# **A long-term survey of heavy metals and specific organic compounds in biofilms, sediments, and surface water in a heavily affected river in the Czech Republic**

**Katerina Kohušová ˇ · Ladislav Havel · Petr Vlasák · Jaroslav Tonika**

Received: 4 March 2009 / Accepted: 20 April 2010 / Published online: 13 May 2010 © Springer Science+Business Media B.V. 2010

**Abstract** To assess the long-term anthropogenic load of the Bílina River (Czech Republic), the concentrations of heavy metals and specific organic compounds in different river ecosystem matrices (water, biofilms, and sediments) were determined. Although the current concentrations of pollutants in surface water are low, frequently below the limits of the quantitative analytical methods used, the river ecosystem is still heavily loaded by anthropogenic pollution, mainly from the chemical and mining industries. This was demonstrated by analyzing biofilms and sediments. These matrices are more accurate representatives of the actual situation in the river and do not depend on hydrological conditions or random variability in water quality. The results indicate that the middle and the lower parts of the river are heavily polluted by mercury, arsenic, vanadium, polychlorinated biphenyls, hexachlorobenzene, and dichloro-diphenyl-trichloroethane. As a tributary

K. Kohušová (⊠) · L. Havel · P. Vlasák T.G. Masaryk Water Research Institute, Public Research Institution, Podbabská 2582/30, 160 00 Praha 6, Czech Republic e-mail: katerina.kohusova@gmail.com

K. Kohušová · J. Tonika Faculty of Science, Institute of Environmental Studies, Charles University in Prague, Benátská 2, 128 01 Praha 2, Czech Republic

of the Elbe River, the Bílina River represents a significant risk for the development of quality in this major European river.

**Keywords** Anthropogenic pollution **·** Biofilm **·** Sediment **·** Bílina River **·** Heavy metals **·** Specific organic compounds

# **Introduction**

The impacts of anthropogenic activity on aquatic environments can be assessed through the contamination of particular ecosystem components. This approach is recommended by the valid European Union legislation—Water Framework Directive 2000/60/EC—in an effort to achieve good ecological potential, where priority pollutants are used to qualify the status of surface water chemistry. In addition, it is recommended to analyze matrices other than just surface water samples (Commission of European Community (CEC) [2000](#page-15-0)). Surface water samples provide evidence of the current situation in a river, whereas the measurement of contamination in solid matrices provides evidence of pollution from a longerterm point of view.

Biofilms in particular are a suitable solid matrix for the monitoring of priority pollutants derived from anthropogenic activity (heavy metals and specific organic compounds), and results can be compared to data on concentrations of pollutants in bottom sediments and surface water. Biofilms are complex, heterogeneous systems consisting of living organisms—bacteria, fungi, algae, and protozoa, which are embedded into an extracellular polymer matrix (EPS) (Characklis and Marshal[l](#page-15-0) [1990\)](#page-15-0). The EPS matrix is a dynamic system that fills and forms the space between cells and is responsible for organization of the biofilm community (Lewandowski et al[.](#page-16-0) [1994](#page-16-0)). It is primarily excreted by bacteria colonizing various surfaces (Flemmin[g](#page-15-0) [1993](#page-15-0)). Biofilms can accumulate on many types of substances (inorganic and organic solutes and particles) from the surrounding water through different processes such as sorption, adhesion, cohesion, uptake of ions, and mechanical entrapment of particulate matters (Schorer and Eisele [1997](#page-16-0); Costerton et al. [1994;](#page-15-0) Neu and Marshall [1990\)](#page-16-0). Sorption sites can include the EPS, cell walls, cell membranes, and cell cytoplasm, with each of these sites displaying different sorption preferences, capacities, and properties (Flemmin[g](#page-15-0) [1995](#page-15-0)).

Biofilms arise on almost every submerged surface in a river. Due to their position between substratum and water, their mixed biotic and abiotic composition, and their position in the food web, they play a fundamental role in the various biogeochemical cycles and dynamics of the aquatic ecosystem (Schorer and Eisel[e](#page-16-0) [1997\)](#page-16-0). Biofilms meet many of the requirements for pollution indicators, such as (a) their ubiquity on almost any surface in the water, (b) a sessile mode of growth that reflects the actual habitat conditions, (c) a short life cycle that enables a more rapid response to environmental changes than in higher level organisms, (d) the species diversity in the community with various environmental tolerances, and (e) the relative ease of collecting biofilm samples (McCormick and Cairn[s](#page-16-0) [1994](#page-16-0); Fuchs et al[.](#page-15-0) [1996\)](#page-15-0).

There are two main approaches to using biofilms for monitoring the effects of pollution: (a) monitoring the impact on the biofilm community (e.g., biomass, diversity, presence or absence of species; e.g., Ivorra et al. [1999;](#page-16-0) Gold et al. [2003](#page-15-0)) and (b) monitoring the self-accumulation of toxic elements in biofilm dry mass (e.g., Kröpfl et al[.](#page-16-0) [2006;](#page-16-0) Mages et al[.](#page-16-0) [2004](#page-16-0); Schorer and Eisel[e](#page-16-0) [1997\)](#page-16-0). Because of their ability to accumulate pollutants,

biofilms represent an important part of the river ecosystem. They generally occupy the primary level of the food chain and so can introduce toxic elements into subsequent trophic levels (Frost and Else[r](#page-15-0) [2002](#page-15-0); Jeppesen et al[.](#page-16-0) [2002](#page-16-0); Pusch et al[.](#page-16-0) [1998;](#page-16-0) Durrieu et al[.](#page-15-0) [2005](#page-15-0)). Bottom sediments have similar properties as biofilms regarding the cycling and fate of pollutants in the aquatic environment: they have the ability to bind different substances, can act as a feeding source for macroinvertebrates or fish, can act as secondary sources of pollution during floods as well as low-water periods, and are a more or less temporal sink for pollutants (e.g., Baudo et al[.](#page-14-0) [1990](#page-14-0); Lotuf[o](#page-16-0) [1998](#page-16-0); Gewurtz et al[.](#page-15-0) [2000](#page-15-0); Baborowski et al[.](#page-14-0) [2004](#page-14-0); Stachel et al[.](#page-16-0) [2004;](#page-16-0) Umlauf et al[.](#page-17-0) [2005\)](#page-17-0). Pollutants accumulated in both biofilms and sediments can be considered bioavailable (e.g., Landrum and Robbin[s](#page-16-0) [1990;](#page-16-0) Farag et al[.](#page-15-0) [2007](#page-15-0)).

The aim of this paper is to use pollution levels in biofilms, sediments, and surface water to assess the long-term anthropogenic load and in a heavily polluted river, which is considered to be one of the most important sources of pollution in the Elbe River catchment area.

## **Materials and methods**

## Site description

The river studied, the Bílina River, is located in the north-west of the Czech Republic (catchment area:  $1,070.9 \text{ km}^2$ , length of river: 84.2 km). Its basin is situated in a highly industrialized area, incorporating primarily coal mining and power and chemical industries. A high population concentration also significantly contributes to the river's pollution. Only the first few kilometers of the river that flow through the original bed are relatively unpolluted. The remaining 71 km (out of 84.2 km) have been more or less influenced by anthropogenic activity (Havlík et al. [1997a,](#page-15-0) [b\)](#page-15-0). Surface coal mining has given rise to extensive changes in the river bed—the bed often had to be solidified, and the flow, redirected or conduited. The first detailed research on the Bilina River (1994–1996) showed it to be an ecologic disaster, with a severely damaged

aquatic ecosystem (no permanent fish population, benthos species with morphological deformations, and hereditary genetic changes; only resistant and exotic species of mollusks are present; etc.), with low surface water quality (Havlík et al. [1997a,](#page-15-0) [b\)](#page-15-0). The Bílina River is a significant tributary of the Elbe River, not in volume but in quality, with pollution from the Bílina River negatively affecting the Elbe River ecosystem. Water quality in certain parts of the Elbe River situated in post-communist countries is influenced by the continuous mobilization of hazardous substances from large amounts of old contaminated deposits (Brügman[n](#page-14-0) [1995](#page-14-0)) and current industrial activities. Currently, several pollutants are considered to be prominent, such as nitrates, suspended sediments, mercury, cadmium, hexachlorobenzene (HCB), dichloro-diphenyl-trichloroethane (DDT), and hexachlorocyclohexane (HCH) isomers (Adams et al[.](#page-14-0) [2001](#page-14-0)). The Bílina River is an important source of PAHs, xenoestrogens (e.g. Bisphenol A), organochlorine compounds (Stachel et al[.](#page-16-0) [2005](#page-16-0); Heemken et al[.](#page-15-0) [2001](#page-15-0)), DDT (Heinisch et al[.](#page-15-0) [2005a](#page-15-0)), and heavy metals (Vink et al[.](#page-17-0) [1999](#page-17-0)). As a result, the Elbe River is considered an important source of contaminants from anthropogenic sources, for example, xenoestrogens, discharging into the North Sea (Stachel et al[.](#page-16-0) [2003;](#page-16-0) Heemken et al[.](#page-15-0) [2001](#page-15-0)). The Bílina River is often mentioned together with the Mulde River (Germany), which is affected by similar anthropogenic load. The Mulde River is polluted by specific organic compounds coming from chemical industry in the Bitterfeld area (Wilken et al[.](#page-17-0) [1994;](#page-17-0) Franke et al[.](#page-15-0) [2005](#page-15-0)). Together with other rivers in the Harz region, which are characterized by high contents of salts (Ca, Mg, Na, and Cl) due to their different geological background, the Mulde River is polluted by heavy metals produced by the mining industry and industrial and urban activities (Kowalik et al[.](#page-16-0) [2003;](#page-16-0) Klemm et al[.](#page-16-0) [2005;](#page-16-0) Hintelmann and Wilke[n](#page-16-0) [1995](#page-16-0)).

## Sample collection

Sampling sites covered the entire course of the Bílina River, from the almost unpolluted source region to the heavily anthropogenically polluted final site in the city of Ústí nad Labem, at the confluence with the Elbe. All matrices (biofilm, sediment, and water) were monitored at four sampling sites (B1, B2, B3, and B4), which represent different sections of the river: B1, the unpolluted, almost natural section; B2, prevailing municipal pollution; B3, industrial and municipal pollution; and B4, the final profile, which provides evidence of the pollution carried by the Bílina River into the Elbe River (Fig. [1\)](#page-3-0).

#### Sample analysis

Samples were collected during the period from 2004 to 2008 as follows: biofilms and sediments, sampled during the growing and non-growing season from 2005 to 2008 (sampling in the winter of 2007 was shifted to the beginning of 2008 because of high water levels); surface water, sampled during the years 2004, 2005, 2006, and 2007. Mixed samples of biofilms were scraped off submerged surfaces by a brush and spatula. Mixed samples of sediments were combined using several point samples collected manually in places where bottom sediments regularly accumulate. The sampling depth for sediments was about 10–15 cm from the surface. Surface water samples were collected from the river's course using glass and PE bottles. All the samples were immediately transported to an accredited laboratory (certified according to  $\overline{CSN}$  EN ISO/IEC 17 025 ([01 5253](#page-15-0)), meeting ISO and EPA standards) and analyzed to determine the contents of selected heavy metals (arsenic (As), cadmium (Cd), mercury (Hg), lead (Pb), vanadium  $(V)$  and zinc  $(Zn)$ ) and specific organic compounds (polychlorinated biphenyls (PCBs), sum of PAHs, and organochlorine pesticides: sum of HCH isomers, HCB, and dichloro-diphenyltrichloroethane ("total DDT")).

Biofilm and sediment samples were homogenized and lyophilized to a constant dry weight. Heavy metals (As, Cd, Pb, V, and Zn) were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES spectrometer IRIS Intrepid II XSP) with total digestion in aqua-regia. Content of mercury was determined by atomic spectrometry in an AMA 254. The following specific organic compounds were measured: sum of polychlorinated biphenyls (PCBs: PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, and PCB

<span id="page-3-0"></span>

**Fig. 1** Map of the study area (Bílina River) and the location of sampling sites (B1–B4)

180), sum of PAHs (fluoranthene, benzo[b] fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene), organochlorine pesticides: sum of HCH isomers (α-HCH, β-HCH, γ-HCH, δ-HCH; HCB), and total DDT, which is used to refer to the sum of all dichloro-diphenyl-trichloroethane (DDT)-related compounds (*o*,*p'*-DDT; *p*,*p'*-DDT; *o*,*p'*-DDD;  $p$ , $p'$ -DDD;  $o$ , $p'$ -DDE;  $p$ , $p'$ -DDE). PAHs were determined by high-performance liquid chromatography (HPLC Waters) with organic solvent extraction. PCBs and organochlorine pesticides were determinated by gas chromatography (GC Agilent 6890 N) with organic solvent extraction. All the concentrations of the pollutants in the solid matrices are reported on a dry-weight basis. Water samples were analyzed by the same methods (but without the preliminary homogenization, lyophilization, and digestion treatments).

## **Results and discussion**

### Surface water

As expected, concentrations of pollutants in surface water differed along the longitudinal profile of the river and reflected existing point and nonpoint pollution sources. According to the average concentrations measured for the survey period, the sampling sites B3 and B4 (Table 1) had the greatest contamination loads. These sites are located in industrialized areas (power and chemical industries, brown coal mining) with a high population concentration. The lowest concentrations of pollutants were found in the B1 site, which is situated in the relatively unpolluted part of the river just downstream of a drinking-water reservoir.

Table 2 shows the average concentrations of heavy metals and specific organic compounds present in surface water measured during the years 2004–2007 at the B4 sampling site. This site is generally the most polluted profile and represents the load of pollutants carried from the Bílina River into the Elbe River. The current concentrations of monitored pollutants in surface water are low and frequently below the detection limits of the analytical methods used (e.g., Cd, Hg, Pb, particular metabolites of DDT: DDE, DDD). However, the average annual concentrations were increased by occasional peaks of higher concentrations (e.g., Pb, in the year 2007; Zn:2007; PAHs:2004; Fig. [2\)](#page-5-0). These peaks can reach considerable values and consequently threaten the river ecosystem.

**Table 2** Average concentrations of heavy metals (microgram per liter) and specific organic compounds (nanogram per liter) measured during the years 2004–2007 in surface water in the B4 sampling site

Metal		Organic	
		compound	
Arsenic	$14.13(11.03)^{a}$	Sum of	$66.72(93.33)^b$
		<b>PAHs</b>	
Cadmium	$0.21(0.18)^{b}$	Sum of	$6.15(4.74)^a$
		<b>PCBs</b>	
Mercury	$0.10(0.12)^a$	Sum of	$2.22 (1.44)^c$
		<b>HCHs</b>	
Lead	7.92 $(12.52)^d$	HCB	$3.95(5.45)^c$
Vanadium	40.33 $(25.31)^e$	Total	9.50 $(16.66)^c$
		<b>DDT</b>	
<b>Zinc</b>	35.26 $(44.95)^{b}$		

Values represent the average from the 2004–2007 period, with SD in parentheses



 $d_n = 12$ 

 $e_n = 9$ 

The average annual concentrations of selected pollutants measured from 2004 to 2007 were compared with the results from the first integrated monitoring of the Bílina River during the years 1994–1996 (Havlík et al. [1997a](#page-15-0), [b\)](#page-15-0). During the intervening decade, the concentrations of most of the selected pollutants decreased distinctly (except for As, concentrations are partly affected by natural background levels; for Pb and Zn, average annual concentrations for 2007 were affected by significant single peaks; Fig. [2a](#page-5-0), b). Similar

Site/metal	Arsenic	Cadmium	Mercury	Lead	Vanadium	Zinc
<b>B1</b>	1.71	0.16	0.04	1.00	2.50	35.95
B <sub>2</sub>	1.91	0.16	0.08	2.76	4.38	24.31
B <sub>3</sub>	11.63	0.23	0.07	2.87	85.56	27.87
<b>B4</b>	14.13	0.21	0.10	7.92	40.33	35.26
Site/organic compound	PAHs	<b>PCBs</b>	<b>HCHs</b>	<b>HCB</b>	<b>Total DDT</b>	
<b>B1</b>	5.18	0.84	0.90	0.15	0.80	
B <sub>2</sub>	10.41	3.36	2.13	2.80	1.08	
B <sub>3</sub>	77.33	6.90	1.33	0.38	1.35	
<b>B4</b>	66.72	6.15	2.22	3.95	9.50	

**Table 1** Average surface water concentrations of heavy metals (microgram per liter) and specific organic compounds (nanogram per liter) in the longitudinal profile of river during the survey (2004–2007)

The bold letters indicate the most contaminated sampling sites

<span id="page-5-0"></span>**Fig. 2 a** Concentrations of heavy metals and specific organic compounds in surface water—comparison of the 1994–1996 period (data from Havlík et al. [1997a](#page-15-0), [b\)](#page-15-0) and the current survey (2004–2007). **b** Concentrations of heavy metals and specific organic compounds in surface water—comparison of the 1994–1996 period (data from Havlík et al. [1997a](#page-15-0), [b\)](#page-15-0) and the current survey (2004–2007)



decreasing trends in water pollution have been described for the Elbe River and other similarly anthropogenically affected rivers in post-communist countries (Adams et al[.](#page-14-0) [2001](#page-14-0); Klemm et al[.](#page-16-0) [2005\)](#page-16-0), and decreasing loads of organic wastes and mercury were already demonstrated soon after 1990 (Simo[n](#page-16-0) [1991\)](#page-16-0).

After the fall of the communist regimes in the former Czechoslovakia and East Germany, many plants and whole industrial complexes were closed or reduced, and stricter requirement accompanied by the introduction of modern water treatment technologies were introduced (Adams et al[.](#page-14-0) [2001;](#page-14-0) Brügman[n](#page-14-0) [1995](#page-14-0)). Moreover, many contaminated sites in this region were subject to clean-up efforts (Brügman[n](#page-14-0) [1995](#page-14-0)).

# Biofilms and sediments

Although the concentrations of pollutants in surface water have decreased (both in average and maximum values), the load to the river ecosystem remains heavy as a consequence of the long-term cumulative effect of pollutants in solid matrices, biofilms, and bottom sediments. Pollutant concentrations in these solid matrices differed from concentrations detected in the water by 3–6 orders of magnitude (Fig. [3a](#page-6-0), b). The greatest difference (six orders of magnitude) was found for specific organic compounds (HCB, total DDT), which could reflect the accumulation process being most effective for these compounds.

Changes in pollutant concentrations measured in solid matrices among the sampling sites were not as clear as differences in water sample concentrations. ANOVA (at  $P < 0.05$ ) showed significant spatial differences among localities for Cd, Hg, V, Zn, HCB, and total DDT measured in biofilms, and for Cd, Hg, V, Zn, HCHs, and HCB in sediments (Tables [3,](#page-7-0) [4\)](#page-7-0). Determining which sampling site was the most contaminated was difficult. In most cases, the sites B3 and B4 <span id="page-6-0"></span>**Fig. 3 a** Comparison of concentrations of heavy metals and specific organic compounds measured in water and solid matrices—biofilms and sediments. **b** Comparison of concentrations of heavy metals and specific organic compounds measured in water and solid matrices—biofilms and sediments



situated in the lower part of the river were the most polluted (as was the case for surface waters), but for some pollutants, the opposite trend was observed (e.g., Cd, concentration in solid matrices decreased from the B1 profile to the final profile B4, probably due to natural sources in the Krušné Hory mountains in the upper part of the river).

According to the average annual concentrations of HCHs, the site B2 was the most polluted profile (which agrees with the relatively higher concentrations in surface water), but this is not unambiguous when evaluating the trends in specific concentrations (Fig. [10\)](#page-13-0). The site B4 had the highest average concentrations of total DDT

	Site/metal	Arsenic	Cadmium <sup>a</sup>	Mercury <sup>a</sup>	Lead	Vanadium <sup>a</sup>	$\rm Zinc^a$
<b>Biofilm</b>	B1	66.50	7.99	0.16	60.83	47.42	495.67
	<b>B2</b>	68.22	2.39	0.26	60.25	82.37	363.67
	B <sub>3</sub>	59.12	0.93	0.98	50.13	398.17	322.17
	B4	50.75	1.12	1.61	67.40	199.67	459.50
Sediment	B1	39.03	4.00	0.16	56.98	44.97	306.67
	<b>B2</b>	79.12	2.97	0.33	64.93	90.67	363.50
	B <sub>3</sub>	77.18	2.46	1.27	54.13	595.17	549.83
	B4	48.80	1.60	2.22	85.38	142.20	470.00

<span id="page-7-0"></span>**Table 3** Average concentrations of heavy metals (milligrams per kilogram dry weight) in solid matrices during the survey (2005–2008)

The bold entries indicate the most contaminated sampling sites

<sup>a</sup>Significant differences among localities (ANOVA test,  $p < 0.05$ )

in sediment (Table 4); however, this difference was not statistically significant due to an isolated extremely high maximum (December 2006,  $>9,000$  μg/kg, but P=0.16). If we disregard this maximum, the differences among the sampling sites become statistically significant. The B4 site would still be much more highly contaminated than the other sites (this newly calculated total DDT concentration would be 572.3 μg/kg, *P* < 0.05).

Although no generally accepted system of classification of concentrations of pollutants in biofilms exists, the contamination of sediments can be assessed by the classification made for the Elbe River as part of the ARGE–Elbe project (Bergemann and Gaumer[t](#page-14-0) [2006\)](#page-14-0). The sediments were divided into seven classes with different values of contamination by heavy metals (As, Cd, Hg, Pb, and Zn) and specific organic compounds

(HCHs, HCB, PCBs, and total DDT; Table [5\)](#page-8-0). Table [6](#page-8-0) shows the development of pollutant concentrations down the river, and it is apparent that the concentrations of heavy metals (except Cd, as is mentioned before) gradually rise, from the almost unpolluted B1 site to the final B4 site. Changes in concentrations of specific organic compounds often corresponded to point sources of pollution in the drainage area. The concentration of HCB greatly increased at the B4 site in the vicinity of a chemical plant. Sources of PCB pollution occur mainly in the lower part of the river (again due to the chemical industry); nevertheless, the concentrations were rather high throughout the whole longitudinal profile (with maximum in the B4 profile). Likewise, concentrations of total DDT gradually increased down the river with maximum at the B4 site, where old deposits related to former production activities are assumed

	Site/organic compound	Sum of PCBs	Sum of PAHs	Sum of HCH <sub>s</sub>	$HCB^a$	Total DDT <sup>a</sup>
Biofilm	B1	47.32	3.43	3.44	22.13	18.48
	B <sub>2</sub>	54.05	0.89	3.90	23.83	34.21
	B3	66.12	2.96	2.08	22.52	25.11
	B4	78.95	2.03	2.62	436.67	746.22
Sediment	B1	29.47	1.94	0.84	5.73	15.12
	<b>B2</b>	85.45	1.24	3.50	6.89	39.72
	B3	111.51	1.70	1.42	11.42	24.57
	B4	208.27	2.37	1.68	1705.50	1978.42

**Table 4** Average concentrations of specific organic compounds (micrograms per kilogram dry weight; PAHs: mg/kg dry weight) in solid matrices during the survey (2005–2008)

The bold values indicate the most contaminated sampling sites

<sup>a</sup>Significant differences among localities (ANOVA test,  $p < 0.05$ )

Indicator (unit)/class		I and II	Н	II and III	Ш	III and IV	IV
As $(mg/kg)$	${<}10$	$<$ 20	$<$ 40	${<}80$	< 160	< 320	>320
$Cd$ (mg/kg)	${<}0.3$	${<}0.6$	${<}1.2$	< 2.4	<4.8	<9.6	>9.6
$Hg$ (mg/kg)	${<}0.2$	${<}0.4$	${<}0.8$	${<}1.6$	< 3.2	<6.4	> 6.4
$Pb$ (mg/kg)	<25	< 50	${<}100$	${<}200$	$<$ 400	< 800	> 800
$Zn$ (mg/kg)	${<}100$	${<}200$	$<$ 400	< 800	< 1600	$<$ 3200	>3200
Sum of HCHs $(\mu g/kg)$		$<$ 5	<10	$<$ 20	< 50	${<}100$	>100
$HCB (\mu g/kg)$		$<$ 20	$<$ 40	${<}100$	${<}200$	$<$ 400	>400
Sum of PCBs $(\mu g/kg)$		$\leq$ 2	$<$ 5	${<}10$	<25	< 50	>50
Total DDT $(\mu g/kg)$		$<$ 20	$<$ 40	${<}100$	${<}200$	$<$ 400	>400

<span id="page-8-0"></span>**Table 5** Classification of sediment contamination—project ARGE–Elbe (Bergemann and Gaumer[t](#page-14-0) [2006\)](#page-14-0)

to exist. Concentrations of HCHs were rather low throughout the whole longitudinal profile of the river.

Although the concentrations of pollutants varied considerably throughout the period of monitoring, some patterns relating to the contamination of particular river ecosystem components by pollutants were found. In particular, there was a relationship between the concentrations of pollutants in biofilms and those in sediments. In fact, biofilm concentrations of Hg, V, and total DDT showed significant linear regressions (Hg:  $R^2$  = 0.63, V:  $R^2 = 0.89$ , and total DDT:  $R^2 = 0.99$ ) with their respective concentrations in sediments (Fig. [4\)](#page-9-0). A weaker relationship was found for As  $(R^{2} = 0.35)$ , Cd  $(R^{2} = 0.41)$  and PCBs  $(R^{2} = 0.51)$ ; Fig. [4\)](#page-9-0).

The relationship between concentrations of pollutants in solid matrices and water were significant only for two substances: between concentrations of vanadium in solid matrices (both in biofilm and sediment) and surface water (biofilm:  $R^2 = 0.87$ , sediment:  $R^2 = 0.90$ ) and between the concentrations of PAHs in biofilm and water  $(R^2 =$ 0.74), though not in the sediment  $(R^2 = 0.22$ ; Fig. [5\)](#page-9-0). These results could be affected by higher variability in surface water sampling, for instance, changes in hydrological conditions and short-term fluctuations in pollutant concentrations.

Interrelationships among the pollutant concentrations detected in particular ecosystem components provide evidence of the distribution of those pollutants, information about target accumulation areas, and about their transfer within the river ecosystem as well as within aquatic food webs. In addition to the above-mentioned biofilm–sediment and water–solid matrices correlations, which have been mentioned by several authors (e.g., Farag et al[.](#page-15-0) [2007;](#page-15-0) Baudo et al[.](#page-14-0) [1990;](#page-14-0) Ivorra et al[.](#page-16-0) [1999](#page-16-0); Behra et al[.](#page-14-0) [2002](#page-14-0); Holding et al[.](#page-16-0) [2003;](#page-16-0) Farag et al[.](#page-15-0) [1998](#page-15-0)), other correlations are described in the literature dealing with river ecosystems, for example, correlations between colloids and biofilm (Farag et al[.](#page-15-0) [2007\)](#page-15-0), sediment and biota (Farag et al. [2007;](#page-15-0) Baudo et al. [1990;](#page-14-0) Farag et al. [1998\)](#page-15-0), biofilm and biota (Durrieu et al[.](#page-15-0) [2005;](#page-15-0)

**Table 6** Evaluation of sediment contamination in the longitudinal profile of the Bílina River according to the classification from the ARGE–Elbe project (Bergemann and Gaumer[t](#page-14-0) [2006\)](#page-14-0)

Indicator/class		I and II	П	II and III	Ш	III and IV	IV
Arsenic			Β1	B1, B2, B3, B4	B <sub>2</sub> , B <sub>3</sub> , B <sub>4</sub>	B <sub>3</sub>	
Cadmium		B4	B4	B1, B2, B3, B4	B1, B2, B3, B4	<b>B</b> 1	
Mercury	B <sub>1</sub>	<b>B1, B2</b>	B <sub>2</sub> , B <sub>3</sub> , B <sub>4</sub>	B <sub>3</sub>	<b>B3, B4</b>	B4	
Lead		B1, B3	B1, B2, B3, B4	<b>B4</b>			
Zinc		Β1	B1, B2, B3, B4	B1, B2, B3, B4	B <sub>3</sub>		
Sum of PCBs					<b>B</b> 1	<b>B1, B2</b>	B <sub>2</sub> , B <sub>3</sub> , B <sub>4</sub>
Sum of HCH <sub>s</sub>		B1, B2, B3, B4	B2				
<b>HCB</b>		B <sub>1</sub> , B <sub>2</sub> , B <sub>3</sub>					B4
<b>Total DDT</b>		B1, B2, B3	B1, B2, B3	<b>B2.</b> B3	<b>B</b> 4		B4

B1, B2, B3, and B4 are the sampling sites

<span id="page-9-0"></span>

**Fig. 4** Relationship between the concentrations of Hg, V, total DDT and PCBs in biofilm and sediment



**Fig. 5** Relationship between concentrations of vanadium and PAHs in solid matrices (biofilm and sediment) and water

Farag et al[.](#page-15-0) [1998\)](#page-15-0), and water and biota (Farag et al. [2007](#page-15-0), [1998](#page-15-0)).

To rule out the possible effect of the composition of the biofilm samples on levels of contamination, microscopy of particular biofilm samples was performed. The biofilms consisted of abioseston, bacteria, algae (green filamentous, spheric algae, and diatoms) cyanobacteria, fungi, *Cilliata*, *Rotatoria*, *Nematoda*, etc. However, all the samples had a very similar species composition, consisting overwhelmingly of diatoms, with the filamentous species *Melosira varians* and the unicellar species *Navicula* sp. comprising the vast majority of the biomass. Therefore, we believe that biofilm sample contaminations provide evidence of the actual pollution load in their environment.

#### Individual aspects of particular pollutants

Concentrations of As, Cd, Pb, and Zn in biofilms and sediment did not show any consistent trends. Loads usually increased in the lower part of the river (the sampling sites B3 and B4), except for cadmium (described above). Natural sources of these metals are located in the Krušné Hory mountains that extend to the upper part of the river (Vesel[ý](#page-17-0) [1994](#page-17-0)). Ecosystem contamination is also caused by anthropogenic sources in the watershed such as combustion of fossil fuels (As, Cd, and Zn), the coal mining and ore-mining industries (As, Cd, Pb), leachates from power plant flyash (As), application of fertilizers (Cd), and the chemical industry and associated trade effluents (Cd, Pb, and Zn).

**Fig. 6** Mercury concentration (milligrams per kilogram dry weight) in biofilms and sediments from 2005–2008

Figure 6 shows mercury concentrations in biofilm and sediment solid matrices in the river. The ecosystem is polluted by mercury derived from anthropogenic sources and old deposits (contaminated sites) in the vicinity of the river. In the past, the site was overloaded with mercury, which is reflected in extremely high mercury concentrations in sediments (maximum values, 27.9 and 13.46 mg/kg dry weight) measured from 1989 to 1996 (Borovec et al[.](#page-14-0) [1998\)](#page-14-0). Although current surface water mercury concentrations are below the detection limit  $(0.05 \mu g/l)$ , except for some isolated fluctuations, mercury was detected regularly in the solid matrices, especially in the lower part of the river, in considerable amounts. Vesel[ý](#page-17-0) [\(1994](#page-17-0)) reported that natural mercury concentration in Czech river sediments is around 0.2 mg/kg. This natural mercury concentration level was found in the upper part of the river at the B1 site and partially at the B2 site. Concentrations at the B3 site (0.6–1.9 mg/kg dry weight sediment) and particularly at the B4 site (0.8–3.6 mg/kg dry weight sediment) were much higher. The biofilm contamination levels were slightly lower (at B3: 0.6– 1.6 mg/kg dry weight biofilm; at B4: 1.3–1.9 mg/kg dry weight biofilm). Big chemical plants represent the main sources of mercury in the drainage area. The first one is located 12 km upstream of the B3 site, and waste waters from organic synthesis where mercury is used as a reaction catalyst could be the cause of increases in concentration in the river. The most considerable source of mercury is a chemical plant producing synthetic resins and inorganic compounds located in the immediate vicinity of the B4 sampling site. Mercury



comes from the production of chlorine (which is a preliminary base material for producing other inorganic and organic compounds, e.g., epoxide resins, hydrochloric acid, perchloroethylene) by an amalgam electrolytic process that produces great amounts of mercury as a waste material. In 2003, pretreated waste waters from the industrial waste water treatment plant situated on the chemical plant's premises were transferred to the municipal waste water treatment plant. In the future (by the year 2012), the situation is expected to improve because of a commitment by the plant to replace the amalgam electrolytic process by a more environmentally friendly diaphragm-based process.

The lower part of the river is contaminated by considerable concentrations of vanadium from anthropogenic sources such as the oil, coal, and chemical industries. Maximum concentrations of vanadium were detected at the B3 site, both in the solid matrices and surface water samples. The source of this contamination was probably industrial waste waters from the chemical plant (situated 12 km upstream), where the vanadium is used as an industrial catalyst for organic synthesis. At the final B4 site, the vanadium concentration was lower, likely due to sedimentation and dilution. Vanadium concentrations at the B3 site showed significant seasonal variation (Fig. 7). During the summer, i.e., the growing season, the concentrations were distinctively lower than in winter. This tendency at the B3 profile was also found for mercury and partly for other metals (As, Cd, and Zn) and some specific organic compounds (PCBs and PAHs). According to a field survey of this site, these variations were probably caused by the accumulation and of pollutants in the biomass of aquatic macrophytes as well as physical filtration and entrapment. The middle and lower parts of the river are overgrown with pondweed (*Potamogeton pectinatus*), which has been shown to accumulate metals (Demirezen and Akso[y](#page-15-0) [2004;](#page-15-0) Greger and Kautsk[y](#page-15-0) [1991;](#page-15-0) Peng et al[.](#page-16-0) [2008\)](#page-16-0) and organic compounds (Vrochinskiy [1970;](#page-17-0) Vrochinskiy et al. [1970](#page-17-0)) from flowing water. The increase in their concentrations outside the growing season is probably caused by reduced accumulation due to the reduced growth of plants, as well as the decomposition of pondweed biomass and subsequent release of accumulated pollutants to the water.

Concentrations of specific organic compounds varied with sampling time and also among the sampling sites. Except for a large increase in HCB and total DDT concentrations at the B4 site (both biofilm and sediment matrices), no trends in the course of concentration for other specific organic compounds were observed. PCB and PAH contamination of the aquatic ecosystem comes probably from the petrochemical industry, fossil fuel combustion, or the chemical industry where these substances are generated as by-products of chemical production. Their concentrations at the B3 site tend to have seasonal variations, similarly to the metals (Hg, V, As, etc.). There was a large increase in HCB and total DDT concentrations

**Fig. 7** Vanadium concentrations (milligrams per kilogram dry weight) in biofilms and sediments from 2005–2008





at the B4 site (Figs. 8, 9). This site is situated in the immediate vicinity of a chemical plant where DDT was produced until 1970 (production of approximately 1,000 tons per year; Heinisch et al. [2005a\)](#page-15-0). The total DDT contamination was caused probably by old deposits in the vicinity of the plant. Sporadically, even higher surface water concentrations of total DDT were measured (e.g., a single maximum of 47.17 ng/l in the year 2007), although the current concentrations are low. These higher concentrations may also derive from the old deposits or reflect some unknown source of DDT despite the fact that this substance has been banned in the Czech Republic for over 30 years. Results from solid matrices show a still significant existent load of DDT in the lower part of the river. The Czech part of the Elbe River (including its drainage basin) is considered an important source of DDT. Based on aquatic environmental contamination (surface water, sediments, and fish biomass) by DDT and its metabolites, the Bilina River is included among the so-called pollution "hot spots," together with the Spittelwasser of the Mulde River (Bitterfeld, Germany) and Teltowkanal (Berlin, Germany). All of these watercourses are in the close vicinity of chemical enterprises in Berlin-Adlershof, Bitterfeld, and Ústí nad Labem (Heinisch et al[.](#page-15-0) [2005a\)](#page-15-0). Data from the Bílina River in Ústí nad Labem in 1999 showed an extreme load of DDT in sediments (total DDT contents: 8 g/kg with the majority being DDT, followed by DDD and then DDE), and this chemical plant was identified as the main source of that pollution. No other Elbe river tributaries were as contaminated (e.g., the Mulde River, 2,100 μg/kg; Heinisch et al. [2005a](#page-15-0)). On the other hand, the present contamination has decreased significantly (sediments: 5–1,500 μg/kg, isolated maximum in 12/2006: 9,000 μg/kg, biofilms: 5–3,400 μg/kg).

An extreme increase in HCB concentration was detected at the B4 site (Fig. 9), again in the vicinity of the chemical plant that is the main source of contamination. In the past, HCB originated during the production of chlorinated pesticides, lindane in particular. The production of HCB was banned in the 1970s (Courtne[y](#page-15-0) [1979\)](#page-15-0). Currently,

**Fig. 9** HCB concentrations (milligrams per kilogram dry weight) in biofilms and sediments from 2005–2008



HCB is generated as a by-product of the production of other industrial chemicals (e.g., chlorine compounds).

The maximum values (4,350 μg/kg dry weight) of current HCB concentrations in sediments from the B4 site approximate the maximum values measured in the 1980s in the Rhine River (5,100 μg/kg dry weight) (BU[A](#page-15-0) [1994](#page-15-0)). Nevertheless, the current average values  $(1,706 \mu g/kg)$ dry weight) are lower by more than one half. It is interesting that the concentrations from the year 2003 had an extremely high maximum value (5,300 μg/kg dry weight), detected in close vicinity of the Ústí nad Labem chemical plant (Petrli[k](#page-16-0) [2006\)](#page-16-0). Current HCB concentrations in sediments are consistently above the concentrations measured for the majority of sediments sampled during the years 1991 and 2001 in the Rhine River and the Elbe River (10-500  $\frac{tg}{kg}$  dry weight) (BU[A](#page-15-0) [1994\)](#page-15-0) and the high maximums still exist. However, they are still lower than the extreme values in the St. Clark River, USA, where HCB concentrations taken near a point source (chemical sewer discharge) were as high as 280,000 μg/kg dry weight (Oliver and Pugsle[y](#page-16-0) [1986](#page-16-0)).

The Bílina River contributes to sediment contamination by organic priority pollutants,  $p, p'$ -DDT and HCB in the Upper Elbe River (Schindler et al. [1997\)](#page-16-0), and influences the pollution distribution, so that there are higher concentrations of these pollutants in the Upper Elbe River (average value from 1991–2001: 758 μg/kg) than in the Middle Elbe River (average value from 1991–2001: 102 μg/kg) (Heininger et al[.](#page-15-0) [2003](#page-15-0)).

<span id="page-13-0"></span>568 Environ Monit Assess (2011) 174:555–572

Pollution by HCH was variable in both space and time (Fig. 10). HCH, especially  $\gamma$ -HCH (lindane), was produced in the chemical plant in Ústí nad Labem. The Bílina River has been implicated as an HCH-polluted river, together with the Mulde River (hotspot area for  $\beta$ -HCH in the Bitterfeld region), the Darmbach River, and slowly flowing waters such as Teltowkanal (Berlin) and Hamburger Hafengewasser (all in Germany), all situated in the vicinity of former manufacturing concerns with HCH/lindane production (Heinisch et al[.](#page-15-0) [2005b;](#page-15-0) Barth et al[.](#page-14-0) [2007\)](#page-14-0). These former industries and redeposition from areas where HCH was used, such as old deposits, dumps, soils, and timber, represent the sources of river contamination. Past levels in the Ústí nad Labem area were many times higher: in 1997, the concentration of the sum of HCHs in the surface water in the Bílina River was about 65 μg/l, with the majority of  $\alpha + \beta + \delta$  HCH and minority of γ-HCH (Heinisch et al[.](#page-15-0) [2005b\)](#page-15-0) (current concentrations are 0.3–5.2 ng/l); the concentration in sediment in 1999 was 425 μg/kg, again with the proportional composition of isomers (γ-HCH share of 38%; Heinisch-etal:2005b; current concentrations are 0.25–6.8 μg/kg in sediments and 0.25–21.6 μg/kg in biofilms). The biggest contribution of HCHs to the Elbe River is via the Mulde River, where these authors detected the loads about 973 μg/kg in sediments in 1999.

Although there has been evident improvement in the quality of surface water in the last decade, the load to the river ecosystem remains heavy because of the contamination of solid matrices by

**Fig. 10** HCH concentrations (milligrams per kilogram dry weight) in biofilms and sediments from 2005–2008



<span id="page-14-0"></span>specific pollutants. The majority of these pollutants are included in the Water Framework Directive 2000/60/EC as "priority" or "hazardous substances" (Commission of European Community (CEC) [2000](#page-15-0)), which are characterized by properties that can negatively affect the environment, such as toxicity, persistence, and the ability to bioaccumulate. Biofilms and sediments serve as a "sink and source" for pollution substances in the environment (Liu et al[.](#page-16-0) [2008;](#page-16-0) Flemmin[g](#page-15-0) [1995\)](#page-15-0). Thus, they may become a secondary source of pollution due to changes in hydrological, chemical, or biological conditions in the river. Biofilm cells can be actively dispersed by the shedding of divided and motile cells or passively detached by erosion or higher shear stress in the form of clumps or small aggregates. The biofilm structure can be damaged by massive removal and abrasion caused by collision with substances moving in the current (Donla[n](#page-15-0) [2002;](#page-15-0) van Loosdrecht et al[.](#page-17-0) [1995;](#page-17-0) Denkhaus et al[.](#page-15-0) [2007](#page-15-0)). Flowing cells or aggregates are carried downstream where they can release accumulated pollutants. In addition, when a biofilm decomposes, it can release sorbed substances, which are subsequently remobilized and can contaminate the water (Flemmin[g](#page-15-0) [1995\)](#page-15-0). Similarly, sediments can release accumulated substances due to changes in chemical conditions (e.g., changes in pH, oxygen concentration, redox potential) or hydrological conditions accompanying changes in flow rate (e.g. during floods or, on the contrary, low-water periods) (Baborowski et al. 2004; Stachel et al[.](#page-16-0) [2004](#page-16-0); Umlauf et al[.](#page-17-0) [2005\)](#page-17-0). Due to high contamination in both biofilms and sediments, the Bílina River continues to be a major source of potential pollution from heavy metals and specific organic compounds.

## **Conclusion**

Anthropogenic load to the Bílina River ecosystem by heavy metals and specific organic compounds is still high even though there has been a significant decrease in the concentrations of most pollutants in surface water over the last 10 years. The continuing significant contamination of solid matrices (biofilms and sediments) reflects existent pollution in the river, both from old deposits in the vicinity and from current pollution sources such as the chemical, mining, and petrochemical industries. The results of contamination of surface water and the solid matrices showed that the middle and lower parts of the river are at the highest risk. This largely corresponds to the point and non-point pollution sources in the drainage area. Concentrations of some pollutants, mainly heavy metals (e.g., vanadium), showed seasonal variations probably caused by the massive occurrence of aquatic macrophytes in the river. Biofilms are a suitable matrix for assessing pollutant contamination in the river; overall, they show similar trends and the levels of most pollutants were well correlated with those in sediments.

**Acknowledgements** This research was supported by the Ministry of the Environment of the Czech Republic by project Nos. MZP0002071101 and SP/1b7/124/08.

## **References**

- Adams, M. S., Ballin, U., Gaumert, T., Hale, B. W., Kausch, H., & Kruse, R. (2001). Monitoring selected indicators of ecological change in the Elbe River since the fall of the Iron Curtain. *Environmental Conservation, 28*(4), 333–344. doi[:10.1017/S0376892901000364.](http://dx.doi.org/10.1017/S0376892901000364)
- Baborowski, M., von Tümpling, W., & Friese, K. (2004). Behaviour of suspended particulate matter (SPM) and selected trace metals during the 2002 summer flood in the River Elbe (Germany) at Magdeburg monitoring station. *Hydrology and Earth System Sciences, 8*(2), 135–150.
- Barth, J. A. C., Steidle, D., Kuntz, D., Gocht, T., Mouvet, C., von Tümpling, W., et al. (2007). Deposition, persistence and turnover of pollutants: First results from the EU project Aqua terra for selected river basins and aquifers. *The Science of the Total Environment, 376*(1– 3), 40–50. doi[:10.1016/j.scitotenv.2007.01.065.](http://dx.doi.org/10.1016/j.scitotenv.2007.01.065)
- Baudo, R., Giesy, J., & Muntau, H. (1990). *Sediments: Chemistry and toxicity of in-place pollutants*. London: CRC Press.
- Behra, R., Landwehrjohann, R., Vogel, K., Wagner, B., & Sigg, L. (2002). Copper and zinc content of periphyton from two rivers as a function of dissolved metal concentration. *Aquatic Sciences-Research Across Boundaries, 64*, 300–306.
- Bergemann, M., & Gaumert, T. (2006). *Gewässergütebericht der Elbe*. Hamburg: Arbetsgemeinschaft für die Reinhaltung der Elbe.
- Borovec, Z., Pivnièka, K., & Fuksa, J. K. (1998). Mercury in sediments and fish in Czech rivers: A review. *Acta Universitatis Carolinae Environmentalica, 12*, 7–40.
- Brügmann, L. (1995). Metals in sediments and suspended matter of the river Elbe. *The Science of the Total*

<span id="page-15-0"></span>*Environment, 159*, 53–65. doi[:10.1016/0048-9697\(94\)](http://dx.doi.org/10.1016/0048-9697(94)04252-I) [04252-I.](http://dx.doi.org/10.1016/0048-9697(94)04252-I)

- BUA (1994). *119 BUA Report: Hexachlorobenzene. CAS-No.118-74-1*. BUA (Advisory Committee on Existing Chemicals of Environmental Relevance; Stuttgart: S. Hirzel Wissenschaftliche Verlagsgesellschaft). In Petrlik, J. (2006). The Spolchemie chloralkali and chlorine based chemical production plant in Usti nad Labem (Czech Republic)—A case study for unintentional production of hexachlorobenzene. [http://www.ipen.org.](http://www.ipen.org)
- Characklis, W. G., & Marshall, K. C. (1990). *Biof ilms*. New York: Wiley.
- Commission of European Community (CEC) (2000). Directive 2000/60/EC of the European (2000). Parliament and of the Council of 23 October 2000 establishing a framework for the community action in the field of water policy. *Off icial Journal of the European Union, L327*, 1–72.
- Costerton, J. W., Lewadowski, Z., De Beer, D., Caldwell, D., Korber, D., & James, G. (1994). Biofilms, the customized microniche. *Journal of Bacteriology, 176*, 2137–2142.
- Courtney, K. D. (1979). Hexachlorobenzene (HCB): A review. *Environmental Research, 20*(2), 225–266. doi[:10.1016/0013-9351\(79\)90001-X.](http://dx.doi.org/10.1016/0013-9351(79)90001-X)
- CSN EN ISO/IEC 17 025 (01 5253). Všeobecné požadavky na způsobilost zkušebních laboratoří. (General standard for assessment of professional capability of laboratories).
- Demirezen, D., & Aksoy, A. (2004). Accumulation of heavy metals in *Typha angustofolia* (L.) and *Potamogeton pectinatus* (L.) Libiny in Sultan Marsh (Kayseri, Turkey). *Chemosphere, 56*(7), 685–696. doi[:10.1016/j.chemosphere.2004.04.011.](http://dx.doi.org/10.1016/j.chemosphere.2004.04.011)
- Denkhaus, E., Meisen, S., Telgheder, U., & Wingender, J. (2007). Chemical and physical methods for characterization of biofilms. *Mikrochimica Acta, 158*(1–2), 1–27. doi[:10.1007/s00604-006-0688-5.](http://dx.doi.org/10.1007/s00604-006-0688-5)
- Donlan, R. M. (2002). Biofilms: Microbial life on surfaces. *Emerging Infectious Diseases, 8*(9), 881–890.
- Durrieu, G., Maury-Brachet, R., Girardin, M., Rochard, E., & Boudou, A. (2005). Contamination by heavy metals (Cd, Zn, Cu and Hg) of eight fish species in the Gironde Estuary (France). *Estuaries, 28*(4), 581–591. doi[:10.1007/BF02696069.](http://dx.doi.org/10.1007/BF02696069)
- Farag, A. M., Woodward, D. F., Goldstein, J. N., Brumbaugh, W. G., & Meyer, J. S. (1998). Concentrations of metals associated with mining waste in sediments, biofilm, benthic invertebrates, and fish from the Coeur d'Alene River Basin, Idaho. *Archives of Environmental Contamination and Toxicology, 34*, 119–127. doi[:10.1007/s002449900295.](http://dx.doi.org/10.1007/s002449900295)
- Farag, A. M., Nimick, D. A., Kimball, B. A., Church, S. E., Harper, D. D., & Brumbaugh, W. G. (2007). Concentrations of metals in water, sediment, biofilm, benthic macroinvertebrates, and fish in the boulder river watershed, Montana, and the role of colloids in metal uptake. *Archives of Environmental Contamination and Toxicology, 52*, 397–409. doi: [10.1007/s00244-005-0021-z.](http://dx.doi.org/10.1007/s00244-005-0021-z)
- Flemming, H.-C. (1993). Biofilms and environmental protection. *Water Science and Technology, 27*(7–8), 1–10.
- Flemming, H.-C. (1995). Sorption sites in biofilms. *Water Science and Technology, 32*(8), 27–33. doi[:10.1016/](http://dx.doi.org/10.1016/0273-1223(96)00004-2) [0273-1223\(96\)00004-2.](http://dx.doi.org/10.1016/0273-1223(96)00004-2)
- Franke, S., Heinzel, N., Specht, M., & Francke, W. (2005). Identification of organic pollutants in waters and sediments from the Lower Mulde River area. *Acta Hydrochimica et Hydrobiologica, 33*(5), 519–542. doi[:10.](http://dx.doi.org/10.1002/aheh.200400588) [1002/aheh.200400588.](http://dx.doi.org/10.1002/aheh.200400588)
- Frost, P. C., & Elser, J. J. (2002). Growth responses of littoral mayflies to the phosphorus content of their food. *Ecology Letters, 5*, 232–240. doi[:10.1046/j.1461-](http://dx.doi.org/10.1046/j.1461-0248.2002.00307.x) [0248.2002.00307.x.](http://dx.doi.org/10.1046/j.1461-0248.2002.00307.x)
- Fuchs, S., Haritopoulou, T., & Wilhelmi, M. (1996). Biofilms in freshwater ecosystems and their use as a pollutant monitor. *Water Science and Technology, 34*(7–8), 137–140. doi[:10.1016/S0273-1223\(96\)00735-4.](http://dx.doi.org/10.1016/S0273-1223(96)00735-4)
- Gewurtz, S. B., Lazar, R., & Haffner, G. D. (2000). Comparison of polycyclic aromatic hydrocarbon and polychlorinated biphenyl dynamics in benthic invertebrates of lake Eire, USA. *Environmental Toxicology and Chemistry, 19*, 2943–2950. doi[:10.1897/1551-5028](http://dx.doi.org/10.1897/1551-5028(2000)019<2943:COPAHA>2.0.CO;2) [\(2000\)019<2943:COPAHA>2.0.CO;2.](http://dx.doi.org/10.1897/1551-5028(2000)019<2943:COPAHA>2.0.CO;2)
- Gold, C., Feurtet-Mazel, A., Coste, M., & Boudou, A. (2003). Effects of cadmium stress on periphytic diatom communities in indoor artificial streams. *Freshwater Biology, 48*, 316–328. doi[:10.1046/j.1365-2427.](http://dx.doi.org/10.1046/j.1365-2427.2003.00980.x) [2003.00980.x.](http://dx.doi.org/10.1046/j.1365-2427.2003.00980.x)
- Greger, M., & Kautsky, L. (1991). Effects of Cu, Pb and Zn on two Potamogeton species grown under field conditions. *Plant Ecology, 97*(2), 173–184. doi[:10.1007/](http://dx.doi.org/10.1007/BF00035390) [BF00035390.](http://dx.doi.org/10.1007/BF00035390)
- Havlík, A., Just, T., & Slavík, O. (1997a). *Ekologická studie povodí Bíliny. 1. díl. Podrobná ekologická studie (Ecological study of the Bílina River. Part 1. Detailed ecological study)*. Prague: T.G. Masaryk Water Research Institution, PRI. (in Czech).
- Havlík, A., Just, T., & Slavík, O. (1997b). *Ekologická studie povodí Bíliny. 2. díl. Kvalita vody a produkce zneèištìní v povodí Bíliny (Ecological study of the Bílina River. Part 2. Water quality and pollution production in the bílina River drainage area)*. Prague: T.G. Masaryk Water Research Institution, PRI.
- Heemken, O. P., Reincke, H., Stachel, B., & Theobald, N. (2001). The occurrence of xenoestrogens in the Elbe River and the North Sea. *Chemosphere, 45*, 245–259. doi[:10.1016/S0045-6535\(00\)00570-1.](http://dx.doi.org/10.1016/S0045-6535(00)00570-1)
- Heininger, P., Pelzer, J., Claus, E., & Pfitzner, S. (2003). Results of long-term sediment quality studies on the River Elbe. *Acta Hydrochimica et Hydrobiologica, 31*(4–5), 356–367. doi[:10.1002/aheh.200300493.](http://dx.doi.org/10.1002/aheh.200300493)
- Heinisch, E., Kettrup, A., Bergheim, W., Martens, D., & Wenzel, S. (2005a). Persistent chlorinated hydrocarbons (PCHC), source-oriented monitoring in aquatic media. 2. The insecticide DDT, constituents, metabolites. *Fresenius Environmental Bulletin, 14*(2), 69–85.
- Heinisch, E., Kettrup, A., Bergheim, W., Martens, D., & Wenzel, S. (2005b). Persistent chlorinated hydrocarbons (PCHC), source-oriented monitoring in aquatic

<span id="page-16-0"></span>media. 3. The isomers of Hexachlorocyclohexane. *Fresenius Environmental Bulletin, 14*(6), 444–462.

- Hintelmann, H., & Wilken, R.-D. (1995). Levels of total mercury and methyl mercury compounds in sediments of the polluted Elbe River: Influence of seasonally and spatially varying environmental factors. *The Science of the Total Environment, 166*, 1–10. doi[:10.1016/0048-9697\(95\)04506-V.](http://dx.doi.org/10.1016/0048-9697(95)04506-V)
- Holding, K. L., Gill, R. A., & Carter, J. (2003). The relationship between epilithic periphyton (Biofilm) bound metals and metals bound to sediments in freshwater systems. *Environmental Geochemistry and Health, 25*, 87–93. doi[:10.1023/A:1021205101133.](http://dx.doi.org/10.1023/A:1021205101133)
- Ivorra, N., Hettelaar, J., Tubbing, G. M. J., Kraak, M. H. S., Sabater, S., & Admiraal, W. (1999). Translocation of microbenthic assemblages used for in situ analysis of metal pollution in rivers. *Archives of Environmental Contamination and Toxicology, 37*, 19–28. doi[:10.1007/s002449900485.](http://dx.doi.org/10.1007/s002449900485)
- Jeppesen, E., Sondergaard, M., Christoffersen, K., Theil-Neilsen, J., & Jürgens, K. (2002). Cascading trophic interactions in the litterol zone: An enclosure experiment in shallow Lake Stigsholm, Denmark. *Archiv fuer Hydrobiologie, 153*, 533–555.
- Klemm, W., Greif, A., Broekaert, J. A. C., Siemens, V., Junge, F. W., van der Veen, A., et al. (2005). A study on arsenic and the heavy metals in the Mulde river system. *Acta Hydrochimica et Hydrobiologica, 33*(5), 475–491. doi[:10.1002/aheh.200400592.](http://dx.doi.org/10.1002/aheh.200400592)
- Kowalik, C., Kraft, J., & Einax, J. W. (2003). The situation of the German Elbe tributaries—Development of the loads in the last 10 years. *Acta Hydrochimica et Hydrobiologica, 31*(4–5), 334–345. doi[:10.1002/aheh.](http://dx.doi.org/10.1002/aheh.200300507) [200300507.](http://dx.doi.org/10.1002/aheh.200300507)
- Kröpfl, K., Vladár, P., Szabó, K., Ács, E., Borsodi, A. K., Szikora, S., et al. (2006). Chemical and biological characterisation of biofilms formed on different substrata in Tisza river (Hungary). *Environmental Pollution, 144*, 626–631. doi[:10.1016/j.envpol.2006.01.031.](http://dx.doi.org/10.1016/j.envpol.2006.01.031)
- Landrum, P. F., & Robbins, J. A. (1990). Bioavailability of sediment-associated contaminants to benthic invertebrates. In R. Baudo, J. Giesy & H. Muntau (Eds.), *Sediments: Chemistry and toxicity of in-place pollutants* (pp. 237–257). London: CRC Press.
- Lewandowski, Z., Stoodley, P., Altobelli, S., & Fukushima, E. (1994). Hydrodynamics and kinetics in biofilm systems—Recent advances and new problems. *Water Science and Technology, 29*(10–11), 223–229.
- Liu, M., Cheng, S., Ou, D., Yang, Y., Liu, H., Hou, L., et al. (2008). Organochlorine pesticides in surface sediments and suspended particulate matters from the Yangtze estuary, China. *Environmental Pollution, 156*, 168–173. doi[:10.1016/j.envpol.2007.12.015.](http://dx.doi.org/10.1016/j.envpol.2007.12.015)
- Lotufo, G. R. (1998). Bioaccumulation of sedimentassociated fluoranthene in benthic copepods: Uptake, elimination and biotransformation. *Aquatic Toxicology (Amsterdam, the Netherlands), 44*, 1–15. doi[:10.](http://dx.doi.org/10.1016/S0166-445X(98)00072-1) [1016/S0166-445X\(98\)00072-1.](http://dx.doi.org/10.1016/S0166-445X(98)00072-1)
- Mages, M., Óvári, M., Tümpling, W., & Kröpfl, K. (2004). Biofilms as bio-indicator for polluted waters? Total reflection X-ray fluorescence analysis of

biofilms of the Tisza river (Hungary). *Analytical and Bioanalytical Chemistry, 378*, 1095–1101. doi[:10.1007/](http://dx.doi.org/10.1007/s00216-003-2291-5) [s00216-003-2291-5.](http://dx.doi.org/10.1007/s00216-003-2291-5)

- McCormick, P. V., & Cairns, J. (1994). Algae as indicators of environmental change. *Journal of Applied Phycology, 6*, 509–526. doi[:10.1007/BF02182405.](http://dx.doi.org/10.1007/BF02182405)
- Neu, T. R., & Marshall, K. C. (1990). Bacterial polymers physicochemical aspects of their interactions at interfaces. *Journal of Biomaterials Applications, 5*(2), 107– 133. doi[:10.1177/088532829000500203.](http://dx.doi.org/10.1177/088532829000500203)
- Oliver, B. G., & Pugsley, C. W. (1986). Chlorinated contaminants in St. Clair River sediments. *Water pollution research journal of Canada, 21*, 368–379. (In Petrlik, J. (2006). The Spolchemie chlor-alkali and chlorine based chemical production plant in Usti nad Labem (Czech Republic)—A case study for unintentional production of hexachlorobenzene. [http://www.](http://www.ipen.org) [ipen.org\)](http://www.ipen.org).
- Peng, K., Luo, C., Lou, L., Li, X., & Shen, Z. (2008). Bioaccumulation of heavy metals by the aquatic plants Potamogeton pectinatus L. and Potamogeton malaianus Miq. and their potential use for contamination indicators and in wastewater treatment. *The Science of the Total Environment, 392*(1), 22–29. doi[:10.1016/j.scitotenv.2007.11.032.](http://dx.doi.org/10.1016/j.scitotenv.2007.11.032)
- Petrlik, J. (2006). The Spolchemie chlor-alkali and chlorine based chemical production plant in Usti nad Labem (Czech Republic)—A case study for unintentional production of hexachlorobenzene. [http://www.](http://www.ipen.org) [ipen.org.](http://www.ipen.org)
- Pusch, M., Fiebig, D., Brettar, I., Eisenmann, H., Ellis, B. K., Kaplan, L. A., et al. (1998). The role of microorganisms in the ecological connectivity of running waters. *Freshwater Biology, 40*, 453–495. doi[:10.1046/j.](http://dx.doi.org/10.1046/j.1365-2427.1998.00372.x) [1365-2427.1998.00372.x.](http://dx.doi.org/10.1046/j.1365-2427.1998.00372.x)
- Schindler, J., Lochovský, P., Tolma, V., Kužílek, V., & Vilimec, J. (1997). *Erfassung und Beurteilung der Belastung der Elbe mit Schadstoffen. (In Teilprojekt: Tschechische Elbenebenflüsse* (pp. 231–238). Prague: T.G. Masaryk Water Research Institution, PRI.
- Schorer, M., & Eisele, M. (1997). Accumulation of inorganic and organic pollutants by biofilms in the aquatic environment. *Water, Air, and Soil Pollution, 99*, 651– 659.
- Simon, M. (1991). Die Belastung der Elbe und ihrer Hauptnebenflüsse auf dem Gebiet der ehemaligen DDR. *Wasserwirtschaft-Wassertech, 41*, 23–27.
- Stachel, B., Ehrhorn, U., Heemken, O. P., Lepom, P., Reincke, H., Sawal, G., et al. (2003). Xenoestrogens in the River Elbe and its tributaries. *Environmental Pollution, 124*(3), 497–507. doi[:10.1016/S0269-7491](http://dx.doi.org/10.1016/S0269-7491(02)00483-9) [\(02\)00483-9.](http://dx.doi.org/10.1016/S0269-7491(02)00483-9)
- Stachel, R., Götz, R., Herrmann, T., Krüger, F., Knoth, W., Päpke, O., et al. (2004). The Elbe flood in August 2002—Occurrence of polychlorinated dibenzop-dioxins, polychlorinated dibenzofurans (PCDD/F) and dioxin-like PCB in suspended particulate matter (SPM), sediment and fish. *Water Science and Technology, 50*(5), 309–316.
- Stachel, B., Jantzen, E., Knoth, W., Krüger, F., Lepom, P., Oetken, M., et al. (2005). The Elbe flood in

<span id="page-17-0"></span>August 2002—Organic contaminants in sediment samples taken after the flood event. Journal of Environmental Science and Health. *Part A, Toxic/Hazardous Substances & Environmental Engineering, 40*(2), 265– 287. doi[:10.1081/ESE-200045531.](http://dx.doi.org/10.1081/ESE-200045531)

- Umlauf, G., Bidoglio, G., Christoph, E. H., Kampheus, J., Krüger, F., Landmann, D., et al. (2005). The situation of PCDD/Fs and dioxin-like PCBs after the flooding of River Elbe and Mulde in 2002. *Acta Hydrochimica et Hydrobiologica, 33*(5), 543–554. doi[:10.1002/aheh.200400597.](http://dx.doi.org/10.1002/aheh.200400597)
- van Loosdrecht, M. C. M., Eikelboom, D., Gjaltema, A., Mulder, A., Tijhuis, L., & Heijnen, J. J. (1995). Biofilm structures. *Water Science and Technology, 32*(8), 35– 43. doi[:10.1016/0273-1223\(96\)00005-4.](http://dx.doi.org/10.1016/0273-1223(96)00005-4)
- Veselý, J. (1994). Kontaminace českých řek stopovými prvky. O prvé regionální studii říčních sedimentů v CR (Contamination of Czech rivers by trace elements.

About the first regional study of the river sediments in the Czech Republic). *Vesmír, 73*(10), 558–560.

- Vink, R. J., Behrendt, H., & Salomons, W. (1999). Point and diffuse source analysis of heavy metals in the Elbe drainage area: Comparing heavy metals emissions with transported river loads. *Hydrobiologia, 410*, 207–314. doi[:10.1023/A:1003703713574.](http://dx.doi.org/10.1023/A:1003703713574)
- Vrochinskiy, K. K. (1970). Accumulation of pesticides in hydrobionts. *Hydrobiological Journal, 6*, 103–107.
- Vrochinskiy, K. K., Grib, I. V., & Grib, A. V. (1970). The content of organochlorine insecticides in aquatic plants. *Hydrobiological Journal, 6*, 91–93.
- Wilken, M., Walkow, F., Jager, E., & Zeschmar-Lahl, B. (1994). Flooding area and sediment contamination of the River Mulde (Germany) with PCDD/F and other organic pollutants. *Chemosphere, 29*(9–11), 2237–2252. doi[:10.1016/0045-6535\(94\)90391-3.](http://dx.doi.org/10.1016/0045-6535(94)90391-3)