive sampling (C_{free}) can be compared with whole water concentrations (C_{total}) determined in composite water samples representative of each of the 14-day sampler deployment periods (Fig. 3). The comparison reveals that C_{free} in water decreases with increasing compound hydrophobicity (Supplementary

information Fig. S5), which reflects the adsorption of hydrophobic compounds on particles or colloids. A significant positive correlation (Table 4) between C_{free} and C_{total} was observed only for the two most hydrophilic compounds (naphthalene and acenaphthylene), which are predominantly present in water in the dissolved phase. While C_{free} was negatively correlated with temperature for most compounds, such trend was not observed for C_{total} . With exception of the most hydrophilic compounds (naphthalene and acenaphthylene), C_{total} of PAHs was positively correlated with total organic carbon (TOC) content in water, which confirms that hydrophobic compounds are associated with organic matter present on particles and in colloids in water. One hypothesis for the absence of correlation between C_{free} and C_{total} is that a fraction of compounds adsorbed on suspended particulate matter is bound irreversibly and cannot partition into dissolved phase, however, such investigation was beyond the scope of this study and more research is needed to prove it. Since whole water concentration measurements were performed with a single composite sample during each sampling period, no data on precision of whole water sampling in one laboratory is available in this study. Collection and analysis of replicate samples would likely reveal whether absence of correlation with free dissolved concentration can be attributed to low precision of sampling and analysis. However, considering the very high sampling and processing effort needed to obtain a representative water sample for a 14 day period, such experiment is practically not feasible.

In addition to samples collected during our study, information is available on concentrations of PAHs in spot samples of whole water (1 L) that were collected monthly in 2010 at the Wolfsthal monitoring station by Water Research Institute Bratislava for the purpose of chemical status assessment in the river Danube (Water

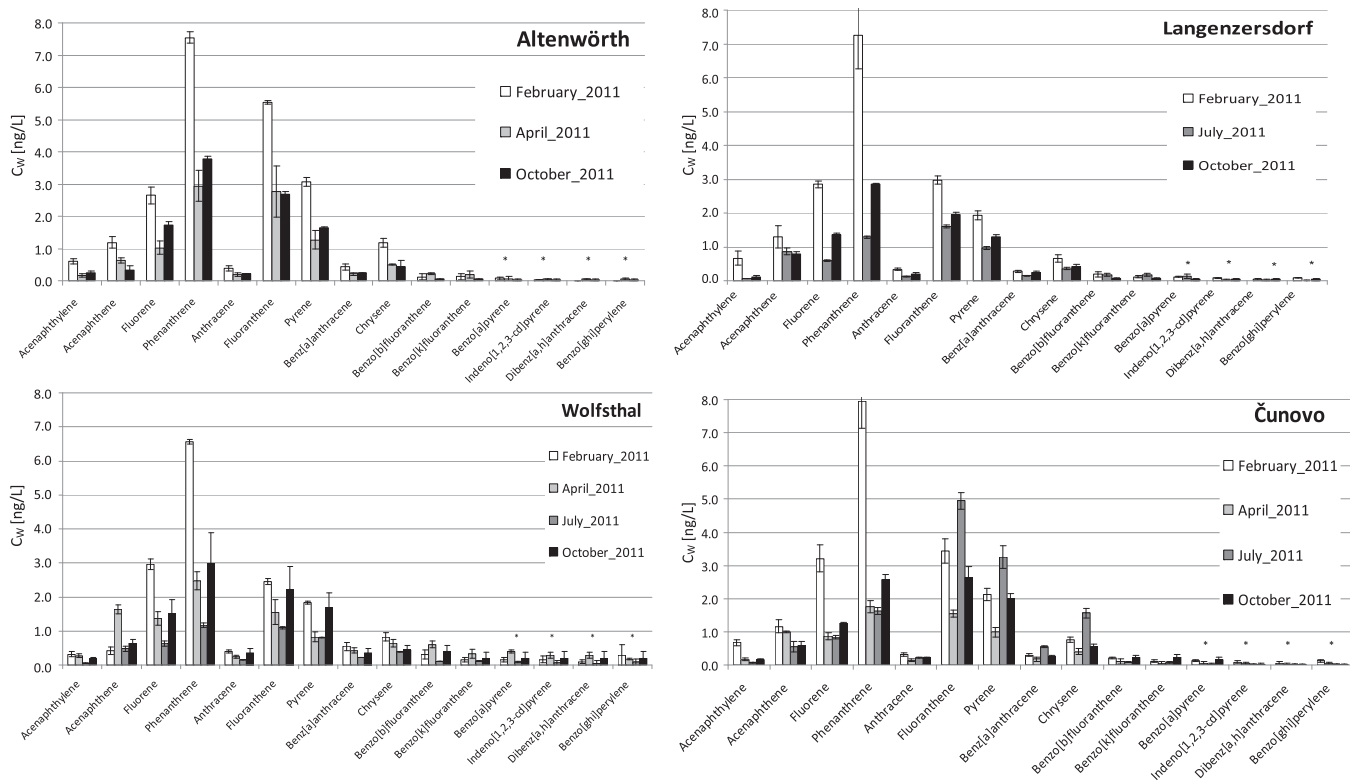


Fig. 4. Temporal variability of free dissolved PAH concentrations, monitored using SPMD passive samplers at four sampling sites along the Danube river in 2011. Data points labelled with asterisks include individual measurements below limit of quantification.

Research Institute, Bratislava, 2013). During the whole duration of sampling campaign, concentrations of all monitored priority pollutant PAHs were below their respective LOQs. The LOQs of individual compounds were relatively high (2–30 ng L⁻¹; Supplementary data, Table S1). The data do not contradict our observations, however, no statements on temporal variability of pollution can be made on their basis. Although data from regulatory monitoring, obtained using low volume spot sampling, can be applied for checking compliance with environmental quality standards, they are not suitable for assessment of temporal and spatial variability of PAHs.

The availability of water discharge data at the Wolfsthal monitoring station enabled to estimate fluxes (as a product of discharge and concentration) of free dissolved as well as total PAHs in the river Danube. The estimated flux of dissolved PAHs (sum of 16 compounds) ranged from 0.9 kg d⁻¹ in October to 6.6 kg d⁻¹ in December 2010, respectively. Estimated total PAH flux in Danube ranged from 3.3 kg d⁻¹ in October to 16.7 kg d⁻¹ in August (period III), respectively. The maximum total flux coincides with the above mentioned elevated water flow event. The average contribution of free dissolved compounds to total flux was 31%. We stress that the ultimate aim of passive sampling is to obtain a measure of the level of pollution that gives a representative measure of the exposure of organisms and compare the contaminant levels in time and space, but not to assess mass balance of compounds in water bodies.

In 2011 the samplers were deployed during four seasons at four sampling sites to characterize the temporal and spatial variability of priority metals, PAHs and PCBs in the water column of the Danube

river between the cities of Vienna and Bratislava. Total concentration of PAHs determined from SPMDs in the campaign conducted at four sampling sites in 2011 were 13–72 ng L⁻¹. A comparison with free dissolved concentrations measured with passive sampling in other urban impacted European rivers shows that the pollution of Danube by PAHs is 1.5–7 times lower than in the rivers for which data is compiled in Table 5. Temporal variability of PAH concentrations at the four sites is shown in Fig. 4. In agreement with observations from 2010 the highest PAH concentrations at all four sampling sites were observed in winter (February) and the lowest ones in summer (July), respectively. A single exception to this general trend were elevated concentrations of fluoranthene, pyrene and chrysene that were observed at Čunovo in July 2011. This event may have been related to on site sediment dredging activities or from accidental release of PAHs from ships, but would require a more detailed investigation. Spatial variability of PAHs during different seasons along the monitored Danube stretch is shown in Fig. 5. To visualize spatial trends of free dissolved concentrations, data from sites downstream the Altenwörth site (AL) were presented as percentual concentration increase or decrease against the levels measured at AL site. Visualisation was performed only for compounds where concentrations exceeded their respective LOQs. No systematic spatial trends in PAH concentrations could be observed along the monitoring stretch since different and often opposite trends were observed during different seasons. The spatial variability of PAH concentration was not dramatic and for most compounds the concentrations varied less than two-fold in both directions in comparison with those measured at the AL site. In

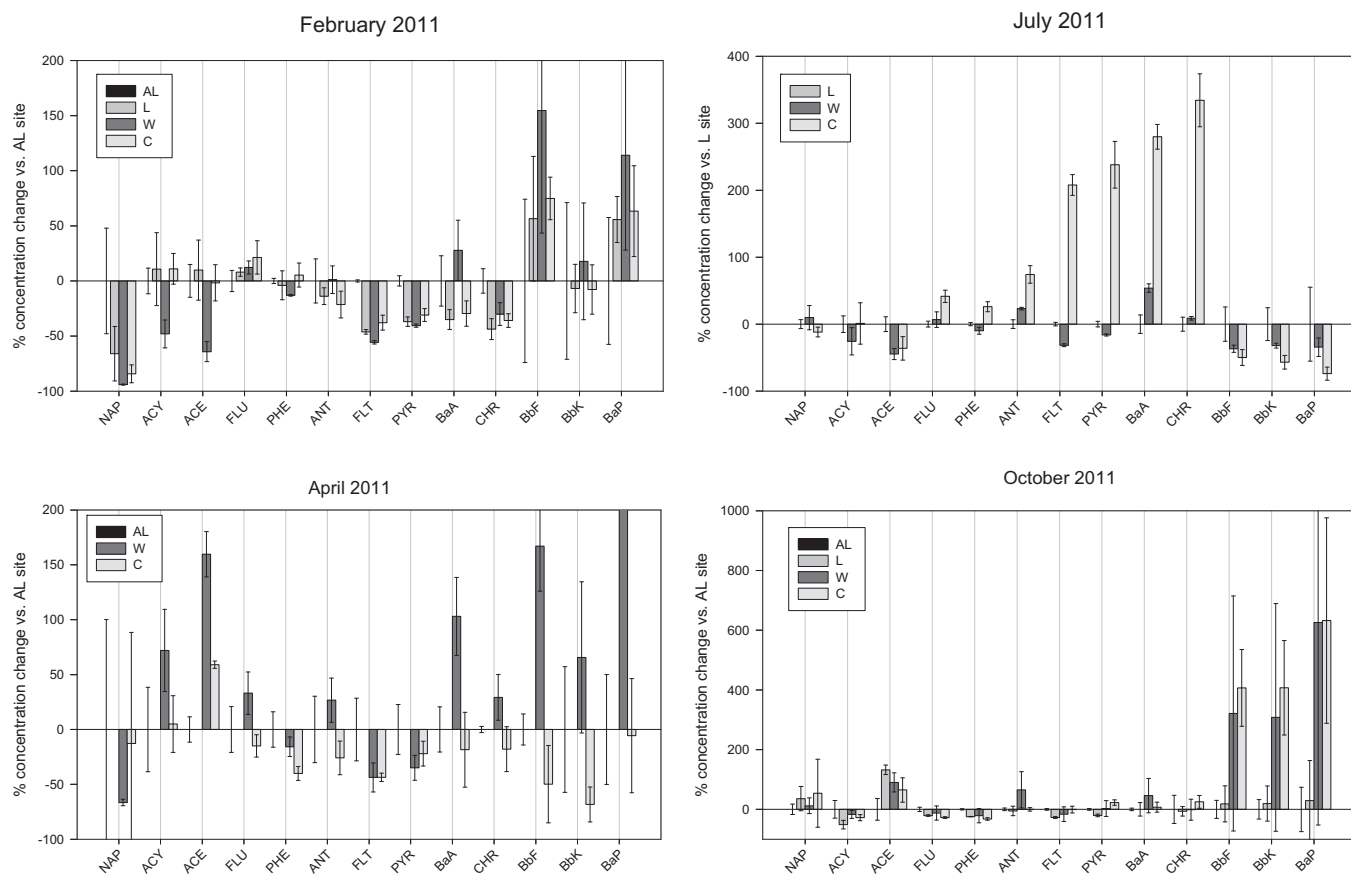


Fig. 5. Spatial variability of free dissolved PAH concentrations along the Danube river, monitored using SPMD passive samplers during four seasons in 2011. Data from sites downstream the Altenwörth site (AL) are presented as percentual concentration increase or decrease against the levels measured at the AL site. For data collected in July 2011, Langenzersdorf (L) was taken as the reference site.

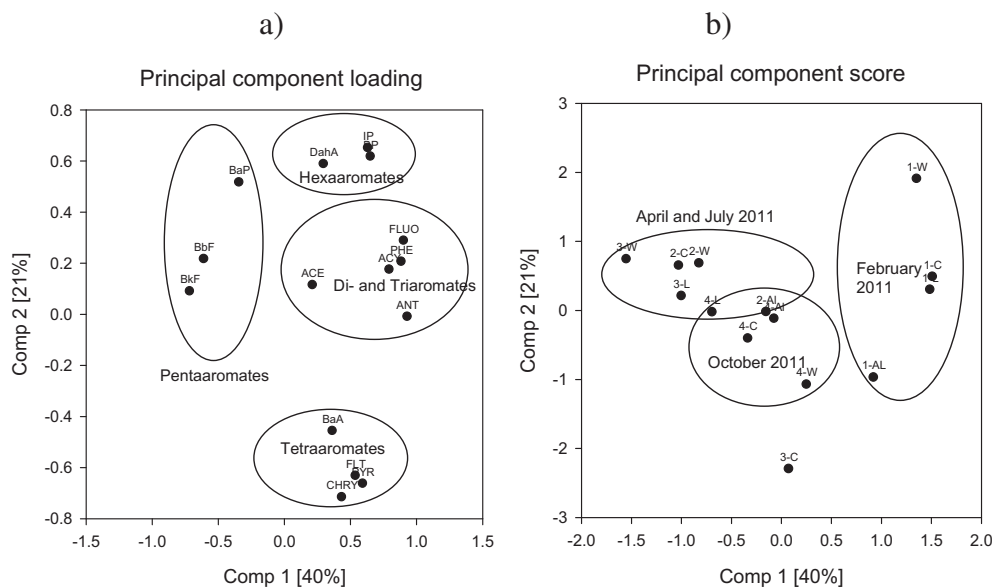


Fig. 6. Principal component plot (Component 1 vs. Component 2) for comparison of the PAH profiles in the dissolved phase at four sampling sites monitored during four seasons in 2011. Graph a) shows loadings for the individual PAHs. Graph b) shows scores of samples. Sampling sites and events are described in Table 3.

many cases these differences were lower than the precision of the passive sampling method and thus not significant. An exception were the above mentioned significantly elevated concentrations of fluoranthene, pyrene, benzo(a)anthracene and chrysene in Čunovo in summer.

From an inspection of the PCA pattern analysis for the samples from the 2011 campaign, the score plot [Component 1 vs. Component 2, Fig. 6(a)] shows the separation of the samples along the principal components. As can be seen in the loading plot [Fig. 6(b)], the compounds (PAHs) are separated on the principal component plane (PC1 vs. PC2) according to their molecular weight or hydrophobicity. Water concentration patterns calculated from SPMD data cluster together on the PCA plot for most samples collected at the four sites along the Danube in April, July and October 2011. Thus, both concentration levels and patterns remain relatively constant during most of the year along the monitored Danube stretch. A distinct contamination pattern of PAHs can be observed in samples collected in February 2011. In winter season, contaminant patterns also differ more between sites. This corresponds with higher concentration levels observed in winter; the differences in PAH fingerprint may correspond with a higher diversity of contaminant sources in winter. A specific case is the PAH pattern observed in Čunovo in July 2011, which was discussed above.

The two city agglomerations of Bratislava and Vienna do not seem to have a significant effect on downstream PAH

concentrations in water. Our observations support the hypothesis that concentrations in the water phase are related to diffusive rather than point pollution sources and the observed periodic annual variability is related to seasonal changes of atmospheric PAH concentrations. Point sources of PAHs in the both cities are likely to be transient rather than continuous and likely related to rain fall, stormwater overflow and direct runoff. It is likely that these point discharges are effectively diluted by the river that has a usual water discharge of more than $2000 \text{ m}^3 \text{ s}^{-1}$ in the area of interest. In addition, the concentrations in the dissolved phase are probably well buffered by contaminant partitioning between water column and bed sediments along the river.

3.3. Temporal and spatial variability of PCBs in the Danube river

SPMD samples from the 2011 campaign were analysed for PCBs. The calculated dissolved PCB concentrations were very in sub ng L^{-1} range (Table 6) and close to method limit of quantification. Sum of 6 indicator PCB congeners ranged from 5 to 16 pg L^{-1} . No temporal or spatial trends of pollution could be observed along the monitored Danube stretch. Better method sensitivity would be required for a better characterization of levels and contaminant patterns of PCBs. The simplest way to achieve this is to significantly extend SPMD exposure up to several months.

Table 6

Dissolved concentrations of PCBs, in water, derived from SPMD passive samplers, at the four sampling sites in Danube during four seasons in 2011.

Campaign	I (February–March 2011)				II (April 2011)				III (July 2011)				IV (October 2011)			
	AL	L	W	C	AL	L ^a	W	C	AL ^a	L	W ^b	C ^b	AL	L	W ^b	C ^b
PCB 28	5.8	5.8	5.9	3.3	6.1		14.0	3.4		1.8			2.6	4.8		
PCB 52	2.7	1.6	<2.1	0.4	2.4		<2.2	0.9		0.5			0.9	1.4		
PCB 101	2.9	1.7	1.4	0.8	4.5		3.1	0.5		2.0			3.0	1.8		
PCB 153	2.2	1.8	<2.3	0.8	3.6		<2.4	0.3		1.4			4.0	1.2		
PCB 138	0.7	<0.9	<2.3	<0.8	1.3		<2.4	<0.6		<0.4			0.3	<0.6		
PCB 180	1.8	1.5	1.6	<0.8	1.8		<2.5	<0.6		0.7			1.9	<0.6		
Σ PCBs	16.1	12.4	8.9	5.2	19.5		17.1	5.0		6.5			12.7	9.1		

^a Not reported because of loss of samplers.

^b Not reported because of bad repeatability of analysis.

3.4. Temporal and spatial variability of heavy metals in the Danube river

DGT fabrication and field blanks contained concentrations of that were below the instrumental detection limit of 0.5, 5 and 5 ng/DGT for Cd, Ni and Pb, respectively. The calculated dissolved Cd, Pb and Ni concentrations measured from metal amount accumulated in DGT samplers were very low and always in the sub $\mu\text{g L}^{-1}$ range. Concentration of mercury was always below the detection limit of the applied method (0.10 ng/DGT sampler). When this limit is applied in Eq. (5) together with the diffusion coefficient of mercury in water $9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Dočekalová and Diviš, 2005), the estimated concentration of mercury in water is less than 0.1 ng L^{-1} . In 2010 concentration of Cd, Pb and Ni were in the range <1 –20, 18–49, and 173–544 ng L^{-1} , respectively (Fig. 7). The repeatability within three parallel determinations of concentrations represented by mean relative standard deviation was 23%. Similarly as was observed for less hydrophobic PAHs, an increase of Cd concentration was measured during the third sampler exposure period (03.08. to 17.08.2010). In August 2010, a local flood occurred at the Danube sampling profile in Wolfsthal and the elevated concentrations may be related to mobilization of these compounds during the event. DGT-derived water concentrations were also compared with composite samples of whole water analysed during the sampling campaign in 2010 as well as with data from spot samples of filtered (through $0.45 \mu\text{m}$ pore size filter) water that were collected monthly at the Wolfsthal monitoring station for the purpose of chemical status assessment (Water Research Institute, Bratislava, 2013). DGT-derived concentrations reflect the dissolved contaminant fraction and were always lower than whole water concentrations. They should be comparable with concentrations found in filtered water samples, but it must be taken into account that spot samples reflect just the concentration in water at one moment, whereas DGT sample provides a time weighted average measure of concentration over 14 days.

For Cd, concentrations in spot samples as well as in composite whole water were below limit of quantification during the whole campaign. For Pb, quantifiable concentration ($4 \mu\text{g L}^{-1}$) was found only in a single spot sample collected during sampling period II. Although elevated whole water concentration was detected during the same period in composite whole water sample, it was lower than in the filtered spot sample. A possible explanation is that spot sampling detected accidentally a peak of Pb contamination that was short enough to be not detected in time averaged DGT and composite water samples. Similarly, elevated concentrations of Ni were measured in spot samples during sampling period II and III. Composite water analysis was available only for period II, with concentration slightly above method LOQ, however, lower than that found in spot sample. Since only five pairs of data were available for comparison, no conclusions can be made on presence or absence of correlation between free dissolved and total metal concentration in water. Estimated total metal flux in Danube ranged from <12 –24, 22–220, and <118 –406 kg d^{-1} for Cd, Pb and Ni, respectively. The mean contribution of free dissolved metals to total flux was 3, 10, and 28% for Cd, Pb and Ni, respectively.

In 2011 concentration of Cd, Pb and Ni were in the range <2 –6, 18–74, and 205–457 ng L^{-1} , respectively. The repeatability within three parallel determination of concentrations represented by mean relative standard deviation was 21%. A comparison with dissolved concentrations measured in other urban impacted European rivers shows that the pollution of Danube by heavy metals is comparable or up to one order of magnitude lower than in the rivers for which data is compiled in Table 5. Monitoring with DGTs confirmed at all sites relatively constant concentrations of the three

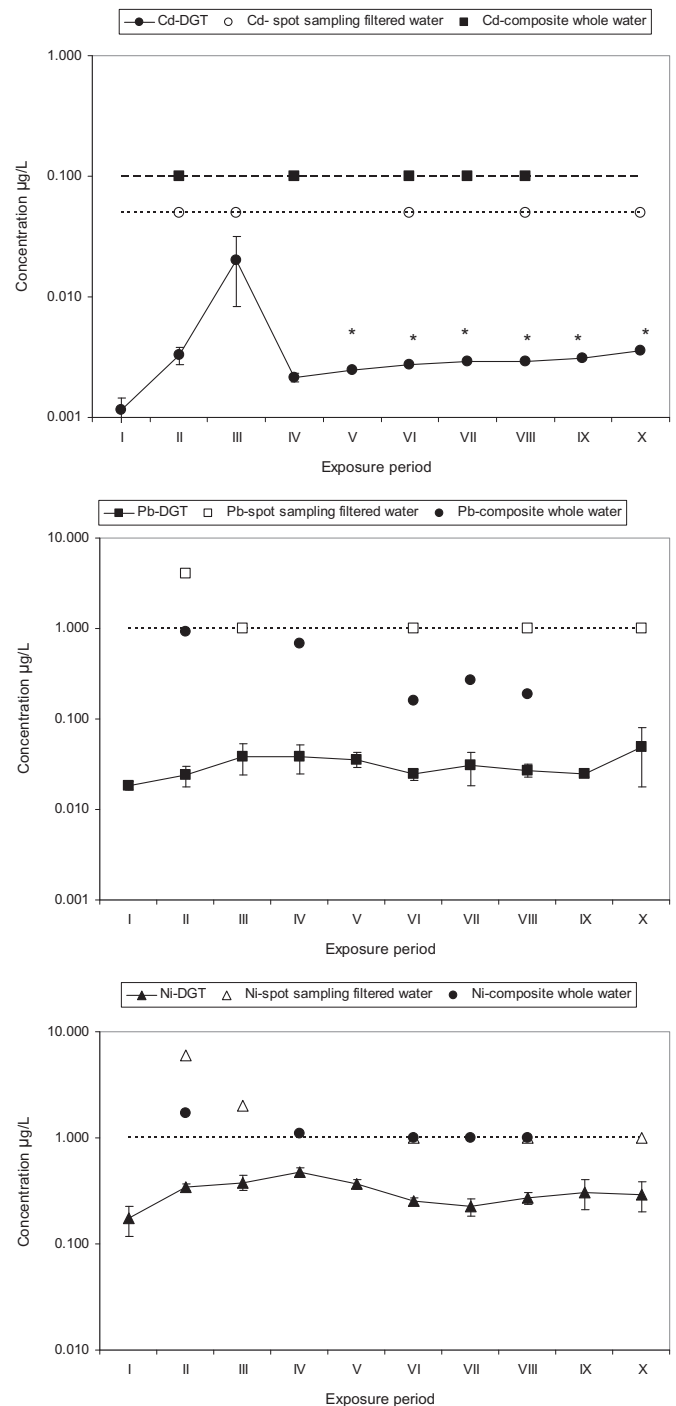


Fig. 7. Temporal variability of dissolved (using DGT), whole water (using continuous water sampler) and filtered water (using monthly spot sampling) metal concentrations, at the online monitoring station in Wolfsthal in July–December 2010. Samplers were continuously exposed in 14-day deployment periods. DGT concentrations labelled with asterisks were lower than limit of quantification. Dotted and dashed lines show the limits of quantification in spot and composite water samples, respectively.

priority pollutant metals and neither a systematic temporal nor a spatial trend of pollution could be observed along the monitored Danube stretch (Fig. 8). The variability of measured metal concentrations was mostly lower than method precision and thus not significant. The data suggest that pollution sources along the monitored stretch do not significantly affect heavy metal concentrations in the dissolved phase.

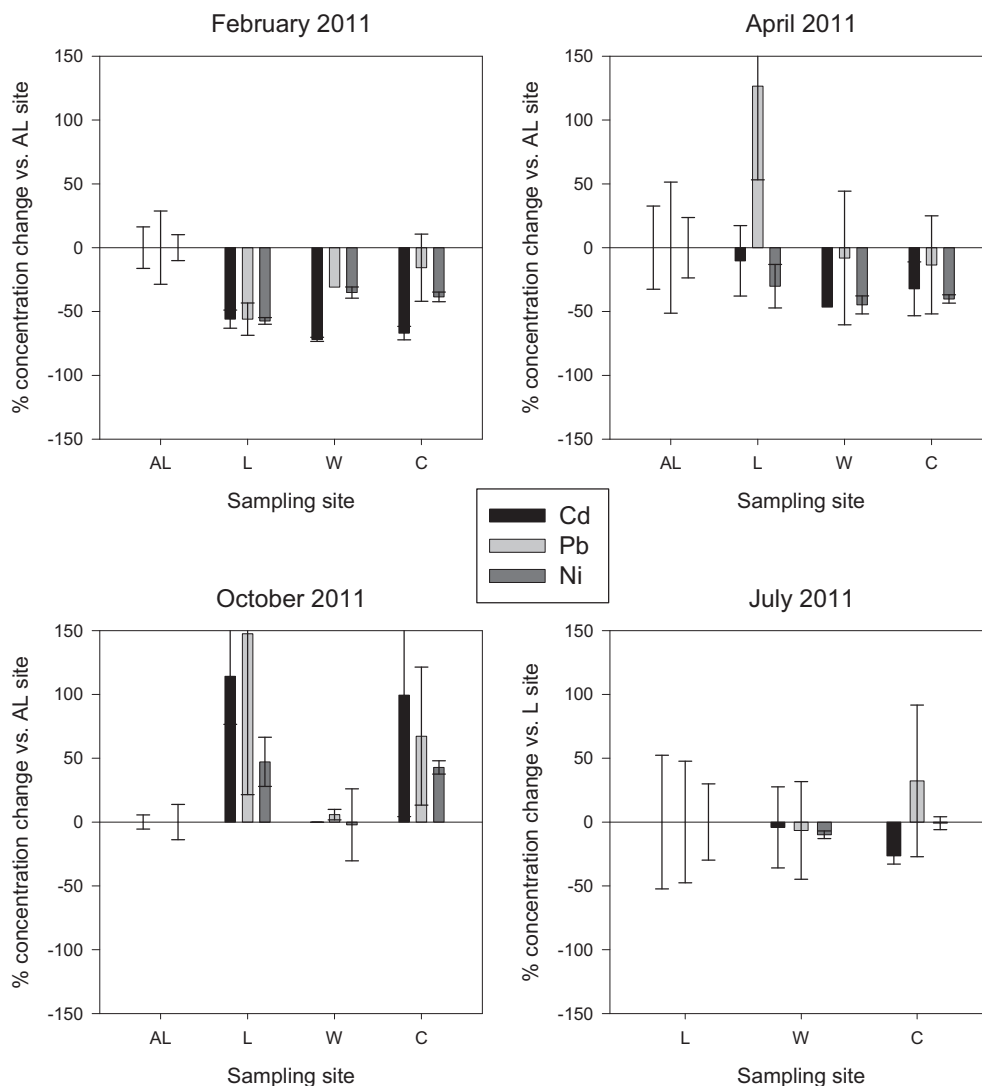


Fig. 8. Spatial variability of free dissolved heavy metal concentrations along the Danube river, monitored using DGT samplers during four seasons in 2011. Data from sites downstream the Altenwörth site (AL) are presented as percentual concentration increase or decrease against the levels measured at the AL site. For data collected in July 2011, Langenzersdorf (L) was taken as the reference site.

4. Conclusions

Passive samplers provide a useful tool for an assessment of pollution status and related temporal and spatial trends within water bodies. They enable to collect information on trace concentrations of priority pollutants with a good precision and, unlike in case of chemical monitoring in biota, the effect of variable exposure conditions can be kept under control. It is possible to directly compare monitoring data obtained at different sites and seasons, which makes passive samplers a promising tool in assessment of spatial and temporal pollutant trends. Passive samplers provide complementary information to chemical monitoring in sediment or suspended particulate matter. Sediment concentration patterns may not be representative for estimation of immediate concentrations in the water column, but they provide a long-term contamination record. On the contrary, the passive samplers integrate water concentrations only during the sampling period and reflect the actual pollution situation in a water body. When total extraction techniques are applied in sediment or suspended particulate matter analysis they cannot distinguish between contaminants that are irreversibly adsorbed to sediment and those that can

be easily partitioned to pore water and then released to the water column.

Spot sampling with a frequency once per month produces often data that are below detection limits and sometimes accidentally detects elevated concentrations that originate from short term concentration variation that is representative only for the moment when sample was collected. This makes spot sampling less suitable for assessment of temporal concentration trends in comparison with techniques that provide an average concentration over extended period, such as continuous water sampling or integrative passive sampling. From the later techniques, passive sampling is much less laborious. Moreover, both DGT and SPMD techniques allow measurements of bioavailable concentrations of pollutants in water with a better sensitivity than can be achieved with conventional water sampling techniques. When accepting that free dissolved concentration is a suitable measure of contaminant levels to which organisms are exposed, absence of a correlation between C_{free} and C_{total} observed for PAHs in this study invokes a question whether whole water concentration is a suitable parameter for assessment of risks associated with pollutants in water.

The spatial variability of dissolved PAHs and heavy metals in the studied region was small, which indicates that diffusive pollution sources dominate over local point sources. Concentrations of PAHs decreased with increasing water temperature in the whole region indicating that atmospheric emission from domestic heating sources and consequent deposition represent an important pathway of PAHs to aquatic ecosystem of the region in the winter period. For PAHs we observed a similar trend in the Danube left bank tributary, the river Morava (Prokeš et al., 2012), which indicates that cyclic seasonal oscillation of PAH concentration occurs in most water bodies in the geographic area. This has an implication for the design of future monitoring programs aimed at assessment of long term trends. For such analysis, based on passive sampling measurements of PAH concentrations, time series should be constructed of data from samples collected always in the same year period. For heavy metals seasonal variability does not seem to be significant.

Our study provided insight into the temporal and spatial variability of bioavailable concentrations of selected priority pollutants in a selected stretch of the Danube river, one of the biggest streams on the European continent. Similar field studies increase the body of information available for assessment of factors that affect distribution and fate of pollutants in the natural environment. Moreover, they support regulators in assessing opportunities for using passive sampling for monitoring water quality within a legislative framework.

Acknowledgements

This research was supported by the EU European Regional Development Fund (ERDF) from the Operational Programme of Cross-Border Cooperation Slovakia-Austria 2007–2013 (project HESTIA), the scientific agency of the Ministry of Education of the Slovak Republic (project VEGA 1/0483/11), and the EU Operational Programme "Research and Development for Innovations", the CETOCOEN project (no.CZ.1.05/2.1.00/01.0001). We further acknowledge Eva Figuliová, Dr. Angelika Kassai, Richard Matula, and Dr. Peter Tarábek from Water Research Institute and Dr. Petr Kukučka from Masaryk University for their technical assistance during sampling and sample analysis. We also thank to Dr. Stefan Schuster from TBS – Water Consult for technical assistance during installation of passive samplers at the online monitoring station at Wolfsthal. We thank to Foppe Smedes from Deltares, the Netherlands for kindly providing the MS EXCEL-based SPMD sampling rate calculator based on nonlinear regression according to Boojj and Smedes (2010).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2013.08.018>.

References

- Boojj, K., Smedes, F., 2010. An improved method for estimating in situ sampling rates of nonpolar passive samplers. *Environ. Sci. Technol.* 44, 6789–6794.
- Boojj, K., Hofmans, H.E., Fischer, C.V., Van Weerlee, E.M., 2003a. Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. *Environ. Sci. Technol.* 37, 361–366.
- Boojj, K., Vrana, B., and Huckins, J.N., 2007. Theory, modeling a calibration of passive samplers used in water monitoring. In: Greenwood, R., Mills, G., Vrana, B. (Eds.), *Passive Sampling Techniques in Environmental Monitoring*. In: D. Barcelo

- (Ed.), *Comprehensive Analytical Chemistry Series vol. 48*. Elsevier, Amsterdam, pp. 141–169.
- Bourgeault, A., Gourlay-Francé, C., 2013. Monitoring PAH contamination in water: comparison of biological and physico-chemical tools. *Sci. Total. Environ.* 454–455, 328–336.
- Chiffolleau, J.-F., Auger, D., Chartier, F., 1999. Fluxes of selected trace metals in the Seine estuary to the eastern English channel during the period August 1994 to July 1995. *Cont. Shelf Res.* 19, 2063–2082.
- DIN 38406–19, 1980–2007. German Standard Methods for the Analysis of Water, Waste Water and Sludge; Cations (Group E); Determination of Cadmium (E 19).
- Dočekalová, H., Diviš, P., 2005. Application of diffusive gradient in thin films technique (DGT) to measurement of mercury in aquatic systems. *Talanta* 65, 1174–1178.
- EU, 2000. Directive 2000/60/EC of the European parliament and of the council of 23 October 2000 establishing a framework for community action in the field of water policy. *Off. J. Euro. Union* L327, 1–72.
- EU, 2008. Directive 2008/105/EC of the European parliament and of the council of 16 December 2008 on environmental quality standards in the field of water policy. *Off. J. Euro. Union* L348, 84–96.
- Greenwood, R., Mills, G., Vrana, B., 2007. Passive sampling techniques in environmental monitoring. In: Barcelo, D. (Ed.), *Comprehensive Analytical Chemistry Series*, vol. 48. Elsevier, Amsterdam.
- Harman, C., Grung, M., Djedjibegovic, J., Marjanovic, A., Sober, M., Sinanovic, K., Fjeld, E., Rognerud, S., Rannekleiv, S.B., Larssen, T., 2013. Screening for Stockholm convention persistent organic pollutants in the Bosna River (Bosnia and Herzegovina). *Environ. Monit. Assess.* 185, 1671–1683.
- Huckins, J.N., Petty, J.D., Lebo, J.A., Almeida, E.V., Boojj, K., Alvarez, D.A., Cranor, W.L., Clark, R.C., Mogenssen, B.B., 2002. Development of the permeability/performance reference compound (PRC) approach for in situ calibration of semi-permeable membrane devices (SPMDs). *Environ. Sci. Technol.* 36, 85–91.
- Huckins, J.N., Boojj, K., Petty, J.D., 2006. Theory and modeling. In: Huckins, J.N., Boojj, K., Petty, J.D. (Eds.), *Monitors of Organic Chemicals in the Environment, Semipermeable Membrane Devices*. Springer, New York, pp. 45–85.
- ISO 15586, 2003. Water Quality – Determination of Trace Elements using Atomic Absorption Spectrometry with Graphite Furnace.
- Lohmann, R., Boojj, K., Smedes, F., Vrana, B., 2012. Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. *Environ. Sci. Pollut. Res.* 19, 1885–1895.
- Mayer, P., Tolls, J., Hermens, L., Mackay, D., 2003. Equilibrium sampling devices. *Environ. Sci. Technol.* 37, 184A–191A.
- Miege, C., Mazzella, N., Schiavone, S., Dabrin, A., Berho, C., Ghestem, J.-P., Gonzalez, C., Gonzalez, J.-L., Lalere, B., Lardy-Fontan, S., Lepot, B., Munaron, D., Tixier, C., Togola, A., Coquery, M., 2012. An in situ intercomparison exercise on passive samplers for monitoring metals, polycyclic aromatic hydrocarbons and pesticides in surface waters. *Trends Anal. Chem.* 36, 128–143.
- Neal, C., Jarvie, H., Whitton, B., Gemmel, J., 2000. The water quality of the River Wear, north-east England. *Sci. Total. Environ.* 251–252, 173–182.
- Prokeš, R., Vrana, B., Klánová, J., 2012. Levels and distribution of dissolved hydrophobic organic contaminants in the Morava River in Zlín district, Czech Republic as derived from their accumulation in silicone rubber passive samplers. *Environ. Pollut.* 166, 157–166.
- Rusina, T., Smedes, F., Koblizkova, M., Klanova, J., 2010. Calibration of silicone rubber passive samplers: experimental and modeled relations between sampling rate and compound properties. *Environ. Sci. Technol.* 44, 362–367.
- Staudinger, J., Roberts, P.V., 2001. A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions. *Chemosphere* 44, 561–576.
- Thévenot, D.R., Meybeck, M., Chesterikov, A., Chevreuil, M., 1998. Métaux: sources multiples et accumulation In la Seine en son bassin. Elsevier, Paris, pp. 391–437.
- Tusseau-Vuillemin, M.-H., Gourlay, C., Lorgeoux, C., Mouchel, J.-M., Buzier, R., Gilbin, R., Seidel, J.-L., Elbaz-Poulichet, F., 2007. Dissolved and bioavailable contaminants in the Seine river basin. *Sci. Total. Environ.* 375, 244–256.
- Vrana, B., Paschke, A., Popp, P., 2001. Polyaromatic hydrocarbon concentrations and patterns in sediments and surface water of the Mansfeld region, Saxony-Anhalt, Germany. *J. Environ. Monit.* 3, 602–609.
- Warnken, K.W., Zhang, H., Davison W. 2007. In situ monitoring and dynamic speciation measurements in solution using DGT. In: Greenwood, R., Mills, G., Vrana, B. (Eds.), *Passive Sampling Techniques in Environmental Monitoring*. In: D. Barcelo (Ed.), *Comprehensive Analytical Chemistry Series vol. 48*. Elsevier, Amsterdam, pp. 251–278.

Further reading

- www.gabcikovo.gov.sk/svdgn/stup_Cun.htm, (accessed 09.07.13.).
- www.umweltbundesamt.at/umweltsituation/hestia_home, (accessed 09.07.13.).
- Framework Program of Monitoring Water Status in Slovakia in 2010–2015, 2013. Water Research Institute, Bratislava, Slovakia. http://www.vuvh.sk/rsv2/index.php?option=com_content&view=article&id=88&Itemid=106&lang=en, (accessed 09.07.13.).