Joint Danube Survey 2

icpdr International Commission for the Protection of the Danube River
iksd Internationale Kommission zum Schutz der Donau

Final Report on:
PAHs and petroleum hydrocarbons contamination in water, suspended particulate matter and sediments

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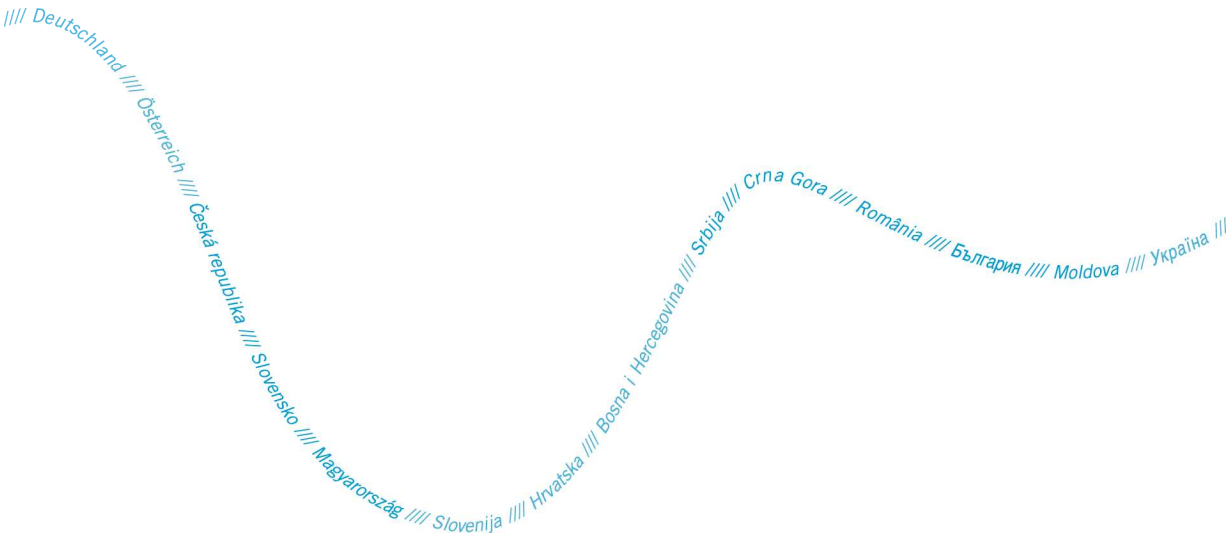

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Table of content

1 Introduction 4

2 Methods 5

3 Results 11

4 Conclusions 15

1 Introduction

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 dealing with priority substances and gives proposals for environmental quality standards (EQS) for eight PAH compounds in water samples, in addition to other organic substances and four heavy metals, and EQS for three compounds in biota. Environmental quality standards are given for different types of waters as "annual averages" and "maximum allowable concentrations."

All 33 priority substances except C10-C13-chloroalkanes (no method available) were analysed in JDS2 water samples. Most of the organic priority substances are discussed in the "Summary Report on: Priority Substances …); however, PAHs, several of them are among the 33 priority substances, are discussed together with other indicators (e.g., fluorescence fingerprints, TEM) of petroleum hydrocarbon contamination. Furthermore, heavy metals that included in the list of priority substances are also discussed in a separate Summary Report together with other heavy metals and Arsenic.

In addition to the analysis of water samples, the in-kind-contributions of the laboratories provided data for different substances, that are included and not included in the list of priority substances. also for suspended particulate matter, sediments and biota.

For most of the priority substances the limits of quantification (LOQ) were below or at the level of the environmental quality standards (EQS). For some compounds the LOQ did not meet the EQS, so that an assessment of water quality is not possible according to WFD rules. Furthermore, since **EQS values are defined for annual average (i.e., mathematical average of 12 measurements within one year), and the JDS2 provided data for single samples from August/September; therefore, the results of JDS2 are reported as an "indication of chemical status at each sampling site".**

Table 1-1 gives an overview on determinands, limits of quantification (LOQ), the corresponding EQS and the laboratories involved. For yellow labelled substances the LOQ was not sufficient for compliance checking except if at least one of the substances was quantified.

Table 1-1 LOQs of analytical methods for WFD target compounds – PAHs - in water samples in comparison to the proposed environmental quality standards

Determinand	Unit	Limit of Quantification (LOQ)	AA-EQS	Laboratory
Anthracene	µg/l	0,005	0,1	WRI Bratislava
Fluoranthen	µg/l	0,004	0,1	WRI Bratislava
Naphthalene	µg/l	0,250	2,4	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		WRI Bratislava
Benzo(ghi)perylene	µg/l	0,002	0,002 (sum of 2)	WRI Bratislava
Indeno(1,2,3-cd)pyrene	µg/l	0,002		WRI Bratislava

LOQ > EQS

2 Methods

PAHs, TEM and fluorescence fingerprints in water and other matrices (suspended particulate matter, sediment, biota) were analysed by international standardised methods whenever possible, or by validated in-house-methods.

2.1 Analysis of PAHs

PAHs were analysed in the laboratories as follows:

- Original water samples in the WRI laboratory in Bratislava, Slovakia;
- SPM samples in the WRI, T.G.M. laboratory in Brno, Czeh Republic;
- Bottom sediment samples in the WRI, T.G.M. laboratory in Prague, Czeh Republic; and
- Dissolved PAHs in water, and PAHs in SPM and bottom sediment in the EC-JRC/IES laboratories in Ispra, Italy.

2.1.1 Analysis of PAHs in water

In the WRI laboratories in Bratislava: The analysis of polycyclic aromatic hydrocarbons in water samples was performed using liquid-liquid extraction (LLE) followed by high performance liquid chromatography (HPLC) and fluorescence or UV detection using a method derived from STN EN ISO 17993. Analytes are extracted from the water sample (1 L) using n-hexane (10 mL) in an Erlenmeyer flask with a magnetic stirrer. Following a 2h extraction, the organic phase is separated using a microseparator device that also provides drying of the extract by its filtration through a layer of anhydrous sodium sulphate. The dried extract is evaporated with a stream of an inert gas to dryness and analytes are redissolved to 200 µL of acetonitrile in ultrasonic bath. 15 µL of the acetonitrile extract are injected to the Agilent HP1100 HPLC (Waldbronn, Germany). The separation of the analytes was performed on a SUPELCOSIL LC-PAH 57945 (25 cm × 2.1 mm, 5µm particle size) column (Supelco) using an acetonitrile-water elution gradient. Detection was performed for PAHs using fluorescence detection (Agilent HP 1200, Waldbronn, Germany). Quantification of analytes was made using external standard calibration curves. Naphthalene was analysed by a direct injection of a filtered water sample (100 µL) to the HPLC system. Table 2-1 shows the performance characteristics of the method used for analysis of PAHs in water.

Table 2-1 Methods used for the analysis of PAHs in water samples

Determinand	Matrix	Method	Unit	Limit of Quantification (LOQ)
Anthracene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,005
Fluoranthen	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,004
Naphthalene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,25
Benzo(a)pyrene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,002
Benzo(b)fluoranthene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,005
Benzo(k)fluoranthene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,005
Benzo(ghi)perylene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,002
Indenopyrene	water	ISO 17993 (LLE, LC-FLD)	µg/l	0,002

Legend: LLE: liquid-liquid-extraction
LC-FLD: liquid chromatography using fluorescence detector

In the EC-JRC/IES laboratories in Ispra: For the analysis of PAHs in the dissolved phase, water samples were collected on XAD 2. Extraction was done with Accelerated Solvent Extraction from 200 ml cells containing 50 g of adsorbent. First Methanol, then n-Hexane was used. Water was added to the combined extracts and the analytes were liquid/liquid-extracted by n-hexane. PAHs were analyzed without clean-up in order to reduce the blank contribution. They were analysed respectively with HRGC/LRMS and HRGC/HRMS.

2.1.2 Analysis of PAHs in SPM

The SPM sample (appr. 1g) was weighed on an analytical ballance and three-times extracted with 30 ml acetonitrile using the fexIKA extractor, based on the principle of fluidized bed extraction, FBE – the extraction material is penetrated by solvent vapour in the range of the solvent boiling point and is then extracted from the solvent condensate.

After adjusting the volume of the extract to around 2 ml with nitrogen gas, clean-up on a silica-gel column was performed. The extract volume after clean-up was adjusted to 1 ml and determination of PAHs in the extract was performed using HPLC (high-performance liquid chromatography) with fluorescence detection (FLD).

Analytical quality control for PAHs

Every batch of 20 samples included a blank extraction and a reference material extraction. As the values of all blank samples were low no blank correction was carried out.

2.1.3 Analysis of PAHs in bottom sediment

Homogenised and freeze-dried sediment samples (less than 63 μm) were stored at room temperature until they were analysed.

For extraction PLE (pressured liquid extraction) was used. Mixture of hexane/acetone 9:1 was used as organic solvent, Florisil® as a sorbent and Hydromatrix as an inert material. The temperature of the extraction was 120 °C, time of extraction cycle was 8 min with 2 cycles and flush 70 % volume.

Extracts were concentrated and after then analysed. Determination of PAHs in the extracts was carried out by liquid chromatography with fluorescent detection. Performance characteristics of the analysis are summarised in Table 2-3.

2.2 Analysis of Total Extractable Matter (TEM)

After solvent extraction, with tetrachloroethylene, of both the SPM and bottom sediment samples, TEM in was determined according to the EPA Method 413.2, using FTIR spectrophotometer. The LoD and LoQ were 1 and 10 mg/kg, respectively.

This analysis was carried out in the laboratories of VITUKI, Budapest.

Table 2-3 Methods and parameters during the determination of PAHs in sediments

Determinand	Unit	CAS No.	Method Used	Method	Limit of Quantification (LOQ)
Benzo(a)pyrene	mg/kg	50-32-8	HPLC-FD	Internal procedure	0.003
Benzo(b)fluoranthene	mg/kg	205-99-2	HPLC-FD		0.006
Benzo(g,h,i)perylene	mg/kg	191-24-2	HPLC-FD		0.003
Benzo(k)fluoranthene	mg/kg	207-08-9	HPLC-FD		0.003
Indeno(1,2,3-c,d)pyrene	mg/kg	193-39-5	HPLC-FD		0.018
Naphthalene	mg/kg	91-20-3	HPLC-FD		0.018
Anthracene	mg/kg	120-12-7	HPLC-FD		0.002
Fluoranthene	mg/kg	206-44-0	HPLC-FD		0.039
Benzo(a)anthracene	mg/kg	56-55-3	HPLC-FD		0.003
Chrysene	mg/kg	218-01-9	HPLC-FD		0.002
Dibenzo(a,h)anthracene	mg/kg	53-70-3	HPLC-FD		0.006
Fluorene	mg/kg	86-73-7	HPLC-FD		0.018
Phenanthrene	mg/kg	85-01-8	HPLC-FD		0.030
Pyrene	mg/kg	129-00-0	HPLC-FD		0.021

2.3 Determination of fluorescence fingerprints

The determination of the excitation-emission matrix (EEM), or fluorescence fingerprints, in cyclohexane extracts of water, SPM and bottom sediments samples collected during JDS2 was carried out in the laboratories of VITUKI, Budapest.

2.3.1 Sample Preparation

Water

Water samples were collected with the built-in pump of the laboratory ship. For the determination of the fluorescence fingerprints (analysis of the petroleum contamination), 100 ml original water sample was extracted on-board with 15 ml cyclohexane in a separatory funnel, the extract dried on anhydrous sodium sulphate, stored in a 7 ml vial and refrigerated until the analysis in the laboratory.

SPM and bottom sediments

After freeze-drying, a typical 1 g sample was mixed with around 1 g anhydrous sodium sulphate and was extracted with 15 ml cyclohexane by sonication for 20 minutes.

2.3.2 Analytical Method

2.3.2.1 Fluorescence Spectroscopy

Excitation Emission Matrix fluorescence spectra (fingerprints) of organic solvent (cyclohexane) extracts of water, suspended solids and bottom sediment samples were recorded according to procedures described in detail elsewhere [Literathy, 2000][1]. A Hitachi F-4500 spectrofluorimeter was used to record the fluorescence spectra in the 220-450 nm excitation and 245-475 nm emission wavelength ranges. Figure 2-1 shows fluorescence fingerprints of petroleum products and PAHs, that can be used as standards for characterization and quantification of petroleum-related environmental contamination.

2.3.2.2 Characterization of the petroleum-related contamination

Determination of contamination type was based on the degree of correlation between fingerprints of water/sediment samples and arbitrary standards and achieved by decomposing each fingerprint into 22 emission spectra (Rayleigh scattering removed) as follows:

Spectrum Number	Excitation Wavelength	Emission Range	Spectrum Number	Excitation Wavelength	Emission Range
Spectrum 1	220 nm	250-365 nm	…	…	…
Spectrum 2	225 nm	255-370 nm	…	…	…
Spectrum 3	230 nm	260-375 nm	Spectrum 19	310 nm	340-455 nm
Spectrum 4	235 nm	265-380 nm	Spectrum 20	315 nm	345-460 nm
…	…	…	Spectrum 21	320 nm	350-465 nm
…	…	…	Spectrum 22	325 nm	355-470 nm

These fluorescence emission spectra were then concatenated. Examples of the concatenated spectra are presented in Figure 2-2 for the candidate arbitrary standards.

[1] Literathy, P. (2000). Polar and non-polar aromatic micropollutants in water (drinking water) resources. 1st World Water Congress of IWA, Paris, 3-7 July, 2000, Conference Preprint Book 2, 71-78; Wat. Sci. Tech.: Water Supply, **1**(4), 149-157.

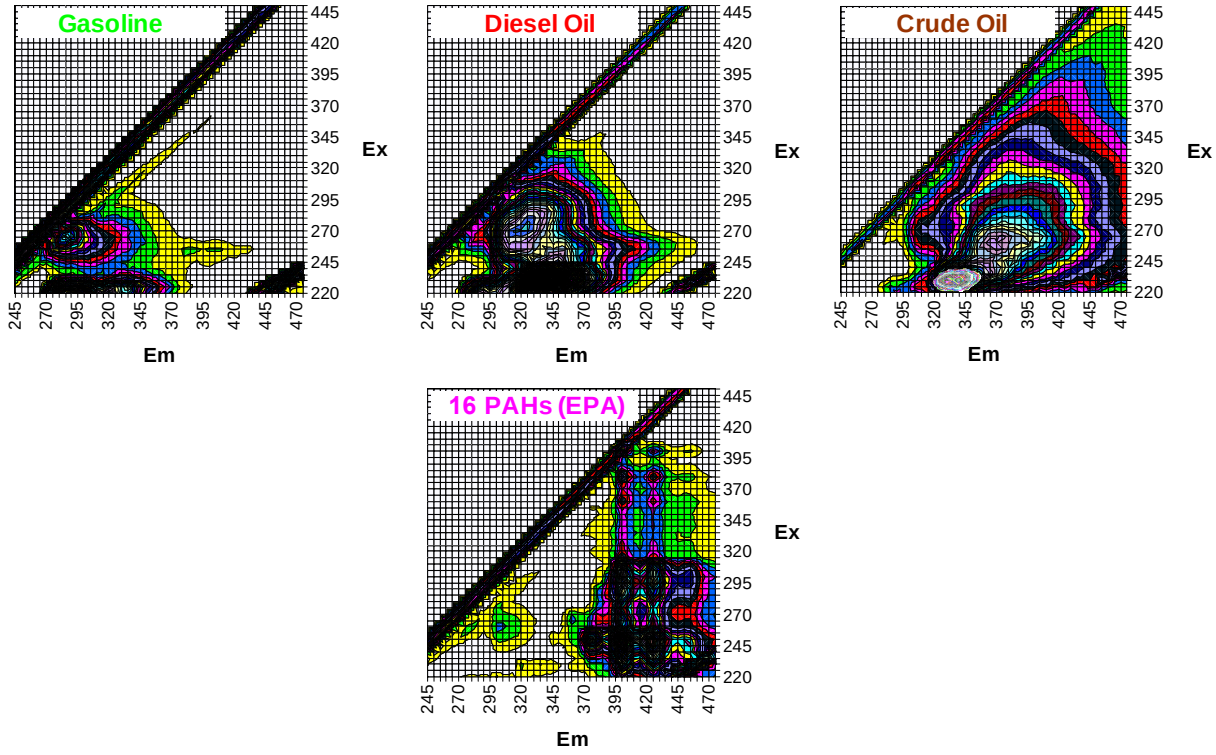

Figure 2-1. Fluorescence fingerprints (contour diagrams) of selected arbitrary – calibration - standards for analysis of petroleum hydrocarbons (Gasoline, Diesel Oil and Crude Oil, each 1 µg/ml, and mixture of 16 PAHs (EPA), each 3 ng/ml, in cyclohexane).

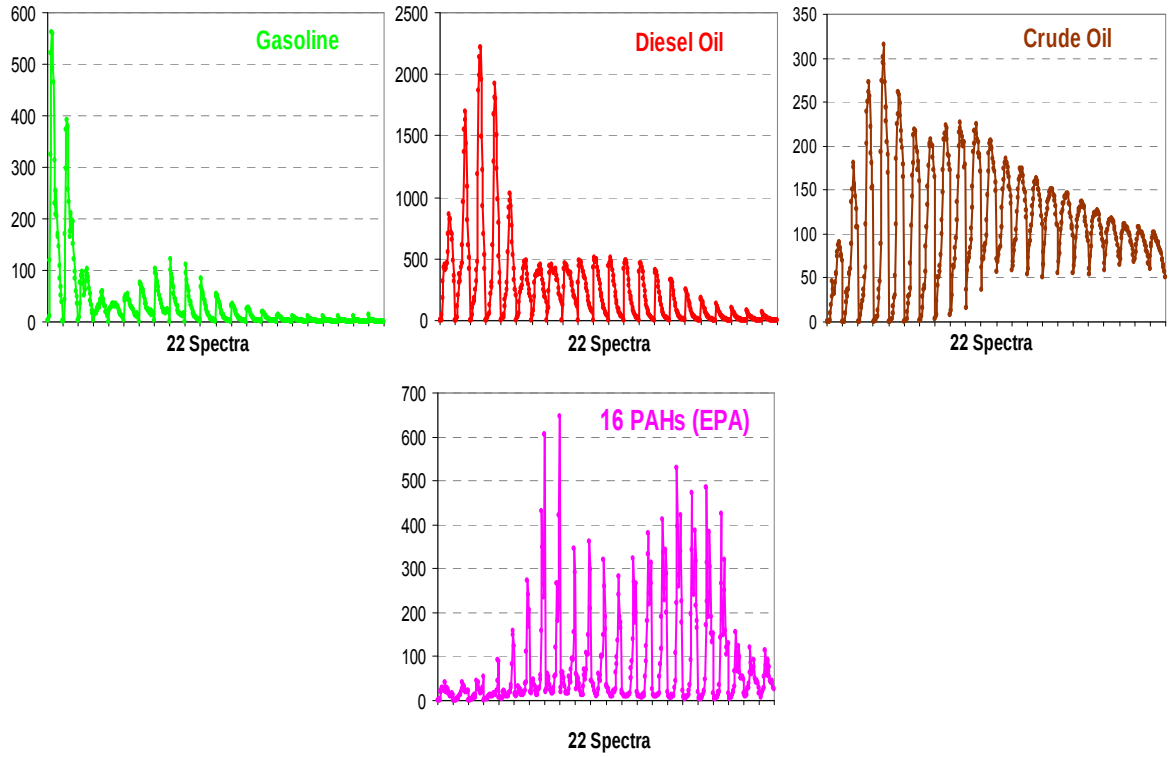

Figure 2-2. Concatenated spectra for the different types of petroleum-related standards, created from the fluorescence fingerprints of the standards shown in Figure 1.

Based on the patterns recognized in the fluorescence fingerprints and on the degree of correlation (quantified as correlation coefficients) between the concatenated spectra of the real world samples and the arbitrary standards, the best matching with the gasoline, diesel oil or crude oil could be used for characterization of the type of oil pollution in environmental sample extracts. Table 2-4 shows the correlation between the arbitrary standards, indicating the significant differences among these standard materials, which will ensure proper characterization of the type of, and differences in the contamination of the real-world samples.

Table 2-4. Correlation coefficients of the concatenated spectra of the arbitrary standards

	Gasoline	Diesel Oil	Crude Oil	16 PAHs (EPA)
Gasoline	1	0,34928	-0,30243	-0,21729
Diesel Oil	0,34928	1	0,285306	-0,30086
Crude Oil	-0,30243	0,285306	1	0,279949
16 PAHs (EPA)	-0,21729	-0,30086	0,279949	1

The level of contamination can be quantified by the fluorescence intensities (FI) at specific characteristic excitation and emission wavelengths. The fluorescence intensities shown in Table 2-5, revealed that the maximum FI of: (a) the gasoline is matching with the maximum FI of benzene; (b) the diesel oil is matching with the highest FI of naphthalene; and (c) the relatively high FI of the diesel and crude oils are matching with the highest FI of chrysene. These could be used as calibration standards. As each standard has a given fluorescence intensity at the Ex/Em wavelength characteristic of the others, therefore, FI ratios, between two calibration standards can be calculated and also used for further characterization of the type of the oil pollution.

Table 2-5. Relative fluorescence intensity of aromatic hydrocarbons and petroleum products, (each 1 µg/ml in cyclohexane) at their characteristic Ex/Em wavelengths.

Compound/Product	Characteristic Excitation/Emission Wavelength, nm		
	260/290	275/335	270/380
Gasoline	**13**	3.8	0.6
Diesel Oil	8.9	**44**	12
Crude Oil	0.8	8.6	**20**
Benzene	**48**	6.0	0.3
Naphthalene	0.3	**85**	2.1
Chrysene	0.2	3.0	**451**

3 Results

3.1 PAHs in water, SPM and bottom sediment

3.1.1 PAHs in water

Most of the PAH in water samples were below the LOQ and far below the AA-EQS values. Danube laboratories quantified some of the PAH substances. The results reveled that the AA-EQS values were exceeded as follows:

- Benzo(g,h,i)perylene alone, without adding the Indeno(1,2,3-cd)pyrene (as indicated in the AA-EQS), exceeded the AA-EQS in the Velika Morava river (JDS56), and
- The sum of the Benzo(b)fluoranthene plus Benzo(k)fluoranthene, and the Benzo(g,h,i)perylene plus Indeno(1,2,3-cd)pyrene exceeded the AA-EQS in the upper section of the Tisa tributary (JDS-TI4).

In addition to the Danube laboratories, the EC-JRC/IES laboratory also analyzed water samples for PAHs and the results revealed that the sum of Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene exceeded the AA-EQS value in five Danube water samples out of the analyzed 23.

3.1.2 PAHs in suspended particular matter and bottom sediments

In the samples collected along the Danube from the 96 JDS2 stations, the concentrations of total PAHs varied between 260 to 1230 µg/kg in the SPM and between 130 to 1850 µg/kg in the bottom sediments. The highest value of total PAHs in the bottom sediments samples was observed in the tributary Morava river (JDS-MO1, at Lanzhot). The concentration of the total PAHs was 5150 µg/kg. This is significantly lower than the maximum (~ 16000 µg/kg) measured during JDS1.

The proposed replacement of Annex X of Directive 2000/60/EC recommends the priority substance Fluoranthene as an indicator of other, more dangerous PAHs. In addition, the proposed Priority Substance data sheet (under serious revision) provide EQS for Benzo(a)pyrene and Benzo(k)fluoranthene for SPM. The corresponding concentrations of these substances for protecting the pelagic community in freshwater are 2940 and 326 µg/kg, respectively. Taking into account these proposals, Figures 3-1 and 3-2 show the longitudinal variation in the concentration of Fluoranthene, and the Benzo(a)pryrene and Benzo(k)fluoranthene, respectively, in the SPM.

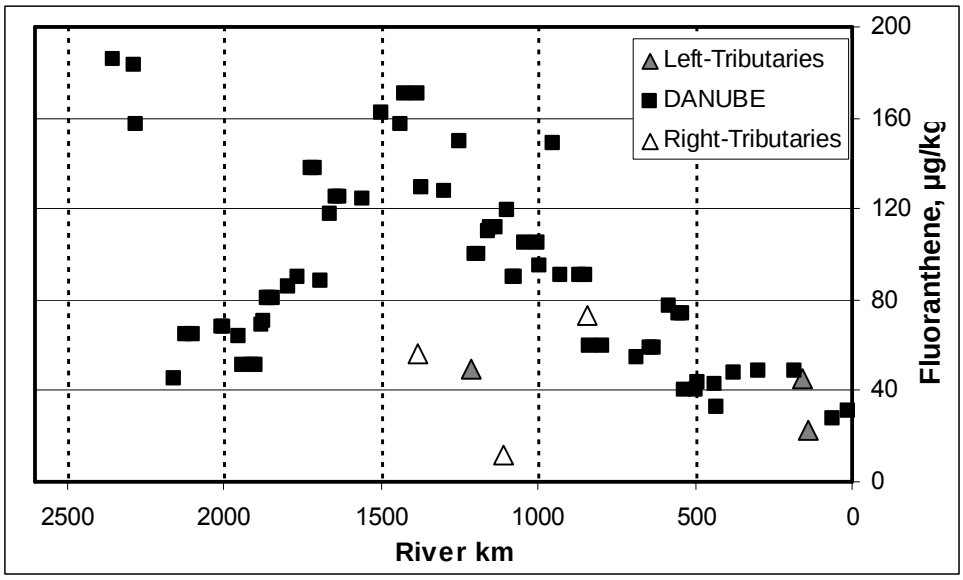

Figure 3-1 Longitudinal variation in Fluoranthene determined in SPM during JDS2

The longitudinal profile of Fluoranthene (Figure 3-1) indicates the highest concentration in the upper Danube reach; however, after a sudden decrease a hump developed along the middle section of the Danube. This distribution pattern is typical for the sum of PAHs as well as the variation in the concentration of the other two PAH compounds, Benzo(a)pyrene and Benzo(k)fluranthene as it is shown in Figure 3-2.

Comparing the concentrations of these two PAH compound with the proposed EQS for SPM, the results indicated that even the maximum concentrations were far below the recommended limit values, i.e., the maximum concentration of Benzo(a)pyrene was more than 20-times less than the EQS, and the concentration of Benzo(k)fluoranthene was about one-fifth of the proposed EQS for SPM.

The concentration of all the three PAH compound was higher in the SPM of the Danube than in the tributaries. The variation in the concentration of the characteristic compound, Fluoranthene, in the bottom sediment is shown in Figure 3-3. Although the overall concentration levels were very similar in the two matrices, but in the bottom sediment of the tributaries contained significantly higher concentration compare to the Danube, reaching the highest measured value of 853 µg/kg in the Iskar river. This indicate the fact that PAHs are accumulating and reaching high concentrations in the bottom sediments of the tributaries and which were not resuspended and transported in the SPM during the low water conditions of the survey. However, they are potentially there in the bottom sediment and could be re-suspended and transported to the Danube during floods.

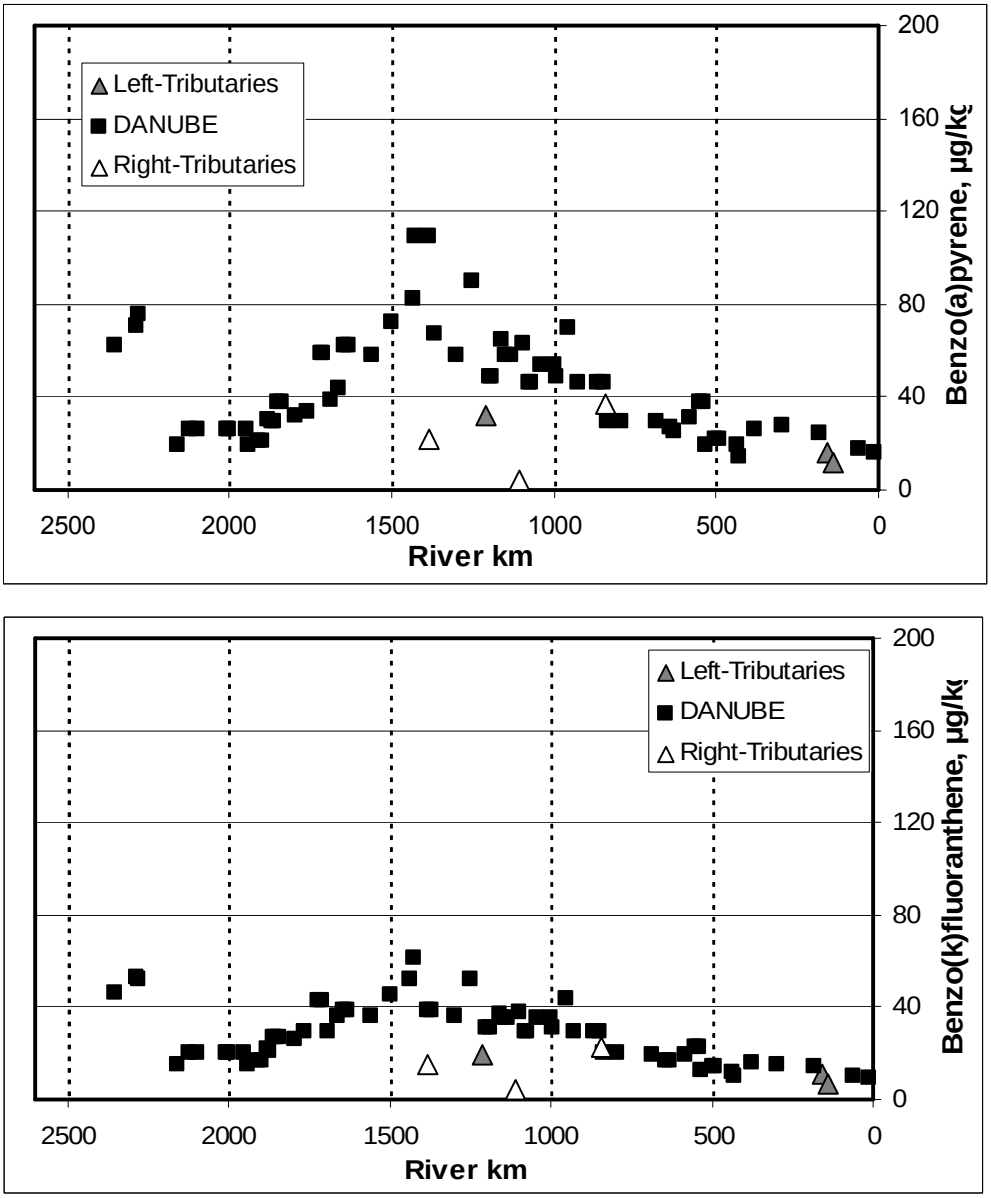

Figure 3-2 Longitudinal variation in Benzo(a)pyrene and Benzo(k)fluoranthene determined in SPM during JDS2

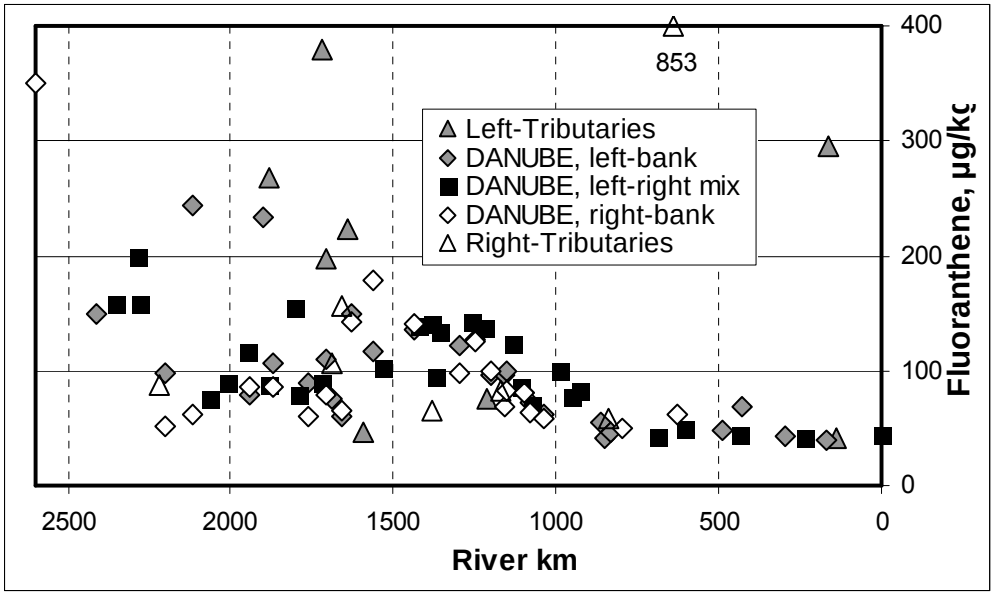

Figure 3-3 Longitudinal variation in Fluoranthene determined in bottom sediment during JDS2

Furthermore, the concentration varied significantly in the bottom sediments along the upper and middle section of Danube and significantly decreased and showed quite uniform distribution downstream the Irongate.

In overall, the concentration levels of the characteristic PAH compounds in both the SPM and the bottom sediment do not show significant problems requiring major concerns. Comparison with the data obtained within JDS1 indicates that there is certain improvement in the central part of the Danube itself, while the tributaries showed higher fluctuation during JDS2.

3.1.3 PAHs Analyzed by EC-JRC/IES

In addition to the Danube laboratories, Ec-JRC6IES also analyzed PAHs in all of the requested samples, which were significantly differed (were less) than those analyzed in the Danube laboratories. The results obtained in the JRC's laboratories, summarized in Table 3-1, revealed the following:

- In the water column, PAHs were more associated with SPM, with average (dissolved and SPM) concentrations of ∑PAH around 17 ng/L and a maximum of 35 ng/L, which is at the lower end of typical findings in the river Elbe (ARGE Elbe Gewaesserguetebericht 2006).
- Most SPM and bottom sediment samples display moderate ∑ PAH concentrations in a range of 250-750 µg/kg with extreme values of up to 2600 µg/kg for SPM, with concentrations in the SPM being slightly higher. For comparison in the German stretch of the River Elbe typical values for ∑ 16 EPA PAHs in SPM and SPM derived sediments are one order of magnitude higher and maximum levels range up to 50 mg/kg. (ARGE Elbe Gewaesserguetebericht 2006: http://www.arge-elbe.de/wge/Download/Berichte/06Guetebericht.pdf).
- Among the PAHs that were quantified in sediments and SPM, the most abundant compounds were Fluoranthene and Pyrene (NB.: This actually justify the use of Fluoranthene as indicator of other PAHs). Lower boiling PAHs such as Fluorene and Phenanthrene have a higher water solubility and are more abundant in the dissolved phase, which results in a higher relative contribution to the pattern in the water (Dissolved phase + SPM). As a result the PAH pattern in water is dominated by Fluorene, Phenanthrene, Fluoranthene and Pyrene.

Table 3-1 PAH concentrations in all abiotic compartments

Sum of all PAHs				
	Sediment (µg/kg)	SPM (µg/kg)	Water, dissolved (ng/L)	Water, dissolved+SPM (ng/L)
Average	493	696	7.8	18
Median	407	590	6.3	17
Min	111	216	0.62	8.9
Max	1135	2665	27	33
25-Percentile	220	436	5.0	13
75-percentile	712	787	8.8	22

3.2 Total Extractable Matter (TEM)

In addition to the PAHs, the characterization of the water pollution by oil, petroleum products, etc., can be estimated with the measurement of the TEM. The measurement results for TEM in SPM and the bottom sediment are demonstrated in Figures 3-4 and 3-5, respectively.

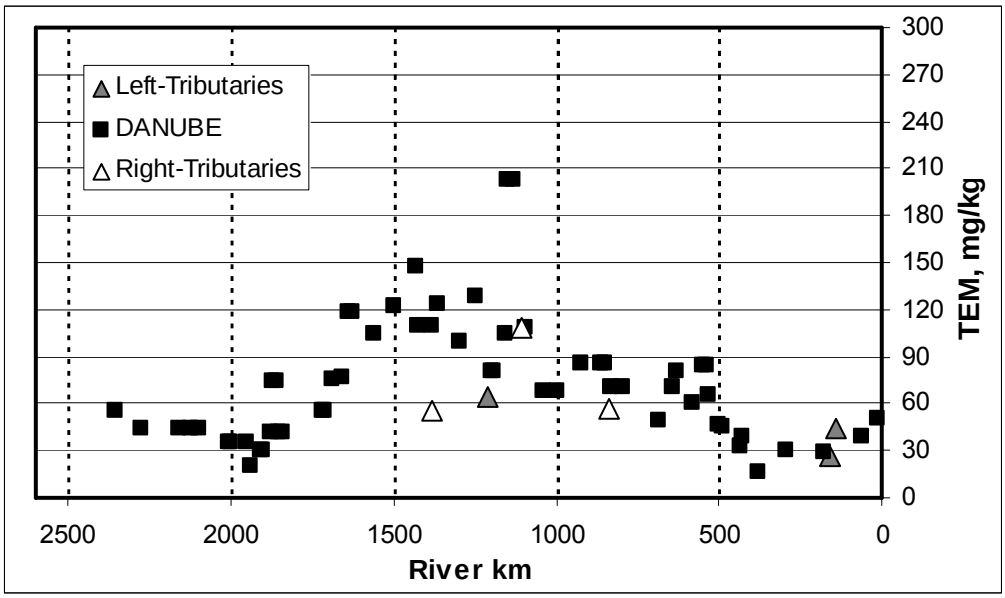

Figure 3-4 Variation in the TEM concentration in the SPM in the Danube and its major tributaries during JDS2

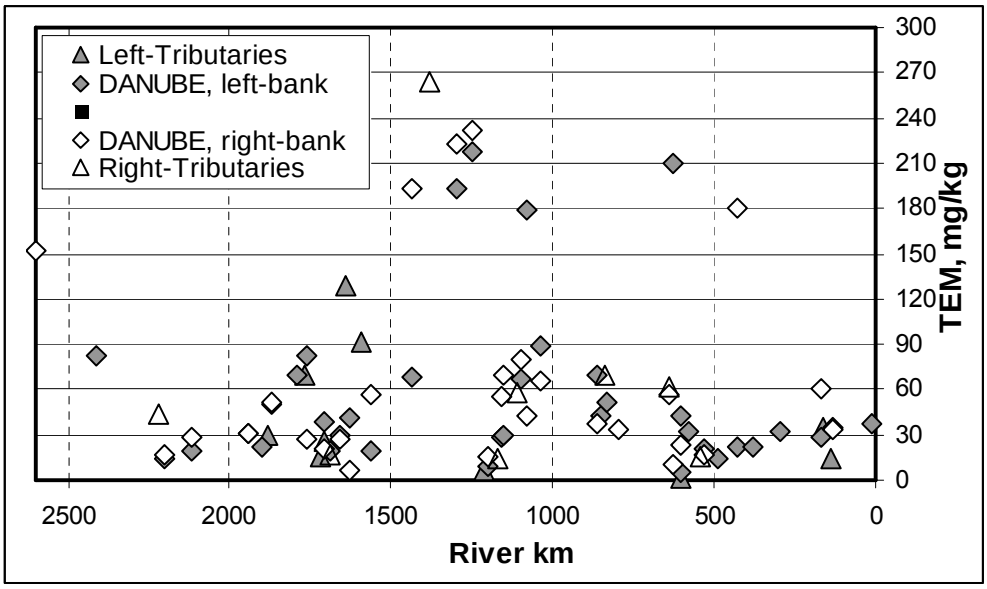

Figure 3-5 Variation in the TEM concentration in the bottom sediments in the Danube and its major tributaries during JDS2

The concentration distribution patterns of TEM in both matrices show similarity to the Fluoranthene concentrations supporting the relationship between the oil-contamination and the PAHs.

3.3 Fluorescence Fingerprints

3.3.1 Characterization of the type of the petroleum-related contamination

The overall profile of each of the fingerprints and their concatenated spectra represents an effective absorption spectral profile. From a comparison of the profiles, at selected sampling sites, it can easily be deduced that the contamination in the water is different from that in the suspended solids, and each could be similar to one of the arbitrary standards presented in Figures 2-1 and 2-2, and can be used for characterization of the type of the petroleum-related contamination in the water body, the SPM, etc.

Fluorescence fingerprint were successfully used for characterizing petroleum-related contamination, and even screeneing for unknown trace organics, as demonstrated later in this section. The total (3D) fluorescence spectra of the cyclohexane extract of water, SPM and bottom sediment were used, compared to arbitrary standards, e.g., gasoline, diesel and crude oil. First the character of the pollutants were evaluated by comparing the concatenated fluorescence spectra of the samples to the arbitrary standards. Figure 3-6 shows the correlation coefficients obtained for the water and SPM samples.

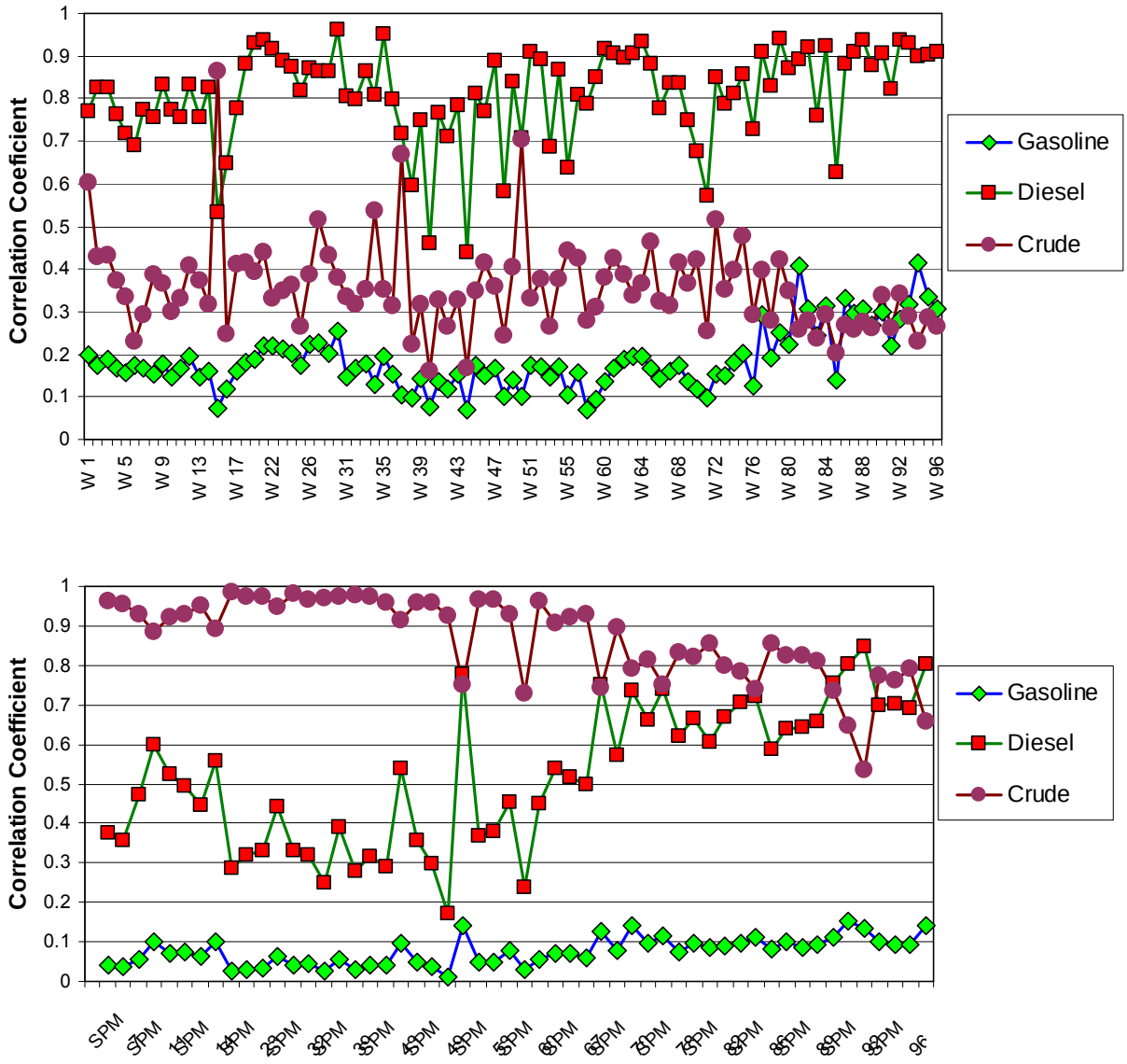

Figure 3-6 Characterization of hydrocarbon contamination by correlating fluorescence spectra of the water (W) and SPM sample extracts with the arbitrary standards

The correlation coefficients obtained by evaluating the concatenated spectra of the arbitrary standards and the JDS2 water and SPM samples revealed the characteristics of the oil pollution. According to the results shown in Figure 3-6, diesel oil type pollution was characteristic in the water column and crude oil type in the SPM, as well as in the bottom sediment. The fluorescence characteristics of the SPM (and also in the bottom sediment) samples show similar distribution patterns to the results of the PAHs (compare Figures 3-8 to Figures 3-1 and 3-2).

3.3.2 Level of the petroleum-related contamination in the water body

After characterizing the type of contamination of the samples, the level (concentration) of the contamination was calculated from the fluorescence intensity of the sample and the standard, at the Ex/Em wavelengths characteristic for the relevant standard. The concentrations for the water and the suspended solids, measured in the Danube and its tributaries, are plotted in Figures 3-7 and 3-8, respectively.

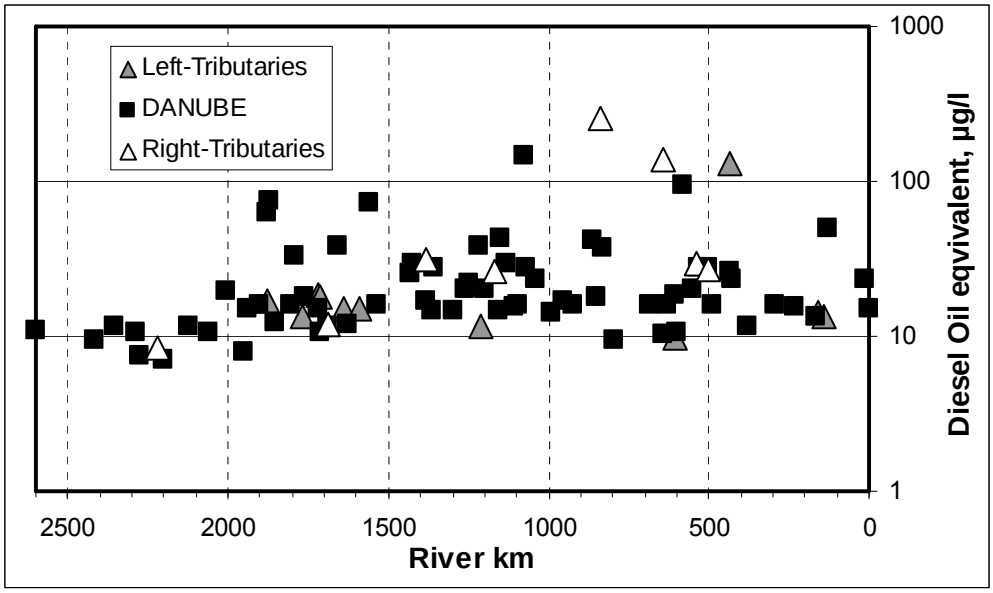

Figure 3-7. Variation in the concentrations of the characteristic petroleum-related contamination, i.e. expressed in the characteristic diesel oil equivalents during JDS2.

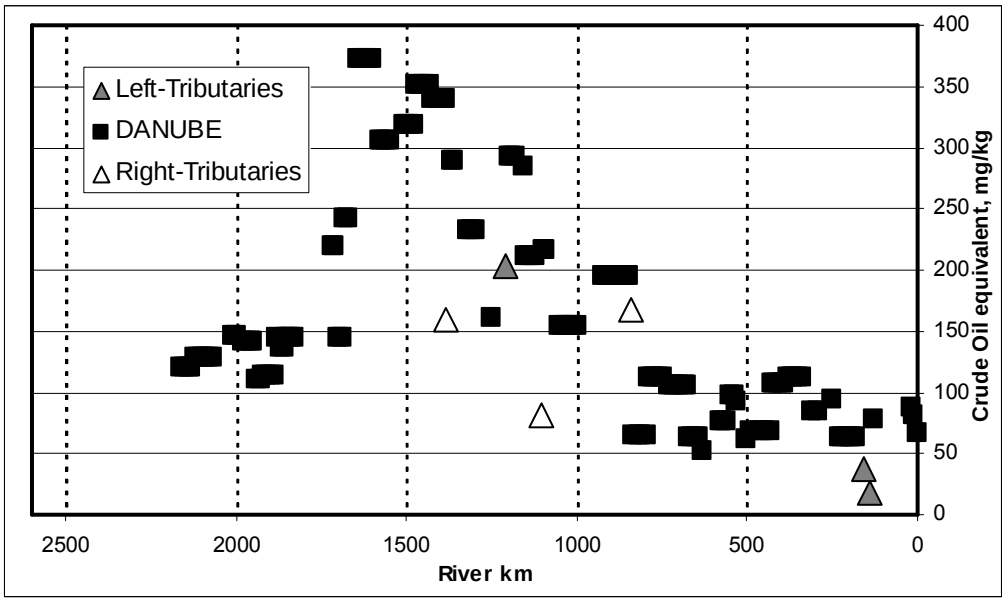

Figure 3-8. Variation in the concentrations of the characteristic petroleum-related contamination, expressed in crude oil equivalents, in the SPM along the Danube and in its tributaries

3.3.3 Screening for trace organic contaminants using fluorescence fingeprints

As an example of using fluorescence fingerprint for screening fluorescing compounds (usually having aromatic rings), Figure 3-9 shows the fluorescence contour diagram of three cyclohexane extracts of Danube water samples collected at river km 1132 (JDS54), 1107 (JDS55) and 1097 (JDS57).

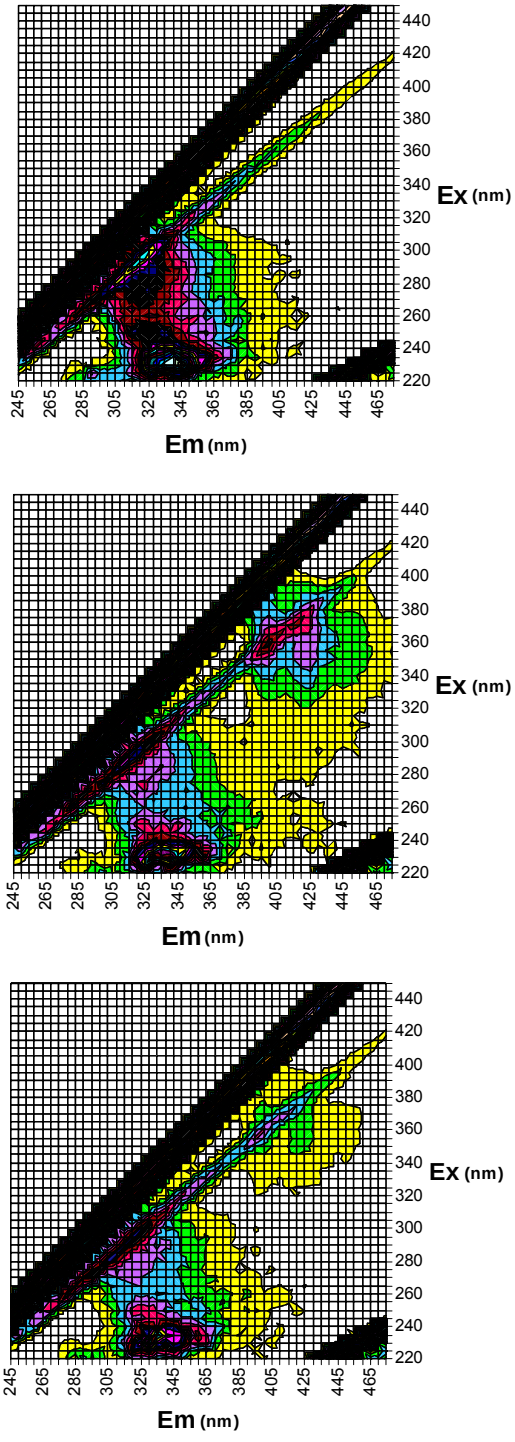

Figure 3-9 Fluorescence fingerprints of cyclohexane extracts of water samples collected from along the Danube reach between river km 1132 and 1097, during JDS2

In addition to the characteristic fluorescence pattern of diesel oil contamination in all the three samples, Figure 3-9 demonstrate the presence of unknown fluorescing compound(s) having a fluorescence intensity peak at Ex/Em = 370/410 nm, in the JDS55 water sample. This compound was not present in the JDS54 sample, however, its presence is indicated in the water sample (JDS57 and even in the samples collected further downstream) downstream of the JDS55 site. The decrease of the fluorescence intensity could be the result of dilution in the Danube.

The identification of this compound could be attempted by the evaluation of the GC/MS scans of the relevant samples.

4 Conclusions

4.1 Compliance checking for priority substances according to WFD

The requirements of the WFD surveillance monitoring of priority substances, according to Annex 4 of the proposed draft EC Directive, is described in more details in the summary report on Priority Substances. With the exception of Anthracene, Fluoranthene and Benzo(a)pyrene, for the other PAH compounds the MAC-EQS is marked as “not applicable.” Therefore, we consider the AA-EQS values for all the PAHs as indicative for being protective against short-term pollution peaks in continuous discharges since they are significantly lower than the values derived on the basis of acute toxicity.

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

Most of the PAH in water samples were far below the AA-EQS values and values in sediments were about one order of magnitude lower than typically found in the River Elbe.

Similarly to the assessment of other priority substances, an **indication** of the chemical status is given for each sampling site by using the proposed AA-EQS for inland waters. Table 4-1 shows the sampling sites where AA-EQS are exceeded in the case of the corresponding PAHs.

Table 4-1 Sampling sites and parameters exceeding AA-EQS values for the priority PAHs

JDS2 Code	PAH Compound	Sampling Station	Concentration [µg/l]
JDS56	∑Benzo(g,h,i) perylene & Indeno(1,2,3-cd)pyrene	/Sava 7.0 rkm	0,004 <0,002
JDS-TI4	∑Benzo(b)fluoranthene & Benzo(k)fluoranthene	/Tisa, upstream Danube	0.074
	∑Benzo(g,h,i)perylene & Indeno(1,2,3-cd)pyrene		0.052
Out of the analytical results of 23 sites' samples, analyzed by EC-JRC/IES			
JDS2	∑Benzo(g,h,i)perylene & Indeno(1,2,3-cd)pyrene	Kelheim – 2415 rkm	> 0.002
JDS16	∑Benzo(g,h,i)perylene & Indeno(1,2,3-cd)pyrene	Bratislava – 1869 rkm	> 0.002
JDS39	∑Benzo(g,h,i)perylene & Indeno(1,2,3-cd)pyrene	Hercegszanto – 1434 rkm	> 0.002
JDS92	∑Benzo(g,h,i)perylene & Indeno(1,2,3-cd)pyrene	Reni – 130 rkm	> 0.002
JDS95	∑Benzo(g,h,i)perylene & Indeno(1,2,3-cd)pyrene	Sulina-arm – 0 rkm	> 0.002

These results are also presented as the indication of the chemical status in map in Chapter 24 of the JDS2 Scientific Report.

Concerning PAHs in the SPM, the proposed Priority Substance data sheet (under serious revision) provide EQS for Benzo(a)pyrene and Benzo(k)fluoranthene. The corresponding concentrations of these substances for protecting the pelagic community in freshwater are 2940 and 326 µg/kg, respectively. Figures 3-1 and 3-2 show the longitudinal variation in the concentration of the Benzo(a)pryrene and Benzo(k)fluoranthene, respectively. Comparing the concentrations of these two PAH compound with the proposed EQS, the results indicated that even the maximum concentrations were far below the recommended limit values, i.e., the maximum concentration of Benzo(a)pyrene was more than 20-times less than the EQS, and the concentration of Benzo(k)fluoranthene was about one-fifth of the proposed EQS for SPM.