5.2.4.2.5 Petroleum Hydrocarbons in Mussels

Mussels samples were analysed for PAHs, as representative for the petroleum hydrocarbons, oil pollution, and the results are shown in Figure C2.4.2.-13.

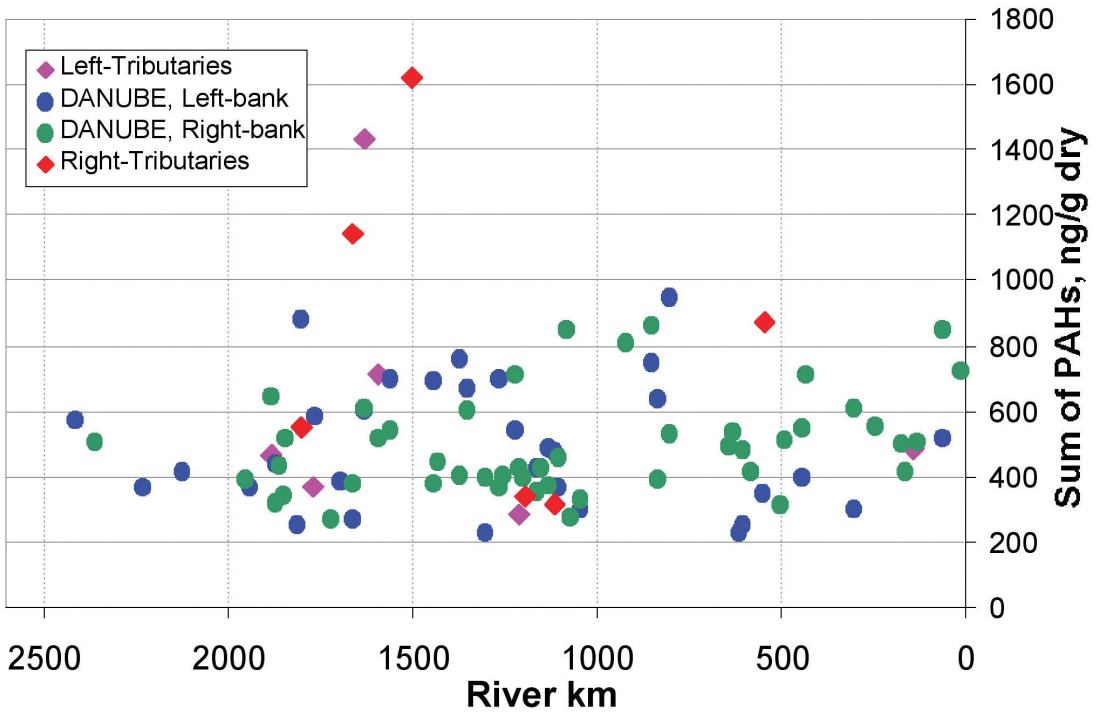

FIGURE C2.4.2.-13: Variation in the concentration of PAHs in mussel samples collected from the Danube and its tributaries during the JDS.

The mussel samples contained PAHs at the similar level as it was observed during the Cousteau and the AR105 surveys. A slight increasing trend can be observed downwards to the Danube Delta, and the highest values were measured in tributaries in the Middle Danube Reach.

5.2.4.3 Volatile Organic Compounds (VOCs)

For the assessment of VOC-results there are proposed water quality target values either from the IWACO-report for the Danube [1], from the Rhine commission or from the Directive 76/464/EEC [2]:

Substance	Unit	Water Quality Target Values			
Benzene	µg/l	2	(Rhine)	10	(76/474)
1,2-Dichloroethane	µg/l	1	(Rhine)	10	(76/464)
Trichloromethane	µg/l	0.6	(IWACO)	12	(76/464)
1,3,5-Trichlorobenzene	µg/l	0.1	(Rhine)	0.4	(76/464)

In general, volatile organic compounds were found in low concentrations in a few JDS samples only. It must be taken into account that the sampling period was in summer where high temperatures support the evaporation of volatile compounds from surface waters.

5.2.4.3.1 1,2-Dichloroethane

In the samples JDS1-JDS35 no 1,2-dichloroethane was found. 1,2-Dichloroethane shows the highest value with 10 µg/l at JDS-36 (Rackeve-Soroksar Danube Arm start) but at the end of this arm it is not detectable. At JDS-39 (Tass) it appears again with 1,5 µg/l and can be followed down to JDS-50 in concentrations less than 0.5 µg/l. The tributaries in this Danube Reach are usually free of 1,2-dichloroethane. Downstream of JDS-50 it appears again in a few samples but in low concentrations. It is worth to mention that 1,2-dichloroethane was one of the major pollutant released to the Danube at Pancevo during the bombing in Yugoslavia during the spring of 1999. At that time, the 1,2-dichloroethane concentration exceeded 50 µg/l in the Danube downstream of the Pancevo wastewater canal.

5.2.4.3.2 Benzene

Benzene was found in 8 samples in concentrations close to the determination limit of 0.1 µg/l with the exception of JDS-69 (tributary Timok) with 0.6 µg/l.

5.2.4.3.3 Trichlorobenzenes

Trichlorobenzenes are found only at three sampling sites (JDS-60; -69 and -84) in concentrations less than 0.5 µg/l. So, this group of substances can be neglected in further investigations.

5.2.4.3.4 Trichloromethane

Trichloromethane was found in 58 samples in concentration not higher than 0.3 µg/l. Higher values can be found in 4 tributaries in the downstream section (0.6-1.3 µg/l) but they obviously do not affect the Danube.

5.2.4.3.5 Dichloromethane

Dichloromethane has not been detected in any of the JDS samples.

References

1. Water Quality Enhancement in the Danube River Basin, Final report, Phare 98-0399.00, February 2000

2. Council Directive 76/464/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community, Official Journal, L129, May 18th 1976

5.2.4.4 Polar Pesticides

All 98 JDS-samples taken from the middle of the Danube or its tributaries were analyzed. From the 23 polar pesticides analyzed only Atrazine and Desethylatrazine were found in concentrations above the limit of determination (see Figures C2.4.4.-1 and C2.4.4.-2).

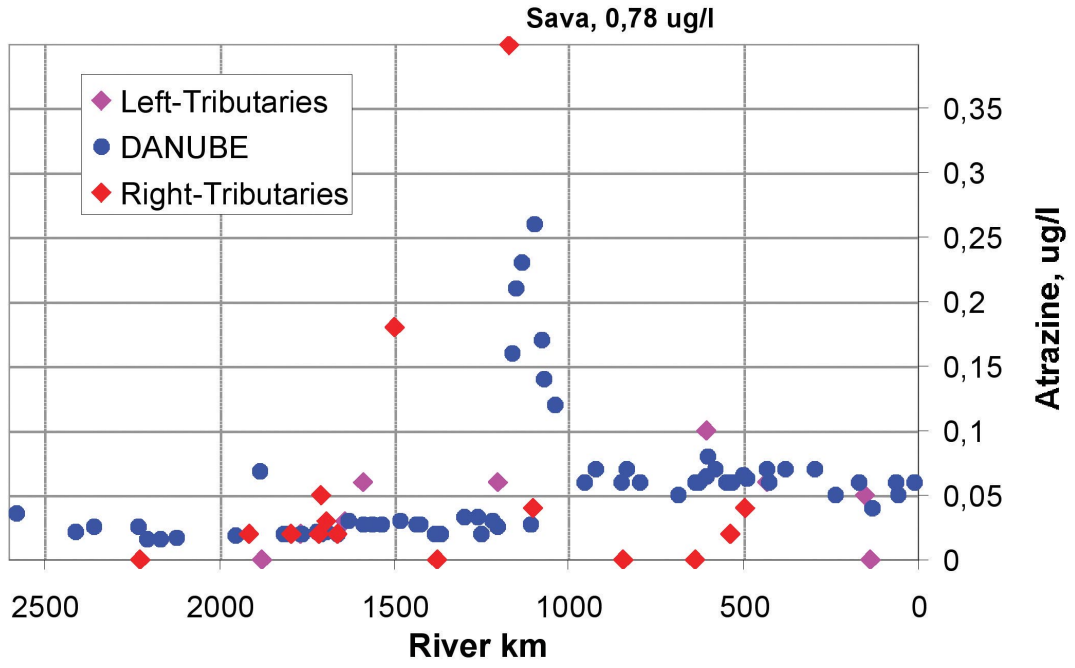

FIGURE C2.4.4.-1: Atrazine concentrations in the Danube and its tributaries

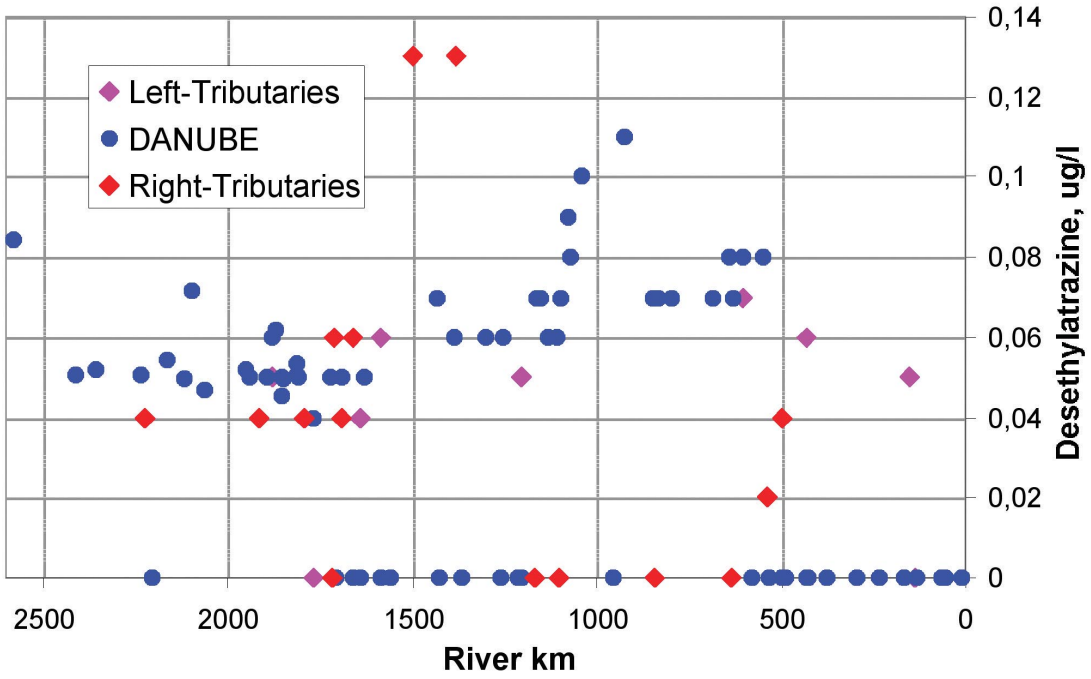

FIGURE C2.4.4.-2: Desethylatrazine concentrations in the Danube and its tributaries

These few positive results are mostly due to the sampling time in summer between August 13th and September 18th. In this summer period the harvest for nearly all important cultures is finished and there is no reason for pesticide application in the fields. So an exposition of the Danube or its tributaries through run-off or drains from agricultural areas can not be expected.

Atrazine was (and in some countries is) a herbicide predominantly used in big amounts in corn fields over decades. It is well known that many soils now contain Atrazine-residues and also residues of the degradation-product Desethylatrazine in the mg/kg-concentration range. This is possible even if the last application was about ten years ago. The residues of Atrazine and Desethylatrazine are eluted continously from the soil and can therefore be found in ground water and surface water on a regular basis.

During JDS Atrazine and Desethylatrazine were found all along the Danube. Atrazine was determined predominantly in the range of 0,02-0,07 µg/l, Desethylatrazine in the range of 0,04-0,08 µg/l. So only few samples show values above the 0,1 µg/l target value, set up by the Rhine commission (IKSR), for Atrazine concerning drinking water purposes and aquatic organisms.

The ratio between Atrazine and the degradation product Desethylatrazine (ratio mostly <1!) proofs the assumption, that there was no recent application of Atrazine. The given concentrations can be regarded as background values, which is confirmed by the results from TNMN during the last years (as far as the data are available). During the Burgund survey in 1998 (sampling between Kelheim and Budapest) Atrazine and Desethylatrazine were found in very similar concentrations (e.g. maximum for atrazine: 0,05 µg/l).

Only the few JDS results above this background value might be explained by recent applications. In Sisak, a town on the river Sava there is an Atrazine-producing factory which might be responsible for the high value in the Sava (JDS56).

In general, the tributaries show higher Atrazine concentration than the water-rich Danube itself. This can be seen from the comparison of the values for the Danube above the tributaries and the tributaries themselves (Table 2.4.4.-1).

TABLE C2.4.4.-1: Comparison of Atrazine-concentrations (µg/l) in tributaries and the adjoined upstream JDS Danube sampling site

Danube sampling site upstream of tributary		Tributary	
JDS41 = Paks	0.03	JDS42 = Sio	0.18
JDS53 = upstream Tisza	0.03	JDS54 = Tisza	0.06
JDS55 = upstream Sava	0.03	JDS56 = Sava	0.78
JDS76 = upstream Olt	0.06	JDS77 = Olt	0.10

The highest value for Atrazine was detected in the tributary Sava with 0,78 µg/l. This high value has an influence on the Danube down to the Iron Gate reservoir (JDS65 = Golubac/Koronin).

The maximum value for Atrazine for the tributary Sava and the elevated values for the Danube down to the Iron Gate were confirmed by GC-MS-analysis done by an independent laboratory (see chapter 5.2.4.8.1).

Concerning Desethylatrazine there are less values above the background value. At the sampling site JDS42 (tributary Sio) the elevated concentration (0,13 ffig/l) corresponds to the value for Atrazine (0,18 ffig/l). In the stretch of the Danube downstream Sava, where Atrazine-values are significantly high, the respective Desethylatrazine-values are not higher, so that a recent emission of Atrazine possibly from the Atrazine-producing factory is proved.

5.2.4.5 Organochlorine Compounds

Organochlorine compounds were analyzed in 63 suspended solids, 187 bottom sediment samples and 143 mussel samples.

5.2.4.5.1 DDT

The average DDT (pp'DDT) concentration in the sediment of the Danube river was 0.0059 mg/kg. Sediment along the German and Austrian section of the river had low pp'DDT content, less than 0.005 mg/kg (N.B. The Canadian limit value for total DDT is 0.007 mg/kg). Concentrations above 0.01 mg/kg were found in the middle and the lower river Reaches as shown in Figure C2.4.5.-1. The maximum value (0.029 mg/kg) was measured at Calafat (rkm 795), on the right bank.

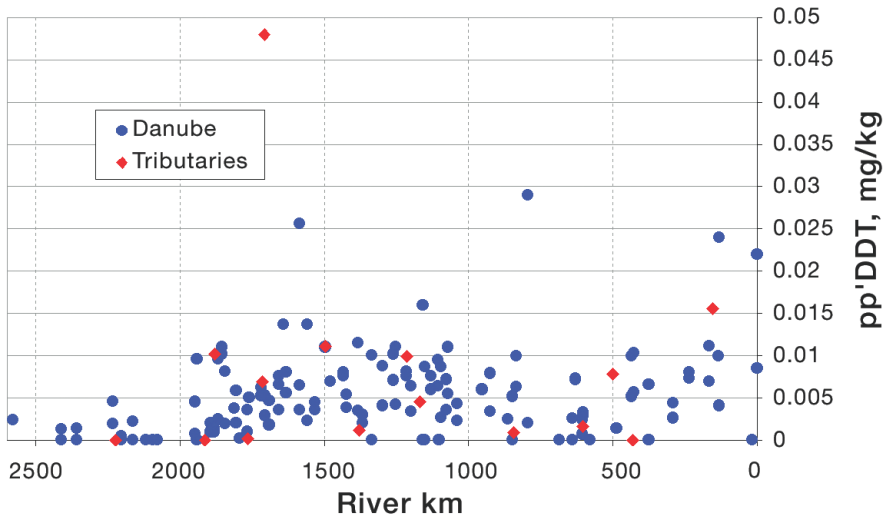

FIGURE C2.4.5.-1: Variation in the concentrations of pp'DDT in the bottom sediments collected from the Danube and its tributaries during the JDS

The pp'DDT levels in the sediments of the tributaries were not very much different from the Danube. The highest concentration (0.048 mg/kg) was measured in the Ipel/Ipoly, however, its expected affect on the Danube sediment, downstream of the Ipel/Ipoly confluence, was not observed.

In the suspended solids of the Danube the pp'DDT mean concentration was approximately two times higher than in the bottom sediment. The highest value was found at Reni (rkm 132) in the Chilia arm of the Danube Delta.

In the suspended solids of the tributaries no remarkable high value of pp'DDT was measured. The highest concentration (0,05 mg/kg) was found in the Siret.

In the mussels wide concentration variation – between 0.02 – 28 μg/kg – was typical in all Danube sections and tributaries as shown in Figure C2.4.5.-2.

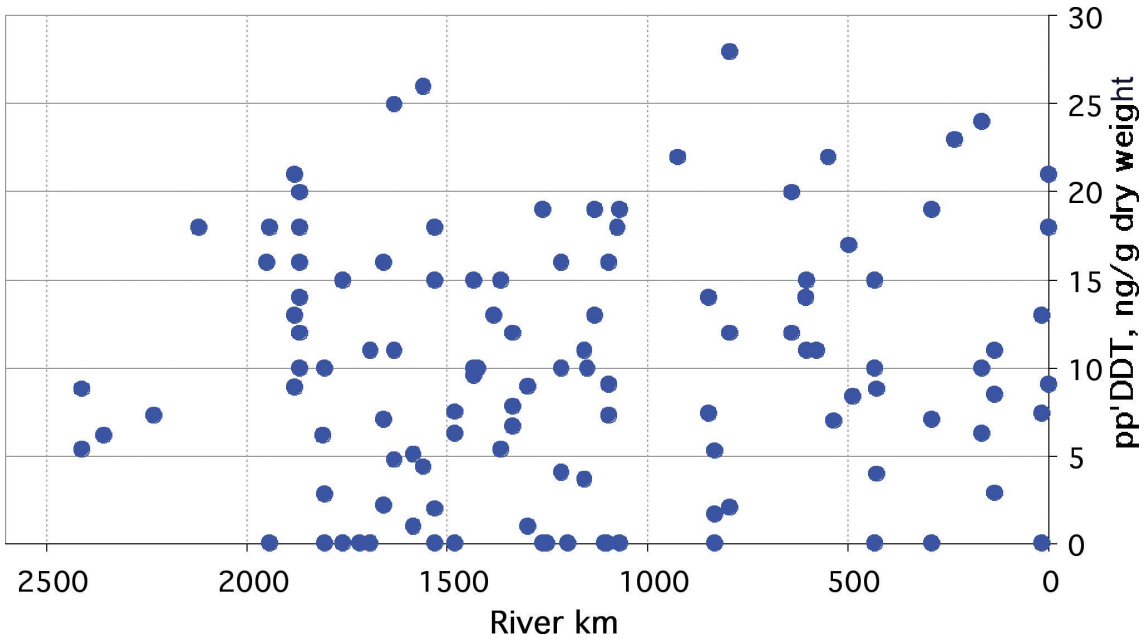

FIGURE C2.4.5.-2: Variation in the concentrations of pp'DDT in the mussel samples collected from the Danube and its tributaries during the JDS

The maximum pp'DDT concentration in mussels was found in Unio Tumidus at Calafat (rkm 795). It should be noted that the sediment pollution level for pp'DDT was also the highest at Calafat.

The results obtained in both matrices indicate that the DDT contamination is very low in the upper Danube Reach, but significantly variable along the middle and lower Reaches.

5.2.4.5.2 Lindane

Lindane concentrations in Danube sediment had 0.0012 mg/kg mean value. The highest concentrations were measured downstream of Belgrade as shown in Figure C2.4.5.-3. Concentrations measured in the tributaries upstream or at Belgrade, e.g., Tisza and Sava, do not indicate significant inputs. The maximum concentration was found downstream of Pancevo (1151 rkm). Even these concentrations are much lower than the Dutch target value (0.05 mg/kg) for Lindane in sediment. In some of tributaries (in the Hron, Olt and Arges) the Lindane content of the sediment slightly exceeded the Dutch limit value.

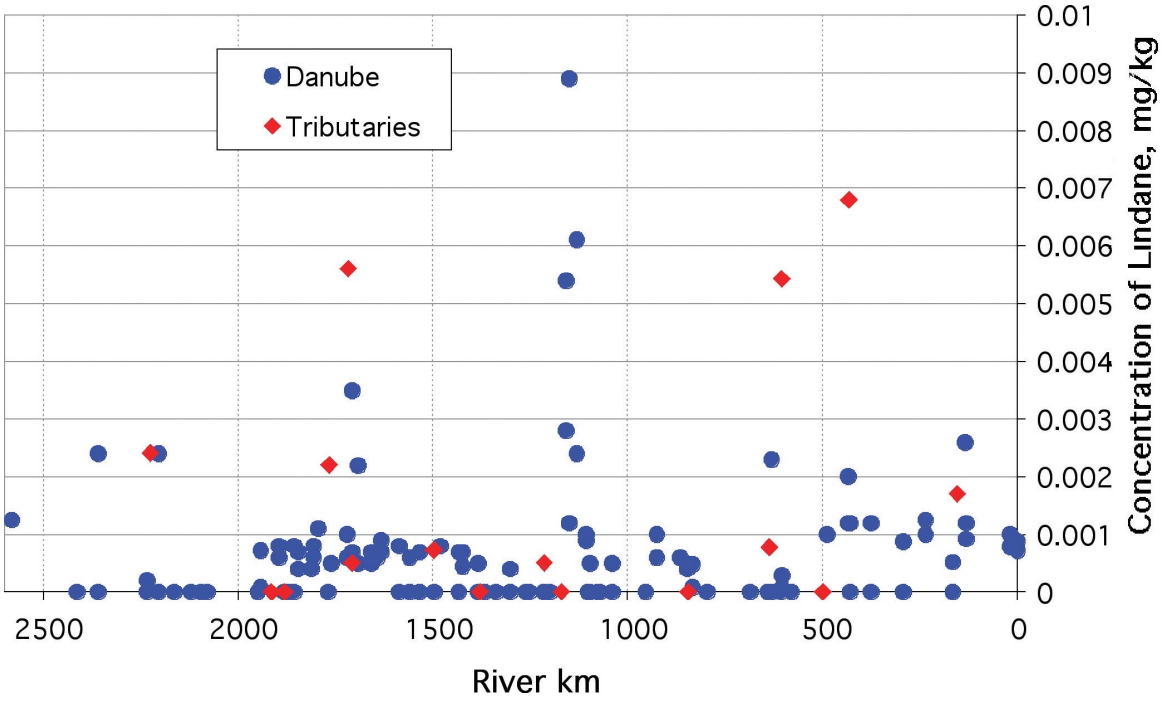

FIGURE C2.4.5.-3: Variation in the concentrations of Lindane in the bottom sediments collected from the Danube and its tributaries during the JDS

In the suspended solids of the Danube and tributaries the mean Lindane concentration was lower than in the bottom sediment.

The Lindane concentration varied between 0.01-24 µg/kg in the mussels of the Danube and tributaries. No characteristic concentration distribution was found. The highest Lindane content (24 µg/kg) was in an Unio Tumidus species in the Iron Gate reservoir at 1040 rkm.

5.2.4.5.3 Hexachlorobenzene (HCB)

HCB concentration in the sediment of the Danube River and its tributaries varied between < 0.0001-0.023 mg/kg. The highest concentration was measured in the sample collected from upstream of Budapest (1659 rkm). This concentration slightly exceeded the Canadian "Lowest Effect Level" for HCB in sediment. Characteristic concentration distribution was not found in the Danube.

The mean HCB concentration in the suspended solids of the Danube and its tributaries was similar to the mean in the sediment. The maximum value, 0.0069 mg/kg was found in the Siret river.

In mussels the HCB concentrations were between 0.01-8.4 µg/kg. The highest values were in an Anadonta Anatina mussel from the Sf Gheorghe Danube arm of the Danube Delta.

5.2.4.5.4 Pentachlorobenzene

Most of the Pentachlorobenzene concentrations were below 0.01 mg/kg in the sediment of the Danube and its tributaries. The concentration range was < 0.0001-0.017 mg/kg, the maximum value was measured in the bottom sediment sample upstream of the Drava river, right bank.

The mean Pentachlorobenzene concentrations in the suspended solids were not very different from the concentrations in the bottom sediment. In the Danube river the maximum (0.028 mg/kg) was at Hercegszántó (1434 rkm). The highest Pentachlorobenzene concentration in suspended solids of the tributaries (0,012 mg/kg) was in the Sio (confluence at 1497 rkm). The impact of the load from the Sio can be suspected on the Pentachlorobenzene concentration in the sediment of the Danube downstream of the Sió confluence.

Pentachlorobenzene concentrations varied between 2.3-115 μg/kg in mussel samples. The maximum was measured in Unio Tumidus species collected from the Danube at JDS-68, upstream of the Timok (849 river km.).

5.2.4.5.5 Hexachlorobutadiene

Hexachlorobutadiene concentrations were below the detection limit in all suspended solids and sediment samples except the sediment from the Danube downstream Budapest, at JDS-37, left side (1632 river km.).

In mussels Hexachlorobutadiene was found above the 0.01 μg/kg detection limit only in an Anadonta Anatina sample (1.2 mg/kg) from Danube at JDS-46 site, upstream of Drava (1384 river km.).

5.2.4.5.6 Polychlorinated biphenyls (PCBs)

The sum of the seven analyzed PCB congeners was below 0,005 mg/kg in most of the bottom sediment and suspended solid samples. 0.005 mg/kg is the Elbe target value for each PCB. The highest PCB-28 value (0.061 mg/kg) was measured at the Gabcikovo reservoir entrance, JDS-18 (at 1856 river km.) as shown in Figure C2.4.5.-4.

The results during the JDS showed the following trends: (a) the PCB concentration were very low along the upper Danube Reach as well as downstream of the Iron Gate dam, and (b) significant variation was observed in the middle Danube Reach and in the second part of the lower Danube Reach.

Particularly the low concentrations in the upper Danube Reach were surprising because during the Cousteau Danube survey in 1991/2 characteristically demonstrated deceasing concentrations along the Danube, and the highest values were found in the more industrialized upper Danube Reach.

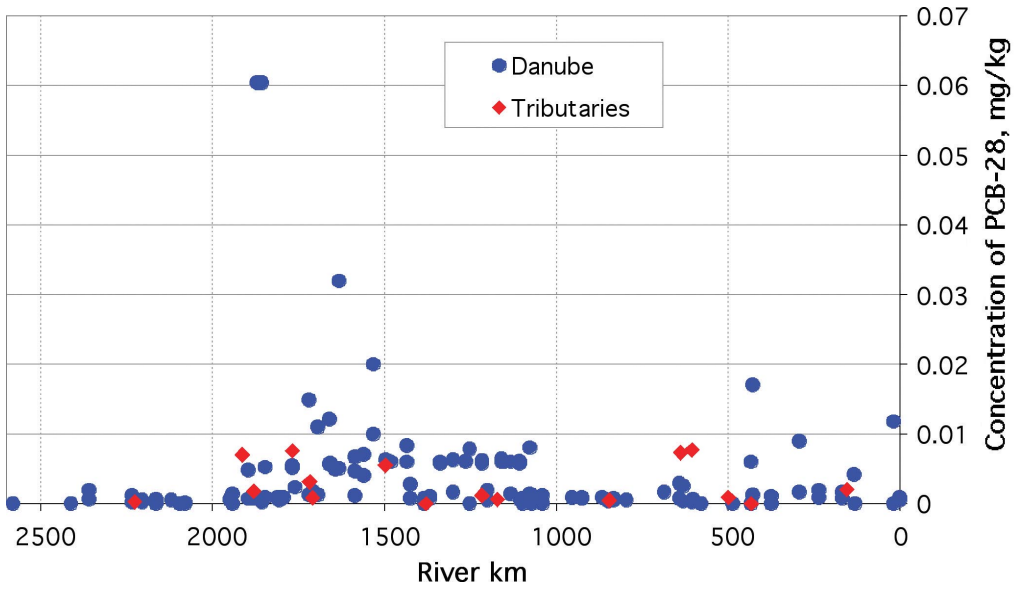

FIGURE C2.4.5.-4: Variation in the concentrations of PCB-28 in the bottom sediments collected from the Danube and its tributaries during the JDS

In the suspended solid samples the sum of the concentrations of the seven analyzed PCB congeners were significantly lower than in the bottom sediment. The concentrations of PCBs were similar to those measured during the Burgund survey.

The mussel results show significant bioaccumulation of PCBs. The ratio of mean total PCB concentration in mussel to the bottom sediment was 6.6.

5.2.4.6 Other WFD Priority Pollutants

During the JDS, 63 suspended matter samples and 187 sediment samples (including 26 core samples) were taken from river Danube and its major tributaries and arms. The dried samples were analysed on the occurrence of the organic compounds para-tert.-octylphenol (OP), para-nonylphenol (NP), di(2-ethylhexyl)phthalate (DEHP), pentachlorophenol (PCP), and pentabromodiphenyl ether (PBDE). Furthermore, Tributhyltin (TBT) was also analysed in the same samples.

A summary of the compounds found in the sediments and suspended matter samples of the river Danube is given in Tables C2.4.6.-1 and C2.4.6.-2.

TABLE C2.4.6.-1: Concentration levels of OP, NP, DEHP, PBDE, PCP and TBT in sediment samples from river Danube and its tributaries

Compound	Concentration Range, mg/kg		Maximum Concentration, mg/kg	
	Danube	Tributaries	Danube	Tributaries
OP	< LOD - 0.84	< LOD - 1.7	0.84 (JDS57)	1.7 (JDS30)
NP	0.016 - 6.8	0.06 - 160	6.8 (JDS2)	160 (JDS84)
DEHP	0.1 - 25	< LOD - 170	25 (JDS86)	170 (JDS87)
PBDE	< LOD	< LOD		
PCP	< LOD	< LOD		
TBT	< LOD - 0.009	< LOD - 0.04	0.009 (JDS92)	0.04 (JDS84)

TABLE C2.4.6.-2: Concentration levels of OP, NP, DEHP, PBDE, PCP and TBT in suspended solids samples from river Danube and its tributaries

Compound	Concentration Range, mg/kg		Maximum Concentration, mg/kg	
	Danube	Tributaries	Danube	Tributaries
OP	< LOD	< LOD		
NP	< LOD – 0.2	< LOD – 1.4	0.2 (JDS55)	1.4 (JDS61)
DEHP	0.021 - 3.0	0.23 – 2.4	3.0 (JDS3)	0.23 (JDS56)
PBDE	< LOD	< LOD		
PCP	< LOD	< LOD		
TBT	< LOD – 0.009	< LOD – 0.04	0.009 (JDS28)	0.04 (JDS56)

It can be seen from the data in Tables C2.4.6.-1 and C2.4.6.-2, that pentabromodiphenyl ether and penta-chlorophenol were neither found in the bottom sediment nor in the suspended solid samples under investigation. All other compounds were detected in at least one sample and, hence, will be discussed in detail.

Octylphenol (OP)

Para-tert-Octylphenol (OP) was not found in suspended solids but in half of the sediment samples. Concentration levels in sediments were between 0.005 and 1.7 mg/kg, but levels above 0.1 mg/kg were only rarely found (Figure 2.4.6.-1). The highest values were found in the tributaries Ipoly (1.7 mg/kg) and Iskar (1.4 mg/kg). An accumulation of values >0.1 mg/kg was detected between JDS53 and JDS62 including the tributaries Tisza and Sava. The results for the two sediment cores at JDS36 and JDS63 show a decreasing OP concentration from older to new sediment layers. At JDS2 (Kelheim, right bank of a sidearm of the Danube carrying water of the tributary Altmühl - in the Danube itself no sediment could be taken!) and at JDS32 (left bank) elevated concentrations were analysed which do not agree with the low concentrations at nearby sampling sites, which is a hint for local point sources.

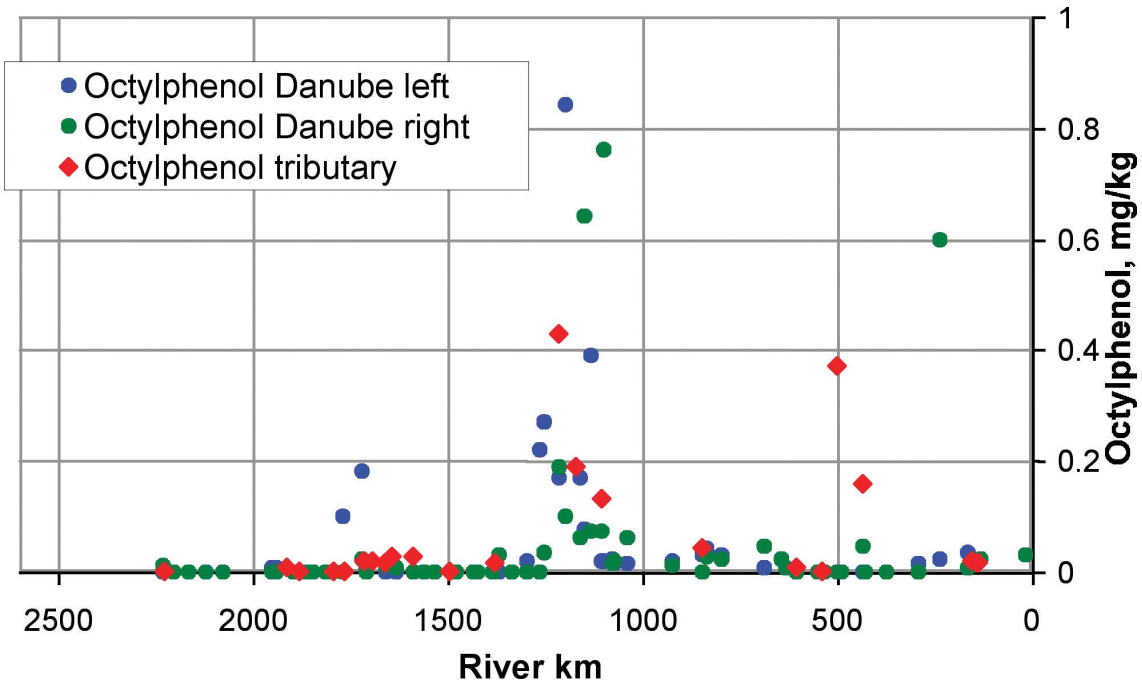

FIGURE 2.4.6.-1: Variation in the Octylphenol concentrations in the bottom sediments collected from the Danube and its tributaries during the JDS

Nonylphenol (NP)

4-iso-Nonylphenol (NP) was found in sediment samples and suspended solids as well in significantly higher concentrations than OP. Concentration levels are given in Figure 2.4.6.-2 and 2.4.6.-3. It can be seen that NP concentrations in sediments were mainly between 0,05 and 0,3 mg/kg. A few "hot spots" could be identified: the highest concentrations were 160 mg/kg (JDS84, Russenski Lom, tributary), 46 mg/kg (JDS87, Arges, tributary), 6.8 mg/kg (JDS2, Kelheim, sidearm of the Danube!) and 2.8 mg/kg (JDS88, downstream Arges). In these areas the sources for NP should be located. NP concentrations in suspended solids were significantly lower than in sediments (usually <0.1 mg/kg).

The hot spots for NP in suspended solids and in sediments do not correspond. The highest value was 1.4 mg/kg at JDS61 (Velika Morava, tributary). Most of the higher concentrations were found in the Yugoslavian section of the Danube (the same was found for OP and NP in sediments) which is a hint for the use of alkylphenol-containing surfactants in this region.

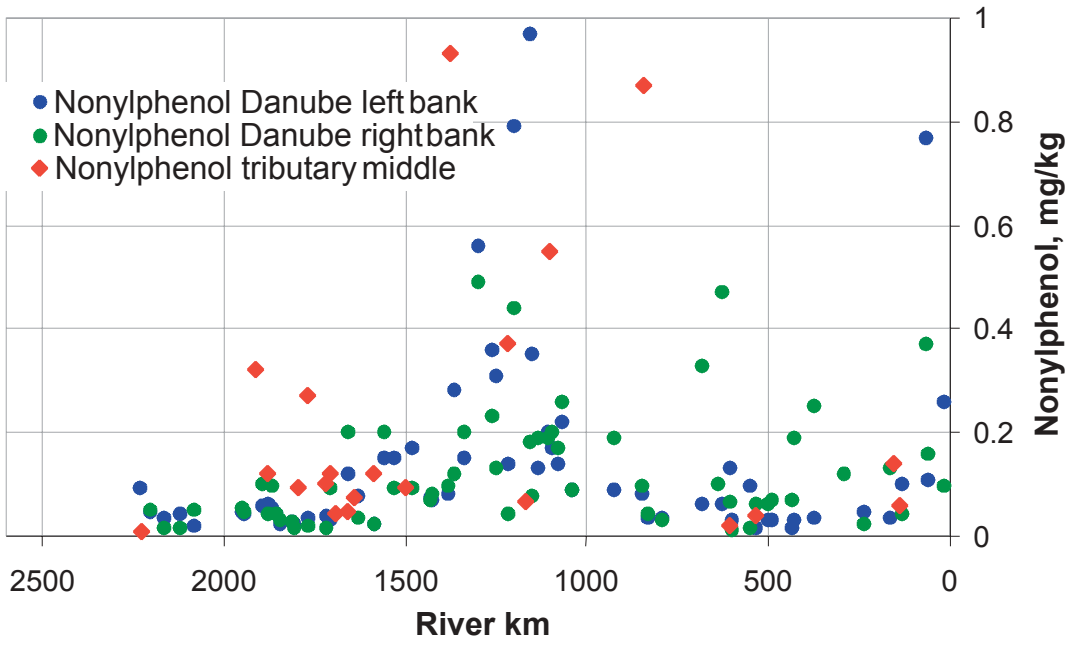

FIGURE 2.4.6.-2: Variation in the Nonylphenol concentrations in the bottom sediments collected from the Danube and its tributaries during the JDS

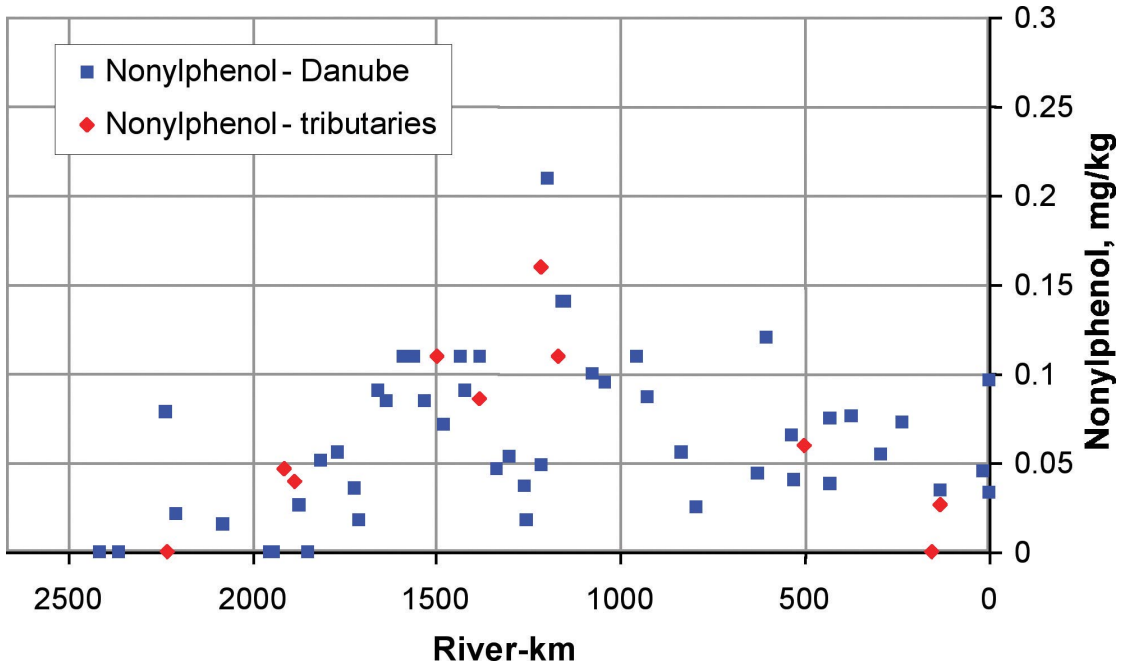

FIGURE 2.4.6.-3: Variation in the Nonylphenol concentrations in the suspended solids collected from the Danube and its tributaries during the JDS

From their use in surfactants and their similar behaviour in the aquatic environment the concentrations of OP and NP should correspond in sediment samples. Figure 2.4.6.-4 shows the values for NP at those sampling sites where OP is high but a clear relationship cannot be stated.

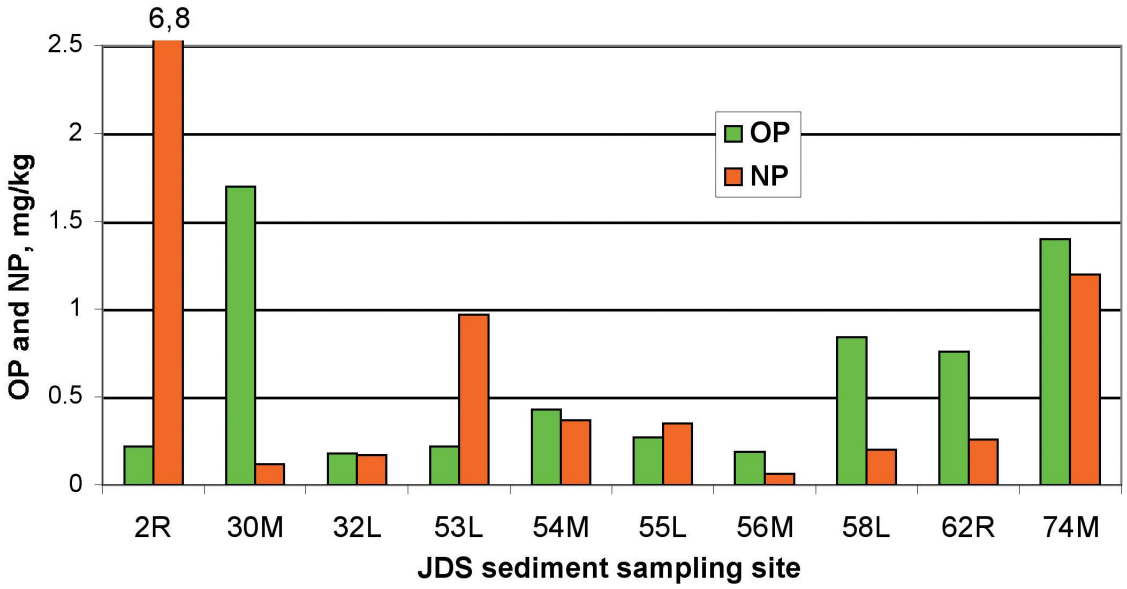

FIGURE 2.4.6.-4: Comparison of OP and NP concentrations in sediments at sampling sites with high OP concentrations

Sediment core collected at JDS-36 (Rackeve-Soroksar Danube-arm) demonstrated decreasing OP and NP concentrations from old to new sediment (Figure 2.4.6.-5).

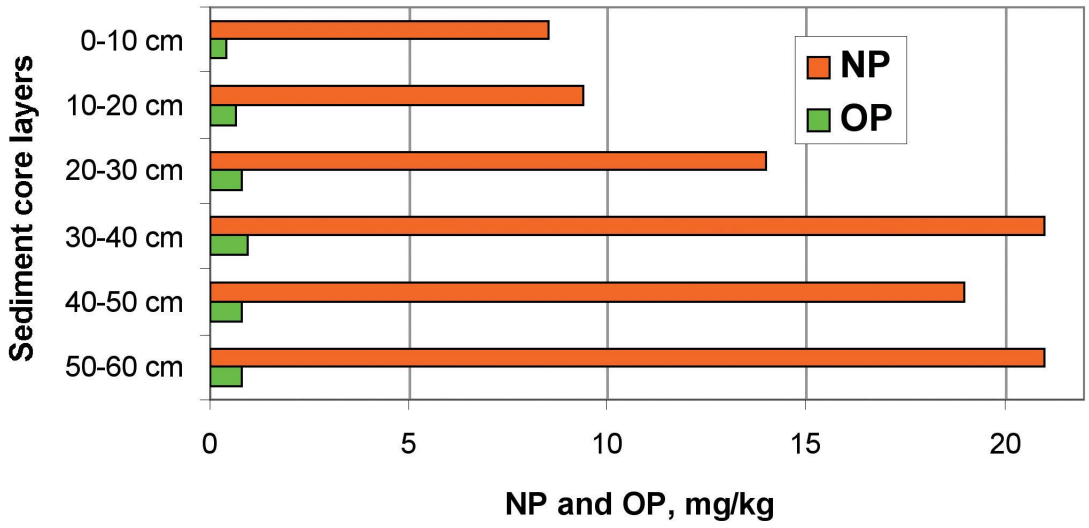

FIGURE 2.4.6.-5: Octylphenol (OP) and Nonylphenol (NP) concentrations in different layers of a sediment core collected at JDS 36

Di[ethylhexyl]phthalate (DEHP)

DEHP was found in nearly all sediment samples with a median concentration of 0.5 mg/kg

(see Figures 2.4.6.-6 and 2.4.6.-7). The hot spots were JDS-87 (Arges, tributary, 170 mg/kg), JDS-86 (upstream Arges, 25 mg/kg), JDS-88 (downstream Arges, 23 mg/kg) and JDS-84 (Russenski Lom, tributary, 17 mg/kg).

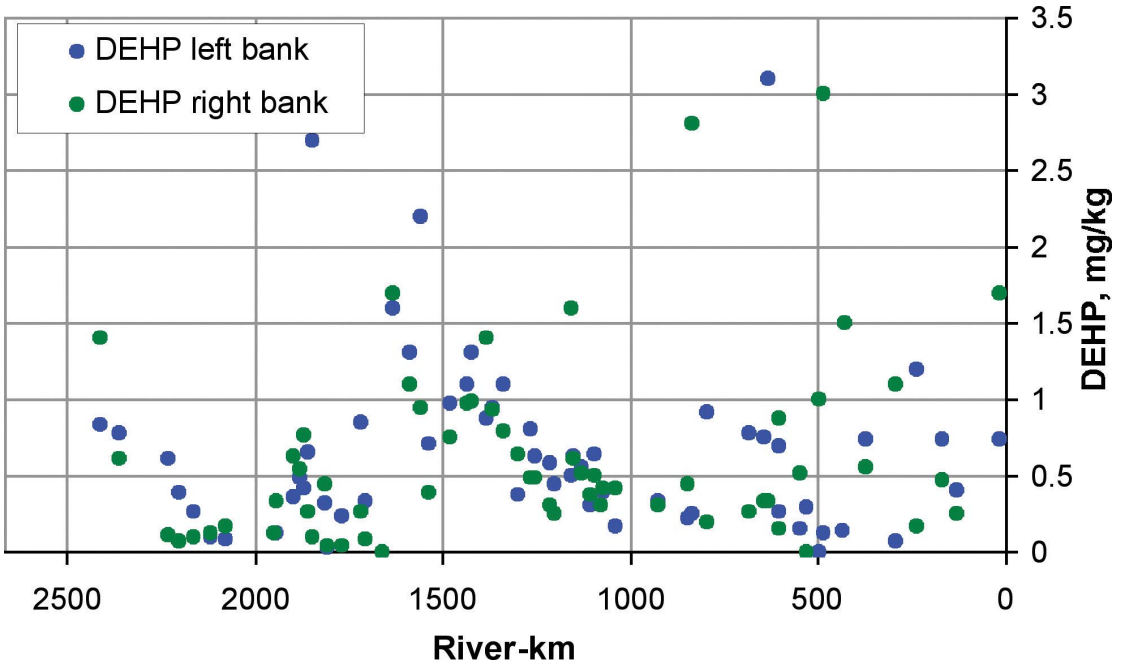

FIGURE 2.4.6.-6: Variation in the Di[ethylhexyl]phthalate (DEHP) concentrations in the bottom sediment samples of river Danube, collected during the JDS

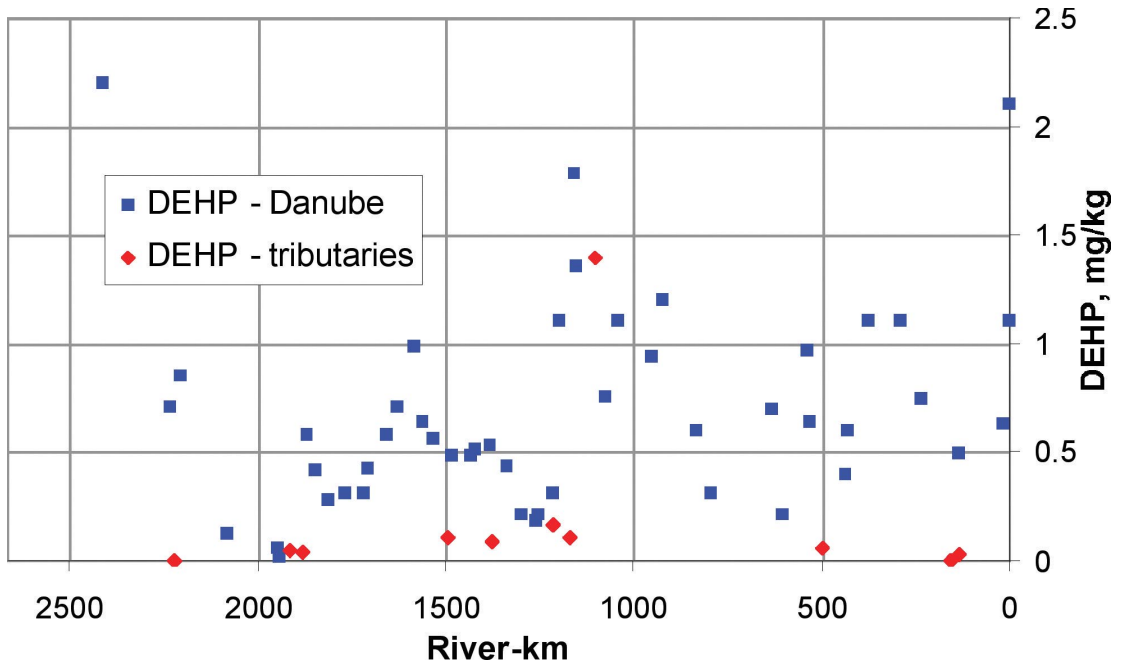

FIGURE 2.4.6.-7: Variation in the Di[ethylhexyl]phthalate (DEHP) concentrations in the suspended solids collected from the Danube and its tributaries during the JDS

At the majority of the sampling sites the DEHP concentrations are about the same at both riversides of the Danube. However, in some regions the influence of emissions from tributaries or industrial effluents on the Danube sediment can be seen.

DEHP is found in all suspended solid samples in concentrations up to 3 mg/kg. Half of the samples show DEHP-values >0.6 mg/kg. The highest concentration was found at JDS3 (upstream Geisling, 3 mg/kg). The very similar concentrations of DEHP all along the Danube reflects the wide-spread use of this substance in all countries. The sediment cores show decreasing DEHP concentrations from old to new sediment layers.

All compounds under investigation are not parameters within the Transnational Monitoring Network (TNMN) for the Danube. Thus, JDS provided the first homogeneous data set for Danube sediments and suspended solids.

Pentachlorophenol (PCP) and Pentabromodiphenyl-ether (PBDE)

Neither the bottom sediment nor the suspended solids samples collected during the JDS contained PCP or PBDE in concentration above the detection limits.

Tributhyltin (TBT)

Tributhyltin in concentrations above 10 µg/kg was found only in two sediment samples and 3 suspended solids. In 31 out of 57 suspended solids tributhyltin was not detected. The low tributhyltin results are distributed all along the Danube. At JDS 36 (Rackeve-Soroksar Danube-arm – upper end) a sediment core was taken and 6 fractions of 10 centimeters were analysed separately. All layers contained tributhyltin in concentrations around 20 µg/kg. Sediment cores at Gabcikovo reservoir and near Iron Gate (JDS 20 and 63) were very low in tributhyltin. The results of the sediment samples correspond to the results of the Burgund survey where sediment samples were taken mainly from harbour sites. In those samples tributhyltin was not higher than 25 µg/kg. From these results it must be concluded that tributhyltin was and is not used in significant amounts in the Danube catchment area.