

UMWELTFORSCHUNGSPLAN DES  
BUNDESMINISTERIUMS FÜR UMWELT,  
NATURSCHUTZ UND REAKTORSICHERHEIT

Forschungsbericht 299 22 286  
UBA-FB 000343e



**International Pilot Study for the  
determination of Riverine Inputs  
of Polycyclic Aromatic  
Hydrocarbons (PAHs) to the  
Maritime Area on the basis of a  
harmonised methodology**

**- Final Report -**

by

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OSPAR-Pilotstudie

On behalf of the Federal Environmental Agency

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Publisher: Federal Environmental Agency (Umweltbundesamt)  
Postfach 33 00 22  
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## Summary

The objectives of this study are the determination of an annual load of the polycyclic aromatic hydrocarbons (PAHs) for the seven selected rivers and the development of a harmonised methodology for the estimation of these riverine loads into the North Sea and the North-east Atlantic. For this purpose Belgium, Denmark, Germany (lead country), the Netherlands, and Spain contributed to this study with measuring programmes on seven rivers. Detailed results of each participating country are described in the Individual Parts in Annexes 2 to 6.

The biggest problem in complying with the above mentioned aims is to face the highly complex suspended sediment dynamics in natural estuaries. For this reasons, a representative sampling inside the tidal reach is possible only in those estuaries, where the suspended matter transport does not distinctly differ from that of the dissolved phase, e.g. in canalized or strongly regulated estuaries. In all other cases, sampling sites should be located directly upstream the tidal limit in a stretch of unidirectional flow. This provides the possibility to quantify the amounts of riverine contaminant transport into the estuary as one contribution to a comprehensive balance of the whole estuary system, the other components being direct inputs into and direct removal from the estuary (dredging etc.), permanent deposition in the tidal flats, and the target value, i.e. the export of contaminants from the estuary into the sea.

Another problem is the distribution of PAHs on the dissolved and the solid phase. Most of the PAHs are bound on particles, during this study the experimentally ascertained portion of this fraction was found to be between 50 and 80 % for the sum of the 16 EPA PAHs. Conversely, this result shows, that the dissolved portion with 20 - 50 % cannot be neglected in estimating the total contamination, too.

Therefore, several techniques for suspended matter sampling and phase separation (dissolved and particle-bound) have been compared. Generally, the use of a flow-through centrifuge can be recommended, because it yields great amounts of representative suspended solids in very short time, and it provides an almost complete separation of one and the same water sample into the dissolved and the solid phase. Filtration, as a low cost and uncomplicated alternative, should only be used, if a representative sampling and reliable analysis in face of very low amounts of sample is ensured.

By means of a correlation analysis, relationships between parameters, that would lead to a possible simplification of the measuring programmes, should be detected. Unfortunately, reliable causal correlations between parameters requiring expensive and sophisticated analysis, and those that can be more easily determined are not universally existent. A desirable simplification on the

basis of the correlations found does not seem to be reasonable at the moment, the more so as a transfer of the individually determined regressions from one river basin to another one is not admissible. At best, one could imagine a reduction of measuring frequencies for PAHs and the interpolation of intermediate values by means of the regressions found.

The possibility for reducing the frequency of PAH measurements in order to decrease the analytical expense is supported by the results of the model calculations with artificially reduced data sets. They show that the frequency of PAH measurements can be reduced (preferably to event related sampling at 5 to 7 times a year), as long as the streamflow and the suspended solids concentration are recorded with sufficient high frequency (preferably daily values). This is due to the fact, that the PAH contaminations in the rivers do not vary to such an extent as the streamflow and the suspended solids concentration do.

The estimated annual total PAH loads range between 7 tons/year (River Rhine; estimated from particle-bound PAH load, which amounts to 5.2 tons/year in River Rhine) and values less than 0.25 tons/year in rivers Guadalquivir and Skjern. The ranking of the rivers according to their annual PAH loads reflects very well the streamflow situations, except for the River Scheldt, which shows a comparable high load due to extreme high suspended solids concentrations. This again is an indication that, because of the wider variations, the streamflow determines the riverine PAH loads to a larger extent than the PAH levels itself do.

Based on the concrete load values, six different mathematical calculation methods are assessed with view to their applicability for annual load calculations. As a result, two of them are rated as recommendable, one of them being the method already introduced by the RID Principles by OSPAR [INPUT, 2000]. The other recommended method, based on linear interpolation, yields additional information about the daily transport rates (in tons/day). These daily rates give insight into the time dependent contaminant transport behavior and open further possibilities of interpretation.

All recommendations, based on the results of this study, are compiled as a Guideline which is attached as Annex 1 to the present report.

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## 1. Introduction

International marine protection programmes grant high priority to the determination of polycyclic aromatic hydrocarbons (PAHs) because of the high persistence and potential cancerogenic and mutagenic effects of these substances. The INPUT Working Group within the Oslo-Paris Commission (OSPAR) gave heed to this fact already in 1995 by supporting pilot studies for the determination of PAH inputs into the North Sea via the atmosphere and rivers. The following OSPAR Member States participate in the studies of the water pathway, which is the exclusive subject of this report: Belgium, Denmark, Germany, the Netherlands, and Spain – with Germany being the lead country of this study.

Sampling in seven rivers flowing into the North Sea or the North-East Atlantic in five European states allows to assess various techniques applied in differently structured areas, what then enables to draw conclusions for the best harmonisation of methods at the international level. Accordingly, the present study gives recommendations and makes proposals for a harmonised methodology of future monitoring programmes. (cf. Chapter 6 and Annex 1).

Nevertheless, these recommendations contain also a portion of compromise and can have merely preliminary character in view of the present limited knowledge in this field, what is due to the extraordinary complexity of the dynamics of suspended solids in estuaries. The fundamental problems that are associated with the issue of waterborne, particle-bound solids inputs into the marine environment are described in detail in the following Chapter 2 together with potential solutions.

In the years 1997-99, the German Federal Institute of Hydrology (BfG) had been commissioned by the Federal Environmental Agency (UBA) to carry out comprehensive pre-studies at the national level in Germany on the River Elbe, using different measuring methods and techniques of suspended-solid sampling and assessing them in a comparison. The outcome of this national study [UBA, 1999] contributed in many regards to the international pilot study under review here. Several preparatory and supplementary workshops during the project life from 2000 to 2001 gave opportunities for exchanges of experiences between all Countries involved in the study and for the necessary coordination between them.

The Participating Countries agreed to present the results of the study in a common part along with five individual parts (Annex 2 to 6). While the individual parts of the report describe in detail the measuring programmes of the individual states, the methods of measurements and analyses, activities for quality assurance, and possibly supplementary parameters that were recorded, as well as the evaluations and the results, which are not shown in the common part, the

latter provides a summary and synthesis of the individual parts focusing mainly on the following topics:

- Comparison and discussion of results regarding the different river systems and varying measuring and computing methods;
- Estimation of annual PAH loads in the individual rivers.

Based on the results of this study, the guidelines presented as annex 1 of this report, give some proposals for future monitoring programmes in order to estimate the riverine PAH transport rates and loads into the North Sea and the North-East Atlantic.



## 2. Problem definition and objectives

Following the mandate by the Oslo-Paris Commission, the objective of the international pilot study is two-fold: **Development of a harmonised methodology** for determination of annual PAH loads carried by rivers into the North Sea and the North-east Atlantic and **determination of an annual load** for the seven selected rivers. In pursuit of the first mentioned of these objectives, a guideline has to be formulated.

The participation of five states in this study and the examination of seven different river systems offer favourable conditions for attaining this ambitious objective. The rivers Scheldt (B), Rhine and Meuse (NL), Elbe and Weser (D) flow through rather densely populated areas and are exposed to comparable anthropogenic impacts. The mean discharge ranges between  $300\text{ m}^3/\text{s}$  (Weser) and  $1,500\text{ m}^3/\text{s}$  (Rhine). The Skjern (DK) and the Guadalquivir (E) are examples of rivers situated in less densely populated landscapes and consequently with lower impacts. The Skjern is a river with lower discharge ( $MQ=29\text{ m}^3/\text{s}$  during this study). However, mean discharge of Guadalquivir river has a great variation depending on the year (from 70 to  $300\text{ m}^3/\text{s}$ ). This characteristic of Guadalquivir river can be explained by the Mediterranean climate of the area, with very irregular rainfalls, which can cause periodic swellings ( $Q>1000\text{ m}^3/\text{s}$ ) and strong erosion of the river banks.

The advantage of a wide variability of the examined river systems is opposed by some drawbacks, so that not all methods could be operated in parallel on every river for reasons of limited capacities. At the example of suspended-solids sampling techniques, three different sampling techniques were used at River Elbe, while in all other cases except Skjern only one method was applied. On the Guadalquivir River, filtration was used, a method exclusively applied there. This means a direct comparison of methods is possible only in one case (Elbe), in all other cases the different methods were evaluated by objective criteria in order to develop a harmonised methodology.

Another "problem" were the sometimes very low PAH concentrations, which were in aqueous samples in many cases below the limit of detection. This fact should be remedied, on the one hand, by keeping the limits of detection as low as the respective situation requires, and on the other hand, by focussing the high effort of sampling and analyses on the rivers with high streamflow and higher contamination (cf. Guidelines in Annex 1).

Probably the most difficult problem in determining the contaminant inputs via rivers into the seas lies in the fact that many contaminants in waters are particle-bound, so that their fate is associated with that of the carrier substances. This applies in particular to poorly soluble, hydrophobic contaminants such as highly condensed PAHs.

The transport behaviour of suspended solids in natural estuaries is characterised by an extraordinary complexity dominated by regularly alternating flow directions with highly variable dynamics.

In dependence on the morphological and hydraulic conditions, deposition and erosion zones emerge: In reaches with intense currents, the solids are kept in suspension and deposited bed material may be additionally remobilised, while in impounded reaches and other still-water zones, more suspended material is deposited.<sup>1</sup>. These mechanisms are typical for all flowing waters with varying morphology [Bagnold, 1968; Celik, 1984; Van Rijn, 1993]. An exception may be the highly canalized, impounded, and dyked estuaries, where hardly any deposition processes occur, such as in the rivers Scheldt, Meuse, and Rhine.

The particular situation in natural estuaries is caused by sometimes very high flow velocities and the regular reversal of the flow direction due to ebb and flood tides. Thus, the described processes of deposition and resuspension are not continuous, and parts of the deposits persist only temporarily: Sediments, that have accumulated over several years and are not yet sufficiently consolidated can become remobilised in short time through extraordinary weather or flow situations.

Neither the short- and medium-term transport processes nor the long-term consolidation and erosion of deposited sediments are fully explicable by theory to date. Experimental studies of these phenomena are not feasible either for the time being, because of the high temporal and spatial heterogeneity of the suspended-matter contents and the flow velocity profiles in the estuaries, moreover, such experiments would require financial, manpower, and logistic resources, that are not available [Jay, 1997].

That is why Jay et al., Ackermann [1998b] and others propose a way out of this situation, which, however, will be practicable only by close cooperation between measurements and modelling: Establishing a comprehensive balance for the estuary system. Balancing elements in this case will be: the input across the tidal limit into the estuary, direct inputs into the estuary, direct removal from the estuary (dredging etc.), and permanent deposition in the tidal flats of the estuary. The positive or negative sum of all these elements corresponds to the target value, i.e. the export from the estuary into the sea.

The choice of the sampling stations, which is often dependent on existing routine programmes, is closely associated with the problem of the tides. In the rivers Guadalquivir, Scheldt, Meuse, and Rhine measurements were made in the ebb current in the tidal zone, while sampling stations in

---

<sup>1</sup> Well-known deposition areas in the Elbe estuary are, among others, the Mühlenberger Loch, the Fährmannsander Watt, and the Schwarztonnensand [Ackermann, 1998a; 2000].

the Elbe, Weser, and Skjern were located upstream of the tidal weirs. This is another example for the diversity, that allows to juxtapose different methods, but does not allow to directly compare these methods. Reasons for the selection of the measuring stations including their assessments are presented in Chapter 4.2.

In general it can be stated that the measuring station should be as far downstream as possible to keep the influences of unidentified effluent discharges possibly low, but where representative measurements cannot be made in the tidal reach, measurements should be made directly at the tidal limit. In such cases, at least one contribution to the above-mentioned balance (namely the input across the tidal limit into the estuary) can be determined with relative high accuracy.

### 3. Parameters

So-called mandatory parameters are those that are indispensable for calculating PAH loads, and parameters which are directly used for interpretations of the results. These mandatory parameters have to be measured by each participating country in sufficient frequency, deviations from this principle are mentioned and explained in the individual parts of this report (see annexes).

In detail, mandatory parameters in this pilot study are:

- Discharge  $Q$  in  $\text{m}^3/\text{s}$ ;
- Suspended matter concentration  $C_{\text{SS}}$  in  $\text{gDW}/\text{m}^3$  (DW: Dry Weight);
- Contaminant concentration
  - in solid samples: 16 PAHs specified by EPA,  $\text{PAH}_{\text{SS}}$  in  $\text{mg}/\text{kgDW}$ ,
  - in liquid samples: naphthalene,  $\text{NAPHT}_{\text{total}}$  (or  $\text{NAPHT}_{\text{filtrate}}$ ) in  $\text{ng}/\text{l}$ ;
- Solids organic carbon content  $C_{\text{OC}}$  in %, (alternatively: loss on ignition LOIN in %);
- Particle size distribution  $C_{<63\mu\text{m}}$ ,  $C_{>63\mu\text{m}}$  in % (Grain Size Analysis GSA).

The 16 compounds according to US EPA list concretely are [EPA, 1984]: Naphthalene (NAPHT), Acenaphthylene (ANAPH), Acenaphthene (ANAPT), Fluorene (FLUOR), Phenanthrene (PHEN), Anthracene (ANTHR), Fluoranthene (FLANTH), Pyrene (PYREN), Benzo[a]anthracene (BENZAA), Chrysene (CHRYSE), Benzo[b]fluoranthene (BENZBF), Benzo[k]fluoranthene (BENZKF), Benzo[a]pyrene (BENZAP), Dibenzo[ah]anthracene (DIBENA), Benzo[ghi]perylene (BENGHI), Indeno[1,2,3-cd]pyrene (INDENO).

In addition to the mandatory parameters, participating countries included optional parameters into their measuring programmes, such as particle size distribution in the fraction  $<20\mu\text{m}$ , the levels of nitrogen, sulphur, and water in suspended solids, oxygen content, pH and salinity, other nutrients and chlorophyll-*a*, as well as other PAH species than those in the mandatory parameters (e.g. alkylated compounds). These optional measurements allow a more precise assessment of the prevailing situation. More details can be found in the individual parts of the report.

## 4. Studied river systems

### 4.1 General characteristics

#### 4.1.1 River Scheldt (B)

The Scheldt river is 435 km long, rising in the north of France and flowing generally in north-east direction across western Belgium and into the North Sea through the western Scheldt estuary in the southwest of the Netherlands. Navigable for most of its length, it covers one of the most populated and industrialized areas of the Europe. The Scheldt and its tributaries drain an area of about 21,860 km<sup>2</sup>. The drainage basin situated in northern France and Belgium is composed of catchments of numerous small streams, feeding larger tributaries such as rivers Leie, Dender and Rupel. It receives its chief tributary, the Lys, at Ghent.

The estuary can be divided into three zones, on the basis of their different physical and chemical characteristics. The first zone, the fluvial estuary, starts upstream from the confluence of the Scheldt and Rupel rivers and is the fresh zone subject to tidal influence. The second zone or the upper estuary, located entirely in Belgium, is heavily polluted by domestic, industrial and agricultural waste loads [Wollast, 1982; Billen et al., 1985]. Finally, the lower estuary is situated between the Dutch-Belgian border and the North Sea.

During the period 1991–2000, the mean streamflow at the gauge Dutch-Belgian border was 120 m<sup>3</sup>/s. The highest streamflow in that period was recorded in December 1993 with a value of 622 m<sup>3</sup>/s, the lowest recorded in September 1991 was 28 m<sup>3</sup>/s. With an average discharge of 158 m<sup>3</sup>/s for 2000 the period of study is rated as a high-flow period.

#### 4.1.2 River Skjern (DK)

River Skjern catchment is situated in the western part of Jutland (see map in chap. 4.2.2) and the area is 2490 km<sup>2</sup>. The catchment area is dominated by farming (Table 4.1) and the population density is low, about 35 inh./km<sup>2</sup>, where 60 % of the population live in the town of Skjern.

Table 4.1: Area distribution in %.

|                                 |      |
|---------------------------------|------|
| Urban area                      | 1.7  |
| Arable land                     | 68.0 |
| Heterogeneous agricultural land | 12.2 |
| Forest                          | 13.6 |
| Heathland                       | 2.5  |
| Inland marshes                  | 1.6  |
| Other                           | 0.4  |

River Skjern is the most water-rich river in Denmark with a length of 93 km. 18 streams drain into the main river with a total length of 1288 km ( see map). The water runs through a marsh delta with shallow lakes into the southeastern part of Ringkoebing fjord. The fjord (290 km<sup>2</sup>) is connected to the North Sea via a sluice, which regulates the water level and salt content of the water in the fjord. In a way the fjord can be looked at as a saltwater lake. The total catchment of Ringkoebing fjord is 3442 km<sup>2</sup>, of which the river Skjern catchment area accounts for 72 %.

#### **4.1.3 River Elbe (D)**

The River Elbe stretches over 1,100 km from the southern slope of the Riesengebirge in the Czech Republic (1,383 m above mean sea level) to the North Sea at Cuxhaven. After 364 km, it crosses the Czech-German border, where the river-km marks again start at zero. The catchment of about 148,000 km<sup>2</sup> is inhabited by some 25 million people, equivalent to a mean population density of 169 inhabitants per km<sup>2</sup>.

The mean streamflow (MQ) of the years 1977 to 2000 at the gauge Neu Darchau (river-km 536.4) was  $MQ = 710 \text{ m}^3/\text{s}$ . The highest streamflow values around  $3,500 \text{ m}^3/\text{s}$  were recorded in March 1981 and in April 1988, the lowest ones amounting to some  $180 \text{ m}^3/\text{s}$  in August 1990. With  $MQ = 508 \text{ m}^3/\text{s}$ , the study period from April 2000 to March 2001 is rated as a low-flow period.

#### **4.1.4 River Weser (D)**

The River Weser begins at Hannoversch Münden with the confluence of the two source-rivers Werra and Fulda, which are 298 km and 218 km long, respectively. The River Weser itself has a length of 432 km, and the tidal limit is at the weir Bremen/Hemelingen (river-km 362). The catchment of 46,300 km<sup>2</sup> has a mean population density of 153 inhabitants per km<sup>2</sup>.

In the long-term average (1941 - 1999), mean streamflow at Intschede was  $MQ = 325 \text{ m}^3/\text{s}$ , the mean lowflow and highflow was around  $117 \text{ m}^3/\text{s}$  and  $1,210 \text{ m}^3/\text{s}$ , respectively, so that the study period from April 2000 to March 2001 with  $MQ = 250 \text{ m}^3/\text{s}$  is here also rated as a low-flow period (cf. River Elbe).

#### **4.1.5 River Rhine (NL)**

The Rhine is 1320 kilometres long. It rises in Switzerland, where it takes the form of a rapid mountain river, fed by Alpine glaciers in the Gotthard massif. Swollen by rainwater and

meltwater from nine different countries, the river makes its way towards the North Sea. The Rhine's basin covers an area of 185,000 square kilometres, some 25,000 square kilometres of it in the Netherlands. The number of inhabitants in the catchment area is nearly 50 millions. Average river currents in the Netherlands vary from 0.5 to 1.5 metres a second, although they can reach more than 2 metres a second in places. At Lobith, an average of 2,300 cubic metres of water flows down the river every second.

A large industrial concentration along the Rhine in The Netherlands is Rotterdam-Europoort. The industries found in the Rotterdam-Europoort are shipbuilding, refineries, chemical industry, metal processing industry and the Rotterdam-Europoort has an important European service sector.

#### **4.1.6 River Meuse (NL)**

The Meuse is 935 kilometres long. It rises about two hundred kilometres north-east of Dijon, some 409 metres above Dutch Ordnance Datum. After passing through France, Luxembourg and Belgium, the river enters the Netherlands at Eijsden, south of Maastricht. The Meuse's course through the Netherlands, measured up to the mouth of the Haringvliet, is approximately 250 kilometres.

The Meuse basin is about 36,000 square kilometres. Within the basin, there are no glaciers or snow accumulations to feed the river. Flow in the Meuse averages 230 cubic metres per second near the Dutch-Belgian border. Because the river is fed by rainfall all year round, flow is much higher in the winter.

The last stretch of the river, the Getijde Maas (Tidal Meuse) downstream of Lith is not canalised and linked to the sea by the Nieuwe Waterweg. The river exhibits tidal influence as far upstream as Lith.

#### **4.1.7 River Guadalquivir (E)**

Guadalquivir is the main river of the South of Spain. It goes over 666 km, towards southwest, since its source till the mouth. Along its downstream route there are big areas of dry farming, specially olive groves, and several urban areas like Córdoba and Seville that are potential sources of PAHs. Its main tributary is Genil river, whose source is situated in "Sierra Nevada", the highest mountain of the Iberian Peninsula (3489 m). Before it runs into the Atlantic ocean, Guadalquivir river flows through the Natural Protected Area of Doñana.

The average annual discharge of Guadalquivir river<sup>1</sup> has been measured as 7818 Hm<sup>3</sup>/year = 248 m<sup>3</sup>/s. Discharge has a wide range of variation during the year, due to the irregular rains of the area, typical of the Mediterranean climate. Usually, minimum values occur in summer, which is extremely dry. On the contrary, maximum discharges take place in winter and springtime, due to the rain events, and to the melting of snow from “Sierra Nevada” mountains.

The surface of Guadalquivir river basin is 52664 km<sup>2</sup>, and the population is 3792000 inhabitants (population density = 72 inhabitants/km<sup>2</sup>)<sup>1</sup>.

## 4.2 Selection of measuring stations

### 4.2.1 River Scheldt (B)

For the purpose of the Belgian contribution to the INPUT pilot study a sampling station in the Scheldt Estuary was selected (51°12.11'N, 4°20.82'E) that lies in the region of Antwerp harbour, near the Dutch-Belgian border (Figure 4.1). The station is situated in the fluvial estuary, close to the confluence of the Scheldt and Rupel rivers, where this zone starts. It is a well-mixed river section, within the tidal reach of the river, and is a regular monitoring point. The station was selected on the basis of influence of tributaries (mainly the Rupel), easy access and the presence of a continuous monitoring station in the vicinity.

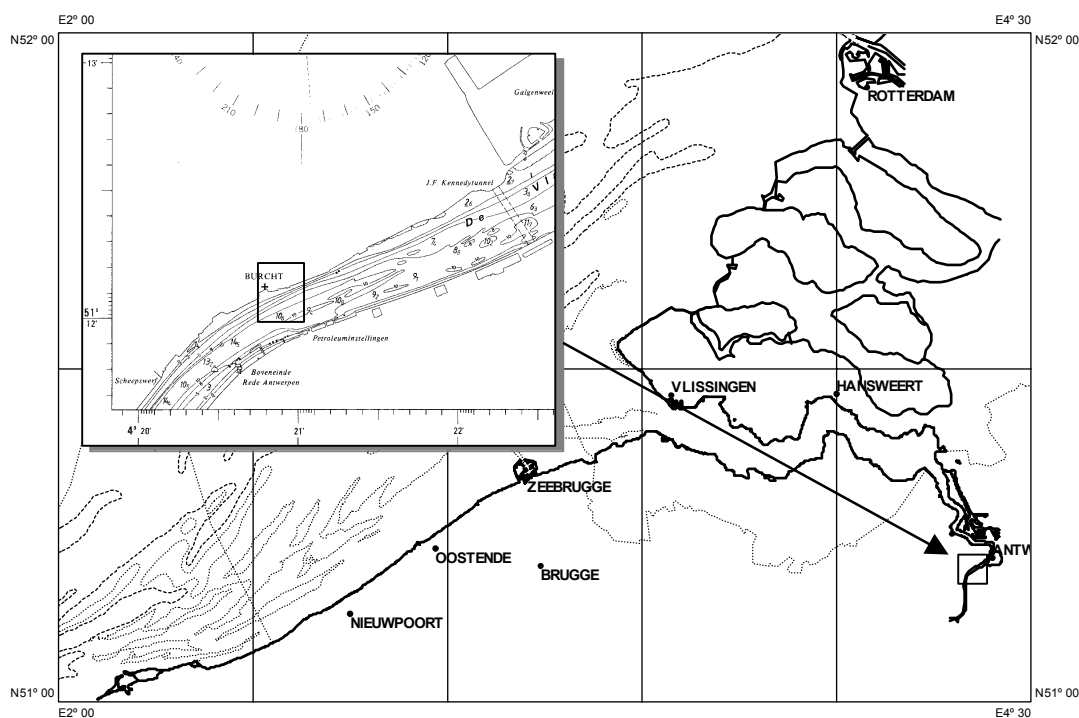


Figure 4.1: Map of sampling location at River Scheldt.

<sup>1</sup> Data supplied by the “Confederación Hidrográfica del Guadalquivir” (Riverine Basin Administration)



### 4.2.2 River Skjern (DK)

The sampling station, Gjaldbaek (marked on the map, Fig. 4.2) is situated at the river Skjern about 20 km from the outlet in Ringkoebing fjord. There is no influence of incoming water from the fjord. The sampling station is included in the Danish national monitoring programme (NOVA 2003) and all sampling and measurements are in accordance with the technical guidelines given in the programme. Only certified laboratories are used for analysing.

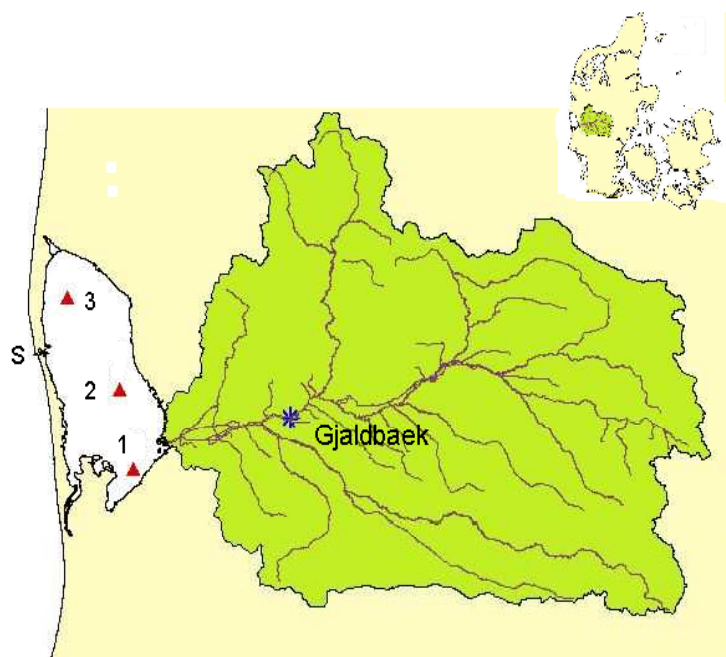


Fig. 4.2:  
River Skjern catchment  
with outlet to Ringkoebing  
Fjord.  
Station Gjaldbaek (\*) and  
3 stations for collecting  
sediment in the fjord (?)  
as well as the sluice (S)  
to the North Sea are  
marked.  
In the upper right corner  
it is indicated where in  
Denmark the catchment  
is situated.

The station Gjaldbaek represents one of the most water-rich rivers in Denmark and is important for estimating loads to the North Sea. Furthermore, annual calculations of discharge are available back to 1920, and from 1993 sediment transport is also included.

The catchment area upstream the station is 1552 km<sup>2</sup>, and represents 62.3 % of the total catchment area. The population density is probably not more than 10-15 inh./km<sup>2</sup> in this area.

### 4.2.3 River Elbe (D)

Wide tidal flats, where suspended solids may settle or may become resuspended during events with stronger currents, characterize the Elbe estuary. Against the background of the extremely complex regime of currents dominated by ebb and flood tide, it is not possible to establish representative estimates of loads transported

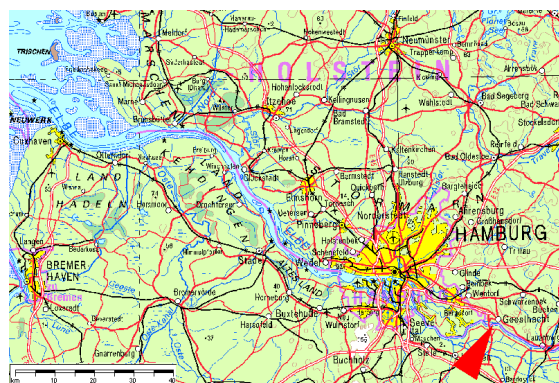


Fig. 4.3: Sampling location at River Elbe

there (cf. "problem definition" in Chapter 2). For this reason the site for the measuring station on the Elbe was selected directly upstream of the tidal weir at Geesthacht (river-km 585.8), so that the PAH input into the estuary beyond the tidal limit - as one element in the desired overall balance, cf. Chapter 2 - may be reliably estimated. The station is marked in Figure 4.3 by a red arrow; for more details refer to the map in Chap. 3.4.2 in the German part of the report, Annex 4.

#### 4.2.4 River Weser (D)

The above-mentioned problem of load estimation on the basis of measurements within the estuary is of nearly universal nature and thus applies also to the Weser estuary [Ackermann, 1998a]. For this reason measurements in the Weser were also made upstream of the tidal weir; the station is marked in Figure 4.4. More details can be found in the individual part of Germany, Annex 4.

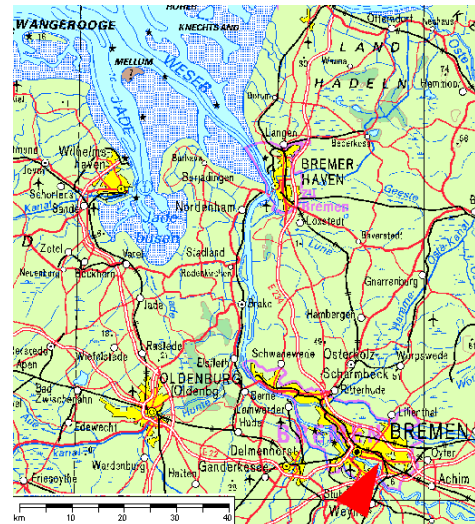


Fig. 4.4: Sampling location at River Weser

#### 4.2.5 River Rhine (NL)

For the river Rhine, the location Maassluis is selected as sampling point. Maassluis is located in the Rotterdam Waterway in the tidal area. This results in a continuously varying water level, and an oscillating water movement with a net flow in the direction of the sea. A certain water mass may pass the monitoring location several times before reaching the sea. The influence of processes such as erosion and sedimentation will vary dependent on the tidal phase.

For the estimation of annual load to the marine area no alternative sampling location was available. The tidal border is as far upstream that the tribute of large industrialised areas to the annual load is missed with a sampling location upstream the tidal border.

The station is marked in the map on the left hand side of Figure 4.5. For more details see Chapter 1 in the Dutch part of the report, Annex 5.

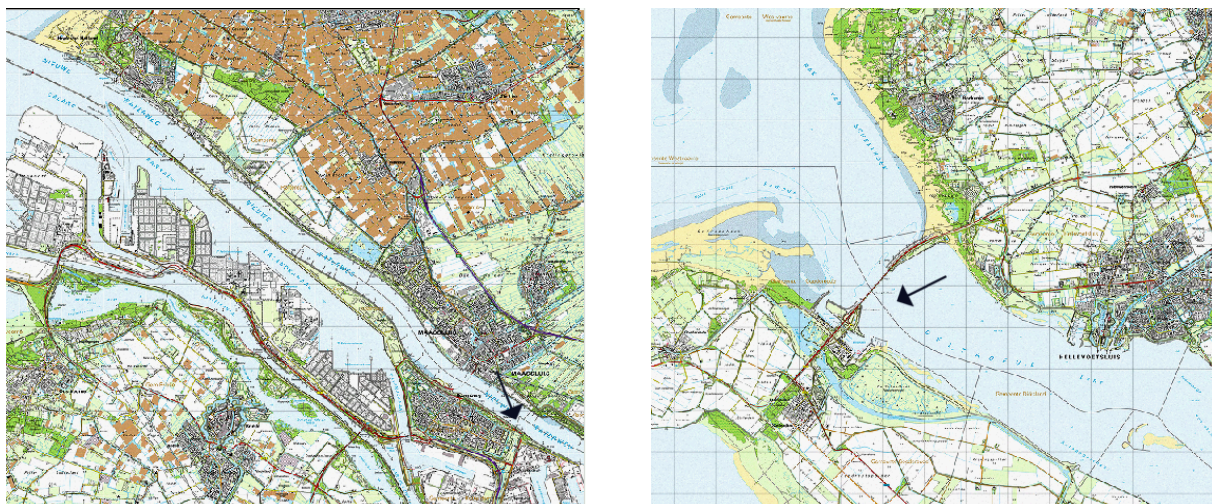


Fig. 4.5: Sampling locations at River Rhine (left) and River Meuse (right).

#### 4.2.6 River Meuse (NL)

For the river Meuse, the location Haringvlietsluis is selected as sampling point. Haringvlietsluis is located in the Haringvliet, upstream of the lock “Haringvlietsluizen”, so outside the tidal area and close to the marine area. Sampling is conducted in circumstances that provide a sample of the water that will proceed through the locks into the marine area.

The station is marked in Figure 4.5, right hand side. For more details see Chapter 1 in the Dutch part of the report, Annex 5.

#### 4.2.7 River Guadalquivir (E)

Site selection was discussed on the basis of the tidal limits in Guadalquivir river, which arrive at 60 km upstream Sevilla. In spite of the problems related to the balance of solids transport under tidal conditions, sampling point was situated in the tidal reach, following the recommendations of the Riverine Basin Administration. The reason is that a point outside

the tidal reach would not have received the main industrial and urban inputs of Guadalquivir river basin, which come from the harbour and the city of Sevilla.

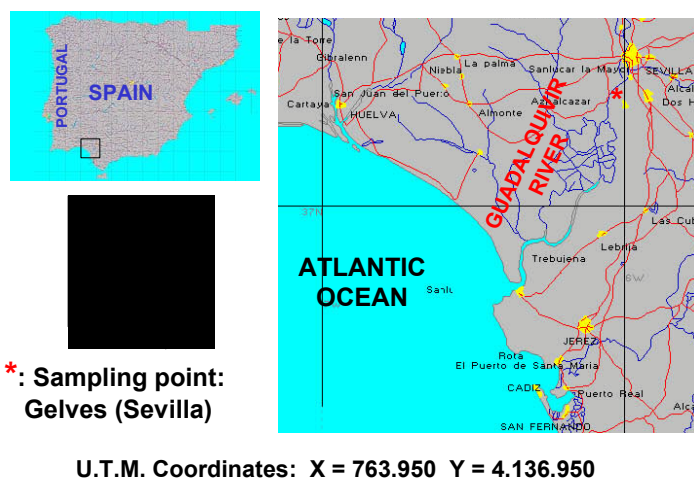


Fig. 4.6: Sampling location at River Guadalquivir

The sampling point was situated in the sportive river port of Gelves, 6 km downstream Seville (37°30'N, 6°W). Samples were collected during low tide in the middle of the river, at a depth of 0.5 m.

## 4.3 PAH situation

### 4.3.1 River Scheldt (B)

The Scheldt is the main input source of contaminants in Belgian coastal waters. In general the two main contributors to PAHs in the environment are fossil fuels, mainly crude oil, and the incomplete combustion of organic materials such as wood, coal and oil. The Scheldt estuary is faced with two main problems. On the one hand, there are extensive dredging operations with dumping of contaminated sediments to keep the port of Antwerp open. On the other hand, there are the large industrial and domestic discharges. The effluents of a number of important Belgian cities such as Brussels, Antwerp and Ghent are either directly or indirectly discharged into the Scheldt. Therefore, the major source of PAHs is the input of freshwater into the estuary at Rupelmonde (south of Antwerp). Other important sources are industrial discharges in Antwerp harbor, the Gent-Terneuzen canal and atmospheric deposition. From a sediment survey, which described the presence of PAHs in twenty-two estuaries in Western Europe, the Scheldt river had among the highest concentrations of total PAHs, with levels over 6 mg/kgDW (QSR 2000). As for other estuaries in Europe, fluoranthene appears to be the most prominent PAH. PAH concentrations in sediments of the estuary often exceed the OSPAR-EAC (Ecotoxicological Assessment Criteria). Although there are many locations with enhanced concentrations in the sediment this cannot always be related to known sources. The physico-chemical properties of PAHs are far more diverse than those of other contaminant groups such as PCBs. Different PAHs tend to behave differently in the estuary showing either a conservative, i.e. decreasing concentrations with increasing salinity, or more complicated patterns (Van Zoest and Van Eck, 1993).

### 4.3.2 River Skjern (DK)

Recent investigations [Henriksen P, 2001] have shown, that the sediment PAH concentration at the stations 1 to 3 (see Fig. 4.2 in chap. 4.2.2) is between 0.2 mg/kg (stat.3) and 1 mg/kg (stat.1) for the sum of the 16 PAHs according to EPA.



#### 4.3.3 River Elbe (D)

The Elbe River Water Quality Board (*ARGE Elbe*) regularly monitors the PAH levels in the Elbe estuary. The summative levels (16 PAHs according to US EPA 1984) in the total samples are around 120 - 280 ng/l, of which around 80 % are bound on particles [ARGE Elbe, 1998], whereas the suspended solids PAH concentration ranges between 0.1 and 1.3 mg/kgDW near-shore and between 1.8 and 8.3 mg/kgDW near the city of Hamburg [ARGE Elbe, 2001].

#### 4.3.4 River Weser (D)

The Working Group for the Protection of the River Weser (*ARGE Weser*) operates a network of 12 stations on the Weser and its major source rivers and tributaries. Since 1995, PAHs have become part of the routine measuring programme; the levels are measured exclusively in sediments. The PAH summative levels (16 PAHs) at the station Hemelingen are in the order of 2-3 mg/kgDW.

#### 4.3.5 River Rhine (NL)

Most of the 16 EPA PAHs are part of the routine monitoring programme conducted by the RIZA. The levels of the sum of the 6 Borneff PAHs vary in Maassluis between 0.9 mg/kgDW (suspended solids) in 1995 and 7.2 mg/kgDW (suspended solids) in 1988. The annual median in the period 1988-1998 of the sum of the 6 Borneff PAHs varies between 2.2 (1994/1995) and 3.2 (1988) mg/kgDW (suspended solids.)

The 6 Borneff PAHs are: Fluoranthene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Benzo[ghi]perylene, Indeno[1,2,3-cd]pyrene.

#### 4.3.6 River Meuse (NL)

Most of the 16 EPA PAHs are part of the routine monitoring programme conducted by the RIZA. The levels of the sum of the 6 Borneff PAHs vary in Haringvlietsluis between <0.1 mg/kg dw (suspended solids) and 8.2 mg/kgDW (suspended solids) in 1988. The annual median in the period 1988-1998 of the suspended solids sum of the 6 Borneff PAHs vary in Haringvlietsluis between 3.0 (1997) and 4.5 mg/kgDW (1992).

#### 4.3.7 River Guadalquivir (E)

Reliable details on PAHs concentrations in Guadalquivir river have not been found in previous studies.

## 5. Results

### 5.1 General

#### 5.1.1 Mandatory parameters

The compilation of the median values of the mandatory parameters introduced in Chapter 3 allows a first classification of the studied areas. A box-and-whiskers plot gives additionally an impression of the variability range of the different parameters in the rivers. Besides the interquartile range (box) and the median value (horizontal line), also values lying further outwards are shown. Among the latter, two groups are distinguished: so-called outliers (o), which are between 1.5 and 3 box length distances away from the upper or lower edge of the box, and extreme values (•), which are more than three box lengths away. The highest and the lowest values that are not yet outliers are connected with the box by vertical lines (whiskers).

Figure 5.1 illustrates the distribution of measuring values during the study period. The study period is always one whole year, but its starting point differs from river to river as Table 5.1 shows.

Table 5.1: Reporting Period in the different countries/ivers

| Belgium<br>(Scheldt) | Denmark<br>(Skjern) | Germany<br>(Elbe/Weser) | The Netherlands<br>(Rhine/Meuse) | Spain<br>(Guadalquivir) |
|----------------------|---------------------|-------------------------|----------------------------------|-------------------------|
| 09/2000 - 08/2001    | The year 2000       | 04/2000 - 03/2001       | The year 2000                    | 06/2000 - 05/2001       |

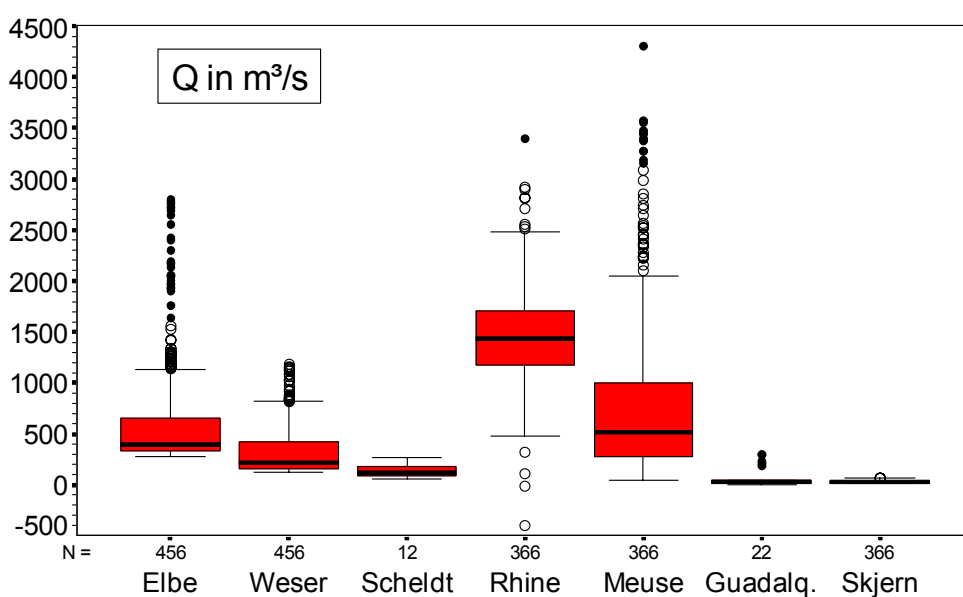


Fig. 5.1: Distribution of mandatory parameters; for legend see last chart

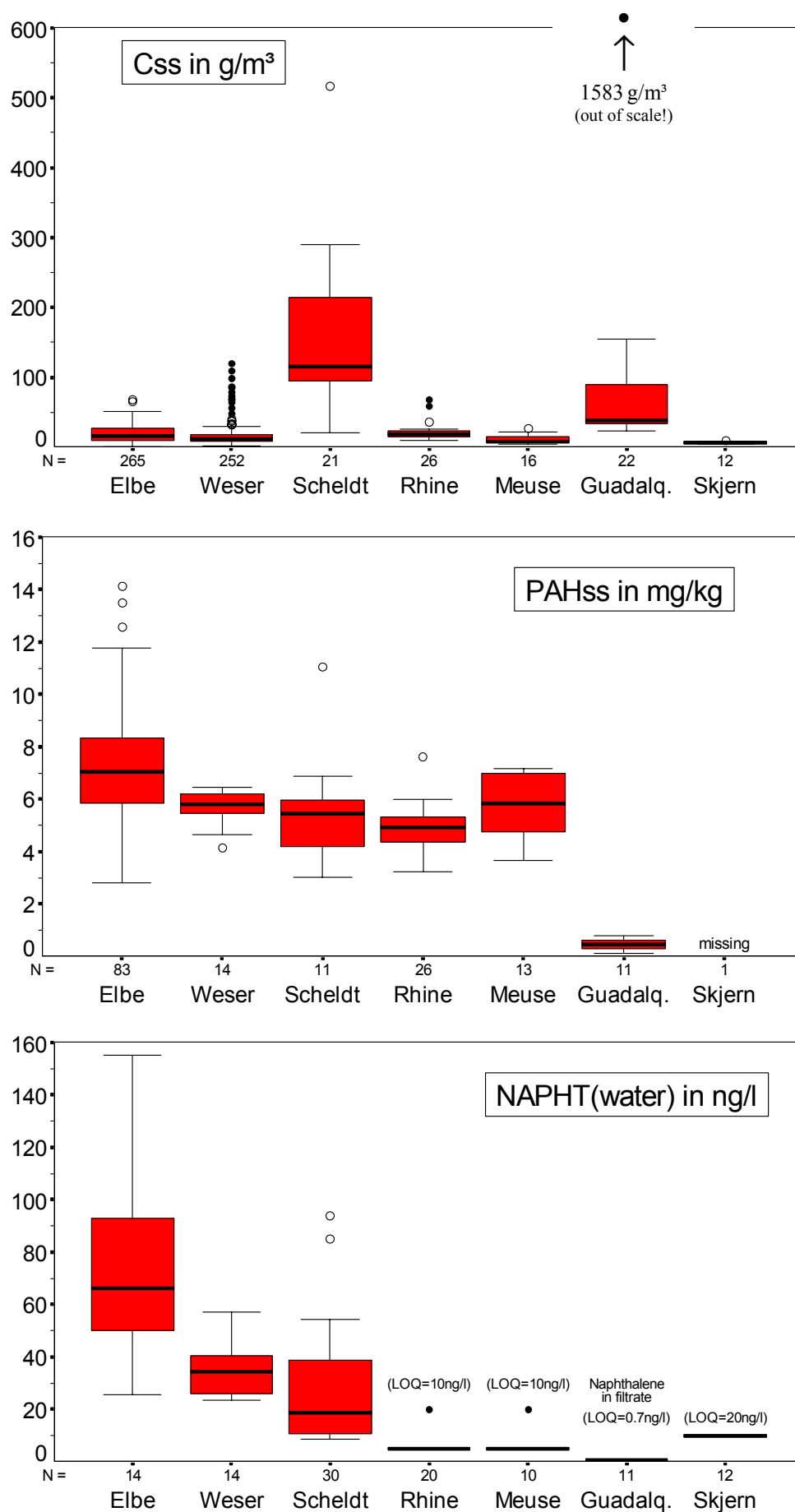


Fig. 5.1 (contd.): Distribution of mandatory parameters; for legend see last chart

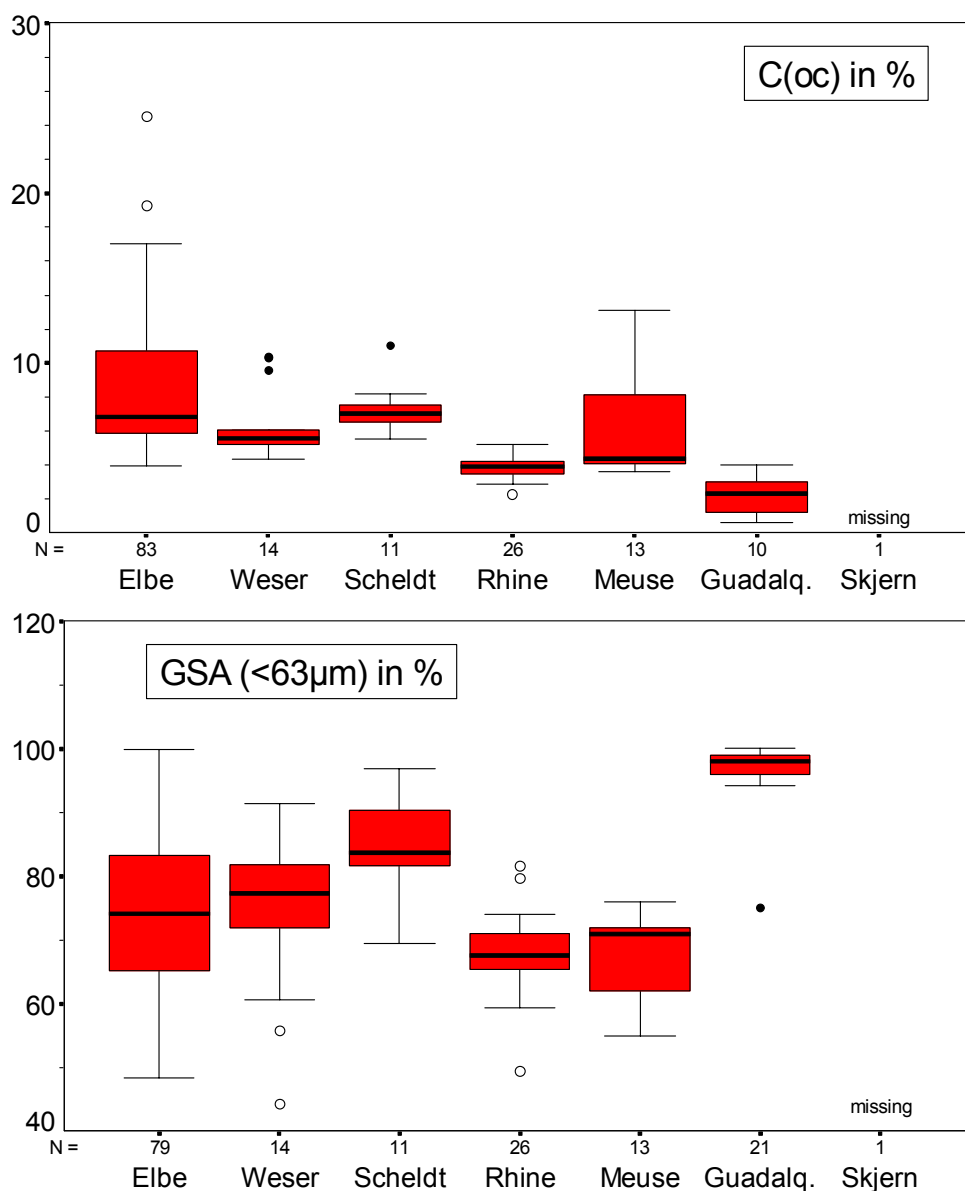


Fig. 5.1 (contd.): Distribution of mandatory parameters.

The medians and variations of the parameters discharge (Q), suspended solids concentration ( $C_{SS}$ ), sum of 16 PAHs concentration in suspended solids ( $PAH_{SS}$ ), Naphthalene concentration in total sample ( $Napht_{water}$ ), suspended solids organic carbon content ( $C_{OC}$ ), and grain size fraction less than  $63\ \mu m$  ( $GSA_{<63\ \mu m}$ ). In cases of measuring values being less than the limit of quantification ( $<LOQ$ ), the LOQ is given explicitly. ("o" and "•" indicate outliers and extreme values, see explanations in the text.)

The examined rivers differ widely in their streamflow characteristics. The rivers with the highest flows Rhine, Meuse, and Elbe showed very strong variations; in the Meuse the peak value is above  $4,000\ m^3/s$ . Guadalquivir and Skjern with mean streamflow values of  $76$  and  $29\ m^3/s$  (median:  $32$  and  $26\ m^3/s$ , resp.), belong to the smaller rivers in this study. For the Guadalquivir River the study period is rated as a low-flow period. As described in Chapter 2, streamflow here is subject to extraordinary strong variations due to climatic reasons, so that the mean streamflow



may reach in some years even  $300\text{ m}^3/\text{s}$ , what is nearly the order of magnitude of the River Weser. In the case of River Rhine, the negative outliers are striking: They are caused by storm events, which may push the water in upstream direction and entail negative daily average discharge values.

Regarding suspended-solids concentrations, the Scheldt and the Guadalquivir with mean values of  $155$  and  $124\text{ g/m}^3$ , respectively, are far at the top end of the list (median:  $115$  and  $39\text{ g/m}^3$ , resp.). The next ones are the Rhine and the Elbe with  $22$  and  $20\text{ g/m}^3$  (median:  $18$  and  $16\text{ g/m}^3$ ), and at the bottom end stands the Skjern with a mean concentration of  $6.5\text{ g/m}^3$  (median:  $6\text{ g/m}^3$ ). By far the widest variations are those of the Guadalquivir with a maximum of  $1,583\text{ g/m}^3$ , measured after a prolonged precipitation period on 29 January 2001. This extreme value is responsible for the great difference between the arithmetic mean ( $124\text{ g/m}^3$ ) and the median ( $39\text{ g/m}^3$ ). The Weser is another example of a river with a hydraulically dominated suspended-solids regime. Already the high number of extreme values in the diagram suggests this, and the correlation analysis in Chapter 5.1.5 confirms it. The connection between the suspended solids and the streamflow dynamics is illustrated in Annex 4 (Chapter 4.2.3.2).

The suspended solids PAH concentration shows a nearly uniform picture in the Elbe, Weser, Scheldt, Rhine, and Meuse. Suspended solids in the Elbe are not only most contaminated with  $7.2\text{ mg/kgDW}$  on average (median:  $7.0\text{ mg/kgDW}$ ), they also display the widest variability: all measurements from the Weser, Scheldt, Rhine, and Meuse lie in the range from  $2.8$  to  $14.1\text{ mg/kgDW}$ , the extremes measured in the Elbe. Completely different conditions prevail in the Guadalquivir, where the measured concentrations are between  $0.1$  and  $0.8\text{ mg/kgDW}$ , with a mean value of  $0.46\text{ mg/kgDW}$  (median:  $0.46\text{ mg/kgDW}$ , as well).

Following the measuring programme on the River Skjern, exclusively total samples were analyzed there, so that no results are available on  $\text{PAH}_{\text{SS}}$  and  $\text{C}_{\text{OC}}$  and  $\text{GSA}_{<63\text{ }\mu\text{m}}$ .

As the naphthalene concentration in the River Skjern is so low that it is not measurable with a limit of quantification (LOQ) of  $20\text{ ng/l}$ , half the LOQ value was entered in the diagram for  $\text{Napht}_{\text{water}}$ . In the Rhine, Meuse, and Guadalquivir, too, the values remained below the limit of quantification. On the Guadalquivir, not the total sample, but the filtrate was analyzed. That is why, unlike on Skjern, Rhine, and Meuse, not half the LOQ but the whole LOQ value, that is very low with  $0.7\text{ ng/l}$ , was entered in the graph. By far the highest naphthalene values were found in the Elbe (cf. also the PAH pattern in the following Chapter 5.1.2). The mean value is  $71.6\text{ ng/l}$  (median:  $66.1\text{ ng/l}$ ), with a range from  $25$  to  $155\text{ ng/l}$ .

The organic portion of suspended solids varies between  $0.7\%$  (Guadalquivir) and  $25\%$  (Elbe), the mean value of all rivers is  $7\%$ . Both in the organic portion and the fine-grain fraction

( $GSA_{<63\mu m}$ ), the rivers Elbe, Weser, Scheldt, Rhine, and Meuse are rather similar, while the Guadalquivir is characterized by a low organic portion and a higher clay and silt content ( $GSA_{<63\mu m}$  between 94 and 100%; one extreme value at 75%). This indicates that the Guadalquivir transports mainly fine mineral and easily erodable material and that biological processes play only a secondary role here.

### 5.1.2 PAH patterns

The PAH contaminations in the rivers considered were compared in the previous chapter by means of their sum ( $\Sigma 16\text{PAH}$  in suspended solids). This chapter examines the species composition of the sum, the PAH pattern.

From the pattern, one can directly see the share in the total sum and the concentration of each individual compound. It facilitates the assessment of the ecological and toxicological relevance, since the effects of the compounds are assessed differently. For instance, cancerogenic and mutagenic effects were proven for benzo

a]anthracene, crysene, benzo[a]pyrene, benzo[k]fluoranthene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]pyrene, while fluoranthene, pyrene, and benzo[ghi]perylene cause primarily genetic changes [Streit, 1991; WHO, 1998].

Beyond the assessment of potential effects, the pattern gives also indications regarding the source of contamination. For instance, the occurrence of the compounds phenanthrene, crysene, and benzo[a]pyrene, which mainly originate from incineration processes, is an indication of diffuse sources, while the compounds naphthalene and fluorene, that are generated in industrial production processes, may come from point sources too.

According to a OSPAR study presented by Norway [OSPAR, 2001], the aluminium industry and the production of creosote- and tar-treated wood are important point sources, whereas road traffic, industrial incineration and home heating as well as the processing of creosote-treated wood (demolition and new construction) are examples of major non-point sources. In the USA more than 50% of the emissions of benzo[a]pyrene derive from combustion of fossil fuels in heat and power generation, refuse burning, and coke ovens. Vehicle emissions contribute as much as 35% to the total PAH emissions [Harvey, 1997].

Figure 5.2 illustrates the PAH patterns on the basis of median values. According to the measuring programmes in the participating states, the patterns are shown for the total samples, the suspended solids, and/or the centrifugate. Cases with values predominantly below the limit of quantification (<LOQ) were not included.

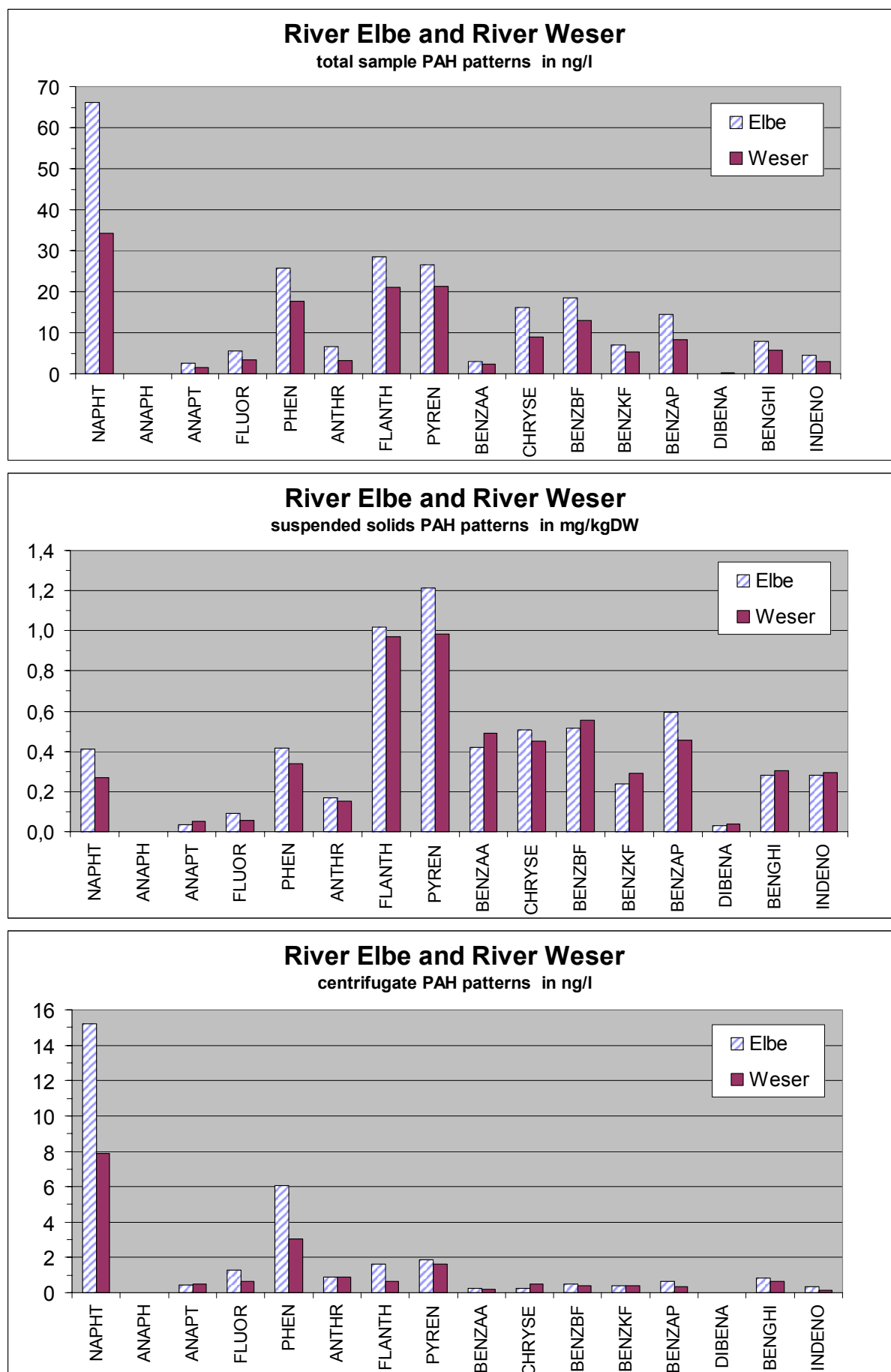


Fig. 5.2: PAH pattern; for legend see last graph

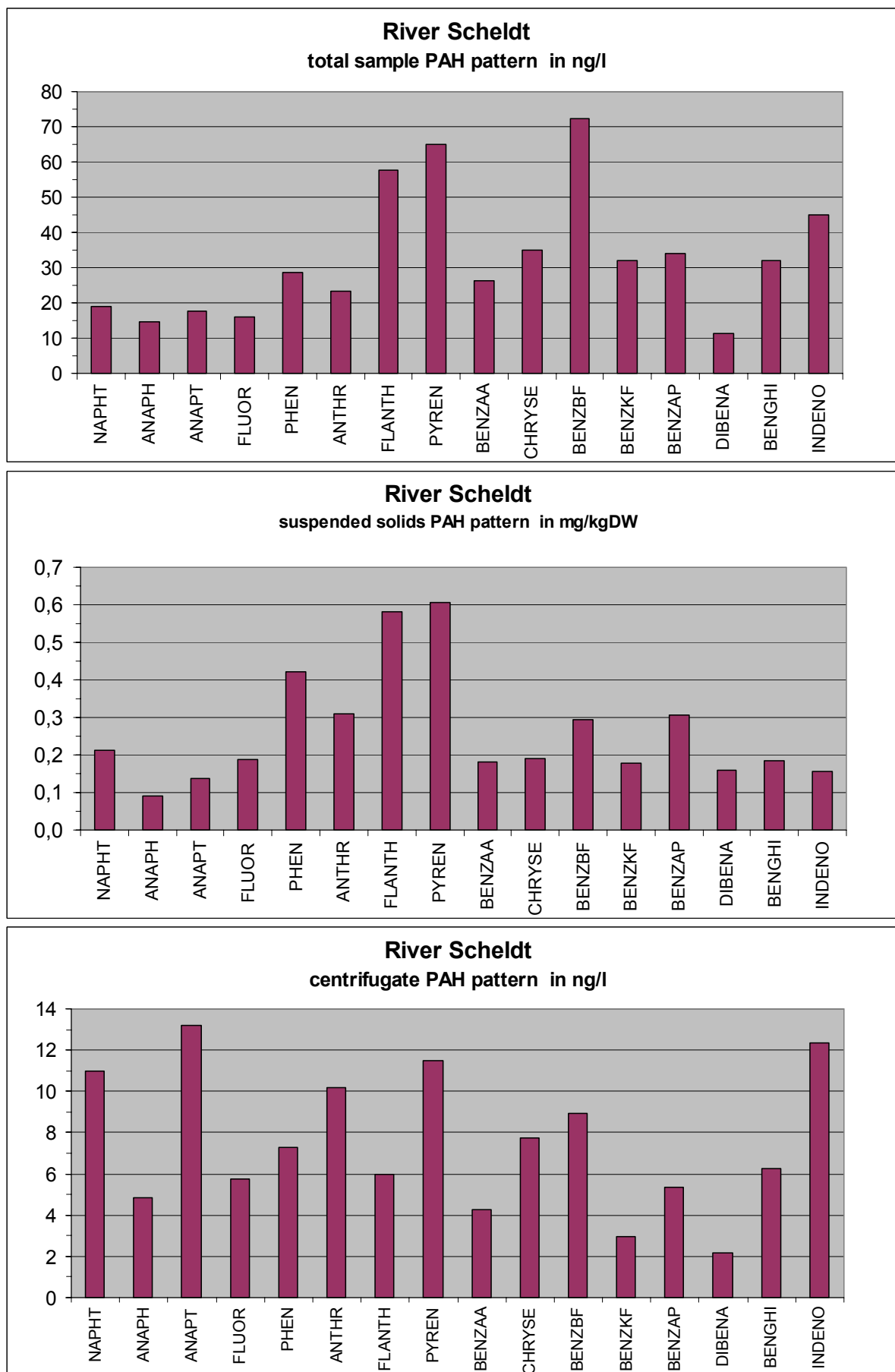


Fig. 5.2: PAH pattern (contd.); for legend see last graph

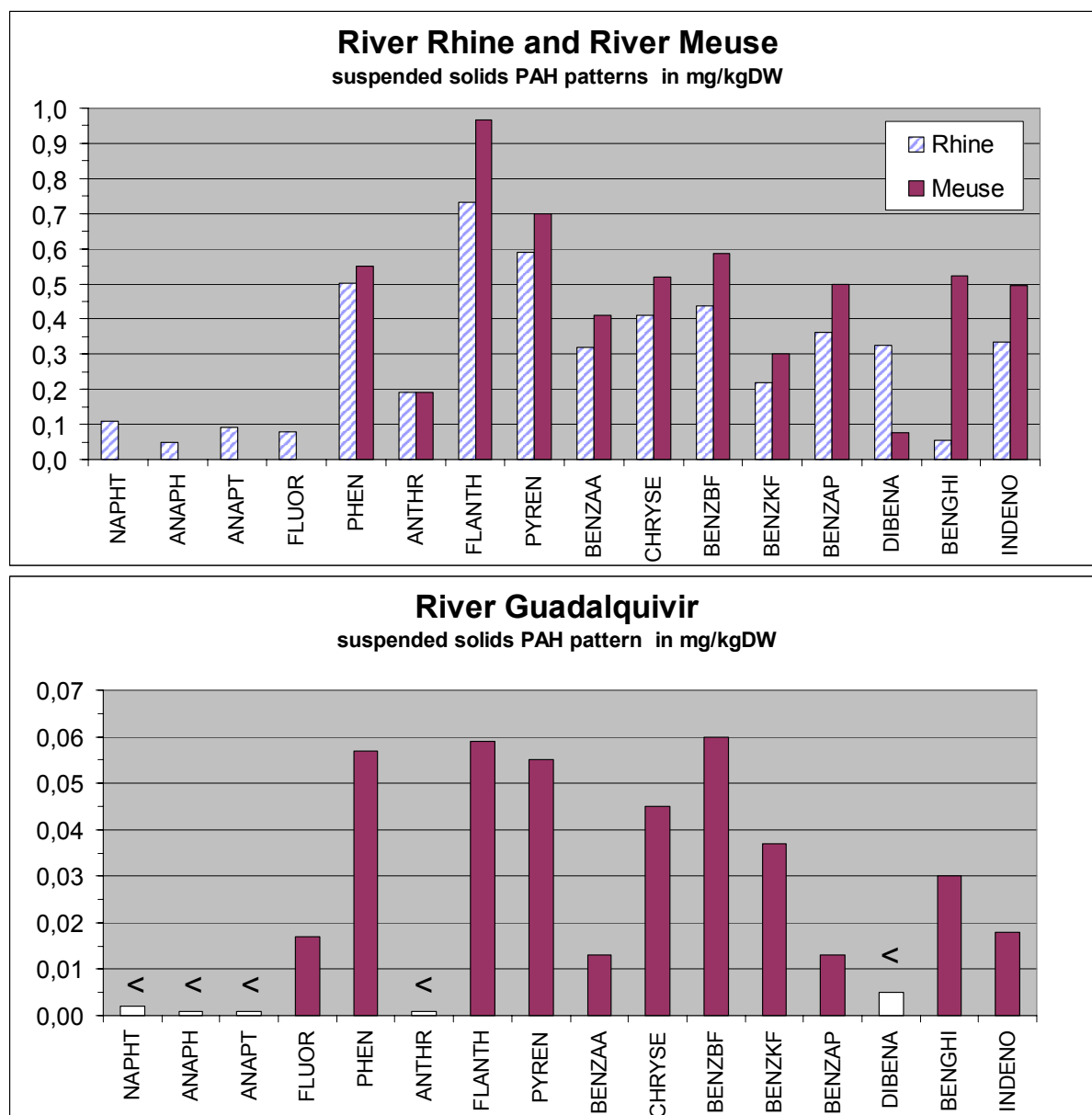


Fig. 5.2: PAH pattern (contd.); PAH patterns in the rivers under investigation. The name of the river and the type of compartment (total sample, suspended solid or centrifugate) are indicated in each single chart.

In case of Guadalquivir river five compounds revealed most of the measured values < LOQ (limit of quantification). Those columns appear in a different color and are indicated with a "<" at the top. They give the values of LOD (limit of detection, which equals 0.3 times the LOQ).

Further results, revealing exclusively values < LOQ, are not shown at all. This concerns the filtrate PAH pattern of Guadalquivir River and the PAH patterns in the total sample of Rivers Meuse and Skjern.

The patterns in the suspended solids of the rivers Elbe, Weser, Scheldt, Rhine, and Meuse are in very good agreement. This suggests comparable diffuse contamination sources as described above. Exceptions are the relatively high values of dibenzo[a,h]anthracene in the Scheldt and the Rhine, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene in the Meuse, and phenanthrene in the Scheldt. With a median value of 0.31 mg/kgDW, anthracene is strongly present in the Scheldt.

The patterns in the suspended solids of the Guadalquivir River are different in that there the portions of phenanthrene, crysene, benzo[b]fluoranthene, and benzo[k]fluoranthene are comparatively high.

The absolute values, too, are similar in the rivers Elbe, Weser, Scheldt, Rhine and Meuse, whereas the PAH levels in suspended solids of the Guadalquivir are by one order of magnitude lower.

In a direct comparison between Elbe and Weser, it is striking that the values from the Elbe are only slightly increased throughout, but that the difference for naphthalene is very distinct (double naphthalene values in aqueous samples from the Elbe). These - also against the other rivers - very high naphthalene values, with 66 ng/l in the total sample and 0.4 mg/kgDW in suspended solids, had been documented already in earlier studies. They derive from sources in the catchments of the tributaries Schwarze Elster and Mulde [ARGE, 1996; 2001].

At the examples of the Elbe and the Weser, the shift in the patterns in the transition from total sample to suspended solids or to centrifugate is obvious: the low condensed compounds (NAPHT - PHEN) occur preferentially in dissolved form, while the high condensed, hardly soluble compounds are stronger attached to suspended solids (cf. also Chapter 5.1.4). This effect can be observed also in the Scheldt, although in weaker form.

### 5.1.3 Seasonality

The results from the studied river basins were analyzed for seasonal variations by means of the PAH sums ( $\Sigma 16\text{PAH}$ ).

In the Elbe and the Weser, the dissolved PAH concentrations (centrifugate) in summer were slightly lower than in winter (Elbe: about 30 ng/l in summer, about 50 ng/l in winter; Weser: about 15 ng/l in summer, about 25 ng/l in winter). Such behaviour was not observed in suspended solids and in the total sample. On River Scheldt, no seasonality was found as well.

Of the rivers Rhine and Meuse, only the results of suspended solids could be examined, because the aqueous samples from the Rhine were not analyzed at all, and in the Meuse the values remained below the limit of quantification. In the Meuse, the highest suspended solids contaminations were observed in winter, and the lowest ones in summer. In the Rhine, however, both the highest value (7.62 mg/kgDW) and the lowest one (3.25 mg/kgDW) were measured in December 2000.

In the Guadalquivir, seasonality of PAH attached on suspended solids could not be found. The dissolved quantities, however, were usually so low that they were below the limit of quantification. Nevertheless, here too the highest measurable concentrations occurred in winter (October-January).

For more details please refer to the individual parts in Annexes 2 - 6.

In conclusion, it may be noted that distinct seasonality was observed in none of the examined rivers. In their tendency, the concentrations – especially those in the dissolved phase – were somewhat lower in summer than in winter. This phenomenon may be explained, on the one hand, in physical terms (temperature-dependent exchange with the atmosphere) and, on the other hand, by anthropogenic impacts (heating in winter increases emissions of PAHs).

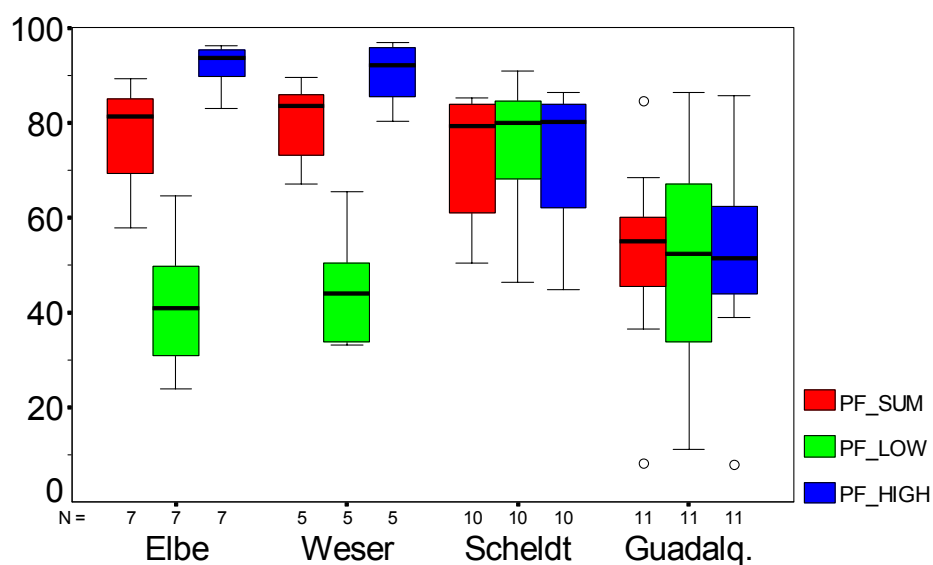
### 5.1.4 Particulate and dissolved fraction

The dispersion behaviour shows which percentage of the PAHs in a water body is particle-bound. The share (dimensionless) or the percentage (%) of particle-bound contaminants in the contaminants content of the total sample is called particulate fraction PF.

The knowledge of the PAH portion that is transported on particles is relevant whenever the suspended solids show another transport behaviour than the dissolved substances. This is the case in nearly all natural water bodies, especially when settling or erosion zones have formed in certain parts of the water bodies. Estuaries, that have kept much of their naturalness and were not canalized, usually show extremely complex suspended-solids dynamics (cf. Chapter 2).

In the rivers Elbe, Weser, Scheldt, and Guadalquivir, the PAH contents were determined in the dissolved phase and in the solid one. The PF values, based on these measurements, are shown as a box-and whiskers-plot in Figure 5.3.

Fig. 5.3:  
Percentage of  
the particulate  
fraction (PF in %)  
for the sum of the  
16 EPA PAHs,  
the group of lower  
(NAPHT-PHEN)  
and the group of  
higher condensed  
(ANTHR-INDENO)  
species (see text).



The low condensed compounds (naphthalene, acenaphthylene, acenaphthene, fluorene, and phenanthrene) have high water-solubility - between 1,290 and 30,000  $\mu\text{g/l}$  at 20°C - and thus occur more often in dissolved form than the higher condensed compounds (water solubility between 0.1 and 260  $\mu\text{g/l}$  at 20°C). This can be seen clearly in the Figure at the examples of the rivers Elbe and Weser. In the Scheldt and the Guadalquivir, however, the measurements do not confirm this expected effect. At Guadalquivir River this behavior may be explicable by taking into account the grain-size analysis and the organic carbon content (cf. Fig. 5.1 in Chapter 5.1.1). Due to the extreme high portion of the clay and silt fraction and the very low organic carbon content it is conceivable that the fine mineral material comes along with a large amount of colloidal particles. These particles are hardly separated from the dissolved phase, so that the adsorbed PAHs impute to the dissolved phase although they belong to the particulate/colloidal



fraction. As a result, the computed PF value decreases and the difference between the low-condensed and the high-condensed PF values are evened out, as well. However, a comprehensive interpretation, particularly with regard to the Scheldt PF values, cannot be given in the frame of the actual study results.

In any case, it becomes obvious that the PF values occurring in nature may range from around 40 % up to 95 %, with extreme values ranging at only 10 %. That is the reason why whenever the dynamics of suspended solids play a role, both the dissolved and particle-bound PAH portions should be measured separately.

### 5.1.5 Relationship between PAH concentrations and other parameters

This chapter looks for possible linear dependencies between the mandatory parameters using bivariate correlations. This is done mainly in pursuit of two aims: On the one hand, existing correlations of easily or frequently measurable parameters allow to draw conclusion about parameters that cannot be easily determined (e.g. from Q and C<sub>SS</sub> to PAHs etc.). On the other hand, the more is known about the relations between the measured parameters, the better and easier can the results be interpreted.

The parameters Q, C<sub>SS</sub>, C<sub>OC</sub>, GSA<sub>(<63 µm)</sub>, PAH<sub>SS</sub>, and NAPHT<sub>total</sub> of each river are compared. Here, it must be kept in mind that not all parameters are available from all rivers. In the River Meuse, only the GSA fraction <16 µm was measured. However, it is included in the correlation analysis, because experience shows that the GSA<sub>(<16 µm)</sub> does not deviate much from GSA<sub>(<63 µm)</sub>. This was demonstrated in the studies on the Rhine, where average values of GSA<sub>(<16 µm)</sub> = 62 % and GSA<sub>(<63 µm)</sub> = 68 % were found. From the Guadalquivir naphthalene values are not available from the total sample (NAPHT<sub>total</sub>) but only from the filtrate (NAPHT<sub>filtrate</sub>). Because all these values are constant (i.e. <LOQ), it is not possible to calculate correlations. From River Skjern useable data (>LOQ) exist only about Q and C<sub>SS</sub>.

For each river, a reduced correlation matrix is established, which includes – for reasons of clarity – only the parameters that show a significant correlation with  $p < 0,005$ . The Pearsons correlation coefficient  $r$ , the number of measurements (N), and the two-tailed significance  $p$  are entered in the fields of the matrix.

#### *Elbe*

In the Elbe, only the particle-bound PAH concentration (PAH<sub>SS</sub>) shows a significant correlation with streamflow Q and the organic carbon level C<sub>OC</sub>. Since the streamflow regime of the Elbe is

primarily controlled by snowmelt and precipitation, the input of PAH contaminated particles (land surface erosion) generates a positive correlation between PAH<sub>SS</sub> and Q. The negative correlation between PAH<sub>SS</sub> and C<sub>OC</sub> is a result of a dilution effect: The organic material in the eutrophic River Elbe consists of freshly grown phytoplankton that is less contaminated than the allochthonous, imported particles. Consequently, a high organic portion is accompanied by a lower specific suspended solids PAH concentration (cf. also Chapter 4.1.3.2 in Annex 4).

| r<br>(N)<br>p     | Q                    | C <sub>OC</sub>       |
|-------------------|----------------------|-----------------------|
| PAH <sub>SS</sub> | .76<br>(034)<br>.000 | -.63<br>(034)<br>.000 |

Tab. 5.2: Significant correlations on River Elbe

### Weser

On the Weser, only one significant result was found: Streamflow is in positive correlation with the content of suspended solids. Due to the high salinity (potash industry), biological processes are irrelevant in the Weser, so that this result is not surprising. Another, only weakly significant correlation was found to exist between Q and NAPHT<sub>total</sub> ( $r=0.90$ ,  $N=5$ ,  $p=0.036$ ).

| r<br>(N)<br>p   | Q                     |
|-----------------|-----------------------|
| C <sub>SS</sub> | .45<br>(0242)<br>.000 |

Tab. 5.3: Significant correlation on River Weser

### Scheldt

No highly significant correlations were discovered on the Scheldt. The most distinct correlation was that between GSA<sub>(<63 μm)</sub> and C<sub>SS</sub> ( $r=-0.66$ ;  $N=11$ ;  $p=0.026$ ) and between GSA<sub>(<63 μm)</sub> and C<sub>OC</sub> ( $r=0.61$ ;  $N=11$ ;  $p=0.048$ ). With increasing content of suspended solids, the fine-grain portion decreases – i.e. the share of coarser material grows – and with higher organic portions, the share of fine-grained material rises. No linear correlation whatsoever was observed between Q and C<sub>SS</sub>; the same applies to the PAH levels.

### Rhine

River Rhine shows a very distinct correlation between PAH<sub>SS</sub> and GSA<sub>(<63 μm)</sub>, and also Q and C<sub>SS</sub> are - like in the case of the Weser - correlated positively. The two other fields in the reduced matrix are printed *in italics*, since these correlations are not highly significant ( $p>0.005$ ). The positive correlation between PAH<sub>SS</sub> and GSA<sub>(<63 μm)</sub> indicates that the

| r<br>(N)<br>p     | Q                     | GSA<br>(<63 μm)       |
|-------------------|-----------------------|-----------------------|
| PAH <sub>SS</sub> | -.33<br>(026)<br>.096 | .72<br>(026)<br>.000  |
| C <sub>SS</sub>   | .62<br>(026)<br>.001  | -.27<br>(026)<br>.179 |

Tab. 5.4: Significant correlations on River Rhine, non significant correlations in italic type.

particle-bound PAHs in the Rhine are preferentially associated with the fine-grain fraction (clay and silt).

### ***Maas***

Besides  $Q \leftrightarrow C_{SS}$  und  $PAK_{SS} \leftrightarrow GSA_{(<16\mu m)}$  (cf. River Rhine), on the Maas significant correlations appear also between  $C_{OC}$  and  $GSA_{(<16\mu m)}$  and between  $C_{OC}$  and  $PAH_{SS}$ . The distinctly negative correlation between  $C_{OC}$  and  $PAH_{SS}$  may indicate - like in the case of the River Elbe, see above - a dilution effect. The negative correlation between  $C_{OC}$  and  $GSA_{(<16\mu m)}$  shows that - other than in the River Scheldt - the organic material is more associated with the fraction  $>16\mu m$ . (Perhaps this result might look another way round, if the fraction  $>63\mu m$  would have been analysed.)

| r<br>(N)<br>p      | Q                    | GSA<br>( $<16\mu m$ ) | $C_{OC}$              |
|--------------------|----------------------|-----------------------|-----------------------|
| $PAH_{SS}$         | .46<br>(013)<br>.115 | .80<br>(013)<br>.001  | -.87<br>(013)<br>.000 |
| $GSA_{(<16\mu m)}$ | .47<br>(013)<br>.107 | 1.0<br>(013)<br>—     | -.95<br>(013)<br>.000 |
| $C_{SS}$           | .85<br>(016)<br>.000 | .45<br>(012)<br>.140  | -.44<br>(012)<br>.152 |

Tab. 5.5: Significant correlations on River Meuse, non significant correlations in italic type.

### ***Guadalquivir***

The Guadalquivir did not show any highly significant correlations. The only noteworthy relation exists between  $Q$  and  $C_{OC}$  ( $r=-0.71$ ;  $N=10$ ;  $p=0.021$ ). This negative correlation supports the thesis mentioned in Chapter 5.1.1, saying that the Guadalquivir transports in the first line mineral material (clay and silt) that is easily eroded at increased streamflow.

### ***Skjern***

Because of the specific measuring programme and the low PAH concentrations in the Skjern, only the parameters  $Q$  and  $C_{SS}$  could be compared there. Here too, only a low correlation was found with an error probability of 13.8 % ( $r=0.45$ ;  $N=12$ ;  $p=0.138$ ).

Conclusion: Reliable causal correlations between parameters that are difficult to measure, like  $PAH_{SS}$  and  $NAPHT_{total}$ , and those that can be easily determined, such as  $Q$ ,  $C_{SS}$ ,  $C_{OC}$ , or  $GSA_{(<63\mu m)}$ , are not universally existent. Merely the particle-bound concentration  $PAH_{SS}$  showed some linear relations: Namely in the Rhine and the Meuse with the clay and silt fraction ( $GSA_{(<63\mu m)}$ ), in the Elbe with streamflow  $Q$ , and in the Elbe and the Meuse with the organic portion  $C_{OC}$ . A desirable simplification on the basis of these correlations does not seem to be

reasonable at the moment. At best, one could imagine a reduction of measuring frequency for PAHs and the interpolation of intermediate values by means of the regressions found. A transfer of the individually determined regressions from one river basin to another one is not admissible. However, the correlations found give valuable information for the interpretation of the processes occurring in the rivers, as those mentioned in the context of the individual rivers, such as land-surface erosion, dilution effect, contaminant association on the fine-grain fraction etc. Measurements of additional parameters, like turbidity or chl-*a* concentration as an indicator of phytoplankton concentration, open further possibilities for interpretation (cf. Chapters 4.1.5.1 and 4.2.4.1 in Annex 4). Here too, it holds true that each river is characterized by its individual processes.

#### **5.1.6 Comparison of suspended matter sampling techniques**

During the study, four different sampling techniques were used: Flow-through centrifuge (FC), filtration, BISAM, and sedimentation tank (ST).

BISAM and ST are passive methods, which function on the principle of sedimentation of the suspended material in artificially created still-water zones. Accordingly, these systems are operated over longer periods (1-4 weeks) and thus present a time-integrated picture of the suspended-solids quality. BISAM is an *in-situ* sampler, while the sedimentation tank is accommodated in a measuring station and is supplied with water by a pump. Both methods were used on the Elbe, and they are described in Chapter 3.2 of Annex 4.

On the rivers Scheldt, Meuse, Rhine, Elbe, and Weser the suspended solids were separated by means of a flow-through centrifuge. The FC may be installed in a monitoring station, or mounted on a trailer, on a vessel, or on a floating pontoon, so that its operation can be either stationary or mobile. The water is fed by a pump into the centrifuge, where the suspended solids deposit on the inner wall of the rotating cylinder. Moreover, the centrifugate can be collected at the centrifuge outlet. A by-pass at the inlet allows to take representative random samples of the water (total sample). With a separation rate of 90-98%, the FC is a system that separates the solid phase of a total sample nearly completely from the liquid one, and makes each compartment (total sample, suspended solids, and centrifugate) available for further analysis. With a typical sampling period of 2-5 hours it presents a "snapshot" of the water quality. The centrifuge used on the Elbe and the Weser is also described in Annex 4. On the rivers Scheldt, Rhine, and Meuse samples were collected at one representative station in the cross-section, while

from the Elbe and Weser besides near-surface and near-bank samples also near-surface mixed samples are available. For load estimates, mixed samples were used exclusively.

On Guadalquivir river phase separation was performed by filtration, following the U.S. Geological Survey standard procedure for phase separation of general trace organic compounds [U.S. Geological Survey, 1999]. It involves the use of two 0.7 µm pore-sized glass microfibre filters, and the processing of 10 l of sample, 5 l through each filter. In principle, the main disadvantages of filtration may be the low representativity of samples collected in situations of high streamflow, or problems related to erosion and near-to-bank effects. To avoid these problems, in this study samples were collected at a depth of 0.5 m, in the middle of the river. In addition, after heavy precipitation events sampling was interrupted for two days to avoid distorted samples. Like the FC, filtration gives a momentary picture and allows the complete separation of one and the same sample into its solid phase and the liquid one. The method is described in Annex 6.

An essential condition that any suspended-sampling technique should meet is the representative collection of the suspended material. This means that the collected suspended material must reflect the real conditions in the river. *A priori* the FC and filtration have the best characteristics in this regard, since these methods are able to separate the suspended matter nearly completely from the water (separation rate nearly 100%; both suspended solids and liquid phase are available). The separation rates of BISAM and ST are not clearly defined; that of the ST is in the order of magnitude of 30%. As predominantly light organic material is not collected, the separation by these passive systems is selective. Annex 4, Chapter 4.1.3 explains in detail that this selectively collected suspended material shows other qualities than material collected by FC (e.g. lower organic portion, higher PAH contents). Another drawback of these two methods is the fact that the water, that was separated from its suspended-solids load, is not available for further analysis.

For these reasons (representativity, separation rate), the sampling techniques BISAM and ST cannot be recommended for purposes of estimating PAH loads. Table 5.6 compares the advantages and drawbacks of the remaining two methods FC and filtration.

Except the yield of suspended solids, filtration has the same advantages like the FC, while only three drawbacks are listed, of which one (snapshot) may also be considered as an advantage of high temporal resolution. Nevertheless, the drawback of "very low SS yield" may be significant. In filtration, the suspended solids from 10 l of water are distributed on two filters, what would correspond at the examples of the rivers examined for the present study to a mean amount of 30 (Skjern) to 750 mgDW (Scheldt) per filter. Artefacts in the analytical findings may occur due to

the unfavourable ratio between sample mass and mass of the filter and due to clogging effects. This artefacts are not observed in this study, but reported elsewhere [Horowitz et al., 1996]. An FC collects at a throughput of 1 m<sup>3</sup>/h already after one hour of sampling the 100-fold amount. This minimizes the error in sampling (representativity) and in analysis.

Table 5.6: Characteristics, advantages and drawbacks of flow-through centrifuge and filtration for the sampling of suspended matter

| System                                       | Specifications                                                                                                                                                                 | Characteristics                                                                                                                                                                                                               |                                                                                                                                                                                                                                                    |
|----------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                              |                                                                                                                                                                                | Advantages                                                                                                                                                                                                                    | Drawbacks                                                                                                                                                                                                                                          |
| <b>(Mobile) Flow-through Centrifuge (FC)</b> | Weight: app. 500 kg<br>Dimensions: app. 100x70x170 cm<br>Separation rate: app. 95 %<br>Rotor speed: 17,000 rpm<br>Rotor diameter: 105 mm (inner)<br>max. throughput: 1,500 l/h | - high time resolution;<br>- mobility (vertical and cross profiles measured by ship);<br>- high SS yield;<br>- high and constant separation rate allowing load estimates and analyses of the liquid phase (total separation); | - "snapshot", not integrating;<br>- high costs;<br>- high maintenance requirement;<br>- in difficult terrain use on boat necessary;<br>- use on boat requires special equipment, as the unit is large, bulky, and hard to handle (e.g. ramp etc.); |
| <b>Filtration</b>                            | two glass fibre filters<br>diameter: 110 mm<br>nominal pore size: 0.7 µm<br>total amount of sample: 10 l                                                                       | - cheap;<br>- easy handling;<br>- high time resolution;<br>- mobility;<br>- high and constant separation rate allowing load estimates and analyses of the liquid phase (total separation);                                    | - "snapshot", not integrating;<br>- very low SS (susp. solids) yield;<br>- analytical findings based on artefacts are possible;                                                                                                                    |

Conclusion: Generally, the use of a flow-through centrifuge can be recommended, because it yields great amounts of representative suspended solids in very short time, and it provides an almost complete separation of one and the same water sample into the dissolved and the solid phase. Filtration, as a low cost and uncomplex alternative, should only be used, as long as a representative sampling and reliable analysis in face of very low amounts of sample is ensured.

## 5.2 Calculation of annual loads

### 5.2.1 Problems in load calculation

The precise determination of the quantity of contaminants transported annually through a given river profile is only possible on the basis of continuous measurements of streamflow and contaminant concentration. In reality, however, at least contaminant concentrations are available only in form of discrete values based on e.g. weekly or monthly measurements at one single point in the river profile.

The problem is consequently to ensure representative sampling (cf. Chapter 2), i.e. to select the sampling site so that it represents the whole profile adequately or – if the spatial inhomogeneities are strong – to sample at several points in the profile. Nevertheless, even provided that the discrete random samples measurements are correct and representative, the mathematical procedure of the subsequent load calculation is not clearly defined.

The following chapter presents six different calculation methods, which had been compared already in earlier studies [Steinebach, 1994; Keller et al., 1997; LAWA, 2002]. All these methods yield more or less close approximations of the real annual load, which – in fact – is usually not known for lack of continuous, highly resolved measurements. The suitability of each method depends on the river system and the questions under consideration (Are the considered substances dissolved or particle-bound? Do concentrations have high temporal variability? Are they correlated with streamflow? etc.)

Two of these methods were selected to compute in the following Chapter 5.2.3 the annual PAH load in the seven studied areas. Moreover, model calculations with reduced data sets should provide evidence on the sampling frequency of PAH and suspended-solids concentrations that should be observed as minimum requirements. Furthermore, the model calculations are expected to give some indications, which of these two selected methods is most robust in response to non-fulfilment of this minimum frequency (Chapter 5.2.4).

## 5.2.2 Calculation methods

### 5.2.2.1 Presentation of the methods

The examples of the PAHs and suspended-solids loads in the rivers Elbe and Weser were used to compare six calculation methods (cf. Chapters 4.1.7 and 4.2.6 in Annex 4) with the following conditions:

- Concentration  $c$  as random sample in mg/l, measured at the times  $t_i$ , with  $i = 1, \dots, N$ ;
- Daily measurement of streamflow  $Q$  in m<sup>3</sup>/s ( $Q_i$ , with  $i = 1, \dots, 364$ );
- Annual load in g; 1 year equals 364 days, with 86,400 s each.

Method #1: product of mean values

$$\text{annual load} = \bar{c} * \bar{Q} * 364 * 86400s$$

This most simple approximation is the product of multiplying the mean values of  $c$  and  $Q$ . By multiplication with 364 days and 86,400 seconds per day one obtains the annual load expressed in grammes (g).

Method #2: mean value of the products

$$\text{annual load} = \frac{1}{N} \sum_{i=1}^N c(t_i) Q(t_i) * 364 * 86400s$$

This method multiplies each measured concentration value with the streamflow value measured at the same time  $t_i$  and then calculates the mean value of the  $N$  products.

The additional information about the daily measured streamflow values is lost in both methods #1 and #2. This shortage is taken into account in different ways by the following methods #2a to #5.

Method #2a: same as #2, but weighed with the "true" annual average of  $Q$

$$\text{annual load} = \frac{1}{N} \sum_{i=1}^N c(t_i) \frac{Q(t_i)}{\bar{Q}} * 364 * 86400s$$

The additional information about the "true" annual streamflow, i.e. the value estimated on the basis of daily mean values  $\bar{Q} = \left( \sum_{i=1}^{364} Q_i \right) / 364$ , is used here by dividing through the mean value of  $Q(t_i)$  and multiplying with  $\bar{Q}$ .



Methode #3: linear interpolation

$$\text{annual load} = \sum_{i=1}^{364} c_{\text{lin},i} Q_i * 86400s$$

The missing concentration values are estimated by means of linear interpolation, so that for each day the product of concentration and streamflow can be calculated.

Methode #4: regression  $c(t) = \tilde{c}(Q(t))$

$$\text{annual load} = \sum_{i=1}^{364} \tilde{c}(Q_i) * Q_i * 86400s$$

Provided a correlation exists between  $c$  and  $Q$ , the daily values of  $c$  ( $= \tilde{c}$ ) can be computed from the daily measurements of  $Q$ . The underlying regression function reads [Keller et al., 1997]:  $\tilde{c}(Q) = a_0 + a_1 \cdot \exp(-a_2 \cdot Q)$

Methode #5: regression  $T(t) \equiv c(t) * Q(t) = \tilde{T}(Q(t))$

$$\text{annual load} = \sum_{i=1}^{364} \tilde{T}(Q_i) * 86400s$$

This method establishes a regression between transport  $T = c \cdot Q$  and streamflow  $Q$ :  $T = a \cdot Q^b$ . The computed daily transport rates in g/s are summed up over the whole year. The cumulative sum gives the estimated annual load in g.

It is the drawback of the two regression methods (#4 and #5) that the streamflow data  $Q(t_i)$  associated with the sampling times  $t_i$  do usually not cover the whole range of streamflow variations of the considered year. This may result in large errors in the evaluation of the regression function within the extrapolation range not covered by data.

Against the first three methods, the methods #3-5 have the advantage that they estimate, besides the annual load, also the daily transport rates, which can be easily visualized by graphical means. The annual load results then from cumulation of the daily transport rates.

### 5.2.2.2 Selection of suitable methods

Method #1 is a very rough approximation, which can yield reliable estimates only if one of the two values  $c$  or  $Q$  is constant. This however, is usually not the case.

Method #2 can be improved with a few tricks by utilizing the information on the daily streamflow values. This results, in the simplest case, in method #2a.

Method #2a is the method recommended by OSPAR in the RID Principles [INPUT, 2000]. Just like in method #3-5, the daily discharge values are included into the calculation.

One drawback of methods #4 and #5 (uncertain extrapolation range) was mentioned in the previous chapter. Moreover, it can be seen from the load calculations on the rivers Elbe and Weser (cf. Annex 4) that the underlying regressions are very poor or non-existent. For these reasons, these two methods cannot be recommended for the present study.

On the basis of the mentioned assessments, the load calculations in the following chapters are performed with methods #2a and #3. It speaks for method #2a that this is a common and widely accepted method. Method #3, conversely, has the advantage that it provides additional valuable information in form of the daily transport rates. It is expected that the concrete application of these two methods at the seven studied areas and the subsequent model calculations with reduced data sets will furnish indications for a deeper evaluation of the two methods.

### 5.2.3 Estimation of annual loads

Table 5.7 gives an overview on the frequency of measurements of the different load-relevant parameters. Only useable data are included, i.e. measurements which are above the LOQ (Limit Of Quantification).

Table 5.7: Frequency of measurements

|                      | Elbe | Weser | Scheldt | Rhine | Meuse | Guadalq. | Skjern |
|----------------------|------|-------|---------|-------|-------|----------|--------|
| Q                    | d    | d     | m       | d     | d     | bw       | d      |
| C <sub>SS</sub>      | "d"  | "d"   | bw      | bw    | m     | bw       | m      |
| PAH <sub>SS</sub>    | er   | er    | m       | bw    | m     | m        | -      |
| PAH <sub>total</sub> | er   | er    | m       | -     | -     | -        | -      |
| PAH <sub>diss</sub>  | er   | er    | m       | -     | -     | m        | -      |

d: daily, "d": working daily, bw: biweekly, m: monthly, er: event related (5 to 7 times a year).

In each of the studied areas, the concentration of suspended solids C<sub>SS</sub> and the 16 PAHs according to EPA were measured in the solid phase (PAH<sub>SS</sub>, ss=suspended solids), except in the River Skjern, where only the total samples were analysed. Moreover, in River Skjern only values below LOQ were found. The limit of quantification is in this case 10 ng/l for each of the compounds, except naphthalene with a LOQ = 20 ng/l. Another exception is PAH<sub>SS</sub> in the River Meuse, where the sum comprises only 12 compounds (i.e. 16 PAHs according to EPA without naphthalene, acenaphthene, acenaphthylene, and fluorene). In the River Guadalquivir, besides the 16 EPA-PAHs, the compounds benzo[e]pyrene and perylene were analysed additionally, so that altogether 18 PAHs were covered there.

The calculation of the annual loads is based on daily measurements of streamflow Q (cf. Chapter 5.2.2.1). From River Scheldt only monthly averages were available, which were used as constant values for the whole month. In the case of River Guadalquivir the fortnightly measurements were linearly interpolated to daily values before the described calculation methods were applied.

#### *Annual suspended-solids load*

Figure 5.4 shows the annual suspended-solids load values obtained by calculation methods #2a and #3 from the studied areas in comparison. Regarding the computation methods, a clear trend cannot be identified: Method #3 produced in comparison with #2a sometimes identical values (Weser, Skjern), as well as lower (Rhine, Meuse, Guadalquivir) or higher ones (Elbe, Scheldt). The result depends on the individual constellation, i.e. on the variations in streamflow and concentrations, and is not easily predictable.

In the River Skjern, both streamflow (29 m<sup>3</sup>/s) and the suspended-solids content (6.5 mg/l) are so low that annual loads of merely 6,226 t (Method #2a) and 6,238 t (Method #3) were recorded. The relatively high annual load in the Guadalquivir (600,000 t) results in the first line from the

heavy rainfall events in January 2001, after which on 29 January a suspended-solids content of 1,583 mg/l was measured. If this measurement is omitted from the computation (one measurement out of 22), the annual load comes to only one third of the actual value (208,006 t by Method #2a and 176,546 t by Method #3).

Method #3 allows to determine

the daily transport rates, what illustrates impressively the enormous influence of this event on the computation of the annual load in the Guadalquivir (Figure 5.5).

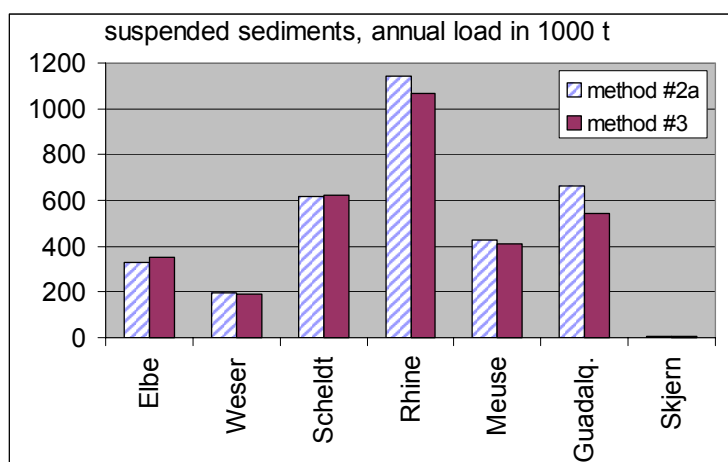


Fig. 5.4: Annual load of suspended sediments, calculated with two different mathematical methods, cf. chapter 5.2.2.

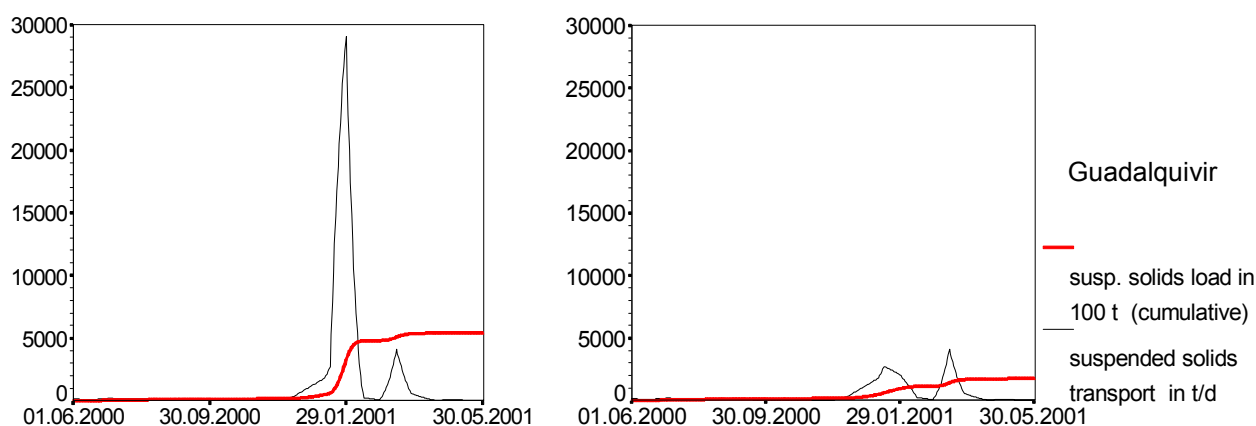


Fig. 5.5: Suspended solids load as cumulative sum of daily transport rates (method #3). Left: with single  $C_{SS}$  event from January 29; Right: without this event

### Annual PAH loads

Figure 5.6 shows the annual loads for the sum of the 16 PAHs, separately for the total, the particle-bound, and the dissolved portions. To calculate the particle-bound load, the suspended solids PAH concentration ( $=PAH_{SS}$  in mg/kgDW) is multiplied with the suspended-solids concentration  $C_{SS}$  (in mg/l) to obtain the particle-bound concentration in ng/l. Since  $C_{SS}$  usually varies more and is measured with higher frequency than  $PAH_{SS}$ , these two parameters must be first linearly interpolated and then be multiplied when Method #3 is used. Otherwise, the valuable information about the variations of  $C_{SS}$  would be lost.

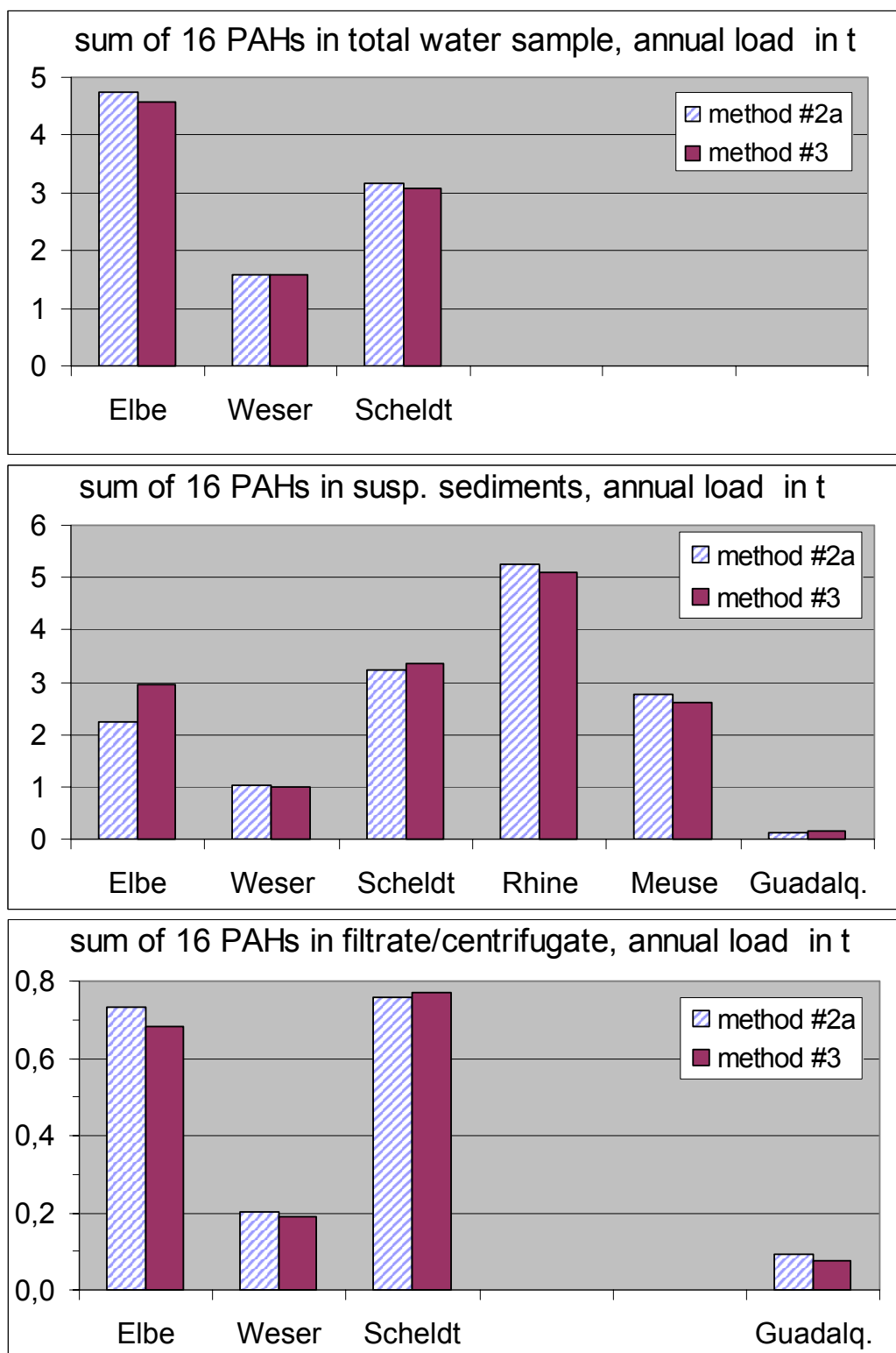


Fig. 5.6: Illustration of annual PAH loads in different rivers, separated in total (top), particulate bound (middle) and dissolved loads (bottom). Each load is calculated by means of two mathematical methods, i.e. Method #2a and #3 (cf. Chapter 5.2.2).

For the same reason some slight modification must be added to method #2a in case of particle-bound load calculation, if the  $C_{SS}$  values are measured with higher frequency than the PAH values are. Method #2a already weights for the "true" average discharge  $\bar{Q}$ , and in the same sense the result must be weighted for the "true" suspended solids concentration  $\bar{C}_{SS}$ . This is done by dividing with the average  $\overline{C_{SS}(t_i)}$  and multiplying with the average  $\overline{C_{SS}(t_k)}$ , where  $t_i$  indicate the times of PAH measurements and  $t_k$  the times of  $C_{SS}$  measurements.

Each of the load values is based on measurements, and thus it is explicable that the balance – dissolved load plus particle-bound load equal total load – does not always work out exactly. In the example of the Elbe, the sum of dissolved load plus particle-bound load amounts to about 75 % of the total load, while it is around 80 % in the Weser. Errors in load estimates may occur in sampling, sample treatment, and analysis. The mentioned deviations of 20-25 % are an indication in which order of magnitude the error has to be expected at least. For River Scheldt, on the other hand, the sum of the dissolved and the particle-bound load overestimates the measured value of the total load by approx. 20 %.

The Rhine carries the highest loads (Figure 5.6, middle). If one assumes a particle-bound portion of 70-80 % (cf. Chapter 5.1.4), the total PAH load in the Rhine can be estimated between 6.5 and 7 tonnes. If the rivers are listed according to their annual PAH loads, the ranking is a very good reflection of the streamflow situations, except for the River Scheldt, where the extreme  $C_{SS}$  values outweigh the discharge dependency (cf. Chapter 5.1.1). It is evident that the loads are more dominated by streamflow than by suspended solids PAH concentration, or in other words, streamflow varies stronger from river to river than the mean contamination level does.

No PAH values are available from the River Skjern. If one uses for a rough estimate of the load for all 16 EPA-PAHs half the limit of quantification (assumed to be constant throughout the year), the result is an annual load of 0.08 t for the sum of PAHs in the total sample. This value – approximately one third of the annual load in the River Guadalquivir – constitutes an upper estimate, because half the limit of quantification (=10 ng/l for naphthalene and 5 ng/l for the remaining PAHs) is probably chosen too high for the sparsely populated and little industrialized catchment of the River Skjern.

For the Guadalquivir, the total load, computed from the particle bound portion and the dissolved one, amounts to 0.255 t per year. The annual particle-bound load amounting to 0.175 t has a share of 69 %. For comparison: Elbe 79 %, Weser 84 %, and Scheldt 80 %. This again confirms the result found in Chapter 5.1.4, namely that the particle-bound portion in the Guadalquivir is the lowest against all the other rivers examined.

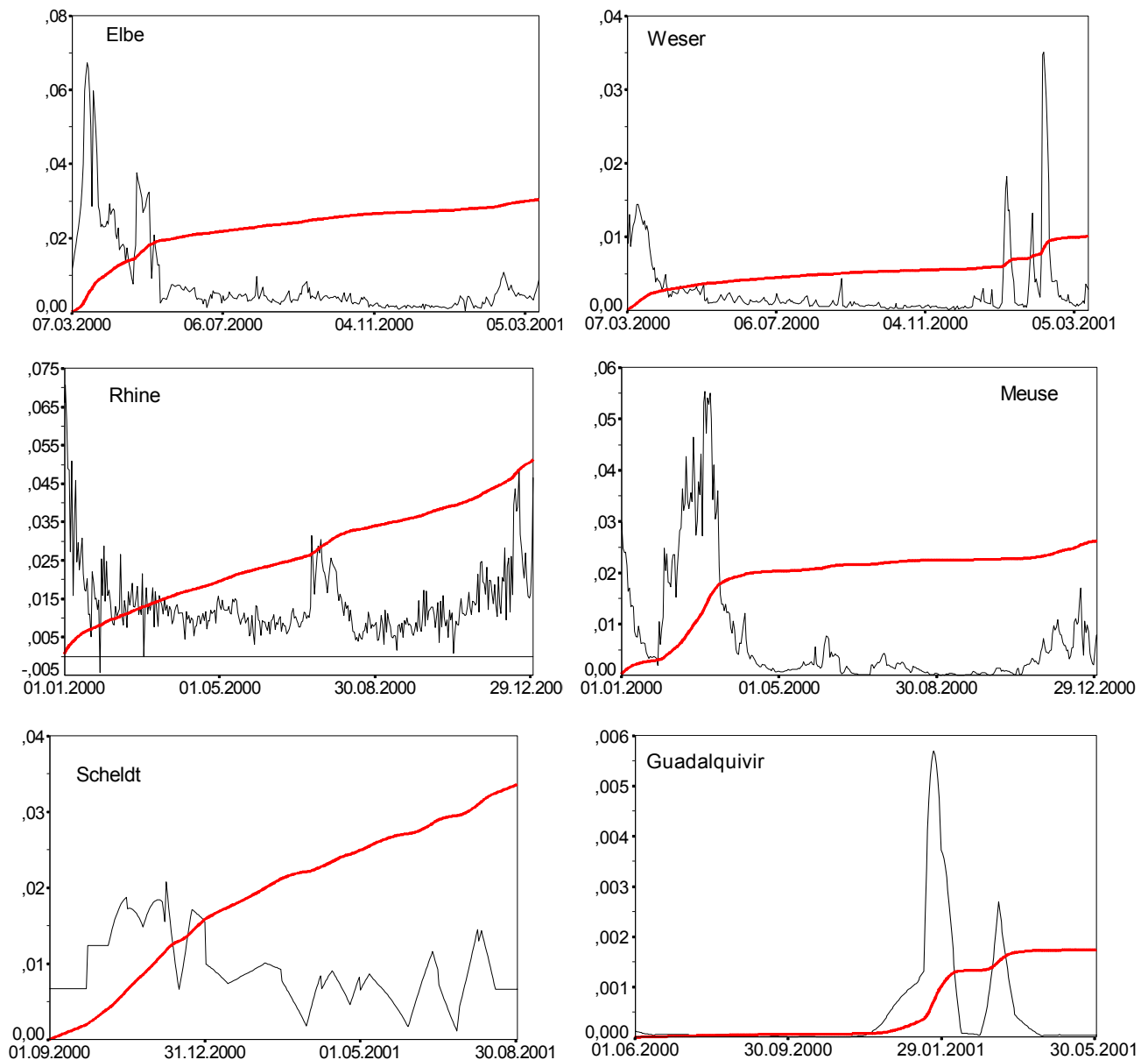


Fig. 5.7: Sum of particulate bound PAHs: daily transport rates and cumulative load.  
 — daily transport rates in t/d      — cumulative load in 100 t.  
 Please note the different scales.

Figure 5.7 gives the daily transport rates of the sum of the particle-bound PAHs of each river under consideration, except river Skjern, where no suspended solids have been analysed. The transport rates are shown together with the loads calculated as the cumulative sum of those rates. Except for the rivers Rhine and Scheldt, which show a nearly continuous increase in the cumulative load, in all other rivers there are only few events – particularly between December and April – that mainly contribute to the annual load. The two exceptions (on rivers Rhine and Scheldt) are probably due to a strong weir regulation. The graphical illustration in Figure 5.7 is based on the calculation method #3.

### 5.2.4 Model calculations with reduced data sets

Model calculations with reduced data sets have been run to provide evidence on the minimum sampling frequencies of PAH and suspended-solids concentrations. Moreover, the model calculations should help to find out, which of the two selected methods is most robust in response to non-fulfilment of the minimum frequency requirement.

According to the abbreviations used in Table 5.7 (Chapter 5.2.3) "d" means working-daily, bw - biweekly (i.e. fortnightly), m - monthly, and er - event-related. In the following, the results of computations with parameters measured in high frequency (suspended solids: "d", PAHs: bw) are called "real" and serve as a scale for assessing those loads computed on the basis of reduced data sets.

Based on the measuring frequencies listed in Table 5.7, three examples were selected, which permit a maximum degree of reduction, with daily streamflow values  $Q$  as a presupposition: suspended-solids loads ( $C_{SS}$ , "d" reduced to bw and m) in the Elbe and the Weser as well as particle-bound PAH loads ( $PAH_{SS}$ , bw reduced to m and er) in the Rhine.

#### *Suspended-solids loads in the Elbe and the Weser*

Applied at the River Elbe, the method #3 showed the expected behaviour, namely that the computed loads deviate with decreasing sampling frequency more and more from the so-called real value (Figure 5.8). In the application of method #2a, the greatest deviation appeared after the reduction to biweekly values (bw). However, one should note the scale of the ordinate axis that does not begin at zero: Even in this extreme case, the deviation never exceeds 7.5 % from the real value. At the River Weser, the expected tendency – the higher the reduction the wider the deviation from the real value – is very distinct, with a stronger influence of reduced sampling frequency in

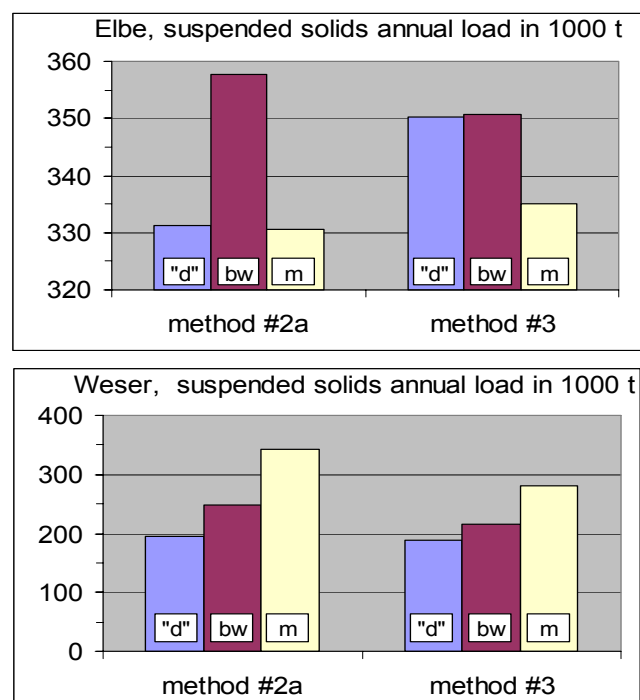


Fig. 5.8: Model calculations with artificially reduced data sets. Suspended solids annual load in rivers Elbe and Weser. For explanation see text.



computations by method #2a than by method #3. For instance, when data are reduced to monthly values (m), method #2a produced deviations of around 80 %.

On the whole, in calculations of suspended-solids loads, method #3 seems to be somewhat more robust against reduced sampling frequency, although the differences to method #2a are only very low, and due to the low number of calculated examples they are certainly not significant.

### ***Particle-bound PAH loads in the Rhine***

At River Rhine the  $C_{SS}$  as well as the  $PAH_{SS}$  measurements took place every two weeks. As the particle-bound PAH concentrations in ng/l are computed from the product of  $C_{SS}$  and  $PAH_{SS}$  (cf. Chapter 5.2.3), two options may be distinguished: Reducing only the  $PAH_{SS}$  sampling frequency (from bw to m and er) or reducing both the  $C_{SS}$  and  $PAH_{SS}$  sampling frequencies (also from bw to m and er). The results are illustrated in Figure 5.9.

In this example too, both the methods #2a and #3 respond similarly to reduced data. It is an interesting result that for the computation of the particle-bound PAH load high-frequency measurements of  $PAH_{SS}$  are not necessarily required as long as  $C_{SS}$  is measured in high frequency (Figure 5.9, top). Even when reducing to event-related sampling, both methods provide load values comparable with the real ones (i.e. bw).

However, as soon as additionally the sampling frequency for  $C_{SS}$  is reduced (Figure 5.9, bottom), both computation methods yield large deviations from the real load values when simulating the reduction to event-related sampling (er). This is due to the fact that for the load, that is computed from the three parameters  $Q$ ,  $C_{SS}$ , and  $PAH_{SS}$ , the variations are mostly those of  $Q$  and  $C_{SS}$ , while the suspended solids PAH concentration  $PAH_{SS}$  shows a narrower range of variability.

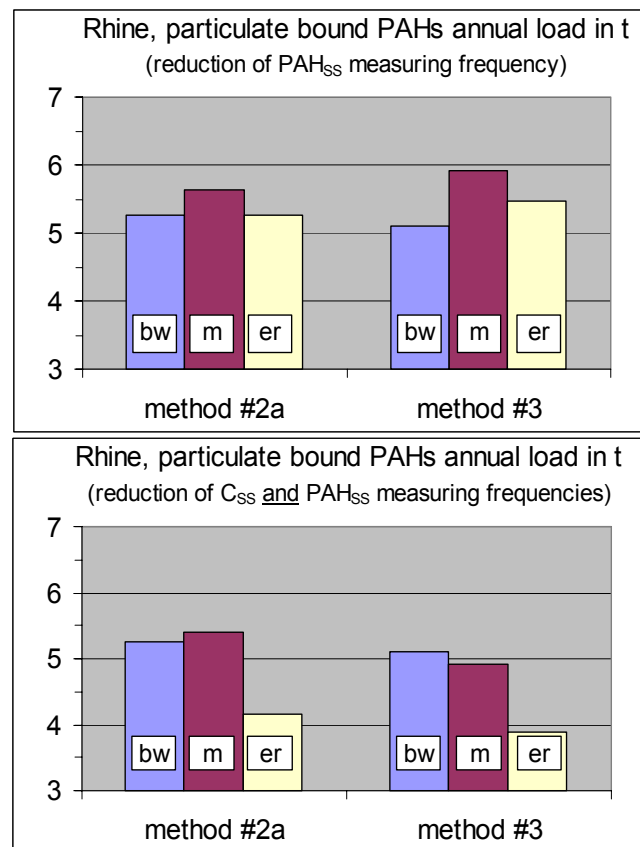


Fig. 5.9: Model calculations with artificially reduced data sets. Particle-bound PAHs annual load in River Rhine. For explanation see text.

Conclusion: In model computations with reduced data sets, too, no significant differences could be found between the methods #2a and #3. Regarding sampling frequency for determination of particle-bound PAH loads, from the analyzed examples it can be noted that frequent  $\text{PAH}_{\text{ss}}$  measurements are not necessary, provided  $C_{\text{ss}}$  is measured with sufficient frequency (daily to fortnightly). If model calculations like these presented here will be done for each individual river under future investigation, perhaps this could enormously reduce analytical efforts in omitting dispensable PAH measurements.

## 6. Conclusions

The objectives of this study are the determination of an annual PAH load for the seven selected rivers and the development of a harmonised methodology for the estimation of these riverine loads into the North Sea and the North-east Atlantic. For this purpose Belgium, Denmark, Germany (lead country), the Netherlands, and Spain contributed to this study with measuring programmes on seven rivers. Detailed results of each participating country are described in the Individual Parts in Annexes 2 to 6.

The biggest problem in complying with the above mentioned aims is to face the highly complex suspended sediment dynamics in natural estuaries, due to multifarious morphology, instationary velocity fields, settling and erosion zones, tidal flats, etc. For this reasons, a representative sampling inside the tidal reach is possible only in those estuaries, where the suspended matter transport does not distinctly differ from that of the dissolved phase, e.g. in canalized or strongly regulated estuaries. In all other cases, sampling sites should be located directly upstream the tidal limit in a stretch of unidirectional flow. This provides the possibility to quantify the amounts of riverine contaminant transport into the estuary as one contribution to a comprehensive balance of the whole estuary system, the other components being direct inputs into and direct removal from the estuary (dredging etc.), permanent deposition in the tidal flats, and the target value, i.e. the export of contaminants from the estuary into the sea (cf. Chapter 2).

Besides these problems, the study concentrates on developing harmonised sampling strategies, wherever the sampling site is located, and on estimating annual PAH loads on the seven European rivers under investigation. Most relevant parameters are the concentrations of the 16 PAHs specified by US EPA, the suspended solids concentration, and the streamflow (Chapter 3).

After a short characterisation of the rivers (Chapter 4), in chapter 5 the results are given, distinguishing between general ones (Chapter 5.1) – as e.g. median values of the mandatory parameters, PAH patterns, seasonality and distribution behaviour of PAHs, correlations between parameters, and a comparison of different suspended matter sampling techniques – and such concerning the load calculations (Chapter 5.2).

Chapter 5.1.1 gives an overview on the median values and the variations of the mandatory parameters of this study. As one result it is shown, that the suspended sediments PAH concentration ( $\text{PAH}_{\text{SS}}$  in  $\text{mg/kgDW}$ ) of the Belgian, Dutch and German rivers feature comparable contamination levels of about 5 to 7  $\text{mg/kgDW}$ . The PAH contamination in the lower populated and less industrialized basins in Denmark and Spain amounts to values less than 1  $\text{mg/kgDW}$ , as expected.

Total Naphthalene concentrations differ from river to river, with the Elbe showing the highest values (median: 70  $\text{ng/l}$ ) and the widest variations, the Weser and Scheldt revealing medium levels (20 to 35  $\text{ng/l}$ ), and the others being lower than 10  $\text{ng/l}$ .

The experimentally ascertained portion of the particle-bound fraction of PAHs was found to be between 50 and 80 % for the sum of the 16 EPA PAHs. Conversely, this result shows, that also the dissolved portion cannot be neglected in estimating the total contamination.

Several techniques for suspended matter sampling and phase separation (dissolved and particle-bound) are compared (Chapter 5.1.6). Generally, the use of a flow-through centrifuge can be recommended, because it yields great amounts of representative suspended solids in very short time, and it provides an almost complete separation of one and the same water sample into the dissolved and the solid phase. Filtration, as a low cost and uncomplicated alternative, should only be used, if a representative sampling and reliable analysis in face of very low amounts of sample is ensured.

The correlation analyses given in chapter 5.1.5 aimed to detect relationships between parameters, that would lead to a possible simplification of the measuring programmes. Unfortunately, reliable causal correlations between parameters requiring expensive and sophisticated analysis, like  $\text{PAH}_{\text{SS}}$  and  $\text{NAPHT}_{\text{total}}$ , and those that can be more easily determined, such as  $Q$ ,  $C_{\text{SS}}$ ,  $C_{\text{OC}}$ , or  $\text{GSA}_{(<63\ \mu\text{m})}$ , are not universally existent. Merely the particle-bound concentration  $\text{PAH}_{\text{SS}}$  shows some linear relations with e.g. the clay and silt fraction  $\text{GSA}_{(<63\ \mu\text{m})}$  (Rhine and Meuse), the streamflow  $Q$  (Elbe), and the organic portion  $C_{\text{OC}}$  (Elbe and the Meuse). A desirable simplification on the basis of these correlations does not seem to be reasonable at the moment. At best, one could imagine a reduction of measuring frequencies for PAHs and the interpolation of intermediate values by means of the regressions found. A transfer of the individually

determined regressions from one river basin to another one is not admissible. However, the correlations found give valuable information for the interpretation of the processes occurring in the individual rivers.

The possibility for reducing the frequency of PAH measurements in order to decrease the analytical expense is supported by the results of chapter 5.2.4. There, the model calculations with artificially reduced data sets show that the frequency of PAH measurements can be reduced (preferably to event related sampling at 5 to 7 times a year), as long as the streamflow and the suspended solids concentration are recorded with sufficient high frequency (preferably daily values). This is due to the fact, that the PAH contaminations in the rivers do not vary to such an extent as the streamflow and the suspended solids concentration do.

The concrete annual suspended solids and PAH loads for the individual rivers are given in chapter 5.2.3. The estimated annual total PAH loads range between 7 tons/year (River Rhine; estimated from particle-bound PAH load, which amounts to 5.2 tons/year in River Rhine) and values less than 0.25 tons/year in rivers Guadalquivir and Skjern. The ranking of the rivers according to their annual PAH loads reflects very well the streamflow situations, except for the River Scheldt, which shows a comparable high load due to extreme high suspended solids concentrations. This again is an indication that, because of the wider variations, the streamflow determines the riverine loads to a larger extent than the PAH levels do.

Together with the concrete load values, six different mathematical calculation methods are assessed in chapter 5.2.3 with view to their applicability for annual load calculations. As a result, two of them are rated as recommendable, one of them being the method already introduced by the RID Principles by OSPAR [INPUT, 2000]. The other recommended method is based on linear interpolation. Both methods provide highly comparable results. The reason for the recommendation of the linear interpolation method, besides the well-proven and accepted OSPAR method, is due to the fact, that it yields additional information about the daily transport rates (in tons/day). These daily rates give insight into the time dependent contaminant transport behavior and open further possibilities of interpretation. Chapter 5.2.3 shows graphical illustrations of these results.

All recommendations, based on the results of this study, are compiled as a Guideline which is attached as Annex 1 to the present report.

## References

- Ackermann F, 1998a. Dynamik der Schwermetallbelastung in feinkörnigen Sedimenten und Schwebstoffen im Tidebereich von Ems, Weser und Elbe. Bundesanstalt für Gewässerkunde, BfG-Report 1188.
- Ackermann F, Schubert B, 1998b. Zur Problematik der Bestimmung von Frachten partikulär gebundener Schadstoffe in die Nordsee. Bundesanstalt für Gewässerkunde, BfG-Report 1177.
- Ackermann F, Schubert B, 2000. Das Elbeästuar: Senke und Quelle für Schadstoffe. ATV-DVWK-Schriftenreihe 22: 298-299.
- ARGE Elbe, 1996. Zeitliche und örtliche Variabilität von organischen Stoffen in schwebstoffbürtigen Sedimenten der Elbe bei Hamburg-Blankenese und der Mulde bei Dessau. Arbeitsgemeinschaft für die Reinhaltung der Elbe, Hamburg.
- ARGE Elbe, 1998. Verteilung von organischen Kontaminanten zwischen wässriger und partikulärer Phase in der Elbe und der Deutschen Bucht. Arbeitsgemeinschaft für die Reinhaltung der Elbe, Hamburg.
- ARGE Elbe, 2001. Wassergütedaten der Elbe. Zahlentafel 1999. Arbeitsgemeinschaft für die Reinhaltung der Elbe, Hamburg.
- Bagnold R A, 1968. Deposition in the process of hydraulic transport. *Sedimentology* 10: 45-56.
- Billen G, Somville M, de Becker E, Sevais P, 1985. A nitrogen budget of the Scheldt hydrographical basin. *Neth. J. Sea Res.*, 19: 223-230.
- Celik I, Rodi W, 1984. A deposition-entrainment model for suspended sediment transport. Report SFB 210/T/6, Strömungstechnische Bemessungsgrundlagen für Bauwerke. University of Karlsruhe.
- Celik I, Rodi W, 1988. Modeling Suspended Sediment Transport in Nonequilibrium Situations. *J. Hydr. Engrg.* 114 (10): 1157-91.
- EPA, 1984. U.S. Environmental Protection Agency: Method 610 – Polynuclear Aromatic Hydrocarbons. 40 CFR Part 136, 43 344; Federal Register 49, No. 209.
- Harvey R G H, 1997. Polycyclic Aromatic Hydrocarbons. WILEY – VCH, New York. Chichester, Weinheim, Brisbane, Singapore, Toronto, p. 8
- Henriksen P (Edt.), 2001. Marine områder 2000 - Miljøtilstanden og udviklingen. Faglig rapport fra DMU. Volume No. 375 (electronically): <http://faglige-rapporter.dmu.dk>
- Horowitz A J, Lum K R, Garbarion J R, Hall G E M, Lemieux C, Demas C R, 1996. The effect of membrane filtration on dissolved trace element concentrations. *Water Air Soil Poll.*, 909: 281-294.
- INPUT, 2000. The Comprehensive Study on Riverine Inputs – (RID) Principles. INPUT 00/7/Info.1-E. Lisbon: 17-21 January 2000.

- Jay D A, Geyer W R, Uncles R J, Vallino J, Largier J, Boynton W R, 1997. A Review of Recent Developments in Estuarine Scalar Flux Estimation. *Estuaries* 20 (2): 262-280.
- Keller M, Hilden M, Joost M, 1997. Vergleich von Schätzmethode für jährliche Stofffrachten am Beispiel des IKS-R-Meßprogrammes 1995. BfG-1078.
- LAWA, 2002. Ermittlung von Stofffrachten in Fließgewässern. Probenahmestrategien und Berechnungsverfahren. Länderarbeitsgemeinschaft Wasser (LAWA), in press.
- OSPAR, 2001. Draft OSPAR Background Document on Polycyclic Aromatic Hydrocarbons (PAH). OSPAR 01/4/6-E. Valencia, 25-29 June 2001.
- QSR, 2000. Quality Status Report 2000 for the North-East Atlantic. OSPAR Commission for the Protection of the Marine Environment of the North-East Atlantic. ISBN 0 946956 52 9 (hardcopy version) or <http://www.ospar.org/eng/html/qsr2000/qec0.htm>, London 2000.
- Steinebach G, 1994. Zur Ermittlung von jährlichen Stofffrachten in großen Fließgewässern am Beispiel der IKS-R-Zahlentafeln 1991. BfG-0827.
- Streit B, 1991. Lexikon der Ökotoxikologie. VCH
- UBA, 1999. Pilot study to elaborate a harmonised method for the determination of water-based inputs of polycyclic aromatic hydrocarbons (PAHs) into the North Sea. Federal Institute for Hydrology Koblenz and Berlin, Berlin Dept., on behalf of the Federal Environmental Agency (UBA). Research project water, report 297 22 529.
- U.S. Geological Survey, 1999. National Field Manual for the Collection of Water-Quality Data. Chapter A5. Processing of Water Samples. Edts.: FD Wilde, DB Radtke, J Gibbs, and RT Iwatsubo.
- Van Rijn L C, 1993. Principles of Sediment Transport in Rivers, Estuaries and Coastal Seas. Aqua Publications, Amsterdam.
- Van Zoest R, Van Eck GTM, 1993. Behaviour of selected PCBs, PAHs and g-HCH in the Scheldt estuary, S.W. Netherlands. *Neth. J. Aquat. Ecol.* 27: 2-4.
- WHO, 1998. Environmental Health Criteria 202. Selected non-heterocyclic polycyclic aromatic hydrocarbons. (Chap. 1.8: Effects on humans). World Health Organization, Geneva.
- Wollast R, 1982. Methodology of research in micropollutants - heavy metals. *Water Sci. Technol.*, 14: 107-125.

**Proposal for a Guideline  
for the Estimation of Riverine PAH Inputs  
into the North Sea  
and the North-East Atlantic**

**Annex 1** to the Final Report of the

**International Pilot Study for the determination of Riverine Inputs  
of Polycyclic Aromatic Hydrocarbons (PAHs) to the Maritime Area  
on the basis of a harmonised methodology**

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## **4. Suspended solids and PAH load calculation methods**



## 1. Introduction

The recommendations given in this guideline refer to an adequate estimation of suspended solids load and particle-bound, dissolved, and total loads of polycyclic aromatic hydrocarbons (PAHs) transported via rivers into the marine environment. The recommendations comprise suitable sampling methods and methods for computing these loads, and they are based on the results of the international PAH pilot study, that were presented in the Common Part of the Final Report and the five Individual Parts (Annexes 2 to 6).

Participating states in the study were Belgium with the River Scheldt, Denmark with the Skjern, Germany (lead country) with the Elbe and the Weser, the Netherlands with the Rhine and the Meuse, and Spain with the Guadalquivir.

The aims of this study have been the determination of an annual PAH load for the seven selected rivers and the development of a harmonised methodology for the estimation of these riverine loads into the North Sea and the North-east Atlantic.

In pursuit of the second mentioned of these objectives, these guidelines have been formulated and attached to the Common Part of the Final Report as Annex 1.

The recommendations given in this Guideline are only briefly explained, literature references were omitted. Instead, reference is made to the contents of the Final Report. References to certain chapters relate, if not mentioned otherwise, to the Common Part of the Final Report.

## 2. Sampling

### 2.1 Sampling location

The sampling site should be as far downstream as possible to include all contaminant discharges and other contamination sources. In some cases the suspended matter dynamics stand in a way of that.

In natural waters, where settling and erosion zones may exist, the dynamics of suspended solids differ considerably from those of the dissolved substances. This applies especially to estuaries that are influenced by tides, and where the strong temporal and spatial heterogeneity of the suspended solids concentrations and the velocity patterns of currents have prevented the experimental determination of the suspended-solids dynamics to date (cf. Chapter 2). As particle-bound PAHs share the fate of the carrying substances, their transport behaviour is completely different from that of dissolved PAHs.

This has the following consequences for the selection of the sampling location:

- Generally, the sampling site should be as far downstream as possible;

but:

- the representativity of sampling must be ensured.

In natural estuaries with complex suspended-solids dynamics (i.e. estuaries with settling and erosion zones, tidal flats, etc.), representative sampling is possible only upstream of the tidal limit. In such cases, the sampling site should be located in the non-tidal zone of unidirectional flow (e.g. upstream of a weir), so that the PAH inputs via the weir into the estuary can be reliably estimated as one component of the overall balance (cf. Chapter 2).

Moreover, it is essential to pay attention to the spatial homogeneity - in particular in the impounded reach upstream of the weir. If inhomogeneities are noted, they should be compensated by selecting one, or if doubts remain several representative sampling sites.

## 2.2 Sample types

Because neither the dissolved portion of PAHs nor the particle-bound PAHs in the river must be neglected (on the distribution cf. Chapter 5.1.4), PAHs may be analyzed either in the dissolved and the solid phase or directly in the total sample. The concentration in the total sample ( $PAH_{total}$ ) equals the sum of the dissolved ( $PAH_{dissolved}$ ) plus the particle-bound ( $PAH_{ss}$ ) concentrations. The decision for one of these options depends on the location of the sampling site and on the analytical preconditions.

location of the sampling site: In cases when the suspended-solids dynamics differ from that of dissolved substances, the suspended solids and the centrifugate/filtrate should be collected and analyzed separately. In all other cases, e.g. in canalized watercourses, where settling processes do not play a role, from a theoretical point of view it is sufficient to analyze the total sample.

Analytical preconditions: However, in praxis it is much more difficult to analyze the total sample than the suspended solids. Problems arise from sample inhomogeneities, changing suspended matter concentrations and from clogging up of the SPE columns (SPE: solid-phase extraction).

Moreover, a flow-through centrifuge collects the suspended solids from several cubic metres of water, so that this integrated sample can be considered as a kind of concentrate and ensures better representativity than e.g. a 5-l or 10-l sample used for analyzing the aqueous phase (total or dissolved).

### Conclusion:

- Provided the local conditions (no settling or erosion zones) and the analytical requirements (quality-assured analysis of total water samples) permit, the analysis of the total sample, on the one hand, and the analysis of the solid and the dissolved phases, on the other hand, can be considered as equally reliable. In all other cases, it is recommended to collect and analyze suspended solids and centrifugate/filtrate separately. In any case, the representativity of sampling must remain guaranteed.

## 2.3 Sampling frequency

The frequency of sampling depends on the type of parameter. Among the parameters that are directly used for contaminant load calculations, streamflow  $Q$  and suspended-solids content  $C_{SS}$  show the widest variations (see e.g. Chapter 5.1.1), so that they should be measured more frequently than the PAH concentrations. Associated parameters, like the contents of the clay and silt fraction ( $GSA_{<63\mu m}$ ) or organic carbon ( $C_{OC}$ ) generally do not vary so widely, but may sometimes change very rapidly (e.g. during beginning algal blooms or flood events).

The following sampling frequencies are recommended (cf. Chapter 5.2.4):

- Daily mean values of streamflow  $Q$ ;
- Suspended-solids concentrations  $C_{SS}$  – daily, if possible, at least fortnightly;
- PAH concentrations ( $PAH_{total}$ ,  $PAH_{dissolved}$ , and  $PAH_{SS}$ ) monthly or event-related.

In order to collect  $C_{SS}$  data in higher frequency, the installation of a continuously recording turbidity probe may be helpful, possibly in combination with a fluorescence probe for estimation of phytoplankton concentrations (cf. Chapter 4.1.5.1 in Annex 4).

Event-related sampling should be sufficient, in particular, for measuring the particle-bound PAH concentration, provided  $C_{SS}$  is measured in high frequency. "Event-related" refers here to the flow situation (measurements at high flow and low flow), and in eutrophic rivers it includes also the biological situation (measurements at times of algal blooms, clear-water stages, winter period).

## 2.4 Sampling methods

Regarding the collection of water samples (total sample) reference is made to well-proven standard methods.

Suspended solids should preferably be sampled by means of a flow-through centrifuge (cf. Chapter 5.1.6). The flow-through centrifuge usually separates within a few hours several grammes of suspended solids (Example:  $C_{SS} = 20 \text{ g/m}^3$ , throughput 800 l/h; separating rate 95 % → suspended-solids yield after two hours: 30 gDW). This simplifies analysis and increases the likelihood that the sample is representative.

Filtration (two  $0.7 \mu\text{m}$  glass-fibre filters, 5 l of water per filter) is a low-cost option, which, however, yields only very small amounts of suspended solids. The subsequent analysis must be able to cope with this unfavourable ratio between sample and filter mass. Moreover, it must be ensured that the 10-l sample is representative for the whole river cross section.

The flow-through centrifuge as well as the filtration provide for an almost complete separation of the total sample into the solid and the liquid phase. Therefore, besides the suspended matter also the liquid phase is available for the subsequent analysis.

### Conclusion:

- Flow-through centrifuges are preferentially used for suspended-solids sampling.
- If the representativity of sampling and a highly resolving analysis are ensured, filtration may be an alternative.

Methods based on the passive settling of suspended solids cannot be recommended, because they collect selectively particles with higher settling velocities. The quality of such material may differ considerably from the suspended solids in the water body (cf. Chapter 4.1.3 in Annex 4). Moreover, a complete separation into the solid and the liquid phase is not possible with these methods.

### 3. Analysis

#### 3.1 Parameters

The relevant parameters for estimating the contaminant load are streamflow  $Q$  in  $\text{m}^3/\text{s}$ , suspended-solids concentration  $C_{\text{SS}}$  in  $\text{g}/\text{m}^3$ , and the concentration of the 16 PAH compounds specified by EPA in  $\text{ng}/\text{l}$  ( $\text{PAH}_{\text{total}}$  in the total sample, and  $\text{PAH}_{\text{dissolved}}$  in the dissolved phase) or in  $\text{mg}/\text{kgDW}$  ( $\text{PAH}_{\text{SS}}$  in suspended solids). For a list of the 16 compounds, please refer to Chapter 3.

For a more detailed interpretation of the results, particularly in terms of hydro-biological processes in the rivers, it is helpful to measure also the parameters  $C_{\text{OC}}$  (organic portion in the suspended solids in %, or as an alternative the loss on ignition in %) and  $\text{GSA}_{<63\mu\text{m}}$  (grain-size fraction  $<63\mu\text{m}$  (clay and silt) in %), as well as the field parameters water temperature, oxygen content, and pH.

Auxiliary parameters for continuous recording of suspended-solids concentrations may be turbidity or chlorophyll-*a* concentration.

#### 3.2 Sample analysis

For sample preparation and analysis of the 16 PAHs specified by EPA, reference is made to national and international standards, as e.g. US EPA Methods 610 and 8270C as well as DIN 38414-21 for suspended sediments or US EPA Method 1625 and DIN 38407-8 for aqueous samples.

#### 3.3 Quality control and limit of quantification

##### ***Quality assurance and control***

Contracting parties should make sure that their data are of sufficient quality. The quality assurance of analytical laboratories who generate data should preferably consist of the following three elements: the use of validated analytical methods, having an in-house or internal quality assurance system, and participation in external quality assurance programmes. Quality assurance should ensure at any time that the analytical method is under control and that analytical results are comparable to those of previous determinations. For that purpose, there are measures which can be carried out regularly such as analysis of certified reference materials, control of precision and repeatability, analysis of blind samples, and determination of analyte

recovery. The main element of external quality assurance is the participation in intercomparison exercises. Such exercises serve as a tool to evaluate the proficiency of a laboratory. Quality assurance systems for analytical laboratories are compiled in several European and international standards (e.g. EN 45 001, 1997).

### ***Limit of quantification***

Values below the limit of quantification (LOQ) enter the load calculation with half the LOQ value. Additionally, minimum and maximum loads may be quoted which are based on computations with the value zero or the LOQ value. Thus, they mark the interval in which the real contamination load may be expected.

If more than 50% of measurements are lower than LOQ, the calculated loads cannot be considered as reliable.

Generally, the limit of quantification should be adjusted to the problem under consideration. Rivers carrying low contaminant loads require analyses with higher sensitivity. If in a river the measurements are below the limit of quantification in more than 50% of all cases, and if the PAH load appears negligibly small in comparison with neighbouring rivers, load calculations should be omitted completely. Otherwise, the sensitivity of measurements had to be increased.

## **4. Suspended solids and PAH load calculation methods**

Provided the parameters  $Q$ ,  $C_{SS}$ , and  $PAH_{total}$ ,  $PAH_{dissolved}$ , and  $PAH_{SS}$  were determined according to the recommendations given in Chapter 2.3 of this Guideline, the remaining problem is the optimum utilization of all the information provided. In the following, the concentration  $c$  in mg/l stands either for the concentration of suspended solids or that of PAHs.

As a result of comparison and evaluation of six different methods of load calculation, two of them were found to be recommendable (cf. Chapter 5.2.2).

While suspended-solids concentration  $C_{SS}$  and PAH concentration in the aqueous phase ( $PAH_{total}$  and  $PAH_{dissolved}$ ) are measured directly in mg/l, the particle-bound PAH concentration in mg/l must be calculated from the product of  $C_{SS}$  and  $PAH_{SS}$ . Consequently, it is appropriate to differentiate between transport in the aqueous phase and in the solid one.

**Total and dissolved loads**

The first of the two methods is designated in the Common Part of the report as #2a. It was recommended already in the RID Principles [INPUT, 2000] and has found wide acceptance:

$$\text{annual load} = \frac{1}{N} \sum_{i=1}^N c(t_i) Q(t_i) \frac{\bar{Q}}{\overline{Q(t_i)}} * 365 * 86400s, \quad (1\text{-aqueous})$$

where: N is the number of samples;

$t_i$  is the time of sampling,  $i = 1, \dots, N$ ;

$c(t_i)$  is the concentration in mg/l at time  $t_i$ ;

$Q(t_i)$  is the corresponding streamflow in  $m^3/s$ ;

$$\overline{Q(t_i)} = \left( \sum_{i=1}^N Q(t_i) \right) / N \quad \text{and} \quad \bar{Q} = \left( \sum_{i=1}^{365} Q_i \right) / 365$$

with  $Q_i$ : daily average values of discharge Q.

One year equals 365 days á 86,400 seconds, the annual load is given in grammes (g).

The additional information about the "true" annual streamflow, i.e. the value estimated on the basis of daily mean values  $Q_i$ , is used here by dividing through the mean value of  $Q(t_i)$  and multiplying with  $\bar{Q}$ .

The second method is named #3 in the Common Part of the report. It is based on linear interpolation of concentration values:

$$\text{annual load} = \sum_{i=1}^{365} c_{\text{lin},i} Q_i * 86400s. \quad (2\text{-aqueous})$$

The missing concentration values are estimated by means of linear interpolation ( $c_{\text{lin},i}$ ), so that for each day the product of concentration and streamflow can be calculated.

**Particle-bound load**

As mentioned above, in case of the particle-bound load calculation, the suspended-solids PAH concentration  $PAH_{SS}(t_i)$  (in mg/kgDW) is multiplied with the correspondent suspended-solids concentration  $C_{SS}(t_i)$  (in mg/l) to obtain the particle-bound concentration  $c(t_i)$  in ng/l. There is one  $C_{SS}$  value available for each  $PAH_{SS}$  measurement, but  $C_{SS}$  was measured in higher frequency than the concentration of PAHs. Then the method (1-aqueous) is modified into

$$\text{annual load} = \frac{1}{N} \sum_{i=1}^N c(t_i) Q(t_i) \frac{\bar{Q}}{\overline{Q(t_i)}} \frac{\overline{C_{SS}(t_k)}}{C_{SS}(t_i)} * 365 * 86400s \quad (1\text{-solid})$$

where:  $t_i$  is the time of sampling for  $PAH_{SS}$  measurement,  $i = 1, \dots, N$ ;

$t_k$  is the time of sampling for  $C_{SS}$  measurement,  $k = 1, \dots, M$  and  $M > N$ ;

All other symbols as explained in Method (1-aqueous).



Besides weighing with the "true" streamflow, an additional correction is made in the suspended-solids concentrations by dividing through the mean value of  $C_{SS}$  over all times  $t_i$  and multiplying with the mean value over all times  $t_k$ .

When the method (2-aqueous) is used for particle-bound loads, the necessity of a modification is also due to the fact that the concentration  $c$  is calculated as the product of  $C_{SS}$  and  $PAH_{SS}$ . Since  $C_{SS}$  usually varies more and is measured with higher frequency than  $PAH_{SS}$ , these two parameters must be first linearly interpolated and then be multiplied. Otherwise, the valuable information about the variations of  $C_{SS}$  would be lost. The modified equation reads:

$$\text{annual load} = \sum_{i=1}^{365} C_{SS,i} PAH_{SS,i} Q_i * 86400s \quad (2\text{-solid})$$

where:  $C_{SS,i}$  is the linear interpolated  $C_{SS}$  value at day  $i$ ,  $i=1, \dots, 365$ ;  
 $PAH_{SS,i}$  is the linear interpolated  $PAH_{SS}$  value at day  $i$ .

The methods designated here as (1) and (2) yielded comparable results in the study and there was no indication of general overestimation or underestimation of annual loads by any of these methods (cf. Chapter 5.2.3 and 5.2.4). The recommendation of linear interpolation, besides the well-proven and accepted method (1), is due to the fact, that method (2) yields additional information about the daily transport rates (in tons/day), what opens further possibilities of interpretation. Chapter 5.2.3 has a graphical illustration of these results. The annual load is then obtained as the cumulative sum over these daily transport rates.



# **OSPAR Pilot study on the INPUT of PAHs to the Marine environment**

## **Individual report from Belgium**

P. Roose

**Annex 2** to the Final Report of the

**International Pilot Study for the determination of Riverine Inputs of Polycyclic Aromatic Hydrocarbons (PAHs) to the Maritime Area on the basis of a harmonised methodology**

**Schelde River**

De Schelde river is 435 km long, rising in N France and flowing generally NE across W Belgium and into the North Sea through the Western Scheldt estuary in the southwest of the Netherlands. Navigable for most of its length, it covers one of the most populated and industrialized areas of the Europe. The tidal difference is 4 to 5 m and the flow varies from 40 to 350 m<sup>3</sup>/s with an average of 90 m<sup>3</sup>/s at Antwerp. The Scheldt and its tributaries drain an area of about 21,860 km<sup>2</sup>. The drainage basin situated in northern France and Belgium is composed of catchments of numerous small streams, feeding larger tributaries such as rivers Leie, Dender and Rupel. It receives its chief tributary, the Leie, at Ghent. The estuary can be divided into three zones, on the basis of their different physical and chemical characteristics. The first zone, the fluvial estuary, starts upstream from the confluence of the Scheldt and Rupel rivers and is the fresh zone subject to tidal influence. The second zone or the upper estuary, located entirely in Belgium, is heavily polluted by domestic, industrial and agricultural waste loads (Wollast 1982, Billen et al. 1985). Finally, the lower estuary is situated between the Dutch-Belgian border and the North Sea.

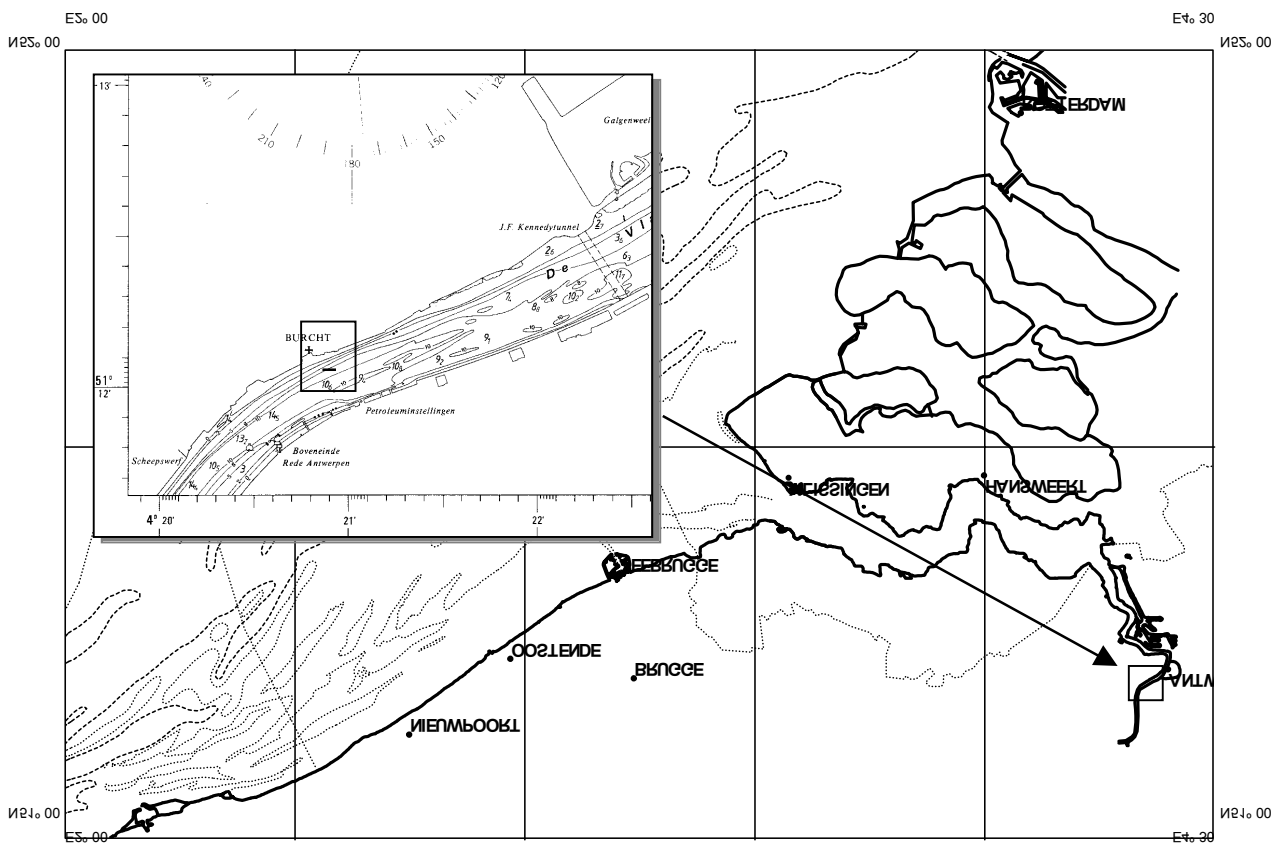
**PAH situation**

The Scheldt is the main input source of contaminants in Belgian coastal waters. In general the two main contributors to PAHs in the environment are fossil fuels, mainly crude oil, and the incomplete combustion of organic materials such as wood, coal and oil. The Scheldt estuary is faced with two main problems. On the one hand, there are extensive dredging operations with dumping of contaminated sediments to keep the port of Antwerp open. On the other hand, there are the large industrial and domestic discharges. The effluents of a number of important Belgian cities such as Brussels, Antwerp and Ghent are either directly or indirectly discharged into the Scheldt. Therefore, the major source of PAHs is the input of freshwater into the estuary at Rupelmonde (south of Antwerp). Other important sources are industrial discharges in Antwerp harbor, the Gent-Terneuzen canal and atmospheric deposition. From a sediment survey, which described the presence of PAHs in twenty-two estuaries in Western Europe, the Scheldt river had among the highest concentrations of total PAHs, with levels over 6000 µg/kg dw (QSR 2000). As for other estuaries in Europe, fluoranthene appears to be the most prominent PAH. PAH concentrations in sediments of the estuary often exceed the OSPAR-EAC (Ecotoxicological Assessment Criteria). Although there are many locations with enhanced concentrations in the sediment this cannot always be related to known sources.

The physic-chemical properties of PAHs are far more diverse than those of other contaminant groups such as PCBs. Different PAHs tend to behave differently in the estuary showing either a conservative, i.e. decreasing concentrations with increasing salinity, or more complicated patterns (Van Zoest and Van Eck, 1993).

## Measuring Programme

For the purpose of the Belgian contribution to the INPUT pilot study a sampling station in the Scheldt Estuary was selected ( $51^{\circ}12'.11$  N,  $4^{\circ}20'.82$  E) that lies in the region of Antwerp harbour, just south of the city center (Figure 1). The station is situated in the fluvial estuary,



**Figure 1:** Sampling station in the Scheldt river.

close to the confluence of the Scheldt and Rupel rivers, where this zone starts. It is a well-mixed river section, within the tidal reach of the river, and is a regular monitoring point. The station was selected on the basis of influence of tributaries (mainly the Ruppel), easy access and the presence of a continuous monitoring station in the vicinity. Sampling was performed

monthly 1 hour after high tide for all samples except suspended matter (SPM) and bimonthly for the latter.

### **Sampling Methods**

Water samples, SPM samples and filtrated water were sampled at a depth of 1 m with an Alfa Laval AS16 flow-through centrifuge mounted in a mobile unit. Raw water was collected at the centrifuge bypass and the filtrate at the centrifuge outlet. Three duplicate water samples of 1 l each were collected on each occasion. SPM was collected at 20,000 rpm for approx. 1.5 hours or a volume of 1500 l.

### **Analytical Methods**

#### *Dry weight determination*

The dry weight percentage was determined using a separate subsample (10-15g) which is weighed into a pre-weighed dish, dried at 105°C in an oven for 16 h (until constant weight), allowed to cool and then reweighed.

#### *PAH determination in suspended matter*

Suspended matter samples are extracted using alkaline saponification. The samples are weighed into a 250 ml round-bottomed flask, and potassium hydroxide pellets added (5 g), along with 100ml of methanol and a few glass anti-bumping granules. Known amounts of the appropriate surrogate standards are added at this stage. The samples are digested under reflux using a heating mantle for 2 hours and allowed to cool. The digests are then filtered through solvent-cleaned filter papers (Whatman 113v) into 250 ml separating funnels fitted with glass stoppers and PTFE stopcocks. The digests are twice extracted with *n*-pentane (2 x 50 ml), the pentane aliquots being used to rinse the round-bottomed flask prior to addition to the separating funnel. After shaking and being allowed to separate, the bottom layer from the first extraction is collected in a clean conical flask. The upper *n*-pentane extract is then collected in a 100 ml conical flask containing solvent-rinsed anhydrous sodium sulphate. The bottom layer is then poured back into the separating funnel and the process repeated. The two *n*-pentane extracts are combined in the 100 ml conical flask and dried over anhydrous sodium sulphate, then transferred quantitatively to a 100 ml volumetric flask and made up to volume prior to UVF analysis.

A procedural blank and a reference material are included with each batch of 12 samples.

The removal of co-extracted material prior to GC-MS analysis is carried out using column chromatography on alumina. The alumina is conditioned by heating to 800°C for 4 h in a quartz dish in a muffle furnace, after which it is allowed to cool in a desiccator. The alumina is then deactivated with 5% water. The sample extracts are concentrated down to 1 ml, by rotary evaporation. Approximately 1 g of 5%-deactivated alumina is poured into Pasteur pipettes plugged with cotton wool and the sides gently tapped to settle it. A beaker is placed under the column and 2 ml of eluent (50% *n*-pentane in dichloromethane) is passed through the column to clean it before use. Once the solvent has drained into the bed of the column, the beaker is replaced with a clean round/flat bottomed flask, and the sample transferred from the rotary evaporator flask to the column using a Pasteur pipette. The sample is allowed to just soak into the alumina and then the hydrocarbons and PAH are eluted with 2 x 1 ml aliquots of the eluent as described above. When all of the eluent has passed through the column the flask is removed. The cleaned extracts are then reduced to a suitable volume (usually between 100 µl and 1 ml) prior to analysis by GC-MS and transferred to crimp-top autosampler vials.

Aliquots of the extracts (1 µl) are analysed using a 20 m x 0.25 mm ID crosslinked fused silica capillary column coated with 100 % dimethyl silicone fluid (0.25 µm film thickness). The carrier gas is helium at a linear flow rate of 1.5 ml/min. Injection is via a PTV injector in the splitless mode, with the split valve being opened to purge the injector 1 minute after injection. The injector temperature programme is as follows: the injector is kept at 65°C during injection and subsequently raised at 10°C min<sup>-1</sup> to 300°C which is held for 1.5 min. Afterwards, the injector is raised at 14.5°C min<sup>-1</sup> to 380°C which is held for 16 min. The injection is made with the column at 50°C, and following injection the oven temperature is held at 50°C for 2 minutes, and subsequently raised at 40°C min<sup>-1</sup> to 120°C. Afterwards, the column is raised at 16°C min<sup>-1</sup> to 320°C where it is held for 10 min. The GC column is directly coupled, via a transfer line heated to 310°C, to the ion source of a Thermoquest Trace MS mass spectrometer. This is interfaced to and controlled by a data system using Excalibur software running under Windows NT. The software controls the GC-MS instrument as well as data acquisition, storage and reduction. The mass spectrometer is operated in selected ion monitoring (SIM) electron-impact ionisation mode (EI). A list of compounds normally analysed and the relevant internal standards used are given in Table 1. In general,

quantification of aromatic hydrocarbons using EI is carried out from mass fragmentograms of the molecular ion for each compound.

**Table 1:** Quantification masses and retention times of selected polycyclic aromatic hydrocarbons.

| Compound                | Mass (m/z) | Retention Time (min) |
|-------------------------|------------|----------------------|
| Naphtalene              | 128        | 3.90                 |
| 1-Methylnaphtalene      | 142        | 4.46                 |
| Biphenyl                | 154        | 4.79                 |
| 2,6-Dimethylnaphtalene  | 156        | 4.93                 |
| Acenaphtylene           | 152        | 5.13                 |
| Acenaphtene             | 153        | 5.32                 |
| 2,3,5-Trimethylnaphtene | 170        | 5.80                 |
| Fluorene                | 166        | 5.87                 |
| Phenanthrene            | 178        | 6.99                 |
| Antracene               | 178        | 7.05                 |
| 1-methylphenanthrene    | 192        | 7.82                 |
| Fluoranthrene           | 202        | 8.55                 |
| Pyrene                  | 202        | 8.82                 |
| Benz(a)anthracene       | 228        | 10.52                |
| Chrysene                | 228        | 10.55                |
| Benzo(b)fluorantene     | 252        | 11.94                |
| Benzo(k)fluorantene     | 252        | 11.96                |
| Benzo(e)pyrene          | 252        | 12.23                |
| Benzo(a)pyrene          | 252        | 12.28                |
| Perylene                | 252        | 12.38                |
| Indeno(1,2,3-cd)pyrene  | 276        | 13.54                |
| Dibenzo(a,h)anthracene  | 278        | 13.58                |
| Benzo(ghi)perylene      | 276        | 13.76                |

#### *PAH determination in water samples*

PAH's are extracted out of the water column using solid phase extraction with Bakerbond Speedisk C<sub>18</sub> extraction cartridges (J.T. Baker). The cartridges are rinsed with ethyl acetate



(10 ml) and conditioned with methanol and organic free water (10 ml each) for about 1 min. Water samples are forced through the disk under vacuum. Up to 3 l of water can be used for this. After all the water has been passed through, about 5 ml of ethyl acetate is added and allowed to soak for 1 min, followed by 5 ml methylene chloride and two 3 ml portions of 1:1 ethyl acetate: methylene chloride. The extract is dried by passing it through a column containing 10 g of anhydrous sodium sulphate and finally concentrated to a suitable volume for extraction under a stream of nitrogen gas. GC-MS analysis is performed as given before.

### *DOC*

Dissolved organic carbon (DOC) is determined using a Skalar continuous flow chain. The sample is automatically injected and pumped through the chain. As a first step, a known ratio of potassium hydroxide and disodiumtetraborate are added and the sample is led through a Quartz tube coiled around an UV-lamp. Afterwards, sulphuric acid is added and the sample is heated to 97°C. The acid is later on neutralised by adding sodium hydroxide in the presence of ascorbic acid to neutralise chlorine. Part of the solution is then resampled and a known ratio of molybdate and ascorbic acid are added. After heating to 40 °C, during which colour formation takes place, the extinction of the sample is measured with a matrix photometer at 880 nm and 1010 nm.

### *DON*

Dissolved nitrogen DON is determined using a Skalar continuous flow chain. The sample is automatically injected and pumped through the chain. As a first step, a known ratio of potassium peroxodisulfide and sodium hydroxide are added and the sample is heated to 90°C. After addition of a known amount of a borate buffer solution the sample is led through a Quartz tube coiled around an UV-lamp. Afterwards, part of the solution is dialysed with ammonium chloride and pumped through a cadmium column where nitrate is reduced to nitrite. After addition of phosphoric acid, sulfanilamide and  $\alpha$ -naphthylene-diamine-dihydrochloride nitrite forms a red-coloured diazo-compound. The extinction of the sample is measured with a matrix photometer at 540 nm.

### *Particulate organic carbon (POC) and particulate total nitrogen (PON)*

Carbon and nitrogen containing compounds in the suspended matter are determined with a Carlo Erba NC 1500 element analyser, which is based on the principle of catalytic oxidation

followed by gas chromatography. In the presence of pure oxygen and tungstenoxide carbon is transformed into carbon dioxide and nitrogen into nitrogen oxides. The nitrogen oxides are further reduced in the presence of Cu to Nitrogen gas and excess oxygen is removed at this stage. Water is removed from the gasses by passing them through a magnesium perchlorate column. N<sub>2</sub> and CO<sub>2</sub> are separated on a packed GC column and detected with a thermal conductivity detector. The concentration is calculated against known amounts of a glycine standard.

### *TOC*

The total organic carbon concentration (TOC) is calculated as the sum of the particulate and the dissolved fraction (see before).

### *SPM*

Suspended matter samples were filtered immediately after sampling on pre-weighed Whatmann GC/C filters. After drying, filters are weighed and the suspended matter concentration is determined.

### *Dissolved oxygen*

Dissolved oxygen was determined with a dedicated YSI-52 dissolved oxygen meter. The YSI dissolved oxygen probes use membrane-covered Clark type polarographic sensors with built in thermistors for temperature measurement and compensation. A thin permeable membrane isolates the sensor elements from the environment, but allows oxygen and certain other gases to enter. When a polarising voltage is applied across the sensor, oxygen that has passed through the membrane reacts at the cathode, causing a current to flow.

Oxygen diffuses through the sensor at a rate proportional to the pressure difference across it. Since oxygen is rapidly consumed at the cathode, it can be assumed that the oxygen pressure inside the membrane is zero. Hence the amount of oxygen diffusing through the membrane is proportional to the absolute pressure of oxygen outside the membrane. If the oxygen pressure increases, more oxygen diffuses through the membrane and more current flows through the sensor. A lower pressure results in less current.

### **Quality Assurance**

The MUMM laboratory used well documented standard operating procedures (SOPs) for all its determinations and is operated conform the rules that apply for accredited laboratories. Every determinant has its own Quality Control and Quality Assessment (QC – QA) scheme that includes regular blanks and calibration checks, the use of certified reference materials and internal reference materials and quality control charts. The lab participates on a regular basis in international intercalibration exercises such as QUASIMEME.

### **Additional parameters**

#### *DON*

Dissolved nitrogen DON is determined using a Skalar continuous flow chain. The sample is automatically injected and pumped through the chain. As a first step, a known ratio of potassium peroxodisulfide and sodium hydroxide are added and the sample is heated to 90°C. After addition of a known amount of a borate buffer solution the sample is led through a Quartz tube coiled around an UV-lamp. Afterwards, part of the solution is dialysed with ammonium chloride and pumped through a cadmium column where nitrate is reduced to nitrite. After addition of phosphoric acid, sulfanilamide and  $\alpha$ -naphthylene-diamine-dihydrochloride nitrite forms a red-coloured diazo-compound. The extinction of the sample is measured with a matrix photometer at 540 nm.

#### *TON*

The total organic carbon concentration (TOC) and total nitrogen concentration (TON) are calculated as the sum of the particulate and the dissolved fractions (see before).

#### *Nutrients*

Nutrients are determined using a Skalar continuous flow chain. The sample is automatically injected and pumped through the chain. To the sample specific chemicals are added while it is being pumped through the system resulting in colored compounds. The extinction of the solution can then be measured and this is representative for the amount of the selected nutrients present in the sample. For nitrate and nitrite the solution is pumped through a cadmium column where nitrate is reduced to nitrite. After addition of phosphoric acid, sulfanilamide and  $\alpha$ -naphthylene-diamine-dihydrochloride nitrite forms a red-coloured diazo-

compound. The extinction of the sample is measured with a matrix photometer at 540 nm. For nitrate only the last step of the previous procedure is used. For phosphate a known amount of molybdate and ascorbic acid are added and the sample is heated to 37°C. In an acid environment and in the presence of antimony Molybdate forms a blue colored compound with ortho phosphate that can be measured at 880 nm. For ammonium EDTA buffer is added to the sample to complex magnesium and calcium ions. Afterward known amounts of sodium salicate, sodium nitroprusside and sodium hypochlorite are added. In a basic environment this results in the formation of a green colored compound that can be measured at 630 nm. For silicate known amounts of a molybdate reagent, ascorbic acid and oxalic acid are added to the sample. In an acid environment molybdate forms with the dissolved Si a compound that is reduced by ascorbic acid to a blue colored compound that can be measured at 660 nm. Oxalic acid removes interfering phosphate ions.

### *pH*

The pH is determined with a Beckman 32 pH meter.

### *Salinity*

The salinity is determined using a Portsal salinometer that measures the conductivity of the sample compared to a standard seawater sample (IAPSO standard seawater, salinity 35, Ocean Scientific).

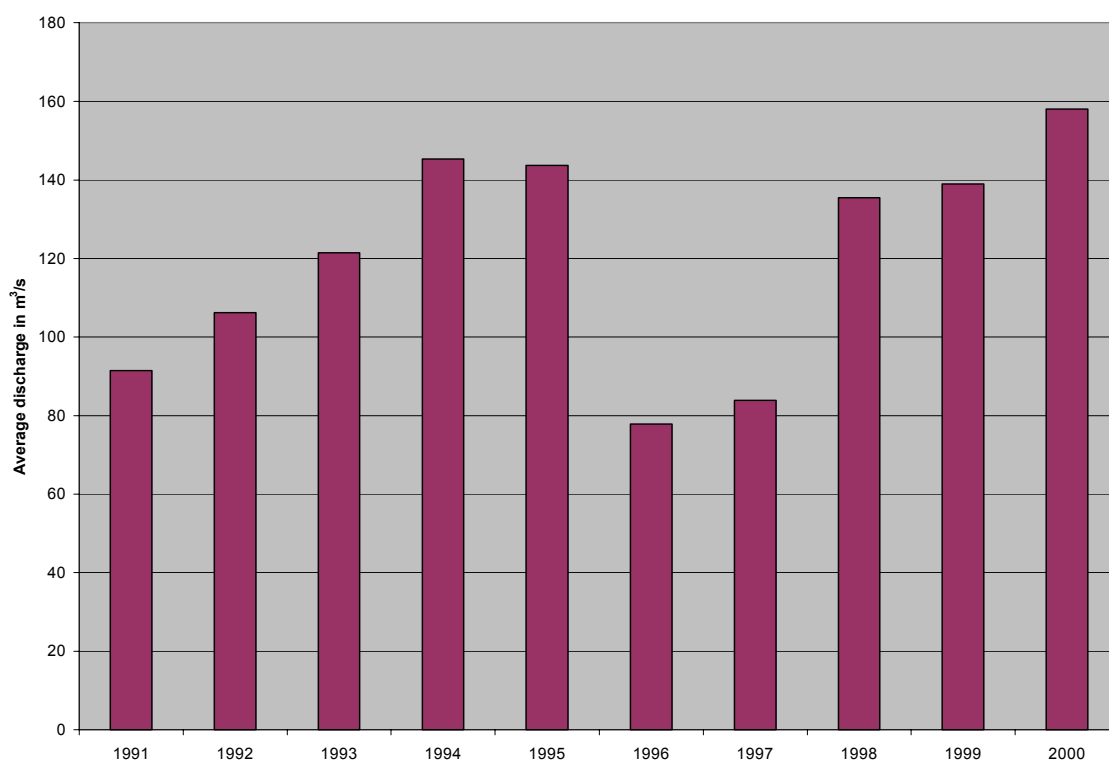
### *Chlorophyll a*

The chlorophyll a determination is based on a spectrometric determination. Algae are filtered out of the water column on Whatman GF/C filters and stored at -80°C prior to extraction. The filters are homogenised in the presence of 90 % acetone with a Braun Potter S homogeniser. The homogenate is left in the refrigerator at 4°C for a period of 48 hours during which chlorophyll is extracted. Afterwards the acetone solution is separated from the debris by centrifugation at 2500 rpm for 30 min. The supernatant is transferred to 4 cm quartz cuvettes and the extinction of the solution is measured at 665 and 750 nm against a blank of 90% acetone. Chlorophyll a is calculated according to the method of Lorenzen (1967).

## Additional evaluation

### *The discharge*

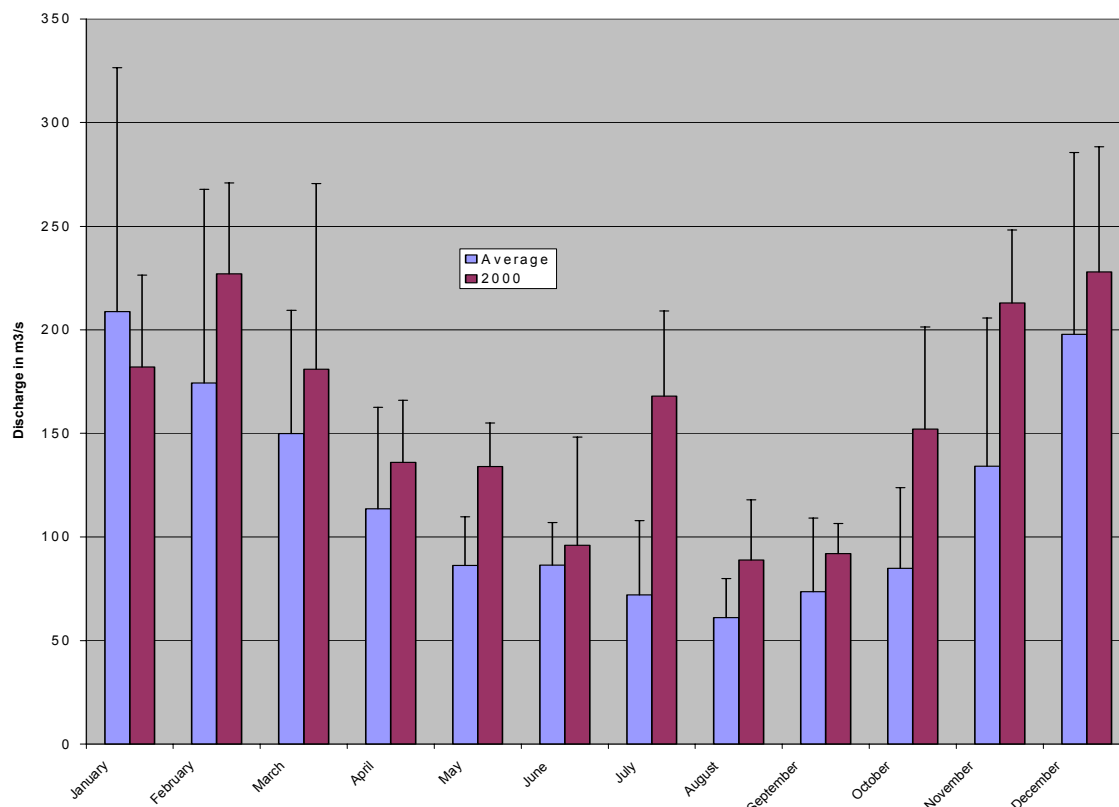
The mean annual discharge during the period 1991 - 2000 is  $120 \text{ m}^3/\text{s}$ , with a minimum in 1996 of  $78 \text{ m}^3/\text{s}$  and a maximum in 2000 of  $158 \text{ m}^3/\text{s}$  (Figure 2). Remarkably enough, the year of the onset of the sampling campaign had the highest mean annual discharge of the last ten years. Nonetheless, there are considerable year-to-year variations. Figure 3 compares the monthly discharges for 2000 with the average of the last ten years. Obviously, the increased discharge is spread over the entire period, with substantial, or even excessive, discharges in the months July ( $168 \text{ m}^3/\text{s}$ ), October ( $152 \text{ m}^3/\text{s}$ ) and November ( $213 \text{ m}^3/\text{s}$ ).



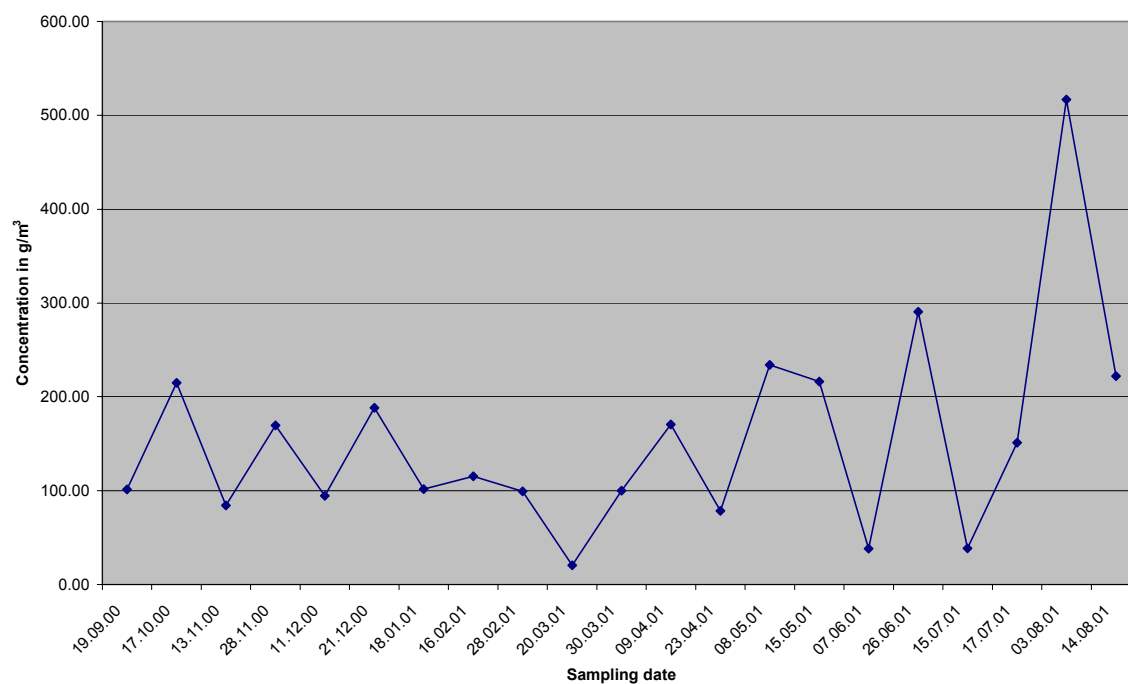
**Figure 2:** average discharges in  $\text{m}^3/\text{s}$  for the years 1991 to 2000 near Antwerp.

### *The concentration of suspended matter at the sampling station*

The concentration of suspended matter at the sampling station varied between  $20 \text{ g}/\text{m}^3$  and  $517 \text{ g}/\text{m}^3$ , with an average of  $155 \text{ g}/\text{m}^3$  and a distinctive peak ( $\text{g}/\text{m}^3$ ) during the sampling occasion at the 3<sup>rd</sup> of August 2001 (Figure 4).



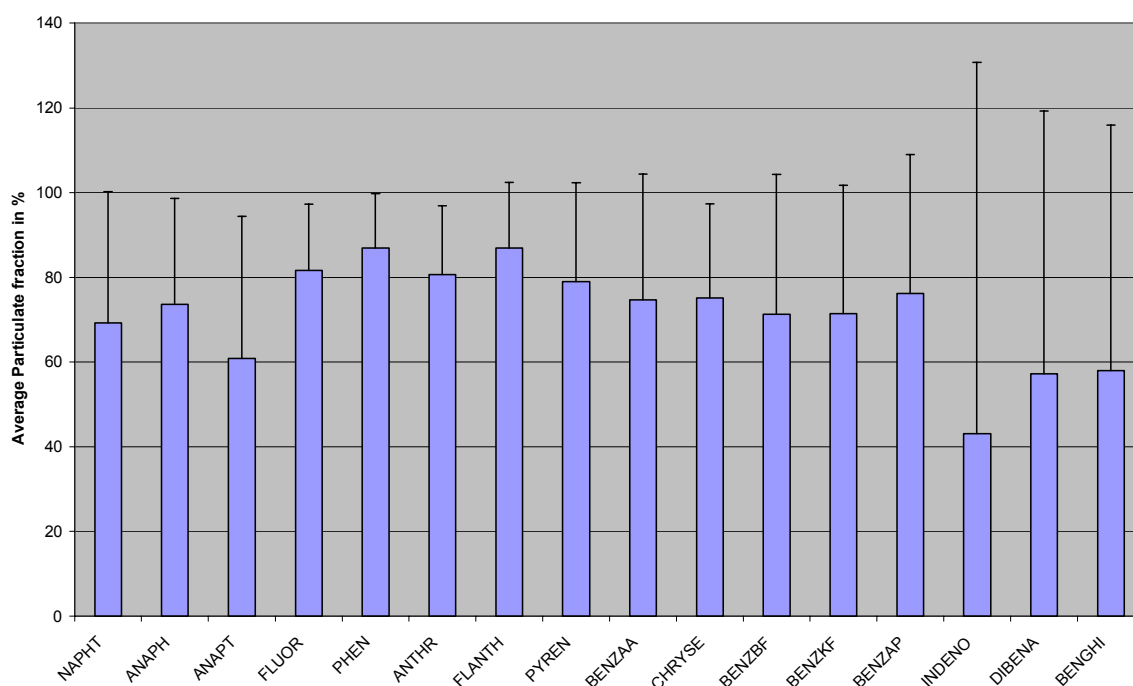
**Figure 3:** Comparison between the average monthly discharges in 2000 and the averages for the period 1991-1999.



**Figure 4:** Concentration of suspended particulate matter during the different sampling occasions.

## *The distribution of PAHs between the water phase and suspended matter*

The distribution of PAHs between the water phase and suspended matter was studied on the basis of PF, i.e. the percentage or share of the particulate fraction. For the calculations only the dissolved and the particulate concentrations were used. Figure 5 shows the average PF for the mandatory PAHs and their sum. For nearly all the cases the majority of the PAHs were mostly present in the particulate fraction (i.e. over 70%). No clear distinction could be made between the lower and the higher molecular weight PAHs for this particular river system (Figure 6). Surprisingly, some of the higher MW PAHs had a significant fraction in the water phase. Nevertheless, the total PAH load was predominantly present in the particulate fraction. The rest of the evaluations were therefore carried out for the PAHs in the suspended matter fraction.

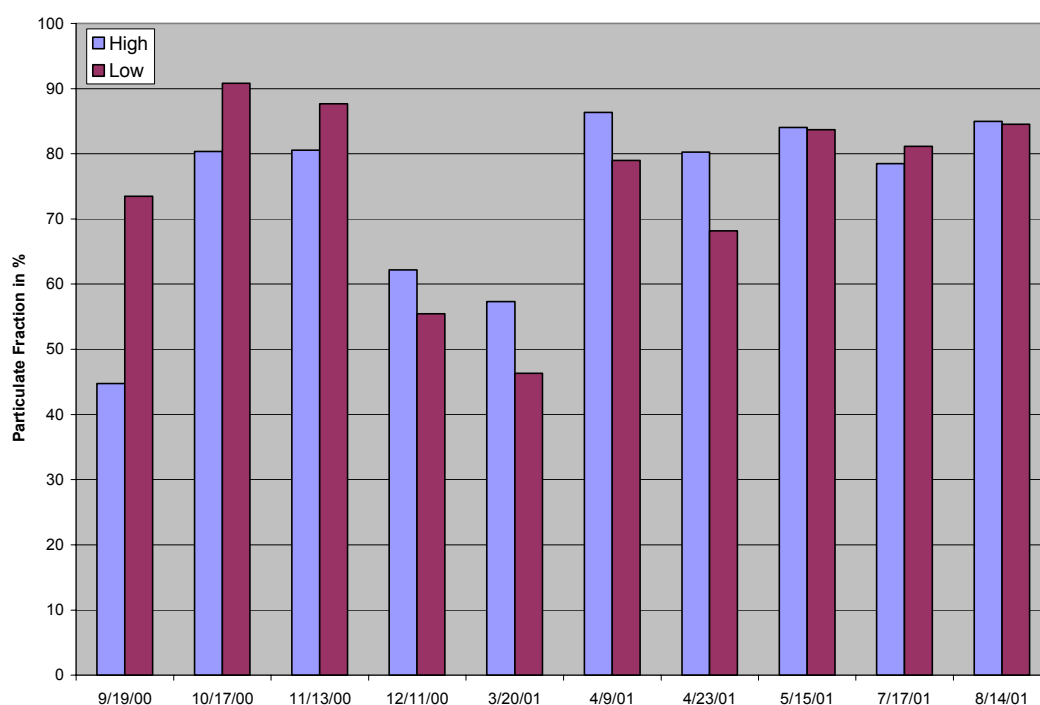


**Figure 5:** Average particulate fraction in % for the 16 mandatory PAHs.

## *Analysis of the PAH patterns*

Median PAH concentrations in in suspended matter varied between 30 and 580  $\mu\text{g/kg}$  with the highest concentrations for medium condensed PAHs. Fluoranthene is the most prominent PAH, closely followed by pyrene. In the dissolved phase, median concentrations varied between 5 and 14  $\mu\text{g/m}^3$  and here the lower condensed PAHs and surprisingly indenopyrene

are the most prominent PAHs. To analyse the PAH patterns concentrations for the different PAHs at the different sampling types were plotted in a box and whisker plot (Fig. 7). The PAHs are arranged according to increasing molecular weight. From the graph it can be seen that the patterns remain fairly constant throughout the sampling period. This is especially so for the lower MW PAHs in the range naphtalene-fluorene, as the boxes of the B&W in those cases are particularly small.

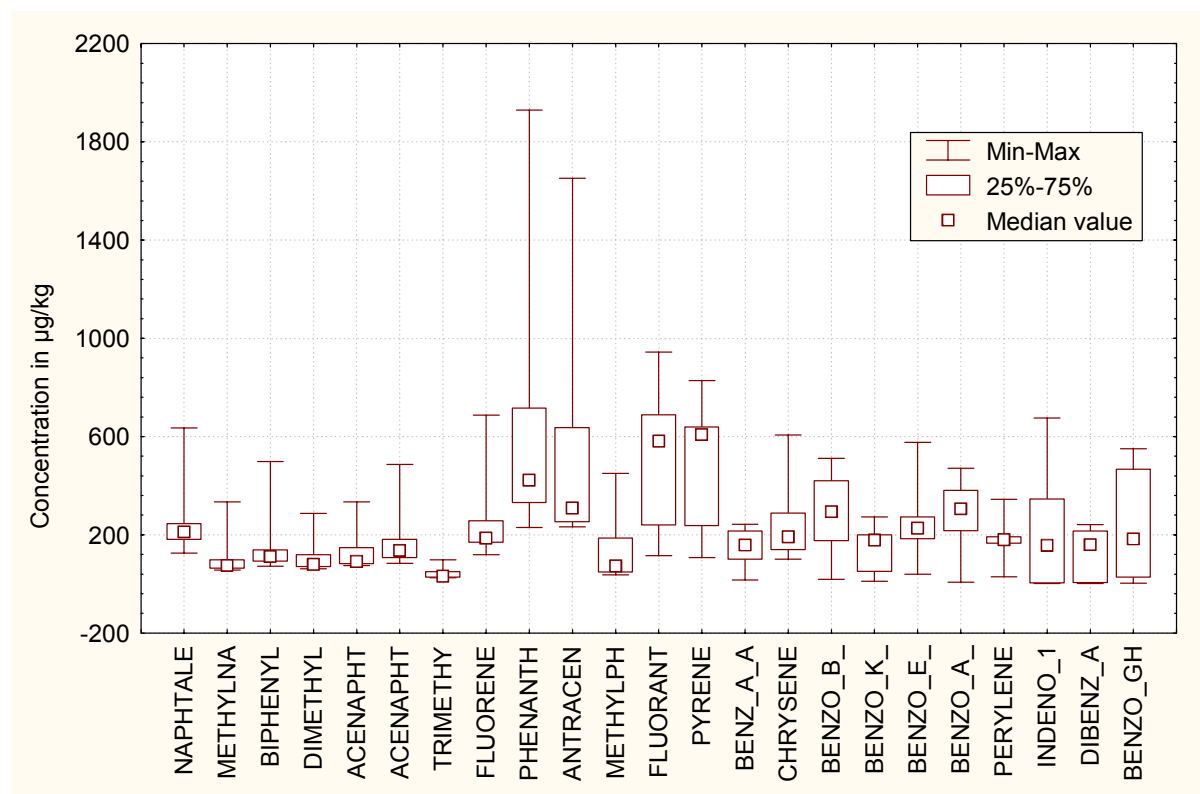


**Figure 6:** Comparison between the particulate fractions in % of the lower condensed PAHs (napthalene – anthracene) and the higher condensed PAHs (from anthracene onwards).

To further study the patterns, a principal component analysis (PCA) was executed. Principal components were extracted when Eigenvalues were greater than one. A picture similar to the above was obtained with the PCA. Here, three factors were identified with Eigenvalues greater than 1. They contributed for 56, 31 and 6 %, respectively of the total variance of all samples. The factor loading plot after varimax rotation for Factor 1 vs. Factor 2 is given in Figure 8. Factor 1 that contributes for the largest variability clearly separates the PAHs in two groups. The rightmost group consists of all the low molecular weight PAHs and also those with the most stable pattern, mentioned above. The leftmost group consists of the PAHs that

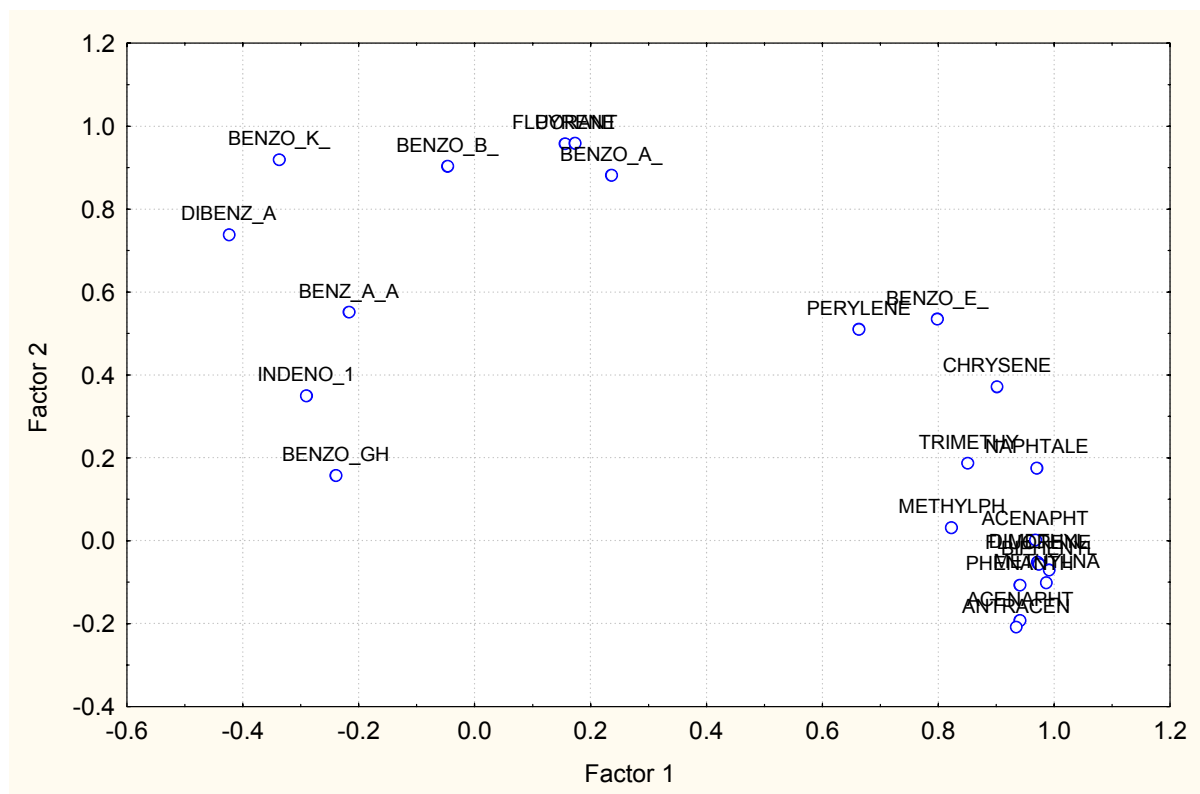


have the highest variability in concentration and therefore a less stable pattern. It also contains the PAHs with the highest concentration.

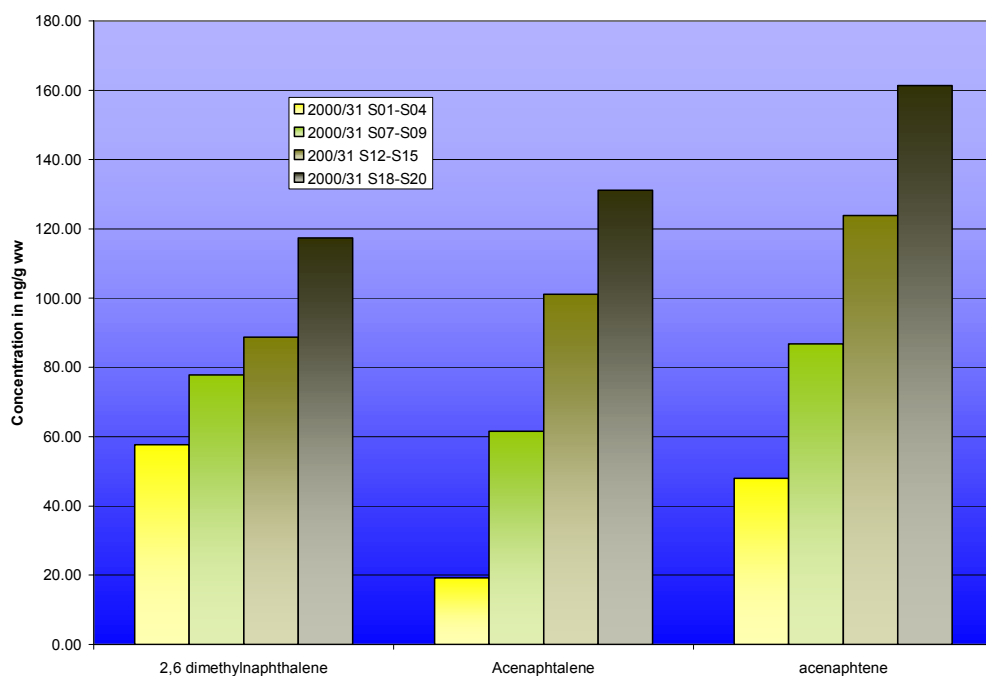


**Figure 7:** Concentrations of the different PAHs in particulate suspended matter.

The PAH patterns found at the sampling location for the pilot study were compared with those further down the lower estuary, all the way up to the North Sea. For this purpose, samples were collected along the Scheldt estuary from the mouth of the river to Antwerp City. Suspended matter was collected in 4 large zones and similarities in the patterns were studied. All in all, no clear similarities were found between the different zones of the Scheldt river, with one exception. The patterns of 2,6 dimethylnaphthalene, acenaphthalene and acenaphtene remained constant throughout the estuary, with decreasing concentrations towards the sea (Fig. 9). Apparently, these PAHs behave in the same way or have the same sources. The results also show a significant increase in the concentrations of mainly higher molecular weight PAHs at the point where the canal Gent-Terneuzen reaches the Scheldt. The latter connects the industrial region of Gent harbour with the Scheldt and this may well explain the increase.



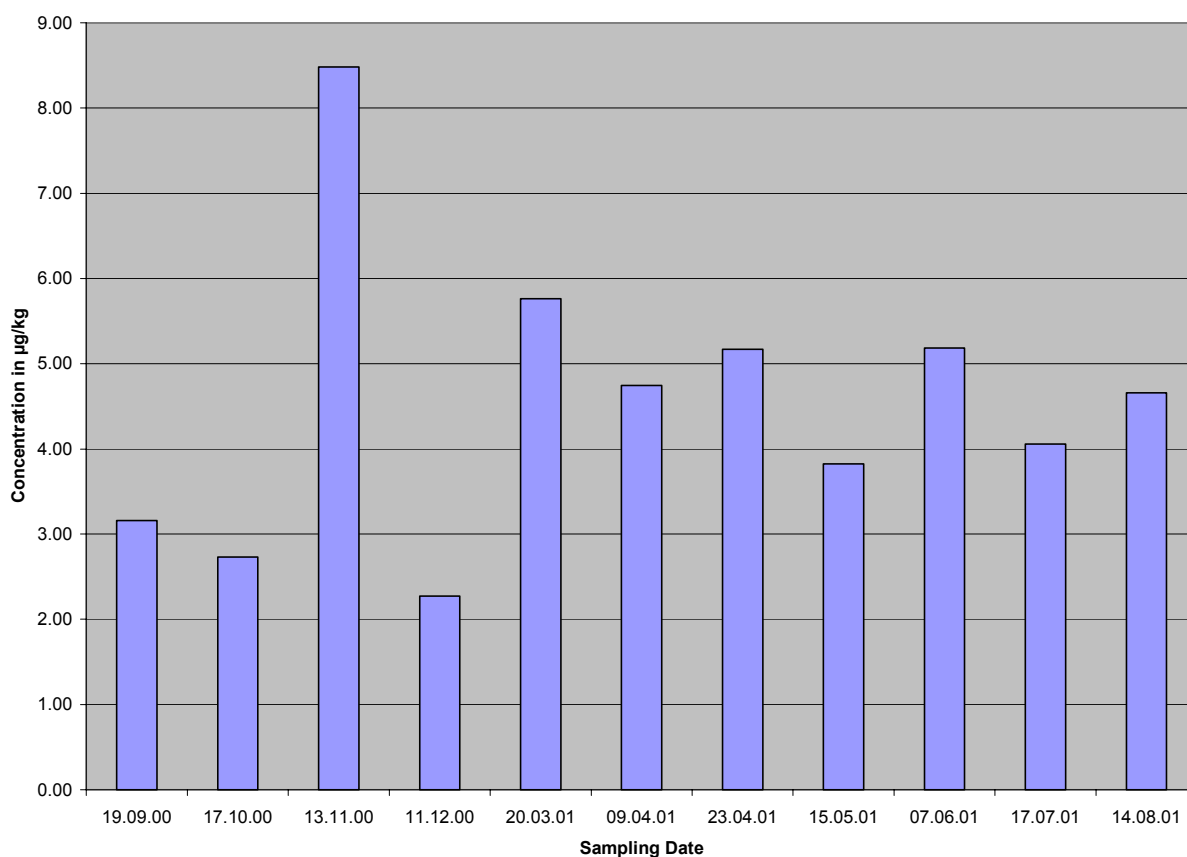
**Figure 8:** Two-dimensional plot (first two factors) of the factor loadings for the different PAHs after varimax rotation.



**Figure 9:** Concentration gradient for three specific PAHs in the Scheldt estuary with S01-S04 the zone nearest to the mouth of the estuary and S18-S20 the zone in the industrial region of Antwerp Harbor.

## *Analysis of the seasonality of PAH concentrations*

No distinct seasonal pattern could be noted during the period of sampling. A higher presence of PAHs might be expected during the wintertime because of the increased use of fossil fuels, but this could not be observed. An overview of the seasonal variation of the sum of the EPA 16 mandatory PAHs is given in Figure 10. It shows roughly lower concentrations in the end of 2000, with the exception of the month of November, and somewhat higher concentrations during 2001. The occasion in November could be linked to a period of heavy rainfall and increased discharges. Apparently, the input of PAH contaminated water from inland sources significantly increased during that period. Causes could be increased runoff and, excess rain-an sewage water bypassing wastewater treatment plants.



**Figure 10:** Concentration in suspended particulate matter of the sum of the 16 EPA PAHs at the different sampling occasions

## Appendix 1

**Table 2:** Median concentrations of the different PAH's in the three matrices.

| Compound                   | Median Concentrations           |          |       |
|----------------------------|---------------------------------|----------|-------|
|                            | Suspended<br>Particulate matter | Filtrate | Water |
| Naphtalene                 | 211                             | 11       | 19    |
| 1-methylnaphthalene        | 74                              | 6.4      | 11    |
| biphenyl                   | 111                             | 6.5      | 8.7   |
| 2,6-dimethylnaphtalene     | 80                              | 6.4      | 14    |
| Acenaphthylene             | 92                              | 4.8      | 15    |
| acenaphthene               | 136                             | 13       | 18    |
| 2,3,5-trimethylnaphthalene | 32                              | 5.0      | 6.2   |
| fluorene                   | 187                             | 5.8      | 16    |
| phenanthrene               | 422                             | 7.3      | 29    |
| anthracene                 | 308                             | 10       | 23    |
| 1-methylphenanthrene       | 73                              | 13       | 13    |
| fluoranthene               | 581                             | 6.0      | 58    |
| pyrene                     | 608                             | 12       | 65    |
| benz(a)anthracene          | 180                             | 4.3      | 26    |
| chrysene                   | 191                             | 7.8      | 35    |
| benzo(b)fluoranthene       | 294                             | 8.9      | 72    |
| benzo(k)fluoranthene       | 179                             | 2.9      | 32    |
| benzo(e)pyrene             | 227                             | 6.6      | 34    |
| benzo(a)pyrene             | 305                             | 5.3      | 34    |
| perylene                   | 179                             | 3.2      | 14    |
| indeno(1,2,3-cd)pyrene     | 156                             | 12       | 45    |
| dibenz(a,h)anthracene      | 159                             | 2.2      | 11    |
| benzo(ghi)perylene         | 184                             | 6.3      | 32    |

## Appendix 2

### List of abbreviations

|                            |         |          |
|----------------------------|---------|----------|
| Naphtalene                 | NAPHT   | NAPHTALE |
| 1-methylnaphthalene        | MNAPH   | METHYLNA |
| biphenyl                   | BEPHEN  | BIPHENYL |
| 2,6-dimethylnaphthalene    | DMNAPH  | DIMETHYL |
| Acenaphtylene              | ANAPH   | ACENAPHT |
| acenaphthene               | ANAPT   | ACENAPHT |
| 2,3,5-trimethylnaphthalene | TMNAPH  | TRIMETHY |
| fluorene                   | FLUOR   | FLUORENE |
| phenanthrene               | PHEN    | PHENANTH |
| anthracene                 | ANTHR   | ANTRACEN |
| 1-methylphenanthrene       | 1MEPHEN | METHYLPH |
| fluorantene                | FLANTH  | FLUORANT |
| pyrene                     | PYREN   | PYRENE   |
| benz(a)anthracene          | BENZAA  | BENZ_A_A |
| chrysene                   | CHRYSE  | CHRYSENE |
| benzo(b)fluoranthene       | BENZBF  | BENZO_B_ |
| benzo(k)fluoranthene       | BENZKF  | BENZO_K_ |
| benzo(e)pyrene             | BENZEP  | BENZO_E_ |
| benzo(a)pyrene             | BENZAP  | BENZO_A_ |
| perylene                   | PERYL   | PERYLENE |
| indeno(1,2,3-cd)pyrene     | INDENO  | INDENO_1 |
| dibenz(a,h)anthracene      | DIBENA  | DIBENZ_A |
| benzo(ghi)perylene         | BENGHI  | BENZO_GH |



**OSPAR: Pilot study on Inputs of PAHs to the maritime area via rivers**

**Measuring programme, Sampling method, Analytical methods, Quality Assurance**

**Final Report: Individual part**

**Contracting Party: Denmark**

NERI, Silkeborg  
Department of Streams and Riparian Areas  
Ole Sortkjær

**Annex 3** to the Final Report of the

**International Pilot Study for the determination of Riverine Inputs  
of Polycyclic Aromatic Hydrocarbons (PAHs) to the Maritime Area  
on the basis of a harmonised methodology**

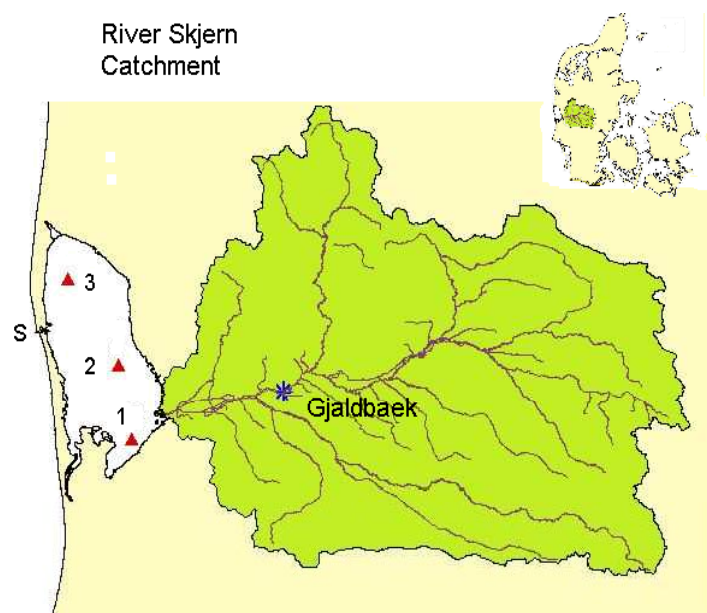


Figure 1: River Skjern catchment with outlet to Ringkøbing Fjord. Station Gjaldbaek (\*) and 3 stations for collecting sediment in the fjord (▲) as well as the sluice (S) to the North Sea are marked. In the upper right corner it is indicated where in Denmark the catchment is situated.

## Measuring Programme for PAHs

The Danish National Monitoring Programme includes all the PAH's mentioned in the pilot project, except Acenaphthylene. Benz( )flouranthenes are for River Skjern measured as Benz(b+J+k)flouranthene and not separated into Benz(b)flouranthene and Benz(K)flouranthene. This is not in accordance with the national monitoring programme (table 1).

Table 1. Monitoring programmes for river Skjern, Danish monitoring programme and the Pilot project

| Parameters               | Danish Monitoring programme | River Skjern | Pilot project |
|--------------------------|-----------------------------|--------------|---------------|
| Suspended matter (CSS)   | x                           | x            | x             |
| Loss on Ignition (LOIN)  | x                           | x            | x             |
| 2-methylphenanthrene     | x                           | x            |               |
| 3,6-dimethylphenanthrene | x                           | x            |               |
| Acenaphthene             | x                           | x            | x             |
| Acenaphthylene           |                             |              | x             |
| Anthracene               | x                           | x            | x             |
| Benz(a)anthranzene       | x                           | x            | x             |
| Benz(a)pyrene            | x                           | x            | x             |
| Benz(e)pyrene            | x                           | x            |               |
| Benz(b)flouranthene      | x                           |              | x             |
| Benz(j)flouranthene      | x                           | (b+j+k) x    |               |
| Benz(k)flouranthene      | x                           |              | x             |
| Benzo(a)flourene         |                             | x            |               |
| Benzo(ghi)perylene       | x                           | x            | x             |
| Chrysene                 | x                           | x            | x             |
| Dibenz(a+h)anthrazene    | x                           | x            | x             |
| Dibenzothiophene         | x                           | x            |               |
| Flouranthene             | x                           | x            | x             |
| Flourene                 | x                           | x            | x             |
| Indeno(1,2,3-cd)pyrene   | x                           | x            | x             |
| Naphtalene               | x                           | x            | x             |
| Perylene                 | x                           | x            |               |
| Phenanthrene             | x                           | x            | x             |
| Pyrene                   | x                           | x            | x             |
| Triphenylene             | x                           | x            |               |



## Sampling Methods

### PAHs

A sample is collected in a 5-l pyrex glass flask with red cap led covered with Teflon. The flask is rinsed 3 times in the river before the sample is taken just under the water surface. The sample is kept below 5°C during transport and in the laboratory before analysing.

Sampling of suspended matter.

A sample is collected in a 1-l polyethylene/teflon flask. The sample is kept below 5° C during transport and in the laboratory before analysing.

## Analytical Methods

Determination of suspended matter concentration in water (mg/l)

Method: Danish Standard (DS-207)

Laboratory: Steins Varde, accreditation no. 305

Determination of Loss on Ignition concentration in water (mg/l)

Method: Danish Standard (DS-207)

Laboratory: Steins Varde, accreditation no. 305

Determination of PAHs

The concentration of PAHs is determined in an unfiltered water sample, which is extracted with dichloromethane and analysed using gas-chromatography with mass spectrometric detector.

Laboratory: Miljøkemi, accreditation no. 168 Detection limits for individual PAHs, see table x  
RSD: 15% by concentrations 10 times the detection limits.

## Quality assurance

Determination of suspended matter concentration in water (mg/l)

Determination of Loss-on-Ignition concentration in water (mg/l)

Determination of PAHs

The Danish EPA has evaluated 11 laboratories based on intercalibration of 26 different PAHs in pure solutions and in water samples. The laboratories were evaluated on repeatability and reproducibility. 6 laboratories meet the requirements and were qualified for analysing PAH in water samples in accordance with the Danish national monitoring programme. So far, there has been no demand for participation in further intercalibrations.

## Catchment area

River Skjern catchment is situated in the western part of Jutland (map) and the area is 2490 km<sup>2</sup>. 40 years ago the lower part of river Skjern was channelized and the area around the river was used as farmland. 5 years ago a restoration project started bringing the river back to its original river beds and establish the wetland areas again. The project which is estimated at 33 mill. euro will be finished in 2002. Many investigations have been made in connection with the project, so river Skjern is now one of the most investigated rivers in Denmark.

The catchment area is dominated by farming (table 2) and the population density is low, about 35/km<sup>2</sup>, where 60% of the population live in the town of Skjern. The population density in Denmark is 127/ km<sup>2</sup>.

Table 2. Area distribution in per cent.

|                                 |      |
|---------------------------------|------|
| Urban area                      | 1.7  |
| Arable land                     | 68.0 |
| Heterogeneous agricultural land | 12.2 |
| Forest                          | 13.6 |
| Heathland                       | 2.5  |
| Inland marshes                  | 1.6  |
| Other                           | 0.4  |

### River Skjern

The river is the most water-rich river in Denmark with a length of 93 km. 18 streams drain into the main river with a total length of 1288 km (map). The water runs through a marsh delta with shallow lakes into the southeastern part of Ringkoebing fjord. The fjord (290 km<sup>2</sup>) is connected to the North Sea via a sluice, which regulates the water level and salt content of the water in the fjord. In a way the fjord can be looked at as a saltwater lake. The total catchment of Ringkoebing fjord is 3442 km<sup>2</sup>, of which the river Skjern catchment area accounts for 72 %.

### The sampling station, Gjaldbaek

The sampling station, Gjaldbaek (marked on the map) is situated at the river Skjern about 20 km from the outlet in Ringkoebing fjord. There is no influence of incoming water from the fjord. The sampling station is included in the Danish national monitoring programme (NOVA 2003) and all sampling and measurements are in accordance with the technical guidelines given in the programme. Only certified laboratories are used for analysing.

The station Gjaldbaek represents one of the most water-rich rivers in Denmark and is important for estimating loads to the North Sea. Furthermore, annual calculations of discharge are available back to 1920, and from 1993 sediment transport is also included.

Monthly sampling was carried out during a year from January to December 2000 and all samples are taken just below the surface to avoid suspended matter from the bottom, so all samples refer to the water phase.

The catchment area upstream the station is 1552 km<sup>2</sup>, and represents 62.3% of the total catchment area. The population density is probably not more than 10-15/ km<sup>2</sup> in this area.

### The discharge

The mean annual discharge during the period 1920 - 1995 is 35.6 m<sup>3</sup>/s, with a minimum in 1929 of 5.9 m<sup>3</sup>/s and a maximum in 1970 of 319 m<sup>3</sup>/s. There are great year-to-year variations. The discharge at Gjaldbaek shows a similar variation and constitutes 62% of the total discharge. The discharge at Gjaldbaek in 2000 is in average 28.9 m<sup>3</sup>/s and the discharge within the year is shown in figure 2. During the higher winter discharge it is possible to have inundated areas along the river.

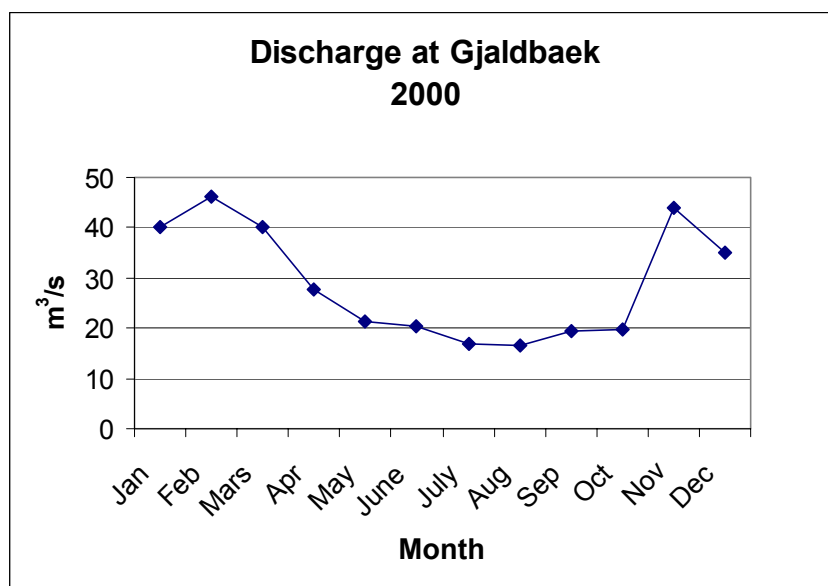


Figure 2. The monthly discharge as mean of daily estimated discharge.

### Sediment transport

The sediment transport can be divided into two, the bed load close to the bottom and the suspended matter transported by the water phase. The suspended load at Gjaldbaek in 1994 and 1995 is estimated both on the basis of every 4h sampling and with a biweekly sampling. Loads based on a biweekly sampling underestimate the loads with 57 % and 63 %, respectively, (Svendsen et al., 1997). In this project, where the load of suspended solids is based on monthly sampling, an underestimation of at least 60 % for river Skjern may be expected. The total load to the fjord is 180 % of the load at the sampling station. In 1994, the bed load was calculated at 21,600 tonnes and the transport of suspended matter at 17,500 tonnes.

An investigation made by Svendsen et al. (1997) in river Skjern concluded that there was no difference in the content of suspended material from samples taken 10 cm above the bottom to 10 cm below the surface. The same could be shown from bank to bank. A single sample will be representative for the cross section.

The suspended matter is rich in phosphorus and iron. Higher plants in the river can catch the particles, which may be sedimented later in the delta. The coarser material from the bed load will to a great extent be sedimented in the lakes before the water flows into the fjord. The vegetation in the Danish streams is dense and the weeds are cut mechanically once a year for river management and due to this and the natural decay during the winter period, considerably fine material is transported down streams.

Subsurface drainage water from Danish streams was found to account for 11-15 % of the annual suspended sediment export from catchments, and the stream bank/bed erosion must therefore have been the major diffuse source of suspended sediment (Kronvang et al., 1997). The fine particles generated by removal of vegetation, and occasionally subsurface drainage, will only be sampled occasionally by using a monthly sampling programme.

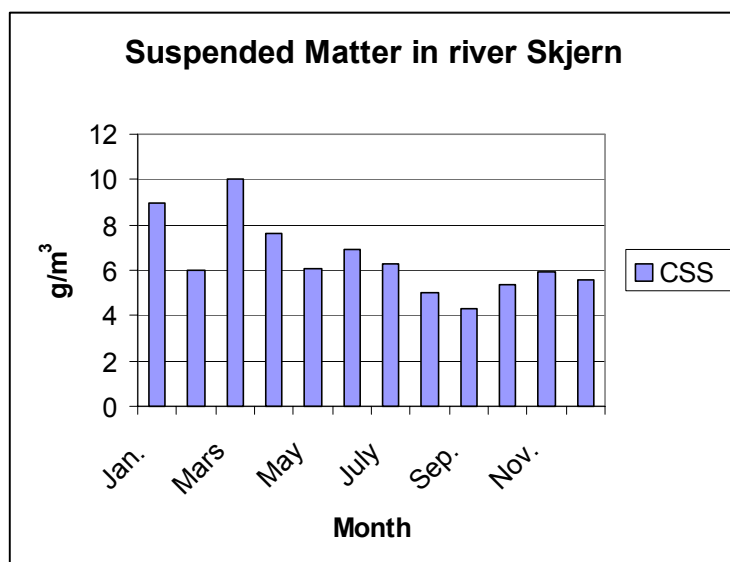


Figure 3. Suspended matter measured once a month during 2000 at station Gjaldbaek

## PAH-Transport

Each month a 5-l sample is taken at Gjaldbaek for analysing of PAH compounds. No compounds could be detected because the sampling technique applied did not collect enough suspended matter, or the analysing methods was not fitted to the extremely small amount in the water sample.

Therefore it is not possible to calculate transport in a traditional way with a model based on discharge. Instead we will try to calculate the annual transport based on the PAH-source. In the part of Denmark where the river Skjern catchment area is situated, the main source of PAH to the area is by precipitation, which again comes from traffic and oil combustion. In 1998, the PAH content in rainwater collected over a period of two months at two stations were measured. One of these stations, Ulborg, is 20 km north of Ringkoebing fjord and represents the same population density as in the river Skjern catchment. The other station is situated close to the city of Aarhus (250,000 citizens) in the eastern part of Jutland.

The total PAH in the precipitation in an area with a low population density (Ulborg) is nearly half of the content of the precipitation in the city of Aarhus, which again is only half of what is found in larger cities.

Let us suppose for the sake of argument that the precipitation is the only source of PAH and that all material will be transported to the fjord by the river connected to the suspended matter. The area of water upstream Gjaldbaek is around 1 km<sup>2</sup> and the flooded area 10 times greater. The total amount of PAHs fallen in this area is:  $11 \cdot 1000 \cdot 1000 \cdot 128.6 \mu\text{g} = 1415 \text{ g}$ . The mean of suspended matter is around 6 g/m<sup>3</sup> and the mean discharge is 28.91 m<sup>3</sup>/s, which roughly gives an annual export of 5.470.235 kg suspended matter.

The total-PAH content per kg suspended matter is averagely 259  $\mu\text{g}$ . If the flooded area alone is 5 times the open water surface, the content will be around 150  $\mu\text{g/kg}$  suspended matter. In some years some areas collect PAHs for several years before it is inundated and such a situation may raise the mean concentration of PAHs. The expected concentration of total PAHs in river Skjern will be in the range of 150-300  $\mu\text{g/kg}$  dry weight of suspended matter, all depending on the flood situation.

The total transport of PAHs to the fjord system may be calculated at 2271 g and consequently the station Gjaldbaek only represents 62.3 per cent of the total area of the river Skjern catchment.

Tabel 3 .PAH precipitation ( $\mu\text{g}/\text{m}^2$ ) and as percentage of the sum at Ulborg and Aarhus

| PAH                      | $\mu\text{g}/\text{m}^2$<br>Ulborg | $\mu\text{g}/\text{m}^2$ Aarhus | %<br>Ulborg | %<br>Aarhus |
|--------------------------|------------------------------------|---------------------------------|-------------|-------------|
| Naphtalen                | 6.8                                | 14.2                            | 5.3         | 6.6         |
| methylnaphtalen          | 8.4                                | 8.6                             | 6.5         | 4.0         |
| dimethylnaphtalener      | 17                                 | 26.9                            | 13.2        | 12.5        |
| trimethylnaphatalener    | 6.6                                | 32.2                            | 5.1         | 14.9        |
| Acenaphtylen             |                                    | 3.9                             | 0.0         | 1.8         |
| Acenaphaten              | 0.6                                |                                 | 0.5         | 0.0         |
| Flouren                  | 4.6                                | 6.1                             | 3.6         | 2.8         |
| Phenathren               | 16.2                               | 24.1                            | 12.6        | 11.2        |
| Anthracen                | 2.9                                | 1.7                             | 2.3         | 0.8         |
| Flouranthen              | 12.9                               | 23.3                            | 10.0        | 10.8        |
| Pyren                    | 9.1                                | 14.7                            | 7.1         | 6.8         |
| Benz(a)anthrazen         | 1.5                                | 3.3                             | 1.2         | 1.5         |
| Chrysen/triphenylen      | 12.2                               | 15.7                            | 9.5         | 7.3         |
| Benz(b+j+k)flouranthener | 17                                 | 22.1                            | 13.2        | 10.2        |
| Benz(a)pyren             | 3                                  | 4.2                             | 2.3         | 1.9         |
| Indeno(1,2,3-cd)pyren    | 4.1                                | 5.8                             | 3.2         | 2.7         |
| Benz(ghi)perylen         | 0.7                                | 7.6                             | 0.5         | 3.5         |
| dibenz(ah)anthracen      | 5                                  | 1.4                             | 3.9         | 0.6         |
| Sum                      | 128.6                              | 215.8                           | 100.0       | 100         |

**PAHs in the fjord systems**

3 stations are situated in the fjord (maps) and in 2000 the first results of PAHs in the sediment were measured. Two of the stations (number 1 and 2) are richer in organic matter (7% loss on ignition) and the third is poor of organic matter (1.2% loss on ignition). The percentage dry weight differs characteristically with 33-37 at station 1 and 2, and 70 at station 3 (table 4). River Skjern probably influences station 1 and 2 and the third station situated in the north of the fjord, far away from the river outlet is probably not influenced. The sedimented material is only 0.25-1 cm deep all over the bottom. It is characteristic in a fjord/lake with an large open area that the resuspension is high, so it is possible for the suspended matter to be transported out of the fjord to the North Sea.

Table 4. Station for sediment in Ringkoebing Fjord

| Station number                | 1                | 2                | 3                |
|-------------------------------|------------------|------------------|------------------|
| co-ordinates                  | 56,02,91/8,10,44 | 55,53,05/8,18,58 | 55,57,53/8,16,71 |
| Depth (m)                     | 3                | 3                | 3.8              |
| % dry weight                  | 36.8             | 33               | 70.2             |
| % loss on ignition            | 7.4              | 7.2              | 1.1              |
| <63 my (%)                    | 95               | 88               | 6.6              |
| Thickness of<br>sediment (mm) | 5                | 7.5              | 7.5              |

Table 5. Content of PAHs and its pattern in the sediment in Ringkoebing fjord at 3 stations

| PAH ug/kg dw                           | St. 1  | St. 2  | St. 3 | St. 1<br>per cent. | St. 2<br>per cent. | St. 3<br>per cent. |
|----------------------------------------|--------|--------|-------|--------------------|--------------------|--------------------|
| Naphtalen                              | 19.0   | 24.5   | 10.9  | 1.5                | 2.7                | 5.4                |
| 2-methylnaphtalen                      | 13.9   | 13.0   | 9.7   | 1.1                | 1.4                | 4.8                |
| 1-methylnaphtalen                      | 8.0    | 7.8    | 5.2   | 0.6                | 0.8                | 2.6                |
| dimethylnaphtalener                    | 66.6   | 79.6   | 13.3  | 5.1                | 8.7                | 6.6                |
| trimethylnaphatalener                  | 50.9   | 43.4   | 22.5  | 3.9                | 4.7                | 11.1               |
| Acenaphtylen                           | 19.6   | 20.1   | 14.0  | 1.5                | 2.2                | 6.9                |
| Acenaphaten                            | 4.2    | 2.6    | 0.6   | 0.3                | 0.3                | 0.3                |
| Flouren                                | 52.1   | 42.7   | 14.3  | 4.0                | 4.7                | 7.1                |
| Dibenzothiophen                        | 3.5    | 5.2    | 1.3   | 0.3                | 0.6                | 0.6                |
| methyldibenzothiophener                | 5.2    | 12.1   | 3.6   | 0.4                | 1.3                | 1.8                |
| Phenathren                             | 77.5   | 49.6   | 18.9  | 5.9                | 5.4                | 9.3                |
| methylphenathrener                     | 23.2   | 9.5    | 2.8   | 1.8                | 1.0                | 1.4                |
| Dimethylphenatrener                    | 1.8    | 1.9    | 0.4   | 0.1                | 0.2                | 0.2                |
| Anthracen                              | 12.9   | 11.0   | 4.8   | 1.0                | 1.2                | 2.3                |
| Benz(a)flouren                         | 3.7    | 2.7    | 0.4   | 0.3                | 0.3                | 0.2                |
| Flouranthen                            | 190.5  | 81.4   | 17.2  | 14.6               | 8.9                | 8.5                |
| Pyren                                  | 134.2  | 64.8   | 14.2  | 10.3               | 7.1                | 7.0                |
| 1-methylpyren                          | 12.0   | 7.7    | 1.2   | 0.9                | 0.8                | 0.6                |
| Benz(a)anthrazen                       | 38.1   | 22.4   | 2.3   | 2.9                | 2.4                | 1.1                |
| Chrysen/triphenylen                    | 50.5   | 35.5   | 1.1   | 3.9                | 3.9                | 0.5                |
| Benz(b+j+k)flouranthener               | 132.8  | 85.0   | 12.5  | 10.2               | 9.3                | 6.2                |
| Benz(e)pyren                           | 64.5   | 39.6   | 5.3   | 5.0                | 4.3                | 2.6                |
| Benz(a)pyren                           | 57.6   | 39.6   | 4.9   | 4.4                | 4.3                | 2.4                |
| Perylen                                | 128.4  | 116.0  | 12.5  | 9.9                | 12.6               | 6.2                |
| Indeno(1,2,3-cd)pyren                  | 69.5   | 52.4   | 5.7   | 5.3                | 5.7                | 2.8                |
| Benz(ghi)perylen                       | 63.0   | 47.5   | 3.2   | 4.8                | 5.2                | 1.6                |
| Sum                                    | 1302.8 | 917.1  | 202.2 | 100.0              | 100.0              | 100.0              |
| Total PAH/per cent loss on<br>ignition | 176.1  | 127.37 | 183.8 |                    |                    |                    |

One kg dry weight at the 3 stations is calculated to wet weight and area, taken in account the dry weight percentage, loss on ignition and mean sediment depth. (table 6).

Table 6. calculations of kg dw to ww and area.

| Station number   | 1     | 2     | 3     |
|------------------|-------|-------|-------|
| Kg dw            | 1     | 1     | 1     |
| Kg ww            | 2.71  | 3.03  | 1.4   |
| Area of sediment | 0.542 | 0.404 | 0.187 |

In table 7 the content of PAHs is calculated per square meter for the PAHs represented in both the precipitation and the sediment and the number of years it will take for the compounds in the precipitation to reach the level found in the sediment for the individual PAHs. In general it takes slightly more than a year for station 1 and 2, and 4 years for station 3. For station 1 and 2, it takes only six months for the smaller PAHs and around 2 years for the highest molecular ones. If we take into account that part of the substances will be dissolved in the water phase (at least for the PAHs with low molecular weight), we will find that for these compounds it will also take around a year to reach the level found in the sediment. Only benz(ghi)perylen differs from this pattern with 12-18

years. But there have probably been difficulties with the measurements of the substance in the precipitation in Ulborg, which is indicated by comparing the data from Aarhus and Ulborg. For the other substances, the values are 50-100 per cent higher in Aarhus than in Ulborg (Table 3), but for benz(ghi)perylene it is 1000 per cent.

Table 7. Content of PAHs calculated per square meter for the PAHs represented in both the precipitation and the sediment and the number of years it will take for precipitation to reach the level found in the sediment for every PAH.

| Station number         | 1                 | 2                 | 3 Ulborg          | 1       | 2       | 3       |      |
|------------------------|-------------------|-------------------|-------------------|---------|---------|---------|------|
| PAHs                   | ug/m <sup>2</sup> | ug/m <sup>2</sup> | ug/m <sup>2</sup> | years   | years   | years   |      |
| Naphtalen              | 2.69077           | 6.5994            | 28.69505          | 6.8     | 0.4     | 1.0     | 4.2  |
| methylnaphtalen        | 3.136531          | 5.445545          | 39.57219          | 8.4     | 0.4     | 0.6     | 4.7  |
| dimethylnaphtalener    | 9.431857          | 21.47167          | 35.04234          | 17      | 0.6     | 1.3     | 2.1  |
| trimethylnaphatalener  | 7.20135           | 11.71427          | 59.50586          | 6.6     | 1.1     | 1.8     | 9.0  |
| Acenaphtylen           | 2.768661          | 5.411778          | 36.89364          | #DIV/0! | #DIV/0! | #DIV/0! |      |
| Acenaphaten            | 0.587721          | 0.688281          | 1.586823          | 0.6     | 1.0     | 1.1     | 2.6  |
| Flouren                | 7.378374          | 11.51184          | 37.81928          | 4.6     | 1.6     | 2.5     | 8.2  |
| Phenathren             | 10.97551          | 13.38774          | 49.85269          | 16.2    | 0.7     | 0.8     | 3.1  |
| Anthracen              | 1.826891          | 2.969055          | 12.56235          | 2.9     | 0.6     | 1.0     | 4.3  |
| Flouranthen            | 26.97851          | 21.97101          | 45.35669          | 12.9    | 2.1     | 1.7     | 3.5  |
| Pyren                  | 19.00533          | 17.49044          | 37.42258          | 9.1     | 2.1     | 1.9     | 4.1  |
| Benz(a)anthrazen       | 5.388621          | 6.046077          | 6.082822          | 1.5     | 3.6     | 4.0     | 4.1  |
| Chrysen/triphenylen    | 7.151783          | 9.568456          | 2.909176          | 12.2    | 0.6     | 0.8     | 0.2  |
| Benz(b+j+k)flouranthen | 18.79998          | 22.9427           | 33.05881          | 17      | 1.1     | 1.3     | 1.9  |
| er                     |                   |                   |                   |         |         |         |      |
| Benz(a)pyren           | 8.1502            | 10.6751           | 12.95905          | 3       | 2.7     | 3.6     | 4.3  |
| Indeno(1,2,3-cd)pyren  | 9.842553          | 14.1435           | 15.07482          | 4.1     | 2.4     | 3.4     | 3.7  |
| Benz(ghi)perylen       | 8.922027          | 12.80743          | 8.463056          | 0.7     | 12.7    | 18.3    | 12.1 |
| Sum                    | 150.2367          | 194.8443          | 462.8572          | 123.6   | 1.2     | 1.6     | 3.7  |

## Loads to the North Sea

There are at least 2 sources of PAHs involved, precipitation and loads from River Skjern. The sediment stations closest to the river are rich in organic material and with a high percentage 88-95 of fine particles <63µm, indicating an influence of sediment from River Skjern. Assuming that ¼ of the fjord area involved receives PAHs from the river, then the content of PAHs will increase with 18 per cent in the sediment, which is in accordance with the concentration found in the sediment close to the river outlet.

Material from the outlet can probably move to other areas in the fjord system, where resuspension may move the finer material further to the North Sea. The sediment station (number 3) furthest away from the river outlet illustrates this, because the sediment lacks fine material and is poor in organic matter leaving only coarse material. 93.4 per cent of the particles are > 63 µm. Nevertheless, the sediment is still able to keep a PAH content equal to 3-4 years' precipitation.

The PAHs from the river contribute annually with around 2.2 kg PAHs compared with the contribution from the precipitation with 37.3 kg to the total loads to the North Sea.

## Conclusion

The scenario set up for calculation of PAHs to the North Sea from river Skjern illustrates that the measured concentration of PAHs in fjord sediment may be explained solely by the PAHs in the precipitation fallen on the river and its occasionally flooded areas and on the surface of the fjord. The river contributes very little to the total loads to the North Sea. The fjord functions only to a minor extent as sink for particles containing PAHs. None of the load calculations methods suggested in this project would account for the situation where a river drains to a fjord (or lake) before it runs to the sea.

It would be helpful to have usable measurements of PAHs of the suspended matter in the river, which was not the case for river Skjern. That can be obtained by using centrifuge instead of water samples taken in bottles or/and using more sensitive analytical methods. In this way, at least the loads to the fjord could be calculated, although an underestimation of at least 60 per cent should be expected. Many of the assumptions made for the Danish part of the report could then be avoided.

## References

Kronvang, B., Laubel, A., and Grant, R., 1997. Suspended sediment and particulate Phosphorus transport and delivery pathways in an arable catchment, Gelbaek stream, Denmark. *Hydrological Processes*, vol. 11, 624-642.

Svendsen, L. M., Andersen, H.E. and Larsen, S. E., 1997. Transport af suspenderet stof og fosfor i den nedre del af Skjern Å-systemet. *Danmarks Miljøundersøgelser. Faglig rapport fra DMU nr. 185*, 90s.



**OSPAR Pilot Study**  
**on Riverine PAH Inputs into the Maritime Area**  
**- German Individual Part -**

Studied areas, measuring programme, sampling methods,  
analytical methods, quality assurance and results

Peter Heininger and Reinhard Schild  
Federal Institute of Hydrology (BfG)  
– Germany –

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# 1. Introduction

The determination of waterborne inputs of polycyclic aromatic hydrocarbons (PAHs) into the marine environment has high priority in international research. For this reason, the INPUT Working Group of the Oslo-Paris Commission (OSPAR) invited Belgium, Denmark, Germany, the Netherlands, and Spain to develop a harmonised methodology for the determination of these inputs [INPUT, 2000a].

In the period 2000-2001, each of the Participating Countries carried out detailed studies over one year on one or two tributaries to the North Sea or the North-East Atlantic. These studies employed different, mutually harmonised measuring methods. The results are presented in a report, consisting of one common and five individual parts. The **common part** of the report constitutes a summary and synthesis of the individual parts and focuses mainly on the following topics:

- Estimation of annual PAH loads in the individual rivers;
- Comparison and discussion of results regarding the different river systems and varying measuring and computing methods;
- Proposals for future monitoring programmes.

The **individual parts** are presented by the five Participating Countries and consist of

- detailed descriptions of the measuring programmes;
- measuring and analytical methods;
- activities for quality assurance;
- possibly supplementary parameters, evaluations or results that are not published in the common report.

The present report is identical with the German individual part and is attached to the common part as annex 4.

## 2. Studied areas

### 2.1 River Elbe

The River Elbe stretches over 1,100 km from the southern slope of the Riesengebirge in the Czech Republic (1,383 m above mean sea level) to the North Sea at Cuxhaven. After a wide bend across the north-east Bohemian basin it takes its largest tributary, the River Moldau, which at this point with 150 m<sup>3</sup>/s has a higher streamflow than the Elbe itself. After 364 km, it crosses the Czech-German border, where the river-km marks again start at zero. In Germany, it flows through the Elbsandsteingebirge, and at Schloss Hirschstein (km 96), i.e. below the city of Meißen, it enters the north-east German lowlands. The following river reach, down to the tidal weir at Geesthacht (km 585.8), is called *Middle Elbe* (Mittlere Elbe), the tidal influenced reach down to Cuxhaven-Kugelbake (km 727) is called *Lower Elbe* (Untere Elbe). Further important tributaries are the rivers Havel (km 423; 115 m<sup>3</sup>/s), the Saale (km 291; 105 m<sup>3</sup>/s) and the Mulde (km 257; 75 m<sup>3</sup>/s). About 25 Mio. people live in the catchment area, which spans an area of 148,268 km<sup>2</sup>, resulting in a mean population density of 169 inhabitants per km<sup>2</sup>.

The mean streamflow of the years 1977 to 2000 at the gauge Neu Darchau (river-km 536.4) was MQ = 710 m<sup>3</sup>/s. The highest streamflow values around 3,500 m<sup>3</sup>/s were recorded in March 1981 and in April 1988, the lowest ones amounting to some 180 m<sup>3</sup>/s in August 1990. Therefore, the year 2000 (mean streamflow 650 m<sup>3</sup>/s) can be rated as averaged, whereas the measuring period from April 2000 to March 2001 with 508 m<sup>3</sup>/s is rated as a low-flow period. The highest streamflow during this period reached 2800 m<sup>3</sup>/s (March 2000), the lowest value was measured with 280 m<sup>3</sup>/s on 30 June 2000.

The summative levels (16 PAHs according to US EPA 1984) in the total samples near Geesthacht (Elbe-km 585,8) are around 120-280 ng/l, of which around 80 % are bound on particles [ARGE Elbe, 1998], whereas the suspended solids PAH concentration ranges between 0.1 and 1.3 mg/kgDW near-shore and between 1.8 and 8.3 mg/kgDW near the city of Hamburg [ARGE Elbe, 2001].

## 2.2 River Weser

The catchment of the 432-km long River Weser comprises 46,306 km<sup>2</sup> and lies exclusively in Germany. About 54 % of the catchment belong to the Federal State of Lower Saxony.

The River Weser is formed by the confluence of the two headwater rivers Werra and Fulda at Hannoversch Münden, which are 298 km and 218 km long. For historical reasons, the kilometre marking of the Weser is divided into two sections: the upper section comprises the Upper and Middle Weser and stretches from Hannoversch Münden to the Wilhelm Kaisen Bridge at Bremen (river-km 366.75). There, the kilometre marking starts again with km-zero, and this second section ends at Bremerhaven (Lower Weser river-km 65.25) with the inflow into the North Sea.

The weir at Bremen-Hemelingen (km 362) forms the tidal limit and marks the beginning of the Lower Weser. Because it is not possible to measure the streamflow in the tidal reach of the river, the load of material transported into the North Sea is estimated by reference to the gauging station Intschede some 32 km upstream of the weir [ARGE Weser, 2000]. At this point, runoff from about 81 % of the Weser catchment is measured.

In the long-term average (1941-99), the mean streamflow (MQ) at Intschede is 325 m<sup>3</sup>/s, while the mean low-flow (LQ) amounts to 117 m<sup>3</sup>/s, and flood-flow (HQ) to 1,210 m<sup>3</sup>/s. Against this background, the calendar year 2000 with 304 m<sup>3</sup>/s (MQ), 127 m<sup>3</sup>/s (LQ), and 1,190 m<sup>3</sup>/s (HQ) can be rated as an average year, the study period 04/00-03/01, however, with 250 m<sup>3</sup>/s (MQ), 127 m<sup>3</sup>/s (LQ), and 858 m<sup>3</sup>/s (HQ) is a period with streamflow below the average. The situation in the study period is similar to that of the hydrological years 1989-92 and 1997-98.

The working group on the protection of the River Weser against pollution (*ARGE Weser*) operates a network of 12 monitoring stations on the rivers Werra, Fulda, Aller, and Weser, i.e. six main and six auxiliary stations. They cover a wide range of physico-chemical and biological-ecological analyses; the results are published in the annual *ARGE Weser* report on water quality. At the six main stations, PAHs have been included in the monitoring programme since 1995, and in the following two years the range of substances was extended from initially 6 PAHs (pursuant to the German drinking water ordinance (Trinkwasserverordnung TVO)) to the 16 priority PAHs according to EPA. These routine measurements of PAH levels are made in half-year intervals (spring/autumn) exclusively in sediments.

In the period from 1997 to 1999, the collective levels (sum of 16 PAHs according to EPA) were measured at Hemelingen in the range from 2 to 3 mg/kg dry weight. Benzo[a]pyrene (BaP) and fluoranthene (F-anth), which are considered as indicator substances because of their outstanding

environmental hazards, occurred in concentrations of 0.14 to 0.23 mg/kg dry weight (BaP) and 0.23 to 0.53 mg/kg dry weight (F-anth).

The TOC (or DOC) levels of the whole samples ranged in the years 1997-99 at Hemelingen between 3 and 12 (or 2 and 8, respectively) mg/l around a mean value of 5.5 (or 3.7) mg/l. The TOC concentrations in suspended solids varied in the same period between 26 and 345 mg/kg (mean value: 115 mg/kg).

The oxygen levels were on average around 10.5 mg/l, pH was around 7.8, and conductivity around 1,630  $\mu\text{S/cm}$ . This extremely high conductivity results from salt effluents from potash mines on the River Werra, although this load has considerably decreased over the past ten years due to closures of plants and technical modifications. For comparison: In the year 1989, the conductivity still ranged between 1,750 and 4,650  $\mu\text{S/cm}$ , with an average of 3,237  $\mu\text{S/cm}$ .

### 3. Parameters, methods and measuring programme

#### 3.1 Parameters

Parameters that are measured in each of the study areas as a minimum requirement of the project are called mandatory parameters. Additionally, other data may be collected optionally.

Mandatory parameters of the international pilot study are:

- Discharge  $Q$  in  $m^3/s$ ;
- Suspended matter concentration  $C_{SS}$  in  $g/m^3$ ;
- Solids organic carbon content  $C_{OC}$  in %, (alternatively loss on ignition LOIN in %);
- Particle size distribution  $C_{<63\mu m}$ ,  $C_{>63\mu m}$  in %; (GSA: Grain Size Analysis)
- Dry weight DW in %;
- Contaminant concentration
  - in solid samples: 16 PAHs specified by EPA,  $PAH_{SS}$  in  $mg/kgDW$ ,
  - in liquid samples: naphthalene,  $NAPHT_{total}$  oder  $NAPHT_{dissolved}$  in  $ng/l$ .

The 16 compounds according to US EPA list are concretely [EPA, 1984]: Naphthalene (NAPHT), Acenaphthylene (ANAPH), Acenaphthene (ANAPT), Fluorene (FLUOR), Phenanthrene (PHEN), Anthracene (ANTHR), Fluoranthene (FLANTH), Pyrene (PYREN), Benzo[a]anthracene (BENZAA), Chrysene (CHRYSE), Benzo[b]fluoranthene (BENZBF), Benzo[k]fluoranthene (BENZKF), Benzo[a]pyrene (BENZAP), Dibenzo[ah]anthracene (DIBENA), Benzo[ghi]perylene (BENGHI), Indeno[1,2,3-cd]pyrene (INDENO).

Additional optional parameters were recorded on the rivers Elbe and Weser:

- Total and dissolved organic carbon TOC und DOC in  $g/m$ ;
- Solids nitrogen and sulfur contents N und S in %;
- Loss on ignition LOIN in %;
- Six particle size fractions  $C_{<20\mu m}$ ,  $C_{20-63\mu m}$ ,  $C_{63-200\mu m}$ ,  $C_{200-630\mu m}$ ,  $C_{630-2000\mu m}$ ,  $C_{>2000\mu m}$  in %
- Solids water content in %;
- 16 PAHs specified by EPA in liquid samples, too.

Further on during flow-through centrifuge operation the electric conductivity in  $\mu S/cm$ , temperature in  $^{\circ}C$ , oxygen concentration in  $mg/l$  and % as well as pH value of the water has been determined with a combined device (Fa. WTW, MultiLine F / Set-3). Continuous chl-*a* (in  $\mu g/l$ ) and turbidity values (in relative units, i.e. volt) have kindly been provided by the GKSS Research Center (measuring station at Elbe km 585,8, left bank), at the River Weser we have been supported by the Bremen municipal government ("*Bremer Senat für Bau und Umwelt*"), who placed some data from the measuring station in Bremen/Hemelingen (Weser km 361, right bank) at our disposal: fortnightly values of chl-*a* (in  $\mu g/l$ ) and daily turbidity values (in NTU).

## 3.2 Methods of suspended-solids sampling

The highly condensed PAHs (four rings and more) in waters are mainly particle-bound, while in the case of aromatics with two to three rings neither the dissolved nor the particle-bound phases should be neglected [UBA, 1999; Kumata et al., 2000] (cf. also partition coefficients in Chapters 4.1.2.4 and 4.2.2.4). Because the dynamics of suspended solids in the estuary differ essentially from that of dissolved substances, it is necessary to analyse these two phases separately.

Three different methods of suspended-solids sampling were used during the study:

- the flow-through centrifuge (FC);
- the sampler BISAM; and
- the sedimentation tank (ST).

While on the River Elbe all three methods were employed, on the River Weser the phases were separated only by means of the flow-through centrifuge. The exact positions at the sampling profiles can be seen in Figures 3.6 and 3.7 in Chapter 3.4.

### 3.2.1 The mobile flow-through centrifuge (FC)

The FC of type Z61, made by Padberg, is mounted on a trailer and may thus be used at any site accessible by ship or car.

FC gives a "snap shot" picture of the suspended solids situation; a typical sampling takes between three and five hours.

With its separation rate of 92 to 98 %, it is suitable for representative sampling of suspended solids.

Since the outflow from the centrifuge can be easily collected, this method allows a complete separation of solids and the dissolved phase.

On the Elbe, water was sampled directly on the right-hand bank and indirectly as a composite sample over the river cross profile. The composite sample had to be filled in barrels on the ship (total volume 1.2 m<sup>3</sup>) and was then treated with the FC on the river bank.



Fig. 3.1: Trailer with mobile flow-through centrifuge (FC)



On the Weser, the centrifuge trailer could be loaded on the measuring boat, so that measurements could be made directly along several points in the cross profile (right hand side/composite sample/left-hand side).

Sampling with FC allows to identify spatial, seasonal, and discharge-related variabilities.

### 3.2.2 The suspended matter sampler BISAM

BISAM (from German word: "Binnensammler", [Reinemann und Schemmer, 1994]) is a passive sampler, that is stationed *in situ* for longer periods (1 to 4 weeks) to collect suspended solids continuously. Via an 8-mm inlet nozzle and two outlet channels the water passes slowly through the body of the "fish". In the wide section of the belly area (settling chamber) the flow velocity decreases and the suspended solids settle to be collected in a 2-l flask.

Throughput and separation rate are not exactly defined.

Three BISAM units were continuously in operation on the River Elbe, distributed across the river profile. They collected suspended solids near the water surface aiming to reveal spatial, seasonal, and discharge-related variations in the suspended-solids quality.

Figure 3.2 shows the BISAM unit with some technical modifications, which had been developed and implemented in the context of a diploma thesis [Harting, 2000] during this project in order to improve the swimming behaviour.

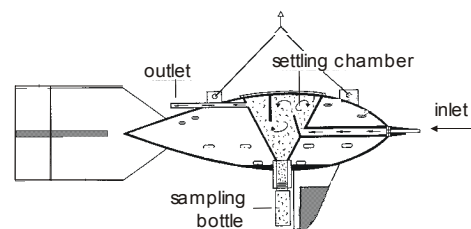
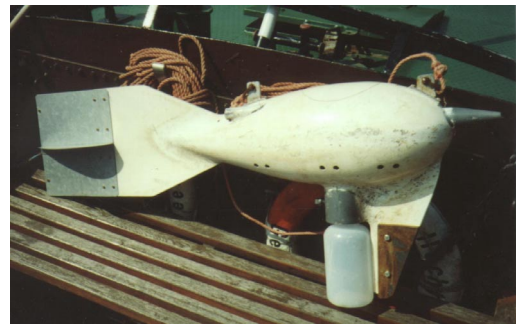


Fig. 3.2: Photo and schematic view of the BISAM sampler

### 3.2.3 The sedimentation tank (ST)

The ST of Type *ARGE Elbe* is also a passive sampler that collects suspended solids continuously over a longer period (1 to 4 weeks).

Inside the weir at Geesthacht there is a measuring station near the right bank of the River Elbe. The station is operated by the WSA Lauenburg, who kindly allowed to install the ST during the measuring period. The water intake is about 2 m below the surface at mean flow conditions.

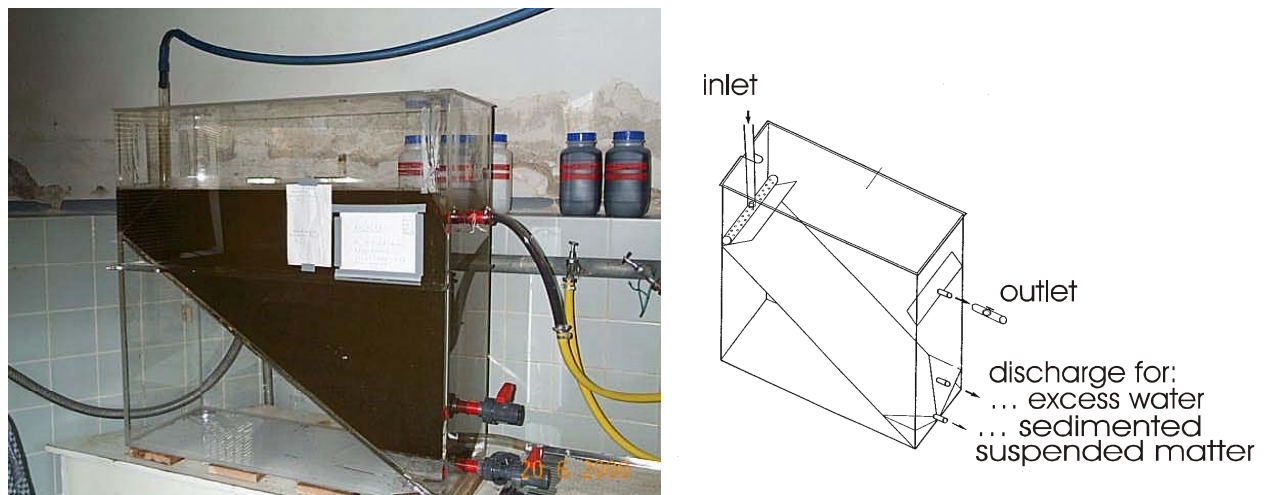


Fig. 3.3: Photo and schematic view of the sedimentation tank (ST) of type *ARGE Elbe*

The inflow and the overflow are located on the upper edge, at the taps near the bottom the suspended solids are extracted.

Throughput may be adjusted variably (typical setting 200 l/h), the separation rate is around 30%.

The material sampled with the ST is used for comparisons with the samples collected by BISAM and FC on the right-hand bank about 800 m upstream of the weir.

### 3.2.4 Comparison of the three sampling techniques

The following table summarizes typical features and advantages or drawbacks of the three methods of suspended-solids sampling:

Table 3.1: Specifications and characteristics of the three sampling techniques

| System                                     | Manufacturer /<br>Type;<br>Specifications                                                                                                                                                                                  | Characteristics                                                                                                                                                                                                               |                                                                                                                                                                                                                                                     |
|--------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                            |                                                                                                                                                                                                                            | Advantages                                                                                                                                                                                                                    | Drawbacks                                                                                                                                                                                                                                           |
| <b>Mobile flow-through centrifuge (FC)</b> | Padberg/<br>Type Z 61;<br><br>Weight: app. 500 kg<br>Dimensions:<br>app. 100x70x170 cm<br>Separation rate:<br>app. 95%<br>Rotor speed:<br>17,000 rpm<br>Rotor diameter:<br>105 mm (inner)<br>max. throughput:<br>1,500 l/h | - high time resolution;<br>- mobility (vertical and cross profiles measured by ship);<br>- high SS yield;<br>- high and constant separation rate allowing load estimates and analyses of the liquid phase (total separation); | - "snap shot", not integrating;<br>- high costs;<br>- high maintenance requirement;<br>- in difficult terrain use on boat necessary;<br>- use on boat requires special equipment, as the unit is large, bulky, and hard to handle (e.g. ramp etc.); |

|                                |                                                                                                                                                                                        |                                                                                                                                                                                                                                        |                                                                                                                                                                                                                        |
|--------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>BISAM</b>                   | BfG development<br><br>Weight: app. 15 kg<br>Dimensions:<br>app. 100x20x60 cm<br>Separation rate:<br>app. 20 - 40 %<br>Throughput:<br>not known                                        | - relatively low cost;<br>- easy handling;<br>- little maintenance;<br>- time-integrative measurement;                                                                                                                                 | - boat use necessary;<br>- operation period 1 -4 weeks;<br>- interference with navigation possible;<br>- device may get lost;<br>- no operation during ice flow etc.;<br>- no load estimate;<br>- no total separation; |
| <b>Sedimentation tank (ST)</b> | Type <i>ARGE Elbe</i> ;<br><br>Weight: app. 40 kg<br>Dimensions:<br>100x40x100 cm<br>Separation rate:<br>app. 20 - 35 %<br>Sample volume:<br>app. 200 l<br>Throughput:<br>app. 200 l/h | - very low costs <sup>*)</sup> ;<br>- little maintenance;<br>- time integrative measurement;<br>- measuring method rather close to natural situation in groin fields and ports;<br><br><sup>*)</sup> provided measuring station exists | - measuring station needed;<br>- operating period 1 -4 weeks;<br>- tanks may need shading and cooling;<br>- load estimates difficult and restricted;<br>- no total separation;                                         |

The advantage of low maintenance requirements of BISAM and ST becomes relative if - as it happened in the summer months - mussels, crustaceans, and other organic matter clog the nozzles of BISAM and the feeder pipelines to the ST. In such cases the pump and the feeder system of the measuring station must be cleared by alternating flushing by the weir-operating staff, often several times per day. Daily inspections of the three BISAM units were not practicable, so that consequently the right-hand, left-hand, and mid-river samplers often yielded considerably deviating amounts of solids, which could be explained only by the clogging of inlet or outlet nozzles. Of course, this fact also reduced the representativity of the suspended solids sampled during this period.

### 3.3 Analyses

The parameters listed in Chapter 2.1 are usually determined by means of generally accepted or standardized procedures. For instance, the loss on ignition is determined according to the German standard DIN 38 414-3 and the total or dissolved organic carbon in liquid samples (TOC or DOC) according to EN 1484:1997 (or DIN 38 409-3).

Suspended matter concentration is determined according to the standard DIN 38 409-2. The water samples were collected near the water surface by staff of the local Districts of the Federal Waterways and Shipping Administrations (WSA) in Geesthacht and Habenhausen on workdays and later filtered in fortnightly intervals in the laboratory of the Federal Institute of Hydrology (BfG).

The official discharge data were provided by courtesy of the competent WSA. These are daily mean values on the basis of 15-minute water level readings and known level-discharge relations. In the following, the procedure for the determination of suspended-solids yields and water contents is described along with the BfG in-house modifications in the determination of organic carbon, nitrogen, and sulfur levels (C, N, and S) in the suspended solids and the grain-size as well as the PAH analysis, which is described in more detail.

#### 3.3.1 Suspended-solids yield / Water content

The suspended-solids enriched content of the 2l flask of the BISAM unit is centrifuged in the laboratory (Heraeus Sepatech "Cryofuge 5000") just like the remains in the sedimentation tank (about 15l, including the water used for rinsing the walls). The mass of the centrifugation residue is called wet yield  $Y_w$ . In case of flow-through centrifuge samples, the centrifugation residue is produced at site, and  $Y_w$  can be determined in the laboratory directly by gravimetry.

After freeze-drying, the dry yield  $Y_D$  is determined by renewed weighing. The percentage of water in the centrifugation residue is computed from:

$$\varphi = \left( 1 - \frac{Y_D}{Y_w} \right) \cdot 100$$

with  $\varphi$  designating the water content of the suspended solids in percent by weight.

#### 3.3.2 Determination of C, N, and S in suspended solids

The determination of organic carbon, nitrogen, and sulfur levels in suspended solids is based on IR detection (C and S) or thermal conductivity (N). Before measuring, the freeze-dried sample is homogenized in a ball grinder (weight of sample 1 g), mixed with de-ionized water into a slurry,

and the inorganic carbon is removed by hydrochloric acid (25%). For detection, the sample is incinerated at 1100 °C in a stream of oxygen (instrument: LECO "CNS 2000").

### 3.3.3 Grain-size analysis (GSA)

The portions of the grain-size classes <20 µm, 20-63 µm, 63-200 µm, 200-630 µm, and 630-2000 µm are measured by laser diffraction with a Coulter Counter, type "LS 200". Following a protective sieving at 2000 µm, the freeze-dried sample is dispersed in a pyrophosphate solution and left for slurring over night. Immediately after ultrasonic treatment over about two minutes (the bath is integrated in the Coulter Counter), the sample is measured for one minute without ultrasonic exposure.

As the fraction >2000 µm is determined gravimetrically <sup>\*)</sup>, the portions of the smaller fractions are also given in percentages by weight. The conversion of the originally determined percentages by volume is based on the assumption of a constant density of suspended solids  $\rho_{SS}=2.65 \text{ g/cm}^3$ .

<sup>\*)</sup> In reality no suspended particles of diameters >2000 µm are found in the river.

### 3.3.4 Polycyclic aromatic hydrocarbons (PAHs)

#### 3.3.4.1 Analytical procedure

The methods applied are suitable for identification and quantification of the 16 PAHs specified by EPA [1984] in sediments, soils, suspended solids, and water. The samples are treated according to DIN 38414-21 and EPA Method 610 in sediments and sludges and DIN 38407-8 in water.

#### *Measuring principle*

The individual components are detected by mass spectrometry (MS) and subsequently identified by gas chromatography (GC) by means of the retention time and the comparison with standardized substances.

#### *Sample preparation for determination of the 16 PAHs in suspended solids by GC/MS*

- Extraction of the freeze-dried powdered sample by means of a Soxhlet apparatus (n-hexane);
- Transferring the sample into a 50 ml flask;
- Concentrating an aliquot in a nitrogen stream to 0.5 ml;
- Purifying the extract by solid-phase extraction (silica-gel phase);
- Elution with dichloromethane / hexane (1 : 1);
- Concentrating the extract under nitrogen;
- Uptake in n-hexane;
- Analysis by GCQ.

*Sample preparation for determination of the 16 PAHs in water by GC/MS*

- Concentrating and purifying the sample by automated solid-phase extraction (SPE, Autotrace SPE Workstation, Zymark) with a solid-phase combination of an amino-C18 phase;
- Volumes used: Inflow 1 l, outflow 5 l;
- After extraction, elution with dichloromethane;
- Concentrating under nitrogen;
- Uptake in n-hexane;
- Analysis by GCQ.

*Instrumental analysis of the 16 PAHs by GCQ*

|                              |                                                                                                       |
|------------------------------|-------------------------------------------------------------------------------------------------------|
| Device:                      | GCQ (Thermoquest),<br>with Autosampler CTC 200 SE (CTC Analytics);                                    |
| Capillary separating column: | MDN- 5S (60m x 0.25 mm ID x 0.25 µm, Supelco);                                                        |
| Ionization:                  | EI, direct coupling;                                                                                  |
| Injection type:              | Splitless;                                                                                            |
| Injector temperature:        | 300°C                                                                                                 |
| Ion source temp.:            | 200°C                                                                                                 |
| Transfer line temp.:         | 300°C                                                                                                 |
| Oven temp. programme.:       | 60°C , 1 min. isothermal<br>10°C/min to 160°C, 0 min isothermal<br>3°C/min to 320°C, 7 min isothermal |

Table 3.2: PAH, determination by GC-MS/MS (SRM)

| Standard compound      | Start Time<br>min | Precursor Ion<br>(m/z) | Product Ion<br>(m/z) |
|------------------------|-------------------|------------------------|----------------------|
| Naphthalene            | 10.50             | 128                    | 102                  |
| Acenaphthylene         | 15.70             | 152                    | 123                  |
| Acenaphthene           | 16.40             | 153                    | 150                  |
| Fluorene               | 18.80             | 166                    | 163                  |
| Phenanthrene           | 23.95             | 178                    | 152                  |
| Anthracene             | 23.95             | 178                    | 152                  |
| Fluoranthene           | 32.00             | 202                    | 198                  |
| Pyrene                 | 32.00             | 202                    | 198                  |
| Benzo[a]anthracene     | 42.80             | 228                    | 224                  |
| Chrysene               | 42.80             | 228                    | 224                  |
| Benzo[b]fluoranthene   | 50.30             | 252                    | 248                  |
| Benzo[k]fluoranthene   | 50.30             | 252                    | 248                  |
| Benzo[a]pyrene         | 52.40             | 252                    | 248                  |
| * Perylene d 12        | 52.40             | 264                    | 260                  |
| Indeno[1,2,3-cd]pyrene | 59.00             | 276                    | 273                  |
| Dibenzo[ah]anthracene  | 60.90             | 278                    | 274                  |
| Benzo[ghi]perylene     | 61.10             | 276                    | 274                  |

\* internal standard

### 3.3.4.2 Quality assurance, analytical error, and selected chromatograms

The analyses are part of the laboratory routine in the Federal Institute of Hydrology and are thus subject to regular in-house quality assurance procedures. These comprise regular analyses with reference materials and comparisons with HPLC analyses.

Quality assurance also consists in regular measurements of standard reference materials and checks with calibrating solutions. Standard reference materials were:

- SRM 1941a (National Institute of Standard and Technology Gaithersburg, USA);
- HS- 4 B (National Research Council of Canada, Institute for Marine Biosciences); and
- HS 6 (National Research Council of Canada, Institute for Marine Biosciences).

The application of the analytical methods mentioned under 3.3.4.1 to suspended-solid samples did not encounter any particular problems. Some difficulties occurred in analyses of aqueous samples; and especially with total samples (containing a high portion of filterable material), the SPE columns became clogged. This problem was avoided by using several SPE columns for one sample.

The quantification followed after the checking of the raw data by means of external standard under inclusion of the recovery rates.

The method is suitable for the quantitative determination of polycyclic aromatic hydrocarbons in suspended solids, sediments, and waters in mass concentrations of  $>0.02$  mg/kg or  $0.02$  ng/l.

Table 3.3 presents the mean value of the recovery rates that were determined over the whole calibration range. For the determination of the recovery rates of the aqueous samples, unpolluted natural surface water samples (River Spree) were concentrated with calibrating solution. The recovery rates of the suspended solids samples were determined with the help of three reference materials (see above). The results are listed in the table separately for the types of the samples, i.e. for suspended solids and aqueous samples (water or centrifugate).

Table 3.3: Mean recovery rates, standard deviations, and variability coefficients in PAH analyses of solid and aqueous samples

| Standard compound      | recovery rate<br>R in % |         | standard deviation<br>SD in % |         | variability coefficient<br>CV = SD / R * 100 |         |
|------------------------|-------------------------|---------|-------------------------------|---------|----------------------------------------------|---------|
|                        | solid                   | aqueous | solid                         | aqueous | solid                                        | aqueous |
| Naphthalene            | 32.4                    | 49.1    | 6.5                           | 10.6    | 20.1                                         | 21.6    |
| Acenaphthylene         | 96.4                    | 42.9    | 19.9                          | 8.1     | 20.6                                         | 18.9    |
| Acenaphthene           | 84.7                    | 61.1    | 13.4                          | 12.1    | 15.8                                         | 19.7    |
| Fluorene               | 98.4                    | 73.2    | 14.0                          | 11.4    | 14.2                                         | 15.5    |
| Phenanthrene           | 99.3                    | 78.6    | 9.9                           | 13.3    | 10.0                                         | 16.9    |
| Anthracene             | 103.9                   | 66.4    | 11.8                          | 14.1    | 11.3                                         | 21.2    |
| Fluoranthene           | 100.6                   | 67.7    | 11.0                          | 8.5     | 10.8                                         | 12.6    |
| Pyrene                 | 78.8                    | 68.9    | 9.9                           | 13.2    | 12.5                                         | 19.2    |
| Benzo[a]anthracene     | 97.9                    | 47.2    | 13.2                          | 7.7     | 13.4                                         | 16.4    |
| Chrysene               | 97.7                    | 62.2    | 13.3                          | 11.6    | 13.6                                         | 18.6    |
| Benzo[b]fluoranthene   | 101.5                   | 54.4    | 10.6                          | 9.1     | 10.4                                         | 16.8    |
| Benzo[k]fluoranthene   | 104.1                   | 69.5    | 14.5                          | 9.4     | 14.0                                         | 13.5    |
| Benzo[a]pyrene         | 111.9                   | 66.6    | 14.9                          | 11.3    | 13.3                                         | 16.9    |
| Indeno[1,2,3-cd]pyrene | 101.1                   | 67.7    | 14.7                          | 14.1    | 14.5                                         | 20.8    |
| Dibenzo[ah]anthracene  | 104.2                   | 63.0    | 12.3                          | 7.5     | 11.8                                         | 11.9    |
| Benzo[ghi]perylene     | 105.8                   | 70.0    | 16.8                          | 8.2     | 15.9                                         | 11.7    |
| Sum of 16 PAHs         | mean value:             |         | 12.9                          | 10.6    | 13.9                                         | 17.0    |

Because the value of the respective recovery rate is included in the quantification of a natural sample, the deviation of this rate from 100 % does not contribute to the analytical error. However, the stochastic scatter of recovery rates must be considered as a measure for the analytical error. For this purpose, the variability coefficient (CV) is listed besides the standard deviation in the right-hand column of the table. Being the ratio between standard deviation and the mean recovery rate, CV stands for the relative error of the analyses and is given in %, too. Consequently, an analytical error is to be expected for solid samples between 10 and 21 % (mean value: 13.9%) and for aqueous samples between 12 and 22 % (mean value: 17.0%).

Figure 3.4 shows chromatograms of the suspended-solids phase, the whole sample, and the centrifugate in comparison with those of a calibrating solution. As the PAH distribution patterns of the Elbe and the Weser do not differ essentially, only the results of the sampling campaign on the Elbe on 10 August 2000 are presented here.



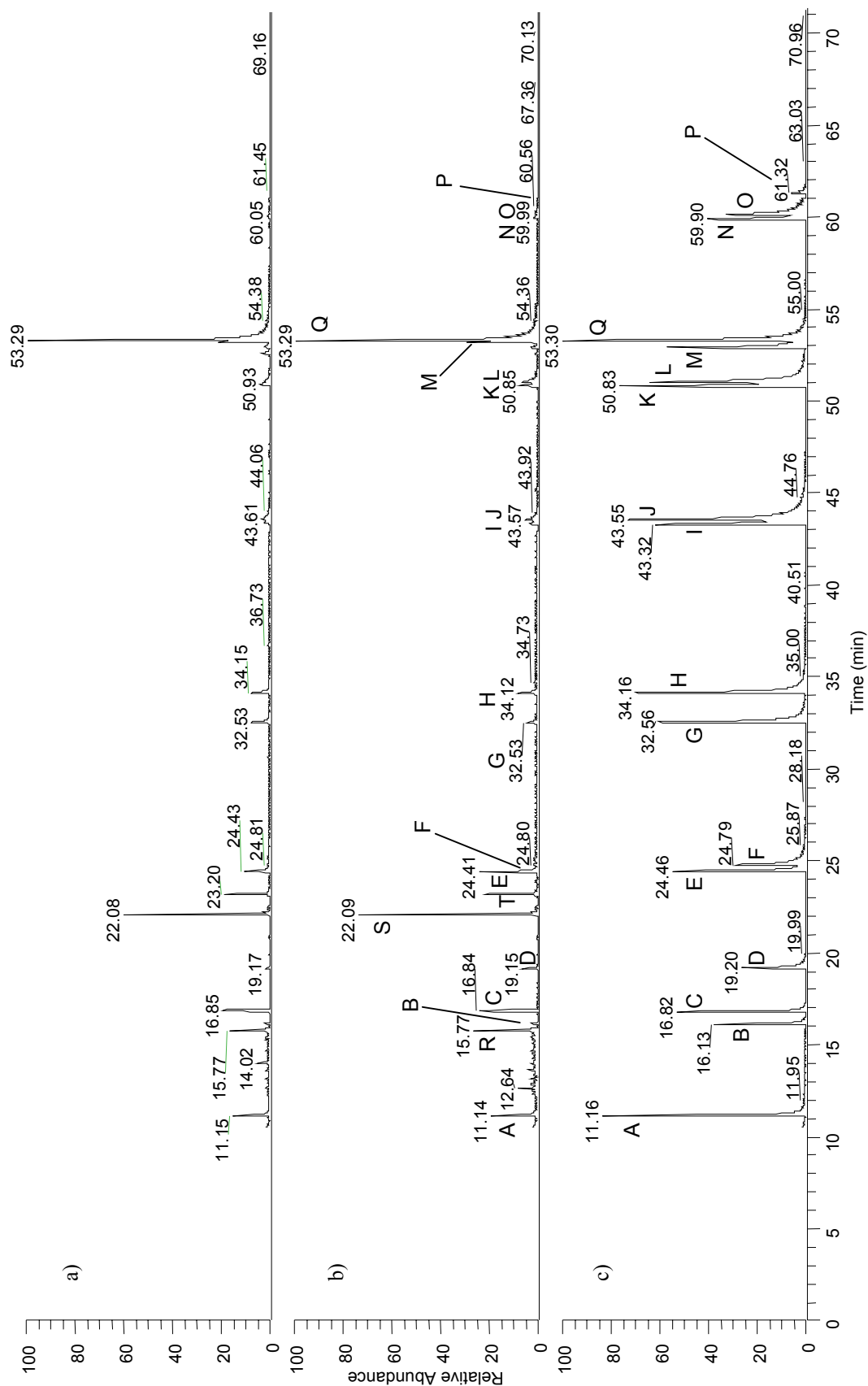


Fig. 3.4: Examples of chromatograms (for legend see next page)



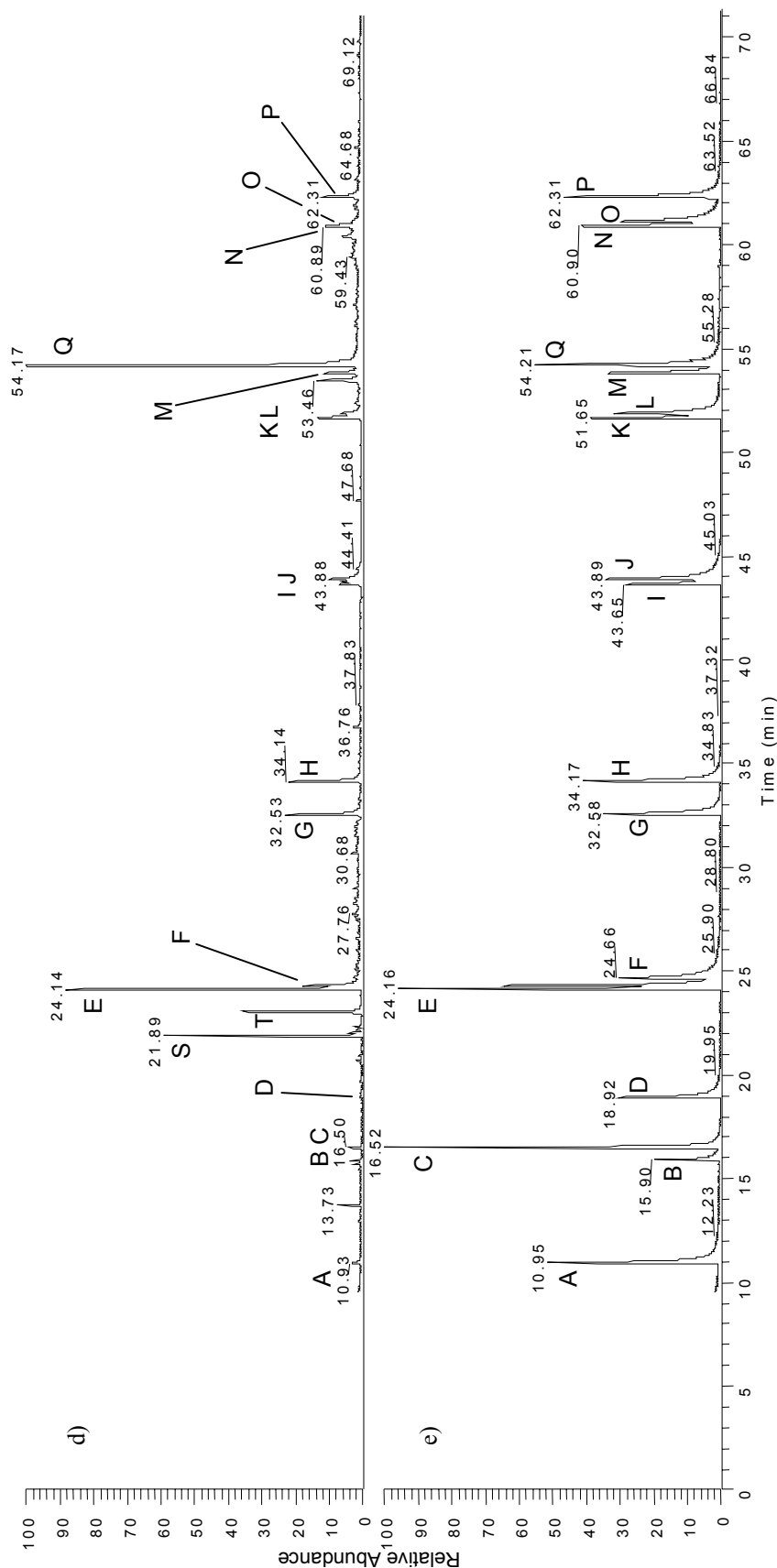


Fig. 3.4 (contd.): Examples of chromatograms (10 August 2000, River Elbe km 585.0, right-hand side):

a) total sample (=FC-inflow), b) centrifugate (=FC-outflow), c) calibrating solution d) solid sample (=FC-residue), e) calibrating solution. Numbers indicate retention times in min, letters the respective compounds:

A: Naphthalene, B: Acenaphthylene, C: Acenaphthene, D: Fluorene, E: Phenanthrene, F: Anthracene, G: Fluoranthene, H: Pyrene, I: Benzo[a]anthracene, J: Chrysene, K: Benzo[b]fluoranthene, L: Benzo[k]fluoranthene, M: Benzo[a]pyrene, N: Indeno[1,2,3-cd]pyrene, O: Dibenzo[a,h]anthracene, P: Benzo[ghi]perylene, Q: Perylene d 12 (internal standard), R, S and T: not identified compounds

### 3.4 Measuring programme

It is known from earlier studies [UBA, 1999] that the variability in particle-bound contaminant transport is primarily dependent on the variability of discharge  $Q$  and concentration of suspended solids  $C_{SS}$ . The variabilities in the composition of suspended solids (organic portion, grain-size spectrum, etc.) or in the contaminant levels of the suspended solids, however, are of secondary significance in practice. This opinion has been repeatedly expressed in the pertinent literature [Knauth, 1993; Keller, 1997; LAWA, 2002].

For this reason, the year-long measuring programme (March 2000 - March 2001) has a (quasi)-continuous part and an event-related one. The quasi-continuous measurements, i.e. the daily mean values of discharge and the random samples of suspended solids concentrations taken on workdays, record in high frequency  $Q$  and  $C_{SS}$  as the essential controlling elements. Event-related measurements, conversely, record discharge-induced and seasonal variations of all measured parameters by means of the flow-through centrifuge (FC). The continuous measurements with the BISAM sampler and the sedimentation tank (ST) give a time-integrating picture of the suspended-solids situation. The simultaneous use of these three methods serves the validation of the measured data and provides the basis for direct comparison of the different sampling techniques.

Measurements have been performed at the two biggest German rivers flowing into the North Sea, i.e. the rivers Elbe and Weser. The sampling locations in Bremen/Hemelingen (Weser) und in Geesthacht (Elbe) are marked with red crosses in Figure 3.5.



Abb. 3.5: Survey map of Germany with the two sampling locations at Elbe and Weser (x).

### 3.4.1 Measuring programme at River Weser

On River Weser measurements took place approx. 2 km upstream of the tidal weir in Bremen/Hemelingen, except the samples for  $C_{SS}$  determination, that are scooped directly upside the weir by the staff of the local Districts of the WSA Bremen in Habenhausen, and the daily mean discharge values, which stem from the gauging station Intschede at kilometre 329.7. The discharge values are based on a level-discharge relationship, they are provided by the WSA Verden.

The locations are illustrated in Figure 3.6. Near-surface samples were collected directly from the ship as near-bank (left/right) or mixed samples with the help of the flow-through centrifuge (FC). In all cases the centrifuge residue from approx. 1 bis 2 m<sup>3</sup> of water as well as the centrifugate and the total sample have been analysed.

The measuring programme is compiled in table 3.4.

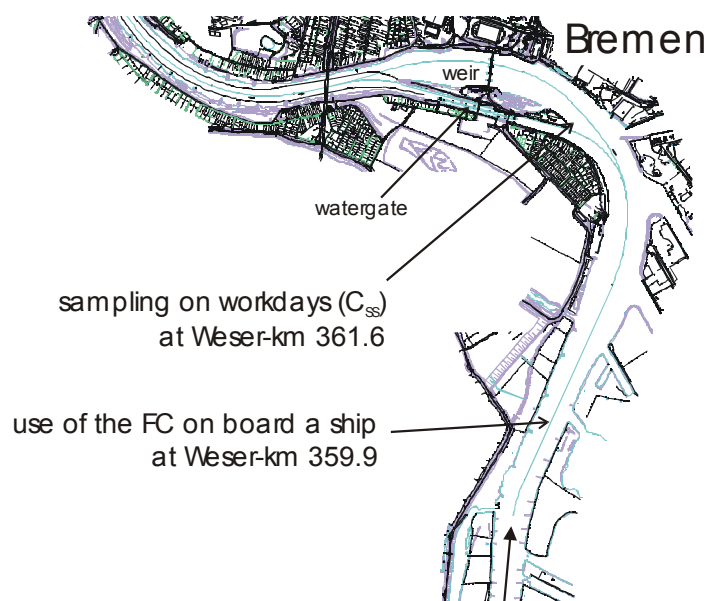


Fig. 3.6:  
Sampling locations at  
the River Weser  
upstream the tidal weir  
in Bremen/Hemelingen  
(53°03'N ; 08°52'E).

Table 3.4: River Weser study programme

| Date (from<br>03.2000 - 03.2001) | Q | $C_{SS}$ | PAH<br>(w) | PAH<br>(ss) | GSA | CNS | LOIN | TOC | DOC | $Y_W$ | $Y_D$ |
|----------------------------------|---|----------|------------|-------------|-----|-----|------|-----|-----|-------|-------|
| Daily                            | X |          |            |             |     |     |      |     |     |       |       |
| Workdays                         |   | X        |            |             |     |     |      |     |     |       |       |
| 9.3.00 (FC)                      |   | X        | X          | X           | X   | X   | X    | X   | X   | X     | X     |
| 6.4.00 (FC)                      |   | X        | X          | X           | X   | X   | X    | X   | X   |       |       |
| 8.6.00 (FC)                      |   | X        | X          | X           | X   | X   | X    | X   | X   | X     | X     |
| 5.9.00 (FC)                      |   | X        | X          | X           | X   | X   | X    | X   | X   | X     | X     |
| 15.3.00 (FC)                     |   | X        | X          | X           | X   | X   | X    | X   | X   | X     | X     |

(w): in aqueous samples; (ss): in suspended solids; GSA: grain size analysis; CNS: C, N, and S determination in suspended solids; LOIN: loss on ignition;  $Y_W$ ,  $Y_D$ : yield wet/dry ( $Y_W$  and  $Y_D \rightarrow$  water content  $\phi$ )

### 3.4.2 Measuring programme at River Elbe

On River Elbe, sampling was performed directly upside the tidal weir in Geesthacht. Sampling locations are shown in Figure 3.7, the measuring programme in table 3.5.

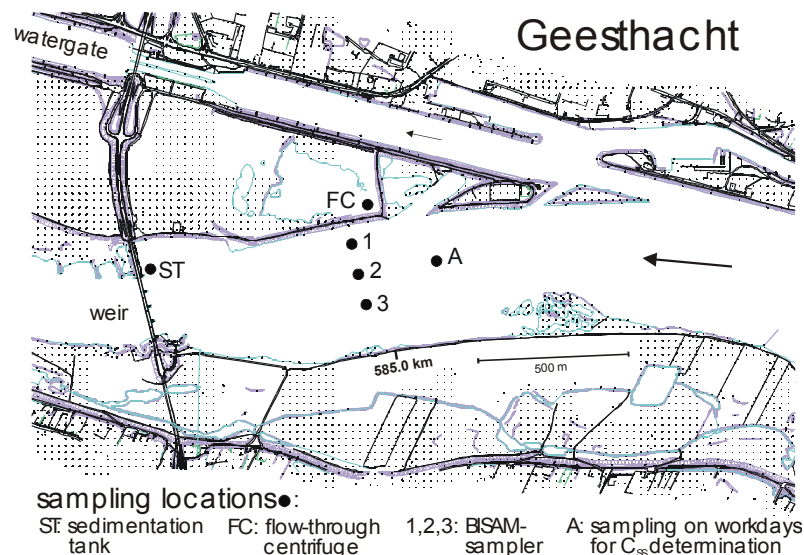


Fig. 3.7:  
Sampling locations at  
the River Elbe  
upstream the tidal  
weir in Geesthacht  
(53°25,5'N ; 10°21'E).

Table 3.5: River Elbe study programme

| Date (from<br>03.2000 - 03.2001)    | Q        | C <sub>SS</sub> | PAH<br>(w) | PAH<br>(ss) | GSA      | CNS      | LOIN     | TOC      | DOC      | Y <sub>W</sub> | Y <sub>D</sub> |
|-------------------------------------|----------|-----------------|------------|-------------|----------|----------|----------|----------|----------|----------------|----------------|
| <b>Daily</b>                        | <b>X</b> |                 |            |             |          |          |          |          |          |                |                |
| <b>Workdays</b>                     |          | <b>X</b>        |            |             |          |          |          |          |          |                |                |
| Continuously<br>(BISAM)             |          |                 |            | X           | X        | X        | X        |          |          | X              | X              |
| Continuously<br>since 16.05.00 (ST) |          |                 |            | X           | X        | X        | X        |          |          | X              | X              |
| <b>7.3.00 (FC)</b>                  |          | <b>X</b>        | <b>X</b>   | <b>X</b>    | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b>       | <b>X</b>       |
| 16.3.00 (FC)                        |          |                 |            | X           |          | X        |          |          |          |                |                |
| 21.3.00 (FC)                        |          |                 |            | X           |          | X        |          |          |          |                |                |
| <b>4.4.00 (FC)</b>                  |          | <b>X</b>        | <b>X</b>   | <b>X</b>    | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b> |                |                |
| <b>6.6.00 (FC)</b>                  |          | <b>X</b>        | <b>X</b>   | <b>X</b>    | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b> |                |                |
| 14.6.00 (MP)                        |          | X               |            | X           | X        | X        | X        |          |          | X              | X              |
| 22.-27.6.00 (FC)                    |          |                 |            | X           | X        | X        | X        |          |          | X              |                |
| 3.7.00 (FC)                         |          | X               | X          | X           | X        | X        | X        | X        | X        | X              | X              |
| 9./10.8.00 (MP)                     |          | X               | X          | X           | X        | X        | X        | X        | X        | X              | X              |
| <b>6.9.00 (FC)</b>                  |          | <b>X</b>        | <b>X</b>   | <b>X</b>    | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b>       | <b>X</b>       |
| 5./6.2.01 (MP)                      |          | X               | X          | X           | X        | X        | X        | X        | X        | X              | X              |
| <b>13.3.01 (FC)</b>                 |          | <b>X</b>        | <b>X</b>   | <b>X</b>    | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b> | <b>X</b>       | <b>X</b>       |

(w): in liquid samples; (ss): in suspended solids; GSA: grain-size analysis; CNS: C, N, and S determination in suspended solids; LOIN: loss on ignition; Y<sub>W</sub>, Y<sub>D</sub>: yield wet/dry (Y<sub>W</sub> and Y<sub>D</sub> → water content  $\phi$ ); MP: multi-point measurement

The regular programme, corresponding to that of the River Weser – i.e. daily discharge measurements, scoop sampling on workdays to determine the suspended matter concentration,

and event-related centrifuging for phase-separated sampling of suspended solids and water – is printed in bold here. Additionally, several special measurements were made on the River Elbe.

For instance, from 22 to 27 June 2000, the FC was operated several times a day under an intensive study programme. Here, the aim was to identify short-term variations in the quality of suspended solids and to obtain a composite sample integrated over one week for comparison with samples taken by the BISAM sampler and the ST.

Moreover, in June and August 2000, as well as in February 2001, multi-point measurements (MP) were made. These comprise simultaneous measurements of flow velocities and suspended solids concentrations along five to six verticals at five levels each with the aim to obtain high resolution data for more precise load estimates. Simultaneous analyses of suspended-solids samples taken by FC near the bottom and the water surface give information about the vertical distribution pattern of contaminants transport.

## 4 Results

The results concerning River Elbe are presented in Chapter 4.1, those from River Weser in Chapter 4.2. But this distinction is not kept up consequently throughout this report. Exceptions are given e.g. with the patterns (Chap. 4.2.2.3.2) and the partition coefficients (Chap. 4.1.2.4), where a joint comparison simplifies the interpretation and assessment of the results.

### 4.1 River Elbe

#### 4.1.1 Mean values of the measured mandatory parameters

The median values and variability ranges of the mandatory parameters measured in this study (cf. Chapter 3.1) and presented in Table 4.1 offer a first overview on the order of magnitude of these parameters in the study area of the River Elbe at Geesthacht (Elbe river-km 585.0). For the sake of better comparability, the respective values are shown for each study area as box-and-whiskers plot in the common report (Chapter 5.1.1 of the Common Report; for River Weser cf. also Table 4.9 in Chapter 4.2.1 of this German individual report).

Tabelle 4.1: Median values and variability of the mandatory parameters, Elbe 585.0 km

|                                     | Minimum | 1. Quartile | Median      | 3.Quartile | Maximum | N   |
|-------------------------------------|---------|-------------|-------------|------------|---------|-----|
| Q in m <sup>3</sup> /s              | 280     | 327         | <b>367</b>  | 504        | 2199    | 365 |
| C <sub>SS</sub> in g/m <sup>3</sup> | 3.1     | 9.1         | <b>15.9</b> | 27.0       | 67.8    | 243 |
| C <sub>OC</sub> in %                | 3.9     | 5.9         | <b>7.4</b>  | 11.3       | 24.5    | 86  |
| GSA <sub>&lt;63µm</sub> in %        | 48      | 65          | <b>74</b>   | 83         | 100     | 82  |
| Σ16PAH <sub>SS</sub> in mg/kgDW     | 2.8     | 5.8         | <b>6.8</b>  | 8.3        | 13.5    | 86  |
| NAPHT <sub>total</sub> in ng/l      | 26      | 47          | <b>62</b>   | 90         | 155     | 16  |



## 4.1.2 Polycyclic aromatic hydrocarbons (PAHs)

### 4.1.2.1 Median values of concentrations

The median values and variability parameters of the total particle-bound and dissolved concentrations of the sum of PAHs according to EPA ( $\Sigma 16\text{PAH}$ ) are shown in Figures 4.1 and 4.2 as box-and-whiskers plots. This presentation shows the interquartile range and the median value (box and horizontal line) as well as the whole variability range ("whiskers"). Values that lie more than one and a half box lengths above or below the box are called outliers (distances of more than three box lengths are called extreme values) and are marked particularly. They are not existent in the figures here.

As the whole sample, the centrifugate, and the suspended solids are compared, only the values measured by flow-through centrifuge are considered here. Thus, there may be minor deviations from the statistics of  $\Sigma 16\text{PAK}_{\text{SS}}$  in Table 4.1.

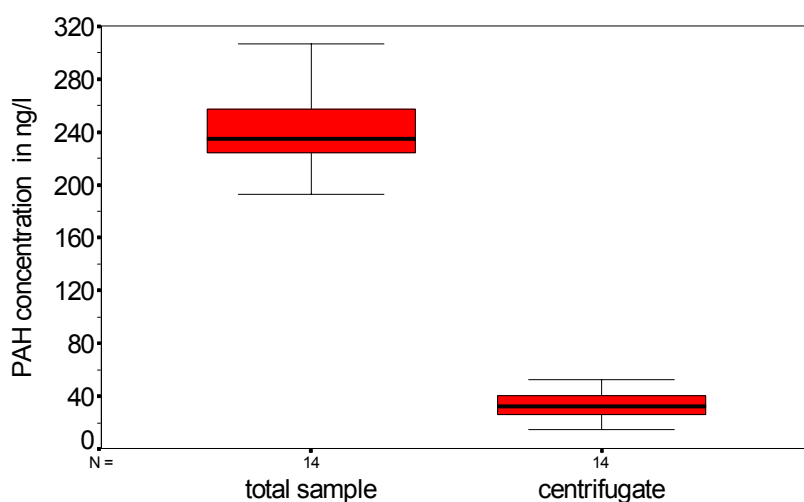


Fig. 4.1: PAH contents in the total sample and in the centrifugate.

In the total sample the median value of 235 ng/l is about seven times higher than in the centrifugate (33 ng/l).

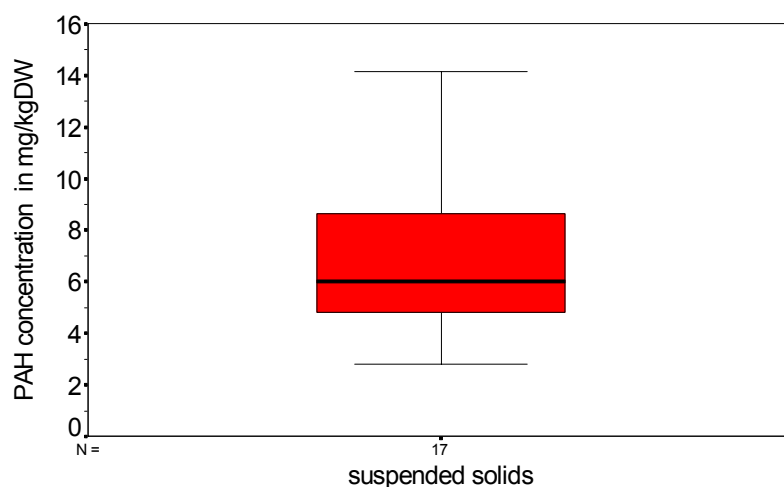


Fig. 4.2: PAH contents in suspended solids. The median value is at 5.9 mg/kg. The three highest values between 12.6 and 14.2 mg/kg were measured in March/April 2000 (not shown here).

#### 4.1.2.2 Seasonality

The temporal development during the study period also is shown by means of the concentration of the sum of the 16 PAHs for each phase separately (total, dissolved, particle-bound) in Figures 4.3 to 4.5. The data were obtained on the basis of all near-surface mixed samples that were gathered with the flow-through centrifuge.

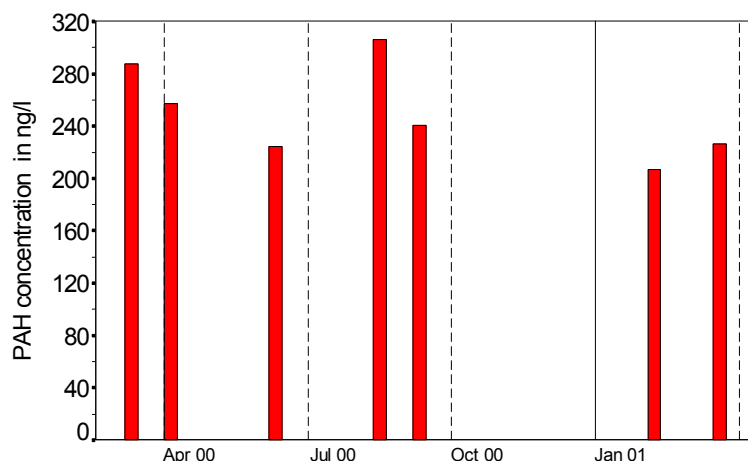


Fig. 4.3:  
PAH concentrations in the total sample in the course of the year. No seasonal patterns can be identified from the measured data.

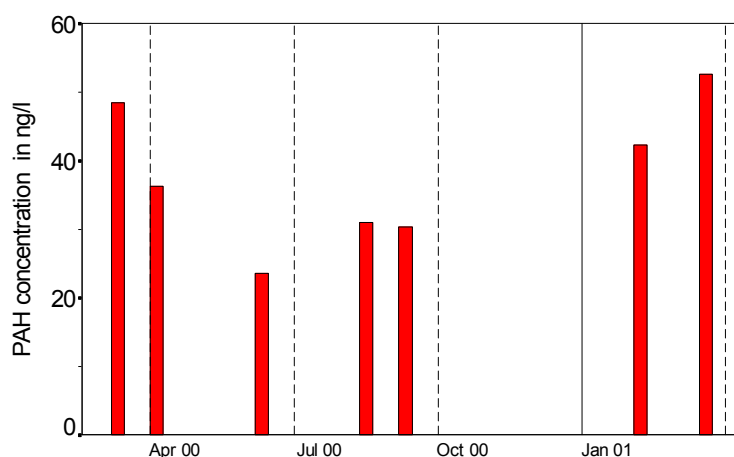


Fig. 4.4:  
PAH concentrations in the centrifugate in the course of the year. A seasonal pattern shows low concentrations in summer and higher ones in winter.

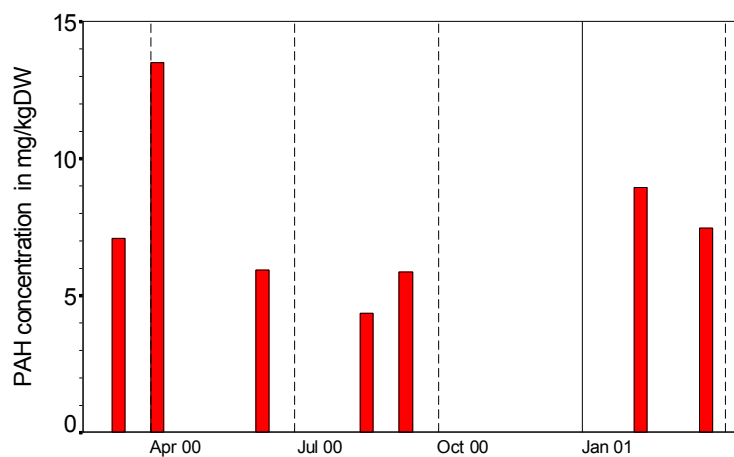


Fig. 4.5:  
PAH concentrations in the suspended solids in the course of the year. A weak seasonal pattern shows lower values in summer.

A distinct seasonal pattern appears only in the centrifugate, a weaker one in suspended solids. A seasonality of PAH loads on suspended solids is distinctly identifiable in connection with homogeneity studies (BISAM), compare here also Figure 4.20 in Chapter 4.1.6.1. Failure to detect seasonal variability in the whole samples may be due to an analytical problem in the first line: The whole samples demand higher standards in sample preparation and analysis than the centrifugate or the suspended solids (cf. Chapter 3.3.4.2).

#### **4.1.2.3 Patterns**

So far, the PAHs were considered in their sum. The PAH pattern illustrates the composition of this sum from the 16 individual compounds. Knowledge of this pattern facilitates the assessment of the ecological and toxicological relevance, as the individual substances produce different effects. Moreover, it gives indications on the sources of PAH pollution.

The Figures 4.6-8 show the mean patterns of the total samples, the dissolved ones, and those of the solids in form of bar diagrams with indication of the variances (interquartile range). Again, values from all samples gathered with the flow-through centrifuge are included.

In the total sample and in the centrifugate Naphthalene shows the highest values, in suspended solids the most frequent compounds are Fluoranthene and Pyrene.

The shift in the patterns from the total samples to the suspended solids or the centrifugate is obvious: The lower-condensed compounds (NAPH-PHEN) occur mostly in solution (centrifugate), while the higher-condensed, poorly soluble ones are more bound on suspended solids.

For a direct comparison of the patterns of the Elbe and the Weser refer to Chapter 4.2.2.3.2.

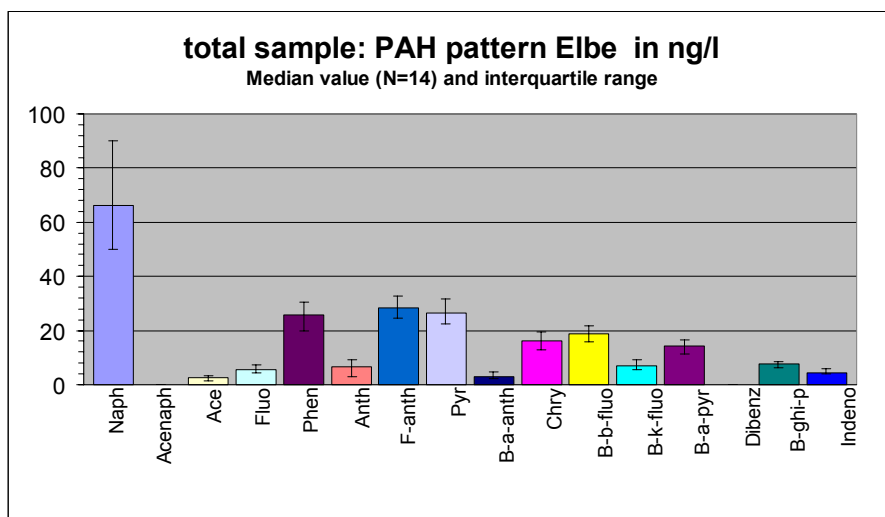


Fig. 4.6:  
Mean PAH pattern  
of the 14 total  
samples  
(centrifuge inflow  
in the study period  
03/00 - 03/01, at  
Elbe 585.0 km).

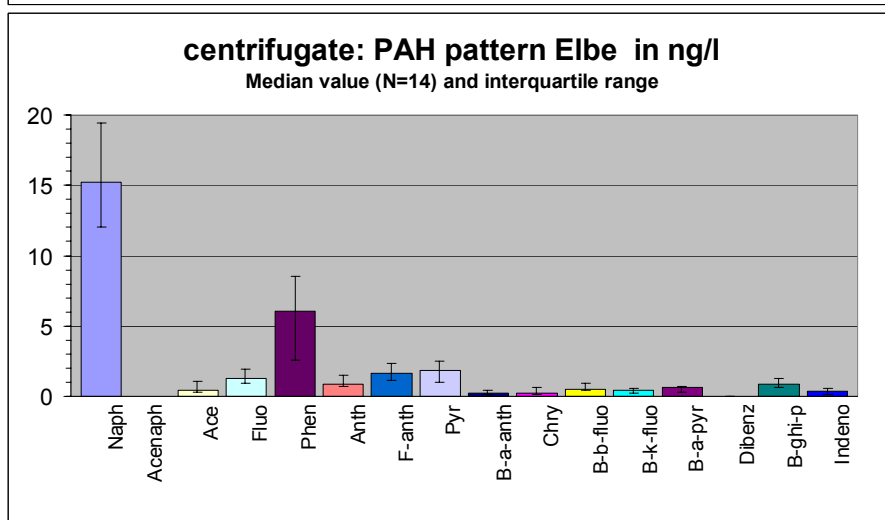


Fig. 4.7:  
Mean PAH pattern  
of the 14 centrifugate  
samples  
(centrifuge outflow  
in the study period  
03/00 - 03/01, at  
Elbe 585.0 km).

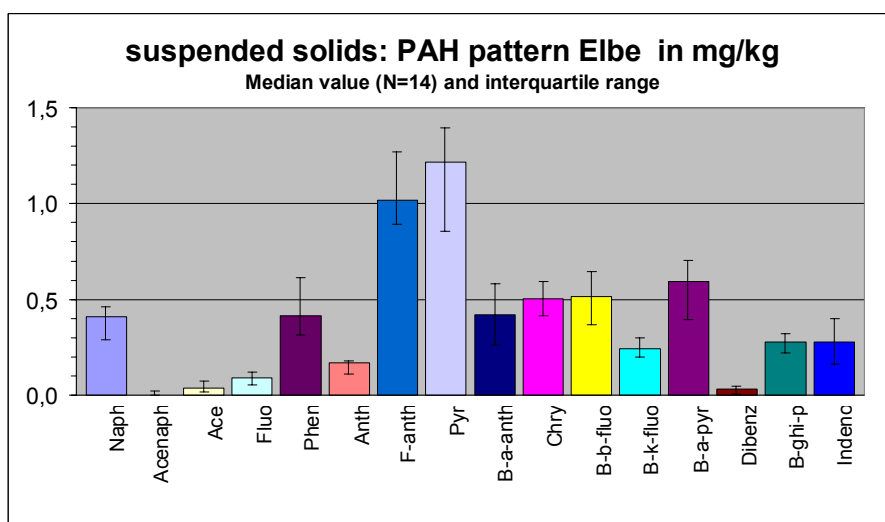


Fig. 4.8:  
Mean PAH pattern  
of the 14 suspended-  
solids samples  
(centrifuge residue  
in the study period  
03/00 - 03/01, at Elbe  
585.0 km).

#### 4.1.2.4 Partition coefficients

The following discussion makes a distinction between the partition coefficient  $K_D$  and the particle-bound fraction PF. Often instead of  $K_D$ , its logarithm (log, base 10) is given, and because confusion can be ruled out, the logarithmic value is called partition coefficient as well.

While the common  $K_D$  value (in l/kg) puts the contamination load of the suspended particles (in mg/kg) into relation with the dissolved concentration (in ng/l), PF (dimensionless) describes the portion of the particle-bound contaminants in the contaminant content of the total sample

These two values are not directly comparable. The connection between  $K_D$  and PF is established via the concentration of suspended solids as shown in Figure 4.9. The percentage of the particle-bound fraction ( $=PF \cdot 100$ ) can be read directly from the diagram when the partition coefficient  $\log K_D$  is known and the suspended-solids concentration  $C_{SS}$  is given.

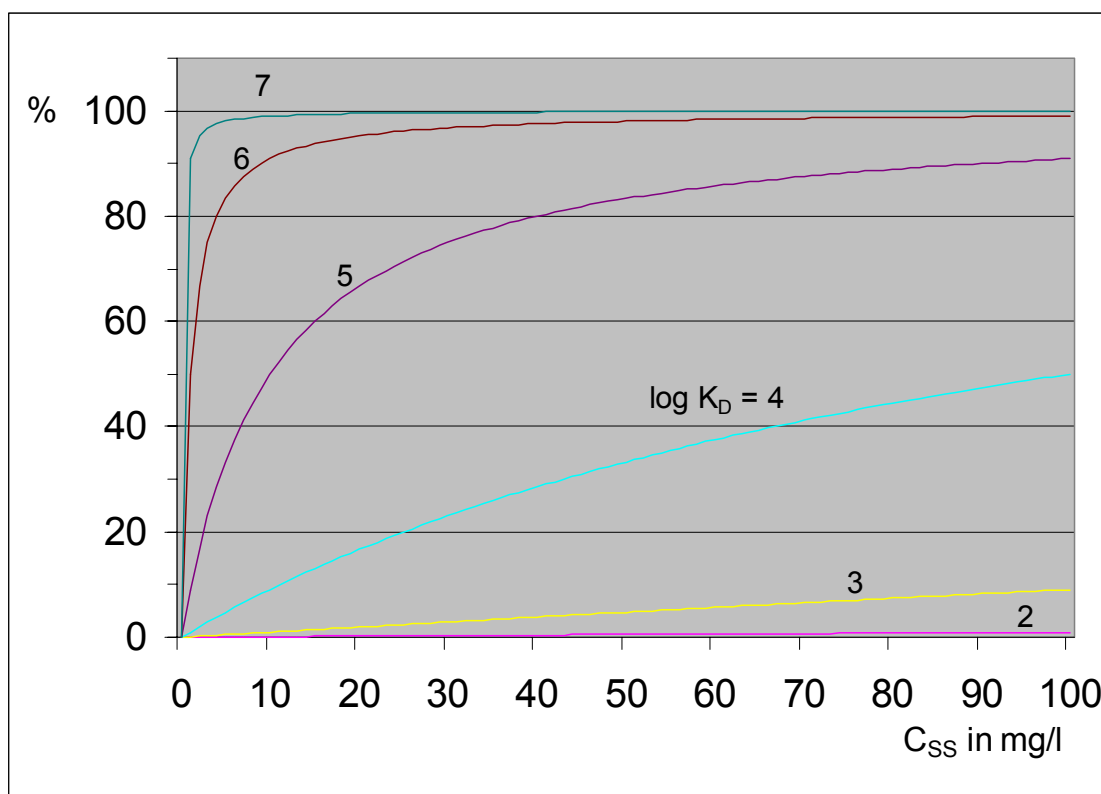


Fig. 4.9: Percentage of the particle-bound portion of contamination in dependence on the concentration of suspended solids  $C_{SS}$  for different partition coefficients  $\log K_D$ .

The following PF calculations are based on measurements of the PAH concentration in the centrifugate (=FC-outlet) and in the FC suspended solids as well as the suspended solids concentration  $C_{SS}$ .

#### 4.1.2.4.1 Distribution of the $\Sigma 16\text{PAH}$ in the rivers Elbe and Weser

Figure 4.10 shows the distribution of PAHs (sum of 16 PAHs according to EPA) between the dissolved and the particulate phases in form of the PF value in percent for each of the 14 measurements made on the Elbe and the Weser, respectively. The samples were collected with the flow-through centrifuge (FC) in the period from March 2000 to March 2001.

Irrespective whether the samples originate from the Elbe or the Weser, they give a very uniform picture with a share of particle-bound PAHs between 60 and 90%. Accordingly, the PAH portion in the dissolved phase ranges between 10 and 40%, so that neither the dissolved portion nor the particle-bound one must be neglected in considerations of the total concentrations or total loads.

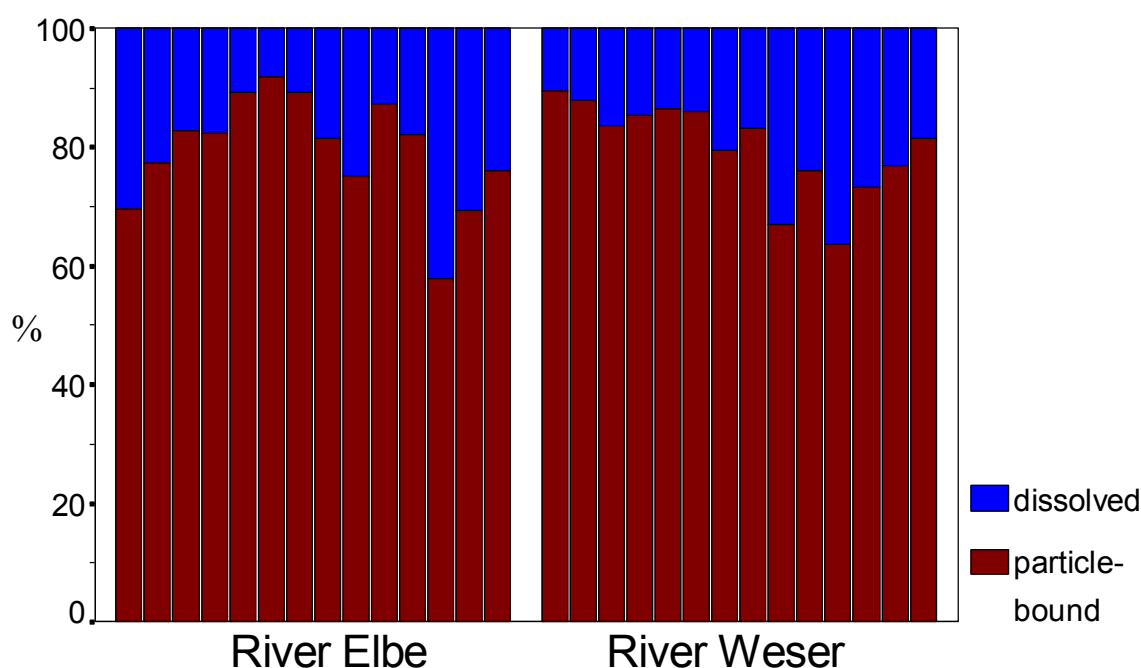


Fig. 4.10: Distribution of PAHs between the particulate phase and the dissolved phase in %. All samples collected with the FC are considered (study period 03/00-03/01).

The following Figure 4.11 presents the PF value (left-hand side) together with the partition coefficient (right-hand side) as box-and-whiskers plots. In contrast to the PF value,  $\log(K_D)$  has on average higher values in the Weser than in the Elbe (median  $\log(K_D)$  Elbe: 5.28; Weser: 5.48). This suggests that PAHs in the Weser have a slightly higher affinity to suspended solids. Due to the fact that the suspended-solids concentration in the Elbe are on average somewhat higher than in the Weser, the particle-bound portions of PAHs in both rivers are comparable, despite the different partition coefficients (median PF Elbe: 0.818; Weser 0.824).

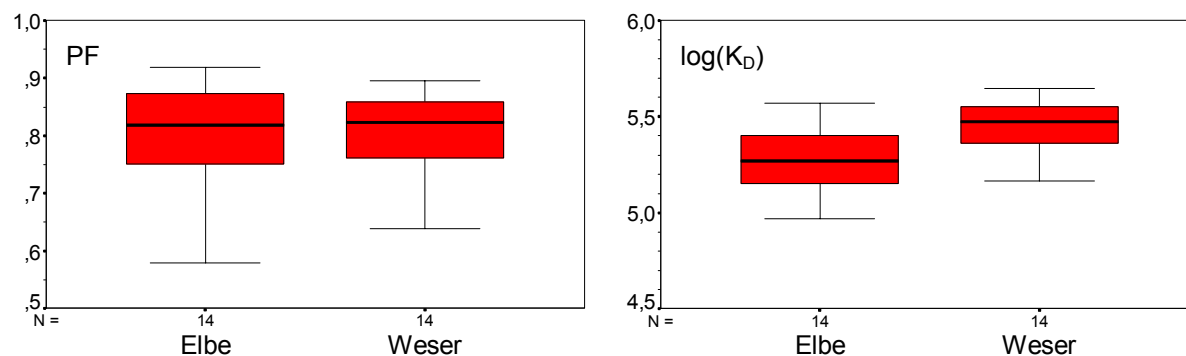


Fig. 4.11: Values of PF and  $\log(K_D)$  from 14 measurements each in the Elbe and the Weser

#### 4.1.2.4.2 Distribution of low- and high-condensed species in the rivers Elbe and Weser

The high-condensed, hardly soluble PAHs have higher PF values than the low-condensed, easily soluble ones. This is clearly visible in Figure 4.12, where the particle-bound and the dissolved PAH portions for low-condensed (sum of NAPH, ANAPH, ANAPT, FLUOR, and PHEN) and the high-condensed compounds (sum of ANTHR, FLANTH, PYREN, BENZAA, CHRYSE, BENZBF, BENZKF, BENZAP, DIBENA, BENGHI, and INDENO) are shown separately.

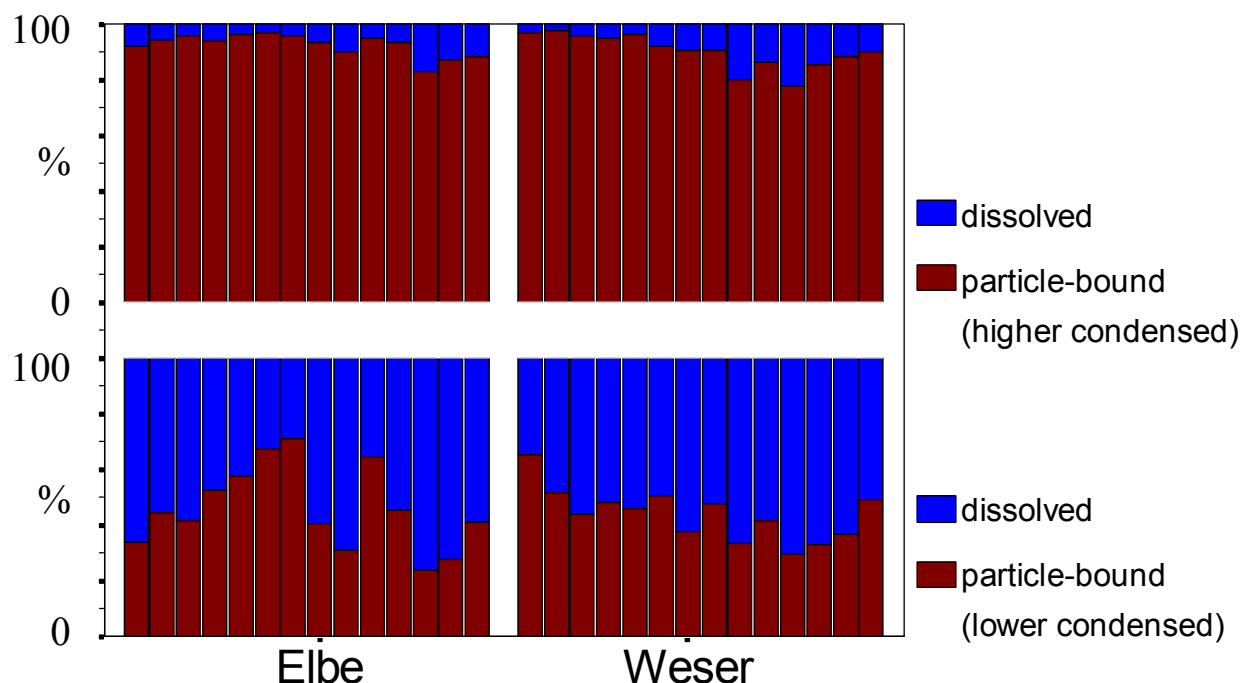


Fig. 4.12: PAHs distribution between the particle-bound phase and dissolved phase in percent; differentiated for low-condensed (bottom) and high-condensed (top) compounds.

Figure 4.13 illustrates the different behaviours of low-condensed and high-condensed compounds. The left-hand picture shows the PF values: Again they are comparable in the Elbe and the Weser and range in the case of easily soluble compounds around 45 %, hardly soluble ones around 90 %. The  $\log(K_D)$  values (right-hand side) of the higher condensed PAHs are by 25 % higher than those of low condensed compounds. Considered within the respective group, the Weser values are slightly elevated against the Elbe data (cf. discussion of the  $\Sigma 16\text{PAH}$  above).

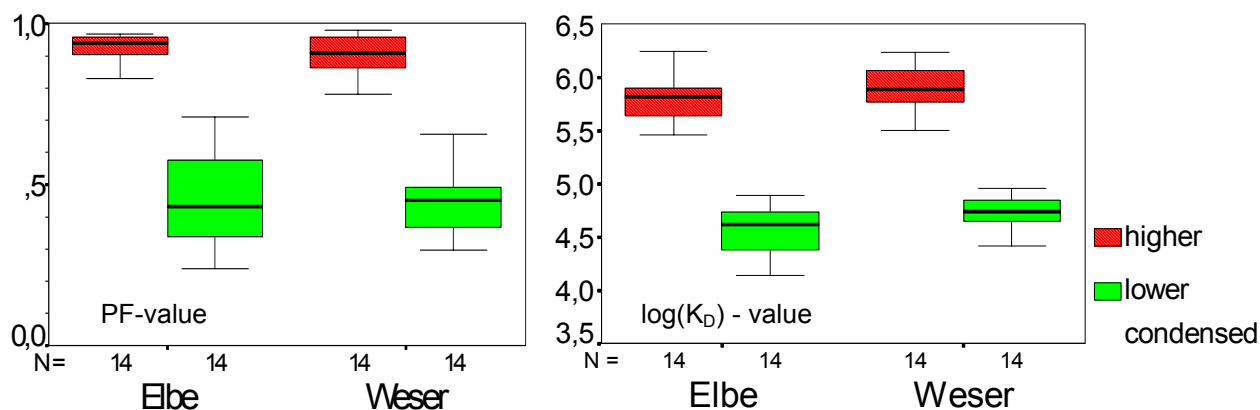


Fig. 4.13: Values of PF and  $\log(K_D)$  from 14 measurements each in the Elbe and the Weser differentiated for low-condensed and high-condensed compounds.



### 4.1.3 Comparison of the three sampling techniques FC, BISAM, and ST

The sites of sampling with flow-through centrifuge (FC), the three BISAM units, and the sedimentation tank (ST) can be seen in Figure 3.7 in Chapter 3.4.2. Because the sedimentation tank is positioned on the right bank of the river and the BISAM samplers float about 1 to 1.5 m below the water surface, the comparison of the sampling methods uses only those FC and BISAM samples that were collected on the right river side near to the surface and the bank. The intake orifice of the sedimentation tank is at mean flow about 2 m below the surface, so that the selected samples allow a comparison of the three techniques.

With view to the problem of clogging in BISAM and SB mentioned in Chapter 3.2.4, the first paragraph describes the yields collected before the following paragraph compares the quality of the suspended solids.

#### 4.1.3.1 *Suspended-solids yield*

In sampling with the centrifuge (FC), the yield obtained depends on the suspended-solids content in the water, the centrifugation time, and the throughput of the centrifuge. Related to 1 m<sup>3</sup> of water, the wet yield ranged between  $Y_W = 62$  g and  $Y_W = 156$  g, with a median of 122 g and number of samples of  $N = 13$ . In the cases of BISAM and ST, the yield again depends on the suspended-solids content, the duration of the sampling interval and the throughput. However, due to the clogging of the pipes – or of the inlet orifice in case of the BISAM – in summer, throughput is often restricted and, above all, it is not defined. The yield related to one week was in the BISAM on the right riverside between  $Y_W = 10$  g and  $Y_W = 80$  g (median: 41 g;  $N = 10$ ) and in the ST between  $Y_W = 8$  g and  $Y_W = 680$  g (median: 54 g;  $N = 11$ ).

The wide variability ranges of the BISAM and ST measurements (factor 8 and 85 in the ratio max:min against the factor 2.5 of the centrifuge) and the comparison of the three BISAM collectors operated in parallel across the river profile, as shown in Figure 4.14, underscore our observation in the field, namely that clogging really impairs the collecting capacity of the samplers. If these restrictions also produce a selective effect, consequences for the quality of the collected suspended solids cannot be ruled out. This should be kept in mind in the assessment of the subsequent comparison.

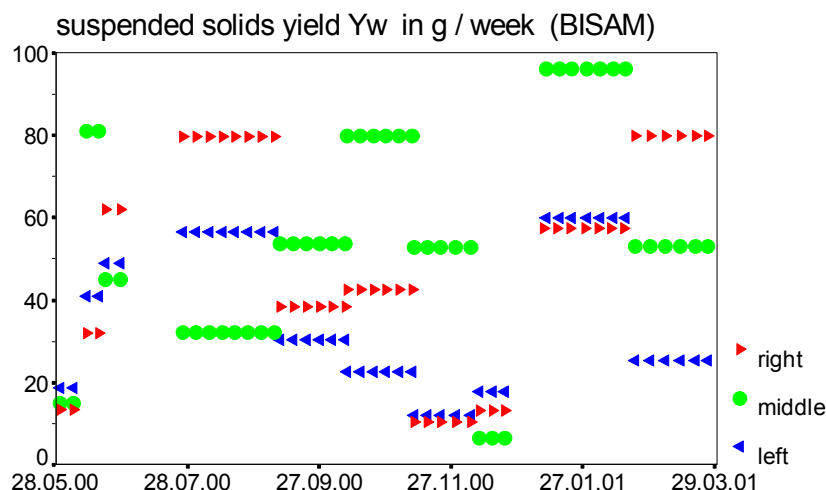


Fig. 4.14: Illustration of stochastically varying yields of three BISAM samplers resulting from varying, undefined flow-through. The three BISAMs are distributed along the cross section at Elbe 585.0 km, and they are sampling in parallel operation. In accordance with the data quoted in the text, the yields were standardized for a sampling period of one week.

#### 4.1.3.2 Suspended-solids quality

When all the data obtained during the study period 03/00-03/01 are used for a comparison of the suspended solids collected by the different techniques, it is striking that the PAH sum contents in the suspended solids collected by FC are significantly lower than those gathered by BISAM or ST (FC: min=2.82; max=8.66; mean value=5.41; N=8; BISAM: min=4.42; max=10.1; mean value=7.43; N=16; SB: min=5.93; max=11.8; mean value=8.35; N=13).

However, a meaningful comparison is only possible with data from those periods when all three methods were applied simultaneously. Thus, the number of available data decreases. According to the results from Chapter 4.1.2.2, the comparison is differentiated for seasons. The result is summarized in Table 4.2.

Table 4.2: PAH sum contents ( $\Sigma 16\text{PAH}$  according to US EPA) in suspended solids collected by the different methods, differentiated for seasons

| $\Sigma \text{ PAH}$<br>in mg/kgDW |             | FC         | BISAM      | ST         |
|------------------------------------|-------------|------------|------------|------------|
| <b>winter</b><br>(Oct - Apr)       | <b>mean</b> | <b>7.3</b> | <b>8.8</b> | <b>8.2</b> |
|                                    | min         | 6.0        | 8.4        | 8.2        |
|                                    | max         | 8.7        | 9.2        | 8.2        |
|                                    | N           | 3          | 2          | 1          |
| <b>summer</b><br>(May - Sep)       | <b>mean</b> | <b>4.3</b> | <b>6.8</b> | <b>8.6</b> |
|                                    | min         | 2.8        | 4.4        | 5.9        |
|                                    | max         | 4.9        | 8.5        | 11.8       |
|                                    | N           | 5          | 8          | 7          |

In this differentiated comparison again the FC data are lower than those of BISAM and ST. The differences are less pronounced in winter than in summer, and because of the limited data available, however, the winter values are less reliable.

For interpretation of these findings it is recommendable to have a look at the other parameters (Table 4.3), in particular the content of organic carbon  $C_{OC}$ .

Table 4.3: Organic carbon content ( $C_{OC}$ ), loss on ignition (LOIN), and fine grain fraction ( $<63\mu m$ , silt and clay) in suspended solids collected by different methods, differentiated for seasons.

| <b><math>C_{OC}</math> in g/kgDW</b>       |             | <b>FC</b> | <b>BISAM</b> | <b>ST</b> |
|--------------------------------------------|-------------|-----------|--------------|-----------|
| <b>winter</b><br>(Oct - Apr)               | <b>mean</b> | 97        | 46           | 53        |
|                                            | min         | 63        | 39           | 53        |
|                                            | max         | 154       | 53           | 53        |
|                                            | N           | 3         | 2            | 1         |
| <b>summer</b><br>(May - Sep)               | <b>mean</b> | 165       | 79           | 62        |
|                                            | min         | 131       | 56           | 45        |
|                                            | max         | 245       | 108          | 91        |
|                                            | N           | 5         | 8            | 7         |
| <b>LOIN in %</b>                           |             | <b>FC</b> | <b>BISAM</b> | <b>ST</b> |
| <b>winter</b><br>(Oct - Apr)               | <b>mean</b> | 28        | 17           | 18        |
|                                            | min         | 21        | 12           | 18        |
|                                            | max         | 37        | 21           | 18        |
|                                            | N           | 3         | 2            | 1         |
| <b>summer</b><br>(May - Sep)               | <b>mean</b> | 35        | 24           | 17        |
|                                            | min         | 22        | 19           | 13        |
|                                            | max         | 43        | 35           | 22        |
|                                            | N           | 5         | 8            | 7         |
| <b>GSA (<math>&lt;63\mu m</math>) in %</b> |             | <b>FC</b> | <b>BISAM</b> | <b>ST</b> |
| <b>winter</b><br>(Oct - Apr)               | <b>mean</b> | 70        | 64           | 69        |
|                                            | min         | 66        | 62           | 69        |
|                                            | max         | 77        | 65           | 69        |
|                                            | N           | 3         | 2            | 1         |
| <b>summer</b><br>(May - Sep)               | <b>mean</b> | 72        | 71           | 73        |
|                                            | min         | 58        | 48           | 61        |
|                                            | max         | 91        | 100          | 84        |
|                                            | N           | 5         | 8            | 7         |

While no significant differences between the methods were noted in the grain-size spectrum (GSA) – in summer and in winter about 70% of fines in suspended solids collected by FC,

BISAM, and ST – the discrepancy is very clear in the case of the levels of carbon: The organic portion in centrifuged solids is roughly double that of BISAM or that of ST. In summer, when the portion of organic material is naturally higher, this difference is more striking than in winter, and this is also supported by the results of ignition loss tests.

#### *Interpretation of results*

If one assumes that organic material has on average a lower density than the inorganic, mineral portion of suspended solids, one can expect that a large portion of it will pass through the passive samplers BISAM and ST without being trapped, while it will be retained in the FC with its high separation rate of 92 to 98 %. This explains the distinct and significant differences in  $C_{OC}$  and LOIN.

The observed differences in the suspended solids PAH concentration may be understood as a result of this selective collection because it can be assumed that in spring and summer fresh-grown phytoplankton, which constitutes a high portion of the organic material, is less contaminated than e.g. fine-grained minerals. The light-weight organic material collected by the centrifuge thus "dilutes" the PAH concentration. This interpretation also helps to explain that the differences in PAH concentrations are less in winter than in summer.

Another interesting phenomenon is the fact that the grain-size analysis (GSA) does not provide significantly different results – neither in the comparison summer/winter nor between the sampling methods. This underlines the assumption that the portion of organic material does not have much influence on the grain-size spectrum, which is in the first line defined by the grain-size distribution of the mineral portion, and that all three methods are suitable to separate the GSA-relevant portion representatively. Problems are encountered with BISAM and ST only when suspended solids have low densities and consequently low settling velocities.

#### 4.1.4 Suspended-solids concentration ( $C_{SS}$ )

##### 4.1.4.1 Median value of concentrations

On 240 working days in the period from 16 March 2000 to 16 March 2001, the concentration of suspended solids ( $C_{SS}$ ) was measured near the water surface, mid-river at Elbe km 585.0. The samples were taken by the staff of the regional waterways administration (WSA Lauenburg, ABz Geesthacht). The distribution pattern of the measurements is shown in Figure 4.15. The median value lies at 15.1 mg/l, the arithmetic mean value (not shown) is 19.0 mg/l. The two outliers date from 8 May and 2 August 2000 (68 and 66 mg/l, respectively).

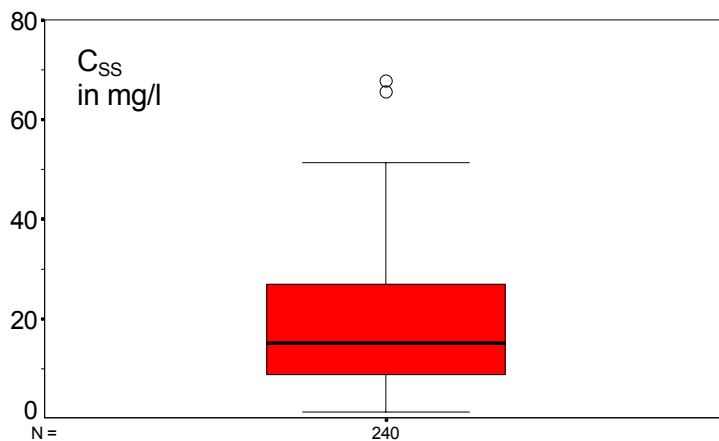


Fig. 4.15: Distribution of  $C_{SS}$  values in the Elbe at km 585.0, workdaily measurements in the period from 03/00 to 03/2001

##### 4.1.4.2 Seasonality

In consideration of the annual course, it is interesting to compare the temporal variation of the suspended-solids concentration with that of streamflow  $Q$  and the concentration of chlorophyll- $a$  (Figure 4.16). The chl- $a$  data were kindly provided by the Research Centre Geesthacht (GKSS), the streamflow data by the WSA Lauenburg.

Being a eutrophic river, the suspended-solids dynamics of the Elbe is dominated in summer months by biological processes. This is reflected by the course of the chl- $a$  concentration (chl- $a$  as indicator of the phytoplankton dynamics), which is correlated with the  $C_{SS}$  dynamics. Regrettably, no chl- $a$  data are available from the winter months, but it can be assumed that the values are negligible between December and March. Accordingly, the variations of suspended solids in these winter months are controlled more by the streamflow dynamics (March 2000 and Jan.-March 2001).

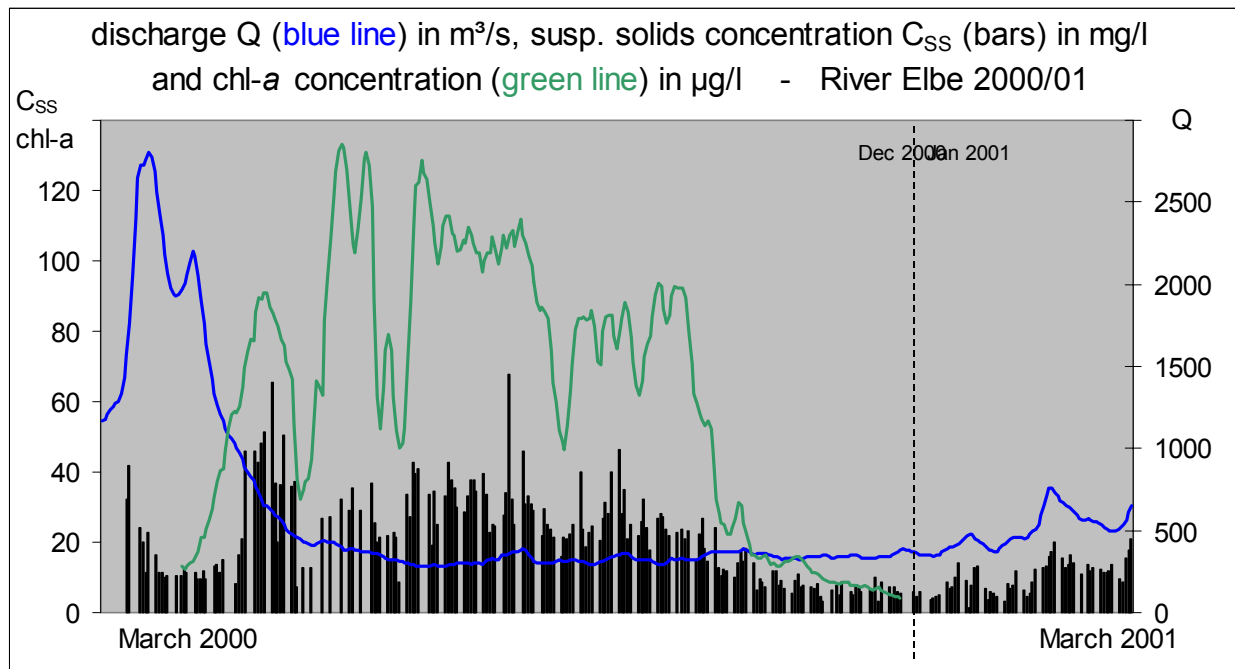


Fig. 4.16: Temporal variation of  $C_{SS}$ ,  $Q$ , and chl-a in the period from 03/00 to 03/01

#### 4.1.4.3 Multi-point measurements

During the study period, three multi-point measurements (MP) were made, two with the survey boat "*Elbegrund*" and one with the buoy-laying vessel "*Herkules*" of the WSA Lauenburg, District Geesthacht. A multi-point measurement comprises simultaneous measurements of flow velocity and suspended solids content, separately for the sand ( $>63\ \mu\text{m}$ ) and fines ( $<63\ \mu\text{m}$ , clay/silt) fractions, along five to six verticals in five horizons each. The aim is to obtain more precise data for the assessment of the suspended-solids transport. Simultaneous analyses of suspended solids collected by FC near the river bottom and near the water surface offer information about the vertical distribution of the contaminant transport (cf. Chapter 4.1.6.2).

An evaluation software (SAUS), developed earlier in the BfG, can interpret the measured data in various regards. Representatively for all three measurements, the findings of the multi-point measurement on 6 February 2001 are shown (Figure 4.17). The two other campaigns in June and August 2000 had only quantitative differences, as in February 2001 one of the lowest suspended-solids concentrations of the whole study period was recorded with  $4.5\ \text{mg/l}$ . Therefore, the maximum unit discharge of suspended sediment in this example was around  $12\ \text{g/m/s}$ , while it was 60 to  $90\ \text{g/m/s}$  in the two other measuring campaigns. (The *unit discharge of suspended sediment* is a vertically integrated value indicating which amounts of suspended solids in grammes are transported per second through an imaginary area (width: 1 m, height: from the bottom to the water surface, and oriented vertical to the flow direction)).

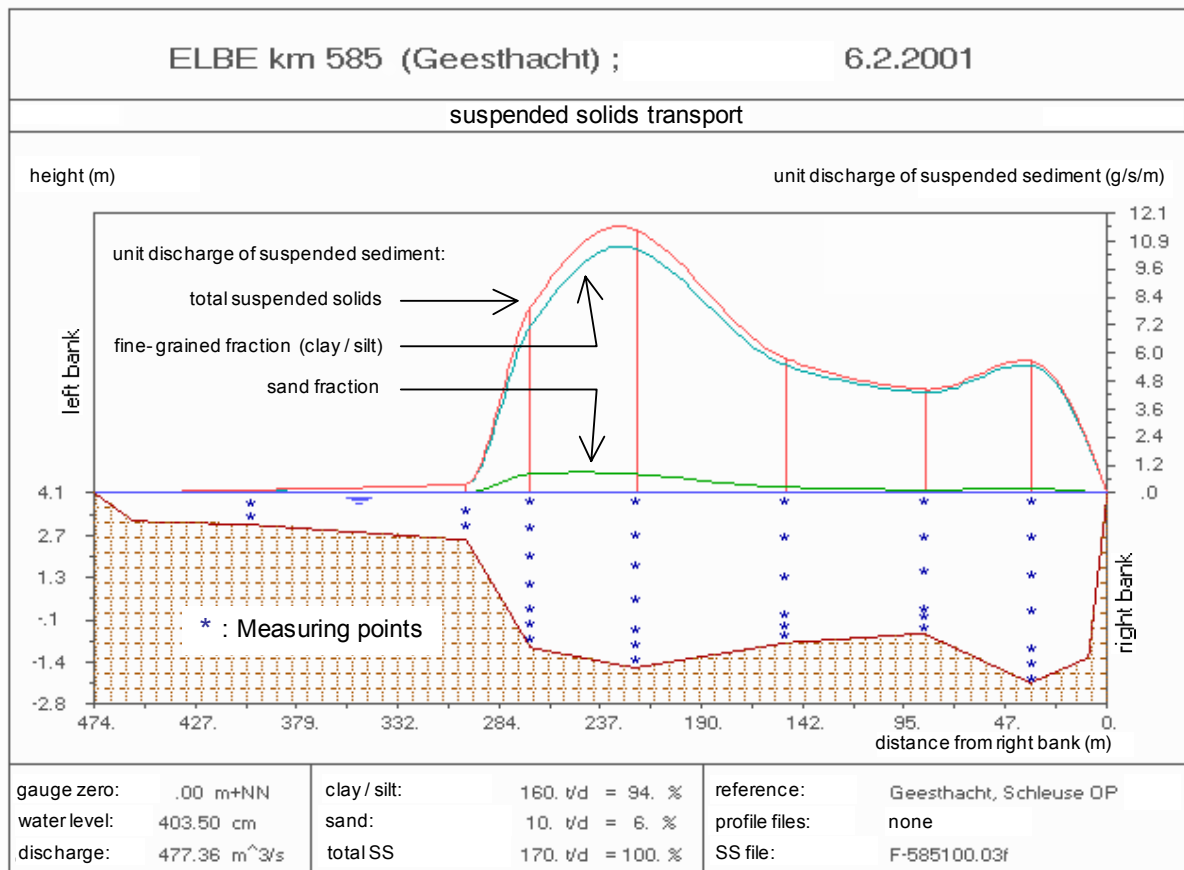


Fig. 4.17: Depth profile and unit discharge of suspended sediment, differentiated for clay/silt and sand fractions, as a result of an MP on 6 February 2001.

In qualitative terms, all three measurements produced the same result: A two-peak distribution of the unit discharge of suspended sediment, which of course reflects the morphology of the riverbed. The left-hand maximum is higher since flow velocities there are faster (not shown in the illustration). The total suspended-solids transport rate in February 2001 was estimated around 170 t/d; during the two other measurements it was due to the higher suspended-solids content near 940 t/d (14 June 2000) and 1,520 t/d (9 August 2000). In all cases, the clay/silt portion was between 94 and 97 %.

Direct information about the amounts of suspended solids transported near the bottom or near the water surface cannot be won by means of SAUS. However, when the averages of the near-bottom values (20 cm and 40 cm above the bottom), the intermediate values at 80 and 60 % of the river depth, and the near-surface values (30 cm below the water surface) are compared, one finds that in the lower half of the water column up to double the amount of suspended material is transported than in the upper half (Table 4.4).

Tab. 4.4: Vertical distribution of  $C_{SS}$  in mg/l, of stream velocity  $v$  in m/s and of the product of these parameters as a measure for transport in  $g/m^2/s$

|                       | 14.06.2000 |      |             | 09.08.2000 |      |              | 06.02.2001 |      |             |
|-----------------------|------------|------|-------------|------------|------|--------------|------------|------|-------------|
|                       | $C_{SS}$   | $v$  | prod.       | $C_{SS}$   | $v$  | prod.        | $C_{SS}$   | $v$  | prod.       |
| 30 cm below surface   | 31.24      | 0.25 | <b>7.72</b> | 27.16      | 0.27 | <b>7.44</b>  | 3.80       | 0.26 | <b>0.98</b> |
| 60% of water depth    | 38.70      | 0.22 | <b>8.47</b> | 52.81      | 0.26 | <b>13.85</b> | 3.93       | 0.35 | <b>1.36</b> |
| 80% of water depth    | 44.66      | 0.18 | <b>8.07</b> | 51.70      | 0.24 | <b>12.20</b> | 5.50       | 0.33 | <b>1.83</b> |
| 40 cm above river bed | 49.16      | 0.15 | <b>7.58</b> | 66.64      | 0.20 | <b>13.06</b> | 6.66       | 0.28 | <b>1.85</b> |
| 20 cm above river bed | 51.42      | 0.14 | <b>7.22</b> | 83.72      | 0.18 | <b>15.30</b> | 8.30       | 0.24 | <b>1.96</b> |

In June 2000, the River Elbe showed good vertical mixing, whereas in February 2001 a very distinct profile formed with high transport rates in the range of about 70 % of river depth and below.

The collection of water samples from different horizons is rather complicated and thus error-prone. The concentration of suspended solids was determined by the "*Melitta*" method used by the BfG and German waterways authorities. For instance, in August 2000 the very abrupt change from nearly 14  $g/m^2/s$  in 60 % of river depth to nearly half that value near the surface may be explained by an error in the determination of  $C_{SS}$ , because the difference between 53 mg/l and 27 mg/l in the transition from 3.30 m to 0.30 m (average river depth 5.60 m) seems rather unlikely.

With some exceptions, usually a vertical profile of transport rates seems to establish in the widening backwater reach of the Elbe upside the weir of Geesthacht. Because the contamination on the suspended solids does not show such a profile (cf. Chapter 4.1.6.2), this effect can be taken into account at best by consideration of a correcting factor, or by applying a mean concentration and flow profile, or by measurements in a mean depth or by vertically differentiated measurements.



### 4.1.5 Correlation analysis

#### 4.1.5.1 Bivariate correlations

The aim of this analysis is the identification of possible dependencies between the individual parameters. If such correlations existed, it would be possible to derive from easily and frequently measurable values more demanding parameters, e.g. calculate PAHs from Q and  $C_{SS}$  or  $C_{SS}$  from turbidity, etc. Moreover, any new knowledge about the interrelations between the measured parameters improves the interpretation of results.

The following parameters are combined in pairs and checked for linear dependencies: Q,  $C_{SS}$ , GSA(<63 $\mu$ m), the product of  $C_{SS}$  and GSA(<63 $\mu$ m), turbidity, chl-*a*,  $C_{OC}$ ,  $\sum 16$ PAH (total),  $\sum 16$ PAH (dissolved),  $\sum 16$ PAH (particle-bound in mg/kgDW) and  $\sum 16$ PAH (particle-bound in ng/l). In the resulting correlation matrix, the Pearson correlation coefficient  $r$ , the number of measurements (N), and the two-tailed significance level  $p$  are given.

Some correlations are based on very few measurements only, what reduced their reliability. In order to achieve objective results anyhow, only such parameters are called clearly correlated which have a significance level of  $p < 0.005$  and  $|r| > 0.5$ . Definitely not correlated are parameters with  $p > 0.5$ , for all other results no definitive statement is given. For sake of clarity, Table 4.5 shows only the reduced matrix, from which all parameters, which do not show clear correlations, are omitted.

As the fine-grain percentage GSA(<63 $\mu$ m) is relatively constant (71 %  $\pm$  8 % standard deviation), this parameter does not show any clear correlations and is not included in the table. No distinct correlations were found for PAH concentrations in the aqueous phase ( $\sum 16$ PAH (total) and  $\sum 16$ PAH (dissolved)), as well.

With the product GSA(<63 $\mu$ m)  $\cdot$   $C_{SS}$ , correlations with the fine-grain concentration in mg/l are tested. Because of the low variability in the fine-grain fraction GSA(<63 $\mu$ m), the product shows – as expected – a similar correlation pattern like  $C_{SS}$ , is strongly correlated with  $C_{SS}$  itself, and thus yields little new information. Deviations only occur in the correlations with turbidity and  $\sum 16$ PAH (particle-bound in ng/l).

For an explanation of these deviations, correlations with the product GSA(>63 $\mu$ m)  $\cdot$   $C_{SS}$  were examined additionally (sand concentration in mg/l). The result, presented in Table 4.6, shows that both turbidity and  $\sum 16$ PAH (particle-bound in ng/l) are more correlated with the fine-grain fraction than with the coarse one. In the case of the particle-bound PAH concentration, the affinity to fine-grained material is so strong that the correlation improves when the fine-grain portion is considered instead of the total suspended-solids concentration.

Table 4.5: Reduced correlation matrix, clear correlations are printed in bold, definitively not correlated parameters are printed in italics.

| r<br>(N)<br>p                                            | Q                                    | C <sub>SS</sub>                      | GSA<br>( $<63\mu\text{m}$ )<br>*C <sub>SS</sub> | turbidity                            | chl- <i>a</i>                        | C <sub>OC</sub>                       | $\Sigma$ 16PAH<br>(particle-b.<br>in mg/kg) | $\Sigma$ 16PAH<br>(particle-b.<br>in ng/l) |
|----------------------------------------------------------|--------------------------------------|--------------------------------------|-------------------------------------------------|--------------------------------------|--------------------------------------|---------------------------------------|---------------------------------------------|--------------------------------------------|
| Q                                                        | 1<br>(440)<br>–                      | -.0985<br>(243)<br>.126              | -.2407<br>(010)<br>.503                         | .1566<br>(342)<br>.004               | -.2529<br>(263)<br>.000              | -.7237<br>(012)<br>.008               | <b>.9066</b><br>(011)<br><b>.000</b>        | .6473<br>(011)<br>.031                     |
| C <sub>SS</sub>                                          | -.0985<br>(243)<br>.126              | 1<br>(243)<br>–                      | <b>.9568</b><br>(010)<br><b>.000</b>            | <b>.7040</b><br>(181)<br><b>.000</b> | <b>.8188</b><br>(175)<br><b>.000</b> | .1557<br>(012)<br>.629                | -.1822<br>(011)<br>.592                     | .6045<br>(011)<br>.049                     |
| GSA( $<63\mu\text{m}$ )<br>*C <sub>SS</sub><br>(Produkt) | -.2407<br>(010)<br>.503              | <b>.9568</b><br>(010)<br><b>.000</b> | 1<br>(010)<br>–                                 | .5655<br>(008)<br>.144               | <b>.9122</b><br>(007)<br><b>.004</b> | .3506<br>(010)<br>.321                | -.5084<br>(009)<br>.162                     | <b>.8676</b><br>(009)<br><b>.002</b>       |
| turbidity                                                | .1566<br>(342)<br>.004               | <b>.7040</b><br>(181)<br><b>.000</b> | .5655<br>(008)<br>.144                          | 1<br>(386)<br>–                      | <b>.5381</b><br>(291)<br><b>.000</b> | -.1310<br>(010)<br>.718               | .3066<br>009<br>.422                        | .6123<br>(009)<br>.080                     |
| chl- <i>a</i>                                            | -.2529<br>(263)<br>.000              | <b>.8188</b><br>(175)<br><b>.000</b> | <b>.9122</b><br>(007)<br><b>.004</b>            | <b>.5381</b><br>(291)<br><b>.000</b> | 1<br>(308)<br>–                      | .3360<br>(007)<br>.461                | -.5951<br>(006)<br>.213                     | .8667<br>(006)<br>.025                     |
| C <sub>OC</sub>                                          | -.7237<br>(012)<br>.008              | .1557<br>(012)<br>.629               | .3506<br>(010)<br>.321                          | -.1310<br>(010)<br>.718              | .3360<br>(007)<br>.461               | 1<br>(012)<br>–                       | <b>-.7817</b><br>(011)<br><b>.004</b>       | -.4797<br>(011)<br>.135                    |
| $\Sigma$ 16PAH<br>(particle-b.<br>in mg/kg)              | <b>.9066</b><br>(011)<br><b>.000</b> | -.1822<br>(011)<br>.592              | -.5084<br>(009)<br>.162                         | .3066<br>009<br>.422                 | -.5951<br>(006)<br>.213              | <b>-.7817</b><br>(011)<br><b>.004</b> | 1<br>(011)<br>–                             | .6351<br>(011)<br>.036                     |
| $\Sigma$ 16PAH<br>(partikulär<br>in ng/l)                | .6473<br>(011)<br>.031               | .6045<br>(011)<br>.049               | <b>.8676</b><br>(009)<br><b>.002</b>            | .6123<br>(009)<br>.080               | .8667<br>(006)<br>.025               | -.4797<br>(011)<br>.135               | .6351<br>(011)<br>.036                      | 1<br>(011)<br>–                            |

A very clear positive correlation appears between streamflow Q and  $\Sigma$ 16PAH (particle-bound in mg/kg). As the Elbe is a river of the snow-rainfall type, its streamflow regime is controlled in the first line by snowmelt and precipitation events.

That is why this result suggests that a major part of the particle-bound PAHs was introduced into the river by land-surface erosion and that these particles from diffuse sources are more contaminated than the autochthonously produced suspended matter.

C<sub>SS</sub> shows clear correlations with turbidity as well as with chl-*a*. However, seen separately, with  $r=0.70$  (turbidity) and  $r=0.82$  (chl-*a*) these correlations are not strong enough to derive C<sub>SS</sub>

Tab. 4.6: Correlation matrix  
(For explanation, refer to the text)

| r<br>(N)<br>p                                            | turbidity                            | $\Sigma$ 16PAH<br>(particle-bounc<br>in ng/l) |
|----------------------------------------------------------|--------------------------------------|-----------------------------------------------|
| C <sub>SS</sub>                                          | <b>.7040</b><br>(181)<br><b>.000</b> | .6045<br>(011)<br>.049                        |
| GSA( $<63\mu\text{m}$ )*<br>C <sub>SS</sub><br>(product) | .5655<br>(008)<br>.144               | <b>.8676</b><br>(009)<br><b>.002</b>          |
| GSA( $>63\mu\text{m}$ )*<br>C <sub>SS</sub><br>(product) | .2278<br>(008)<br>.587               | .5320<br>(009)<br>.140                        |

reliably from turbidity or chl-*a*. Nevertheless, for further investigations it seems promising to analysis the multiple regressions ( $C_{SS}$  in dependence on turbidity and chl-*a*), in order to achieve a continuous and reliable estimate of suspended solids concentrations from automated measurements of turbidity and fluorescence.

The correlation between  $C_{SS}$  and chl-*a* reflects the fact that the Elbe reach under consideration is a eutrophic lowland river, whose suspended-solids regime is controlled to a high degree by biological processes.

Finally the clear correlation between  $C_{OC}$  and  $\Sigma 16PAH$  (particle-bound in mg/kg) is to be mentioned. This negative correlation follows the interpretation presented in Chapter 4.1.3.2, saying that low PAH concentrations in suspended solids are a consequence of a "dilution process" induced by high organic portions.

#### 4.1.5.2 Cross correlation between Q and $C_{SS}$

Because the suspended-solids regime of natural rivers is also determined by sedimentation and resuspension processes, a positive correlation between Q and  $C_{SS}$  may be expected. This correlation, however, is superimposed by other influences, for instance very distinctly by chl-*a* (see above and Figure 4.16 in Chapter 4.1.4.2) and is, moreover, not linear. Suspended-solids peaks are often observed in the rising limb of flood events, but during the stagnating flood already concentrations slightly decrease. Regrettably, it was not possible in March 2000 to observe the entire flood event (a rapid rise of streamflow began already before the study period), and no further flood occurred until March 2001.

If the data set is reduced, at first to the biologically inactive winter season (March 2000 and Dec 2000 - March 2001) and then to the winter period without the falling flood limb, the linear correlation rises drastically (Table 4.7).

Tab. 4.7: Correlation Q ↔  $C_{SS}$  with restricted data set

| r<br>(N)<br>p | $C_{SS}$<br>(all data)  | $C_{SS}$<br>(03/00 and<br>12/00 - 03/01) | $C_{SS}$<br>(12/00 - 03/) |
|---------------|-------------------------|------------------------------------------|---------------------------|
| Q             | -,0985<br>(243)<br>,126 | ,4854<br>(065)<br>,000                   | ,8004<br>(53)<br>,000     |

This result highlights the fact that besides biological processes also hydraulic conditions influence the suspended-solids regime, what however is masked during periods of biological growth.

Accordingly, on the basis of the whole data set it is not possible to identify a temporarily delayed relationship between  $C_{SS}$  and Q by means of cross correlations.

The cross-correlation function  $r(\tau)$  is shown in Figure 4.18 for the restricted data set Dec 2000 - March 2001. It appears as a positively skewed distribution with its maximum at  $\tau=1$ , so that one can conclude that the "response" of the suspended-solid regime of the Elbe to a flood event occurs with a delay of a few hours to one day. So, for a detailed examination of this phenomenon, in case of a flood event prompt measurements of  $Q$  and  $C_{SS}$  are needed in higher measuring frequency (e.g. hourly values).

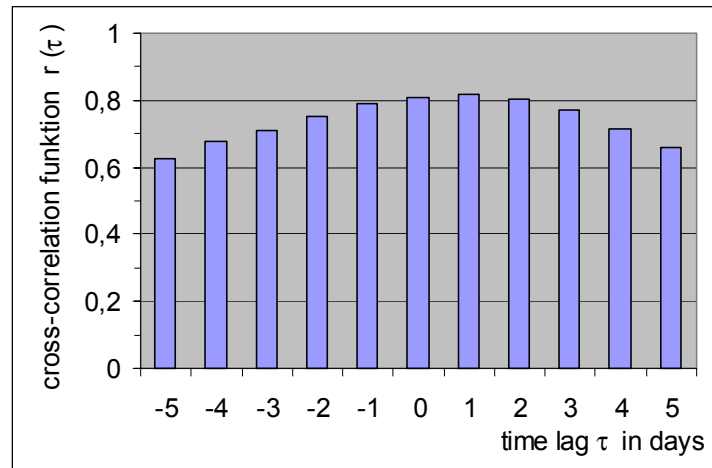


Fig. 4.18: Cross correlation between  $Q$  and  $C_{SS}$  (Dec 2000 - March 2001)

### 4.1.6 Spatial homogeneity

#### 4.1.6.1 Horizontal homogeneity

Testing for horizontal homogeneity uses the PAH contents in suspended solids ( $\Sigma 16\text{PAH}_{\text{SS}}$ ) collected in the three BISAMs that are distributed over the river profile (left bank, mid-river, right bank). The statistical distribution of these values is shown as box-and-whiskers plot in Figure 4.19.

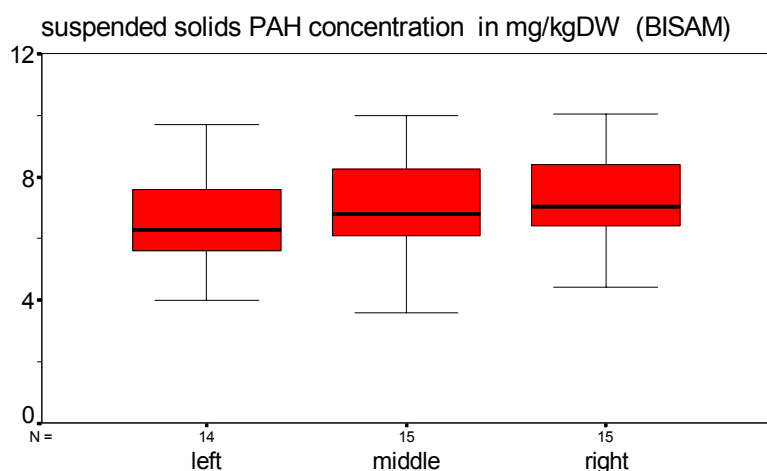


Fig. 4.19:  
Spatial distribution of the suspended solids PAH concentration across the profile of the River Elbe at river-km 585.0. Near-surface sampling in the period April 2000 to March 2001.

Considering the span of the measured values, the differences between the median values appear negligible. A paired-samples T-test shows a low two tailed significance ( $p=0.012$ ) only for the difference between the median values "left" and "right".

The, at first, eye-catching trend – increasing PAH contamination from left to right – appears to be more accidental and not significant, too, if the small differences are compared with the wide seasonal variations (Figure 4.20).

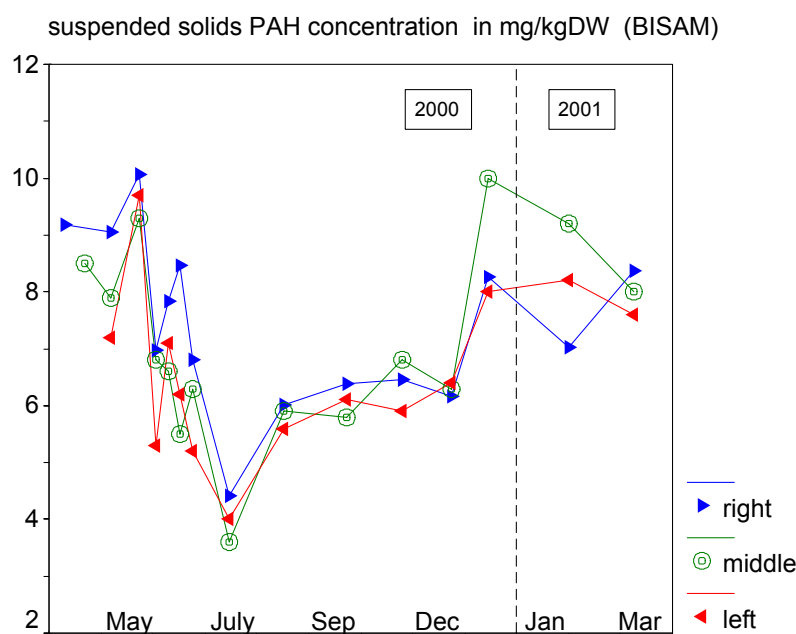


Fig. 4.20:  
Annual variation of PAH contamination in suspended solids (Elbe 585.0 km; near-surface sampling)

Besides the PAH concentrations, also the parameters GSA, LOIN, C<sub>OC</sub>, N, S, and water content do not show significant horizontal gradients at this sampling site. In a unique cross-profile measurement (28 March 2001, five near-surface sampling points across the river cross section) the parameters O<sub>2</sub>, T<sub>w</sub>, pH, and conductivity were found to be also extremely evenly distributed.

#### 4.1.6.2 Vertical homogeneity

Among other things, the three multi-point measurements MP (cf. Chapter 3.4.2 and Chapter 4.1.4.3) tried to identify possible differences in PAH contamination in samples collected near the surface and those from near the river bottom. The near-surface samples were collected approx. 1 m below the water surface, the near-bottom samples 40 to 50 cm above the river bed, each as a mixed sample along the cross section. The findings of the MPs are summarized in Table 4.8.

Tab. 4.8: PAH concentrations in near-surface and near-bottom samples  
( $\Sigma$ 16PAH according to EPA, solid samples in mg/kgDW, aqueous samples in ng/l)

| Date        | sample type                  | suspended matter<br>(solid) | total sample<br>(aqueous) | centrifugate<br>(aqueous) |
|-------------|------------------------------|-----------------------------|---------------------------|---------------------------|
| 6.6.2000    | near-surface<br>mixed sample | 5.93                        | –                         | –                         |
| 14.6.2000   | near-bottom<br>mixed sample  | 6.35                        | –                         | –                         |
| 10.8.2000   | near-surface<br>mixed sample | 4.34                        | 306                       | 31                        |
| 10.8.2000   | near-bottom<br>mixed sample  | 4.69                        | 245                       | 24                        |
| 5.2.2001    | near-surface<br>mixed sample | 8.95                        | 207                       | 42                        |
| 5./6.2.2001 | near-bottom<br>mixed sample  | 8.89                        | 201                       | 34                        |

Sampling took place at streamflow between 350 and 480 m<sup>3</sup>/s, i.e. in the range of median-flow, although in different seasons, what explains the variations in the particle-bound PAH concentration (cf. Chapter 4.1.2.2). With view to these variations, the vertical differences appear negligible, so that for the solid samples none of the conditions could be called "stratified". For the aqueous samples there is a slight tendency towards a higher contamination in the upper layer. However, because of the analytical uncertainties, that are much higher in aqueous samples than in the solid ones (cf. Chapter 3.3.4.2), this result is somewhat put into perspective.

### 4.1.7 Annual loads

#### 4.1.7.1 Mathematical methods of load calculation

Chapter 5.2.1 of the Common Report refers to several problems encountered in computing loads. One problem is the calculation method itself, as no clearly defined optimum mathematical method exists. The examples of suspended-solids loads and PAH loads in the Elbe and the Weser used six different calculation methods, which had been examined and compared already earlier [STEINEBACH, 1994; KELLER et al., 1997; LAWA, 2002] or were recommended by OSPAR [INPUT, 2000]. The following preconditions apply to all methods:

- Concentration  $c$  as random sample in mg/l, measured at the times  $t_i$ , with  $i=1,...,N$ ;
- Daily measurements of streamflow  $Q$  in m<sup>3</sup>/s ( $Q_i$ , with  $i=1,...,364$ );
- Annual load in g; 1 year corresponds to 365 days á 86,400 seconds.

In the following, the methods used are presented:

Method #1: Product of the mean values

$$\text{annual load} = \bar{c} * \bar{Q} * 365 * 86400s$$

This most simple approximation means the multiplication product of the mean values of  $c$  and  $Q$ . By multiplying with 365 days and 86,400 seconds per day, the annual load is obtained in the unit gram (g).

Method #2: Mean value of the products

$$\text{annual load} = \frac{1}{N} \sum_{i=1}^N c(t_i) Q(t_i) * 365 * 86400s$$

In this method, each measured concentration value is multiplied with the streamflow value measured at the same time  $t_i$ , and then the mean value of these  $N$  products is computed.

The additional information about the daily measurements of streamflow is lost in the methods #1 and #2. This drawback is compensated in the following methods #2a to #5 in different ways.

Method #2a: same like #2 but weighted with the "true" annual mean value of  $\bar{Q}$

$$\text{annual load} = \frac{1}{N} \sum_{i=1}^N c(t_i) \frac{Q(t_i)}{\bar{Q}} \bar{Q} * 365 * 86400s$$

The additional information about the "true" (i.e. estimated on the basis of 365 daily mean values) annual streamflow  $\bar{Q} = \left( \sum_{i=1}^{365} Q_i \right) / 365$  is utilized here by dividing by the mean value of  $Q(t_i)$  and multiplying with  $\bar{Q}$ . This method is currently recommended by OSPAR in the RID Principles [INPUT, 2000b].

## Method #3: Linear interpolation

$$\text{annual load} = \sum_{i=1}^{365} c_{\text{lin},i} Q_i * 86400s$$

Missing concentration values are estimated by linear interpolation, so that the product of concentration and streamflow can be computed for every day.

Method #4: Regression  $c(t) = \tilde{c}(Q(t))$ 

$$\text{annual load} = \sum_{i=1}^{365} \tilde{c}(Q_i) * Q_i * 86400s$$

Provided a correlation exists between  $c$  and  $Q$ , daily  $c$  values ( $= \tilde{c}$ ) can be computed from the daily measurements of  $Q$ . A recommended regression function [KELLER et al., 1997], on which the following computations are based reads:  $\tilde{c}(Q) = a_0 + a_1 \cdot \exp(-a_2 \cdot Q)$ .

Method #5: Regression  $T(t) \equiv c(t) * Q(t) = \tilde{T}(Q(t))$ 

$$\text{annual load} = \sum_{i=1}^{365} \tilde{T}(Q_i) * 86400s$$

With this method, a regression between transport  $T = c \cdot Q$  and streamflow  $Q$  is established:  $T = a \cdot Q^b$ . The daily transport rates in g/s thus computed are summed-up over the whole year, and the cumulative sum gives the estimated annual load in g.

The two regression methods (#4 and #5) have the drawback that the streamflow values  $Q(t_i)$  associated with the sampling times  $t_i$  usually do not cover the entire streamflow spectrum of the considered year. This may entail great errors in the evaluation of the regression function in the extrapolation range not supported by data.

The methods #3 - #5 have against the first three methods the advantage that they estimate – besides the annual loads – also the daily transport rates, which may be presented graphically without any problem. In these cases, the annual load is the cumulative sum over the daily transport rates.



#### 4.1.7.2 *Suspended-solids loads*

In the Elbe, the suspended-solids loads were during the study period from March 2000 to March 2001 in the order of 340,000 t per year, irrespective of the calculation method applied (Figure 4.21). It is remarkable that here even the simplifying methods #1 and #2 yield comparable results.

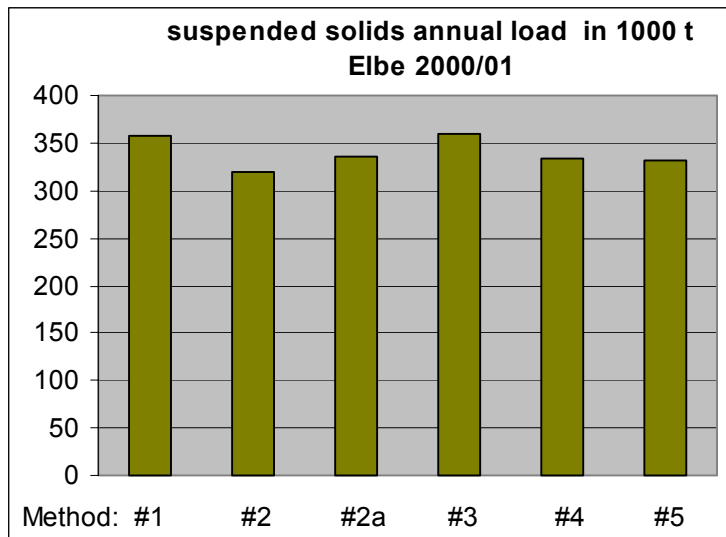


Fig. 4.21: Annual loads of suspended solids in the Elbe at Geesthacht (km 585.0) in the study period from 03/00 to 03/01, computed by six different mathematical methods.

As the suspended-solids load is controlled by streamflow  $Q$  and the suspended-solids concentration  $C_{SS}$ , one can expect that the individual contributions to the total annual load may vary in the course of the year with  $Q$  and  $C_{SS}$ . As to be seen in Figure 4.22, the computations by methods #3 to #5 allow graphic presentations of these "individual contributions" to the annual load as daily transport rates.

It is clearly visible that the main portion of the annual load originates from the flood events in spring of the year 2000 (on streamflow, see Figure 4.16 in Chapter 4.1.4.2).

The variation of suspended-solids transport appears much more differentiatedly in the computations by method #3 than by methods #4 and #5. This is due to the fact that  $C_{SS}$  was measured on workdays and that the green curve in the upper graph of Figure 4.22 is mainly based on measurements, while on the two lower graphs the green line appears strongly smoothed as a consequence of the regression.

The regressions themselves are extremely weak, see Figure 4.23.

With  $r^2=0.01$ ,  $C_{SS}$  is hardly correlated with  $Q$ , so that the extreme regression coefficients indicated in the Figure are accordingly artefacts of the computation software (SPSS) and depend, moreover, partially on the initial values. Conversely, the regression of  $T$  on  $Q$  looks much better ( $r^2=0.53$ ), what is of course due to the implicit self-correlation of  $C_{SS} \cdot Q$  with  $Q$ .

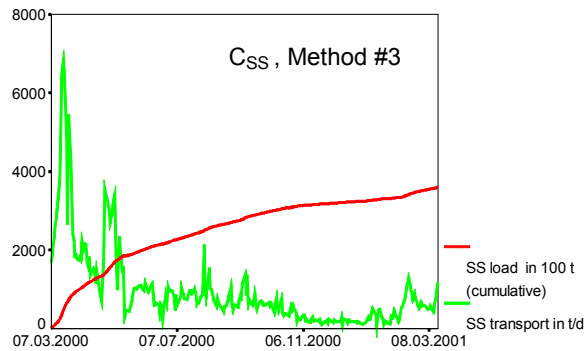


Fig. 4.22: Suspended-solids load in t (red curve) as cumulative sum over the daily transport rates in t/d (green curve). Cumulation over one year corresponds to the annual loads obtained by the respective calculation methods as shown in Figure 4.21

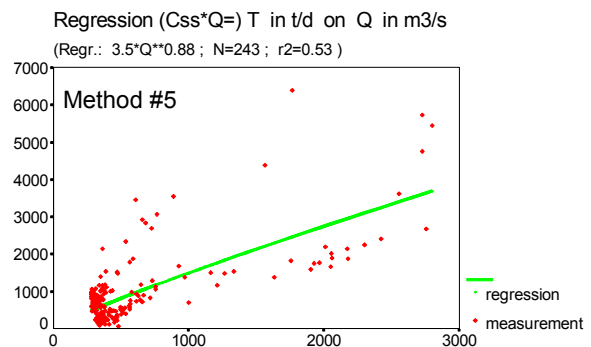
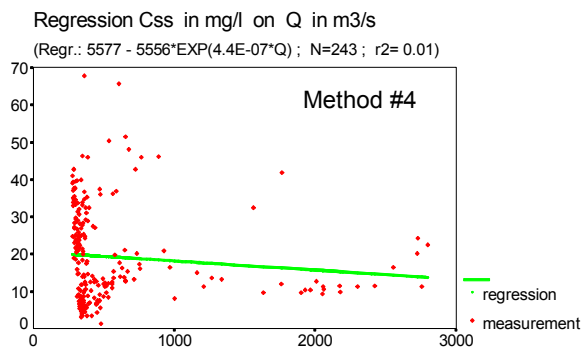
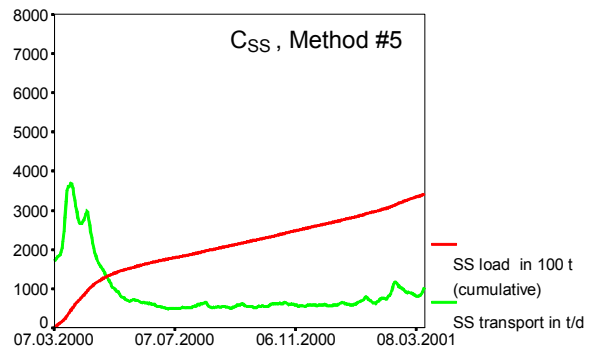
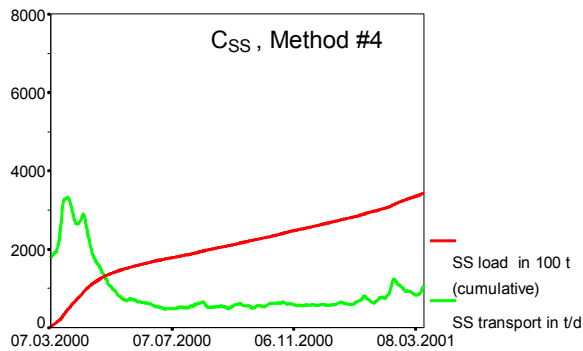


Fig. 4.23: Representation of the regressions  $C_{SS}(Q)$  and  $T(Q)$ , with  $T=C_{SS} \cdot Q$ . (cf. presentation of the methods #4 and #5 in Chapter 4.1.7.1).

How is it possible to estimate meaningful annual loads on the basis of such poor regressions? It is due to the fact that the regression shown in Figure 4.23 assigns to each value of  $Q$  a mean value of  $C_{SS}$  (left-hand graph) or of transport  $T$  (right-hand graph). Thus the methods #4 and #5 – with regression curves nearly horizontal or proportional to  $Q$  – become comparable with methods #1 and #2.

#### 4.1.7.3 PAH loads

The PAH loads in the Elbe are given differentiatedly as total load, particle-bound load and dissolved load. The computation of the total load is based on measurements of the PAH levels in the whole samples (centrifuge inflow,  $\Sigma 16\text{PAH}$ ) and uses again the methods #1 to #5. With the exception of method #2, which had results about 20 % above, all other methods found PAH loads around 4.5 t per year (Figure 4.24).

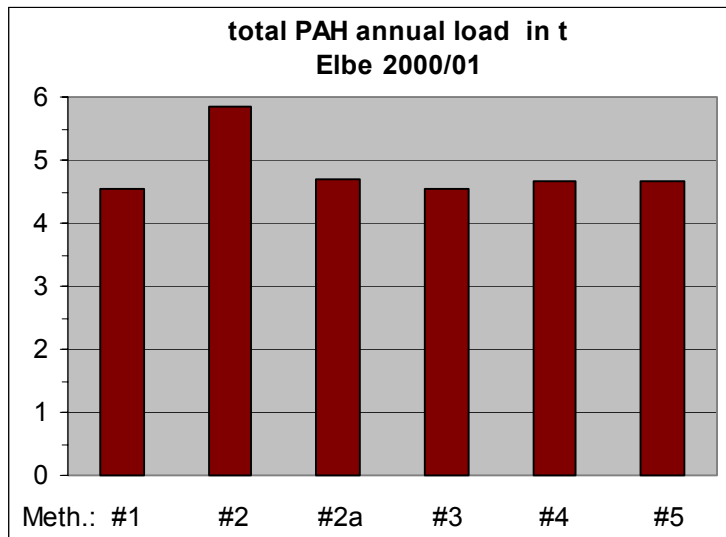


Fig. 4.24: Total annual PAH load in the Elbe at Geesthacht (km 585.0) in the study period from 03/00 to 03/01, computed by six different mathematical methods.

Figure 4.25 presents the temporal development of the daily PAH transport rates. Like in the case of suspended-solids loads, the streamflow  $Q$  can be identified as the main controlling factor. The transport rates computed by method #3 run as smooth as those based on regressions, since in contrast to suspended solids only seven PAH measurements are available (for comparison: suspended-solids  $N=243$ ), so that the method of linear interpolation appears as smoothing as the two regression-based methods.

Figure 4.26 shows the regressions underlying the methods #4 and #5. Because the PAH concentrations vary relatively little in the course of the year, the regression of  $\text{PAH}_{\text{total}}$  on  $Q$  is very poor, the regression of  $T$  on  $Q$ , however, is very good because of the above mentioned self-correlation, and with 1.054 the exponent is close to 1. This proves again that the regression methods produce acceptable results, whereas the regressions themselves are not very well founded.

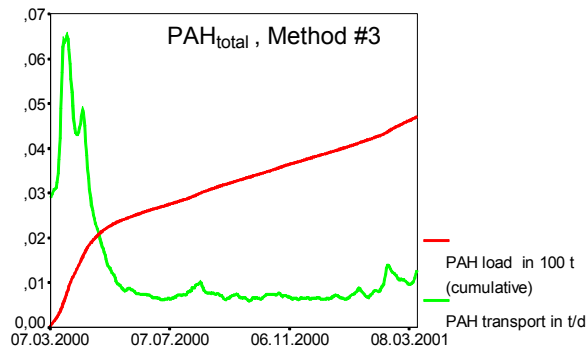


Fig. 4.25: Total PAH load in 100 t (red curve) as cumulative sum over the daily transport rates in t/d (green curve). Cumulation over one year corresponds to the annual loads obtained by the respective calculation methods as shown in Figure 4.24.

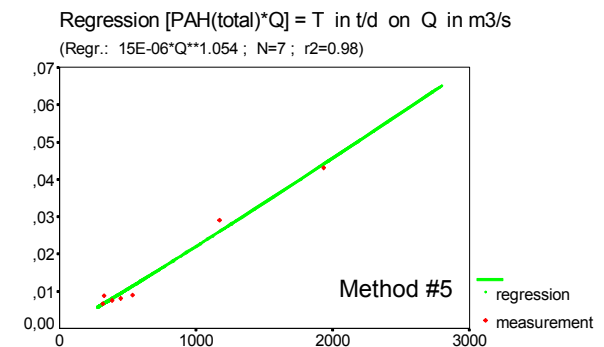
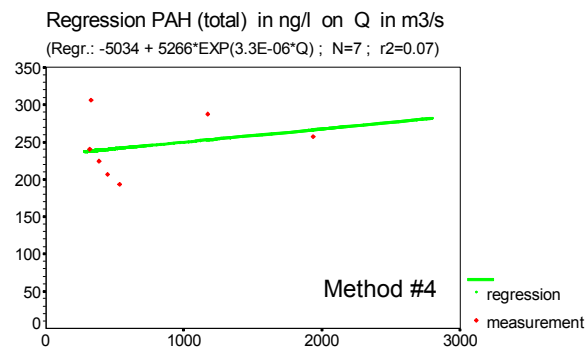
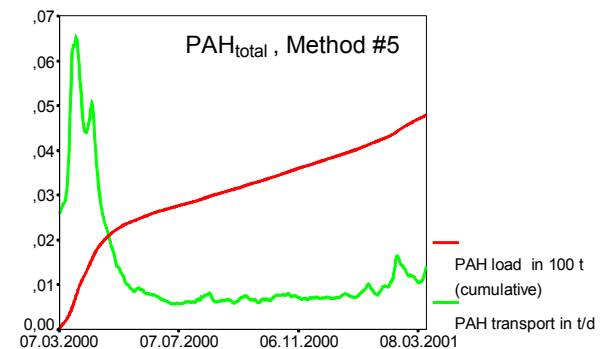
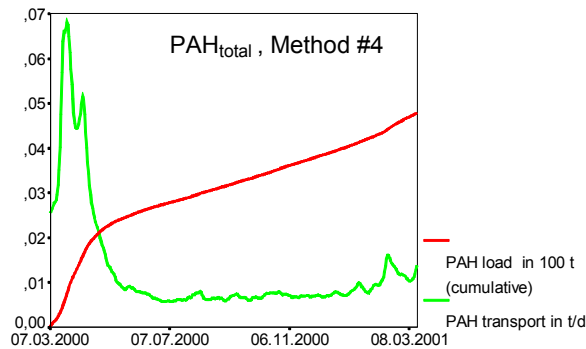


Fig. 4.26: Representation of the regressions  $PAH_{total}(Q)$  and  $T(Q)$ , with  $T = PAH_{total} \cdot Q$ . (cf. presentation of the methods #4 and #5 in Chapter 4.1.7.1).

In the case of particle-bound PAHs, the determined loads vary about  $\pm 15\%$  around a mean value of 2.6 t per year; cf. Figure 4.27. The computation of the annual load is somewhat more difficult here, as besides the streamflow value  $Q$  and the suspended-solids PAH concentration  $PAH_{SS}$ , the suspended-solids concentration  $C_{SS}$  itself is also included. Therefore, by analogous application of the methods presented in Chapter 4.1.7.1, first the PAH concentration in ng/l is computed as the product of  $PAH_{SS}$  (in mg/kgDW) and  $C_{SS}$  (in mg/l).

Method #2 now does not weight only with the "true" annual mean value of  $Q$ , but additionally with that of the suspended-solids concentration  $C_{SS}$ , as usually also  $C_{SS}$  is measured in higher

frequency, and this information would be lost otherwise. For the same reason, it is essential that in method #3 first  $C_{SS}$  and  $PAH_{SS}$  are interpolated linearly and then the product of these interpolated values is calculated.

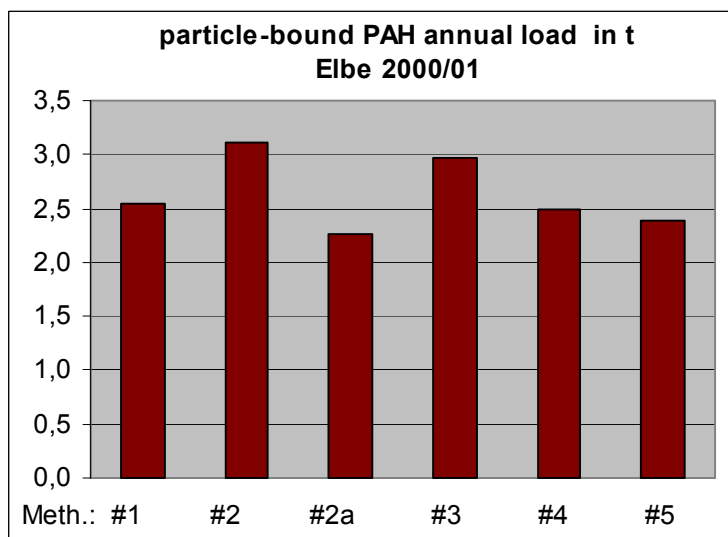


Fig. 4.27: Annual load of particle-bound PAHs in the Elbe at Geesthacht (km 585.0) in the study period from 03/00 to 03/01, computed by six different mathematical methods.

The annual load as the result of the cumulative sum over the daily transport rates of particle-bound PAHs is depicted in Figure 4.28. The application of the regression based on few PAH measurements only (methods #4 and #5) leads to smoothing, whereas the presentation is more differentiated in the upper chart (method #3), because of the higher sampling frequency of  $C_{SS}$ . The regressions for methods #4 and #5 are shown in Figure 4.29.

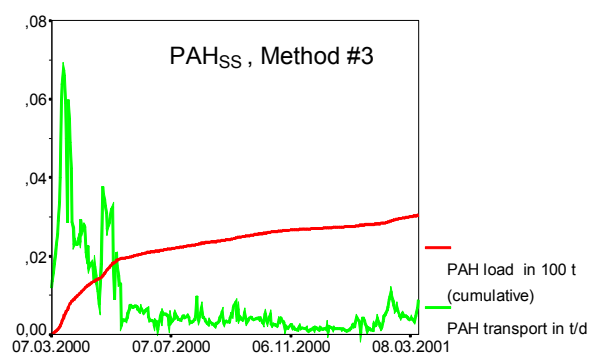
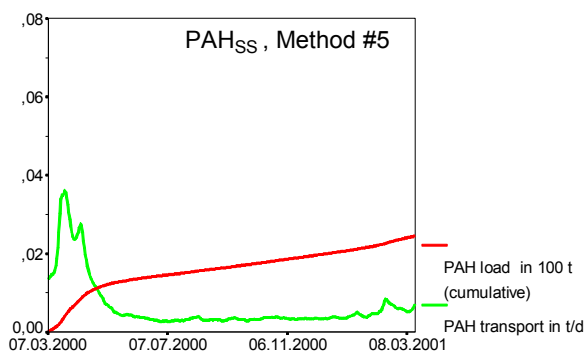
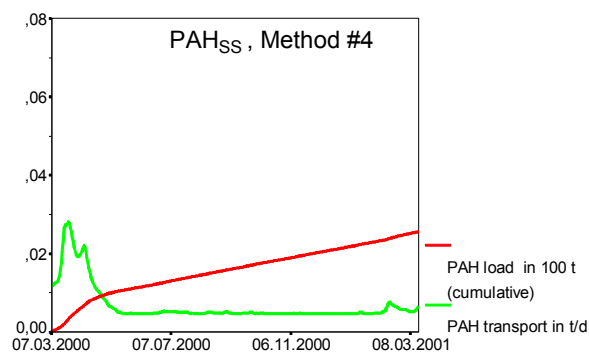


Fig. 4.28: Particle-bound PAH load in 100 t (red curve) as cumulative sum over the daily transport rates in t/d (green curve). Cumulation over one year corresponds to the annual loads obtained by the respective calculation methods as shown in Figure 4.27.



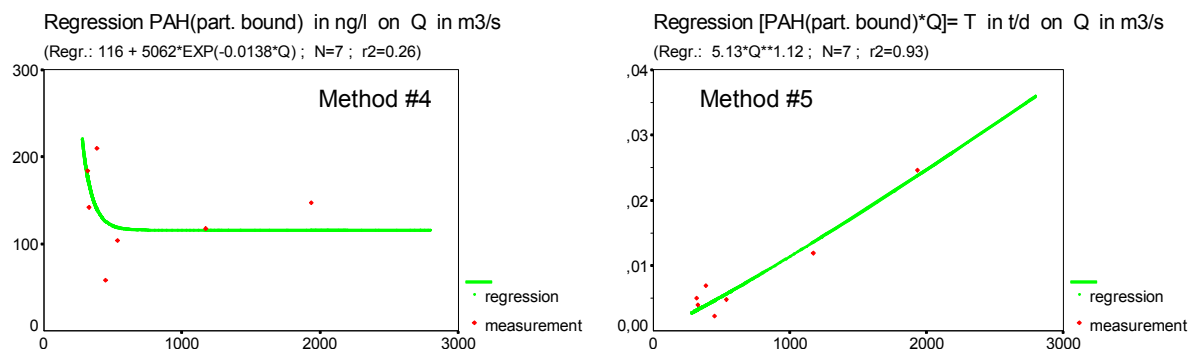


Fig. 4.29: Representation of the regressions  $PAH_{SS}(Q)$  and  $T(Q)$ , with  $T=PAH_{SS} \cdot Q$  (cf. presentation of the methods #4 and #5 in Chapter 4.1.7.1).

The annual load of dissolved PAHs in the study period is estimated in the order of 0.72 t per year. Like in the case of the total PAH load, also for the dissolved load method #2 with a 25 % higher value is the exception, while all other methods yield comparable results (Figure 4.30).

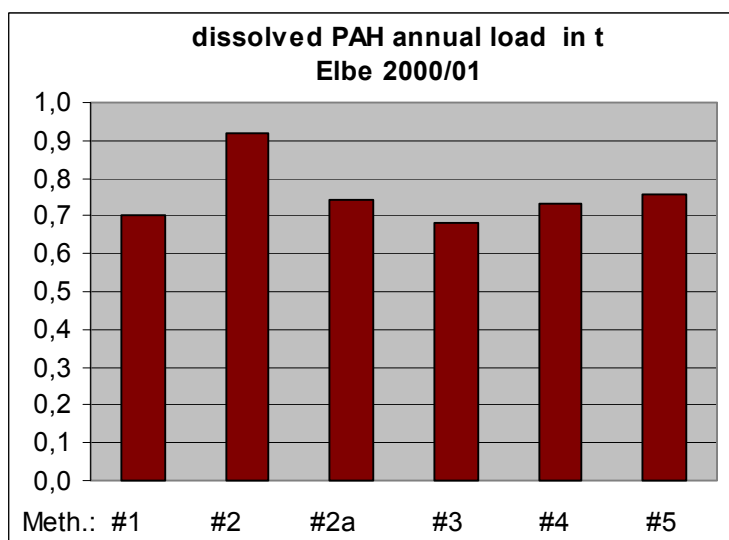


Fig. 4.30: Annual load of dissolved PAHs in the River Elbe at Geesthacht (km 585.0) in the study period from 03/00 to 03/01, computed by six different mathematical methods.

Finally, the daily transport rates of dissolved PAHs (Figure 4.31) and the regressions for the methods #4 and #5 (Figure 4.32) are presented.

Also in the example of the dissolved PAH load, streamflow  $Q$  can be identified as the main controlling factor (compare Figure 4.31 with Figure 4.16 in Chapter 4.1.4.2). The transport rates computed by method #3 have just as smooth curves as those based on the regressions, as only seven measurements of dissolved PAH concentrations exist, so that the method of linear interpolation has the same smoothing effect like the regression methods.

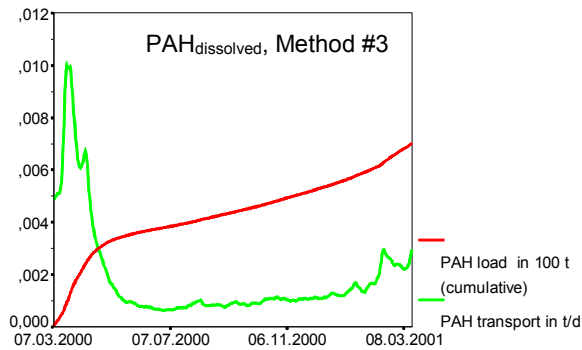


Fig. 4.31: Dissolved PAH load in 100 t (red curve) as cumulative sum over the daily transport rates in t/d (green curve). Cumulation over one year corresponds to the annual loads obtained by the respective calculation methods as shown in Figure 4.30.

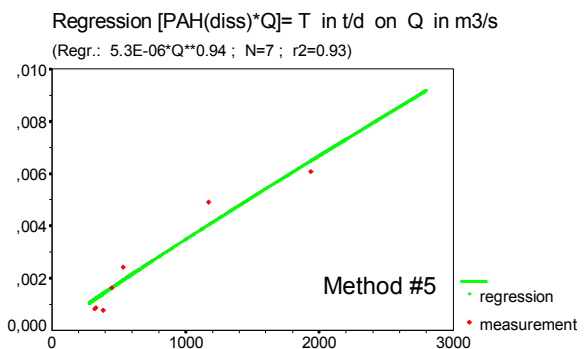
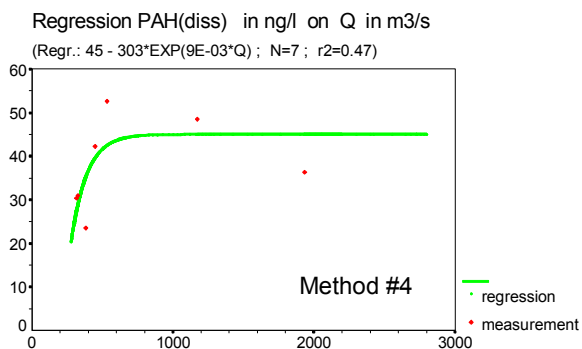
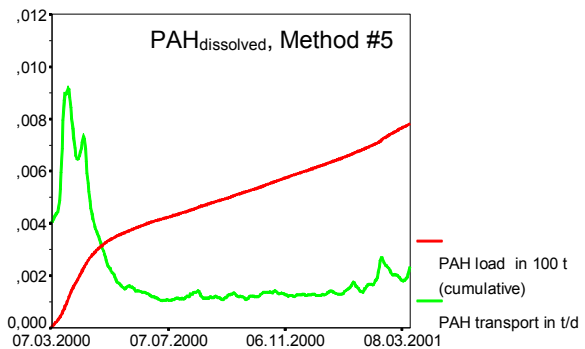
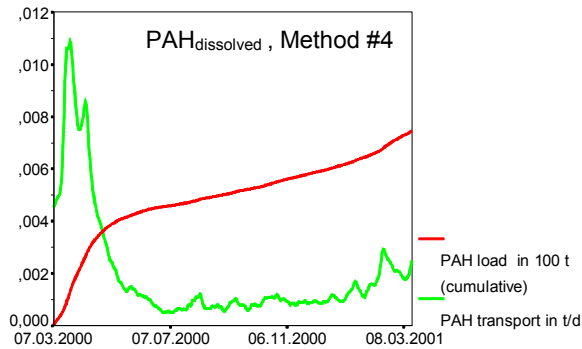


Fig. 4.32: Representation of the regressions  $PAH_{dissolved}(Q)$  and  $T(Q)$ , with  $T = PAH_{dissolved} \cdot Q$  (cf. presentation of the methods #4 and #5 in Chapter 4.1.7.1).

The balance (particle-bound + dissolved = total) does not exactly come out in the presented study of PAH loads in the River Elbe. The determined annual total load was about 1.2 t (i.e. 35 %) higher than the sum of particle-bound plus dissolved PAH loads (4.5 t versus  $2.6 \text{ t} + 0.72 \text{ t} = 3.32 \text{ t}$ ). The reason should be sought in measuring errors, beginning with sampling, sample treatment, to analysis. Here, the aqueous samples are more problematic than the solid ones: Representativity of sampling is best ensured for solid samples (high throughput), sample treatment is most difficult with the total samples (cf. Chapter 3.3.4.2), and analysis meets its limits at first with dissolved samples because of the low concentrations.

With view to the many possible sources of errors, deviations of 35 % may be considered as acceptable, however.

All six mathematical methods of calculating loads were used comparatively for each of the four parameters:  $C_{SS}$ ,  $PAH_{total}$ ,  $PAH_{SS}$ , and  $PAH_{dissolved}$ . A final assessment of the calculation methods applied is given in Chapter 4.2.6.4 after the discussion of the data from the River Weser.



## 4.2 River Weser

### 4.2.1 Mean values of the measured mandatory parameters

The mean values and variability ranges listed in Table 4.9 give a first overview on the order of magnitude of the mandatory parameters (cf. Chapter 3.1) measured in the study area on the River Weser at Bremen/Hemelingen (for River Elbe cf. Chapter 4.1.1).

Tabelle 4.9: Median values and variability of mandatory parameters, Weser 359.9 km

|                                 | Minimum | 1. Quartile | Median      | 3.Quartile | Maximum | N   |
|---------------------------------|---------|-------------|-------------|------------|---------|-----|
| Q in m³/s                       | 127     | 155         | <b>182</b>  | 304        | 858     | 365 |
| C <sub>SS</sub> in g/m³         | 1.7     | 8.3         | <b>12.0</b> | 17.4       | 120     | 241 |
| C <sub>OC</sub> in %            | 4.3     | 5.1         | <b>5.5</b>  | 6.1        | 10.4    | 15  |
| < 63µm in %                     | 44      | 72          | <b>77</b>   | 82         | 91      | 15  |
| ∑16PAK <sub>SS</sub> in mg/kgDW | 4.2     | 5.4         | <b>5.8</b>  | 6.2        | 6.5     | 14  |
| NAPHT <sub>total</sub> in ng/l  | 24      | 26          | <b>34</b>   | 41         | 57      | 15  |

### 4.2.2 Polycyclic aromatic hydrocarbons (PAHs)

#### 4.2.2.1 Median values of concentrations

The median values and variability parameters of the total, the particle-bound, and the dissolved concentrations of the sum of the 16 PAHs according to EPA (∑16PAH) are shown in the Figures 4.33 and 4.34 as box-and-whiskers plots.

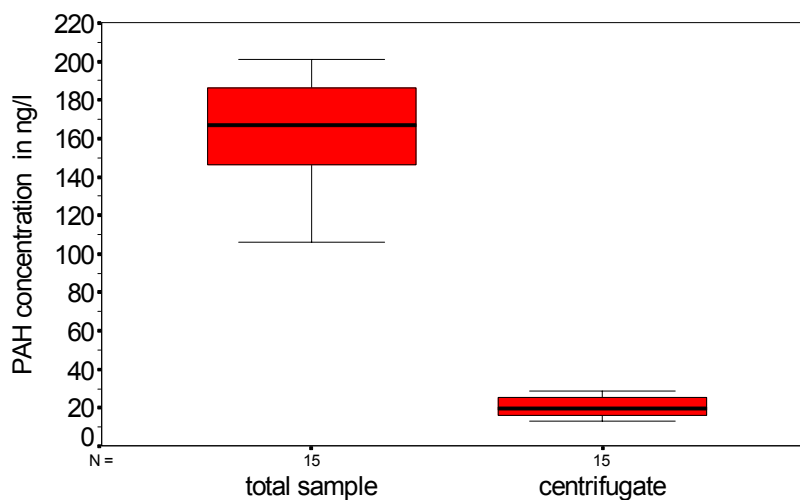


Fig. 4.33: PAH contents in the total sample and in the centrifugate. In the total sample the median value of 167 ng/l is about eight times higher than in the centrifugate (20 ng/l).

The graphs are based on all samples collected by flow-trough centrifuge (FC), and differentiated for whole sample, centrifugate, and suspended solids.

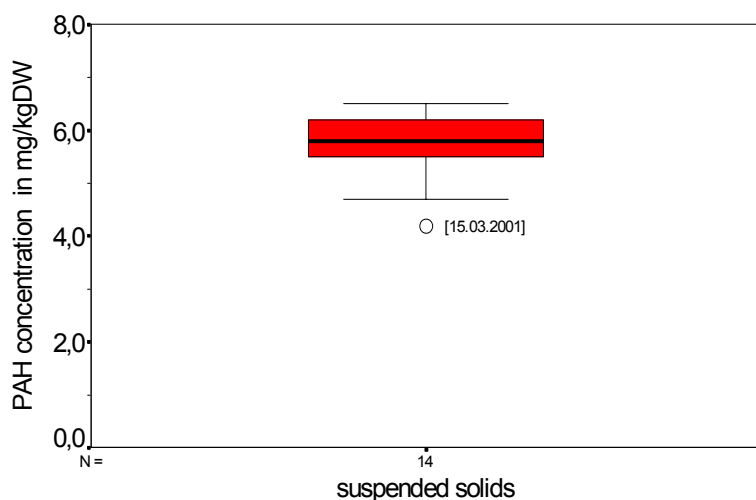


Fig. 4.34: PAH contents in suspended solids. The median value is at 5.8 mg/kg. The outlier comes from the near-surface mixed sample of 15 March 2001.

#### 4.2.2.2 Seasonality

Basis for the consideration of the seasonal variability of PAH concentrations are all mixed samples (composite samples along the cross section) from the water surface collected by FC. The Figures 4.35-37 show the seasonal variations of total, dissolved, and particle-bound concentrations.

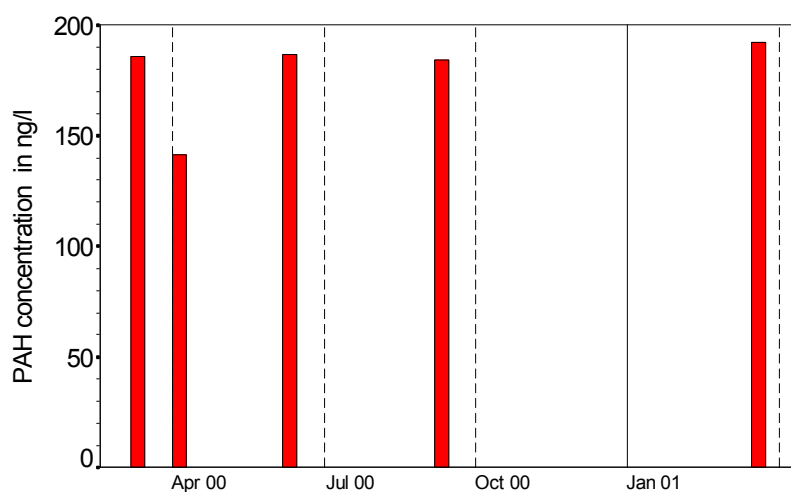


Fig. 4.35: PAH concentration in the total sample in the course of the year (PAH<sub>total</sub>). The measured data do not suggest seasonality.

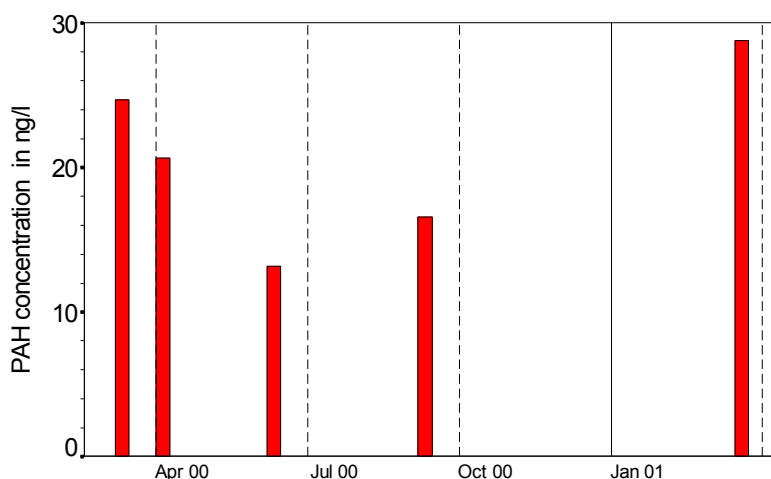


Fig. 4.36: PAH concentration in the centrifugate in the course of the year (PAH<sub>dissolved</sub>). Seasonality is notable, with low concentrations in summer and higher values in winter.

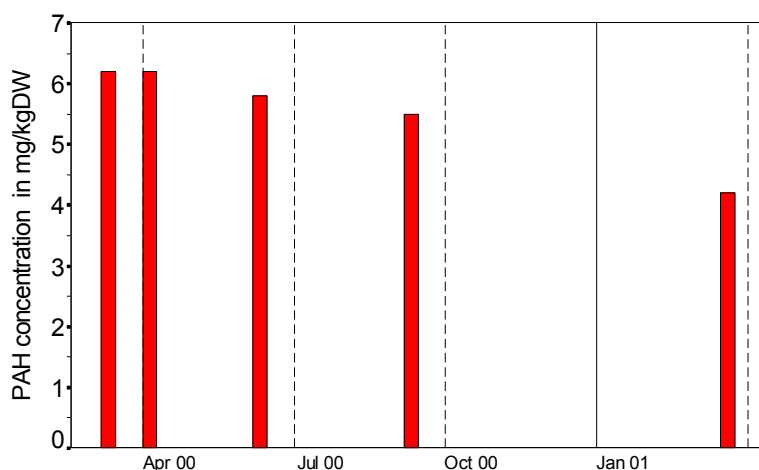


Fig. 4.37: PAH concentrations in suspended solids in the course of the year ( $PAH_{ss}$ ). There is no seasonality noticeable, but a decreasing tendency. This tendency, however, is weakly supported due to the short study period.

A distinct seasonal variability was found - just like in the Elbe - only in the centrifugate (concentration of dissolved PAHs). The total sample shows relatively constant values around 180 ng/l, while the particle-bound concentrations have a decreasing bias. However, to substantiate this observed trend continuously collecting samplers, like BISAM or the sedimentation tank (ST), would be needed or the sampling frequency with the FC would have to be increased. Because of the small number of measurements, this is more likely an accidental development. If one considers, for instance, only the first four values until October 2000, one might expect also a seasonal variability with a minimum in summer (cf. Chapter 4.1.2.2). Moreover, the PAH concentrations in suspended solids measured on the right-hand bank and the left-hand one on 15 March 2001 are with 4.7 and 6.0 mg/kgDW, respectively, both higher than the mixed sample value presented here with 4.2 mg/kgDW (cf. also Chapter 4.2.5).

#### 4.2.2.3 *Patterns*

##### 4.2.2.3.1 PAH patterns in the River Weser

The Figures 4.38 - 4.40 show mean patterns of the total, dissolved, and solid samples in form of bar diagrams with indication of the variations (interquartile range). Again all data collected by FC were considered.

Here too, naphthalene proved to be the richest fraction in the aqueous samples (total and dissolved), and fluoranthene and pyrene in the suspended solids.

Like in the case of the Elbe, the shift in the patterns in the transition from the total sample to the suspended solids and to the centrifugate is obvious: The lower condensed compounds (NAPH-PHEN) occur more in dissolved form (centrifugate), while the higher condensed, hardly soluble ones are preferentially bound on suspended solids.

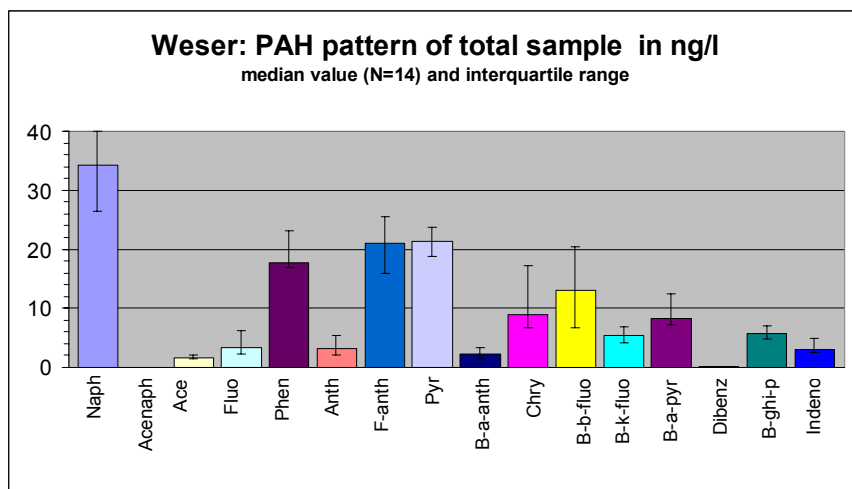


Fig. 4.38:  
Mean PAH pattern of  
the 14 total samples  
(centrifuge inflow;  
study period  
03/00 - 03/01,  
Weser km 359.9).

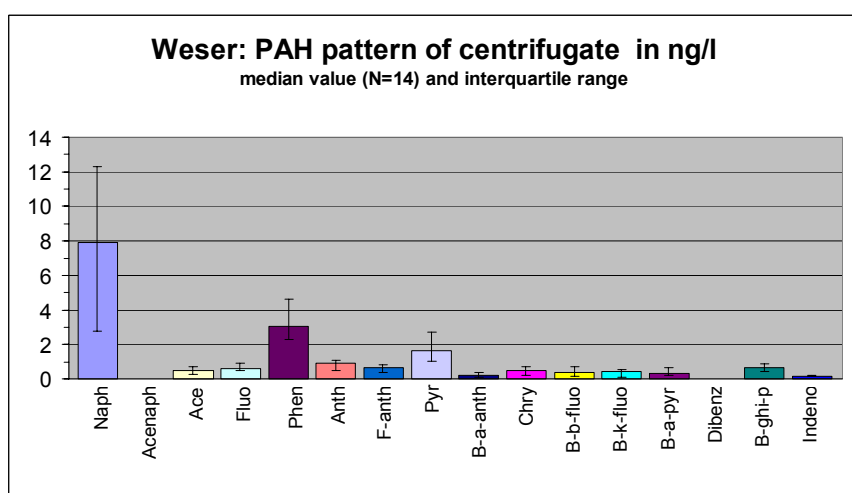


Fig. 4.39:  
Mean PAH pattern of  
the 14 centrifugate  
samples (centrifuge  
outflow; study period  
03/00 - 03/01,  
Weser km 359.9).

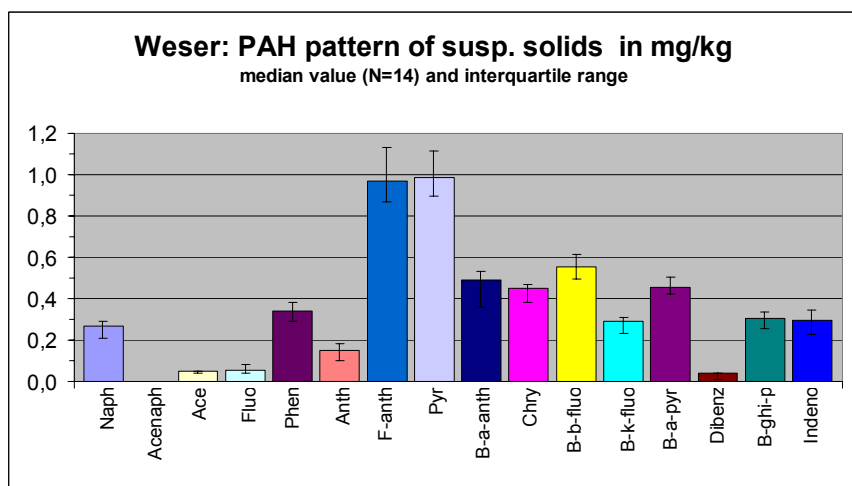


Fig. 4.40:  
Mean PAH pattern of  
the 14 suspended-  
solids samples  
(centrifuge residue;  
study period  
03/00 - 03/01,  
Weser km 359.9).

#### 4.2.2.3.2 Direct comparison of PAH patterns in the rivers Elbe and Weser

The juxtaposition of the Figures 4.41 -43 gives a good possibility to compare the PAH patterns in the Elbe and in the Weser.

The similarity of the patterns, that appears in all three compartments, is striking. The aqueous samples (total and dissolved) from the Elbe have on average 1.5 times higher values, except in the case of naphthalene that has the double concentration in the Elbe against the Weser.

In the case of suspended solids, this ratio is not so wide (on average 1.1-times higher values in the Elbe), and sometimes it is even reversed: acenenaphthene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenzo[ah]anthracene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene are compounds which are more frequent in the Weser than in the Elbe.

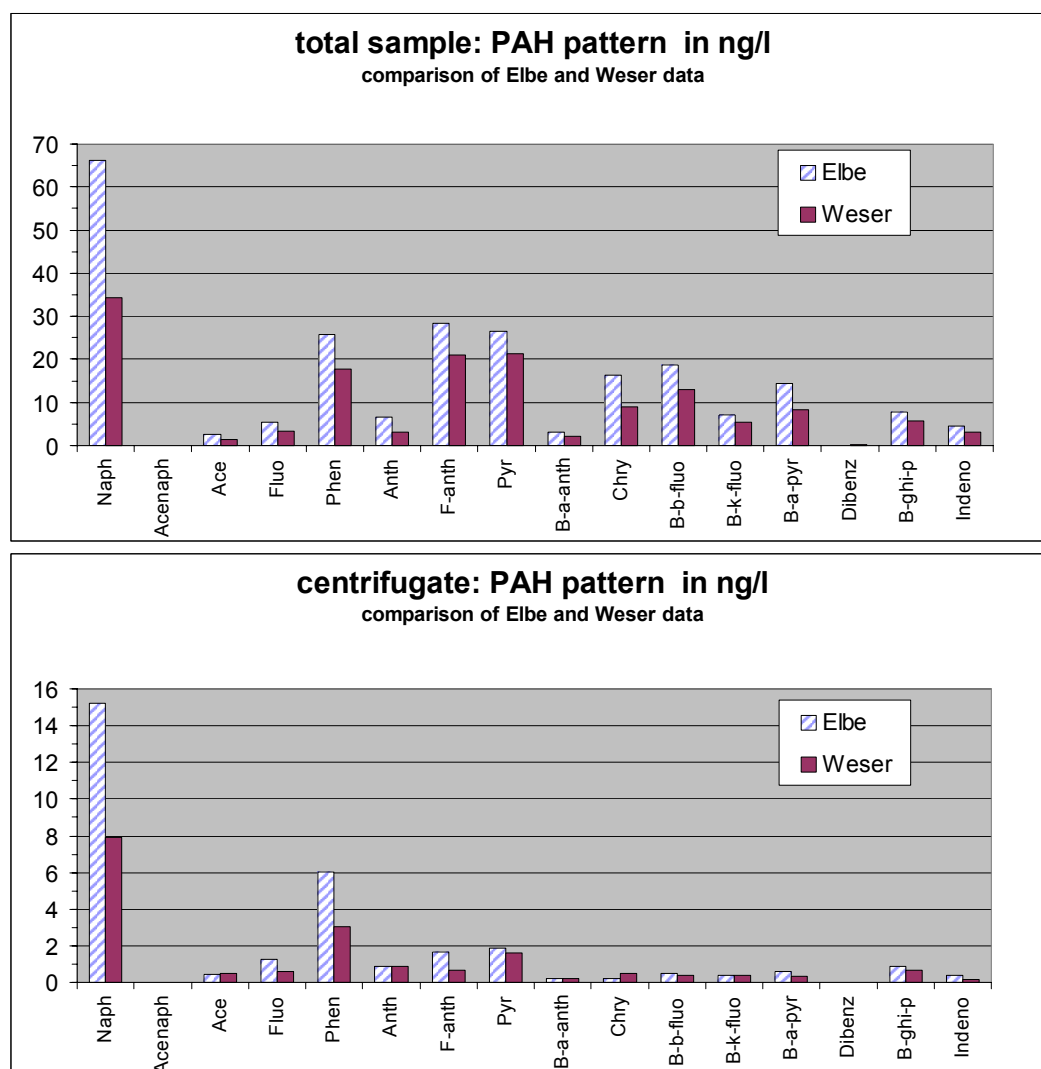


Fig. 4.41a: Direct comparison of PAH patterns of the Elbe and those of the Weser in the total sample and in the centrifugate. (to be contd., see next page)

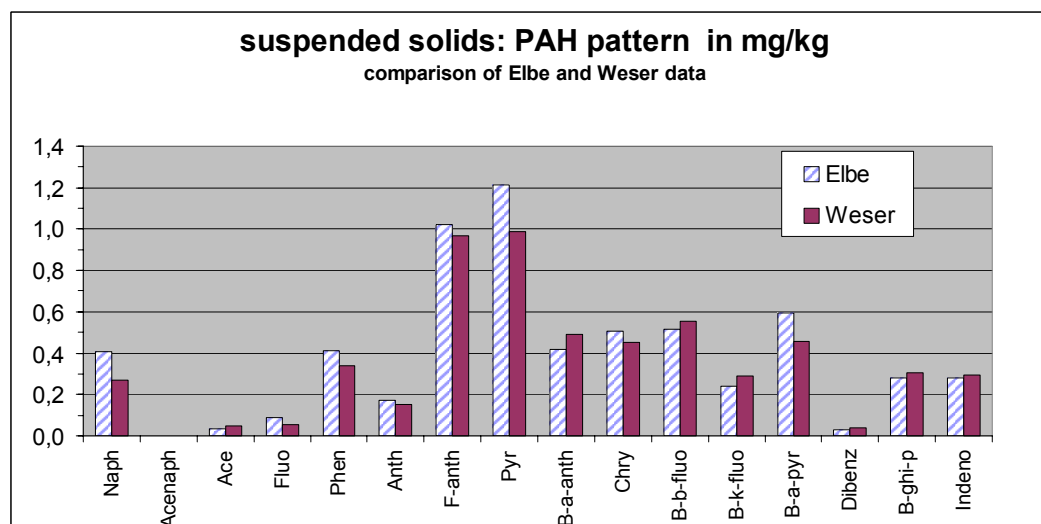


Fig. 4.41b: Direct comparison of PAH patterns of the Elbe and those of the Weser in the suspended solids.

#### 4.2.2.4 Partition coefficients

The distribution of PAHs in the Weser in relation to the data from the Elbe between the solid phase and the dissolved one was discussed regarding the particulate fraction (PF value) and the  $K_D$  value for the sum of the 16 PAHs defined by EPA and differentiatedly for the sum of lower and the sum of higher condensed PAHs in Chapter 4.1.2.4 (see there).

### 4.2.3 Suspended-solids concentration ( $C_{SS}$ )

#### 4.2.3.1 Median value of concentrations

In the period between 8 March 2000 and 16 March 2001, the suspended-solids concentration ( $C_{SS}$ ) was measured near the surface on 241 workdays at Weser km 361.6. The samples were taken by the staff of the local waterways administration (WSA Bremen/ABz Habenhausen). The distribution of the measured values is shown in Figure 4.42.

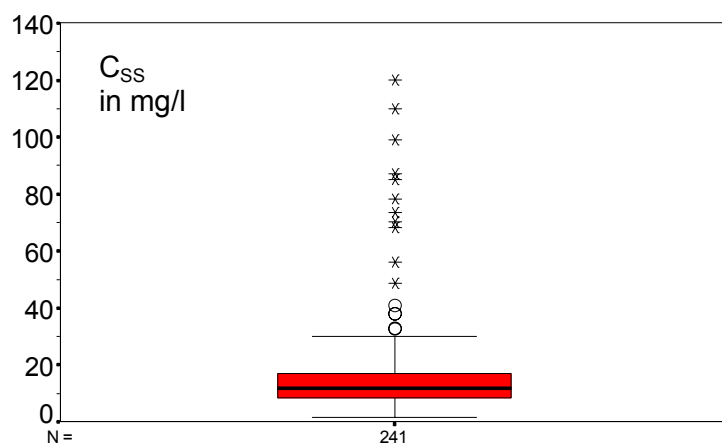


Fig. 4.42: Distribution of  $C_{SS}$  values in the Weser at km 361.6. Measurements on workdays in the period 03/00-03/01. Box-and-whiskers plot with 5 outliers and 11 extreme values (for definition see Chapter 4.1.2.1).

The median value is 12 mg/l, the arithmetic mean (not shown) is 16.1 mg/l. The strong dynamics in the variation of suspended-solids concentrations, expressed in the high number of outliers and extreme values, is striking. Two outliers date from December 2000, all other outliers and extremes stem from the period January to February 2001 (cf. Figure 4.43).

#### 4.2.3.2 Seasonality

The annual variation of suspended-solids concentrations is confronted in Figure 4.43 with the temporal development of streamflow  $Q$  and the chlorophyll- $a$  concentration. The usually fortnightly chl- $a$  data were kindly provided by the Bremen Senate for Building and the Environment, the streamflow data were provided by the WSA Verden.

The limit of detection (LOD) for chl- $a$  measurements is around 10  $\mu\text{g/l}$ ; in cases when the limit of detection was not reached, half the value of LOD was entered into the diagram.

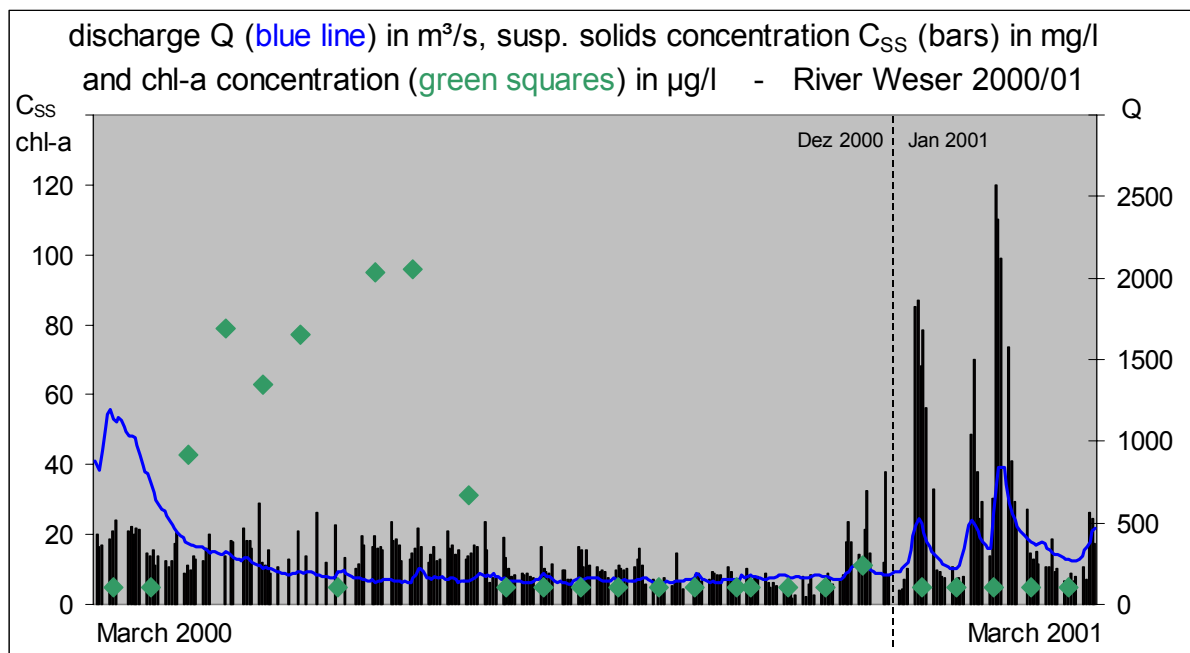


Fig. 4.43: Temporal variations of  $C_{SS}$ ,  $Q$ , and chl- $a$  in the period 03/00 - 03/01.

In contrast to the Elbe, in the Weser the phytoplankton dynamics plays a secondary role, although with 100  $\mu\text{g/l}$  the concentrations are comparable with those of the Elbe, but such values were measured only in the months from April to July. During the rest of the year, the values are nearly exclusively below the limit of detection, i.e. in contrast to the Elbe, the Weser does not experience a second algal bloom in the summer.

In January and February 2001, there are very high peaks of suspended-solids concentrations due to only slightly increasing streamflow values. From that it becomes clear that the dynamics of suspended solids in the Weser is essentially dominated by the streamflow regime and hardly by biological processes (phytoplankton dynamics).

#### 4.2.4 Correlation analysis

##### 4.2.4.1 Bivariate correlations

Like in the evaluation of the data from the River Elbe presented in Chapter 4.1.5.1, for the River Weser the same parameters are pairwise correlated:  $Q$ ,  $C_{SS}$ , GSA ( $<63\mu\text{m}$ ), the product of  $C_{SS}$  and GSA ( $<63\mu\text{m}$ ), turbidity, chl- $a$ ,  $C_{OC}$ ,  $\Sigma 16\text{PAH}$  (total),  $\Sigma 16\text{PAH}$  (dissolved),  $\Sigma 16\text{PAH}$  (particle-bound in mg/kgDW) and  $\Sigma 16\text{PAH}$  (particle-bound in ng/l).

Again those parameters are called clearly correlated which have a significance level of  $p < 0.005$  and  $|r| > 0.5$ . Definitively not correlated are parameters with  $p > 0.5$ , for all other results no explicit answer is given.

In contrast to the data from the Elbe, those from the Weser showed less distinct correlations. These are restricted to the connection between  $Q$ ,  $C_{SS}$ , and turbidity, that are shown in a matrix in Table 4.10, with  $r$ : meaning Pearson correlation coefficient; (N) number of measurements, and  $p$ : level of two-tailed significance.

The linear relation between  $C_{SS}$  and turbidity in the Weser is similar to that in the Elbe, while the correlations with streamflow values  $Q$  are more pronounced.

All other parameters do not show any distinct correlations and are not included in the Table. In particular chl- $a$  is definitely not correlated with  $C_{SS}$  ( $r = 0.07$ ;  $N = 26$ ;  $p = 0.75$ ), so that the suspended-solids

regime in the Weser may be characterized as mainly hydraulically dominated. One reason lies certainly in the unfavourable environmental conditions for the potamoplankton due to the high salinity. This phenomenon is in agreement with the observation that neither the PAH concentrations in suspended solids nor the concentrations of suspended solids themselves do show distinct seasonality in the Weser.

Table 4.10: Correlation matrix  
(For explanation, refer to the text.)

| r<br>(N)<br>p | $C_{SS}$               | turbidity              |
|---------------|------------------------|------------------------|
| $Q$           | .4547<br>(242)<br>.000 | .7879<br>(209)<br>.000 |
| $C_{SS}$      | 1<br>(242)<br>–        | .7514<br>(132)<br>.000 |



Among the PAH-relevant parameters none is clearly correlated. On the Elbe, at least the particle-bound PAH components showed a correlation (with  $Q$  or the product of  $C_{SS}$  and  $GSA(<63\mu m)$ ). In order to facilitate the comparison with the data from the Elbe, Table 4.11 presents the respective parts of the correlation matrix.

Table 4.11:  
PAH-relevant  
correlations

| $r$<br>(N)<br>$p$                              | $Q$                    | $C_{SS}$                | $GSA$<br>( $<63\mu m$ )<br>$*C_{SS}$ | turbidity              | chl- $a$        | $C_{OC}$                |
|------------------------------------------------|------------------------|-------------------------|--------------------------------------|------------------------|-----------------|-------------------------|
| $\Sigma 16PAK$<br>(particle-bound<br>in mg/kg) | .4902<br>(005)<br>.402 | -.3190<br>(005)<br>.601 | -.3039<br>(005)<br>.619              | .2109<br>(003)<br>.865 | –<br>(002)<br>– | -.2947<br>(005)<br>.630 |
| $\Sigma 16PAK$<br>(particle-bound<br>in ng/l)  | .8477<br>(005)<br>.070 | .8846<br>(005)<br>.046  | .7792<br>(005)<br>.120               | .8070<br>(003)<br>.402 | –<br>(002)<br>– | -.8341<br>(005)<br>.079 |

The very low significances (high values of  $p$ ) are certainly due to the low number of measurements; although one can note that the correlations with  $\Sigma 16PAH$  (particle-bound in ng/l) are always stronger than those with  $\Sigma 16PAH$  (particle-bound in mg/kgDW). This means that regarding the PAH contamination in the Weser, the parameters  $Q$ ,  $C_{SS}$ , product of  $C_{SS}$  and  $GSA(<63\mu m)$ , turbidity, and  $C_{OC}$  are more correlated with the quantity of the suspended solids than with their quality. This effect was not so obvious in the River Elbe.

#### 4.2.4.2 Cross correlation between $Q$ and $C_{SS}$

If the falling limb of floods and the times of increased chl- $a$  concentration are left out of account following the argumentation given in Chapter 4.1.5.2 for the River Elbe, the linear correlation between  $Q$  and  $C_{SS}$  increases to  $r=0.82$  with  $N=158$  and  $p<0.0005$ .

The result of the cross correlation made on this data basis (Aug. 2000 - March 2001) is depicted in Figure 4.44.

A nearly symmetric distribution appears, so that it can be assumed - like on the Elbe - that  $C_{SS}$  responds to variations of  $Q$  in the order of a few hours.

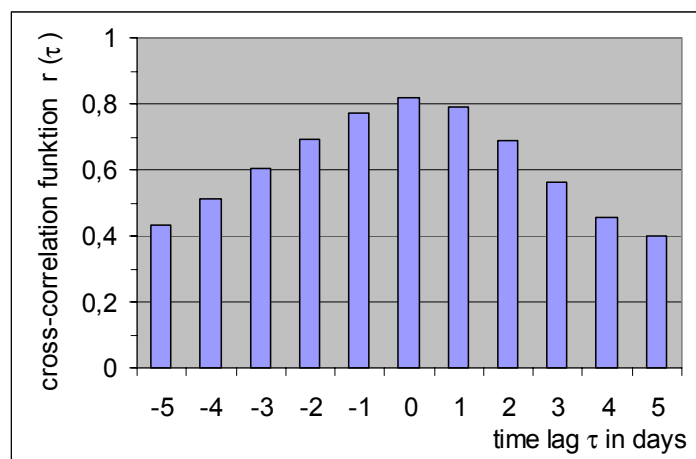


Fig. 4.44: Cross correlation between  $Q$  and  $C_{SS}$   
(Aug. 2000 - March 2001)

#### 4.2.5 Spatial homogeneity

The horizontal homogeneity is examined by means of the PAH levels in suspended solids from the centrifuged samples. These samples were collected near the water surface on the right-hand and left-hand banks, as well as in form of mixed surface samples (composite samples along the cross section near the water surface). The statistical distribution of these values is shown as box-and-whiskers plots in Figure 4.45.

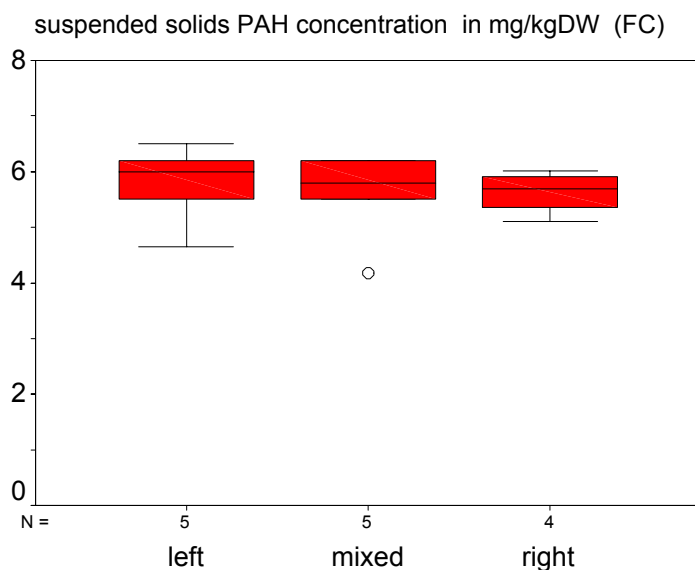


Fig. 4.45: Spatial distribution of the suspended-solids PAH concentration across the Weser river profile at km 359.9. Samples collected near the water surface in the period from April 2000 to March 2001.

The available data do not give any indication of horizontal differences in the PAH contamination of suspended solids. The median values are 6.0 (left-hand bank), 5.8 (mixed sample), and 5.7 mg/kgDW (right-hand bank).

The outlier in the composite sample dates from 15 March 2002. In the discussion of the seasonal variations in Chapter 4.2.2.2, this value was responsible for the seemingly decreasing temporal trend.

Also the illustration of the seasonal development (Figure 4.46) shows that the variations of differences in the PAH loads between the right-hand bank and the left-hand one are irregular. The same applies to the PAH concentration in the aqueous phase (Figure 4.27).

Like the PAH concentration, the other parameters GSA, LOIN, C<sub>OC</sub>, N, S, and water content do not show a significant gradient, too. In a unique cross profile measurement (15 March 2001, five points in the cross profile near the water surface), the environmental parameters O<sub>2</sub>, T<sub>w</sub>, pH, and conductivity were also extremely homogeneously distributed.

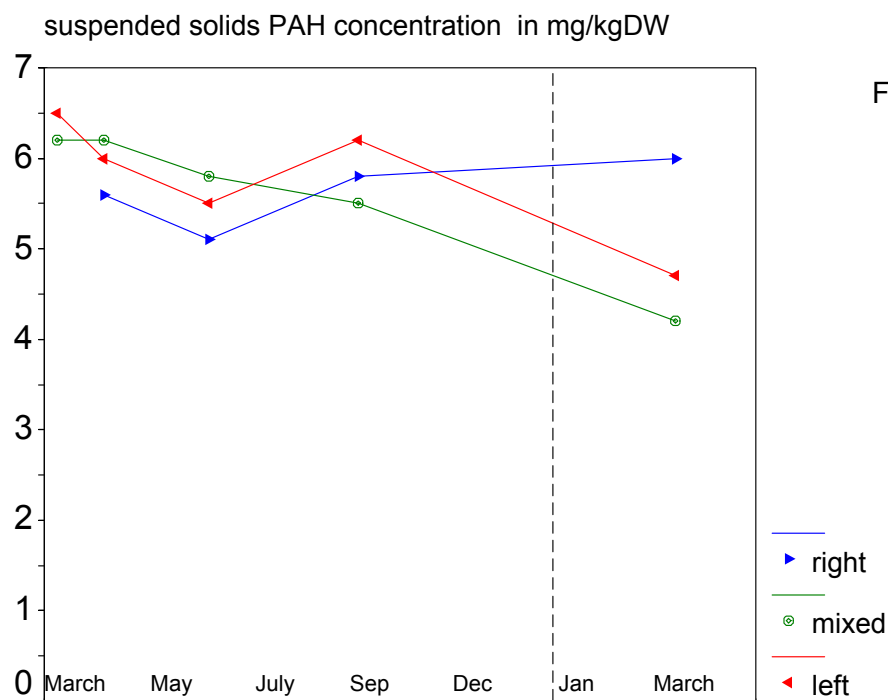


Fig. 4.46: Annual variation of the suspended-solids PAH concentration (Weser km 359; data from samples collected near the water surface).

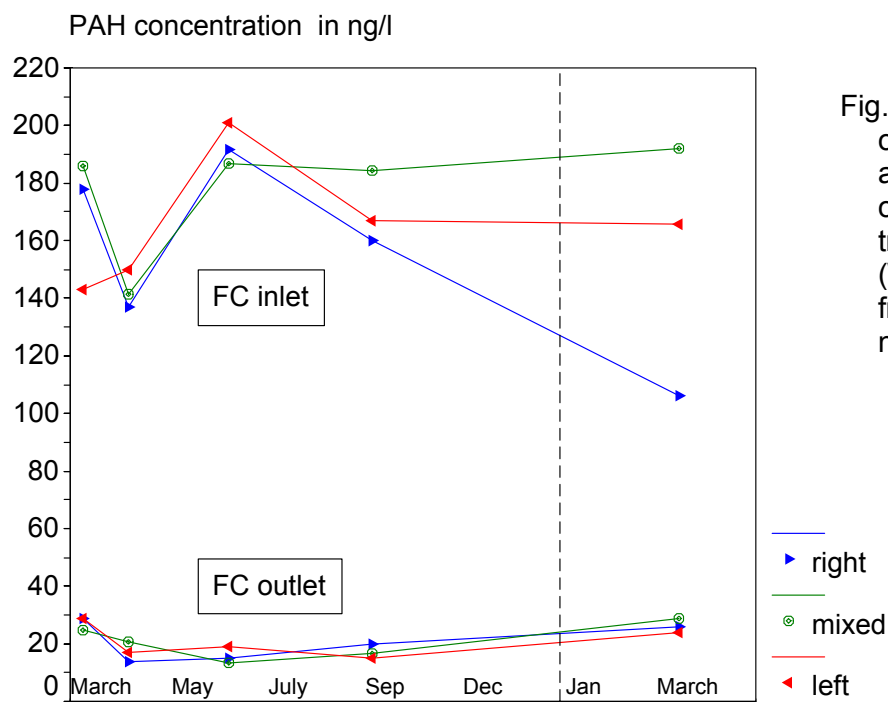


Fig. 4.47: Annual variation of the total (FC inlet) and the dissolved (FC outlet) PAH concentration (Weser km 359; data from samples collected near the water surface).

## 4.2.6 Annual loads

### 4.2.6.1 Mathematical methods of load calculation

The same six methods that were presented in Chapter 4.1.7.1 were used on the River Weser. In the following two chapters they are compared using the examples of suspended-solids load and PAHs loads.

### 4.2.6.2 Suspended-solids loads

The suspended solids loads computed by six different mathematical methods were in the range of 190,000 t per year in the study period from March 2000 to March 2001 (Figure 4.48). The lowest value was computed by method #1 with 143,000 t/a, the highest one with 214,000 t/a by method #6. Unlike the results on the Elbe, the data on the Weser displayed a distinct dependence on the computation method. This is certainly due to more pronounced dynamics of suspended solids in the Weser, so that even slight weighting of single measurements caused by the different calculation methods may produce larger effects.

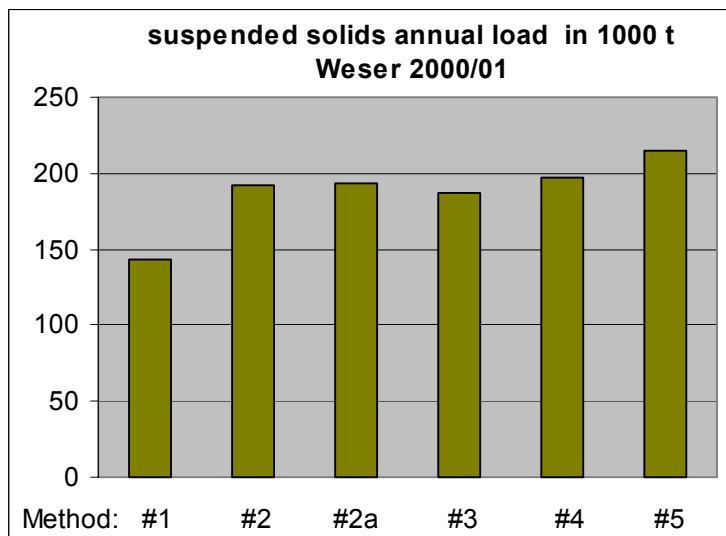


Fig. 4.48: Annual suspended-solids load in the Weser at Bremen (km 359.9) in the study period 03/00 - 03/01, computed by six different mathematical methods.

The fact that short flood events, accompanied by an increase in suspended-solids concentration  $C_{SS}$ , influence the annual load essentially is visible in the illustrations of daily transport rates in Figure 4.49, which were based on computations with the methods #3 to #5. The comparison with Figure 4.43 in Chapter 4.2.3.2 highlights the connection between transport rates on the one hand and streamflow  $Q$  (March 2000), as well as  $Q$  and  $C_{SS}$  (January/February 2001), on the other hand. This applies in particular to the upper illustration in Figure 4.49 (Method #3).

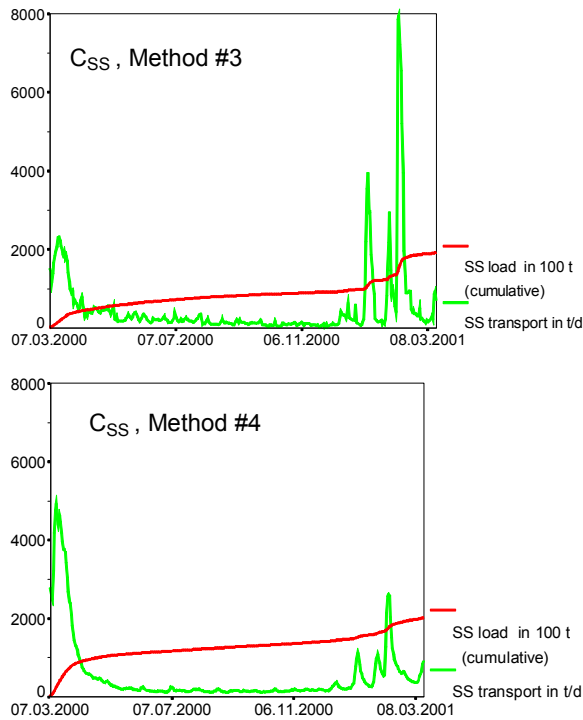
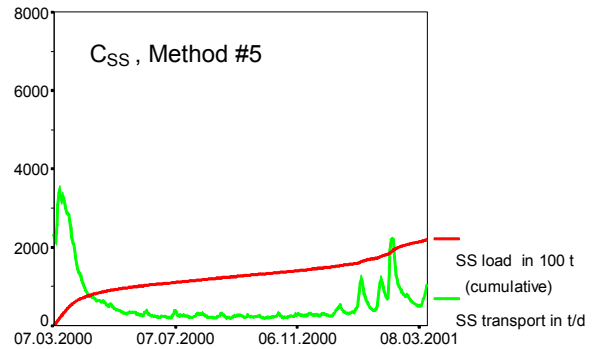


Fig. 4.49: Suspended-solids load in 100t (red curve) as cumulative sum over the daily transport rates in t/d (green curve). The cumulation over one year corresponds to the annual load given in Figure 4.48 for the respective calculation methods.



The two illustrations below (methods #4 and #5) point more at the connection with streamflow  $Q$ . This is due to the fact that the correlation between  $Q$  and  $C_{SS}$  is very weak ( $r^2=0.2$ ) and that the existing suspended solids dynamics is not represented by the very weak regressions of methods #4 and #5.

The regressions themselves are illustrated in Figure 4.50. Like in the case of the River Elbe, the regression parameters reflect here too the fact that  $C_{SS}$  and  $Q$  are only weakly correlated.

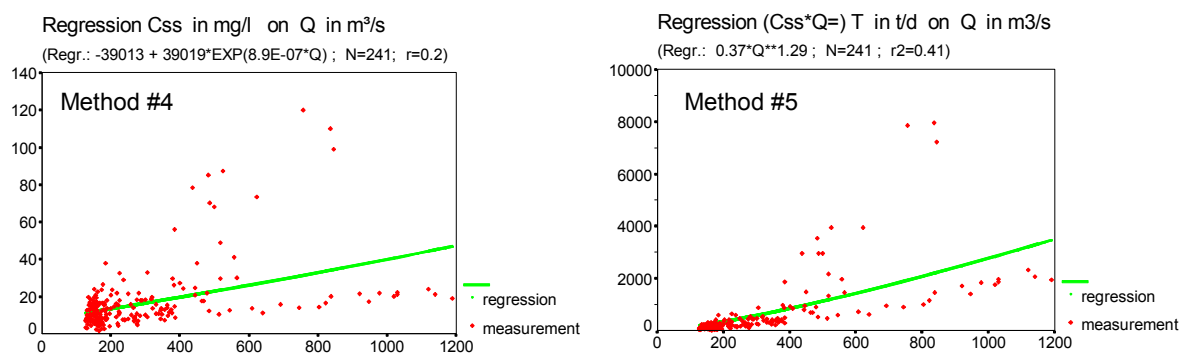


Fig. 4.50: Regressions  $C_{SS}(Q)$  and  $T(Q)$ , with  $T=C_{SS} \cdot Q$  (cf. presentation of the methods #4 and #5 in Chapter 4.1.7.1).

#### 4.2.6.3 PAH loads

The PAH loads in the Weser are given differentiatedly for total load, particle-bound load, and dissolved load. The computation of the total load rests on measurements of the PAH content in the total sample (centrifuge inflow,  $\Sigma 16\text{PAH}$ ) using again methods #1 to #5. With the exception of method #2, which similar to the case of the Elbe, produces 45 % higher values than the other methods, the loads are equally near 1.6 t per year (Figure 4.51).

Thus, the load in the Elbe is with 4.5 t per year about three times as high as the load in the Weser.

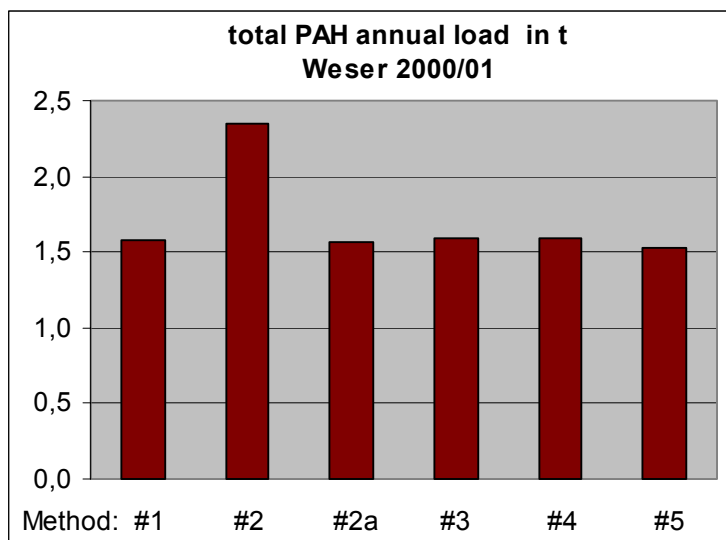


Fig. 4.51: Annual total PAH load in the Weser at Bremen (km 359.9) in the study period 03/00 - 03/01, calculated with six different mathematical methods.

The analysis of the daily transport rates reveals (Figure 4.52) that the events in March 2000 and in January/February 2001 play an important role also for the PAH load.

However, here streamflow  $Q$  seems to be the decisive factor, while the peaks of suspended solids at the beginning of the year 2001 are not reflected in the PAH transport, as regrettably no PAH measurements were made in these periods.

The daily transport rates and the resulting cumulative loads of the three methods #3 - #5 are comparable. This is so because the five measured PAH concentrations are all in the same order of magnitude. Consequently, the linear interpolation produces just like the regression method #4 similar, nearly constant values, which are then multiplied with  $Q$ , or the regression values are proportional to  $Q$  (method #5). The regressions of the methods #4 and #5 are shown in Figure 4.53.

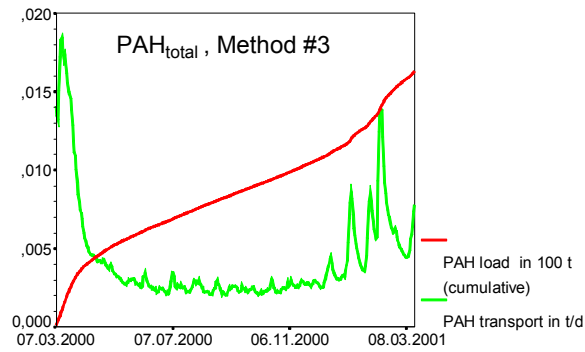


Fig. 4.52: Total PAH load in 100 t (red curve) as cumulative sum over the daily transport rates in t/d (green curve). The cumulation over one year corresponds to the annual load given in Figure 4.51 for the respective calculation methods.

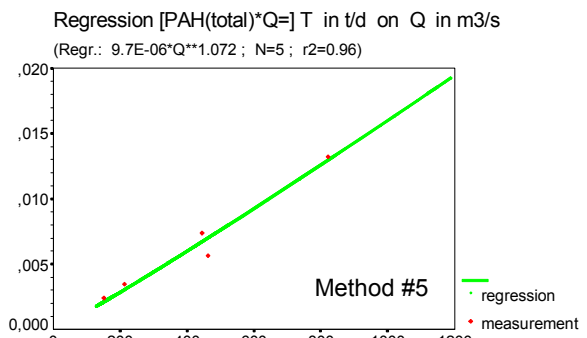
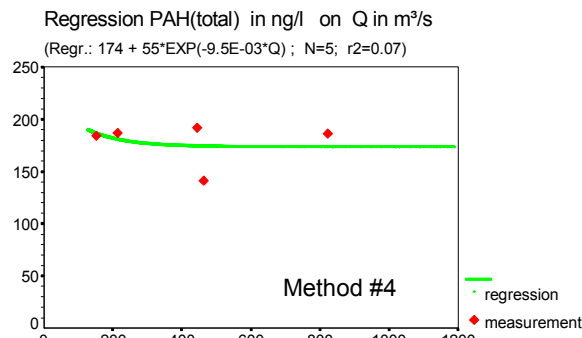
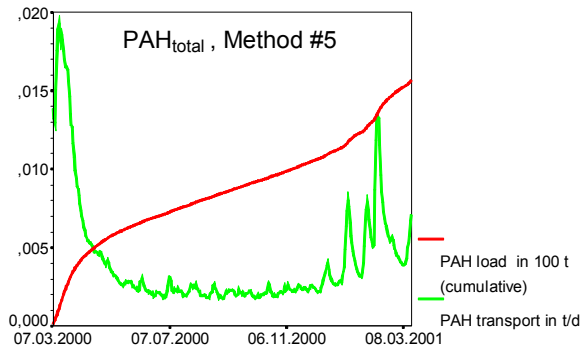
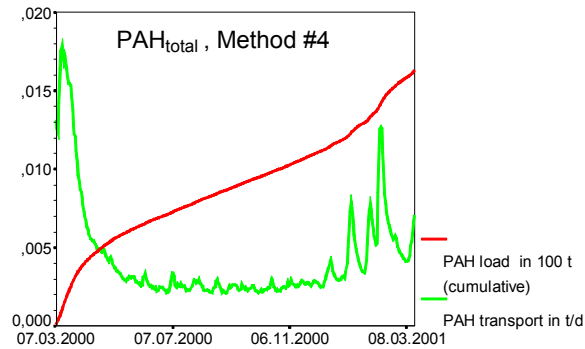


Fig. 4.53: Regressions  $PAH_{total}(Q)$  and  $T(Q)$ , with  $T = PAK_{total} \cdot Q$  (cf. presentation of the methods #4 and #5 in Chapter 4.1.7.1).

The particle-bound PAH loads are in the order of nearly 1 t per year (Figure 4.54). The result of the calculation method #2 of 1.66 t per year is in this case 68 % too high. The outputs of the other five methods vary between 0.89 and 1.04 t per year.

As for the calculation of the particle-bound loads the parameters  $Q$ ,  $PAH_{SS}$ , and  $C_{SS}$  are used, the calculation methods presented in Chapter 4.1.7.1, and especially methods #2a and #3, need some modification. These modifications are described in the context of the particle-bound loads in the River Elbe in Chapter 4.1.7.2.

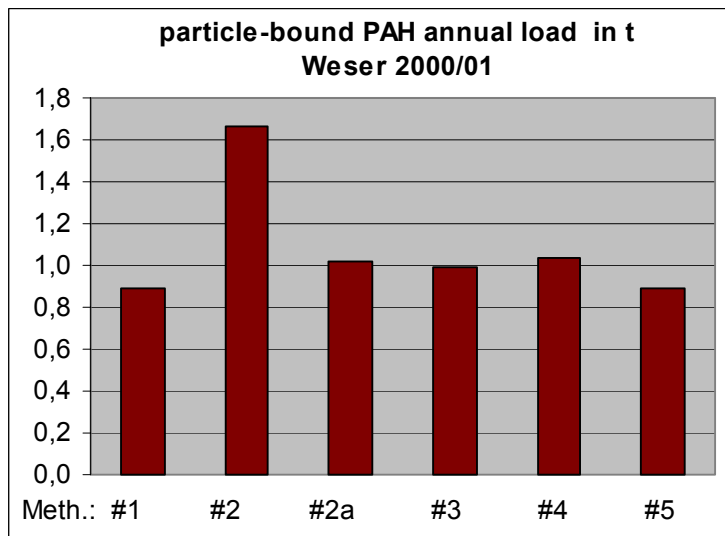


Fig. 4.54: Annual particle-bound PAH load in the Weser (km 359.9) in the study period 03/00-03/01, computed with six different mathematical methods.

The daily transport rates are shown in Figure 4.55. As in the application of method #3 the suspended-solids concentrations  $C_{SS}$  measured on workdays are used, the dependence of the transport rates on  $Q$  and on  $C_{SS}$  is very obvious, as a comparison with Figure 4.43 in Chapter 4.2.3.2 reveals. In the regressions on the basis of merely five measurements, this differentiated information is of course lost and only the dependence on  $Q$  is noticeable (cf. the two lower pictures in Figure 4.55).

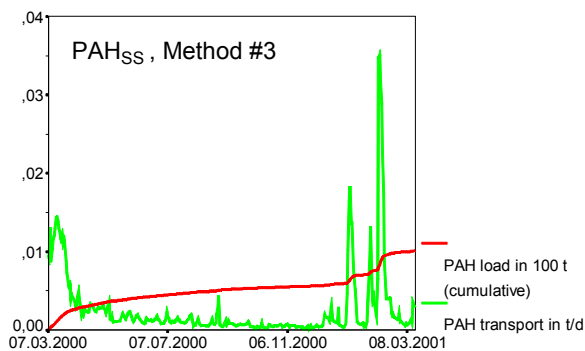
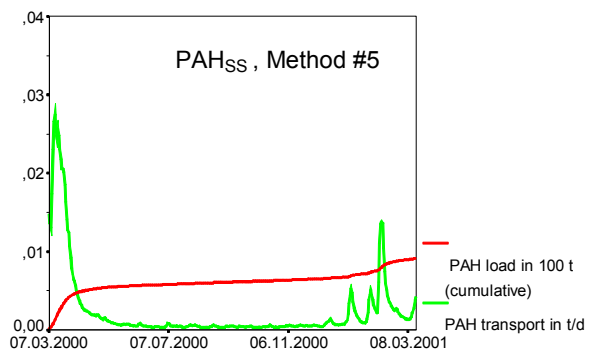
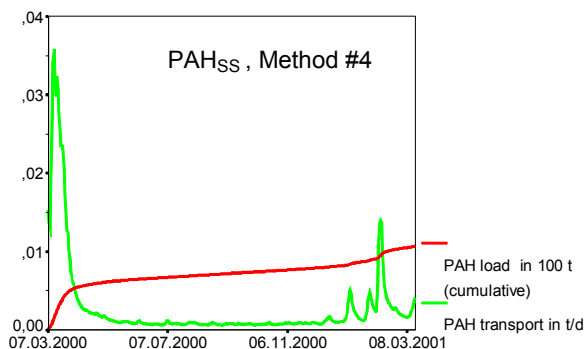


Fig. 4.55: Particle-bound PAH load in 100t (red curve) as cumulative sum over the daily transport rates in t/d (green curve). The cumulation over one year corresponds to the annual load given in Figure 4.54 for the respective calculation methods.



The regressions of the methods #4 and #5 are illustrated in Figure 4.56. Against the regressions shown so far, they appear very good. Although not significant because of the low number of



values, the high linear correlation between  $\text{PAH}_{\text{SS}}$  in ng/l and  $Q$  amounting to  $r=0.85$  ( $r^2=0.72$ ) was already visible in the correlation analysis in Chapter 4.2.4.1 (see there).

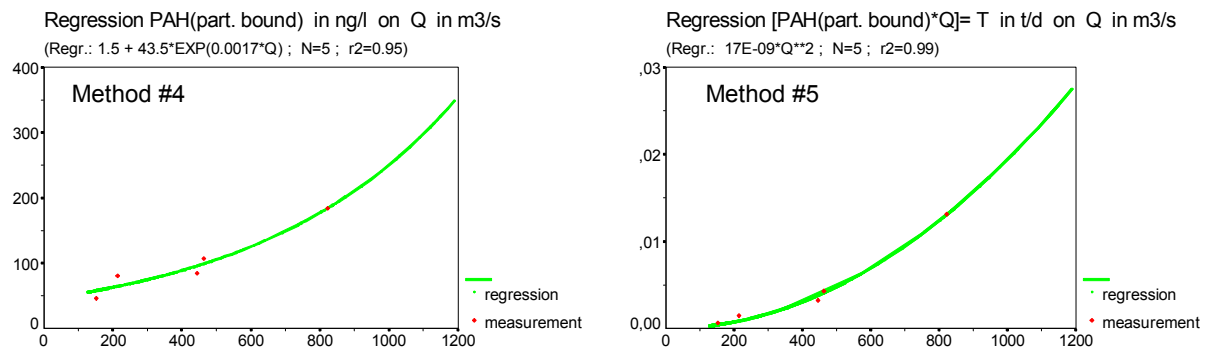


Fig. 4.56: Representation of the regressions  $\text{PAH}_{\text{SS}}(Q)$  and  $T(Q)$ , with  $T=\text{PAK}_{\text{SS}} \cdot Q$  (cf. presentation of the methods #4 and #5 in Chapter 4.1.7.1).

Figure 4.57 shows the annual dissolved PAH load in the order of magnitude of 0.19 t per year with a uniform result of all calculation methods except method #2, which again gives load values more than 50 % higher.

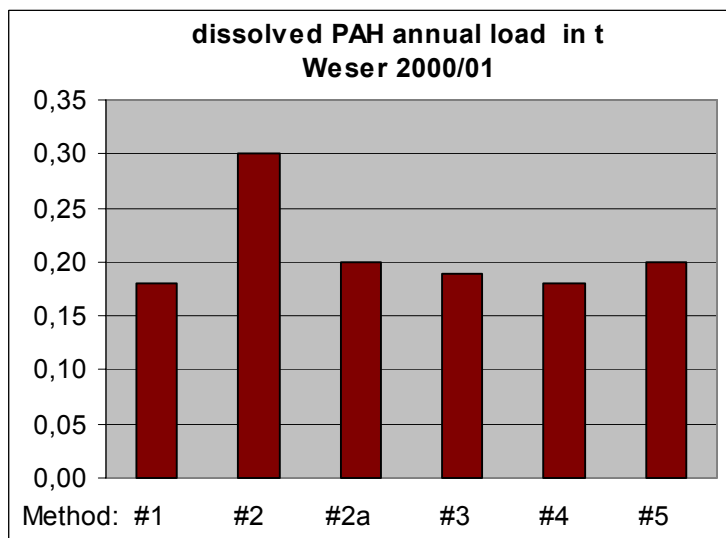


Fig. 4.57: Annual dissolved PAH load in the Weser at Bremen (km 359.9) in the study period 03/00 - 03/01, computed by six different mathematical methods.

As suspended solids do not play any role in the case of the dissolved load, the seasonal course of the transport rates reflects in the first line the streamflow regime (compare Figure 4.58 with Figure 4.43 in Chapter 4.2.3.2). The regressions for methods #4 and #5 are shown in Figure 4.59.

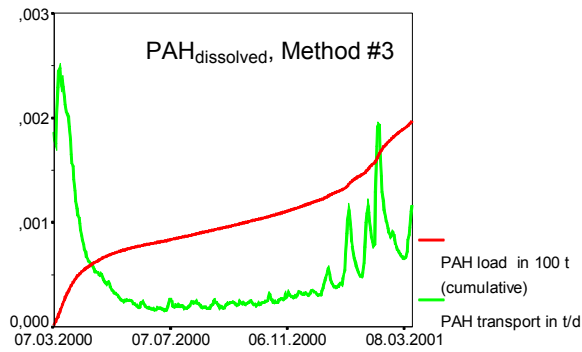


Fig. 4.58: Dissolved PAH load in 100 t (red curve) as cumulative sum over the daily transport rates in t/d (green curve). The cumulation over one year corresponds to the annual load given in Figure 4.57 for the respective calculation methods.

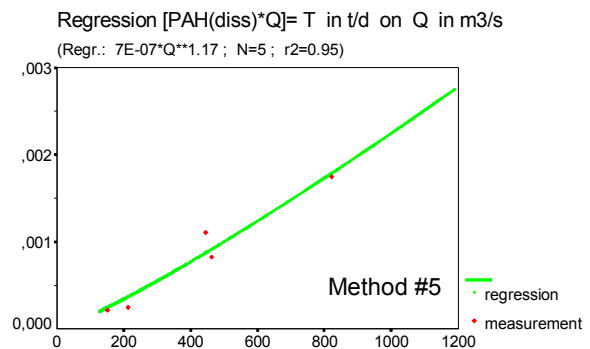
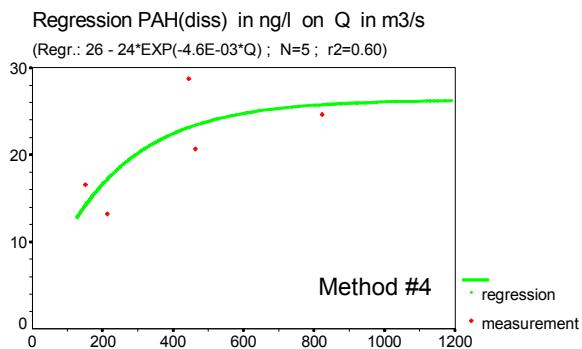
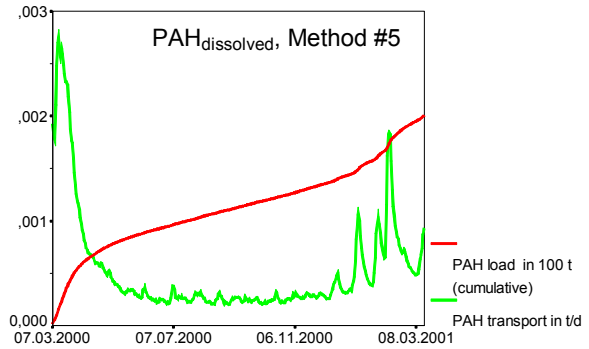
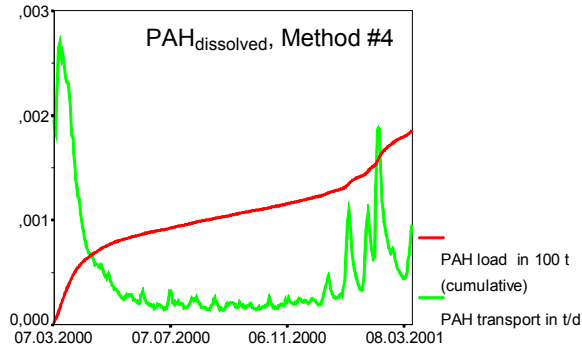


Fig. 4.59: Representation of the regressions  $\text{PAH}_{\text{dissolved}}(Q)$  and  $T(Q)$ , with  $T = \text{PAH}_{\text{dissolved}} \cdot Q$  (cf. presentation of the methods #4 and #5 in Chapter 4.1.7.1).

Regarding the balance, one can note for the Weser, too, that the total PAH load estimated is about 35% higher than the sum of particle-bound plus dissolved loads ( $1.6\text{ t}$  against  $1\text{ t} + 0.2\text{ t} = 1.2\text{ t}$ ). For interpretation and assessment of these results see the closing commentaries in Chapter 4.1.7.3.

#### ***4.2.6.4 Assessment of calculation methods***

In the load calculations (suspended solids and PAHs) the methods employed yielded comparable results on the Elbe and the Weser. The only exception was method #2 that produces especially for PAH loads in the Weser much too high values. With view to the results on the rivers Elbe and Weser alone, the methods #1 and #2a-#5 appear equally valid. The following argumentation tries to find further differentiations and preferences for certain methods.

Method #1 is a very rough approximation, which yields reliable estimates only if one of the factors  $c$  or  $Q$  is constant. In the case of PAH loads ( $c$  = PAH concentrations),  $c$  is in fact relatively constant, what is, however, not necessarily the case with other parameters. That is why method #1 should be rejected for computations of suspended-solids and PAH loads, the more as sufficient alternatives are available.

Method #2 cannot be recommended for the reasons mentioned above (frequently deviating results). Moreover, this method can be easily improved by harnessing the information on daily streamflow, what in the simplest case leads to method #2a.

Method #2a is the method recommended by the OSPAR Convention in the RID Principles [INPUT, 2000b]. Like in the methods #1 and #3-5, the daily streamflow data are included in the computation.

Method #3 has - just like methods #4 and #5 - the advantage that during the computation the daily transport rates are available. This additional information about the transport rates opens more possibilities for interpretation, as the examples of the rivers Elbe and Weser show.

As mentioned in the presentation of the methods in Chapter 4.1.7.1, the two regression methods (#4 and #5) have the drawback that the streamflow values  $Q(t_i)$  associated with the times of sampling  $t_i$  do usually not cover the whole streamflow spectrum of the respective year. This may cause large errors in the evaluation of the regression function in the extrapolation range not supported by data. For the transport rates this has the consequence that single peaks are smoothed by the regression and are not reflected adequately. Moreover, the examples of the Elbe and the Weser showed that the regressions are often not sounded. This led to sometimes extreme regression parameters (artefacts) and simultaneously very small regression coefficients ( $r^2$ ).

On the basis of these arguments, the methods #2a and #3 can be recommended for the computation of suspended-solids and PAH loads. The method #2a is favoured by the fact that it is an accepted and generally practiced method. Conversely, method #3 has the advantage that with the daily transport rates it yields additional valuable information.

The load estimates in the five other European rivers are accordingly be made by means of methods #2a and #3 and the results are presented together with those of the rivers Elbe and Weser in the common part of the report.

## References

ARGE Elbe, 1998. Verteilung von organischen Kontaminanten zwischen wässriger und partikulärer Phase in der Elbe und der Deutschen Bucht. Arbeitsgemeinschaft für die Reinhaltung der Elbe, Hamburg.

ARGE Elbe, 2001. Wassergütedaten der Elbe. Zahlentafel 1999. Arbeitsgemeinschaft für die Reinhaltung der Elbe, Hamburg.

ARGE Weser, 2000. Wesergütebericht 1999. Wassergütestelle Weser im NLÖ, Hildesheim.

EPA, 1984. U.S. Environmental Protection Agency: Method 610 – Polynuclear Aromatic Hydrocarbons. 40 CFR Part 136, 43 344; Federal Register 49, No. 209.

Harting H, 2000. Untersuchung der Einsatzmöglichkeiten des Schwebstoffsammlers BISAM zur repräsentativen Gewinnung von Schwebstoffen in Geesthacht/Elbe. Bundesanstalt für Gewässerkunde. Diplomarbeit an der Fachhochschule für Technik und Wirtschaft, Berlin.

INPUT, 2000a. Meeting of the working group on inputs to the marine environment – Summary Record. INPUT 00/16/1-E. Lisbon: 17-21 January 2000.

INPUT, 2000b. The Comprehensive Study on Riverine Inputs – (RID) Principles. INPUT 00/7/Info.1-E. Lisbon: 17-21 January 2000.

Keller M, Hilden M, Joost M, 1997. Vergleich von Schätzmethoden für jährliche Stofffrachten am Beispiel des IKS-R-Meßprogrammes 1995. BfG-1078.

Knauth HD, Gandraß J, Sturm R, 1993. Vorkommen und Verhalten organischer und anorganischer Mikroverunreinigungen in der mittleren und unteren Elbe. GKSS. Forschungsbericht des BMU Nr. 102 04 363. UBA-FB 93-122.

Kumata H, Masuda K, Yamada J, Takada H, 2000. Water-particle distribution of hydrophobic micro pollutants in storm water runoff. Polycyclic Aromatic Compounds 20 (1-4): 39-54.

LAWA, 2002. Ermittlung von Stofffrachten in Fließgewässern. Probenahmestrategien und Berechnungsverfahren. Länderarbeitsgemeinschaft Wasser (LAWA), in press.

Reinemann L, Schemmer H, 1994. Neuartige Schwebstoffsammler zur Gewinnung von Schwebstoffen aus fließenden Gewässern. DGM 38 (4/5): 22-25.

Steinebach G, 1994. Zur Ermittlung von jährlichen Stofffrachten in großen Fließgewässern am Beispiel der IKS-R-Zahlentafeln 1991. BfG-0827.

UBA, 1999. Pilot study to elaborate a harmonised method for the determination of water-based inputs of polycyclic aromatic hydrocarbons (PAHs) into the North Sea. Federal Institute for Hydrology Koblenz and Berlin, Berlin Dept., on behalf of the Federal Environmental Agency (UBA). Research project water, report 297 22 529.

**OSPAR: Pilot study on Inputs of PAHs to the  
maritime area via rivers**

**Final Report: Individual part**

**Measuring programme, Sampling method,  
Analytical methods, Quality Assurance and  
Results**

**Contracting Party: The Netherlands**

PAH Pilot Study  
Lelystad, November 29th 2001  
RIZA, Karin de Beer

**Annex 5** to the Final Report of the

**International Pilot Study for the determination of Riverine Inputs  
of Polycyclic Aromatic Hydrocarbons (PAHs) to the Maritime Area  
on the basis of a harmonised methodology**

## **1. DESCRIPTION OF THE MEASURING PROGRAMME**

According to the meeting held in Berlin (Workshop on PAH Inputs, 18-19 April 2000), the selected sampling points in The Netherlands for the Pilot Study on Inputs of PAHs are located in the delta of the rivers Rhine and Meuse.

For the river Meuse, Haringvlietsluis is selected as sampling point (X coordinate: 63.400, Y coordinate 427.600 RD or 51°49'46,10" N - 04°03'29,98" E, coordinates in WGS84) The sampling station is located in the Haringvliet, upstream of the locks (Haringvlietsluizen).

For the river Rhine, Maassluis is selected as sampling point (X coordinate 77.700, Y coordinate 435.720 RD or 51°54'19,50" N - 04°15'50,12" E coordinates in WGS84). Maassluis is located in the Rotterdam Waterway in the tidal area of the river Rhine.

Both sampling points are part of the regular monitoring program of RIZA. Samples were collected during the ebb current in the fresh water part, to avoid that sampling takes place in the incoming sea water. Samples are taken at a depth of 1 meter. Maps of the sampling site are given in chapter 4.2.5 and 4.2.6 of the common part of this report.

The sampling sites are considered as representative. This was studied in 1993 in an optimisation study of the Dutch monitoring program by RIZA. Maassluis and Haringvlietsluis are within the regular monitoring program both important locations for calculating the loads of riverine loads to the North-Sea. Data of Maassluis are exchanged within the international commission for the protection of the Rhine (IRC), data of Haringvlietsluis are exchanged within the international commission for the protection of the Meuse.

Sampling was carried out for a year (from January to December 2000). Determination of the 16 PAHs according to the EPA list is only carried out in Maassluis in the suspended solids. In Haringvlietsluis samples and in total water samples (not filtered) only 12 of the 16 EPA PAHs are determined. Naphtalene, Acenaphtene, Acenaphthylene and Fluorene are not analysed. In water samples in Haringvlietsluis and Maassluis Naphtalene is determined additional [see table 1].

Table 1: Monitoring program in 2000

|                             | Parameter           | Rhine<br>Maassluis | Meuse<br>Haringvlietsluis |
|-----------------------------|---------------------|--------------------|---------------------------|
| <b>Suspended<br/>solids</b> | PAH (16)            | 26/year *          | -                         |
|                             | PAH (12)            | 26/year**          | 13/year**                 |
|                             | % organic<br>carbon | 26/year            | 13/year                   |
|                             | % <,> 63 µm         | 13/year            | -                         |
|                             | % <,> 16 µm         | 26/year            | 13/year                   |
|                             |                     |                    |                           |
| <b>Water</b>                | PAH (12)            | -                  | 13/year *                 |
|                             | Naphthalene         | 26/year***         | 13/year***                |
|                             | Suspend solids      | 26/year            | 16/year                   |
|                             | Discharge           | daily (calc.)      | daily (calc.)             |

\*.: Analysed at commercial laboratory by HPLC-Flu/UV

\*\*.: Analysed at the RIZA laboratory by HPLC-Flu

\*\*\*.: Analysed at the RIZA laboratory by GC-MS



## **2. SAMPLING METHOD**

The sampling was carried out only during low tide to prevent sampling incoming sea-water instead of the river water.

Sampling is carried out according to internal procedures (Directorate-General for Public Works and Water Management).

Sampling the water samples (procedure 913.00.W002)

- Sampling from a measuring ship
- Samples 50-100 cm under the water surface
- Sampling with a plunger membrane pump
- Inlet orientated to the flow direction of the water
- Water will be pumped to the centrifuge with a minimal velocity of 1.5 m/s
- Water will be mixed homogeneously and bottles are filled.
- Samples are cooled (1-5 °C) and transported to the laboratory for analysis

Sampling the suspended solids (procedure 913.00.W005)

- Sampling from a measuring ship
- Samples 50-100 cm under the water surface
- Sampling with two parallel positioned flow-through centrifuges in combination with a pump
- Inlet orientated to the flow direction of the water
- Water will be pumped to the centrifuge with a minimal velocity of 1.5 m/s
- Suspended particle matter gathered and kept in a glass jar (1-5 °C) and transported to the laboratory for analysis

### **3. ANALYTICAL METHODS**

#### **3.1 Determination of suspended matter concentration in water (ZS, mg/l)**

Method: N6484, Filtration/gravimetric determination

Laboratory: Commercial laboratory, OMEGAM

#### **3.2 Particle size distribution of the suspended solids (%KGF63, %KGF16, %)**

Method: W1445, Sedigraph (X-ray diffraction), conform NEN 5753

The freeze-dried sample is treated with peroxide to oxidise the organic content. Subsequently the sample is treated with HCl to remove the carbonates. The residue is freeze-dried and resuspended in a solvent in which a peptised device is added. The particle-size distribution is subsequently analysed with the Sedigraph 5100

Laboratory: RIZA, IMLA

#### **3.2 Determination of organic carbon content (%OC,%)**

Method: W1415, GC determination by elementary analysis, conform NEN 5756

Laboratory: RIZA, IMLA

#### **3.3 Determination of PAHs**

The concentration of PAHs was determined in **suspended solids** and in **water (total sample)** using HPLC with Fluorescence or UV detection. Naphtalene in water is determined with GC-MS

##### Water

##### *Naphthalene*

Method: W6016, GC-MS analysis of volatile compounds, related to NEN 6407

Purge and Trap injection combined with GC-MS. Volatile compounds are purged with a gasflow from the water phase into a Tenax column. Subsequently this will be heated quickly and the absorbed compounds are led into the GC-column. After separation compounds are detected with MS.

Laboratory: RIZA, IMLO

##### *12 of the 16 EPA PAHs*

Method: W5353, HPLC-UV/Flu

Laboratory: Commercial laboratory, OMEGAM

##### Suspended solids

##### *16 EPA PAHs*

Method: W5352, HPLC-UV/Flu

Laboratory: Commercial laboratory, OMEGAM

##### *12 of the 16 EPA PAHs*

Method: W5352, HPLC-Flu

Extraction of PAHs is carried out with the Accelerated Solvent Extractor. The extraction solvent is dichloromethane/acetone (1/1). After extraction an aliquot is dissolved in acetonitrile and analysed at the HPLC with fluorescence detection. Separation is obtained with a Vydac 201 TP5 column.

Laboratory: RIZA, IMLO

## **4. QUALITY ASSURANCE**

### **4.1 Determination of suspended matter concentration in water (ZS, mg/l)**

Inter-laboratory research

### **4.2 Particle size distribution of the suspended solids (%KGF63, %KGF16, %)**

Validation with reference materials

Second-line quality assurance

Inter-laboratory research of RIZA and ISE

### **4.3 Determination of organic carbon content (%OC,%)**

Validation with reference materials

Second-line quality assurance

Inter-laboratory research of RIZA and ISE

### **4.4 Determination of PAHs**

#### Water

*Naphtalene (W6016)*

Second-line quality assurance, 3 times/year by IMLK

Inter-laboratory research of RIZA

*12 of the 16 EPA PAHs (W8140 5.353)*

Sterlab accreditation for this analysis, Inter-laboratory research

#### Suspended solids

*16 EPA PAHs (W5352, OMEGAM))*

Inter-laboratory research

*12 of the 16 EPA PAHs (W5352, RIZA, IMLO)*

First-line quality assurance with reference materials.

Second-line quality assurance, 3 times/year by IMLK

Inter-laboratory research of RIZA (3 times/year) and SETOC (4 times/year)

## 5. RESULTS MANDATORY PARAMETERS

In this paragraph the results of the mandatory parameters are given as temporal mean values (minimum, first quartile, median, third quartile, maximum) of the individual parameters.

Tabel 2: Results of river Rhine (Maassluis)

|                     | MIN   | P25   | MED   | P75   | MAX   | N   |
|---------------------|-------|-------|-------|-------|-------|-----|
| Q in m3/s           | -391  | 1180  | 1439  | 1702  | 3402  | 366 |
| CSS in g/m3         | 10    | 15    | 18    | 23    | 68    | 26  |
| Corg in %           | 2,3   | 3,5   | 3,9   | 4,2   | 5,2   | 26  |
| C<63 in %           | 49,5  | 65,4  | 67,6  | 71,0  | 81,7  | 26  |
| ANAPH in mg/kg DWT  | <0,05 | <0,05 | <0,05 | <0,05 | <0,96 | 25  |
| ANAPT in mg/kg DWT  | <0,05 | <0,05 | 0,09  | 0,21  | 0,29  | 25  |
| ANTHR in mg/kg DWT  | 0,10  | 0,15  | 0,19  | 0,24  | 0,28  | 26  |
| BENGHI in mg/kg DWT | 0,20  | 0,30  | 0,33  | 0,38  | 0,45  | 26  |
| BENZAA in mg/kg DWT | 0,22  | 0,31  | 0,32  | 0,37  | 0,51  | 26  |
| BENZAP in mg/kg DWT | 0,26  | 0,34  | 0,36  | 0,40  | 0,53  | 26  |
| BENZBF in mg/kg DWT | 0,32  | 0,38  | 0,44  | 0,51  | 0,66  | 26  |
| BENZKF in mg/kg DWT | 0,15  | 0,19  | 0,22  | 0,23  | 0,31  | 26  |
| CHRYSE in mg/kg DWT | 0,28  | 0,37  | 0,41  | 0,44  | 0,64  | 26  |
| DIBENA in mg/kg DWT | 0,04  | 0,05  | 0,05  | 0,06  | 0,08  | 26  |
| FLANTH in mg/kg DWT | 0,46  | 0,67  | 0,73  | 0,79  | 1,08  | 26  |
| FLUOR in mg/kg DWT  | <0,05 | <0,06 | 0,08  | 0,11  | 0,22  | 25  |
| INDENO in mg/kg DWT | 0,25  | 0,29  | 0,33  | 0,38  | 0,50  | 26  |
| NAPHT in mg/kg DWT  | <0,05 | 0,06  | 0,11  | 0,15  | <0,37 | 25  |
| PHEN in mg/kg DWT   | 0,26  | 0,43  | 0,50  | 0,56  | 0,81  | 26  |
| PYREN in mg/kg DWT  | 0,40  | 0,51  | 0,59  | 0,70  | 1,10  | 26  |
| NAPHT in µg/m³      | <10   | <10   | <10   | <10   | 20    | 10  |

Tabel 3: Results of river Meuse (Haringvlietsluis)

|                     | MIN  | P25  | MED  | P75  | MAX  | N   |
|---------------------|------|------|------|------|------|-----|
| Q in m3/s           | 49   | 277  | 522  | 995  | 4301 | 366 |
| CSS in g/m3         | 4    | 7,1  | 8,5  | 14,5 | 27   | 16  |
| Corg in %           | 3,6  | 4,1  | 4,4  | 8,1  | 13,1 | 13  |
| ANTHR in mg/kg DWT  | 0,12 | 0,17 | 0,19 | 0,21 | 0,27 | 13  |
| BENGHI in mg/kg DWT | 0,34 | 0,42 | 0,52 | 0,55 | 0,60 | 13  |
| BENZAA in mg/kg DWT | 0,25 | 0,31 | 0,41 | 0,47 | 0,52 | 13  |
| BENZAP in mg/kg DWT | 0,28 | 0,39 | 0,50 | 0,59 | 0,62 | 13  |
| BENZBF in mg/kg DWT | 0,40 | 0,54 | 0,59 | 0,76 | 0,81 | 13  |
| BENZKF in mg/kg DWT | 0,20 | 0,26 | 0,30 | 0,34 | 0,37 | 13  |
| CHRYSE in mg/kg DWT | 0,33 | 0,40 | 0,52 | 0,61 | 0,66 | 13  |
| DIBENA in mg/kg DWT | 0,05 | 0,07 | 0,08 | 0,09 | 0,10 | 13  |
| FLANTH in mg/kg DWT | 0,62 | 0,71 | 0,97 | 1,03 | 1,23 | 13  |
| INDENO in mg/kg DWT | 0,29 | 0,46 | 0,50 | 0,53 | 0,66 | 13  |
| PHEN in mg/kg DWT   | 0,37 | 0,52 | 0,55 | 0,61 | 0,74 | 13  |
| PYREN in mg/kg DWT  | 0,43 | 0,61 | 0,70 | 0,87 | 1,00 | 13  |
| NAPHT in µg/m³      | <10  | <10  | <10  | <10  | 20   | 10  |

**OSPAR: Pilot study on Inputs of PAHs to the maritime area via  
rivers**

**Final Report: Individual part**

**I - Measuring programme, Sampling method, Analytical methods,  
Quality Assurance**

**Contracting Party: SPAIN**

**Barcelona, November 27<sup>nd</sup> 2001**

**Carles Planas**

**Dr. Josep Caixach**

**Annex 6** to the Final Report of the

**International Pilot Study for the determination of Riverine Inputs  
of Polycyclic Aromatic Hydrocarbons (PAHs) to the Maritime Area  
on the basis of a harmonised methodology**

## **1. DESCRIPTION OF THE MEASURING PROGRAMME**

According to the OSPAR meeting held in Berlin (18-19 April 2000), the selected sampling point in Spain for the Pilot Study on Inputs of PAHs was situated in the Guadalquivir river (SW of Spain). The sampling site was the sportive river port of Gelves, 6 km downstream of Sevilla, in the tidal reach of the river\*. Samples were collected during low tide in the middle of the river, at a depth of 0.5 m. More details about the sampling site are given in the enclosed map.

Each month, a sample (12 L of water) was collected for the determination of suspended matter concentration ( $C_{ss}$ , g/m<sup>3</sup>), particle size distribution ( $C_{<60\mu m}$ ,  $C_{>60\mu m}$ , %), organic carbon content ( $C_{oc}$ , %) and contaminant concentration in both; particulate ( $C_{PAH}$ , mg/kg dry weight) and filtered water ( $C_{PAH}$ , mg/m<sup>3</sup>).

Furthermore, a biweekly sampling (2 L of water) was carried out in order to determine suspended matter concentration ( $C_{ss}$ , g/m<sup>3</sup>) and particle size distribution ( $C_{<60\mu m}$ ,  $C_{>60\mu m}$ , %).

Sampling was carried out for a year (from June 2000 to May 2001). Discharges ( $Q$ , m<sup>3</sup>/s) were determined in the moment of every sampling (biweekly). Determination of PAHs is carried out for the 16 PAHs according to the EPA list plus benzo[e]pyrene and perylene (18 compounds).

\* The sampling site was recommended by the „Confederación Hidrográfica del Guadalquivir“ (Riverine Basin Administration)

## **2. SAMPLING METHOD**

Sampling was carried out using teflon capped dark glass bottles of 2.5L. When pouring, sampling was done 2 or 3 days after the event.

**Phase separation** was performed by filtration using two tared glass-microfiber filters, 110 mm diameter, 0.7 µm nominal pore size (Whatman Inc., Clifton, N.J., GF/F grade, No 1825 110). Filters were rinsed and conditioned with 20 mL of Milli-Q water and 100 mL of sample. The rinse water was discarded. 5 L of sample was passed through each filter (10 L total volume), collecting the filtrate in 5 L amber glass bottles\*. Filters with the particulate were dried at room temperature during 24 h. PAHs were analysed in the **solid phase (particulate)** and in the **filtered water**.

\* USGS. National Field Manual for the Collection of Water-Quality Data. Edited by F.D. Wilde, D.B. Radtke, J. Gibbs and R.T. Iwatsubo. pp. 36-74

### **3. ANALYTICAL METHODS**

#### **3.1 Determination of suspended matter concentration ( $C_{ss}$ , g/m<sup>3</sup>) and particle size distribution ( $C_{<60\mu m}$ , $C_{>60\mu m}$ , %)**

2 L of sample were successively passed through a tared **nylon filter**, 120 mm diameter, **60  $\mu m$**  nominal pore size (Millipore, ref. NY60 000 10), and through a tared **microfiber filter**, 110 mm diameter, **0.7  $\mu m$**  nominal pore size (Whatman Inc., Clifton, N.J., GF/F grade, No 1825 110). Both filters were dried at 103-105°C and weighted. Suspended matter concentration and particle size distribution were calculated.

Suspended matter concentration:

$$C_{ss} \text{ (g/m}^3\text{)} = \text{Total weight of particulate in both filters (g)} / \text{Volume of sample (m}^3\text{)}$$

Particle size distribution:

$$C_{>60\mu m} \text{ (%) } = \text{Weight of particulate in the 60 } \mu m \text{ filter (g)} / \text{Total weight of particulate in both filters (g)}$$

$$C_{<60\mu m} \text{ (%) } = \text{Weight of particulate in the 0.7 } \mu m \text{ filter (g)} / \text{Total weight of particulate in both filters (g)}$$

#### **3.2 Determination of organic carbon content ( $C_{oc}$ , %)**

Several drops of 10% hydrochloric acid were added to a small part of the dry particulate (see 2. Sampling method) to eliminate the carbonates. The particulate was dried at 70°C during 24 h.

Organic carbon content was determined in the particulate free of carbonates using a EA 1108-Elemental Analyzer (Thermo Instruments).

#### **3.3 Determination of PAHs**

The concentration of PAHs was determined in **particulate** and in **filtered water** using isotope dilution HRGC/MS.

##### **3.3.1 Instrumentation**

The analyses were carried out on an integrated system GC/MS MD800 (Thermo, Manchester, U.K.), which consists on a Quadrupolar Analyser coupled to a Gas Chromatograph GC-8000.

Data were processed with Masslab software, which includes the spectra libraries Wiley 6 (229119 spectra) and NIST 98 (129136 spectra).



### 3.3.2 Analysis of particulate

The procedure was based on method 8270C from U.S.E.P.A.

5 labelled PAHs (*d*-PAHs) were added as internal standards to the dry particulate, which was extracted by sonication with dichloromethane. After a clean-up using silica deactivated with 5% of water and concentration, anthracene-*d*<sub>10</sub> was added to the extract as recovery standard. Finally, the extract was analysed by HRGC/MS in the SCAN mode. Instrumental conditions were optimized to obtain method detection limits of 1-5 ng/g.

### 3.3.3 Analysis of filtered water

The analysis was based on method 1625 from U.S.E.P.A.

5 *d*-PAHs were added to 1.5 L of filtered water as internal standards. Liquid-liquid extraction was carried out using dichloromethane as extraction solvent. After concentration and addition of anthracene-*d*<sub>10</sub> as recovery standard, the extract was analysed by HRGC/MS in the SCAN mode. Instrumental conditions were optimized to obtain method detection limits of 0.1-0.5 ng/L.

### 3.3.4 Quantification

Quantitative analysis was carried out with the molecular ion of each compound (M), using the relative responses of PAHs related to the respective internal standard (*d*-PAHs). The ions M+1 or M-1 were used as confirmation masses. Quantification masses of PAHs and *d*-PAHs are shown in the next table.

| COMPOUND                | LISTS OF PRIORITY POLLUTANTS | QUANTIFICATION MASS* (m/z) | INTERNAL STANDARD                      |
|-------------------------|------------------------------|----------------------------|----------------------------------------|
| Naphtahlene             | U.S.E.P.A.                   | 128                        | Naphthalene-d <sub>8</sub> (m/z=136)   |
| Acenaphthylene          | U.S.E.P.A.                   | 152                        | Acenaphthene-d <sub>10</sub> (m/z=162) |
| Acenaphthene            | U.S.E.P.A.                   | 153                        |                                        |
| Fluorene                | U.S.E.P.A.                   | 165                        |                                        |
| Phenanthrene            | U.S.E.P.A.                   | 178                        | Phenanthrene-d <sub>10</sub> (m/z=188) |
| Anthracene              | U.S.E.P.A.                   | 178                        |                                        |
| Fluoranthene            | U.S.E.P.A./U.E.              | 202                        |                                        |
| Pyrene                  | U.S.E.P.A.                   | 202                        |                                        |
| Benzo[a]anthracene      | U.S.E.P.A.                   | 228                        | Chrysene-d <sub>12</sub> (m/z=240)     |
| Chrysene                | U.S.E.P.A.                   | 228                        |                                        |
| Benzo[b]fluoranthene    | U.S.E.P.A./U.E.              | 252                        | Perylene-d <sub>12</sub> (m/z=264)     |
| Benzo[k]fluoranthene    | U.S.E.P.A./U.E.              | 252                        |                                        |
| Benzo[e]pyrene          | -                            | 252                        |                                        |
| Benzo[a]pyrene          | U.S.E.P.A./U.E.              | 252                        |                                        |
| Perylene                | -                            | 252                        |                                        |
| Indeno[1,2,3-c,d]pyrene | U.S.E.P.A./U.E.              | 276                        |                                        |
| Dibenzo[ah]anthracene   | U.S.E.P.A.                   | 278                        |                                        |
| Benzo[ghi]perylene      | U.S.E.P.A./U.E.              | 276                        |                                        |

## QUALITY ASSURANCE

Quality of determinations was assessed by different ways. Firstly, **recoveries of internal standards** (*d*-PAHs) were calculated in each analysed sample. Furthermore, the **linearity range**, the **method detection limit** and the **method quantification limit** of each PAH were determined. Finally, PAHs were analysed in **certified reference materials** and in samples from **interlaboratorium studies**.

### 4.1 Recoveries of internal standards

As an example, recoveries of *d*-PAHs related to the first 3 samples analysed are shown in the next table.

### 4.2 Linearity range of PAHs

| COMPOUND                     | RECOVERY (%)     |         |         |                |         |         |
|------------------------------|------------------|---------|---------|----------------|---------|---------|
|                              | Suspended Matter |         |         | Filtered Water |         |         |
|                              | 1.06.00          | 1.07.00 | 4.09.00 | 1.06.00        | 1.07.00 | 4.09.00 |
| Naphthalene-d <sub>8</sub>   | 89.3             | 51.8    | 64.9    | 90.3           | 71.7    | 77.5    |
| Acenaphthene-d <sub>10</sub> | 84.8             | 58.0    | 70.9    | 72.3           | 82.6    | 84.4    |
| Phenanthrene-d <sub>10</sub> | 95.4             | 77.0    | 79.1    | 80.9           | 99.9    | 93.3    |
| Chrysene-d <sub>12</sub>     | 46.8             | 98.8    | 92.7    | 42.5           | 108.0   | 75.2    |
| Perylene-d <sub>12</sub>     | 48.8             | 90.0    | 83.2    | 58.8           | 91.9    | 63.1    |

Solutions containing 0, 0.1, 0.5, 1, 5 and 10 ng/μL of PAHs and 1 ng/μL of *d*-PAHs were analysed by HRGC/MS in the SCAN mode (injection of 1 μL). Relative response of PAHs related to the amount injected (ng) were represented and regression coefficients (*r*) were calculated.

The linearity range was 0-5 ng injected for indeno[123-cd]pyrene, dibenzo[ah]anthracene and benzo[ghi]perylene, and 0-10 ng injected for the rest of the compounds.

These intervals enclose the range of PAH concentrations found in the samples analysed during the measuring programme (particulate and filtered water).

#### **4.3 Method detection limit (MDL) and method quantification limit (MQL)**

**MDL:** 3 times the standard deviation of the noise

**MQL:** 10 times the standard deviation of the noise

Both parameters were calculated in real samples

| ❏<br>COMPOUND           | Suspended Matter<br>(ng/g) |     | Filtered Water ❏<br>(ng/L) |     |
|-------------------------|----------------------------|-----|----------------------------|-----|
|                         | MDL                        | MQL | MDL                        | MQL |
| Naphthalene             | 2                          | 5   | 0.2                        | 0.7 |
| Acenaphthylene          | 1                          | 2   | 0.3                        | 1.0 |
| Acenaphthene            | 1                          | 3   | 0.2                        | 0.6 |
| Fluorene                | 3                          | 9   | 0.2                        | 0.4 |
| Phenanthrene            | 1                          | 3   | 0.2                        | 0.6 |
| Anthracene              | 1                          | 2   | 0.3                        | 1.0 |
| Fluoranthene            | 3                          | 9   | 0.2                        | 0.5 |
| Pyrene                  | 3                          | 9   | 0.2                        | 0.5 |
| Benzo[a]anthracene      | 1                          | 2   | 0.6                        | 2.0 |
| Chrysene                | 1                          | 3   | 0.8                        | 2.5 |
| Benzo[b]fluoranthene    | 2                          | 5   | 0.1                        | 0.3 |
| Benzo[k]fluoranthene    | 2                          | 5   | 0.1                        | 0.3 |
| Benzo[e]pyrene          | 1                          | 3   | 0.2                        | 0.5 |
| Benzo[a]pyrene          | 1                          | 3   | 0.2                        | 0.5 |
| Perylene                | 1                          | 3   | 0.1                        | 0.3 |
| Indeno[1,2,3-c,d]pyrene | 3                          | 8   | 0.5                        | 1.7 |
| Dibenzo[ah]anthracene   | 5                          | 14  | 1.2                        | 3.8 |
| Benzo[ghi]perylene      | 5                          | 15  | 0.8                        | 2.6 |

#### **4.4 Analysis of certified reference materials and interlaboratorium studies**

The reliability of PAH determination was periodically assessed by the analysis of certified reference materials:

- \* SRM 1944 (NIST)**

New York/ New Jersey waterway sediment

- \* HS-6 (National Research Council Canada)**

Harbour marine sediment reference material for PAHs

Furthermore, water samples containing PAHs were analysed within a spanish interlaboratorium study (February-March 2001):

- \* CALITAX-LABAQUA. Drinking water B - 2001**

**OSPAR: Pilot study on Inputs of PAHs to the maritime area via  
rivers**

**Final Report: Individual part**

**II - Concentration of PAHs, Parameters  
(Sampling point: Guadalquivir river, SW Spain)**

**Contracting Party: SPAIN**

**Barcelona, November 27<sup>th</sup> 2001**

**Carles Planas**

**Dr. Josep Caixach**

## Concentration of PAHs

### Sampling point: Guadalquivir river in Gelves (Sevilla)

| COMPOUND              | Filtered water<br>(ng/L) |         |         | Suspended Matter<br>(ng/g) |         |         |
|-----------------------|--------------------------|---------|---------|----------------------------|---------|---------|
|                       | 1.06.00                  | 1.07.00 | 4.09.00 | 1.06.00                    | 1.07.00 | 4.09.00 |
| Naphthalene           | < L.D.                   | < L.D.  | < L.D.  | < L.D.                     | < L.D.  | < L.D.  |
| Acenaphthylene        | < L.D.                   | 0.9     | < L.D.  | < L.D.                     | 2       | 3       |
| Acenaphthene          | < L.D.                   | 0.5     | < L.D.  | < L.D.                     | 2       | 6       |
| Fluorene              | 1.8                      | 1.0     | < L.D.  | 8                          | 13      | 19      |
| Phenanthrene          | 2.2                      | 3.6     | 3.0     | 39                         | 77      | 84      |
| Anthracene            | < L.D.                   | < L.D.  | < L.D.  | 1                          | < L.D.  | 3       |
| Fluoranthene          | 2.9                      | 2.0     | 2.1     | 59                         | 32      | 59      |
| Pyrene                | 4.2                      | 2.7     | 2.7     | 56                         | 30      | 48      |
| Benzo[a]anthracene    | < L.D.                   | < L.D.  | < L.D.  | 37                         | 6       | 12      |
| Chrysene              | < L.D.                   | < L.D.  | < L.D.  | 183                        | 18      | 62      |
| Benzo[b]fluoranthene  | < L.D.                   | 0.1     | < L.D.  | 87                         | 11      | 40      |
| Benzo[k]fluoranthene  | < L.D.                   | 0.3     | < L.D.  | 59                         | 9       | 27      |
| Benzo[e]pyrene        | < L.D.                   | 0.3     | < L.D.  | 59                         | 7       | 25      |
| Benzo[a]pyrene        | < L.D.                   | 0.4     | < L.D.  | 20                         | 6       | 14      |
| Perylene              | < L.D.                   | 0.4     | < L.D.  | 51                         | 39      | 43      |
| Indeno[123-cd]pyrene  | < L.D.                   | < L.D.  | < L.D.  | 34                         | 10      | 14      |
| Dibenzo[ah]anthracene | < L.D.                   | < L.D.  | < L.D.  | < L.D.                     | 8       | < L.D.  |
| Benzo[ghi]perylene    | < L.D.                   | < L.D.  | < L.D.  | 67                         | 20      | 30      |
| PAHs*                 | 16.7                     | 16.6    | 13.6    | 769                        | 293     | 496     |

L.D.: Limit of Detection

\* Sum of PAHs includes the Limits of Detection of the compounds not detected

In blue: Compounds from the E.P.A. list

In red: Compounds included in the Directive 75/440/EC

## Concentration of PAHs

Sampling point: Guadalquivir river in Gelves (Sevilla)

| COMPOUND              | Filtered water<br>(ng/L) |          |          | Suspended Matter<br>(ng/g) |          |          |
|-----------------------|--------------------------|----------|----------|----------------------------|----------|----------|
|                       | 16.10.00                 | 31.10.00 | 29.11.00 | 16.10.00                   | 31.10.00 | 29.11.00 |
| Naphthalene           | < L.D.                   | < L.D.   | < L.D.   | < L.D.                     | < L.D.   | < L.D.   |
| Acenaphthylene        | < L.D.                   | 1.6      | < L.D.   | < L.D.                     | < L.D.   | < L.D.   |
| Acenaphthene          | 3.4                      | < L.D.   | 3.0      | < L.D.                     | < L.D.   | < L.D.   |
| Fluorene              | < L.D.                   | < L.D.   | < L.D.   | 20                         | < L.D.   | 58       |
| Phenanthrene          | < L.D.                   | < L.D.   | < L.D.   | 51                         | < L.D.   | 140      |
| Anthracene            | < L.D.                   | 2.2      | < L.D.   | < L.D.                     | 10       | < L.D.   |
| Fluoranthene          | 2.7                      | 10.1     | 2.9      | 49                         | < L.D.   | 70       |
| Pyrene                | 2.4                      | 10.8     | 3.8      | 50                         | < L.D.   | 78       |
| Benzo[a]anthracene    | < L.D.                   | 16.2     | < L.D.   | 20                         | < L.D.   | 29       |
| Chrysene              | < L.D.                   | 14.3     | < L.D.   | 50                         | < L.D.   | 45       |
| Benzo[b]fluoranthene  | < L.D.                   | < L.D.   | < L.D.   | 60                         | < L.D.   | 95       |
| Benzo[k]fluoranthene  | < L.D.                   | < L.D.   | < L.D.   | 37                         | < L.D.   | 74       |
| Benzo[e]pyrene        | < L.D.                   | < L.D.   | < L.D.   | 40                         | < L.D.   | 62       |
| Benzo[a]pyrene        | < L.D.                   | < L.D.   | < L.D.   | 28                         | < L.D.   | 62       |
| Perylene              | < L.D.                   | < L.D.   | < L.D.   | 92                         | 45       | 54       |
| Indeno[123-cd]pyrene  | < L.D.                   | < L.D.   | < L.D.   | < L.D.                     | 34       | 33       |
| Dibenzo[ah]anthracene | < L.D.                   | 10.7     | < L.D.   | < L.D.                     | 27       | 27       |
| Benzo[ghi]perylene    | < L.D.                   | < L.D.   | < L.D.   | < L.D.                     | 49       | 96       |
| PAHs*                 | 14.3                     | 68.7     | 15.5     | 515                        | 187      | 928      |

L.D.: Límit of Detection

\* Sum of PAHs includes the Limits of Detection of the compounds not detected

In blue: Compounds from the E.P.A. list

In red: Compounds included in the Directive 75/440/EC



## Concentration of PAHs

Sampling point: Guadalquivir river in Gelves (Sevilla)

| COMPOUND              | Filtered water<br>(ng/L) |          |          | Suspended Matter<br>(ng/g) |          |          |
|-----------------------|--------------------------|----------|----------|----------------------------|----------|----------|
|                       | 10.01.01                 | 29.01.01 | 27.02.01 | 10.01.01                   | 29.01.01 | 27.02.01 |
| Naphthalene           | < L.D.                   | < L.D.   | < L.D.   | < L.D.                     | < L.D.   | < L.D.   |
| Acenaphthylene        | 8.1                      | < L.D.   | < L.D.   | < L.D.                     | 1        | < L.D.   |
| Acenaphthene          | < L.D.                   | < L.D.   | 2.1      | 4                          | 2        | < L.D.   |
| Fluorene              | 8.0                      | < L.D.   | < L.D.   | 17                         | 6        | 26       |
| Phenanthrene          | 14.8                     | 8.5      | < L.D.   | 51                         | 13       | 159      |
| Anthracene            | 0.9                      | 0.4      | 1.1      | 2                          | 1        | 7        |
| Fluoranthene          | 14.4                     | 4.9      | 5.5      | 72                         | 13       | 59       |
| Pyrene                | 24.5                     | 9.3      | 8.1      | 84                         | 14       | 55       |
| Benzo[a]anthracene    | 2.3                      | < L.D.   | < L.D.   | 13                         | 3        | 6        |
| Chrysene              | 4.3                      | 3.6      | 3.8      | 44                         | 12       | 24       |
| Benzo[b]fluoranthene  | < L.D.                   | < L.D.   | < L.D.   | 92                         | 12       | 41       |
| Benzo[k]fluoranthene  | < L.D.                   | < L.D.   | < L.D.   | 57                         | 9        | 29       |
| Benzo[e]pyrene        | < L.D.                   | < L.D.   | < L.D.   | 61                         | 8        | 29       |
| Benzo[a]pyrene        | < L.D.                   | < L.D.   | < L.D.   | 13                         | 3        | 6        |
| Perylene              | < L.D.                   | < L.D.   | < L.D.   | 21                         | 13       | 49       |
| Indeno[123-cd]pyrene  | < L.D.                   | < L.D.   | < L.D.   | 25                         | 5        | 18       |
| Dibenzo[ah]anthracene | < L.D.                   | < L.D.   | < L.D.   | < L.D.                     | < L.D.   | < L.D.   |
| Benzo[ghi]perylene    | < L.D.                   | < L.D.   | < L.D.   | 39                         | 6        | 23       |
| PAHs*                 | 80.9                     | 31.4     | 25.3     | 603                        | 128      | 540      |

L.D.: Límit of Detection

\* Sum of PAHs includes the Limits of Detection of the compounds not detected

In blue: Compounds from the E.P.A. list

In red: Compounds included in the Directive 75/440/EC

## Concentration of PAHs

Sampling point: Guadalquivir river in Gelves (Sevilla)

| COMPOUND              | Filtered water<br>(ng/L) |         | Suspended Matter<br>(ng/g) |         |
|-----------------------|--------------------------|---------|----------------------------|---------|
|                       | 28.03.01                 | 2.05.01 | 28.03.01                   | 2.05.01 |
| Naphthalene           | < L.D.                   | < L.D.  | < L.D.                     | < L.D.  |
| Acenaphthylene        | < L.D.                   | < L.D.  | 5                          | < L.D.  |
| Acenaphthene          | < L.D.                   | < L.D.  | 6                          | < L.D.  |
| Fluorene              | < L.D.                   | < L.D.  | 43                         | < L.D.  |
| Phenanthrene          | < L.D.                   | < L.D.  | 138                        | 57      |
| Anthracene            | < L.D.                   | < L.D.  | < L.D.                     | < L.D.  |
| Fluoranthene          | 2.7                      | < L.D.  | 119                        | 87      |
| Pyrene                | 3.8                      | < L.D.  | 114                        | 94      |
| Benzo[a]anthracene    | < L.D.                   | < L.D.  | 16                         | 41      |
| Chrysene              | 2.2                      | < L.D.  | 68                         | 68      |
| Benzo[b]fluoranthene  | 2.6                      | 0.4     | 71                         | 70      |
| Benzo[k]fluoranthene  | 1.4                      | 0.3     | 53                         | 62      |
| Benzo[e]pyrene        | 0.7                      | < L.D.  | 49                         | 34      |
| Benzo[a]pyrene        | 0.7                      | < L.D.  | < L.D.                     | 45      |
| Perylene              | 0.3                      | < L.D.  | 40                         | 19      |
| Indeno[123-cd]pyrene  | < L.D.                   | < L.D.  | 17                         | 28      |
| Dibenzo[ah]anthracene | < L.D.                   | < L.D.  | < L.D.                     | 14      |
| Benzo[ghi]perylene    | < L.D.                   | < L.D.  | 17                         | 33      |
| PAHs*                 | 18.9                     | 6.9     | 765                        | 660     |

L.D.: Límit of Detection

\* Sum of PAHs includes the Limits of Detection of the compounds not detected

In blue: Compounds from the E.P.A. list

In red: Compounds included in the Directive 75/440/EC

## PARAMETERS

| SAMPLE   | Q<br>(m <sup>3</sup> /s) | C <sub>ss</sub><br>(g/m <sup>3</sup> ) | C <sub>oc</sub><br>(%) | C <sub>&lt;60µm</sub><br>(%) | C <sub>&gt;60µm</sub><br>(%) | C <sub>PAH,SS</sub><br>(mg/Kg) | C <sub>PAH,W</sub><br>(mg/m <sup>3</sup> ) |
|----------|--------------------------|----------------------------------------|------------------------|------------------------------|------------------------------|--------------------------------|--------------------------------------------|
| 1.06.00  | 43.66                    | 42.1                                   | 2.13                   | 94.3                         | 5.7                          | 0.769                          | 0.0167                                     |
| 15.06.00 | 24.90                    | 40.0                                   | -                      | 99.0                         | 1.0                          | -                              | -                                          |
| 4.07.00  | 49.04                    | 48.7                                   | 2.06                   | 98.2                         | 1.8                          | 0.293                          | 0.0166                                     |
| 18.07.00 | 42.11                    | 38.0                                   | -                      | 98.0                         | 2.0                          | -                              | -                                          |
| 4.09.00  | 35.26                    | 38.0                                   | 2.62                   | 98.4                         | 1.6                          | 0.496                          | 0.0136                                     |
| 19.09.00 | 19.16                    | 38.0                                   | -                      | 97.9                         | 2.1                          | -                              | -                                          |
| 2.10.00  | 5.56                     | 34.5                                   | -                      | 75.1                         | 24.9                         | -                              | -                                          |
| 16.10.00 | 11.77                    | 33.4                                   | 3.86                   | 94.6                         | 5.4                          | 0.515                          | 0.0143                                     |
| 31.10.00 | 8.18                     | 42.7                                   | 3.04                   | 96.0                         | 4.0                          | 0.187                          | 0.0687                                     |
| 15.11.00 | 3.04                     | 35.0                                   | -                      | 95.9                         | 4.1                          | -                              | -                                          |
| 30.11.00 | 21.81                    | 23.7                                   | 2.52                   | 96.8                         | 3.2                          | 0.928                          | 0.0155                                     |
| 13.12.00 | 42.36                    | 90.0                                   | -                      | 99.0                         | 1.0                          | -                              | -                                          |
| 10.01.01 | 234.39                   | 89.5                                   | 0.90                   | 100                          | 0                            | 0.603                          | 0.0809                                     |
| 15.01.01 | 299.21                   | 106.0                                  | -                      | 98.0                         | 2.0                          | -                              | -                                          |
| 29.01.01 | 212.47                   | 1583.0                                 | 0.66                   | 99.9                         | 0.1                          | 0.128                          | 0.0314                                     |
| 14.02.01 | 23.10                    | 124.0                                  | -                      | 99.9                         | 0.1                          | -                              | -                                          |
| 28.02.01 | 19.22                    | 51.2                                   | 1.20                   | 99.9                         | 0.1                          | 0.540                          | 0.0253                                     |
| 15.03.01 | 305.021                  | 155.0                                  | -                      | 99.9                         | 0.1                          | -                              | -                                          |
| 28.03.01 | 190.07                   | 35.9                                   | 1.65                   | 99.0                         | 1.0                          | 0.765                          | 0.0189                                     |
| 18.04.01 | 26.51                    | 22.6                                   | -                      | 95.4                         | 4.6                          | -                              | -                                          |
| 2.05.01  | 38.30                    | 23.5                                   | 4.04                   | 98.0                         | 2.0                          | 0.660                          | 0.0069                                     |
| 16.05.01 | 28.67                    | 24.0                                   | -                      | 98.0                         | 2.0                          | -                              | -                                          |

Q (m<sup>3</sup>/s): Discharge

C<sub>ss</sub> (g/m<sup>3</sup>): Suspended Matter Concentration

C<sub>oc</sub> (%): Organic Carbon Content

C<sub><60µm</sub> (%): Percentaje of particulate below 60µm

C<sub>>60µm</sub> (%): Percentaje of particulate above 60µm

C<sub>PAH,SS</sub> (mg/Kg): Total Concentration of PAHs in particulate

C<sub>PAH,W</sub> (g/m<sup>3</sup>): Total Concentration of PAHs in filtered water