
Joint Danube Survey 2

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International
Commission
for the Protection
of the Danube River

Internationale
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der Donau



Organic compounds in water, suspended particulate matter, sediments and biota

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1 Introduction

Organic pollutants are a huge group of very different organic compounds which are used e.g. for industrial or household purposes, for agriculture, as pharmaceuticals etc.. Residues of many organic compounds can be found in waste water, river water, suspended particulate matter, sediments or biota. More than 30 of these organic pollutants are compiled in Annexes IX and X of the WFD and were the main target substances for chemical analysis during JDS 2. Proposals for environmental quality standards are given in a draft directive still under discussion.

Depending on analytical capacities besides WFD target substances additional organic compounds were under investigation as they might be present in the Danube catchment area in significant concentrations.

The following subchapters provide general information about the organic parameters analysed. Details on analytical methods used by the different laboratories can be seen in the summary report “Methods for the analysis of organic compounds”.

1.1 Alkylphenoles and alkylphenol ethoxylates

Alkylphenol polyethoxylates (APEOs) are commercially important surfactants with industrial, agricultural and domestic applications. Nonylphenol polyethoxylates (NPEOs) account for about 80 % of APEOs, and octylphenol polyethoxylates (OPEOs) for most of the remaining 20 %.

During sewage treatment by aerobic digestion, NPEOs are degraded to lower ethoxymers (nonylphenol monoethoxylate (NP1EOs), nonylphenol diethoxylate (NP2EOs)) and subsequently anaerobically to nonylphenol (NP) which are known to exert estrogenic effects in aquatic organisms and in mammals and birds. The same fate can be expected for OPEOs which are subsequently degraded to octylphenol (OP).

It has been estimated that one half of the APEOs production is emitted via wastewater treatment plants (WWTPs) into surface waters. Therefore, water courses may be acting as environmental sinks for those compounds by receiving treated and/or untreated effluents.

Usually NP and in a few cases OP are found in river water in low concentrations. Due to their partly hydrophobic nature, NP, OP and their lower ethoxylate homologues are also associated with organic matter in sediments and suspended/colloidal particulate matter. Suspended particles and colloids especially play a significant role in the transport of those compounds in the river systems including their settlement. Subsequently, bottom sediments may act as the sink and/or source of NP, NP1EOs, NP2EOs, OP, OP1EOs and OP2EOs.

NP and OP were investigated for the first time in the Danube River during the Joint Danube Survey in the year 2001 and during the Aquaterra Danube Survey in the year 2004, when the river stretch from river kilometre 1942 to 795 has been investigated.

In many European countries these compounds were banned from house-hold products but they are still used in products for industrial use. OP and NP are listed as WFD priority substances and the proposed environmental quality standards for OP and NP for inland waters are 0,1 µg/l and 0,3 µg/l respectively.

1.2 Polybrominated diphenylethers (PBDEs)

Polybrominated diphenylethers are used as flame retardants in plastic materials, especially in plastics for electrical and electronic products. Worldwide, only three types of polybrominated diphenylethers are commercially used: decabromo-diphenylether, octabromodiphenylether, and pentabromodiphenylether. It is imported by two companies and its total use (especially in polyurethane foams) is estimated to be around 250 tons per year. The main polybrominated diphenylethers produced and used in Europe are the higher brominated ones (estimated amounts for EU: octabromodiphenylether 450 tons/a, decabromodiphenylether 7500 tons/a). Some years ago the use of pentabromodiphenylether as well as octabromodiphenylether was banned in the European Union. Concerning risk assessment, PDBEs were identified to carry unacceptable risks from use in polyurethane foams. Under the proposed Directive on Waste Electrical and Electronic Equipment, it is suggested that PDBEs should be substituted by other substances by 2008.

1.3 Phthalates

Di-(2-ethylhexyl)phthalate (DEHP) is one of the most important plastifiers especially used in PVC. DEHP can be found in all environmental compartments.

Di-(iso-nonyl)phthalate is an important substitute for DEHP. The production of Di-(iso-nonyl)phthalate in Europe was about 500.000 tons in 2005. Up to now only few data about Di-(iso-nonyl)phthalate are reported for environmental matrices.

1.4 VOCs

The following compounds were analysed: 1,2-dichloroethane, benzene, dichloromethane, trichloromethane, tetrachloroethylene, tetrachloromethane, trichloroethylene, trichlorobenzenes (all isomers)

Volatile organic compounds are used in industrial, commercial and domestic fields, and can enter a water body via waste water and may consequently contaminate drinking water. Furthermore, they may originate from the use of chlorine as an oxidizing agent in water and waste water treatment.

- 1,2-Dichloroethane is mainly used as a solvent and an intermediary in the production of vinylchloride,
- Dichloromethane and trichloromethane are important solvents used in various industries. Because of their toxic effects they are being replaced in most applications,
- Trichlorobenzenes are important intermediaries in chemical industrial processes,
- Benzene was widely used as a solvent in the past. Because of its high carcinogenicity, in several countries benzene has been banned for industrial use for many years. Benzene is an important component of the gasoline.
- Trichloroethylene is an effective industrial solvent for a variety of organic materials.
- Tetrachloroethylene is a manufactured chemical compound that is widely used for the dry cleaning of fabrics and for metal-degreasing. It is also used to make other chemicals and is used in some consumer products.
- Tetrachloromethane is a reagent in synthetic chemistry and was formerly widely used in fire extinguishers and as a precursor to refrigerants.
- Hexachlorobutadiene (HCBD) is mostly used as a solvent for longer-chain hydrocarbons and elastomers, as hydraulic fluid, as heat transfer liquid and insulating fluid, and as a chemical intermediary in the production of chlorofluorocarbons and lubricants. HCBD is mostly released as a by-product in the production of tetrachloroethylene. It could be found in the fly ash during refuse combustion. Due to its hydrophobic nature, HCBD will not remain in water for long periods and will partition into the atmosphere or be adsorbed to sediments. Its half-life in water

is proportional to organic matter and ranges from 4 to 52 weeks. It is expected that HCBd persists in sediments with high organic content. Sediment accumulation factors are estimated at 200-10 000. Its log K_{OC} of 4.9 leads to sorption to suspended particulates, which settle on bottom sediments. Although HCBd bioconcentrates in tissues of freshwater invertebrates and fish, it does not biomagnify to any appreciable extent, possibly because of its fast depuration rate.

1.5 Organochlorine compounds (OCDs)

The following organochlorine compounds from Annex X and IX WFD were analysed in water samples:

Chlorpyrifos, chlorfenvinfos, α -endosulfan, lindane (gamma-hexachloro-cyclohexane), hexachlorobenzene, pentachlorobenzene, trifluralin, DDT isomers, aldrine, endrine, dieldrine and isodrine.

The commercial use of the majority of these substances is banned for many years.

- Lindane, the gamma isomer of hexachlorocyclohexane (γ -HCH), is a synthetic organochlorine pesticide that has been used since the early 1950s as a treatment for the control of a variety of insects. Lindane enters aquatic systems mainly as surface runoff from treated lands, and deposition following volatilisation and aerial transport. Due to its affinity to organic materials, lindane in aquatic systems tends to become associated with particulate matter and accumulates in bed sediments. Due to its relatively high water solubility, however, lindane accumulates in bed sediments to a lesser extent than many other organochlorines. Because a wide variety of organisms live in bed sediments or are in contact with them, sediments act as an important route of exposure to aquatic organisms. Adverse biological effects of lindane include decreased benthic invertebrate diversity, reduced abundance, increased mortality, and behavioral changes.
- Hexachlorobenzene (HCB) is a selective fungicide. In many countries, its production and use as a fungicide were forbidden. At present, its main importance appears to be as a by-product of several chemical processes or an impurity in some pesticides. HCB is a widespread contaminant. It has very low solubility in water and a relatively low vapour pressure. The main chemical reaction in water is slow photolysis, whereas hydrolysis and oxidation appear to be unimportant. Biotransformation of HCB in surface water, sludge, or soil suspensions is extremely low because HCB is strongly adsorbed by soil and sediments. Because of its resistance to both abiotic and biotic degradation, and very high octanol-water partition coefficient, it can bioaccumulate in aquatic organisms.
- DDT (Dichlorodiphenyltrichloroethane) is a chlorinated hydrocarbon compound that exhibits broad-spectrum insecticidal properties. There are several possible configurations of the chlorine atoms on the DDT molecule, resulting in several isomeric forms: p,p'-DDT, o,p'-DDT, and m,p'-DDT. The general term "DDT" is applied to a variety of commercial pesticide formulations that consist predominantly of p,p'-DDT and o,p'-DDT, but may also contain minor amounts of dichloro-diphenyl-dichloroethylene (DDE) and dichlorodiphenyl-dichloroethane (DDD). In the present study, p,p'-DDT was measured as dominant and representative DDT compound. In general, DDTs are chemically stable under ambient environmental conditions. The physicochemical properties of these substances, such as low solubility in water and high solubility in lipids (i.e., high K_{OW}) and high K_{OC} , are such that DDT and its metabolites are preferentially incorporated into bed sediments and accumulate in biota. Benthic organisms may be exposed to both particulate and dissolved forms of DDTs in interstitial or overlying waters, as well as to sediment-bound DDTs through surface contact and ingestion of sediment during feeding. Sediments and porewater are believed to represent the primary routes of exposure for infaunal and epibenthic species. Several properties of DDTs influence their bioavailability to aquatic organisms. Hydrophobicity, as represented by the K_{OW} , and water solubility, have been identified as the two most important factors.

Accordingly, substances with high K_{ow} and low water solubilities are considered to be the most readily bioavailable to benthic organisms. Based on their physicochemical properties, p,p'-DDT and o,p'-DDT are likely to be the most readily bioavailable of the six isomers discussed in this fact sheet. Sediment characteristics, including TOC, particle size distribution, and clay content, may affect the bioavailability of DDTs in sediments.

- Chlorpyrifos is a toxic crystalline organophosphate insecticide that inhibits the enzyme acetylcholinesterase and is used to control insect pests. Chlorpyrifos is a broad-spectrum organophosphate insecticide. Chlorpyrifos is effective in controlling cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites, fire ants, and lice. It is used as an insecticide on grain, cotton, field, fruit, nut and vegetable crops, and well as on lawns and ornamental plants. It is also registered for direct use on sheep and turkeys, for horse site treatment, dog kennels, domestic dwellings, farm buildings, storage bins, and commercial establishments.
- Chlorfenvinfos is amber-colored liquid with a mild chemical odour. It is used for control of ticks, flies, lice, and mites on cattle and for blowfly, lice, ked, and itchmite on sheep. Chlorfenvinfos controls fleas and mites on dogs but not on cats. It is applied on organic wastes and breeding places of fly larvae and also used as a foliage insecticide for potatoes, rice, maize, and sugar cane. It can be used to control soil insects. (EPA, 1998)
- Endosulfan is a neurotoxic organochlorine insecticide of the cyclodiene family of pesticides. It is highly toxic and an endocrine disruptor, and it is banned in the European Union and several other countries. It is still used extensively in many countries. Because of its high toxicity and high potential for bioaccumulation and environmental contamination, a global ban on the use and manufacture of endosulfan is being considered under the Stockholm Convention on Persistent Organic Pollutants (POP)..
- Trifluralin is used on winter wheat and barley, set-aside (arable land temporarily taken out of cultivation), oil-seed rape, brassicas, carrots, lettuce, sugar beet, and beans. It is also applied to outdoor bulbs and flowers, fodder crops, glasshouse crops, Christmas trees, herbaceous plants, soft fruit and vegetables. In other countries it is used on cotton, soybean, sunflower, canola, turf, alfalfa, tomatoes and vines. Trifluralin is almost exclusively a single-application, ground-applied or soil-incorporated treatment.
- Aldrin and dieldrin are insecticides with similar chemical structures. They are discussed together in this fact sheet because aldrin quickly breaks down to dieldrin in the body and in the environment. Exposure to aldrin and dieldrin happens mostly from eating contaminated foods, such as root crops, fish, or seafood. Aldrin and dieldrin build up in the body after years of exposure and can affect the nervous system.
- Isodrin is a stereoisomer of aldrin
- Endrin is a solid, white, almost odorless substance that was used as a pesticide to control insects, rodents, and birds. Exposure to endrin can cause various harmful effects including death and severe central nervous system injury.
- Pentachlorophenol (PCP) has been used as bactericide and fungicide with a variety of applications, e.g. as wood preservative. Since 1987, it is banned in Germany and in recent years, most developed countries have restricted the use of PCP, especially for agricultural and domestic applications.

HCB, DDT, aldrin, dieldrin and endrin are banned worldwide according to the Stockholm Convention on Persistent Organic Pollutants (POP).

1.6 Organotin compounds

Tributyltin (TBT) was mainly used in antifouling paints (especially on vessels) and as antifouling agent in connection with different materials (e.g. paper). TBT is classified as a compound with

endocrine disruptin potential (category I). As it is banned in the EU concentrations in the environment should decrease in time.

1.7 Polar pesticides

The “polar” pesticides alachlor, isoproturon, diuron, atrazin and simazin are listed as priority substances in Annex X of WFD. The use of atrazine is banned in the EU because of widespread residues in groundwaters after intensive use for decades. Isoproturon is one of the most-used herbicides for growing crops.

Together with these five pesticides, other substances like terbutylazin, desethylterbutylazin, bentazone, desethylatrazin, 2,4-D and mecoprop were also analysed by the LC-MS/MS-method used.

1.8 Additional organic compounds

1.8.1 Polychlorinated biphenyls (PCB)

Polychlorinated biphenyls (PCB) were widely used technical mixtures of biphenyls with variable chlorine content. They were used e.g. as transformer oils, hydraulic oils in minery, plastifier etc. Its use is banned in the European Union because of the extreme stability in the environment. Traces of PCB can be found nearly everywhere in the aquatic system.

1.8.2 HHCB (Galaxolide®)

HHCB (Galaxolide®) is a polycyclic musk compound which is predominantly used in personal care products. As it cannot be eliminated completely in waste water treatment plants, HHCB reaches the surface waters continuously. It is mostly adsorbed to suspended particulate matter and sediments and may be accumulated in biota.

1.8.3 Triclosan and methyl-triclosan

Triclosan is a widely used biocide (e.g. in toothpastes and other personal care products). It is readily degraded (>90%) in standard waste water treatment plants. Triclosan is further degraded in river waters. During waste water transportation and treatment methylation occurs and the more stable metabolite methyl-triclosan is formed. Methyl-triclosan is stable in surface waters and shows accumulation on suspended particulate matter/sediments and in biota.

2 Results

2.1 Alkylphenols and alkylphenol ethoxylates in water, suspended particulate matter and sediments

2.1.1 Alkylphenols in water

During JDS 2 octylphenol (OP) and nonylphenol (NP) were analysed in whole water samples for the first time. The limits of quantification were well below the WFD environmental quality standards.

OP was found at only three sampling sites in concentrations above the limit of quantification (5 ng/l, see table 2.1-1). The WFD EQS of 0,1 µg/l is not exceeded.

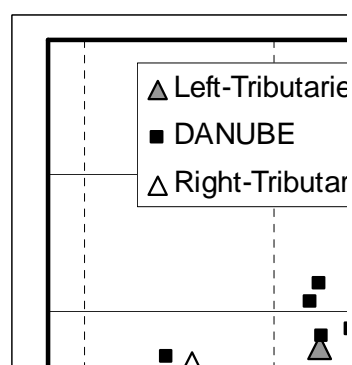
On the other hand NP was found in all water samples and concentrations up to 3280 ng/l (sampling site JDS AR2). The highest concentration in the Danube was measured at sampling station JDS 47 (downstream Novi-Sad, 141 ng/l). The WFD EQS is exceeded at that three sampling station where also OP is found (tributaries Arges and Russenski Lom).

NP and OP concentration show that Arges and Russenski Lom are the tributaries with the most serious organic pollution caused by direct discharge of untreated or inadequately treated wastewater from industry and municipalities.

Table 2.1-1: Sampling Stations with the highest concentration of alkylphenols

| determinand | JDS 2 code | sampling station | concentration (ng/l) | WFD EQS (ng/l) |
|-------------|------------|-----------------------------------|----------------------|----------------|
| octylphenol | JDS AR2 | Arges – downstream Bucharest | 22 | 100 |
| | JDS84 | /Arges – above confluence | 11 | 100 |
| | JDS81 | /Russenski Lom – above confluence | 5 | 100 |
| nonylphenol | JDS AR2 | Arges – downstream Bucharest | 3280 | 330 |
| | JDS84 | /Arges – above confluence | 1380 | 330 |
| | JDS81 | /Russenski Lom – above confluence | 418 | 330 |

Figure 2.1-1 Nonylphenols in water samples



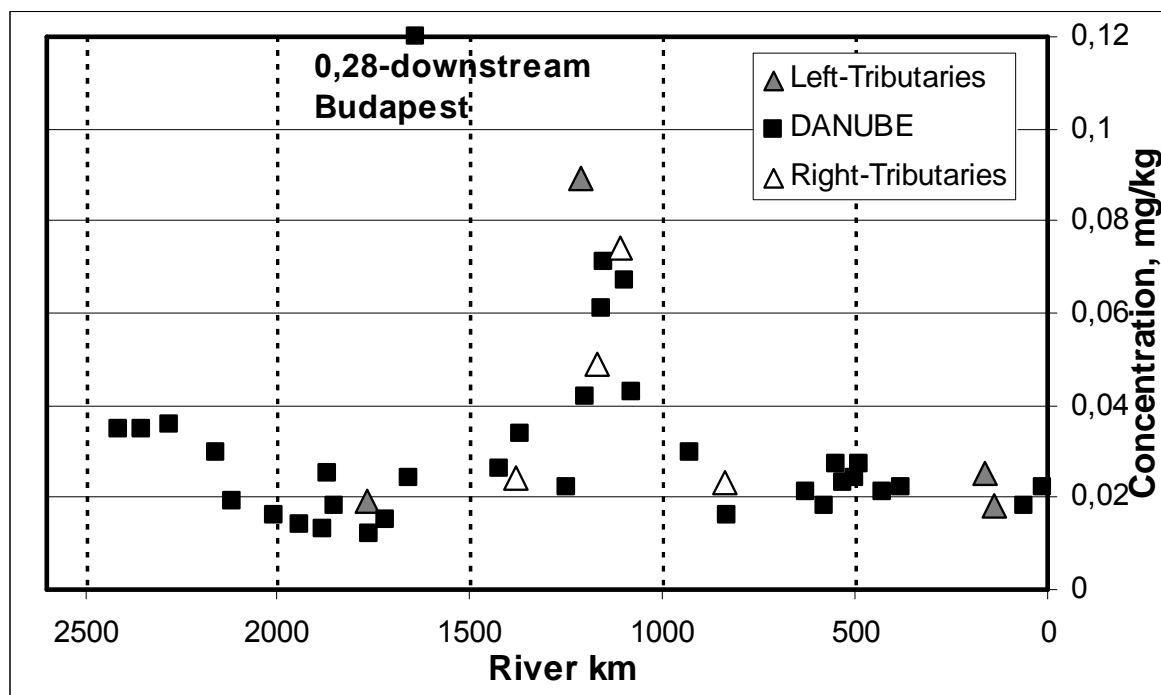
2.1.2 Alkylphenols in suspended particulate matter

NP and OP in suspended particulate matter were analysed by LfU Munich (all available samples) and University of Vienna (21 selected samples).

4-iso-Nonylphenol can be found all along the Danube. Sewage treatment plants are the main point sources for this compound. The highest value (0,280 mg/kg dry matter) is found downstream Budapest where the main sewage plant is still under construction.

The impact of the Budapest sewage can be seen for more than 200 kilometres. Also Tisza (89 mg/kg dry matter) and Velika Morava (74 mg/kg dry matter) are obviously receiving untreated or insufficiently treated sewage. In the upper part and the lower part of the Danube NP concentrations always are under 0,05 mg/kg dry matter with small variations.

Figure 2.1-2 Nonylphenol in suspended particulate matter



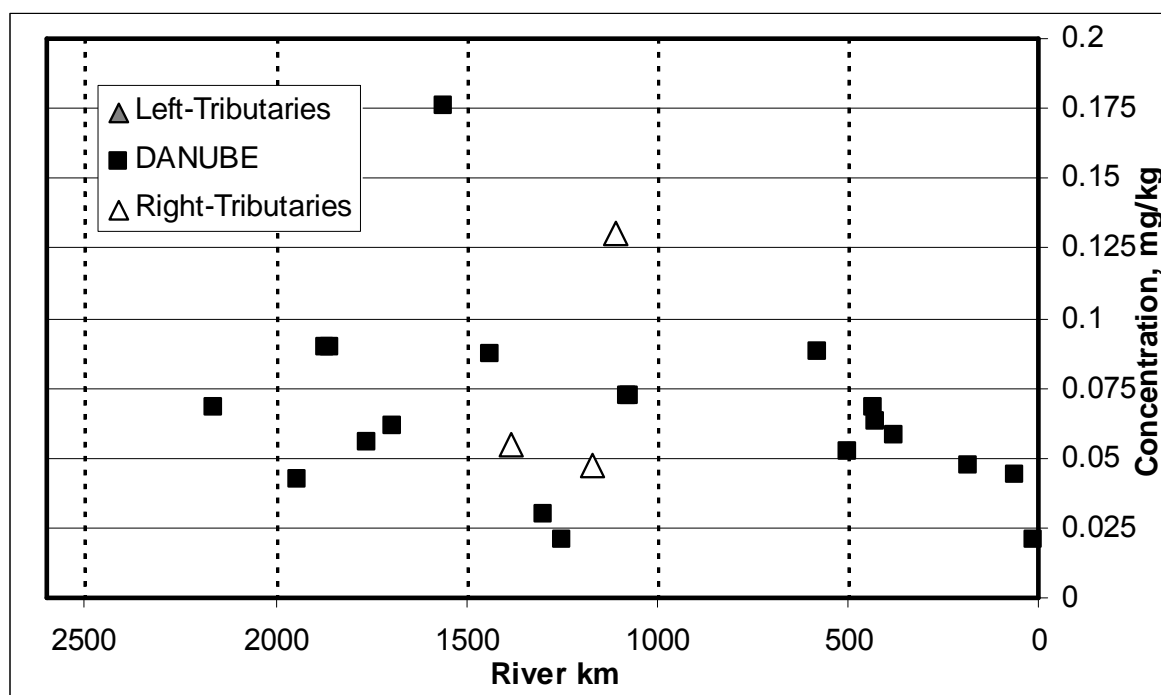
During Aquaterra Survey concentrations in all samples were <0,01 mg/kg dry matter whereas during JDS 2 all samples showed concentrations above 0,01 mg/kg dry matter. This discrepancy should be followed and cleared.

Remark: Analysis of NP in suspended particulate matter from sampling station JDS 7 (Danube/Jochenstein) done from 2002-2007 by LfU Munich (2 samples from each year gathered with a high performance centrifuge) showed NP concentrations > 0,01 mg/kg dry matter with a median value of 0,026 mg/kg dry matter. Taking into account these values and JDS 2 results the Aquaterra Survey results for NP in suspended particulate matter are not reliable.

No EQS was defined for NP in suspended particulate matter or sediments.

NP and OP were also analysed by University of Vienna at 21 selected sampling sites (figure 2.1-3).

Figure 2.1-3 Longitudinal variations in NPs concentrations in SPM at the selected 23 JDS 2 stations (University of Vienna)



Comparing the analytical results from LfU Munich and University of Vienna about 2/3 of the overlapping samples showed significant differences of more than 35%. These differences might be explained by the analytical methods used (see figure 2.1-4). As there is no standard for the analyses of NP and OP in suspended particulate matter different solvents and extraction techniques were used in the laboratories.

Figure 2.1-4 Nonylphenol in suspended particulate matter: comparison of samples analysed by LfU/Munich and University of Vienna

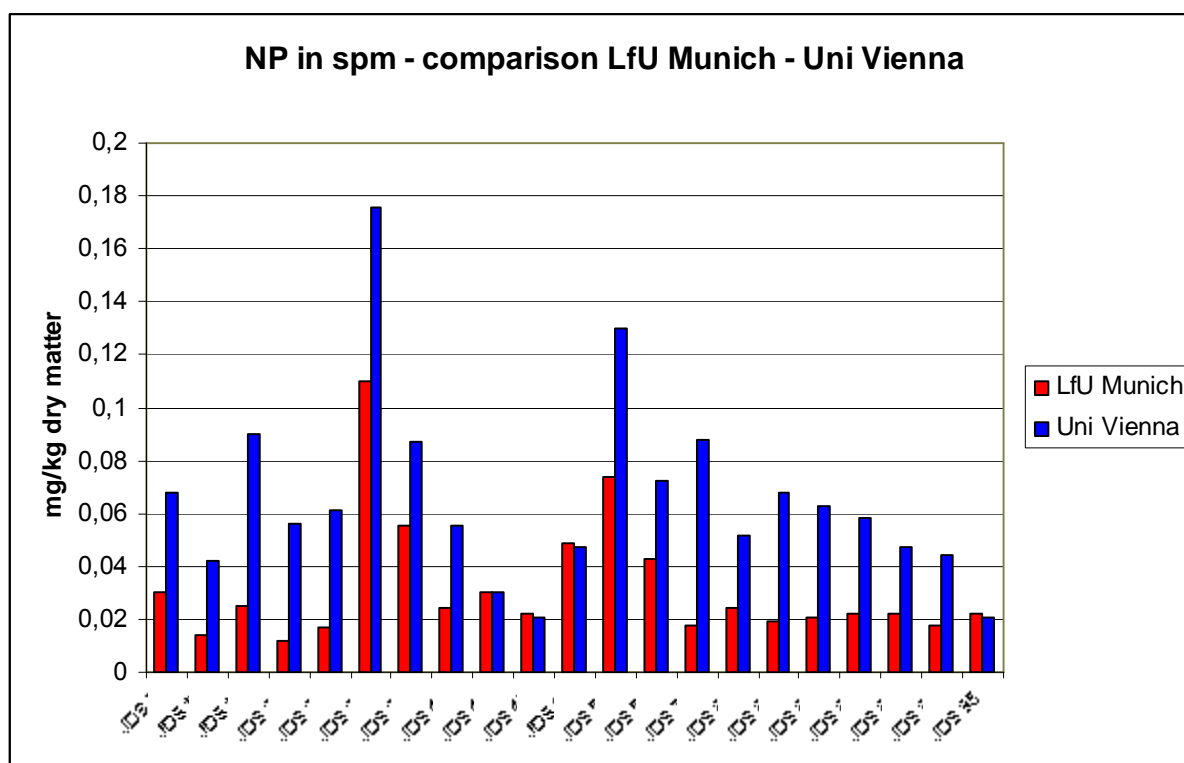


Figure 2.1-5 Nonylphenol in suspended particulate matter: comparison of 39 sampling sites analysed during JDS 1 (2001) and JDS 2 (2007)

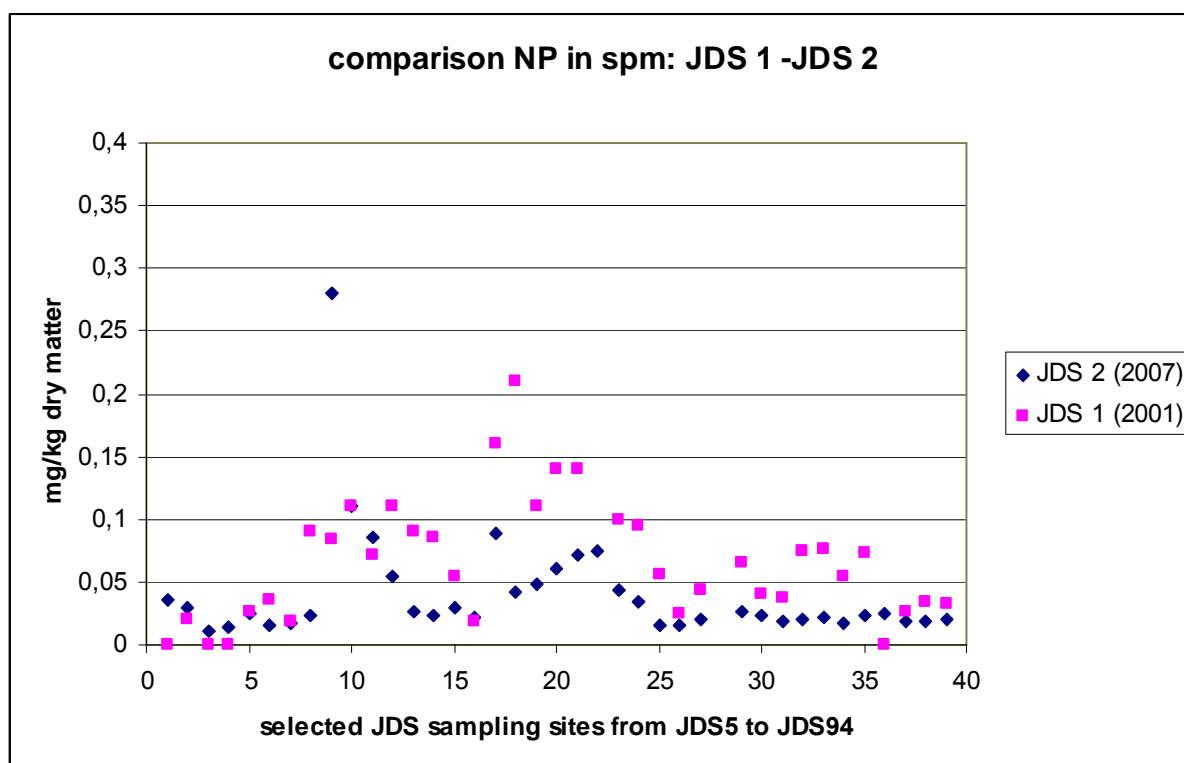


Figure 2.1-5 shows a comparison of NP-concentrations of 39 sampling sites sampled during JDS 1 (2001) and JDS 2 (2007). As the sampling sites represent a certain stretch of the Danube where sampling was done during the movement of the ships the results are not perfectly comparable. In general the concentrations of NP 2007 were slightly lower than during JDS 1 in 2001. These

differences might be explained by the use of different methods by the labs (2001: TZW/Karlsruhe; 2007: LfU/Munich). The distribution of the values along the Danube is similar.

For p-tert-octylphenol (OP) only 17 out of 60 samples of suspended particulate matter showed positive results. The highest concentrations were found downstream Budapest with a maximum value of 0,043 mg/kg dry matter at the station Baja. The concentration of OP is more or less correlated to the concentration of NP indicating the use of mixed tensides. The concentration of OP usually is 2-10 times smaller than the concentration of NP. The ratio NP/OP from 2:1 to 10:1 fits to the production rate NPEOs/OPEOs of 8:2.

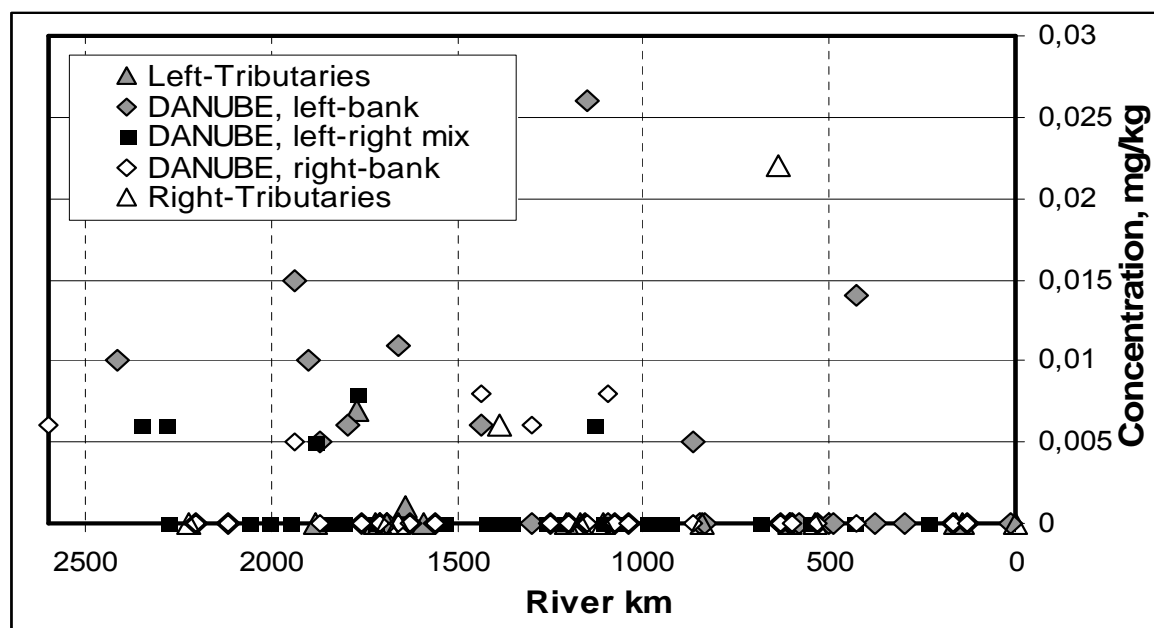
During Aquaterra Survey all samples showed OP concentrations <0,01 mg/kg dry matter including the sampling site downstream Budapest where now during JDS 2 higher OP-concentrations were found. This discrepancy should be followed and cleared.

2.1.3 Alkylphenols in sediments

135 sediment samples from river Danube and its major tributaries were analysed during JDS2 for tert.-octylphenol and iso-nonylphenol (laboratory: TZW Karlsruhe).

OP was only found in 20% of the sediment samples under investigation with a maximum concentration of 0.026 mg/kg dry weight. Positive findings of OP are arbitrarily distributed along the course of river Danube and no hot-spot can be identified. During JDS1, OP was detected in Danube sediments at concentration levels between <0.005 mg/kg and 1.8 mg/kg, whereby levels above 0.1 mg/kg dry weight were only rarely found and most of the elevated concentrations occurred in sediments from lower Danube. Thus, the results of JDS2 (see Figure 2.1-6) indicate a reduction in OP levels of Danube sediments during the recent years. For a statistically sound evaluation of current OP contaminations, however, this data base is not sufficient.

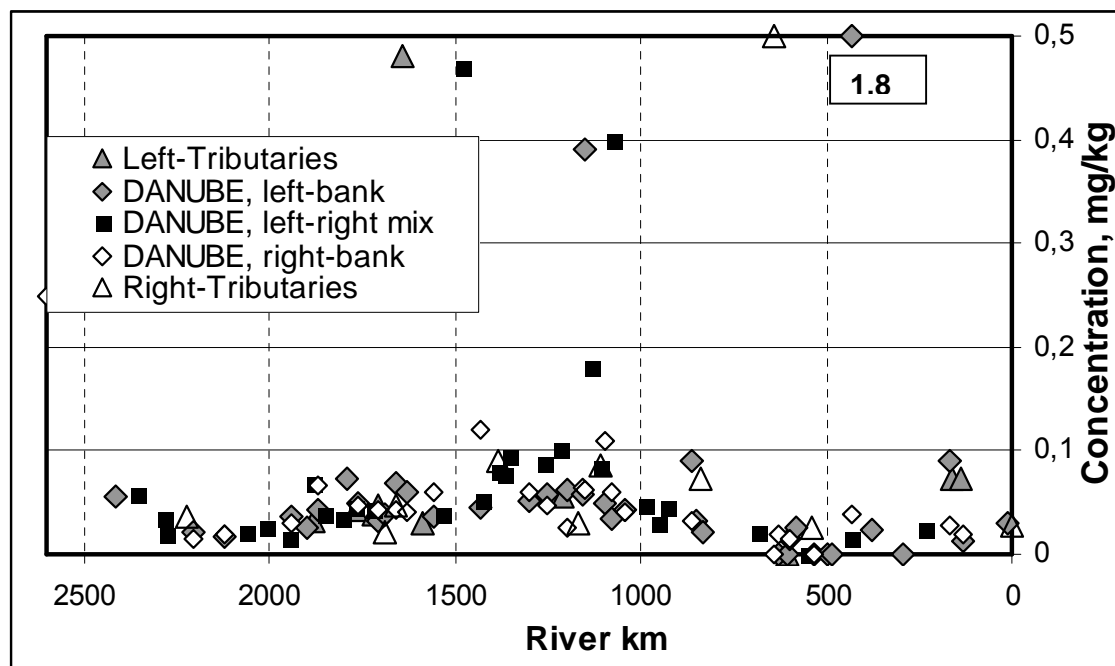
Figure 2.1-6 Occurrence of OP in sediments of the Danube and its major tributaries



In contrast to OP, NP could be detected in almost all sediment samples under investigation. Median and maximum concentration of NP were much higher than for OP, being 0.039 mg/kg dry weight and 1.8 mg/kg dry weight, respectively. Figure 2 gives an overview on the NP concentrations found in the

Danube sediments and its major tributaries during JDS2. It can be seen that for most of the sediment samples, NP concentrations are in the range of 0.01 to 0.1 mg/kg dry weight, and only for few samples higher NP levels were observed. The maximum concentration of NP which was 1.8 mg/kg dry weight was found for the sample JDS 85 which was taken at river km 429 (Oltenita, downstream of Arges in Romania).

Figure 2.1-7 Occurrence of NP in sediments of the Danube and its major tributaries



During JDS1, highest NP levels in sediments were found at river km 432, and thus the latest results are in good accordance with the previous findings. The results from JDS2 indicate that sediment contamination with NP has decreased during the last years. As for OP, this effect is also for NP most pronounced in the lower part of river Danube.

The University of Vienna analysed sediments from 23 selected sampling sites. For 7 sampling sites bottom sediments from the left and right river banks were mixed before analyses. For 16 sampling sites the sediment samples from left and/or right bank were analysed separately.

OP is found in 1/3 of the sediment samples in low concentrations, with the maximum concentration of 0,036 mg/kg dry matter at the same location where the maximum OP level was reported by TZW/Karlsruhe. NP was found in 24 out of 29 samples in the concentration range from <LOQ – 2,83 mg/kg dry matter (JDS 85, downstream Arges, left bank of the Danube – similar to the JDS 1 findings). Concentrations and distribution of NP and OP, as well as the sampling sites showing the highest concentrations, are in good agreement between the laboratories of University of Vienna and TZW/Karlsruhe.

The distribution of NP at the selected sampling sites analysed by University of Vienna is shown in figure 2.1-8, the distribution of OP in figure 2.1-9.

Figure 2.1-8 Longitudinal variations of NP-concentrations in bottom sediments at 23 selected JDS2 stations

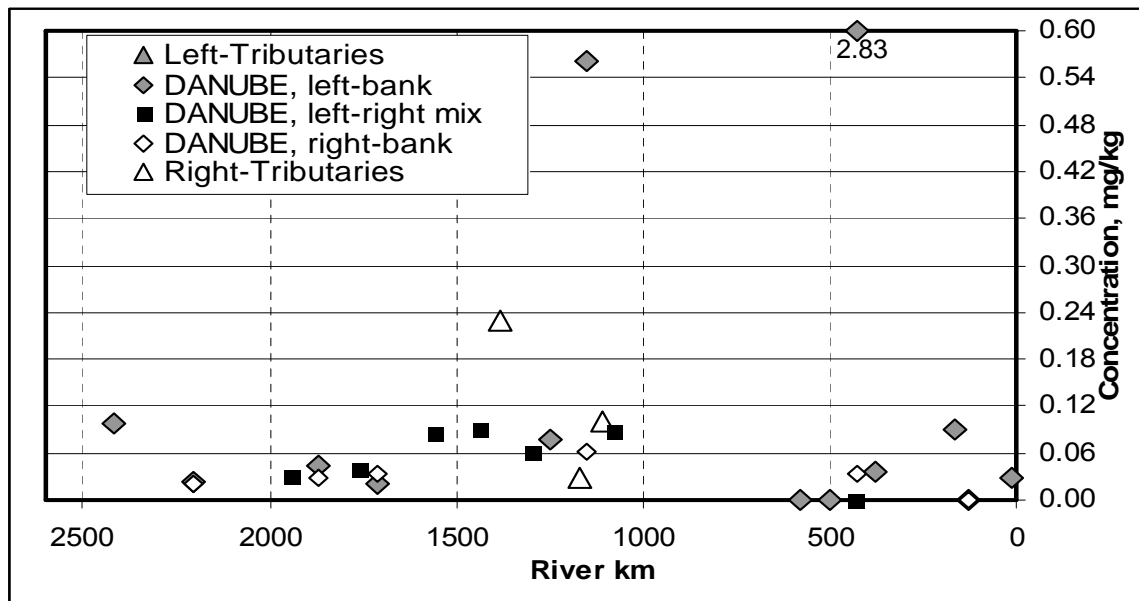
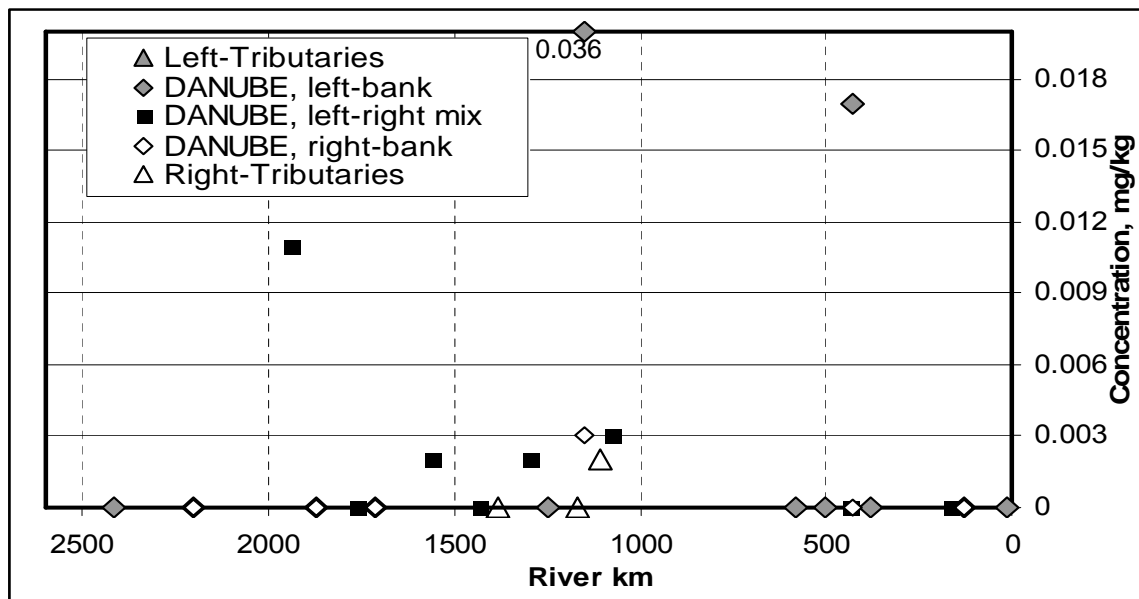


Figure 2.1-9 Longitudinal variations of OP-concentrations in bottom sediments at 23 selected JDS2 stations



The Aquaterra Survey reported that the occurrence of nonylphenol was occasional and random not exceeding 0,06 mg/kg dry matter and that octylphenol results were below the detection limit. Taking into account that NP was found in sediment samples in concentrations above 0,06 mg/kg dry matter by both laboratories involved, this discrepancy should be followed and clarified.

2.1.4 Alkylphenoethoxylates in suspended particulate matter and sediments

NP1EOs are found in sediments within the concentration range of 0.021 – 2.096 mg/kg while NP2EO ranged from 0.024 – 0.280 mg/kg (Figure 2.1-10). The highest values have been found in the sample from the left river bank downstream Arges where also the highest NP concentrations was found (2,83 mg/kg dry matter). Therefore it can be assumed that the alkylphenol pollution enters the Danube through the river Arges. Concentrations higher than 0.040 mg/kg are mostly found in the middle part of the Danube (rkm 1500-1000) at the locations of high NP concentrations.

In the suspended particulate matter samples NP1EOs were found in the range from 0.020 to 0.125 mg/kg dry matter. NP2EOs were mostly found at concentration below 0.035 mg/kg dry matter and at only few sampling sites at concentrations from 0.040 – 0.099 mg/kg dry matter. The highest NP1EOs and NP2EOs concentrations were found at the Dunaföldvár (1560 river km) where the highest NP concentration was also found (Figure 2.1-10).

Figure 2.1-10 Longitudinal variations of NP1EOs concentrations in bottom sediments at the selected JDS 2 stations

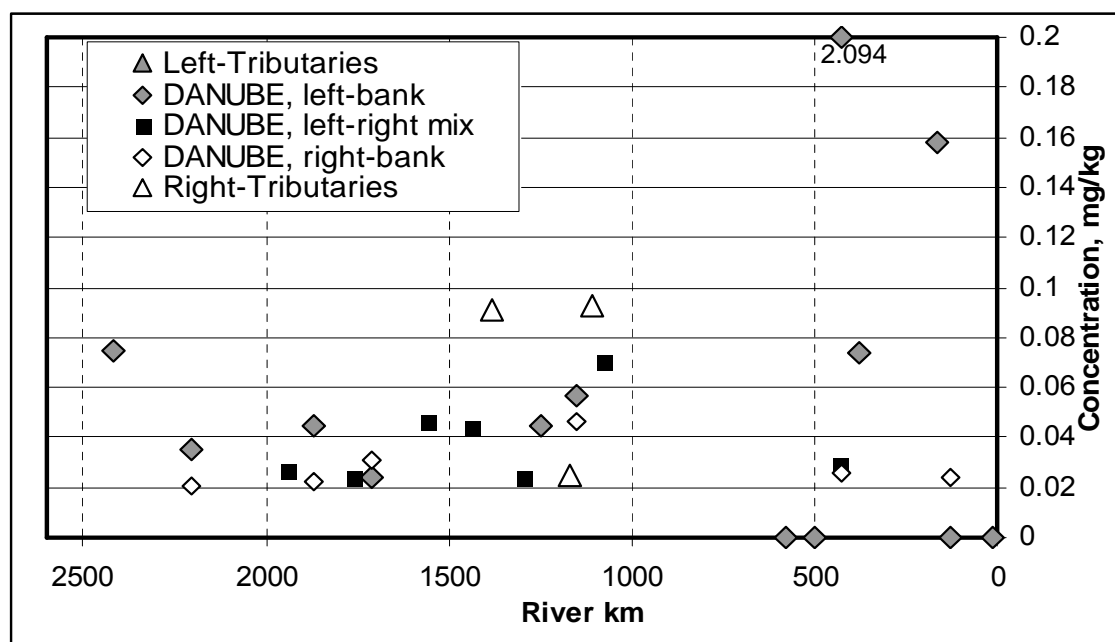


Figure 2.1-11 Longitudinal variations of NP2EOs concentrations in bottom sediments at the selected JDS 2 stations

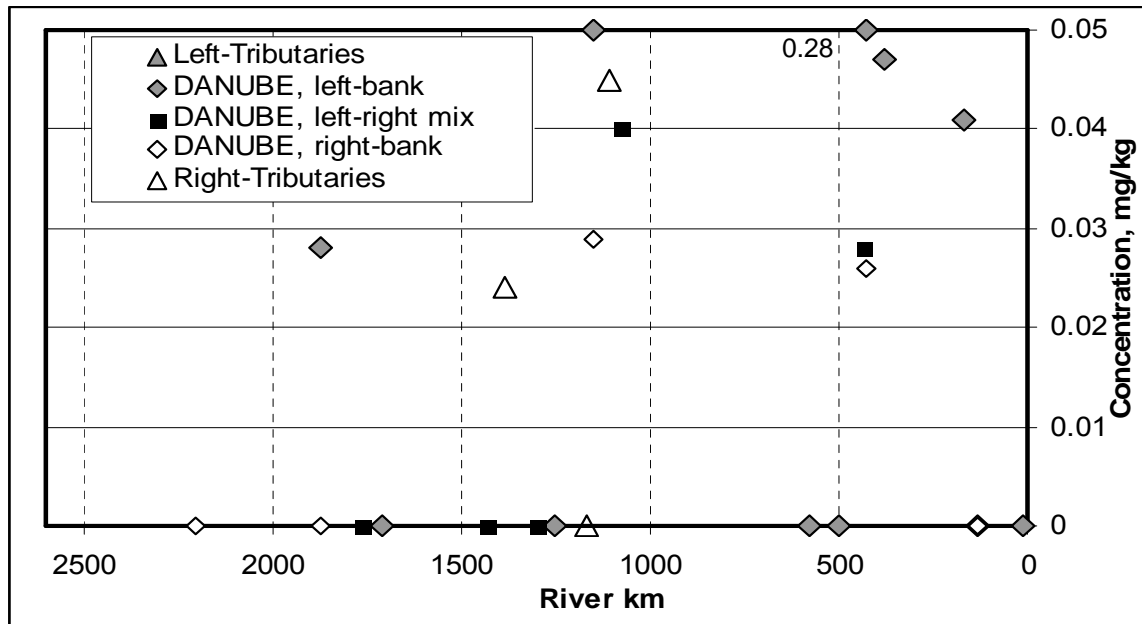


Figure 2.1-12 Longitudinal variations of NP1EOs concentrations in suspended particulate matter at the selected 23 JDS 2 stations

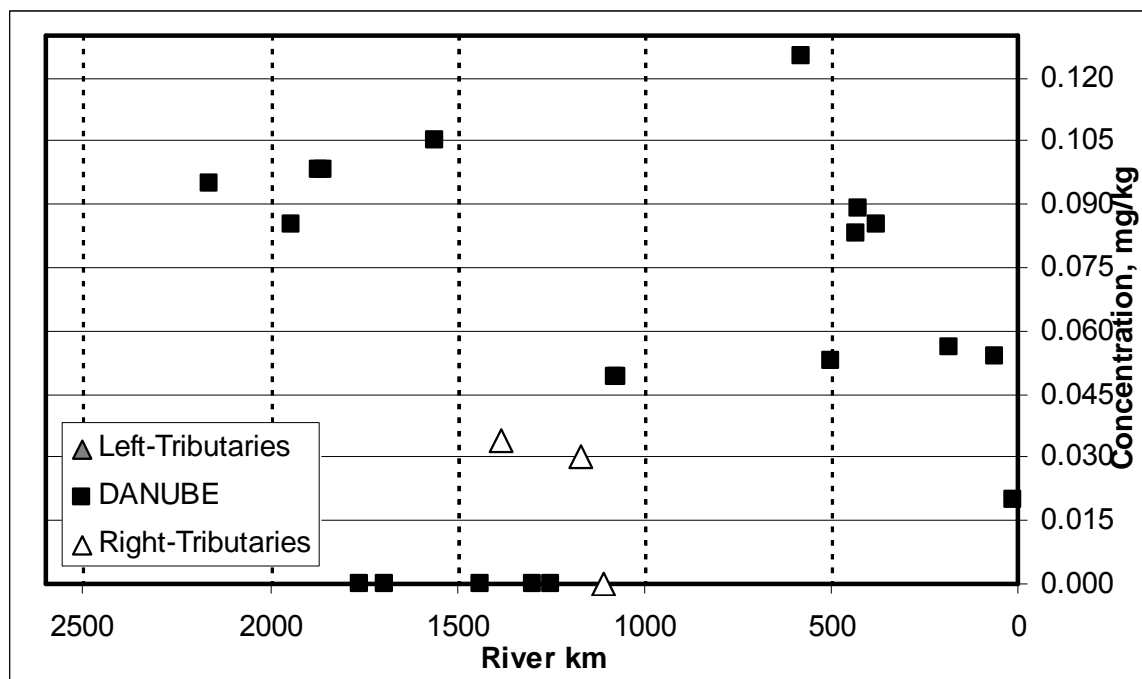
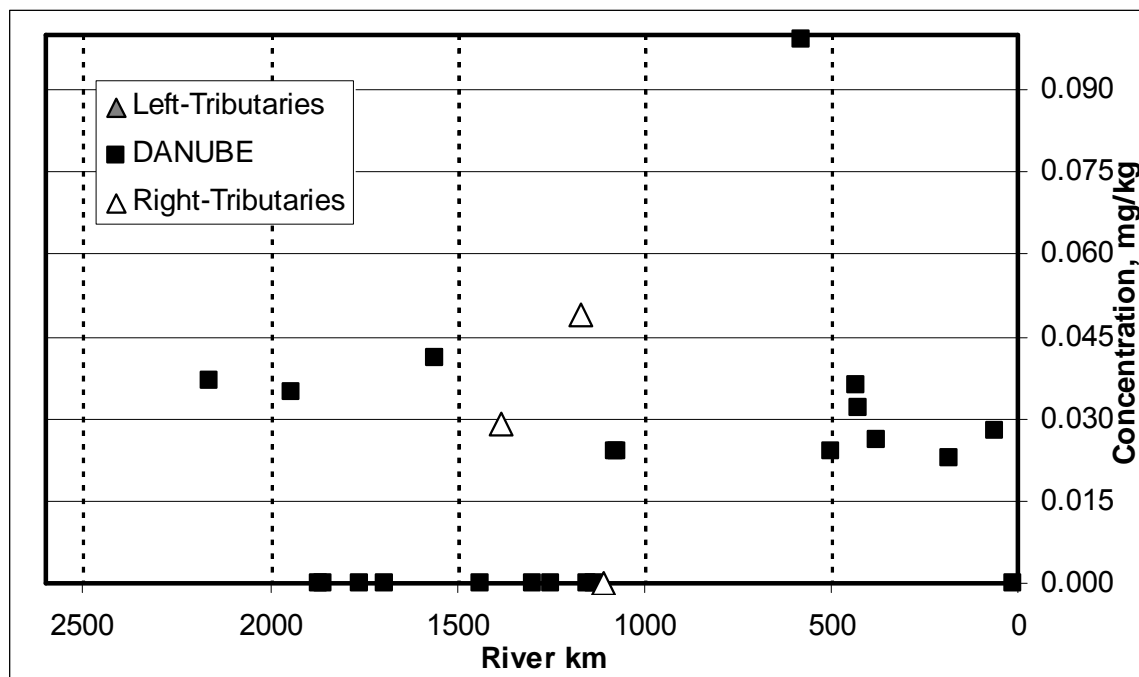


Figure 2.1-13 Longitudinal variations of NP2EOs concentrations in suspended particulate matter at the selected 23 JDS 2 stations



OP1EO and OP2EO in the bottom sediments investigated were only found at one of the selected sampling sites at the left river bank downstream the River Arges (JDS 85). OP1EO was detected at a concentration of 0.005 mg/kg dry matter and OP2EO at a concentration of 0.007 mg/kg on the same sampling site.

In none of the investigated suspended particulate matter samples OP1EO and OP2EO were found.

2.2 Polybrominated diphenylethers (PBDEs)

2.2.1 Polybrominated diphenylethers in water

Polybrominated diphenylethers are persistent, they show a low water solubility but a high binding affinity to particles and a distinct tendency to accumulate in sediments. Because of their very low solubility in water there is only few information about the concentration of PBDEs in water. In literature sums of PBDEs in water samples range from 3 to 153 pg/l.

In this investigation 8 different PBDE-congeners were analysed. The limits of quantification for JDS2-samples were 0,002 µg/l (BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183) and 0,005 µg/l (BDE 203, BDE 205).

PBDEs were not found in amounts above the limit of quantification in any water sample. In several samples PBDEs were measured in concentrations between LOQ and LOD. Pentabromodiphenylether (BDE 99) was detected in four water samples from tributaries and two samples from the Danube.

Table 2.2-1 PBDE-results in water samples (* = concentrations between LOD and LOQ)

| JDS 2 | Sampling | BDE47 | BDE100 | BDE99 | BDE154 | BDE153 | BDE183 | BDE203 | BDE205 |
|-------|----------|-------|--------|-------|--------|--------|--------|--------|--------|
|-------|----------|-------|--------|-------|--------|--------|--------|--------|--------|

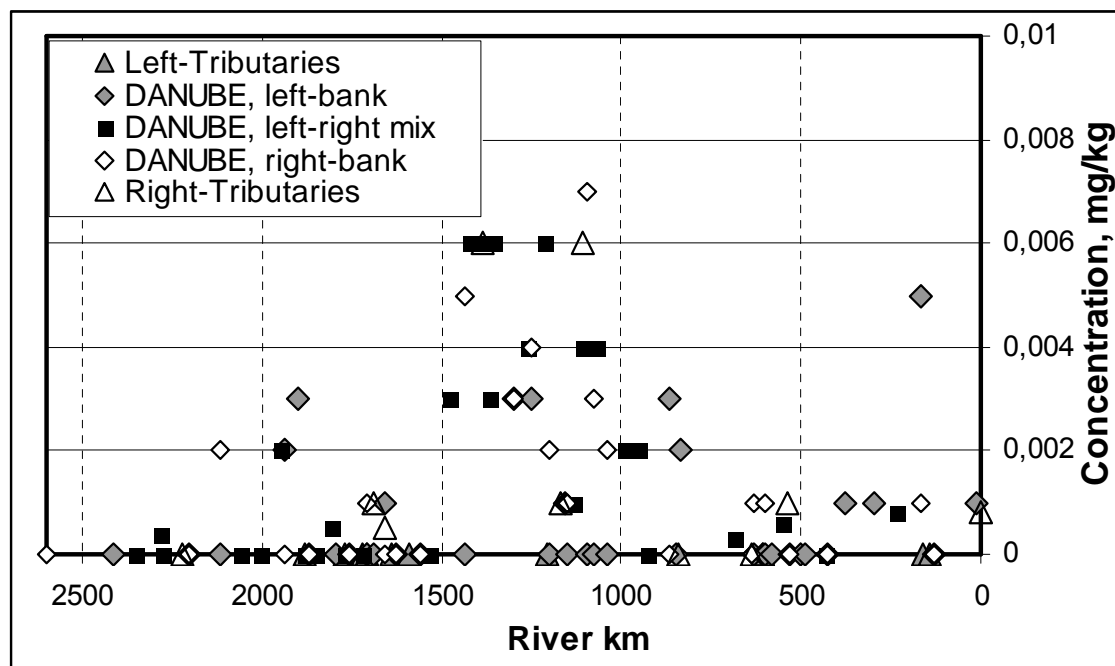
| Code | Station | ng/l | ng/l | ng/l | ng/l | ng/l | ng/l | ng/l | ng/l |
|--------------|-------------------------|-----------|------|-----------|------|------|------|-----------|------|
| JDS - 54 | Grocka | 0 | 0 | 0 | 0 | 0 | 0 | detected* | 0 |
| JDS - 82 - M | Downstream Ruse/Giurgiu | 0 | 0 | detected* | 0 | 0 | 0 | 0 | 0 |
| JDS - 84 - M | /Arges | 0 | 0 | detected* | 0 | 0 | 0 | 0 | 0 |
| JDS - AR - 2 | Upstream Bucharest | 0 | 0 | detected* | 0 | 0 | 0 | 0 | 0 |
| JDS - RL - 1 | Basarbovo | 0 | 0 | detected* | 0 | 0 | 0 | 0 | 0 |
| JDS - 91 - M | /Prut | detected* | 0 | detected* | 0 | 0 | 0 | 0 | 0 |

During JDS 1 neither the bottom sediment nor the suspended particulate matter samples contained PBDEs in concentration above the limits of detection. Water samples in JDS 1 were not analysed.

2.2.2 Polybrominated diphenylethers in sediments

From the list of target PBDEs, only BDE-209, i.e. decabromodiphenyl ether, turned out to be relevant for contamination of river Danube sediments. Besides BDE-209, BDE-99 and BDE-100 were found in one sediment sample (JDS29, i.e. river Danube upstream of Budapest) at a concentration close to the LOQ, whereas all other PBDEs under investigation couldn't be detected at all. During JDS1, only the pentabrominated diphenyl ethers which are listed in Annex 10 of the WFD have been analysed. These compounds were not detected during both surveys, indicating that they have low relevance for sediments contamination of river Danube.

Figure 2.2-1 Occurrence of BDE-209 in sediments of river Danube and its major tributaries



The results for BDE-209 in sediments from river Danube are summarized in Figure 2.2-1. It can be seen that for most of the samples 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 for a sediment sample from the tributary Velika Morava (sampling location: Varvarin). As these results seem to be the first data on sediment contamination in river Danube with BDE-209, no comparison with former data is feasible.

2.3 Phthalates

2.3.1 Di-(2-ethylhexyl)phthalate (DEHP)

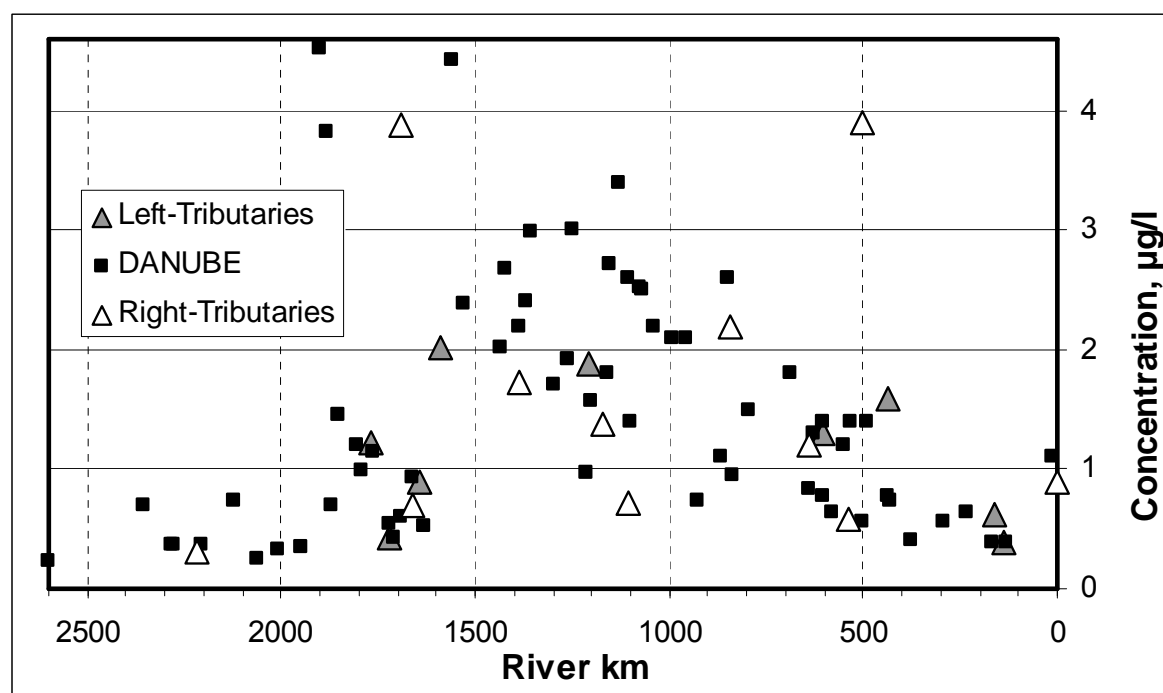
2.3.1.1 Di-(2-ethylhexyl)phthalate in water

It is well known, that Di-(2-ethylhexyl)phthalate (DEHP) is used worldwide in huge quantities and that it can be found in high concentrations in different environmental samples (soil, sewage sludge, water, biota). Because of its ubiquitous presence in plastics blanks are a serious problem in analytical laboratories. For this reason a limit of quantification of $0,30$ mg/kg dry matter was achieved for suspended particulate matter and $0,2$ µg/l for whole water samples.

In all water samples – except of 4 samples from the upper reach of the Danube – DEHP was detected. The highest concentration were found at JDS13 (Wildungsmauer, $4,53$ µg/l) and JDS35 (Dunavoldfar, $4,42$ µg/l). Relatively higher concentrations of DEHP were detected in the middle stretch of the Danube whereas the concentrations in the upper part and the lower part are <1 µg/l.

Water concentrations for DEHP at single sampling sites do not really correspond to the data in suspended particulate matter which might be explained by sampling suspended particulate matter during hours over a certain distance of the river.

Figure 2.3-1 DEHP concentrations in water

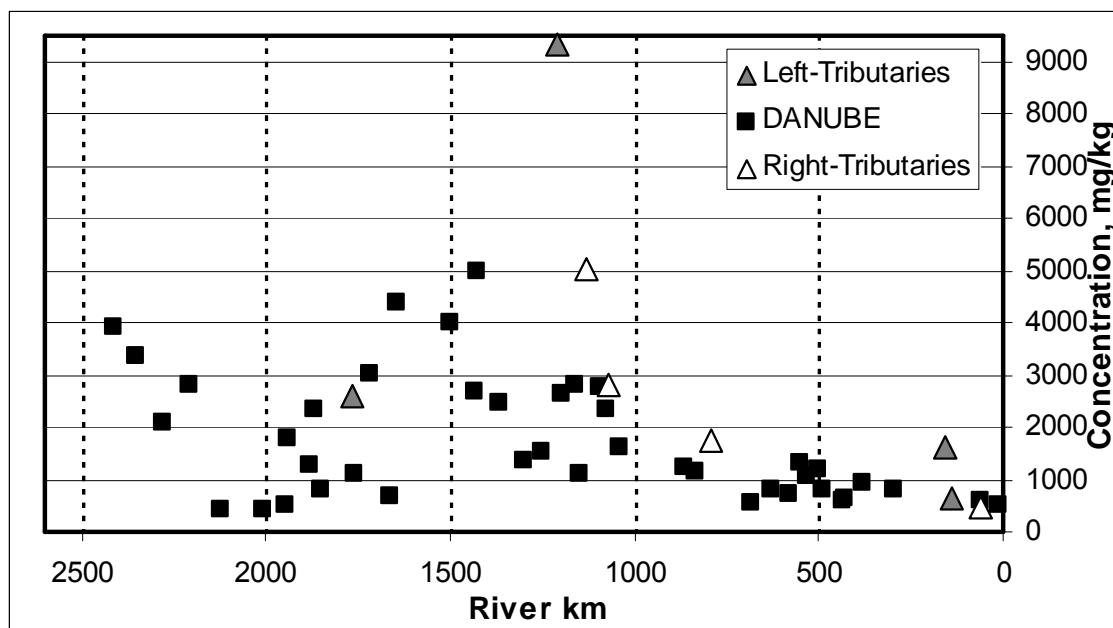


2.3.1.2 Di-(2-ethylhexyl)phthalate in suspended particulate matter

In all JDS 2 samples DEHP can be found in concentrations $>0,30$ mg/kg dry matter. The highest value is almost 10 mg/kg dry matter at the Tisza sampling station (JDS49). Also Sava showing a DEHP-concentration of 5,03 mg/kg dry matter contributes an important load to the Danube.

High concentrations are found in the German stretch of the Danube and again in the middle section of the Danube. The huge difference in concentrations regarding upstream and downstream Budapest hints at insufficient treated sewage and industrial activities as the main source.

Figure 2.3-2 DEHP concentrations in suspended particulate matter



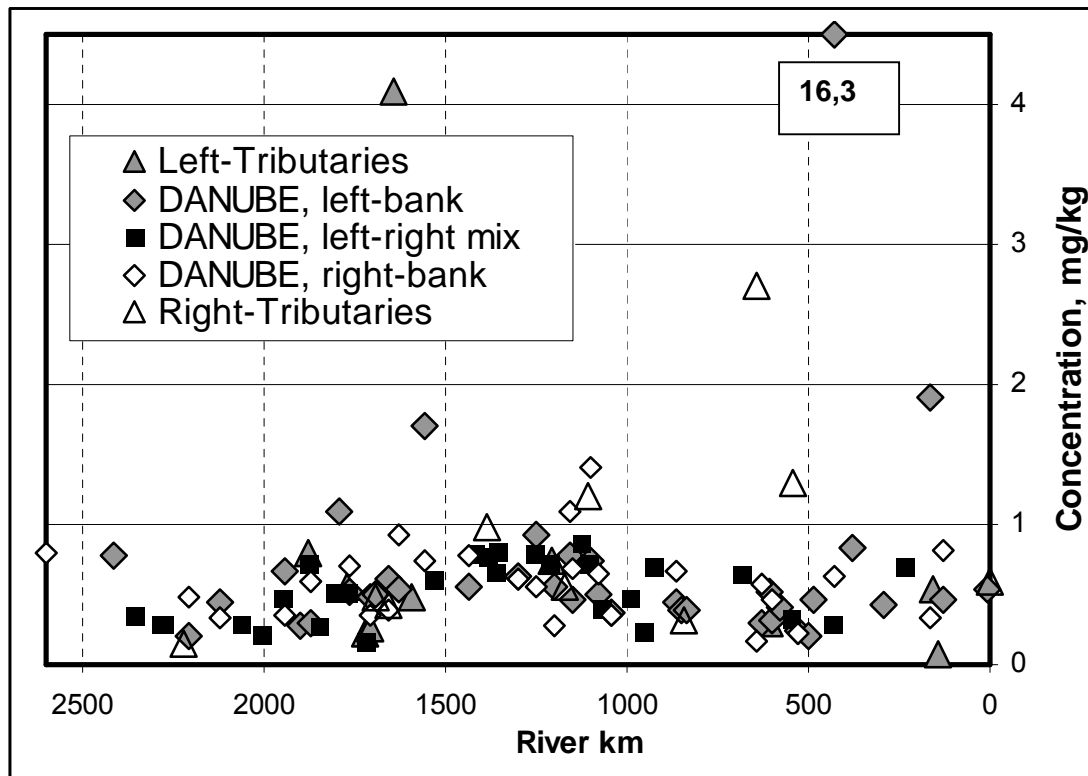
JDS 2 (21 samples > 2 mg/kg dry matter) generally showed higher concentrations of DEHP than JDS 1 (3 samples > 2 mg/kg dry matter) and Aquaterra Survey. In comparison to JDS 1 more sampling stations with relevant concentrations were now found in the middle stretch of the Danube.

2.3.1.3 Di-(2-ethylhexyl)phthalate in sediments

During JDS2, DEHP was found in all samples under investigation, indicating the ubiquitous occurrence of phthalates and underlining the relevance of DEHP as priority substance for sediment contamination in river Danube. 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, as the data in Figure 2.3-3 show, no clear trend in DEHP contamination along the course of river Danube can be identified. Maximum DEHP levels of more than 16 mg/kg dry matter were found for sample JDS85 (downstream Arges), 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 again was found in a sediment sample from river km 429. Thus, as for NP a good correlation between the results of JDS1 and JDS2 can be observed. The levels of contamination, however, seem to have significantly decreased.

Figure 2.3-3 Occurrence of DEHP in sediment

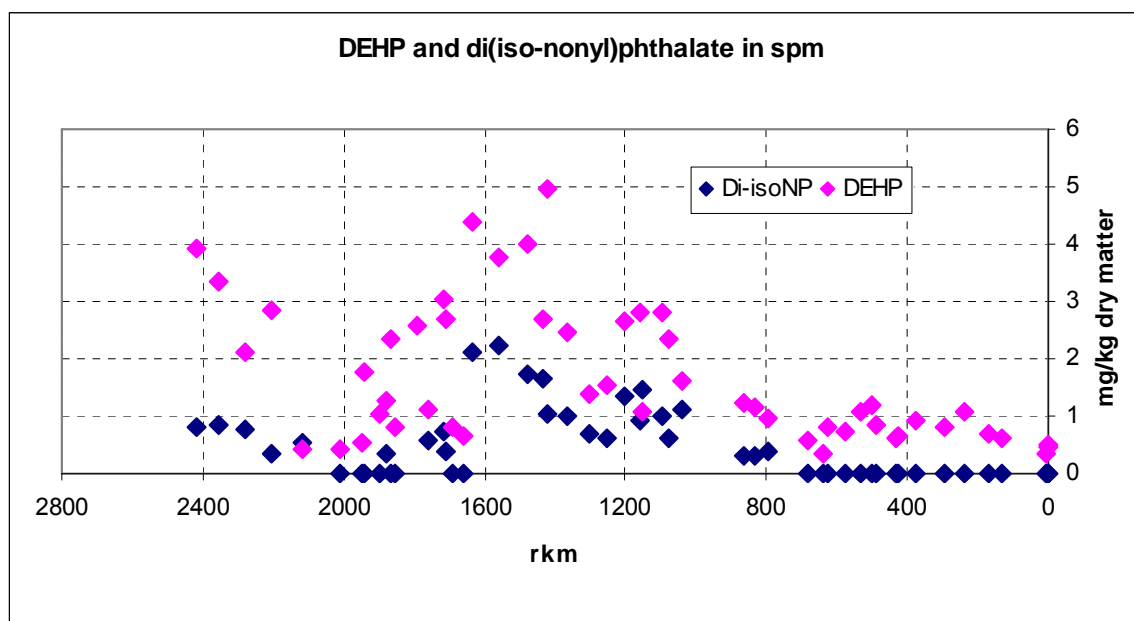


2.3.2 Di-(iso-nonyl)phthalate

Di-(iso-nonyl)phthalate was analysed for the first time at LfU/Munich in suspended particulate matter. In whole water samples it is usually detectable at one third of the concentration of DEHP.

The concentrations of both plastifiers in suspended particulate matter show a good correlation. Di(iso-nonyl)phthalate concentrations are always lower than DEHP by a factor of about 3.

Fig. 2.3-4 Comparison of DEHP and Di-(iso-nonyl)phthalate in suspended particulate matter



There is no EQS for di(iso-nonyl)phthalate in suspended particulate matter available.

2.4 Volatile organic carbons (VOCs)

Volatile organic compounds were found in low concentrations close to limit of quantification only in a few JDS2 samples.

Table 2.4-1 Limits of quantification and EQS for volatile organic carbons

| Substance | Unit | Limit of quantification (LOQ) | EQS |
|--------------------------------|------|-------------------------------|-----|
| 1,2-dichloroethane | µg/l | 0.7 | 10 |
| benzene | µg/l | 0.3 | 10 |
| dichloromethane | µg/l | 0.5 | 20 |
| trichloromethane | µg/l | 1.8 | 2,5 |
| tetrachloroethylene | µg/l | 0.5 | 10 |
| tetrachloromethane | µg/l | 1.2 | 12 |
| trichloroethylene | µg/l | 1.7 | 10 |
| hexachlorobutadiene | µg/l | 0,1 | 0,1 |
| trichlorobenzene (all isomers) | µg/l | 0.5 | 0,4 |

1,2-Dichloroethane, benzene, dichloromethane, hexachlorobutadien, trichloromethane, tetrachloromethane and trichloromethane were **not** detected in any of the JDS2 samples.

Tetrachloroethylene was found in 2 samples (JDS2-84M, JDS2-AR2) at a concentration of 0.8 µg/L. This concentration is close to limit of quantification.

1,2,4-Trichlorobenzene was found only in one sample (JDS2-10M) showing a concentration close to limit of quantification (0,6 µg/l). The other isomers of trichlorobenzene have not been detected in any of the JDS2 samples.

These results approve the findings of JDS1 when VOCs were found only in some samples at low concentrations. As the environmental quality standards for VOCs are relatively high not a single exceedance was detected.

2.5 Organochlorine compounds

2.5.1 Organochlorine compounds in water

Organochlorine compounds were not found in concentrations above the limit of quantification (LOQ). The LOQ and the corresponding EQS are shown in Table 2.5-1. For some compounds the LOQ is higher than the proposed EQS.

Only trifluralin was found in one single sample (JDS2-M0 1) at a concentration of 0,01 µg/L.

Table 2.5-1 Limits of quantification and EQS for organochlorine compounds in water samples

| compound | unit | LOQ | EQS |
|----------------------------------|------|-------|-----------------|
| α- endosulfane | µg/l | 0.005 | 0,005 |
| aldrin | µg/l | 0.01 | 0,01 (sum of 4) |
| dieldrin | µg/l | 0.021 | 0,01 (sum of 4) |
| endrin | µg/l | 0.023 | 0,01 (sum of 4) |
| isodrin | µg/l | 0,005 | 0,01 (sum of 4) |
| pentachlorobenzene | µg/l | 0,018 | 0,007 |
| hexachlorobenzene | µg/l | 0.02 | 0,01 |
| chlorfenvinphos | µg/l | 0.005 | 0,1 |
| chlorpyrifos | µg/l | 0.005 | 0,03 |
| DDT(all isomers and metabolites) | µg/l | 0.007 | 0,025 |
| lindane | µg/l | 0.02 | 0,02 |
| trifluraline | µg/l | 0,005 | 0,03 |
| pentachlorophenole | µg/l | 0,1 | 0,4 |

In order to have a reliable risk assessment according to WFD for these substances with a LOQ > EQS the data from other matrices must be taken into regard.

2.5.2 Organochlorine compounds in sediments and suspended particulate matter

The results of this survey of 135 sediment samples show that pentachlorophenol could not be found in the solid samples under investigation at concentration levels above the limit of quantification (0.005 mg/kg dry mass). This result is in accordance with the data from the JDS1, where also no PCP was

found in the sediments from river Danube. Based on the results of both surveys, the relevance of PCP for the contamination of sediments in river Danube and its tributaries seems to be rather low.

DDT and its metabolites analysed in 123 sediment and 23 suspended particulate matter samples showed positive results only at a few sampling sites mostly in the lower part of the Danube.

Aldrin, dieldrin and isodrin was detected in very few samples. The highest concentrations of isodrin were found at the German sampling sites JDS1, JDS2 and JDS 5. The maximum concentration for isodrin was 94 µg/kg dry matter at JDS 1 in sediment from the right bank. Endrin could not be found in any sample.

Trichlorobenzenes, pentachlorobenzene and hexachlorobenzene showed only few positive results at the lower µg/kg dry matter level. The findings are located in the middle stretch of the Danube.

The insecticides chlorpyrifos and chlorfenvinfos also appear at some sites along the middle stretch of the Danube. The highest concentration for chlorfenvinfos was detected at JDS 69 at a concentration of 42 µg/kg dry matter.

The only sampling station where trifluralin was found in suspended particulate matter was JDS 35 (15 µg/kg dry matter).

Pentachlorophenole (PCP) could not be found in the sediment samples under investigation at concentration levels above the limit of quantification (0.005 mg/kg dry mass). This result is in accordance with the data from the JDS1, where also no PCP was found in the sediments from river Danube. Based on the results of both surveys, the relevance of PCP for the contamination of sediments in river Danube and its tributaries seems to be rather low.

2.6 Organotin compounds

2.6.1 Organotin compounds in water

23 water samples were finally selected for the analysis of 5 organotin compounds. Table 2.6-1 shows a statistically evaluation of mean, maximum and minimum values. Mean values were calculated only in cases where more than 50 % of the analyzed samples were above the LOQ of 0,2 ng/l. LOD or zero were taken for values below LOQ or LOD, respectively.

Table 2.6-1 Results for organotin compounds in water

| as cation in ng/l | Dibutyltin | Tributyltin | Tetrabutyltin | Diphenyltin | Triphenyltin |
|----------------------|------------|-------------|---------------|-------------|--------------|
| MEAN | 1.1 | | | | |
| MAX | 9.2 | 14 | < 0.2 | n.d. | < 0.2 |
| MIN | n.d. | n.d. | n.d. | n.d. | n.d. |

LOD 0,1 ng/l, LOQ 0,2 ng/l, n.d. = not detected

Only dibutyltin was found in most of the water samples with a maximum concentration of 9,2 ng/l which is below the EQS of 10 ng/l. Except dibutyltin, tributyltin was found occasionally in the water samples. In 8 out of 23 samples tributyltin could be determined above the LQQ of 0,2 ng/l. A maximum concentration of 14 ng/l could be detected. All other measured compounds could not be detected or were below LOQ in the water samples.

2.6.2 Organotin compounds in sediments

Overall 124 sediment samples were analysed for organotin compounds. In table 6.2-2 the maximum as well as the minimum concentrations are listed for each substance. Moreover, the numbers of samples

with detected concentrations above the limit of quantification (LOQ) are listed. Tinorganic compounds were found all along the Danube in comparable concentrations.

Table 2.6-2 Results for organotin compounds in sediment samples

| as cation in µg/kg dm. | Monobutyl- tin | Dibutyltin | Tributyltin | Tetrabutyltin | Diphenyltin | Triphenyl- tin |
|------------------------------|-------------------|------------|-------------|---------------|-------------|-------------------|
| number > LOQ | 22 | 13 | 9 | 0 | 2 | 3 |
| MAX | 38 | 19 | 12 | n.d. | 7,7 | 10 |
| MIN | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |

LOD: 2.5 µg/kg dm.; LOQ: 5 µg/kg dm.

As it can be clearly seen, monobutyltin and dibutyltin were the most abundant compounds found in the sediment samples. Maximum concentration for these substances of 38 and 19 µg/kg dry matter could be determined. On the other side, tetrabutyltin was not detected at all. Contamination of di- and triphenyltin were also very seldom with only 2 or 3 out of 124 sediments, respectively with concentrations above the LOQ.

2.6.3 Organotin compounds in suspended particulate matter

23 suspended matter samples at the same sample sites like the water samples were analysed for organotin compounds. In table 2.6-3 the results are shown.

Table 2.6-3 Results for organotin compounds in suspended particulate matter

| as cation in µg/kg dm. | Monobutyl- tin | Dibutyltin | Tributyltin | Tetrabutyltin | Diphenyltin | Triphenylti n |
|------------------------------|-------------------|------------|-------------|---------------|-------------|------------------|
| number < LoQ | 9 | 4 | 3 | 0 | 0 | 4 |
| MAX | 37 | 75 | 230 | 0 | 0 | 11 |
| MIN | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |

LoD: 2.5 µg/kg dm.; LoQ: 5 µg/kg dm.

Like sediment samples the investigated compounds were only occasionally found in the suspended matter. Mono-, di-, tributyltin and triphenyltin compounds were again the most abundant compounds analysed, whereas tetrabutyl- and diphenyltin were not detected at all. The maximum concentration with 230 µg/kg dry matter. were found for tributyltin. This high level was determined for the suspended matter JDS 53_M (downstream Pancevo). The sample showed also the highest level for mono- and dibutyltin. The rest of samples showed contamination patterns which are comparable to those of the sediment samples.

2.6.4 Organotin compounds in mussels

Overall 25 mussel samples were analysed and were statistically evaluated in Table 4. Mean values were calculated only in cases where more than 50 % of the analyzed samples were above the LOQ of 0,2 ng/l. LoD or zero were taken for values below LOQ or LOD, respectively.

Table 2.6-4 Results for organotin compounds in mussels

| as cation in µg/kg | Monobutyl- tin | Dibutyltin | Tributyltin | Tetrabutyltin | Diphenyltin | Triphenylti n |
|-----------------------|-------------------|------------|-------------|---------------|-------------|------------------|
|-----------------------|-------------------|------------|-------------|---------------|-------------|------------------|

| | | | | | | |
|-----------------|------|------|------|------|------|------|
| dm. | | | | | | |
| number < LoQ | 10 | 14 | 24 | 0 | 0 | 1 |
| MEAN | | 19 | 112 | | | |
| MAX | 160 | 200 | 1200 | 0 | 0 | 0 |
| MIN | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |

Mono-, di-, tributyltin and triphenyltin compounds were once again the most abundant compounds analysed, whereas tetrabutyl- and diphenyltin were not detected at all. Concentration up to 1200 µg/kg dm. could be determined, especially for the mussel samples from JDS site 47.

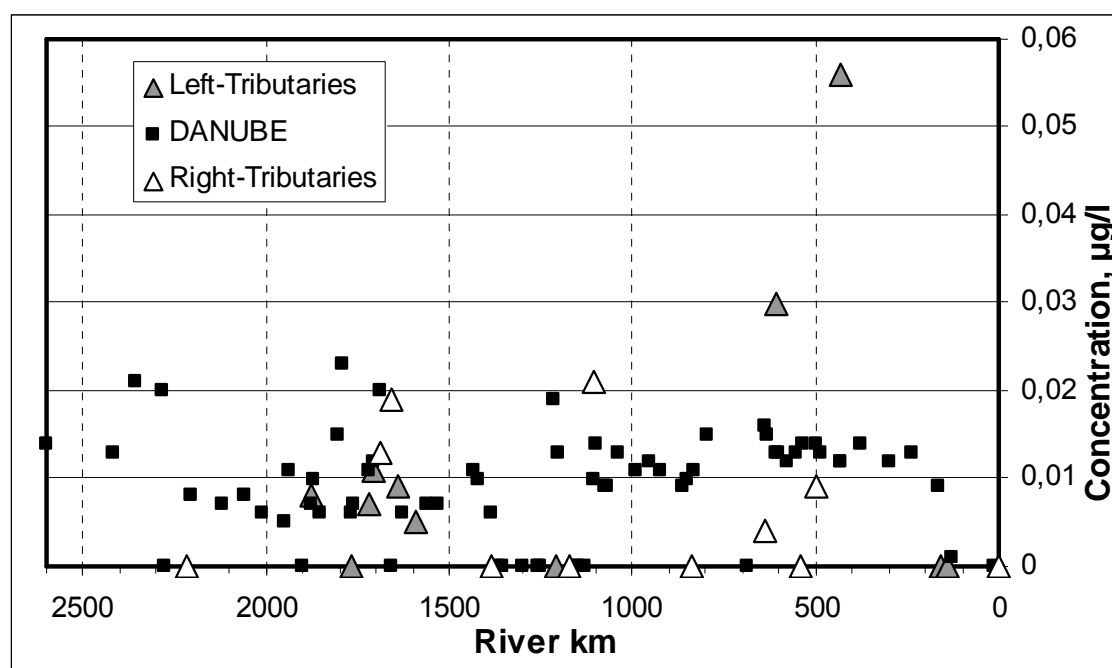
2.7 Polar pesticides

Atrazine, simazin and alachlor were analysed in dissolved water samples. According to their chemical-physical properties these pesticides should not be adsorbed to suspended particulate matter.

Alachlor was absent in all water samples whereas simazine was found only in three samples in low concentrations (JDS7 0,015 µg/l; JDS25 0,026 µg/l; JDS 27 0,055 µg/l).

Atrazine can be detected in most of the samples mostly in concentrations around 0,01 µg/l.

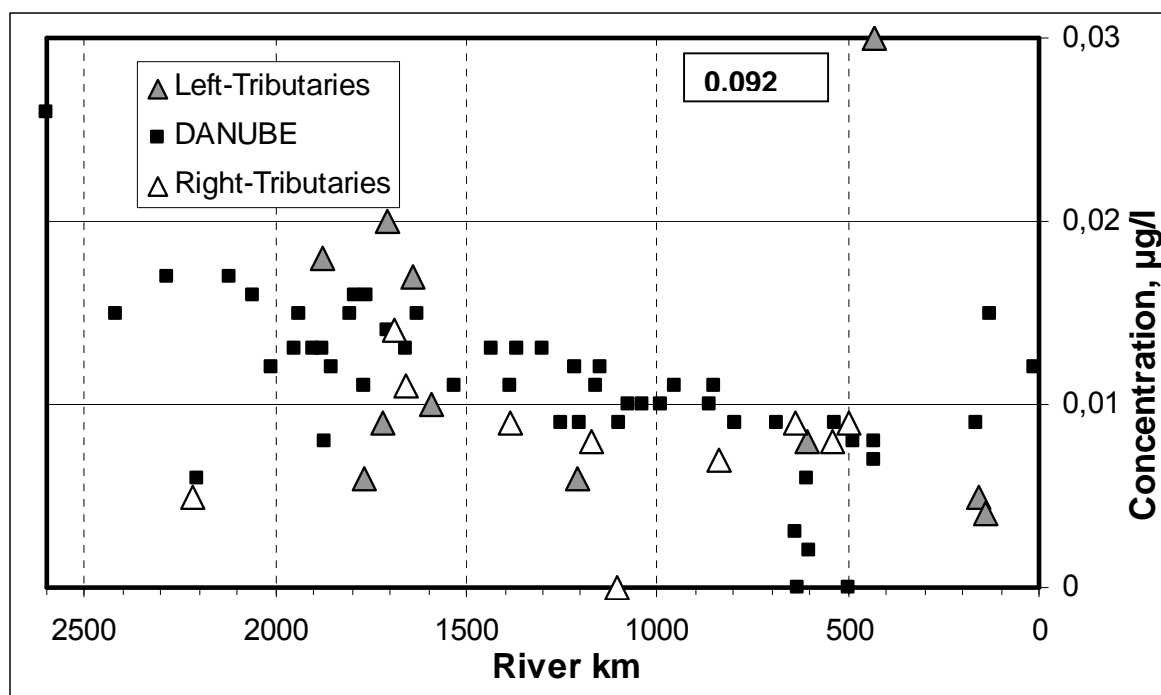
Fig. 2.7-1 Atrazine concentrations in water samples



The tributary Arges shows the highest concentration (0,056 µg/l) but all findings are well below the EQS of 0,6 µg/l.

Joint Research Centre in Ispra also analysed desethylatrazine, which is the main metabolite of atrazine. The concentrations of desethylatrazine are very comparable to the atrazine finding. This indicates that atrazine found in river water doesn't come from fresh applications. Comparable concentrations of atrazine and desethylatrazine are found in many groundwaters due to the longterm use of atrazine in agriculture and the degradation process in soils. There is no EQS for desethylatrazine given.

Fig. 2.7-2 Desethylatrazine concentrations in water samples



Two other herbicides listed in Annex X of the WFD, isoproturon and diuron, were analysed by JRC. Using modern LC-MS/MS-techniques a LOQ of 0,001 µg/l was achieved.

In most of the water samples both isoproturon and diuron were detected in trace concentrations below 0,01 µg/l. Isoproturon was found in concentrations of 0,011-0,016 µg/l in three samples and diuron just in one single sample above 0,01 µg/l (JDS11 0,012 µg/l).

The EQS for isoproturon and diuron are 0,3 µg/l and 0,2 µg/l respectively. All concentrations are clearly below the EQS.

2.8 Additional organic compounds

2.8.1 Polychlorinated biphenyls (PCB)

2.8.1.1 Polychlorinated biphenyls in water

Nine PCB congeners (PCB-8, PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180, PCB-203) were analysed in water samples. The LOQs for each compound were 0,003-0,005 µg/l.

PCB congeners were below the limit of quantification. Only one of the analysed congeners (PCB 8) was found in two JDS2 samples at concentrations of 0,066 µg/l (JDS2-90M) and 0,046 µg/l (JDS2-AR2), respectively. PCBs in river water – especially higher chlorinated congeners – are readily accumulated to suspended particulate matter and sediments.

2.8.1.2 Polychlorinated biphenyls in fish

PCB were not under investigation in fish tissue during JDS 1 but PCB were analysed in mussels. Although fish muscle tissue cannot be compared directly to mussle tissue the order of magnitude is quite similar.

PCB could be found in all fish samples. In most of the fish (pools) concentrations in liver is higher than in muscle tissue. The results for PCB 28, 52, 153 and 180 are shown in figures 2.8-1 to 2.8-4.

Figure 2.8-1 PCB 28 in fish muscle and liver

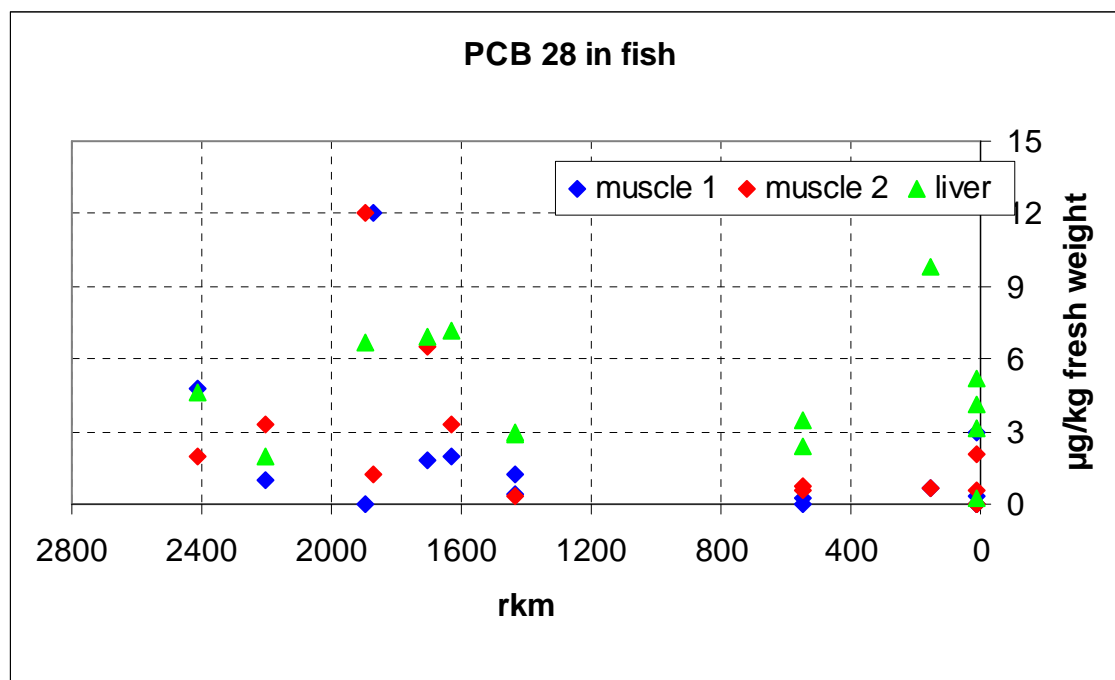


Figure 2.8-1 PCB 52 in fish muscle and liver

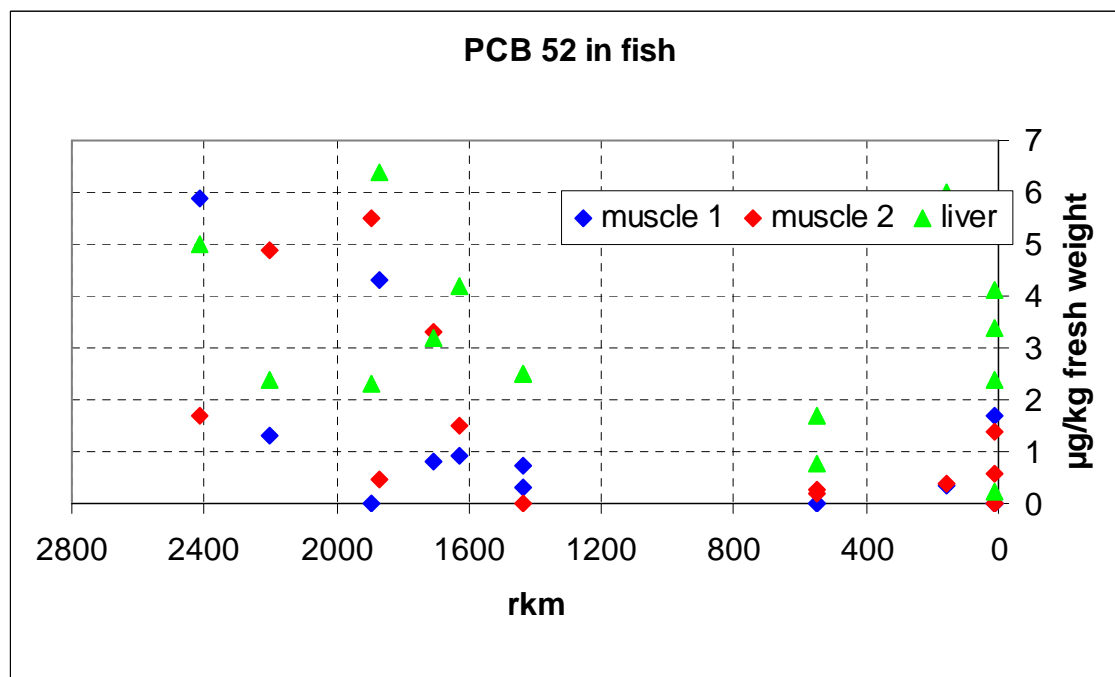
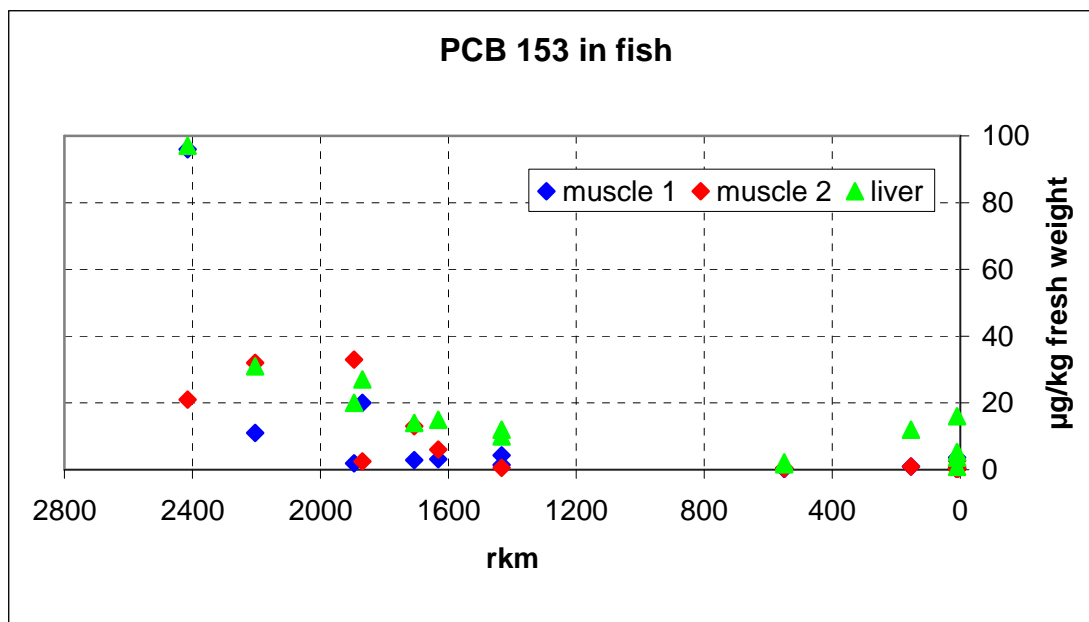
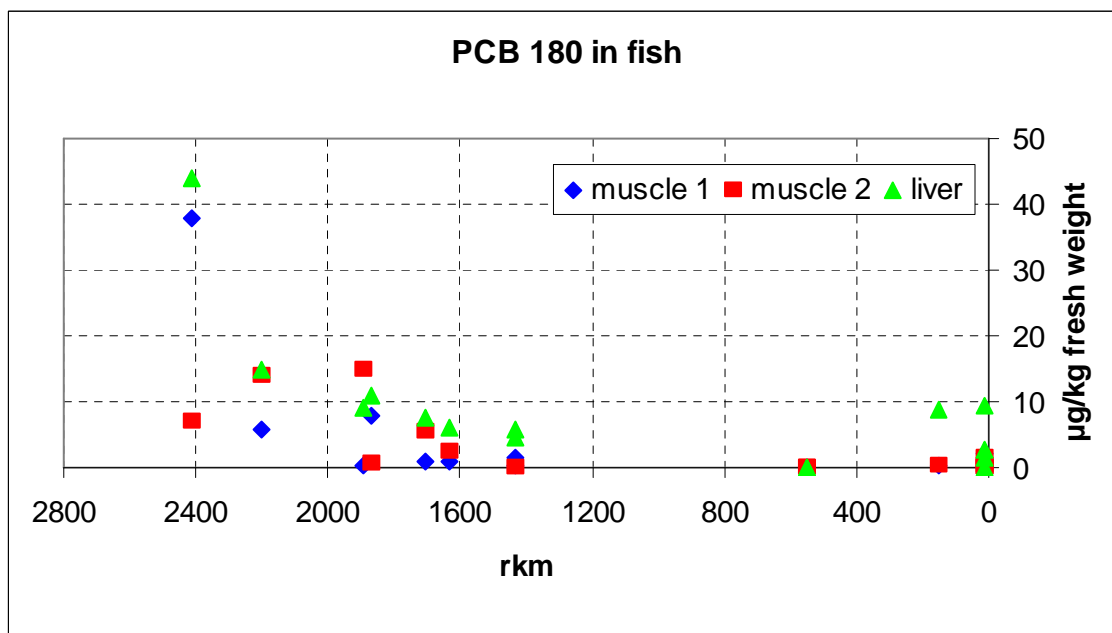


Figure 2.8-3 PCB 153 in fish muscle and liver



In mussle samples from JDS 1 PCB 153 was found in the concentration range 2 – 75 µg/kg, most of the samples were around 10 µg/kg.

Figure 2.8-4 PCB 180 in fish muscle and liver



PCBs are well adsorbed to sediments. According to their persistence they can be remobilized over a long period of time. Data at JDS 7 compared to national data from fish analysis during the last 10 years at the sampling site Donau/Jochenstein do not show a trend towards lower concentrations. The

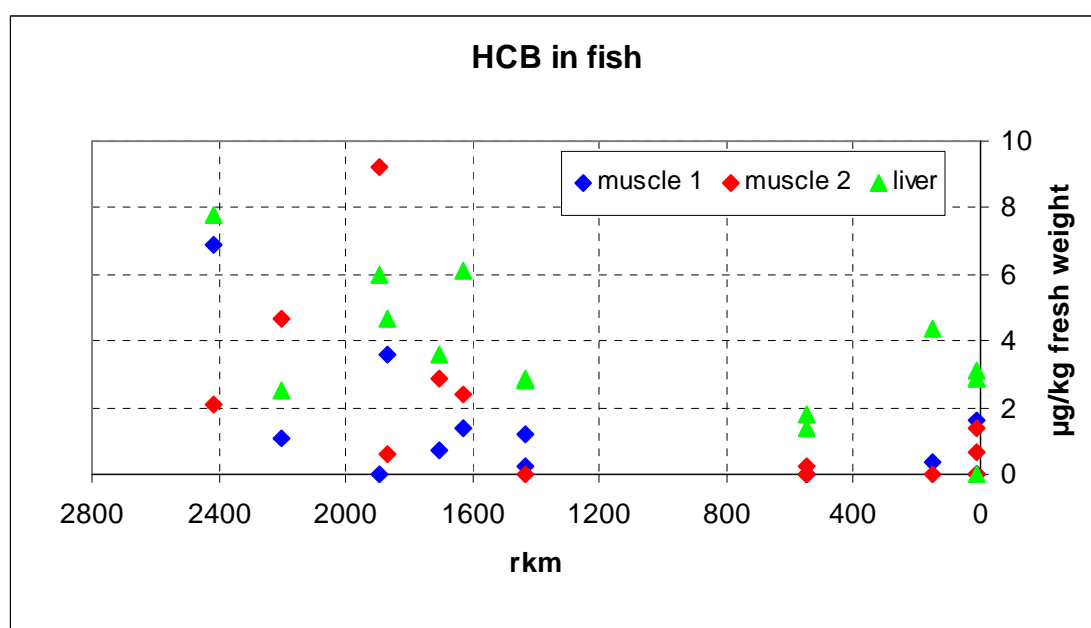
variability between single fish samples even of one species is very large. This might be explained by age, sex, fat-content and nutrition status.

2.8.2 Hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD) in fish

The draft “Directive on environmental quality standards in the field of water policy and amending 2000/60/EC” is proposing environmental quality standards for HCB (10 µg/kg wet weight) and HCBD (55 µg/kg wet weight). The “wet weight” is referring to “prey tissue”, which is not exactly defined. When analysing filet the focus is held on “eatable matter” according to regulations for human food.

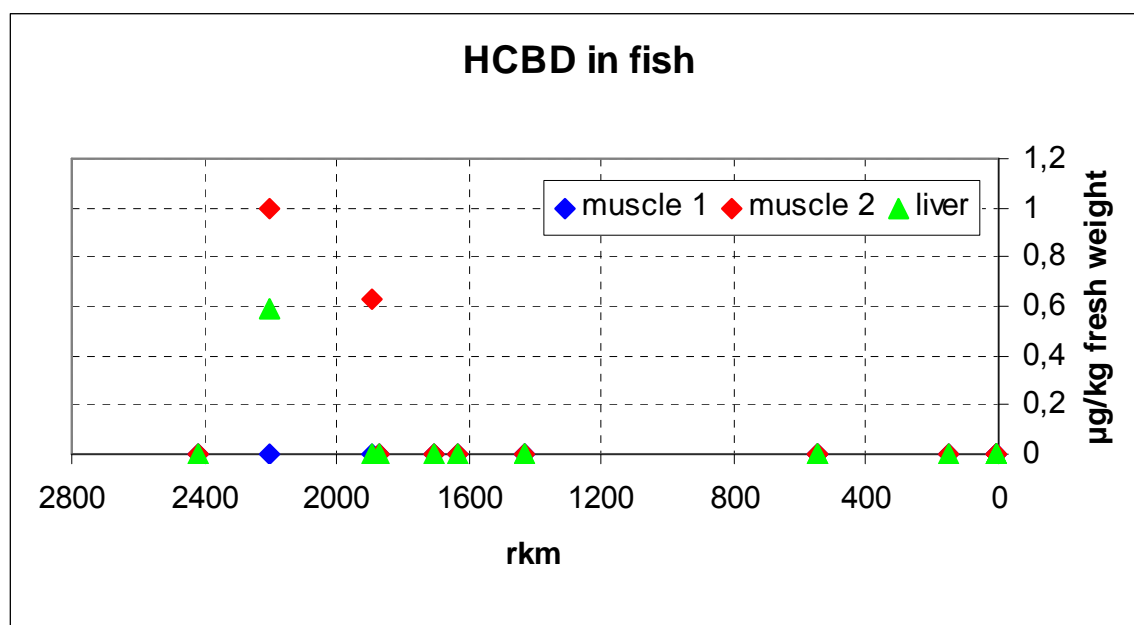
When applying the EQS für HCB not a single sample is exceeding a concentration of 10 µg/kg fresh weight, only a few results get close to the EQS.

Figure 2.8-5 Hexachlorobenzene (HCB) in fish



In most of the samples HCBD was not found. The positive results from the upper Danube can be explained by a leaching waste dumping ground (chemical industry) within the Inn river basin. This site is under investigation and decontamination for more than 15 years. Leachate of this dumping ground is treated separately. HCBD-concentrations are decreasing from year to year which can also be demonstrated by low HCBD concentrations in fish muscle tissues.

Figure 2.8-6 Hexachlorobutadiene (HCBD) in fish



2.8.3 1,2,4-Trichlorobenzene and pentachlorobenzene in fish

1,2,4-Trichlorobenzene and pentachlorobenzene were found only in few fish samples showing low concentrations. As these concentrations are lower than concentrations for HCB, HCB can be seen as an indicator for the group of chlorinated benzenes. The results in fish correspond to low concentrations in the water phase.

2.8.4 HHCB (Galaxolide), triclosan and methyl-triclosan in suspended particulate matter

As HHCB is predominantly used in household products the main source of HHCB contamination is waste water. Most of the HHCB is adsorbed to sewage sludge but about 20% of the HHCB is discharged into rivers with treated waste water. So HHCB is a clear indicator for waste water influence. HHCB can be found along the Danube down to the Iron Gate Reservoir. The highest concentration is found downstream Budapest where a new waste water treatment plant is under construction but not yet in operation. In the lower Danube HHCB concentrations are below the LOQ of 5 $\mu\text{g/kg}$ dry matter.

Figure 2.8-7 HHCB (Galaxolide) in suspended particulate matter ($\mu\text{g/kg}$ dry matter)

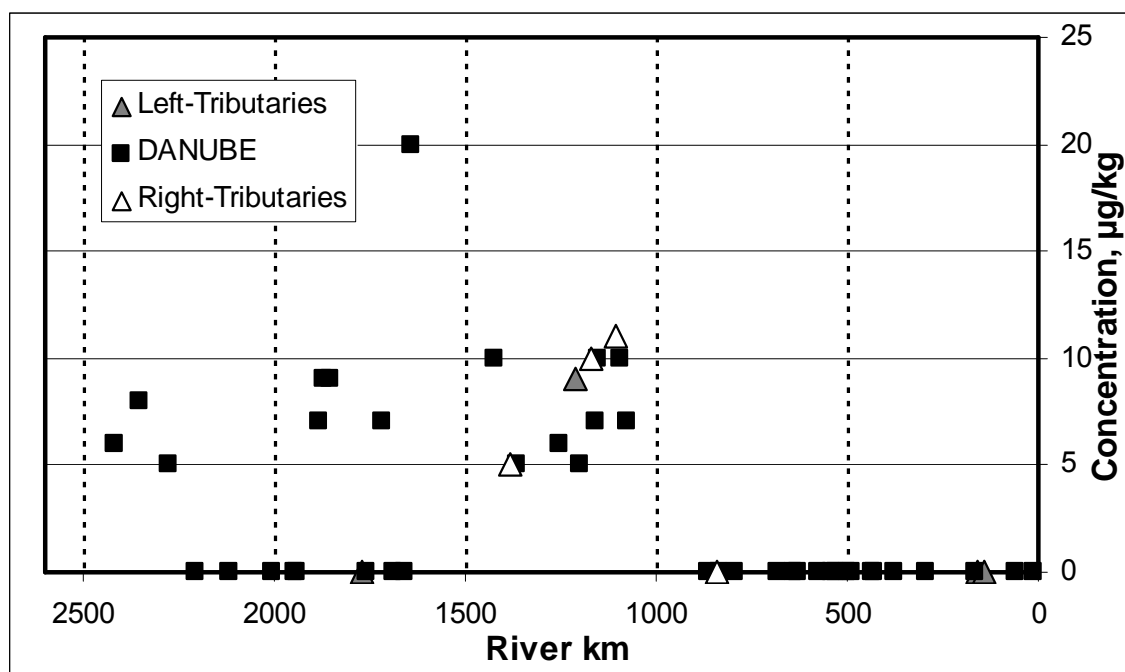
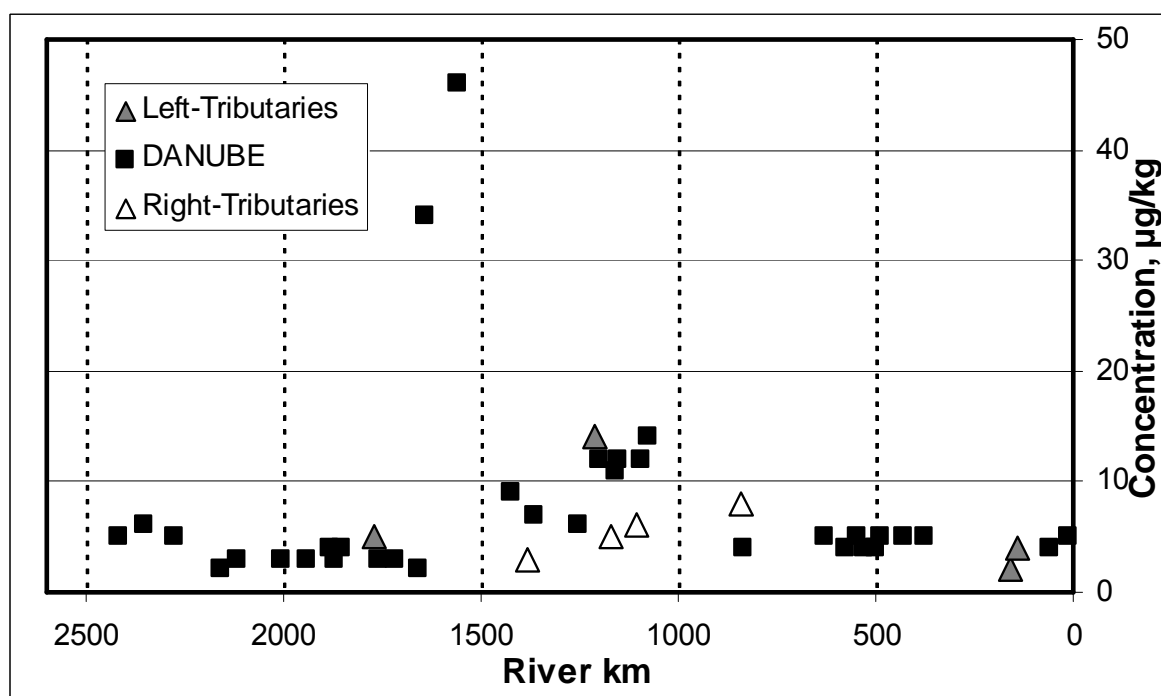


Figure 2.8-8 Triclosan in suspended particulate matter (µg/kg dry weight)



3 Conclusions

One important objective of JDS 2 was to get a complete dataset for priority pollutants according to the daughter directive of the WFD concerning priority pollutants (“Proposal for a Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC”). In this proposal environmental quality standards are given for different types of waters as “annual averages” and “maximum allowable concentrations”.. The environmental quality standards refer to analysis of whole water samples (except for metals, which must be analysed from the filtered sample).

All priority pollutants except C10-C13-chloroalkanes (no method available) and fluoranthene (not analysed) were analysed in JDS2 water samples. For most of the priority pollutants the limits of quantification (LOQ) were below or at the level of the environmental quality standards (EQS). For some compounds the LOQ didn't meet the EQS, so that an assessment of water quality is not possible according to WFD rules (see ANNEX 1). It has to be annotated that EQS are defined for an average value of 12 measurements within one year. JDS2 provided a single sample from the months August/September which may be not representative for the time period of one year (e.g. pesticide application in certain periods of the year). It is not according to WFD rules to assess the chemical status from one single measurement.

The cited proposal also gives three EQS for biota (mercury 20 µg/kg; hexachlorobenzene 10 µg/kg; hexachlorobutadiene 55 µg/kg), these EQS being for “prey tissue”. Hexachlorobenzene and Hexachlorobutadiene were under investigation in JDS 2 fish samples.

3.1 Alkylphenols

4-iso-Nonylphenol can be found in nearly all water samples along the Danube, but only two tributaries (Timok and Arges) show concentrations above the EQS of 0,3 µg/l. p-Octylphenol is of less importance and EQS is by far not exceeded.

4-iso-Nonylphenol should be further monitored in the future whereas p-octylphenol can be excluded from regular monitoring programs.

3.2 Polybrominated diphenylethers (PBDEs)

In JDS 2 PBDEs were analysed in water and sediment samples.

The EQS for PBDEs for inland waters is extremely low (0,0005 µg/l). The limits of quantification in JDS 2 were at the level of the EQS or above. For this reason more sensitive analytical methodologies must be tested.

PBDEs in water showed positive results only in six samples. Although very low LODs were achieved the concentration of these samples was between LOD and LOQ.

Taking into account the accumulative qualities of PBDEs they should be further analysed in suspended particulate matter and/or sediments in future.

From the list of target PBDEs under investigation, only BDE-209, i.e. decabromodiphenyl ether, turned out to be relevant for contamination of river Danube sediments. This compound, however, is not included in the list of WFD priority pollutants which only refers to the pentabrominated diphenyl ethers (defining the congeners 28, 47, 99, 100, 153 and 154 as relevant for assessment).

BDE-209 should be a candidate for the next revision of Annex X WFD.

3.3 Phthalates

Di-(2-ethylhexyl)phthalate (DEHP) is found in nearly all JDS 2 water samples in high concentrations. In the middle stretch of the Danube the DEHP pollution is significantly higher than in the upper and lower part. In more than 30% of the water samples the rather high EQS (1,3 µg/l) is exceeded. The highest concentration were found at JDS13 (Wildungsmauer, 4,53 µg/l) and JDS35 (Dunavoldfar, 4,42 µg/l).

As DEHP is readily accumulating to organic matter also high concentrations can be detected in suspended particulate matter and sediments.

Among the priority pollutants listed in Annexes XI and X WFD DEHP is the most critical substance in water samples and measures have to be taken to reduce the input into the aquatic environment.

Together with DEHP also Di(iso-nonyl)phthalate was detected in most of the suspended particulate matter samples showing concentrations of about 1/3 of the DEHP concentrations. So this phthalate should be integrated in future monitoring programs.

3.4 VOCs

Most of the results obtained for the WFD priority substances in sediments during JDS2 are in good accordance with the data from JDS1. For the most relevant compounds OP, NP, and DEHP the contamination profile of both surveys is rather similar. Looking at the concentration levels, however, a significant improvement of the situation can be observed. For all of the priority substances, average sediment concentrations during JDS2 were lower than during JDS1. Concentrations observed at the former “hot spots” still are elevated, but the concentrations during JDS2 are much lower than before and thus measures taken to reduce contamination levels on a local scale seem to be successful. In conclusion, the results for WFD priority substances in river Danube sediments indicate a slight improvement of the overall water quality of river Danube and a significant reduction of contamination at the former hot spots.

3.5 Chlororganic compounds

Only few chlororganic compounds were detected in water, sediments and suspended solids. This result shows that most of these compounds are out of use but some residues can be found in sediments and suspended particulate matter. Some compounds can be addressed to a certain stretch of the Danube (e.g. DDT and metabolites in the lower Danube, isodrin at German sampling sites) and should be regarded in national monitoring programmes.

3.6 Organotin compounds

The proposal for the EQS for tributyltin is extremely low (0,0002 µg/l). The analytical method used showed a LOD of 0,0002 µg/l. In 8 out of 23 water samples the EQS was exceeded. These findings are supported by analysis of suspended particulate matter, sediments and mussels where tributyltin showed the highest concentrations among the tinorganic compounds under investigation.

Tributyltin-cation is listed in Annex X WFD as “priority hazardous substance” which means that its use, emissions and losses must be stopped until 2020. According to JDS 2 results tributyltin must be monitored in future and measures have to be taken to stop further inputs into the aquatic environment.

3.7 Polar pesticides

The pesticides alachlor, atrazine, simazine, diuron and isoproturon could be analysed in water samples with LOQs well below the EQS values. The EQS was never exceeded.

On the other hand the during sampling period in August/September pesticide application is generally low. So these findings may not be typical and pressures by pesticides are clearly underestimated. But national monitoring data show that also during the time of the year when most of the pesticides are used the EQS are not exceeded.

As these pesticides are quite water-soluble compounds they don't tend to accumulate in suspended particulate matter or sediments so that the analysis of these materials give no additional information.

3.8 Additional organic compounds

3.8.1 Polychlorinated biphenyls (PCB)

PCB were analysed in fish for the first time. Higher chlorinated congeners show a stronger tendency to accumulate in muscle and liver tissue. The highest concentrations were found for PCB 153 at sampling station JDS 2 (Kelheim, liver, pooled: 97 µg/kg fresh weight, muscle 1: 96 µg/kg fresh weight).

PCB contamination in fish is mainly found in the upper and middle stretch of the Danube whereas PCB concentrations are low in the lower Danube.

3.8.2 Hexachlorobenzene (HCB) and hexachlorobutadiene (HCBd) in fish

The proposed environmental quality standards for HCB and HCBd are not exceeded. The source for HCBd in the upper Danube (old dumping ground in the German Inn catchment area) is identified for many years and HCBd concentrations are decreasing.

3.9 Compliance checking for priority substances according to WFD

According to Annex 4 WFD surveillance monitoring of priority substances must be done on a monthly basis for the period of one year.

The draft directive ("Proposal for a Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy and amending Directive 2000/60/EC") is defining the application of the EQS in the following way:

- for any given surface water body, applying the EQS-AA ("EQS-annual average") means that, for each representative monitoring point within the water body, the arithmetic mean if the concentrations measured at different times during the year does not exceed the standard"
- for any given surface water body, applying the EQS-MAC ("EQS-maximum allowable concentration") means that the measured concentration at any representative monitoring point within the water body does not exceed the standard"

For about half of the priority substances the EQS-MAC is marked as "not applicable". In these cases the EQS-AA 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.

The draft directive "laying down technical specifications for chemical analysis and monitoring of water status" defines the procedure for the calculation of mean values, For results below the limit of quantification half of the value of the limit of quantification shall be used.

3.10 Assessment of the indication of the chemical status from JDS2 results

For JDS2 one single water sample was taken at each sampling site. For this reason the assessment of the chemical status cannot be done in-line with the WFD requirements.

The following procedure was decided:

- an **indication** of the chemical status is given for each sampling site (not water body)

- for compliance checking the proposed EQS-AA for inland waters is used

Table 4.2-1 shows the sampling sites where EQS are exceeded as well as the corresponding parameters.

Table 4.2-1 Sampling sites and parameters exceeding EQS for priority substances

| sampling station | parameter/s > EQS |
|-------------------------|-----------------------------|
| JDS13 | DEHP |
| JDS14 | DEHP |
| JDS17 | DEHP |
| JDS26 | tributyltin |
| JDS34 | DEHP |
| JDS35 | DEHP, tributyltin |
| JDS36 | DEHP |
| JDS38 | DEHP |
| JDS39 | DEHP |
| JDS40 | DEHP |
| JDS41 | DEHP |
| JDS42 | DEHP |
| JDS43 | DEHP |
| JDS44 | DEHP |
| JDS45 | DEHP, tributyltin |
| JDS46 | DEHP |
| JDS47 | DEHP |
| JDS49 | DEHP |
| JDS50 | DEHP |
| JDS51 | DEHP |
| JDS52 | DEHP |
| JDS53 | DEHP |
| JDS54 | DEHP |
| JDS55 | DEHP |
| JDS57 | DEHP |
| JDS58 | DEHP |
| JDS59 | DEHP |
| JDS60 | DEHP |
| JDS61 | DEHP |
| JDS62 | DEHP |
| JDS65 | DEHP |
| JDS66 | DEHP |
| JDS68 | DEHP |
| JDS69 | DEHP |
| JDS72 | DEHP |
| JDS73 | DEHP |
| JDS74 | DEHP |
| JDS76 | tributyltin |
| JDS79 | DEHP |
| JDS80 | tributyltin |
| JDS81 | nonylphenol, DEHP |
| JDS82 | DEHP |

| | |
|-------|-------------------|
| JDS83 | tributyltin |
| JDS84 | nonylphenol, DEHP |
| JDS92 | tributyltin |
| JDS94 | DEHP |
| JDS95 | tributyltin |

These results are also presented as the indication of the chemical status in map xxx.

3.11 Assessment of other organic pollutants

For some of the other organic pollutants only national EQS or EQS-proposals might be used for assessment.

From the compounds analysed HHCB and di-(iso-nonyl)phthalate should be discussed as candidates for a revision of the priority substances list.

ANNEX 1 LOQs of analytical methods for WFD target compounds in water samples in comparison to the proposed environmental quality standards

| determinand | unit | limit of quantification (LOQ) | EQS | laboratory |
|----------------------|------|-------------------------------|------------------|----------------|
| alachlor | µg/l | 0,05 | 0,3 | VITUKI |
| anthracene | µg/l | 0,005 | 0,1 | WRI Bratislava |
| atrazine | µg/l | 0,005 | 0,6 | VITUKI |
| benzene | µg/l | 0,3 | 10 | WRI Bratislava |
| BDE-47 | µg/l | 0,002 | 0,0005 | WRI Prague |
| BDE-99 | µg/l | 0,002 | 0,0005 | WRI Prague |
| BDE-100 | µg/l | 0,002 | 0,0005 | WRI Prague |
| BDE-153 | µg/l | 0,002 | 0,0005 | WRI Prague |
| BDE-154 | µg/l | 0,002 | 0,0005 | WRI Prague |
| BDE-183 | µg/l | 0,002 | 0,0005 | WRI Prague |
| C10-13-chloroalkanes | | no method | | |
| chlorphenvinfos | µg/l | 0,005 | 0,1 | WRI Bratislava |
| chlorpyriphos | µg/l | 0,005 | 0,03 | WRI Bratislava |
| 1,2-dichloroethan | µg/l | 0,7 | 10 | WRI Bratislava |
| dichloromethane | µg/l | 0,5 | 20 | WRI Bratislava |
| DEHP | µg/l | 0,2 | 1,3 | WRI Bratislava |
| diuron | µg/l | 0,001 | 0,2 | JRC |
| alpha-endosulfan | µg/l | 0,005 | 0,005 | WRI Bratislava |
| fluoranthen | | not analysed | | |
| hexachlorobenzene | µg/l | 0,02 | 0,01 | WRI Bratislava |
| hexachlorobutadiene | µg/l | 0,1 | 0,1 | WRI Bratislava |
| lindan | µg/l | 0,02 | 0,02 | WRI Bratislava |
| isoproturon | µg/l | 0,001 | 0,3 | JRC |
| naphthalene | µg/l | 0,25 | 2,4 | WRI Bratislava |
| 4-iso-nonylphenol | µg/l | 0,02 | 0,3 | WRI Prague |
| p-octylphenol | µg/l | 0,005 | 0,1 | WRI Prague |
| pentachlorobenzene | µg/l | 0,018 | 0,007 | WRI Bratislava |
| pentachlorophenol | µg/l | 0,1 | 0,4 | WRI Bratislava |
| benzo(a)pyrene | µg/l | 0,002 | 0,05 | WRI Bratislava |
| benzo(b)fluoranthene | µg/l | 0,005 | 0,03 (sum of 2) | WRI Bratislava |
| benzo(k)fluoranthene | µg/l | 0,005 | 0,03 (sum of 2) | WRI Bratislava |
| benzo(ghi)perylene | µg/l | 0,002 | 0,002 (sum of 2) | WRI Bratislava |

| determinand | unit | limit of quantification (LOQ) | EQS | laboratory |
|------------------------|------|-------------------------------|------------------|----------------|
| indenopyrene | µg/l | 0,002 | 0,002 (sum of 2) | WRI Bratislava |
| simazine | µg/l | 0,01 | 1 | VITUKI |
| tributyltin | µg/l | 0,0002 | 0,0002 | UBA Vienna |
| 1,2,4-trichlorobenzene | µg/l | 0,5 | 0,4 | WRI Bratislava |
| trichloromethan | µg/l | 1,8 | 2,5 | WRI Bratislava |
| trifluralin | µg/l | 0,005 | 0,03 | WRI Bratislava |
| DDT total | µg/l | | 0,025 | |
| p-p'-DDT | µg/l | 0,007 | 0,01 | WRI Bratislava |
| isodrin | µg/l | 0,005 | 0,01 (sum of 4) | WRI Bratislava |
| endrin | µg/l | 0,023 | 0,01 (sum of 4) | WRI Bratislava |
| dieldrin | µg/l | 0,021 | 0,01 (sum of 4) | WRI Bratislava |
| aldrin | µg/l | 0,01 | 0,01 (sum of 4) | WRI Bratislava |
| tetrachloroethylene | µg/l | 0,5 | 10 | WRI Bratislava |
| tetrachloromethane | µg/l | 1,2 | 12 | WRI Bratislava |
| trichloroethylene | µg/l | 1,7 | 10 | WRI Bratislava |

| | |
|--|-----------|
| | LOQ > EQS |
| | LOQ = EQS |