29 Passive sampling: chemical analysis and toxicological profiling

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29.1 Introduction
Organic pollutants are often present in the water column at trace concentrations that are difficult to detect when conventional low volume spot sampling of water is applied. The scope of the sampling campaign performed using passive samplers was the screening of trace organic pollutants and their toxic potentials in the water column of the Danube, as well as the assessment of their spatial distribution along the river.

Freely dissolved concentrations of priority substances in the water phase \( C_{\text{free}} \) can be derived from the uptake of these substances by passive samplers, and because accumulated contaminants represent a large water volume, low limits of quantification can be obtained. \( C_{\text{free}} \) is a more stable parameter than a concentration measured in whole water as the level is not influenced by variable amounts of the substance bound to dissolved and suspended particulate organic matter. Thus, it is very suitable for assessment of trends. \( C_{\text{free}} \) is further considered to play a key role in chemical uptake by aquatic organisms. It is proportional to the chemical activity (Mayer et al., 2003) and if in equilibrium with surrounding environmental compartments it also represents chemical activity of those environmental compartments, including the biota at the base of the food chain (Reichenberg and Mayer, 2006).

We used an “active” passive sampling system (APS) for temporally and spatially integrative sampling of trace organic pollutants. APS is used in a concept similar to that of a Ferry-Box (“Website of the European Ferrybox Community,” 2014) to obtain a representative picture of pollution situation along defined stretches or transects of large water bodies including rivers, lakes or seas. The uptake principle in the APS remains the same as in classical static passive sampling and the monitoring results can be evaluated using usual passive sampler calibration parameters. The APS enhances the uptake rate of contaminants into passive samplers, thereby allowing to drastically reduce the exposure time needed for accumulation of sufficient chemicals for analysis.

The application of temporal- and spatial- integrative passive sampling approach resulted in samples that provide a representative picture of pollution situation in eight defined stretches of the Danube River.

29.2 Methods

29.2.1 Passive samplers
Three types of passive samplers were applied: two partitioning samplers for hydrophobic compounds (silicone rubber (SR) and low density polyethylene (LDPE) sheets), and an adsorption sampler for polar compounds based on styrene-divinylbenzene solid phase extraction disks, SDB-RPS Empore disks (ED), respectively.

The SR sampler consisted of a single Altesil\textsuperscript{®} SR sheet with dimensions 14×28 cm and 0.5 mm thickness. The mass of a sampler was cca 23 g and the surface area exposed to water was 392 cm\(^2\) (one side of the sheet). SR samplers (except those intended for the ecotoxicological analysis) were spiked...
prior to exposure with a number of Performance Reference Compounds (PRCs) that are partially released during exposure. The residual concentration of PRC is compared with the initial amount of PRCs analysed in samplers that have not been exposed.

The LDPE sampler consisted of two strips 4×28 cm and 80 µm thickness (cut from 2.5 cm wide lay-flat LDPE tubing from Brentwood Plastics Inc, St. Louis, USA). LDPE samplers were also spiked with PRCs and were used for chemical analysis only.

The ED sampler consisted of 10 solid phase extraction disks Empore® SDB-RPS with 47 mm diameter. The mass of a sampler was cca 3.2 g and the surface area exposed to water was 173 cm². Before exposure samplers were pre-conditioned and kept immersed in MilliQ water until exposure. These samplers were not spiked with PRCs.

29.2.2 Sampling operation

The “active” passive sampling system was installed on board of the expedition ship Argus to obtain enhanced passive sampler uptake rates in order to achieve sufficient sensitivity despite the short time available for sampling.

The APS device consists of a rectangular stainless steel plate box. During operation the box remained open from two sides and it was fully immersed in water. One end of the box was connected to a submersible pump (cca 9 m³ h⁻¹) that forced water at high flow velocity (1-2 m s⁻¹) through the exposure chamber. A submersible temperature and light intensity logger was attached to the box during the entire cruise. Two parallel APS devices were in operation during each sampling period. The samplers exposed in one device were used for chemical analysis, and those from the other one for ecotoxicological analysis, respectively.

The APS device was deployed on the frontal deck of the Argus. For sampling, the device was immersed in a flow-through system that consisted of a 600 l stainless steel tank. The river water in the tank was exchanged at a rate cca 3 m³ h⁻¹ by a high performance pump. The water intake to the chamber was by a vertical steel pipe positioned in front of the ship. The water sampling depth was cca 0.5 m below the water level.

The device was operated only during the cruising of the ship or when the ship anchored outside harbours (e.g. for sampling) in areas not visibly impacted by point sources of pollution, e.g. discharge pipes, industrial areas next to the river, oil film visible on the water surface. The device was switched off before the ship entered harbours and switched on again when the cruise resumed. Samplers were mounted to the APS device just before exposure and removed immediately after recovery. The recovered samplers were placed back into their storage containers. They were stored in a refrigerator at 4°C on board of the ship and transported to the processing laboratory once per week, where they were stored in a freezer at -20°C.

Each individual water sampling period took approximately 5 days. During this period ship moved downstream along a defined stretch. The obtained sample contained water pollutants integrated in time and space along that stretch. Samplers were exchanged every 5 days, which resulted in total of eight samples of each type (SR, LDPE and ED) representing eight stretches of the Danube (Table 89). Sampling periods were planned so that exposure was avoided during days when ships stopped in harbours for one day or longer.
### Table 89: River stretches sampled with passive samplers deployed from the Argus ship

<table>
<thead>
<tr>
<th>Stretch number</th>
<th>Stretch start and end</th>
<th>River km</th>
<th>Dates of cruise</th>
<th>Mean water temperature [°C]</th>
<th>Exposure time [d]</th>
<th>Volume extracted by SR [l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Regensburg-Passau</td>
<td>2375-2225</td>
<td>13.8.-16.8.</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Passau-Bratislava</td>
<td>2203-1852</td>
<td>17.8.-22.8.</td>
<td>21.3</td>
<td>2.0</td>
<td>169</td>
</tr>
<tr>
<td>3</td>
<td>Bratislava-Budapest</td>
<td>1852-1632</td>
<td>22.8.-26.8.</td>
<td>22.0</td>
<td>1.2</td>
<td>84</td>
</tr>
<tr>
<td>4</td>
<td>Budapest-Vukovar</td>
<td>1648-1297</td>
<td>26.8.-2.9.</td>
<td>21.9</td>
<td>1.7</td>
<td>139</td>
</tr>
<tr>
<td>5</td>
<td>Vukovar-Belgrade</td>
<td>1297-1154</td>
<td>2.9.-6.9.</td>
<td>22.8</td>
<td>1.6</td>
<td>133</td>
</tr>
<tr>
<td>6</td>
<td>Belgrade-Turnu-Severin</td>
<td>1154-930</td>
<td>6.9.-10.9.</td>
<td>22.1</td>
<td>2.0</td>
<td>139</td>
</tr>
<tr>
<td>7</td>
<td>Turnu-Severin-Ruse</td>
<td>930-495</td>
<td>11.9.-17.9.</td>
<td>21.9</td>
<td>2.0</td>
<td>129</td>
</tr>
<tr>
<td>8</td>
<td>Ruse-Braila</td>
<td>495-170</td>
<td>17.9.-21.9.</td>
<td>19.2</td>
<td>1.4</td>
<td>79</td>
</tr>
<tr>
<td>9</td>
<td>Braila-Tulcea</td>
<td>170-71</td>
<td>21.9.-26.9.</td>
<td>18.7</td>
<td>1.3</td>
<td>72</td>
</tr>
</tbody>
</table>

1 Volume of water extracted by the SR sampler during exposure; it is calculated for a model compound with molecular mass of 300.

2 The stretch from Regensburg to Passau was not sampled due to initial technical difficulties with sampler installation.

#### 29.2.3 Sample processing

SR samplers (except those intended for the ecotoxicological analysis) were spiked with recovery internal standards. Compounds sorbed in the SR sheet were extracted for 8 hours in methanol using Soxhlet extraction. The volume of the extract was reduced using Kuderna-Danish (K-D) apparatus and under nitrogen flow to a volume of 2 ml. For ecotoxicological analyses, the sample in methanol was divided to aliquots for different types of bioassays. For chemical analyses, a 20% aliquot of the sample was used for instrumental analysis by LC/MS methods. The remaining 80% aliquot of samples for chemical analysis was azeotropically transferred to hexane using K-D apparatus. Aliquots of the extract were divided into vials for different types of GC/MS analysis. The extract aliquots for analysis of PAHs were further cleaned-up by a silica gel column clean up step using diethylether/acetone elution. The extract aliquots for analysis of organochlorine compounds (OCs), PCBs, BDE and PRCs were purified by a cleanup using activated silica gel modified with sulphuric acid. Following cleanup, addition of internal standards and volume reduction using a K-D apparatus, samples were analysed using a GC-MS/MS method for indicator PCBs, BDEs, OCPs and PRCs.

LDPE samplers, including trip controls, were extracted twice by soaking overnight with n-pentane (100 ml). Recovery standards (deuterated PAHs and PCBs that do not occur in the environment) were added to the extraction jar during the first extraction. The volume of pentane was reduced to 2 ml by a gentle stream of nitrogen at room temperature.

Extracts were split into two, with one fraction kept for non-target screening. For target analyses, extracts were first split into two equal fractions by volume. One fraction received a general clean-up using gel permeation chromatography (GPC). This post GPC sample was again split into two equal fractions by volume; the first of these was reduced in volume using nitrogen and analysed for PAH; the second received treatment with 2 × 1 ml concentrated sulphuric acid, was reduced in volume, and analysed for PCBs and OCs (Allan et al., 2013).

For non-target analyses, the extracts from samplers without PRCs were reduced by a gentle stream of nitrogen to 50-100 μl, with no clean up in order to preserve the integrity of the samples as much as possible. The extracts were stored at -20 °C until analysis by gas chromatography coupled to high resolution time of flight mass spectrometry (GC-HR ToFMS).

ED samplers for chemical analysis (but not those for ecotoxicological analysis) were spiked with RIS (C13 caffeine, C13 triclosan, M8PFOA, M8PFOS, D13-alachlor, D6-diuron, D10-simazine, deuterated EE2, n-nonylphenol). All samplers where then freeze dried for 24 hours in the original containers that were used for sample storage and transport. The disks were extracted three times by overnight (12 h) slow shaking at room temperature with 70 ml acetone. Combined extracts were reduced by vacuum rotary evaporation. After removal of particles by filtration through a layer of anhydrous Na2SO4 the extract was further reduced in volume to cca 1 ml. The acetone extract was transferred to methanol by
addition of methanol (20 ml) and subsequent evaporation and a nitrogen flow to further reduce in volume to 2 ml. Aliquots of the extract were divided into vials for different types of analysis.

### 29.2.4 Sample analysis

#### 29.2.4.1 Analysis of hydrophobic compounds
SR and LDPE sampler extracts were analysed using a GC-MS/MS (GC 7890 / MS-MS Triple Quadrupole 7000B (Agilent), equipped with an HT8 SGE Analytical Science column for PCBs and OCs. PAHs were analysed using GC 7890 / MS5975 (Agilent) equipped with a J&W Scientific fused silica column DB-5MS column. PBDEs were analysed by a GC equipped with a 15m × 0.25 mm × 0.10 µm RTX-1614 column (Restek, USA) HRMS (AutoSpec Premier) was operated in EI+ mode at the resolution of >10 000.

#### 29.2.4.2 Analysis of polar compounds
Polar pesticides and pharmaceuticals were analysed by liquid chromatography (Waters Acquity) with MS detection (Waters Xevo TQ-S). Analytes were separated on reverse phase column (Waters Acquity UPLC BEH-C18) using gradient elution with methanol and water, both with 0.1% formic acid. Eluting analytes were ionized using electrospray in positive mode and detected in MRM mode.

#### 29.2.4.3 Toxicological profiling
For toxicological profiling, a battery of bioassays has been established. The same tests are employed for assessment of toxic potential of samples from high volume active sampling (Chapter 27). The set consists of eight assays provided by four laboratories (INERIS, RECETOX, RWTH, and University of Queensland (UQ)). The selected bioassays cover several important steps in the toxicity pathway including induction of xenobiotic metabolism, specific and reactive modes of toxic action, activation of adaptive stress response pathways. The diverse modes of action provide broad range of information on toxic potential.

Specifically, there are assays for assessment of endocrine disruptive potential (anti-estrogenicity (MELN) and (anti-)androgenicity (MDA-kb2), activation of receptors for xenobiotics (CAFLUX and HG5LN-hPXR), immune response (NF-xb-bla THP-1), mutagenicity and DNA damage –related apoptosis (Ames fluctuation assay and p53-bla HCT-116, resp.) and detection of response to oxidative stress (ARE-bla Hep G2). The model cell lines are exposed to dilution series of the ED and SR extracts to describe dose-response relationship of the effects. The potentials are quantified in comparison with negative control and positive control describing the effect of a model chemical with known toxic potency specific for each of the bioassay endpoints.

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Bioassay</th>
<th>Endpoint</th>
</tr>
</thead>
<tbody>
<tr>
<td>INERIS</td>
<td>MELN</td>
<td>Binding to and activation of human estrogen receptor (ER)¹</td>
</tr>
<tr>
<td></td>
<td>HG5LN-hPXR</td>
<td>Binding to and activation of the human pregnane X receptor (PXR)²</td>
</tr>
<tr>
<td>RECETOX</td>
<td>CAFLUX</td>
<td>Binding to and activation of aryl hydrocarbon receptor (AhR)³</td>
</tr>
<tr>
<td></td>
<td>MDA-kb2</td>
<td>Binding to and activation or inhibition of activity of human androgen receptor (AR)⁴</td>
</tr>
<tr>
<td>RWTH</td>
<td>Ames fluctuation assay</td>
<td>Assessment of mutagenic activity in Salmonella typhimurium after metabolic activation of compounds with S9 liver fraction⁵</td>
</tr>
<tr>
<td>UQ</td>
<td>p53-bla HCT-116</td>
<td>Assessment of p53-mediated apoptosis rate in response to DNA damage⁶</td>
</tr>
<tr>
<td></td>
<td>ARE-bla Hep G2</td>
<td>Induction of the Nrf-2-mediated oxidative stress pathway⁷</td>
</tr>
<tr>
<td></td>
<td>NF-xB-bla THP-1</td>
<td>Induction of inflammatory response⁸</td>
</tr>
</tbody>
</table>

¹(Balaguer et al., 1999), ²(Lemaire et al., 2006), ³(Aarts et al., 1998), ⁴(Wilson et al., 2002), ⁵(Reifferscheid et al., 2012), ⁶(Yeh et al., 2014), ⁷(http://tools.lifetechnologies.com/content/sfs/manuals/cellsensor_AREblaHepG2_man.pdf, n.d.), ⁸(http://tools.lifetechnologies.com/content/sfs/manuals/CellSensor_NFxBbla_THP1_man.pdf,” n.d.)
29.2.5 QA/QC
The applied quality control measures included the analysis of procedural solvent blanks, fabrication controls, field controls and matrix spikes.

29.2.6 Data analysis
Dissolved water concentrations of were calculated from analyte amounts accumulated in SR and LDPE samplers, the in situ sampling rate ($R_s$) of the compounds and their sampler-water partition coefficients (Smedes et al., 2009) as described in Smedes and Booij (2012). Sampling rates were estimated from dissipation of PRCs from samplers during exposure using methods described by Booij and Smedes (2010).

For ED samplers calibration data are not available so far. For compounds under investigation we assumed an integrative uptake with a constant sampling rate. Identification of pollutant gradients along the Danube was performed based on the amount of a compound sampled by the ED in individual stretches, normalised to an average sampler exposure time (1.6 days).

29.3 Results

29.3.1 Analysis of hydrophobic compounds- use of silicone rubber samplers
SR samplers were deployed at 8 successive Danube stretches to characterise the spatial variability of hydrophobic compounds in the water column of the river.

29.3.1.1 Polychlorinated biphenyls and brominated diphenyl ethers
Calculated dissolved PCB concentrations were in sub ng l$^{-1}$ range (Figure 150). Sums of 6 indicator PCB congeners ranged from 158 to 369 pg l$^{-1}$. Over the set of PCBs investigated there is a decrease in free dissolved concentration as hydrophobicity increases. The highest spatial variability is observed for the more water soluble congeners PCB28, 52 and 101. There was no clear spatial trend of PCB contamination along the river.

Concentrations of freely dissolved PBDEs (referring to the sum of the concentrations of congener numbers 28, 47, 99, 100, 153 and 154) were below the limit of quantification of 3 pg l$^{-1}$ with the exception of the stretch Passau to Bratislava, where the summed concentration of the 6 congeners was 12 pg l$^{-1}$. Measurement of such low concentrations would require longer exposure times for integrative sampling, which was not available during the JDS3 cruise. A parallel 43 day sampling using a caged SR sampler statically deployed at a sampling site downstream Bratislava in the period August-October 2013 provided a concentration estimate of 2 pg l$^{-1}$ for the sum of 6 PBDE congeners (Vrana, unpublished data).

![Figure 150: Free dissolved concentration of PCBs measured by SR samplers in 8 Danube stretches](image-url)
29.3.1.2 Organochlorine compounds
The free dissolved concentrations of OCs were in sub ng l⁻¹ range (Figure 151). The highest concentration of pentachlorobenzene (PeCB) up to 96 pg l⁻¹ was observed in the stretch between Budapest and Belgrade whereas the highest level of hexachlorobenzene (HCB) of 97 pg l⁻¹ was measured in the lowest Danube stretch between Ruse and Tulcea. The spatial variability of PeCB concentration was higher than that of HCB. Among the hexachlorocyclohexane (HCH) congeners, only β-HCH is reported because of low extraction recovery of the remaining isomers. There is an increasing trend of β-HCH concentration along the river, ranging between 9 pg l⁻¹ in the upper stretches and 259 pg l⁻¹ in the river delta area, respectively. The same spatial trend can be observed also for the sum of total DDT (given as sum of 4 isomers according to the Directive 2008/105/EC) as well as for p,p'-DDT. Concentrations of p,p'-DDT (1-21 pg l⁻¹) comprised only 2-7% of the total DDT, which indicates no current use of DDT in the Danube catchment. In the delta area concentration of DDT metabolites reach levels up to 864 pg l⁻¹.

![Figure 151: Free dissolved concentration of OCPs measured by SR samplers in 8 Danube stretches](image)

29.3.1.3 Polycyclic aromatic hydrocarbons
Summed concentrations (Σ 16 US EPA PAHs) of free dissolved PAHs in the water column ranged between 10.6 ng l⁻¹ in stretch 7 and 45.1 ng l⁻¹ in stretch 4, respectively. Summed concentrations were largely composed of PAHs with up to 4 aromatic rings. As for PCBs there is a strong decrease of free dissolved concentration with increasing compound hydrophobicity (Figure 152). Concentrations of compounds with 6 aromatic rings were mostly below the limit of quantification (tens of pg l⁻¹). Elevated PAH concentrations were observed in the stretches 4 and 5 (Budapest to Vukovar) and stretch 5 (Vukovar to Belgrade) with distinct pollutant patterns, which indicates different sources of PAHs along those river stretches. Concentrations of individual PAHs measured in stretch 2 (Passau to Bratislava) are within the concentration range that was measured in that stretch in spring till autumn 2011 using SPMD passive samplers (Vrana et al., 2014). This indicates that free dissolved PAH concentrations and their patterns in that Danube stretch in the summer period remained stable over a period of several years. A comparison with free dissolved concentrations measured using passive sampling in other European rivers (Vrana et al., 2014) shows that the concentrations of PAHs in the Danube is comparable to about 10 times lower.
29.3.1.4 Alkylphenols

The highest concentrations of free dissolved 4-nonylphenol (4-NP; 9.2 ng l\textsuperscript{-1}) and that of 4-tert-octylphenol (4-t-OP; 0.36 ng l\textsuperscript{-1}) was observed in the stretch between Vukovar and Belgrade (Figure 153). Concentration of 4-t-OP was on average 50 times lower than that of 4-NP.
29.3.2 Analysis of polar compounds – use of Empore disk samplers

29.3.2.1 Polar pesticides
A suite of 40 polar pesticides was analysed in extracts from the ED samplers. Results of analysis of five WFD priority pollutant polar pesticides, namely alachlor, atrazine, diuron, isoproturon and simazine are shown in Figure 154. Alachlor and diuron were present at concentrations less than or close to limit of quantification, which roughly corresponds to concentrations less than 100 pg l\(^{-1}\) in water. Estimated concentrations of atrazine, simazine and isoproturon in water were in the order of units of ng l\(^{-1}\) with the maxima of these pesticides in the stretch from Ruse to Braila. The results indicate that concentrations of the priority polar pesticides were far below their EQS values. It has to be noted that the main period of pesticide application is April-July and therefore the JDS results are not representative for the application season of these compounds.

Figure 154: Spatial variability of WFD priority pollutant polar pesticides in the water column measured by ED samplers in 8 Danube stretches. Data is expressed as amount of compound taken up by an integrative sampler during an average sampler exposure (1.6 days)

29.3.2.2 Alkylphenols
The longitudinal relative concentration profile of alkylphenols in the Danube, measured by ED samplers (Figure 155), was similar to that reported by SR samplers. The highest concentrations of both 4-t-OP and 4-NP, but also of bisphenol A was measured in the stretch from Vukovar to Belgrade. In ED samplers concentration of 4-t-OP was on average 40 times lower than that of 4-NP.
29.3.2.3 Pharmaceuticals

Results of analysis of caffeine and two pharmaceuticals, carbamazepine and diclofenac in extracts from the ED samplers are shown in Figure 156. The trend of caffeine concentration in the water column along the river was similar to that of bisphenol A. Estimated caffeine concentration levels were up to several tens of ng l-1 with the maximum observed concentration in the stretch from Vukovar to Belgrade. For comparison, analyses of caffeine in discrete spot samples taken collected the cruise and analysed by ELISA showed median concentration in Danube of 93 ng l-1 (Chapter 26). Estimated concentrations of carbamazepine along the river were in units of ng l-1 and less variable than that of caffeine. In agreement with the measurements made during JDS2 diclofenac was present at concentrations less than or close to limit of quantification, which can be explained by the biodegradability of this compound (Loos et al., 2008).

![Figure 155: Spatial variability of alkylphenols in the water column measured by ED samplers in 8 Danube stretches. Data is expressed as amount of compound taken up by an integrative sampler during an average sampler exposure (1.6 days)](image1)

![Figure 156: Spatial variability of caffeine and selected pharmaceuticals in the water column measured by ED samplers in 8 Danube stretches. Data is expressed as amount of compound taken up by an integrative sampler during an average sampler exposure (1.6 days)](image2)
29.3.3 Toxicological profiling

Selected toxic/bioactive potentials (see Table 90) of extracts of SR and ED passive samples are currently under evaluation. Preliminary results indicate that SR extracts contain significant amounts of dioxin-like compounds assessed by CAFLUX bioassay (Figure 157). Estimated toxic equivalents (bioTEQ) of samples recalculated for the sampled volume are between 6-10 pg l\(^{-1}\). MELN bioassay has indicated estrogenic activity in SR samples. The specific estrogenic potential needs to be quantified yet. Available data from HG5LN-hPXR bioassay show that some SR extracts can significantly activate pregnane X receptor, but not the androgenic receptor. Negative results have been obtained in case of mutagenicity of SR extracts in Ames assay. Preliminary data indicate that at least some of the ED samples possess quantifiable estrogenic and PXR-related potential significantly higher than field blank samples.

![Figure 157: Estimate of toxic equivalent of TCDD in the water column measured by SR samplers in eight Danube stretches determined in CAFLUX bioassay](image)

29.4 Conclusions

Despite the low or sub-ng l\(^{-1}\) concentrations of most organic pollutants present in the free dissolved phase, passive sampling enabled to clearly identify spatial gradients of a broad range of organic pollutants in the water column, including PCBs, OCs, PAHs, alkylphenols, selected polar pesticides and pharmaceuticals. In many cases, the integrative character of passive sampling allowed measurement of compounds down to pg l\(^{-1}\) levels where methods based on low volume spot sampling of water applied in the previous JDS2 survey failed to detect them (Sengl, 2008).

Passive samplers in most cases confirmed similar spatial distribution of pollutants along the river, as was observed in JDS2. The highest levels of PAHs, alkylphenols and caffeine in passive samplers were observed in the Danube stretches between Budapest and Belgrade. In agreement with JDS2, the downstream profile of PCBs and HCB showed a low variability and did not suggest particular emission maxima (Umlauf et al., 2008). In accordance with the findings during the JDS1 and JDS2, the downstream profile of \(\beta\)-HCH, DDT and its metabolites displays a sharp increase in the water column downstream Braila towards the Black Sea (Umlauf et al., 2008). The low percentage of p,p'-DDT of the total DDT concentration indicates that there was no current use of DDT in the area. The levels of priority pollutant polar pesticides alachlor, atrazine, diuron, isoproturon and simazine were comparable with the levels found in water samples during JDS2 and well below their respective EQS values (Loos et al., 2008).

Whereas data from spot sampling reflects the pollution at the individual JDS sampling sites at a single moment of time, passive samplers continuously sampled pollutants for several days, including river
stretches between individual JDS sampling sites. Thus, the information provided by spot sampling and passive sampling should be considered as complementary.

Finally, the combination of passive samplers with bioassays presents a very promising approach for detection of various trace organic pollutants and toxic potentials along the river and for identification of areas of concern for further investigation.

29.5 References


Acknowledgments

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