

EU WFD Organic Priority Substances in Water, Suspended Particulate Matter, Sediments, and Biota in the Danube

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Abstract Since its publication in the year 2000, the EU Water Framework Directive (WFD) became the most important legal act for water protection not only within the European Union but also in the Danube River Basin. In its strategy against water pollution, the WFD identifies priority substances (PS). PS are hazardous chemical compounds forming a special threat to the quality of surface waters. The goal is to reduce concentrations of all PS at least below substance-specific environmental quality standards (EQS). EQS are concentration limit values derived on the basis of ecotoxicological substance data and additional information. In the Danube River Basin, the level of contamination of the Danube and its tributaries by PS was investigated within the monitoring activities of the International Commission for the Protection of the Danube River Basin (ICPDR). Especially the results of ICPDR's research expeditions in 2001 and 2007, the Joint Danube Surveys, revealed the exposure situation for PS in different aquatic matrices. For the subgroup of organic PS, widespread pollution problems with partial exceedance of the respective water EQS were found for nonylphenol, a decomposition product of surfactants, the plasticizer di(2-ethylhexyl) phthalate, and tributyltin compounds, formerly used in antifouling paints for ships. The mostly banned pesticide atrazine could also be found in many water samples. For all other PS, only local problems were identified or they have not been detected at all. The results for suspended particulate matter, sediment, and biota support the findings above.

Keywords Danube, Joint Danube Survey, Pollution, Priority substance, Water framework directive

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1 The Water Framework Directive

In the 1970s, the first legal instrument of the European Union to protect surface waters against pollution by hazardous substances was introduced with the enforcement of the Dangerous Substances Directive (DSD) [1] and its daughter directives. In the following years, these legal acts were supplemented by a number of use-oriented directives and decisions which covered different other aspects of water protection (e.g., Nitrates Directive [2], Industrial Emissions Directive [3]). With increasing pressures on surface waters and groundwater, it became clear that existing legislation was not capable to guarantee the preservation and improvement of European waters in the long term. In the 1990s, therefore, work started on reshaping water legislation, and in December 2000, eventually, the Water Framework Directive (WFD) [4] of the European Union was enforced (more details can be found in [5]). This legal act forms the basis for a new and comprehensive water policy within the EU.

The outstanding goal of the WFD is to achieve a good status for all surface waters and groundwater until 2015. For the status assessment, surface waters and groundwater are formally divided into “water bodies,” coherent subunits of the river basin district [6]. For each water body, a set of quality elements has to be evaluated and compared to the environmental objectives given for all types of waters in Annex V of the WFD. The quality elements are grouped to define the ecological status (biological, hydromorphological, and physicochemical quality elements including hazardous substances of relevance in a specific river basin) and the chemical status (hazardous substances regulated on community level). The

combination of these two assessments leads to the overall result revealing whether a water body has achieved good status.

The operational tool to pursue the WFD goals is the River Basin Management Plans (RBMPs). To set up this plan for a catchment area, several consecutive steps have to be carried out: identification of pressures, analysis of impacts, identification of risks to fail good status, monitoring and assessment of status, and development and implementation of measures to improve water bodies in bad status. The results of these analyses and the necessary measures for improvement are compiled in the RBMPs. According to the WFD, the first edition of the RBMPs had to be put into force in 2009. Currently, the second cycle of analysis and assessment for update of the RBMPs in 2015 is ongoing. The results of river basin characterization and the coordinated measures for the international catchment area of the Danube River were summarized in the Danube RBMP 2009, prepared by the International Commission for the Protection of the Danube River (ICPDR) [7].

2 Priority Substances

The WFD defines hazardous substances as “substances or group of substances that are toxic, persistent and liable to bio-accumulate and other substances or group of substances which give rise to an equivalent level of concern.” Two groups of hazardous substances are defined: According to the subsidiary principle, on community level, only substances shall be regulated posing a threat to a majority of European waters, therefore named priority substances (PS). Pollutants with only local or regional impacts have to be handled on member state level (belonging to the quality elements of the ecological surface water status). According to WFD Article 16, the European Commission is obliged to submit a proposal for a PS list ranking substances according to their risk to the aquatic environment due to their intrinsic properties and exposure.

The selection and prioritization for PS are challenging because of the large number of potential candidates and the huge amount of high-quality data needed to assess risk and exposure. The basic measure for the ranking of candidate substances is the ratio of the predicted environmental concentration (PEC) to the predicted no-effect concentration (PNEC). PEC values are calculated with the help of exposure models taking into account data on production, use, and release potential for a certain substance. Ideally, instead of PEC values, data of monitored concentrations of a pollutant can be used. PNECs are derived, *inter alia*, based on ecotoxicological endpoints for water organism, determined to the greater part in standardized laboratory tests (see Sect. 3). Substances with a PEC/PNEC ratio greater than 1 pose a risk to the aquatic environment.

In 2001, the EC submitted a first proposal [8] identifying 33 substances and substance groups as PS of which 11 were designated as priority hazardous substances (PHS) and 14 as PHS candidates (in the meantime, this decision process has been finalized resulting in 13 PHS). For PHS, due to their extremely dangerous

properties, the phase-out and cessation of discharges, emissions, and losses is the midterm goal of the WFD. For PS, the WFD demands a continuous reduction of emissions into the aquatic environment.

3 Derivation of Environmental Quality Standards

The environmental quality standards (EQS) provide legally binding concentration limits for hazardous substances in surface waters ensuring protection of the environment and humans, mainly derived on the basis of ecotoxicological effect data.

For hazardous substances, the basic principles for derivation of EQS are laid down in Annex V, point 1.2.6 of the WFD. The development of a detailed method for the first PS list was carried out by a consultant [9, 10]. Based on this work and after a tedious legislative procedure, the EQS for PS were put into force in December 2008 (“EQS Directive” [11]). The directive lays down EQS for inland surface waters and other surface waters (transitional, coastal, and marine waters). Both sets of EQS comprise Annual Average-EQS (AA-EQS) protecting against long-term/chronic exposure to PS and Maximum Allowable Concentration-EQS (MAC-EQS) protecting against short-term/acute effects due to pollutant concentration peaks. In addition, the directive includes EQS for 8 remaining substances of the 17 dangerous substances of the DSD, which have not been identified as PS. The existing standards for these substances have proved to be useful, so their regulation on community level was maintained.

The AA-EQS is compared to the annual average concentration of monthly measurements of 1 year and the MAC-EQS to the single measurement of the same period. Only if in both assessments the monitoring results do not exceed the respective EQS values for all 41 hazardous substances the water body is assigned “good chemical status.” Table 1 summarizes the 41 substances regulated on community level for the time being, the substance status, and the EQS for inland surface waters.

While MAC-EQS are based on acute ecotoxicological effects, AA-EQS take into account both chronic and acute effects. Figure 1 gives an overview of the derivation process for freshwater AA-EQS.

In the first step, on the basis of substance properties and agreed trigger criteria, it is decided which additional risk scenarios besides the water phase (pelagic community) are relevant (sediment/benthic community, top predators via prey/biota, and humans via food intake/biota and drinking water). For example, if the substance has no potential to bioaccumulate, the risk for top predators via prey and humans via food intake need not to be considered.

In the next step, the necessary data are compiled and checked for their usability (relevance and reliability). On the basis of this filtered data set, specific quality standards (SQS, synonymous to PNEC) for the relevant risk scenarios are derived: The lowest no-effect concentration (NOEC) is identified and an appropriate

Table 1 Hazardous substances regulated on community level, substance status, and environmental quality standards for inland surface waters [11]

No.	Name of substance	Status ^a	CAS number ^b	AA-EQS ^c Inland surface waters ^d	MAC-EQS ^e Inland surface waters ^d
(1)	Alachlor	PS	15972-60-8	0.3	0.7
(2)	Anthracene	PHS	120-12-7	0.1	0.4
(3)	Atrazine	PS	1912-24-9	0.6	2.0
(4)	Benzene	PS	71-43-2	10	50
(5)	Brominated diphenylether ^f	PHS	32534-81-9	0.0005	Not applicable
(6)	Cadmium and its compounds (depending on water hardness classes) ^g	PHS	7440-43-9	≤0.08 (Class 1) 0.08 (Class 2) 0.09 (Class 3) 0.15 (Class 4) 0.25 (Class 5)	≤0.45 (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)
(6a)	Carbon tetrachloride	OP	56-23-5	12	Not applicable
(7)	C10-C13 chloroalkanes	PHS	85535-84-8	0.4	1.4
(8)	Chlorfenvinphos	PS	470-90-6	0.1	0.3
(9)	Chlorpyrifos (chlorpyrifos-ethyl)	PS	2921-88-2	0.03	0.1
(9a)	Cyclodiene pesticides	OP		Σ = 0.01	Not applicable
	Aldrin		309-00-2		
	Dieldrin		60-57-1		
	Endrin		72-20-8		
	Isodrin		465-73-6		
(9b)	DDT total ^h	OP	Not applicable	0.025	Not applicable
	<i>para-para'</i> -DDT	OP	50-29-3	0.01	Not applicable
(10)	1,2-Dichloroethane	PS	107-06-2	10	Not applicable
(11)	Dichloromethane	PS	75-09-2	20	Not applicable
(12)	Di(2-ethylhexyl)-phthalate (DEHP)	PS	117-81-7	1.3	Not applicable

(continued)

Table 1 (continued)

No.	Name of substance	Status ^a	CAS number ^b	AA-EQS ^c Inland surface waters ^d	MAC-EQS ^e Inland surface waters ^d
(13)	Diuron	PS	330-54-1	0.2	1.8
(14)	Endosulfan	PS	115-29-7	0.005	0.01
(15)	Fluoranthene	PS	206-44-0	0.1	1
(16)	Hexachlorobenzene	PHS	118-74-1	0.01 ⁱ	0.05
(17)	Hexachlorobutadiene	PHS	87-68-3	0.1 ^j	0.6
(18)	Hexachlorocyclohexane	PHS	608-73-1	0.02	0.04
(19)	Isoproturon	PS	34123-59-6	0.3	1.0
(20)	Lead and its compounds	PS	7439-92-1	7.2	Not applicable
(21)	Mercury and its compounds	PHS	7439-97-6	0.05 ^k	0.07
(22)	Naphthalene	PS	91-20-3	2.4	Not applicable
(23)	Nickel and its compounds	PS	7440-02-0	20	Not applicable
(24)	Nonylphenol (4-nonylphenol)	PHS	104-40-5	0.3	2.0
(25)	Octylphenol ((4-(1,1',3,3'-tetramethylbutyl)-phenol))	PS	140-66-9	0.1	Not applicable
(26)	Pentaclorobenzene	PHS	608-93-5	0.007	Not applicable
(27)	Pentaclorophenol	PS	87-86-5	0.4	1
(28)	Polyaromatic hydrocarbons (PAH) ^l	PHS	Not applicable	Not applicable	Not applicable
	Benzo(a)pyrene	PHS	50-32-8	0.05	0.1
	Benzo(b)fluoranthene	PHS	205-99-2	Σ = 0.03	Not applicable
	Benzo(k)fluoranthene	PHS	207-08-9		
	Benzo(g,h,i)perylene	PHS	191-24-2	Σ = 0.002	Not applicable
	Indeno(1,2,3-cd)pyrene	PHS	193-39-5		
(29)	Simazine	PS	122-34-9	1	4
(29a)	Tetrachloroethylene	OP	127-18-4	10	Not applicable
(29b)	Trichloroethylene	OP	79-01-6	10	Not applicable
(30)	Tributyltin compounds (tributyltin cation)	PHS	36643-28-4	0.0002	0.0015

(31)	Trichlorobenzenes	PS	12002-48-1	0.4	Not applicable
(32)	Trichloromethane	PS	67-66-3	2.5	Not applicable
(33)	Trifluralin	PS	1582-09-8	0.03	Not applicable

^aOP other pollutant: substance formerly regulated by DSD and not identified as PS, PS priority substance, PHS priority hazardous substance

^bCAS Chemical Abstracts Service

^cThis parameter is the EQS expressed as an annual average value (AA-EQS). Unless otherwise specified, it applies to the total concentration of all isomers
^dInland surface waters encompass rivers and lakes and related artificial or heavily modified water bodies

^eThis parameter is the EQS expressed as a maximum allowable concentration (MAC-EQS). Where the MAC-EQS are marked as “not applicable,” the AA-EQS values are considered protective against short-term pollution peaks in continuous discharges since they are significantly lower than the values derived on the basis of acute toxicity

^fFor the group of priority substances covered by brominated diphenylethers (No. 5) listed in Decision No. 2455/2001/EC, an EQS is established only for the sum of congener numbers BDE 28, 47, 99, 100, 153, and 154

^gFor cadmium and its compounds (No. 6), the EQS values vary depending on the hardness of the water as specified in five class categories (Class 1, <40 mg CaCO₃/L; Class 2, 40 to <50 mg CaCO₃/L; Class 3, 50 to <100 mg CaCO₃/L; Class 4, 100 to <200 mg CaCO₃/L; and Class 5, ≥200 mg CaCO₃/L)

^hDDT total comprises the sum of the isomers 1,1,1-trichloro-2,2-bis (*p*-chlorophenyl) ethane (CAS number 50-29-3; EU number 200-024-3); 1,1,1-trichloro-2-(*o*-chlorophenyl)-2-(*p*-chlorophenyl) ethane (CAS number 789-02-6; EU number 212-332-5); 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethylene (CAS number 72-55-9; EU number 200-784-6); and 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethane (CAS number 72-54-8; EU number 200-783-0)

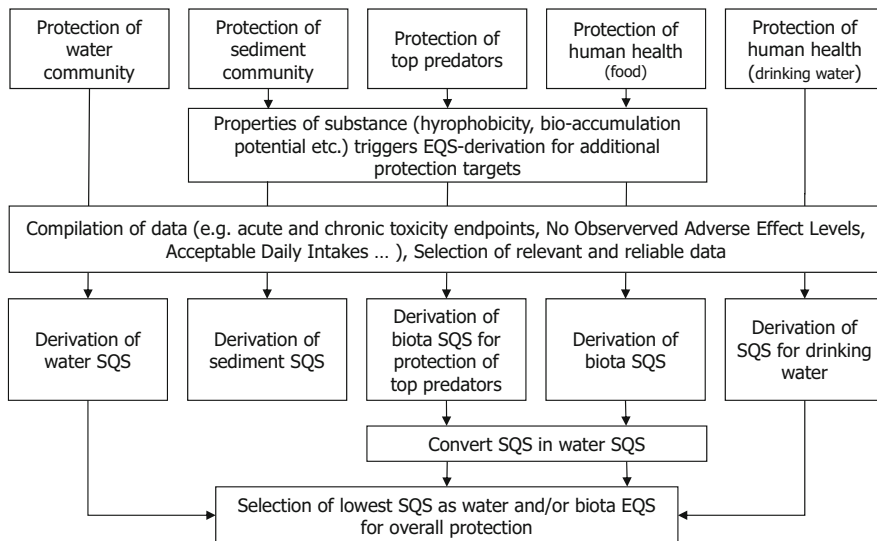
ⁱWater EQS may only be applied in combination with biota EQS for hexachlorobenzene: 10 µg/kg (wet weight)

^jWater EQS may only be applied in combination with biota EQS for hexachlorobutadiene: 55 µg/kg (wet weight)

^kWater EQS may only be applied in combination with biota EQS for mercury and its compounds: 20 µg/kg (wet weight)

^lFor the group of priority substances of polycyclic aromatic hydrocarbons (PAH) (No. 28), each individual EQS is applicable, i.e., the EQS for benzo(a)pyrene, the EQS for the sum of benzo(b)fluoranthene and benzo(k)fluoranthene, and the EQS for the sum of benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene must be met

Overview – Derivation of Environmental Quality Standards



SQS: Specific Quality Standard
EQS: Environmental Quality Standard

Fig. 1 Overview of derivation steps for environmental quality standards according to [12]

assessment factor (AF) in the range 2–1,000 applied (i.e., division of the lowest concentration by AF) to obtain the SQS/PNEC. The AFs account for:

- Uncertainties in transfer of ecotoxicological endpoints from laboratory tests to the environment
- Completeness of data set (data gaps)
- Effects on endocrine system of aquatic organisms
- Synergistic toxic effects of pollutant mixtures (no consolidated approach for assessment of pollution mixtures is available presently)

The “assessment factor method” was developed to deal with limited data sets for pollutants of interest. In the meantime, many substances are well characterized regarding their adverse environmental effects, and large data sets are available for risk assessment and QS derivation. In this case, a statistical method can be applied, the so-called species sensitivity distribution, where the SQS/PNEC is derived as percentile of ecotoxicity data distribution.

The SQS for other matrices than water are back-calculated to the water phase with the help of bioaccumulation factors, etc. The SQS with the lowest (corresponding) water value is selected as water and/or biota EQS for the substance ensuring overall protection.

More details on EQS derivation (MAC-EQS, metals, etc.) can be found in the EU CIS Guidance Document No. 27 “Technical Guidance for Deriving

Environmental Quality Standards” [12]. This document lays down the advanced methodology of EQS setting for the revision of the PS list based on the original method [9, 10].

4 Monitoring of Priority Substances in the Danube River Basin

4.1 Routine Monitoring Programs

The first coordinated monitoring program within the Danube River Basin was already initiated under the Bucharest Declaration, which was signed by the Danube riparian countries in 1985. The focus of this monitoring network was to evaluate water quality in the cross section of the river at the borders of the riparian states. Monitoring activities were heavily intensified after the signing of the Danube Convention in 1994 eventually leading the setup of the “Trans-National Monitoring Network” (TNMN) in 1996. In 2007, the monitoring network was reshaped to adapt it to the requirements of the WFD. Within the joint monitoring under TNMN, the water quality is determined at over 100 sampling sites at the Danube River and its tributaries 12 times per year, at selected monitoring stations 26 times per year for reliable load calculations. The list of determinants comprises basic physicochemical parameters, nutrients, metals and selected pollutants (all measurements in the water phase), and biological parameters. Up to now, only a few WFD priority substances (namely, cadmium, lead, nickel, mercury, atrazine, lindane (γ -hexachlorocyclohexane), PAH, and trichloromethane) and some EU-regulated “other pollutants” (carbon tetrachloride, *p,p'*-DDT, tetrachloroethylene, trichloroethylene) are monitored within the framework of TNMN. Analyses are carried out by national reference laboratories in the riparian countries. With regard to the mentioned organic priority substances, it has to be noted that these substances were only partly analyzed at TNMN stations and the assessment of available data is additionally complicated by varying limits of quantification (LOQ). Nevertheless, the available data show that lindane and trichloromethane can hardly be detected. Atrazine can be quantified in some cases, but only single values exceed the AA-EQS in some tributaries. The mean values are well below the EQS. Result details of the TNMN program can be found in the annual TNMN reports starting from 1996 [13].

Another part of TNMN functions as surveillance and operational monitoring according to WFD providing data for the Danube River Basin Management Plan. The priority substances which were identified in the first Danube River Basin Management Plan as causing poor chemical status in the surface water bodies in catchments larger than 4,000 km² are described in the chapter by Liska [14].

4.2 *Joint Danube Surveys*

At the end of the 1990s, the idea came up to supplement the results of the existing monitoring programs with a research expedition to give a longitudinal multidisciplinary overview of the water quality of the Danube River. The need to close the data gaps regarding priority substances, geographically and with respect to the substances not monitored within TNMN, was one of the important motivations for the organization of the first Joint Danube Survey of the ICPDR in 2001 (JDS 1) and remained as one of the most important goals for the second survey in 2007 (JDS 2).

The lessons learned in the first years of routine monitoring led to a different approach for analysis during the Joint Danube Surveys: Within these measurement campaigns, groups of substances are measured by one laboratory for all samples of the same type of the survey. This avoids problems with bias and differing LOQs and guarantees comparability of data along the whole stretch of the Danube River. The results of both surveys can be found in the respective scientific reports [15, 16].

4.3 *Results and Assessment of Organic Priority Substances According to WFD*

During JDS1 (2001), lots of experience were gained regarding sampling and analysis of PS. This knowledge, the even broader scope of investigation with respect to matrices analyzed combined with the comparability of data due to the “one substance-one laboratory” principle, makes the results for priority substances of JDS2 (2007) the most valuable data set for the basin-wide assessment of this substance group. The following summary assessments are therefore based on JDS2 results, with a comparison of JDS1 outcome, where possible.

It is the character of the survey to provide only a snapshot of the exposure situation (one result for a single sample per sampling site and matrix). For full chemical status assessment, the WFD demands 12 monthly measurements per year. It therefore has to be stressed that the JDS results can only give an indication of the chemical status at each sampling site and must not be mixed up with chemical status assessment on a water body basis which lies within the responsibility of the riparian states.

In this chapter, most of the organic PS are addressed. The findings for metals are discussed in the chapter by László [17] and the results for polycyclic aromatic hydrocarbons (PAH) in the chapter by Literathy [18].

Table 2 summarizes the analytical results of organic PS in the water phase. For these PS, the whole water sample (including suspended particulate matter) was analyzed because due to their hydrophobic properties for most of these substances, the partition equilibrium is shifted from the dissolved to the adsorbed state. For each substance, the range of concentrations found and the percentage of results above LOQ are given. Many results were below the respective LOQ. In these cases, for the

Table 2 Summary of results of JDS2 for priority substances and certain other pollutants in the water phase of the Danube River and its tributaries

No.	Name of substance	JDS2 results	% >LOQ	AA- EQS	MAC- EQS
(1)	Alachlor	(0.05)	0	0.3	0.7
(3)	Atrazine	(0.005)–0.56	>50	0.6	2.0
(4)	Benzene	(0.3)	0	10	50
(5)	Brominated diphenylether	(0.002) ^a	0	0.0005	–
(6a)	Carbon tetrachloride	(1.2)	0	12	–
(7)	C10–C13 chloroalkanes	n.a	–	0.4	1.4
(8)	Chlorfenvinphos	(0.005)	0	0.1	0.3
(9)	Chlorpyrifos (chlorpyrifos-ethyl)	(0.005)	0	0.03	0.1
(9a)	Cyclodiene pesticides			Σ = 0.01	–
	Aldrin	(0.01)	0		
	Dieldrin	(0.021)	0		
	Endrin	(0.023)	0		
	Isodrin	(0.005)	0		
(9b)	DDT total	(0.007)	0	0.025	–
	<i>para-para</i> -DDT	(0.007)	0	0.01	–
(10)	1,2-Dichloroethane	(0.7)	0	10	–
(11)	Dichloromethane	(0.5)	0	20	–
(12)	Di(2-ethylhexyl)-phthalate (DEHP)	(0.2)– 4.53	~100	1.3	–
(13)	Diuron	(0.001)	0	0.2	1.8
(14)	Endosulfan	(0.005)	0	0.005	0.01
(16)	Hexachlorobenzene	(0.02)	0	001	0.05
(17)	Hexachlorobutadiene	(0.1)	0	0.1	0.6
(18)	Hexachlorocyclohexane	(0.02)	0	0.02	0.04
(19)	Isoproturon	(0.001)–0.016	<1	0.3	1.0
(24)	Nonylphenol (4-nonylphenol)	0.02– 3.28	100	0.3	2.0
(25)	Octylphenol ((4-(1,1',3,3'- '-tetramethylbutyl)-phenol))	(0.005)–0.022	20	0.1	–
(26)	Pentachlorobenzene	(0.018)	0	0.007	–
(27)	Pentachlorophenol	(0.1)	0	0.4	1
(29)	Simazine	(001)–0.055	3	1	4
(29a)	Tetrachloroethylene	(0.5)–0.8	2	10	–
(29b)	Trichloroethylene	(1.7)	0	10	–
(30)	Tributyltin compounds (tributyltin-cation)	(0.0002)– 0.014	34	0.0002	0.0015
(31)	Trichlorobenzenes	(0.5)– 0.6	<1	0.4	–
(32)	Trichloromethane	< (1.8)	0	2.5	–
(33)	Trifluralin	(0.005)–0.01	<1	0.03	–

^aDetected in some water samples in concentrations between limit of detection and LOQ

lower end of the range, the LOQ in parenthesis is filled in. If all values were <LOQ, only the LOQ in parenthesis is given. If the maximum of results exceeds the respective EQS, the figure is displayed in bold.

The results of Table 2 show that for the major part of PS no or only local pollution problems could be identified in the water phase (no or only a few percent of results above LOQ). In contrast, for atrazine, alkylphenols, DEHP, and tributyltin compounds the results indicate a basin-wide pollution. Another group of substances where a widespread environmental contamination can be anticipated due to production and use is brominated diphenylethers. The real extent of pollution is concealed by the lack of analytical routine methods with sufficient analytical performance. Relevant concentrations can only be quantified with sophisticated analytical techniques. For some other compounds with high adsorption and bioaccumulation potential, water data alone are not sufficient to assess the real extent of pollution. For these compounds, supplementary data in sediment, suspended particulate matter, and/or biota were collected. These results are assessed in combination with the water data in the following sections.

4.4 Alkylphenols: Nonylphenol, Octylphenol

Nonylphenol, predominantly 4-iso-nonylphenol (NP), is a decomposition product of alkylphenol ethoxylates (APEO), surface active substances which were in widespread use in the last decades. More than 50% of produced NP went to manufacture of APEO. Other uses of NP were modified phenolic resins, plastics, stabilizers, and phenolic oximes. In 1997, 73,500 t of NP was produced within the EU; 3,500 t of exports and 8,500 t of imports give 78,500 t of NP used [19]. Of all possible octylphenol (OP) isomers, only 4-(1,1,3,3-tetramethylbutyl)-phenol (4-*tert*-octylphenol) seems to be of relevance due to the manufacturing process. Production in the EU is reported to be 6,800 t in 1998; thereof, 5,000 t is estimated to be used for the production of octylphenoxyethoxylates [19]. The use pattern seems to differ to some extent from NP. The ratio of NP and OP production is reflected in analytical results of environmental samples for these compounds. In the meantime, alkylphenols were banned in the EU [20] due to their endocrine-damaging potential.

JDS2 results of NP and OP revealed that at least NP was ubiquitous in the water phase in the whole catchment area at the time of investigation. NP was found in nearly all water samples at concentrations up to a maximum value of 3.28 µg/L. The highest concentrations, exceeding the AA-EQS and MAC-EQS for NP, were found in tributaries in the lower Danube region. The highest NP concentration in the Danube was measured at a sampling station downstream Novi Sad in Serbia (0.14 µg/L). OP could be only found in quantifiable concentrations at three sampling sites: the same sites where NP EQS were exceeded.

The main source for NP and OP are untreated urban and industrial waste waters. But even effluents of waste water treatment plants (WWTP) contribute remarkably

to NP pollution of the aquatic environment. High concentrations in the intake of the WWTP result in relevant concentrations in the effluent, despite of high removal rates for NP.

The findings in suspended particulate matter (SPM) and sediment support the water results for NP. Quantifiable amounts in SPM can be found at all sampling sites along the Danube. The maximum value (0.280 mg/kg dry matter) was found downstream Budapest where the main sewage plant was under construction at the time of the survey. The impact of the Budapest sewage could be seen for more than 200 km. Also the tributaries Tisza (89 mg/kg dry matter) and Velika Morava (74 mg/kg dry matter) were obviously influenced by untreated or insufficiently treated waste water. The level of NP in SPM samples of the upper part and the lower part of the Danube was always lower than 0.05 mg/kg dry matter with small variations. OP was only found in some 30% of SPM samples, with a maximum value of 0.043 mg/kg also downstream of Budapest.

Sediment results give a similar ratio of detectable concentrations for NP and OP as for SPM. NP could be quantified in nearly all sediment samples, OP only in 20% of the samples. Concentration ranges from LOQ (0.01 mg/kg dry weight) up to 1.8 mg/kg for NP and from LOQ (0.005 mg/kg) to 0.026 mg/kg. Hot spots are sampling sites in tributaries and in the lower stretch of the Danube.

4.5 *Di(2-Ethylhexyl)Phthalate (DEHP)*

The main use of di(2-ethylhexyl)phthalate (DEHP) was as plasticizer, mainly in polyvinylchloride (PVC) polymers. The content in flexible polymer materials was up to 30–40% (w/w). In the 1990s, the production in Western Europe was in the order of magnitude of several 100,000 t/year [21]. The global release into the environment via air was estimated between 10,000 and 150,000 t/year [22]. Therefore, it is not surprising that DEHP can still be found in high concentrations in different environmental samples (soil, sewage sludge, water, biota).

As a consequence of the widespread use of DEHP-containing plastics and the relatively high volatility of phthalate, it is ubiquitously present. This also creates a serious problem for analytical laboratories. Due to high blank values, additional uncertainty is introduced in the analytical process, which is reflected in elevated quantification limits. For this reason, LOQs of 0.2 µg/L for whole water samples and of 0.30 mg/kg dry matter were achieved for suspended particulate matter for analysis of JDS2 samples.

In all water samples of JDS2 – except four samples from the upper reach of the Danube – DEHP was detected. The highest concentration was found at the Austrian–Slovakian border (Wildungsmauer, 4.5 µg/L) and downstream Budapest (Dunavoldfar, 4.4 µg/L). Elevated concentrations of DEHP were detected in the middle stretch of the Danube, whereas the concentrations in the upper part and the lower part of the river were below 1 µg/L. Quite a number of single measurements

exceed the AA-EQS for DEHP of 1.3 µg/L which is a strong indication that the good chemical status could be failed in some water bodies.

DEHP could be quantified in all suspended matter samples of JDS2 concentrations above 0.3 mg/kg dry matter. Samples of the tributaries Tisza (10 mg/kg dry matter) and Sava (5.0 mg/kg dry matter) showed the highest values of all samples. Elevated concentrations were also found in the German stretch and in the middle section of the Danube. The sharp rise of DEHP concentrations downstream Budapest again indicated the influence of insufficiently treated household and industrial sewage.

During JDS2, DEHP was also found in all sediment samples analyzed. The ubiquitous occurrence of DEHP in all water, suspended matter, and sediment samples underlines the relevance of DEHP as a priority substance for contaminating the Danube River. For most of the sediments, concentrations ranged between 0.1 and 1.0 mg/kg dry mass, and only few samples exhibited significantly higher amounts of DEHP. However, no clear trend in DEHP contamination along the course of the Danube River could be identified. Maximum DEHP levels of more than 16 mg/kg dry matter were found in a sample collected downstream Arges in Romania, i.e., the same sediment that already exhibited elevated amounts of NP. During JDS1, DEHP was also found in almost all sediments under investigation with a maximum concentration of 170 mg/kg dry weight which also was found in a sediment sample near Arges. Comparing JDS1 and JDS2 results for DEHP, suspended matter show higher concentrations especially in the middle part of the Danube, whereas sediment samples indicate an improvement of sediment quality with regard to phthalates.

4.6 Tributyltin Compounds

Tributyltin compounds (TBT) were used as antifouling paints (80%), fungicides, and various biocides used in preparations and products. In 2002, the use of tri-substituted organotin compounds was about 1,600 t in the EU. In the meantime, the use of TBT as antifouling agent was forbidden by EU chemicals law (REACH [20]). Therefore, the application of tri-substituted organotins decreased to about 350 t/a and of TBT to about 250 t/a. According to its use as antifouling agent, the pollution by TBT is mainly caused by diffuse emissions from ship hulls and emissions of TBT during activities in shipyards and dockyards. Despite the ban as a biocide in antifouling paints, diffuse emissions of TBT from ship hulls and contaminated harbor and river sediments still go on although they will gradually diminish [23].

During JDS2, TBT was analyzed in 23 selected water samples together with 4 other organotin compounds and was found only in 8 of the 23 samples in concentrations above the LOQ of 0.2 ng/L with a maximum concentration of 14 ng/L. All other organotin compounds analyzed could not be detected or were below LOQ in the water samples. For TBT the LOQ of the method applied during

JDS2 and the AA-EQS were equal, which means that all positive results were an indication of good chemical status failure. The EQS for acute effects of 15 ng/L was not exceeded by the single measurements.

Suspended matter samples were collected at the same sample sites which were selected for water analysis of organotin compounds. Tributyltin compounds could only be found in 3 of the 23 samples but with a maximum concentration of 230 µg/kg dry matter. This high level was determined for the suspended matter collected in Serbia downstream Belgrade.

The fraction of samples with concentrations of TBT above LOQ was even lower for sediments. Only 9 of 124 samples showed positive evidence for TBT with a maximum of 12 µg/L dry matter.

TBT was additionally analyzed in mussel samples. In contrast to the other matrices in mussel tissue, TBT was the organotin compound with the highest abundance of all organotin compounds investigated. Out of 25 mussel samples, 24 showed positive results with a maximum value of 1,200 µg/kg dry weight and with mean and maximum value a factor 6 higher than concentrations of other organotins. The maximum for TBT in mussel samples was detected at a site downstream Novi Sad in Serbia.

4.7 Polybrominated Diphenylethers

Polybrominated diphenylethers (PBDE, in the context of the WFD also named brominated diphenylethers – BDE) were broadly used as flame retardants in polyurethane foams for furniture and upholstery as well as in plastic housings of electronic equipment in recent decades. Combined figures for production and import of PBDE in the EU were some 10,000 t/year at the end of the 1980s [24]. In the meantime, due to the identified risks, the amount used went down to several hundred t/year; eventually, production and use were banned. Huge amounts of PBDE are still physically bound in products and enter the environment by diffusion.

PBDEs are persistent. They show low water solubility but a high binding affinity to particles and a distinct tendency to accumulate in sediments and biota. The decisive-specific quality standard was the one for protection of human health via food consumption. Due to the high accumulation potential in fish, mussels, etc., the back-calculation from biota SQS led to very low AA-EQS for the water phase of 0.0005 µg/L.

Three technical mixtures of PBDEs were used as flame retardants referred to as pentabromo diphenylether, octabromo diphenylether, and decabromo diphenylether. At the time of preparation of the first PS list only for pentabromo diphenylether, a risk to the aquatic environment was identified and the substance group therefore included in the PS list. The technical products contain a mixture of several congeners of brominated diphenylethers (compounds based on the same chemical structure, a diphenylether, but with differing number and position of

bromine atoms; the 209 possible different congeners are identified, besides their correct nomenclature names, via number codes). For the commercial product pentabromo diphenylether, tetra- and pentabromo compounds were identified as the main components and tri-, hexa-, and heptabromo congeners as impurities. For monitoring purposes, the six most important congeners of pentabromo diphenylether have been selected (BDE 28, 47, 99, 100, 153, 154; see also Table 1, footnote f). The sum of measured concentrations has to be compared with the AA-EQS.

PBDE water concentrations at EQS level are hardly accessible with analytical routine techniques; therefore, water data for PBDE are scarce. Also during JDS2, the achievable LOQ for lower and medium brominated diphenylethers was 0.002 µg/L (BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183; BDE 28 was not analyzed) and for highly brominated diphenylethers 0.005 µg/L (BDE 203, BDE 205), a factor 4–10 above the AA-EQS. PBDEs were not found in amounts above the respective LOQs in any water sample. Only in a few samples, BDE 47 and BDE 99 were measured in concentrations between LOD and LOQ (Romanian reach of Danube). Comparison with former data is not possible because PBDE was not analyzed in water samples in JDS1.

Also in sediments, just two compounds of the regulated PBDE group (BDE 99, BDE 100) could be detected in only one sample. Conversely, decabromo diphenylether (BDE 209) was quantified in all sediment samples and turned out to be relevant for contamination of the Danube River sediment. The concentrations are between <0.00025 and 0.005 mg/kg dry mass with generally higher concentrations in the middle stretch of the Danube. The highest level of BDE 209 was found in a sediment sample from the Serbian tributary Velika Morava. Detailed analysis of the results of polybrominated diphenylethers received from JDS2 is provided in the chapter by Umlauf et al. [25].

4.8 Organochlorine Compounds

Chlorinated compounds form the biggest group of the PS list (including the “other pollutants”) and comprise of substances used mainly as solvents (carbon tetrachloride, 1,2-dichloroethane, dichloromethane, tetrachloroethylene, trichlorobenzene, trichloroethylene, trichloromethane), insecticides (chlorfenvinphos, chlorpyrifos, aldrin, dieldrin, endrin, isodrin, DDT, endosulfan), bactericides/fungicides (hexachlorobenzene, pentachlorophenol), and intermediates in chemical processes (pentachlorobenzene, trichlorobenzenes). The main use of C10–C13 chloroalkanes was as cooling lubricant in metal works. The commercial product is a mixture of several thousand isomers with different chain length and chlorination degree. As an agreed method has been made available only recently, this substance group was not analyzed during JDS2.

With exception of chlorpyrifos, the production and use of the listed organochlorine compound are banned or restricted, for some of them since decades (e.g.,

DDT). The use of chlorinated solvents is allowed in part but only in closed-loop circuits to minimize emissions to air and water. The bans and restrictions for organochlorine compounds are laid down in international treaties (Stockholm Convention [26], Convention on Long-range Transboundary Air Pollution [27]) and EU regulations (Regulation on persistent organic pollutants [28], REACH [20]).

For all organochlorine compounds, the results of JDS2 target analyses (Table 2) revealed that these substances were hardly detectable in the water phase and all quantifiable concentrations are well below the respective EQS. But for some of the substances, the LOQ of the applied method was higher than the EQS (dieldrin, endrin, pentachlorobenzene, hexachlorobenzene, trichlorobenzene). Furthermore, organochlorine compounds with higher molecular weight and chlorination degree tend to adsorb on sediment and suspended matter and have a high bioaccumulation potential (for hexachlorobenzene and hexachlorobutadiene biota, EQS of 10 and 55 $\mu\text{g}/\text{kg}$ wet weight are stipulated, respectively). Accordingly, data on organochlorine compounds in sediment, SPM, and biota are an important supplement to water monitoring results. Target analysis of sediment and SPM showed only a low content of organochlorine compounds in a few samples, mainly in the middle and lower stretch of the Danube River. Fish samples, in the contrary, show quantifiable concentrations of hexachlorobenzene > hexachlorobutadiene > 1,2,4-trichlorobenzene and pentachlorobenzene in muscle tissue and liver. The concentrations for hexachlorobenzene come close but did not exceed the biota EQS. The higher concentrations of hexachlorobenzene in the upper reach of the Danube River were assigned to historic pollution stemming from chemical industry facilities already under remediation. These data for organochlorine compounds are supplemented by an in-depth analysis which is given in the chapter by Umlauf et al. [25].

4.9 Polar Pesticides

The herbicides alachlor, atrazine, diuron, isoproturon, simazine, and trifluralin were broadly used in agriculture and other applications in recent decades. Mainly due to their persistence in soil and the resulting groundwater contamination in combination with their toxicity to aquatic organisms, the authorizations on the basis of the EU Plant Protection Products Regulation [29] for alachlor, atrazine, simazine, and trifluralin were withdrawn between 2004 and 2007. Atrazine and simazine were already banned in some member states since the 1990s and 2000, respectively. Diuron and isoproturon are still authorized. While isoproturon-containing products are approved in most EU countries, the number of diuron-containing formulations on the markets has been successively reduced in the last years.

According to their polarity, the water solubility of these compounds is moderate to high with a low tendency to adsorb to SPM, showing only moderate bioaccumulation potential. Analysis is therefore focused on the water phase. Despite its ban, atrazine and its most important degradation product

desethylatrazine were found in many water samples during JDS2. Most concentrations were in the range 0.01–0.02 µg/L with a maximum for atrazine of 0.056 µg/L in a Romanian tributary, more than a factor of 10 below the AA-EQS. For all the herbicides, the overview in Table 2 reveals that they hardly could be detected. The concentrations of the few positive results were far below the respective EQS. It has to be noticed that monitoring during JDS2 took place in August and September. At least for the two authorized pesticides, it can be anticipated that the concentrations in surface waters are probably higher during the application periods, mainly in spring.

4.10 Benzene

In the meantime, the use of benzene is largely restricted according to Annex XVII of the REACH regulation with two exceptions: motor fuels and industrial uses (when legal emission limit values are not exceeded). In both application fields, rather huge amounts of benzene are used. Nevertheless, during JDS2, benzene was not detected in any of the analyzed water samples.

5 Conclusions and Outlook

5.1 Trends in Environmental Concentrations for PS

As already mentioned in the discussion of substances and substance groups, PS production and use are limited or even banned. Especially for the frequently detected alkylphenols, DEHP, tributyltin compounds, and atrazine, it can be expected that environmental concentrations will further go down. Due to the low AA-EQS in water for brominated diphenylethers, the actual exposure situation could only be partly evaluated, but also PBDE use is limited and an improvement of the environmental status with regard to this substance group is likely. Despite these trends toward a meaningful long-term monitoring, it is important to further shift the focus from the water phase to suspended matter, sediment, and/or biota depending on physical properties and behavior of the respective pollutants. This is also reflected on the European level in the increasing number of EQS laid down for biota (see below).

The development in concentrations of identified local pressures for some of the other PS depends on the source of the respective pollution. It's up to the riparian countries to identify these sources and develop measures for their sanitation. For EU member states, this is already obligatory, and the first River Basin Management Plans (RBMPs) addressing these problems are in place since 2009. The 2015 update of the RBMPs is currently in preparation. During this exercise, the efficiency of the

actual reduction measures have to be assessed and the measures modified if necessary.

Pollution problems affecting more than one riparian state are addressed in the Danube RBMP prepared by the ICPDR in 2009 [30]. Although this document is based on the obligations of the Water Framework Directive, also information on the water quality status and measures for non-EU member states within the Danube River Basin are included.

For some of the PS, however, even basin-wide measures might not be sufficient. Due to the physical properties, certain PS are subject to long-range air transport and therefore could be found even in remote areas far away from the location of their production and use. From the list of organic PS relevant for the Danube River Basin, tributyltin compounds and PBDE have been marked as such “ubiquitous persistent, bioaccumulative, and toxic” substances (uPBT) by the European Commission [31]. Thus, the goal of reduction and phase-out of emissions for these substances can only be reached if the measures already implemented on an international level are intensified and effectuated [26, 27].

5.2 *New PS and Revision of Existing PS*

Identification and regulation of PS is a dynamic process. WFD Article 16 provides for a regular revision of the PS list. Although the first revision was delayed in August 2013, the new PS Directive was published eventually [31]. The new directive will extend the PS list with 12 substances, 6 of them were identified as PHS (underlined below):

- Pesticides and biocides: aconifen, bifenox, cybutryne, cypermethrin, dichlorvos, dicofol, heptachlor and heptachlor epoxide, quinoxifen, terbutryn
- Industrial chemicals: hexabromcyclododecane (HBCDD), perfluorooctane sulfonic acid, and its derivatives (PFOS)
- Byproducts of combustion processes: dioxins and dioxin-like compounds

For dicofol, PFOS, dioxins, and dioxin-like compounds, HBCDD and heptachlor and heptachlor epoxide biota EQS were derived.

In the revision proposal, also pharmaceutical substances (α -ethinyl estradiol, β -estradiol, diclofenac) were included for the first time, but their regulation in the PS list was postponed due to uncertainties regarding the exposure situation.

In parallel, also the existing PS have been revised. On the basis of new data, EQS have been adapted and lowered in most cases. For brominated diphenylethers, fluoranthene, and PAH, biota EQS were defined. Water AA-EQS for brominated diphenylethers, hexachlorobenzene, hexachlorobutadiene, mercury and its compound, and some compounds belonging to PAH were withdrawn. New substance information led to a change of status of 2 PS (DEHP, Trifluralin) to PHS. The new directive has to be transposed into national law of the member states until September 2015.

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