

Temporal Variability of Organic Micropollutants in Suspended Particulate Matter of the River Elbe at Hamburg and the River Mulde at Dessau, Germany

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Abstract. The compound classes of n-alkanes, polycyclic aromatic hydrocarbons (PAHs), and a number of chlorinated hydrocarbons (CHs) in the River Elbe and its tributary Mulde were investigated on the basis of monthly mixed samples of suspended particulate matter (SPM). Covering the period from September 1994 to August 1995, samples from the River Elbe were taken at Hamburg, those from the River Mulde at Dessau. The samples were extracted by supercritical fluid extraction (SFE). Analysis of all substance groups were performed by high-performance liquid chromatography (HPLC), followed by gas chromatography with mass spectrometric detection (GC/MSD). As a statistical approach for the interpretation of data, hierarchical cluster analysis of the individual compound classes were performed to determine differences or similarities between the sampling sites Hamburg and Dessau to find spatial and seasonal concentration patterns. These analysis showed that, with a high significance, the concentration patterns of n-alkanes, PAHs, and CHs were sampling site-specific in both the Elbe and Mulde throughout the entire sampling period. In all cases, clustering of mostly consecutive months indicated continuous, slow changes of input, which moreover showed a constancy with respect to annual cycles. Correlation analysis of pollutant loads with different hydrographic parameters showed a number of linear dependencies of the contaminants with temperature, SPM content, and water discharge. Annual fluxes of particle-bound pollutants were calculated for each sampling site, taking into account the average monthly SPM levels and the water discharge. The particle-bound pollutant loads for the River Elbe at Hamburg were estimated to 13.4 t/a n-alkanes, 4.1 t/a PAHs, and 175.8 kg/a CHs. The pollutant loads for the River Mulde at Dessau amounted 0.55 t/a n-alkanes, 0.14 t/a PAHs, and 15.5 kg/a CHs during the monitoring period. The input of n-alkanes originated from different sources. The n-alkane pattern of samples of the River Elbe showed a predominance of odd-numbered compounds in the range of C-20 and C-30 originating from terrestrial plants and, depending on the season, high concentrations of C-15 and C-17 due to aquatic organisms. Only a small proportion of n-alkane input originated from

petroleum sources. Samples from the River Mulde showed high amounts of the n-alkanes C-12 to C-15, indicating the input of light oil throughout the entire sampling period, constituting approximately 25% of the total n-alkane concentration. PAHs, which are considered combustion products, were widely distributed in all samples. Although the major inputs of PAHs were probably combustion sources and urban runoff, unusually high concentrations were found for some PAHs, which can be explained by point sources. A comparison of the standardized PAH patterns in samples from both stations clearly showed that higher fused ring systems, which mainly originate from combustion processes (four- to six-ring systems), had considerably higher relative concentrations in SPM from the Elbe than from the Mulde, where higher relative concentrations of the two- and three-ring systems were measured. This confirms findings that petroleum input was higher in the Mulde than in the Elbe. Concentrations of chlorinated hydrocarbons in SPM samples from the river Mulde had comparatively high levels. The largest differences were found for p,p'-DDT and its metabolites p,p'-DDD and p,p'-DDE. On average, concentrations of p,p'-DDT, p,p'-DDD, and p,p'-DDE in the Mulde were about 10, 15, and 25 times higher, respectively, than in the Elbe. Concentrations of HCB, which in the samples from Hamburg had the highest concentrations of all CHs, were found to be higher by about a factor of 3 in the Mulde River. The PCB levels in samples from the Mulde and Elbe were about equal, although there were differences in the pattern of PCB congeners.

A large number of environmentally relevant classes of organic compounds are lipophilic and hence have a strong tendency to adsorb at suspended particulate matter and sediments. Such compounds adsorb preferably at the organic and lipophilic components of the particulate phase. Therefore, to describe the quality of aquatic systems, it is common practice to determine concentrations of lipophilic, organic trace substances in suspended particulate matter and sediments. In a number of studies, the adsorption behavior of different micropollutants have been related to chemical/physical properties, *e.g.*, water

solubility, or to n-octanol/water partition coefficients (as log K_{ow}), in order to obtain estimates of the enrichment rates (Schulz-Bull *et al.* 1995; Kayal and Connell 1990). Considering their n-octanol/water partition coefficients, the substance groups of alkanes, PAHs, and the CHs selected for this study belong to the lipophilic compounds (Doucette and Andren 1988; Sangster 1989; Noble 1993).

Alkanes

Aliphatic hydrocarbons represent a class of compounds that are ubiquitously present in the aquatic environment. Sources of n-alkanes are anthropogenic or biogenic inputs. Anthropogenic inputs are mineral oils or their products. Input paths are atmospheric deposition, pollution from shipping, and industrial wastes (NCR 1985). Biogenic inputs may be of terrestrial or marine origin, *e.g.*, vascular plants, animals, and various algae species. Alkanes are also produced by bacteria and are formed in decomposition processes of naturally occurring lipids.

Depending on the alkane pattern, subdivisions can be made with a view to identifying input sources. The most important identification criterion is the ratio of odd- and even-numbered hydrocarbons. Input sources can be characterized by forming the “carbon preference index” (CPI) for n-alkanes $> C-20$. Terrestrial plants show a characteristic predominance of odd-numbered n-alkanes in the range from C-21 to C-35, the maximum being mostly at C-29 or C-31. CPI values equal or greater than 4 thus indicate input of such plant components as an essential source of n-alkanes (Saliot *et al.* 1988). Such patterns are often encountered in rivers, estuaries, or coastal areas.

By contrast, low CPI values of approximately 1 indicate a petroleum source of the n-alkanes because petroleum and petroleum products do not show a predominance of odd-numbered n-alkanes (Saliot 1981; Saliot *et al.* 1988; Lipiatou and Saliot 1991). Depending on the oil’s origin, the maximum is around C-20; that of light oils, *e.g.*, heating oil or diesel fuel, is in the range of C-12 to C-14 (Ladendorf 1962; Sonchik 1983; Binder and Weis 1984).

Aquatic organisms (zooplankton, phytoplankton) have a characteristic predominance of C-15 or C-17 compounds, whereas longer-chain n-alkanes are missing almost completely. In several red and brown algae species, the percentage of C-15 or C-17 amounted to 60 to 99% of all quantified n-alkanes in the C-14 to C-32 range (Clark and Blumer 1967).

Since n-alkanes generally stem from different sources, a clear identification of petrogenic inputs based solely on the pattern of n-alkanes often is not possible. For that reason, PAHs and their alkylated homologues as well as alkenes, alcohols, or hopanes are taken into account as well (BSH 1993). Additional useful indicators proved to be the isoprenoid hydrocarbons pristane (C-19) and phytane (C-20), which have markedly longer degradation rates than unbranched hydrocarbons (Osterroht and Petrick 1982; Steinhauer and Boehm 1992).

PAHs

PAHs are formed in several different processes. Incomplete combustion of organic material leads to the formation of PAHs.

Large areas of the environment are affected by emissions from combustion engines, home heating, power generation from fossil fuels, emissions from industrial activities like aluminium and steel production, and the petroleum and coal industries. PAH enter the aquatic environment through atmospheric deposition, industrial and residential waste waters, oil pollution by ships, or by urban runoff. It is also assumed that some PAHs may be of biogenic origin, *e.g.*, retene, cadalene (Yunker *et al.* 1995), fluorene (LaFlamme and Hites 1978), or perylene (Aizenshtat 1973; Venkatesan 1988). To document changing environmental impacts and locate emission sources, a widely used practice is to examine PAH patterns of selected compounds. To differentiate between inputs from combustion processes and from petroleum sources in aquatic systems, two criteria can be used: PAHs from combustion processes mainly contain thermodynamically more stable, nonalkylated PAHs, whereas petrogenic PAHs are composed primarily of alkylated PAH (LaFlamme and Hites 1978). Thus, the ratio of mono-substituted phenanthrenes to phenanthrene in petroleum ranges between 2 and 6, while PAHs from combustion processes shows values from approximately 0.5 to 1, with concentrations decreasing exponentially in the following sequence: unsubstituted phenanthrene, sums of mono-, di-, and trimethyl-substituted phenanthrenes. Another criterion is the number of fused rings. Petroleum has a strong predominance of one-, two-, and three-ring systems. In analyses of 11 different petroleum types, it was found that PAH concentrations (including monocyclic aromatics) ranges between 7.4 and 34% by weight. Of these total PAHs, the proportion of three- to six-ring systems was only about 3–20%, on average 10%. Monocyclic aromatics, followed by the sums of di- and trimethylnaphthalene, were the predominant components (Neff 1979). PAHs from combustion processes were found to have high proportions of three-ring PAHs (phenanthrene, anthracene), four-ring PAHs (pyrene, fluoranthene), and five-ring PAHs (benzofluoranthenes, benzo-pyrenes). Especially the presence of an alicyclic five-membered ring in the PAH (as given in fluorene and fluoranthene) indicates a pyrolytic source.

As in the case of n-alkanes, it is not always possible to precisely identify a specific source of PAHs because in aquatic environments there are generally many overlapping input sources. Besides, the individual PAHs differ in their rates of adsorption to the particulate phase and in their biodegradability (Cerniglia 1992; Siron *et al.* 1995), so that contaminant patterns in the environment need not be identical with that of the primary sources.

Chlorinated Hydrocarbons

The CHs analyzed in this study include the α - and γ -isomers of hexachlorocyclohexane (HCH); hexachlorobenzene (HCB); DDT and its metabolites, DDD and DDE; as well as the polychlorinated biphenyls (PCBs): PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 105, PCB 138, PCB 1546, and PCB 180.

PCBs are a group of compounds comprising 209 congeners. Owing to their thermal stability, resistance to chemicals, high permittivity, flame-retardant properties, etc., they are widely used as cooling fluids and liquid dielectrics in transformers, plasticizers in varnishes and adhesives, and as hydraulic fluids and heat transfer agents. Since 1929, about 750,000 t of PCBs

have been manufactured worldwide, and it is estimated that by 1970, 30,000 t of PCBs had been released into the atmosphere, 60,000 t into surface water, and 300,000 into the soil. In view of the toxicity or even carcinogenic effect of PCBs, their use was restricted considerably by the EC Directive of 1976 and the 10th Ordinance on the Federal Pollution Control Act of 1978. PCB production in Germany was stopped in 1983.

For decades, DDT was the most important insecticide worldwide; almost 100,000 t of DDT was produced and used in 1963. The main metabolites of DDT are DDD and DDE, of which the latter does not have a pesticide effect. In Germany, the DDT Act came into force in 1972, prohibiting the production, use, import, and export of DDT. The developing countries continue to produce DDT (1984: approximately 30,000 t) because a low-cost alternative for fighting the malaria-transmitting anopheles mosquito is not available presently. Because of their persistence (half-life time estimates range from 10 to 100 years), DDT, like PCBs, today are among the ubiquitous environmental pollutants.

Hexachlorocyclohexanes (HCHs) are formed in the manufacture of the insecticide "lindane" (γ -HCH). A mixture of eight stereoisomers is formed (65–70% α -HCH, 7–10% β -HCH, 14–15% γ -HCH, approximately 7% δ -HCH, 1–2% ϵ -HCH, and 1–2% other compounds). In 1974 to 1978, use of technical HCH in Germany was banned for agricultural, forestry, and veterinary uses.

Objectives of This Study

It was the purpose of this study to investigate the distribution patterns of the substance groups of n-alkanes, PAHs, and a number of low-volatility CHs in suspended particulate matter (SPM) of the River Elbe and its tributary Mulde on the basis of monthly samples. The samples from the River Elbe were taken at Hamburg, those from the Mulde at Dessau, covering the period from September 1994 to August 1995. The measurements were recorded and interpreted under the following aspects:

- Determination of pollutant levels of n-alkanes, PAHs, and CHs based on dry mass (DM) and on the content of total organic carbon (TOC).
- Identification of anthropogenic or biogenic sources of n-alkanes taking into account terrigenous and aquatic inputs.
- Distinction of input sources of PAH between combustion or pyrolytic processes and petroleum sources.
- Calculation of SPM-bound pollutant loads of the Rivers Elbe and Mulde.
- Cluster analysis of substance groups to determine differences/similarities between the sampling sites Hamburg and Dessau in order to find local and seasonal pollution patterns.
- Cluster analysis to determine differences/similarities between single compounds within the individual substance groups, performed separately for the sampling sites Hamburg and Dessau.
- Correlation analysis of pollutants with various hydrographic parameters to estimate linear dependencies.
- Considering the partitioning of organic micropollutants between aqueous and particulate phases.

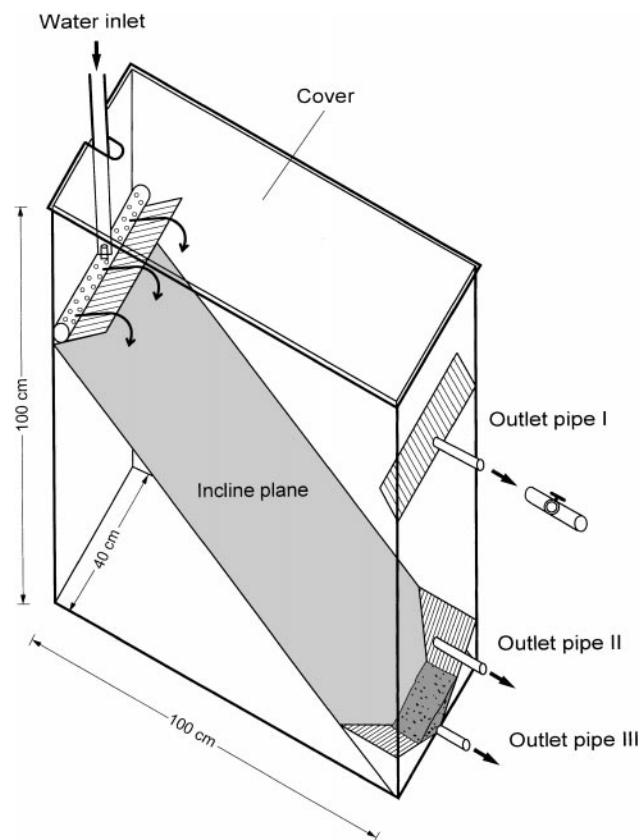


Fig. 1. Sample device for collecting SPM. Pipe I = overflow for passing water, pipe II = outlet for supernatant water, pipe III = outlet for collected SPM

Materials and Methods

Sampling

Monthly samples of suspended particulate matter were collected from September 1994 to August 1995. The samples from the River Elbe were taken at Hamburg (river km 634.3), those from the River Mulde were collected at Dessau (river km 7.6). The sampling was performed with sedimentation traps made of plexiglass (Figure 1) (Stachel *et al.* 1995). A volume of approximately 5 m³ d⁻¹ water was conducted through the traps with a flow of 1 cm/s. The separation efficiency was 20–30%, collecting 30–40 g SPM per day. After 1 month the collected SPM was transferred into glass bottles by opening the outlet valve. The supernatant water was decanted, and the SPM samples were centrifuged at 5,000 rpm for 15 min. Again, the supernatant water was decanted, and then the samples were dried in a clean bench at room temperature for 4 days. After drying, the water content of the SPM was determined following DIN 38414. Another part of the sample was used to determine the content of TOC. For sampling sites, see Figure 2.

Supercritical Fluid Extraction

Samples were extracted with a Suprex SFE 50 (Suprex GmbH, Duisburg, Germany). SFE conditions were: 30 min static and 60 min dynamic mode at 80°C and 400 atm. Carbon dioxide 5.5 grade (Messer/Grießheim, Duisburg, Germany) modified with 10% (by volume) methanol was used as fluid. Prior to extraction, 1.5 ml toluene

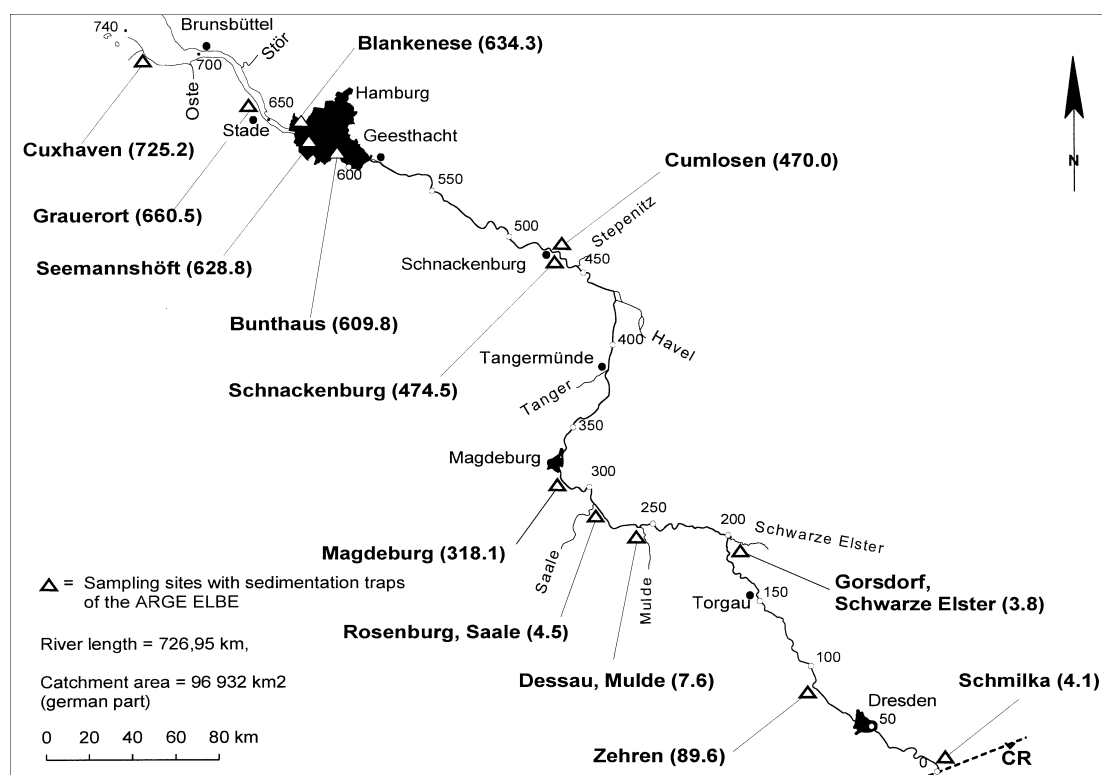


Fig. 2. Sampling sites and catchment area of the River Elbe and tributaries

was placed directly into the vessel. The flow rate was 1 ml/min (liquid CO₂), the total amount of fluid was 60 ml per extraction. About 1 g of dried SPM was extracted using a 3-ml stainless steel vessel. To remove elemental sulfur, 200 mg of activated copper powder was placed at the outlet side of the vessel. Five to three milliliter of n-hexane with 3 to 5 ml internal standard was used as trapping solvent. Trapping was performed with a Dewar condenser as described in Wenclawiak *et al.* (1995).

HPLC Cleanup

After concentrating the extracts to 100 μ l, samples were fractionated by HPLC, consisting of a pump (L 6200, Merck/Hitachi, Darmstadt, Germany), an autosampler (HP Series 1050, Hewlett Packard, Waldbronn, Germany), a fraction collector (L 5200, Merck/Hitachi), a diode-array detector (HP 1040 M Series II, Hewlett Packard) and a column oven (Techlab). The column was a Nucleosil 100-5 (Macherey/Nagel, Dülmen, Germany). HPLC parameters were as follows: 2 min n-hexane/methylene chloride (6:4 v/v; 1 ml/min); in 6 min to 100% methylene chloride (1 ml/min); 4 min 100% methylene chloride (1 ml/min); 5 min 100% acetone (1.5 ml/min); 10 min n-hexane/methylene chloride (6:4 v/v; 1.5 ml/min) for equilibration. Temperature was 20°C. The fraction containing the analytes was taken from 1 to 3.5 min and reduced to 100 μ l again.

GC/MSD Quantification

All extracts were analyzed with a gas chromatograph (Hewlett Packard 5890 Series II) and a mass spectrometer (MSD 5971 A). The GC system was equipped with a 5% phenylmethyl silicon capillary column, 0.25 mm ID, 0.5 μ m film thickness, and 25 m length (SE 52, Macherey/Nagel). Helium was used as carrier gas. The GC temperature

program was: 40°C, 5°C/min to 310°C, 310°C for 20 min. Parameters for the cold injection system KAS 3 (Gerstel GmbH, Mühlheim a.d. Ruhr, Germany) were: 30°C; 1°C/s to 70°C; 70°C for 20 s; 12°C/s to 320°C; 320°C for 120 s; splitless time 120 s; injection volume 2 μ l. The mass spectrometer was operated in selected ion monitoring mode, detecting the following ion masses: m/z = 66, 85, 128, 136, 142, 152, 154, 156, 164, 166, 178, 181, 183, 184, 188, 192, 202, 212, 228, 235, 240, 246, 252, 256, 264, 266, 276, 278, 284, 288, 292, 300, 312, 326, 360, and 396. Three calibration standard solutions were used to generate response factors for each compound relative to internal standards. The analytes in the samples were identified by matching the retention time of each compound with those in calibration standards. Concentrations of analytes were calculated according to recoveries of the internal standards.

Standards and Chemicals

Standards. The internal standard contained ϵ -HCH, TCN, PCB 185 (Lab. Dr. Ehrenstorfer, Augsburg, Germany) and the perdeuterated compounds C-12, C-16, C-20, C-30, Naph, Ace, Phen, Ant, Fluor, BaA, BeP, Per, BghiP, Cor (MSD Isotops, Montreal, Canada). Concentrations were in the range of 80 ng/ml for aliphatic, 20 ng/ml for aromatic and 10 ng/ml for chlorinated compounds. The calibration standards consisted of n-alkanes C-12 to C-30, Pri, Phy (Alltech Associates Inc., Unterhachingen, Germany), the PAHs (Aldrich Chemie GmbH, Steinheim, Germany and EGA Chemie, Steinheim, Germany), and the internal standard compounds. For the quantification of chlorinated compounds, a second set of calibration standards containing the target analytes as well as ϵ -HCH, TCN, and PCB 185 was used. Concentrations in the calibration standard solutions were in the range from 2 to 20 ng/ μ l for n-alkanes, 0.2 to 6 ng/ μ l for PAHs, and for halogenated compounds from 10 to 100 pg/ μ l. All standards were prepared in n-hexane. (For abbreviations see the sections following.)

Chemicals. Solvents: acetone, toluene, n-hexane (Nanograde, Promochem, Wesel, Germany); methylene chloride, methanol, iso-propanol (Lichrosolv, Merck, Darmstadt, Germany); water (HPLC, Baker). All solvents except water and isopropanol were fractionally distilled prior to use.

Copper powder (Baker) was activated with diluted nitric acid and subsequently rinsed with water, acetone, and n-hexane. The quality of Na₂SO₄ (Baker) was controlled by fluorescence measurements of n-hexane extracts.

Cluster Analysis

Among the methods of multivariate statistics, cluster analysis is a suitable tool for structuring large data sets. In the hierarchical cluster analysis, the distances between the observables or variables of a data set are computed and compared with each other. Small distances between the observables indicate similarities, whereas big distances indicate differences. It is the purpose of cluster analysis to obtain natural groupings of similar properties within data sets.

The most common methods for computing the difference between two observables are the Manhattan and the Eukclidean methods. In the Eukclidean method, the difference d_{ab} between two observables a and b is determined by computing the differences of all m variables:

$$d_{ab} = \sum_{j=1}^m [(x_{aj} - x_{bj})^2]^{1/2} \quad (\text{Eq. 1})$$

Standardization of each variable is carried out by subtracting the mean value \bar{x} from each variable x_i of the data matrix, and by subsequent division by the standard deviation σ :

$$s_i = \frac{x_i - \bar{x}}{\sigma} \quad (\text{Eq. 2})$$

After computation of all differences, the two observables exhibiting most similarities are combined to a cluster. The distances d between this newly formed cluster AB and other existing clusters C (or observables) are computed, and the two clusters closest to each other are combined to a new cluster. Several algorithms exist for cluster linkage. In this work, the complete linkage method has been used:

$$d_{AB=C} = 0.5 \times d_{AC} + 0.5 \times d_{BC} + 0.5 \times |d_{AC} - d_{BC}| \quad (\text{Eq. 3})$$

This process is continued until all clusters have been combined. Results of cluster analysis are shown graphically in the form of dendrograms. The software used in the evaluations was Statgraphics Plus 1.0.

Method Validation and Quality Control

The entire procedure of sample preparation (extraction, cleanup, and quantification) was accompanied with suitable methods of quality assurance. All relevant steps of analysis were checked for recovery rates and contaminations.

Method validation of SFE was performed in different ways. Accuracy and precision were estimated on the basis of extraction results starting with spiked samples, followed by the extraction of a certified sediment (HS-6), and finally by comparison with the classical methods soxhlet, ultrasonic, and methanolic saponification extractions. In three SPM samples used for method validation the average recoveries of PAH ranged from 96–105%, the relative standard deviations (RSD) being below 5% in most cases. For alkanes the SFE achieved recoveries in the range of 93–115% with an average RSD of about 5%.

For detailed information see Heemken *et al.* (1997). In SFE, blanks showed concentrations below 0.5 ng/g for all PAH, alkanes had concentrations of about 5 ng/g per compound. Recovery rates for HPLC were estimated to be within the range of 93–102%, the concentrations of target analytes in blanks were negligible. For detailed information see Heemken (1997). In this study all extractions were performed in triplicate, the RSDs are listed in Tables 1 and 2 as mean values over all extractions. Solvents used for SFE and HPLC were fractionally distilled prior to use and checked for target analytes as contaminants by GC/MSD.

The accuracy of GC/MSD quantification was ascertained by measuring certified standard solutions (US EPA). The detection limits of the GC/MSD were determined as the 10-fold value of the underground next to the target signals in extracts. When extracting 1 g of SPM and concentrating the extracts to a volume of 100 μ l the detection limits were as follows: alkanes 1.5 ng/g, PAHs 0.7 ng/g, and CHs 0.4 ng/g DM.

A further quality control for the analysis of PAHs and CHs in SPM and sediment samples is permanently performed in the course of a quality assurance program called QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe). These intercalibrations and interlaboratory studies showed good agreements with analytical results (mean values) generated by the other participants, the z scores being <2 for most compounds (QUASIMEME 1999).

Abbreviations

Ace	Acenaphthene
Acy	Acenaphthylene
AH	Aliphatic hydrocarbons
Ant	Anthracene
BaA	Benzo[a]anthracene
BaP	Benzo[a]pyrene
BbF	Benzo[b]fluoranthene
BeP	Benzo[e]pyrene
BghiP	Benzo[g,h,i]perylene
Chr/Tri	Chrysene/triphenylene
Cor	Coronene
DMN	2,6-Dimethylnaphthalene
DBaCA	Dibenz[a,c]anthracene
DBT	Dibenzothiophene
DDE	2,2-Bis-(4-chlorophenyl)-1,1-dichloroethene
DDD	2,2-Bis-(4-chlorophenyl)-1,1-dichloroethane
DDT	2,2-Bis-(4-chlorophenyl)-1,1,1-trichloroethane
DM	Dry mass
Flu	Fluorene
Fluor	Fluoranthene
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
I123P	Indeno[1,2,3-c,d]pyrene
M1N	1-Methylnaphthalene
M1P	1-Methylphenanthrene
M2N	2-Methylnaphthalene
Naph	Naphthalene
Per	Perylene
Phen	Phenanthrene
Phy	Phytane
Pri	Pristane
Pyr	Pyrene
TCN	Tetrachloronaphthalene
TOC	Total organic carbon (weight %)

Table 1. River Elbe concentrations (ng/g DM) of n-alkanes, PAHs, and CHs in SPM of the sampling site Hamburg

	Sep 94	Oct 94	Nov 94	Dec 94	Jan 95	Feb 95	Mar 95	Apr 95	May 95	Jun 95	Jul 95	Aug 95	RSD (%)*
C-12	124	287	319	158	113	531	120	390	169	408	255	162	7.4
C-13	139	162	177	223	121	643	183	401	325	350	161	113	7.7
C-14	132	97	98	219	134	845	212	337	385	255	94	70	10.1
C-15	407	231	193	391	235	1,528	378	614	1,550	627	536	331	10.8
C-16	126	87	89	118	72	281	175	191	289	178	148	104	3.8
C-17	2,390	1,434	618	491	305	1,213	362	769	2,422	1,186	2,152	1,674	4.2
Pri	157	205	225	167	154	1,344	182	374	476	266	139	112	4.4
C-18	623	277	151	112	92	300	104	242	293	187	175	308	4.8
Phy	88	134	146	127	118	483	131	327	391	225	107	76	5.0
C-19	188	169	158	111	101	294	100	233	302	183	151	179	5.1
C-20	124	120	135	125	79	256	128	218	250	179	107	102	4.1
C-21	296	287	296	271	151	473	246	413	486	356	223	237	3.8
C-22	200	205	278	218	119	381	200	323	347	267	152	164	4.0
C-23	812	779	695	719	348	1,068	583	901	1,041	829	507	594	4.6
C-24	352	343	436	431	196	704	350	562	597	456	238	287	4.6
C-25	1,551	1,405	1,264	1,479	683	2,596	1,258	2,135	3,372	1,929	1,017	1,258	5.3
C-26	486	522	584	518	324	1,099	551	898	943	739	407	374	3.2
C-27	2,323	2,441	2,064	2,161	1,567	4,753	1,918	3,703	3,629	3,326	1,900	1,850	4.3
C-28	618	610	707	727	369	1,399	666	1,154	1,238	950	509	457	4.5
C-29	2,973	3,041	2,580	3,132	1,592	6,104	2,807	7,790	5,605	5,639	2,376	2,518	3.6
C-30	685	554	647	677	326	1,333	586	1,128	1,160	945	519	417	4.2
Naph	172	162	149	199	134	526	213	344	358	317	120	114	4.6
M2N	106	92	92	169	103	337	139	178	204	162	60	59	6.9
M1N	51	47	48	84	54	178	69	94	110	83	30	30	7.6
DMN	97	64	62	131	77	238	110	111	204	130	142	66	9.9
Acy	20	16	14	27	15	58	30	39	42	35	14	13	7.1
Ace	20	19	18	26	16	60	29	43	44	36	14	13	5.9
Flu	53	44	39	67	50	163	66	109	108	95	40	37	6.2
DBT	27	25	23	34	19	72	36	53	51	45	18	18	3.9
Phen	286	301	256	363	285	789	410	730	779	581	217	201	4.5
M1P	26	30	27	34	22	82	39	59	68	52	25	23	4.9
Ant	66	69	61	97	50	183	101	146	136	118	46	48	5.5
Fluor	464	457	414	509	352	1,159	566	1,147	937	922	385	352	5.3
Pyr	415	403	386	569	288	1,430	489	952	938	772	337	306	5.1
BaA	188	180	178	247	137	477	268	385	372	330	174	162	5.8
Chr/Tri	281	248	247	442	172	633	477	511	458	439	237	219	4.9
BbF	236	202	178	211	131	424	195	390	389	322	163	152	8.8
BeP	312	211	199	405	123	506	421	416	386	360	193	185	5.9
BaP	244	197	196	344	146	524	382	422	393	364	193	181	6.3
Per	201	198	185	248	114	221	181	194	175	171	122	182	6.3
I123P	150	149	140	180	104	378	196	285	319	245	125	122	8.7
DBacA	54	54	50	69	39	147	66	119	120	98	47	44	8.1
BghiP	136	118	110	177	88	291	194	235	234	202	107	101	6.7
Cor	45	37	34	58	26	103	60	79	76	74	40	34	8.9
α -HCH	17	20	12	15	14	47	23	30	28	25	10	10	11.2
γ -HCH	10	15	15	14	8.5	33	22	25	26	22	n.d.	9.1	11.3
HCB	32	25	21	30	12	64	28	92	69	51	27	22	8.5
DDE	12	7.4	4.9	7.6	5.8	14	6.3	13	16	12	8.8	6.4	7.4
DDD	21	14	10	16	11	35	11	30	28	29	17	15	6.3
DDT	13	10	6.1	7.8	6.6	37	18	50	28	69	8.9	3.7	10.9
PCB 28	2.7	2.8	2.3	0.87	2.2	4.8	2.8	4.2	5.9	6.2	4.5	2.6	9.4
PCB 52	17	6.0	5.9	10	8.6	17	10	20	25	18	12	10	7.3
PCB 101	4.5	2.8	2.1	3.6	2.6	3.9	2.4	4.3	7.2	4.3	1.3	1.7	9.0
PCB 118	1.7	1.6	1.3	1.4	0.99	2.0	0.39	1.8	2.2	2.2	0.9	0.96	10.2
PCB 153	19	14	13	19	10	27	15	22	30	20	15	12	7.0
PCB 105	2.8	1.7	1.8	1.8	1.3	3.6	2.0	3.2	3.1	3.5	2.5	2.0	9.7
PCB 138	19	15	14	20	10	30	17	25	43	23	15	13	7.5
PCB 156	4.0	2.3	1.4	2.6	1.5	4.6	2.3	3.8	4.0	2.5	3.1	1.9	11.6
PCB 180	13	8.1	8.1	13	6.8	17	10	13	23	11	6.4	5.5	8.7

* Average of all triplicate extractions

Table 2. River Mulde concentrations (ng/g DM) of n-alkanes, PAHs, and CHs in SPM of the sampling site Dessau

	Sep 94	Oct 94	Nov 94	Dec 94	Jan 95	Feb 95	Mar 95	Apr 95	May 95	Jun 95	Jul 95	Aug 95	RSD (%)*
C-12	2,650	2,980	3,994	3,982	5,615	6,337	6,659	7,799	1,991	4,568	1,604	1,952	17.5
C-13	2,477	2,869	2,196	2,875	4,199	7,744	3,161	6,529	1,987	4,117	1,777	1,407	16.7
C-14	1,112	1,510	787	1,084	1,952	2,044	1,065	2,970	828	1,528	888	929	12.5
C-15	1,334	2,942	1,291	1,815	2,396	2,727	1,911	3,528	925	1,693	1,289	1,496	11.6
C-16	786	1,330	1,188	1,093	1,220	1,312	1,070	1,579	494	805	459	652	7.0
C-17	1,751	3,039	2,281	1,932	1,621	1,704	2,903	1,531	908	1,045	1,563	2,508	4.6
Pri	303	590	795	1,069	594	733	1,408	622	256	343	198	209	3.8
C-18	638	1,000	941	812	645	738	1,053	683	302	536	366	384	6.1
Phy	381	570	791	1,053	553	670	1,313	536	281	301	130	123	4.9
C-19	436	742	727	606	494	596	1,250	508	277	448	265	368	3.7
C-20	415	642	595	526	392	433	751	383	203	355	235	222	4.1
C-21	627	1,009	929	796	617	681	1,511	595	448	574	392	427	4.3
C-22	468	769	644	638	534	564	960	489	293	493	249	267	6.9
C-23	1,337	1,678	1,569	1,456	1,243	1,264	2,101	1,342	948	1,093	954	1,096	3.2
C-24	878	1,195	1,231	1,250	1,099	1,205	1,976	1,166	639	934	465	513	6.0
C-25	4,684	4,716	6,789	4,750	4,037	4,491	7,495	3,212	3,297	3,127	2,010	2,545	4.2
C-26	1,745	2,314	2,151	2,214	1,705	1,892	2,795	1,654	1,122	1,497	987	1,085	4.2
C-27	6,681	10,977	8,698	7,831	6,624	6,213	8,570	5,786	4,352	4,916	4,721	5,495	3.0
C-28	2,088	2,907	2,684	2,644	2,112	2,461	3,463	2,194	1,404	1,979	1,260	1,322	4.0
C-29	9,506	27,205	18,491	12,521	9,826	10,296	14,258	7,173	5,154	7,539	5,549	6,321	3.1
C-30	1,987	2,412	2,345	2,394	1,925	2,489	3,483	2,072	1,392	1,995	1,336	1,394	4.7
Naph	1,603	1,692	2,062	3,090	3,574	2,669	2,260	5,620	2,403	4,249	1,180	1,076	9.0
M2N	296	272	260	364	531	434	332	633	209	457	217	193	6.1
M1N	173	160	156	223	330	260	199	383	127	274	130	118	6.2
DMN	118	165	172	158	227	190	232	160	62	177	107	124	9.2
Acy	77	78	131	160	140	104	80	107	49	96	42	40	6.3
Ace	45	33	43	54	76	70	81	86	30	71	33	34	3.8
Flu	93	87	91	149	169	163	155	197	72	182	79	75	6.9
DBT	83	67	102	132	138	125	105	141	52	105	58	54	3.1
Phen	907	680	910	1,254	1,749	1,412	1,282	1,429	559	1,409	646	622	4.7
M1P	81	63	71	90	127	131	113	155	52	122	66	64	3.8
Ant	147	104	140	241	236	214	207	263	81	203	100	101	5.8
Fluor	1,333	916	1,186	1,498	2,016	1,600	1,565	1,648	624	1,432	901	953	3.3
Pyr	1,019	842	1,018	1,181	1,392	1,478	1,315	1,408	543	1,275	706	776	3.6
BaA	486	383	424	486	568	565	585	591	221	506	343	381	3.3
Chr/Tri	575	512	502	542	593	679	686	761	278	593	454	469	2.9
BbF	453	359	412	434	483	458	499	530	182	464	288	313	7.2
BeP	412	315	351	395	410	522	525	585	195	449	321	351	3.5
BaP	531	394	425	532	605	539	541	610	206	490	357	402	4.4
Per	163	108	125	148	191	200	180	201	67	172	113	125	6.6
I123P	314	200	213	276	391	453	400	454	132	411	245	268	7.1
DBacA	109	66	78	103	162	208	171	177	52	172	97	110	7.5
BghiP	279	201	210	255	308	324	325	337	80	300	199	229	6.7
Cor	80	61	55	73	81	71	110	102	28	88	61	73	8.1
α-HCH	132	105	138	112	136	177	157	97	100	201	110	111	11.4
γ-HCH	95	52	64	51	51	51	63	50	46	38	31	34	13.4
HCB	151	91	165	135	137	192	159	79	170	184	104	123	11.7
DDE	184	138	134	121	112	83	88	86	60	73	63	63	6.2
DDD	542	515	398	330	309	228	216	323	186	233	200	197	5.0
DDT	842	656	474	426	353	528	359	805	515	548	262	223	9.0
PCB 28	1.4	3.5	3.5	3.2	2.6	0.9	1.1	3.1	0.2	0.7	2.3	3.1	8.5
PCB 52	8.1	10	16	14	7.5	13	22	6.7	9.0	6.6	10	7.4	19.4
PCB 101	9.0	1.9	5.6	5.2	5.2	4.1	3.4	5.4	2.4	3.4	2.4	2.6	9.5
PCB 118	6.4	3.4	4.1	3.1	3.3	3.2	2.5	3.1	1.4	2.5	2.6	2.8	10.5
PCB 153	37	21	26	22	23	23	21	28	13	18	13	14	7.0
PCB 105	4.5	3.3	3.8	3.3	2.8	3.3	2.6	4.2	1.8	3.2	4.5	5.0	14.4
PCB 138	46	25	28	26	28	29	25	34	17	23	18	16	6.9
PCB 156	5.7	5.8	4.0	5.7	4.6	7.3	3.0	6.5	1.6	2.7	1.7	1.9	22.7
PCB 180	15	8.0	10	9.0	10	11	8.2	21	5.2	7.2	5.5	5.1	10.2

* Average of all triplicate extractions

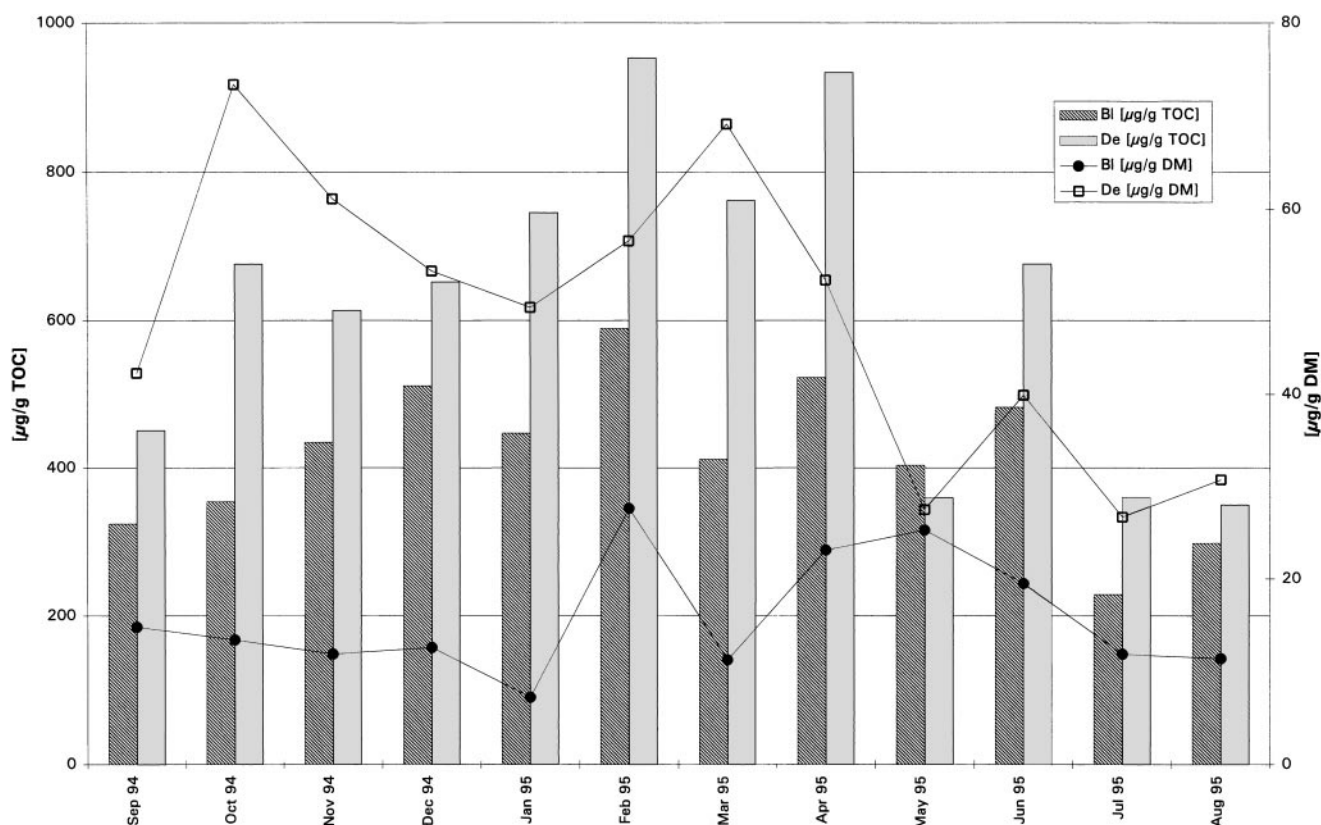


Fig. 3. Sum of n-alkanes in SPM of the sampling sites Hamburg (BI) and Dessau (De) related to TOC and DM

Results and Discussion

Input of n-Alkanes

The concentrations of n-alkanes related to DM in samples of the River Elbe are given in Table 1, of the River Mulde in Table 2. A graphic representation of total n-alkanes is shown in Figure 3. Table 3 shows that the sum of quantified n-alkanes (C-12 to C-30, Pri, Phy) at Hamburg averaged 15.8 µg/g DM, with levels ranging from 7.2 µg/g (January) to 27.6 µg/g DM (February). Related to contents of TOC, the concentrations ranged from 229 µg/g (July) to 589 µg/g (February). The mean value was 417 µg/g TOC. In the River Mulde at Dessau, the average n-alkane level was 48.5 µg/g DM, the lowest value of 26.6 µg/g being recorded in July and the highest value of 73.4 µg/g DM in October. The annual average of concentrations, related to TOC, was 628 µg/g, with a minimum of 350 µg/g in August and a maximum of 953 µg/g in February. Though mean concentrations per DM at the two stations differed by about a factor of 3, concentration levels as a function of TOC differed only by about 1.5. This is attributable to markedly higher TOC levels in suspended matter from Dessau, where average TOC levels of 8.0 weight % were found (5.6 to 10.9 weight %), as compared to Hamburg, where the average TOC value was 3.9 weight % (1.6 to 6.3 weight %). The n-alkane levels, related to TOC, at both sampling sites showed a similar pattern over the year (Figure 3). Both had their maximum in February (second maximum in April), and the lowest concentrations were measured in the months from July to September. Among the single

compounds highest concentrations at both sampling sites were measured for C-29, followed by C-27, C-25, and C-23. Depending on seasonal factors (algal bloom), C-17 and C-15 levels were high as well, mainly in the summer months. Moreover, at Dessau, high levels of C-12, C-13, and C-14 (Table 2) were measured throughout the year.

To estimate the relative amount of this light oil input, the ratio of the alkanes C-12, C-13, and C-14 divided by C-18, C-19, and C-20 was calculated. The alkanes C-15 and C-17 have been excluded because they are of biogenic origin. At Hamburg, the values ranged from 0.42 (September) to 2.37 (February), with a mean value of 1.33. At Dessau, values between 3.08 (November) and 10.98 (April) were measured, with a mean value of 5.74. This value, which exceeds that at Hamburg by about a factor of 4, clearly indicates light oil input during the whole sampling period.

To estimate inputs of aquatic algae, the ratio of C-17/C-18 was computed. The C-17/C-18 ratio at Hamburg ranged from 3.2 (April) to 12.3 (July), with a mean value of 5.32. At Dessau the average C-17/C-18 ratio, at 3.01, was lower than in Hamburg. Here, the minimum was measured in June, at 1.95, and the maximum in August, at 6.53.

The carbon preference index (CPI), in this case as the quotient from odd-numbered hydrocarbons from C-21 to C-29 divided by even-numbered n-alkanes from C-22 to C-30, was determined to indicate input of mineral or crude oil. Table 3 shows that the average CPI value for Hamburg was 3.29, that for Dessau 3.15. CPI values below 4 generally indicate that there are not only biogenic but also anthropogenic input

Table 3. Hydrographic parameters and sum contents of n-alkanes, PAHs, and CHs of the Rivers Elbe at Hamburg and Mulde at Dessau

	Sep 94	Oct 94	Nov 94	Dec 94	Jan 95	Feb 95	Mar 95	Apr 95	May 95	Jun 95	Jul 95	Aug 95	Min	Max	Mean
Blankenese															
TOC [weight %]	4.56	3.78	2.73	2.46	1.61	4.69	2.73	4.42	6.26	4.04	5.19	3.82	1.61 (Jan)	6.26 (May)	3.86
SPM [mg/L]*	38.8	29.4	29.0	20.9	26.1	32.7	22.6	20.5	24.4	25.4	43.1	39.4	20.5 (Apr)	43.1 (Jul)	29.4
Temp [°C]	16.1	10.9	8.8	5.9	2.4	4.9	5.5	9.4	14.8	17.7	23.0	23.5	2.4 (Jan)	23.5 (Jul)	11.9
Discharge [m ³ /s]**	480	390	470	640	890	1,740	710	1,410	1,010	1,300	670	330	330 (Aug)	1,740 (Feb)	837
Conduct. [µS/cm]	998	1,043	1,048	917	842	713	811	707	711	668	804	982	668 (Jun)	1,048 (Nov)	854
pH	7.70	7.80	7.80	7.80	7.80	7.70	8.00	8.10	8.10	7.60	7.70	7.60	7.6 (Jun)	8.1 (Apr)	7.81
CPI	3.4	3.6	2.6	3.0	3.3	3.0	2.9	3.7	3.3	3.6	3.3	3.8	2.6 (Nov)	3.8 (Aug)	3.29
C-17/C-18	3.8	5.2	4.1	4.4	3.3	4.0	3.5	3.2	8.3	6.4	12.3	5.4	3.2 (Apr)	12.3 (Jul)	5.32
C12–C14/C18–C20	0.4	1.0	1.3	1.7	1.3	2.4	1.6	1.6	1.0	1.8	1.2	0.6	0.42 (Sep)	2.37 (Feb)	1.33
Sum AH [µg/g DM]	14.8	13.4	11.9	12.6	7.2	27.6	11.2	23.1	25.3	19.5	11.9	11.4	7.2 (Jan)	27.6 (Feb)	15.8
Sum AH [µg/g TOC]	324	354	435	511	447	589	412	523	404	482	229	298	228 (Jul)	589 (Feb)	417
Loads [kg/month]	724	404	424	442	440	4,131	474	1,752	1,638	1,690	901	389		Sum [t/a]=	13.4
Sum PAH [µg/g DM]	3.6	3.3	3.1	4.7	2.5	9.0	4.7	7.0	6.9	6.0	2.9	2.7	2.54 (Jan)	8.98 (Feb)	4.7
Sum PAH [µg/g TOC]	80.0	87.9	113.8	190.7	158.1	191.5	173.5	159.3	110.2	147.3	54.9	69.7	55 (Jul)	191 (Feb)	128
Loads [kg/month]	179	100	111	165	155	1,343	200	534	447	517	216	91		Sum [t/a]=	4.1
Sum CH [µg/g DM]	0.19	0.15	0.12	0.16	0.10	0.34	0.17	0.34	0.34	0.30	0.13	0.12	0.10 (Jan)	0.34 (Feb)	0.20
Sum CH [µg/g TOC]	4.1	3.9	4.4	6.7	6.4	7.3	6.2	7.6	5.4	7.4	2.6	3.0	2.55 (Jul)	7.64 (Apr)	5.41
Loads [kg/month]	9.3	4.4	4.3	5.8	6.3	51.1	7.2	25.6	21.9	26.0	10.1	4.0		Sum [kg/a]=	176
Dessau															
TOC [weight %]	9.38	10.86	9.97	8.18	6.63	5.94	9.08	5.61	7.64	5.90	7.41	8.78	5.61 (Apr)	10.86 (Oct)	7.95
SPM [mg/L]	2.5	1.0	1.5	2.5	2.0	8.5	1.5	4.0	5.0	2.5	8.0	7.0	1.0 (Oct)	8.5 (Feb)	3.8
Temp [°C]	16.8	11.8	8.9	5.5	2.7	4.7	5.1	7.9	12.4	16.8	21.7	20.6	2.7 (Jan)	21.7 (Aug)	11.2
Discharge [m ³ /s]***	31.2	21.9	28	60	88.7	120	50	197	99	168	49.6	29.7	21.9 (Oct)	197 (Apr)	79
Conduct. [µS/cm]	546	544	524	546	507	480	554	438	466	422	554	624	422 (Jun)	624 (Aug)	517
pH	7.53	7.35	7.46	7.47	7.45	7.35	7.29	7.14	7.15	7.27	7.42	7.06	7.06 (Aug)	7.53 (Sep)	7.33
CPI	3.2	4.8	4.0	3.0	3.0	2.7	2.7	2.4	2.9	2.5	3.2	3.5	2.39 (Apr)	4.75 (Okt)	3.15
C-17/C-18	2.7	3.0	2.4	2.4	2.5	2.3	2.8	2.2	3.0	2.0	4.3	6.5	1.95 (Jun)	6.53 (Aug)	3.01
C12–C14/C18–C20	4.2	3.1	3.1	4.1	7.7	9.1	3.6	11.0	6.1	7.6	4.9	4.4	3.08 (Nov)	10.98 (Apr)	5.74
Sum AH [µg/g DM]	42.3	73.4	61.1	53.3	49.4	56.6	69.2	52.3	27.5	39.9	26.7	30.7	26.7 (Jul)	73.4 (Okt)	48.5
Sum AH [µg/g TOC]	451	676	613	652	745	953	762	933	360	676	360	350	350 (Aug)	953 (Feb)	628
Loads [kg/month]	10.3	5.0	8.0	25.0	27.4	180.4	16.2	128.9	42.5	52.3	33.1	20.0		Sum [t/a]=	0.55
Sum PAH [µg/g DM]	9.4	7.8	9.1	11.8	14.5	12.9	11.9	16.6	6.3	13.7	6.7	6.9	6.30 (May)	16.57 (Apr)	10.6
Sum PAH [µg/g TOC]	100.0	71.4	91.6	144.7	218.6	216.6	131.6	295.5	82.5	232.2	91.0	79.2	71.4 (Oct)	296 (Apr)	146
Loads [kg/month]	2.3	0.5	1.2	5.5	8.0	41.0	2.8	40.8	9.8	18.0	8.4	4.5		Sum [t/a]=	0.14
Sum CH [µg/g DM]	2.08	1.64	1.47	1.27	1.19	1.35	1.13	1.55	1.13	1.34	0.83	0.81	0.81 (Aug)	2.08 (Sep)	1.32
Sum CH [µg/g TOC]	22.0	15.0	14.7	15.4	17.7	22.6	12.4	27.3	14.7	22.7	11.1	9.1	9.15 (Aug)	27.28 (Apr)	17.1
Loads [kg/month]	0.5	0.1	0.2	0.6	0.7	4.3	0.3	3.8	1.7	1.8	1.0	0.5		Sum [kg/a]=	15.5

* Seemannshöft

** Neu Darchau

*** Bad Dübren

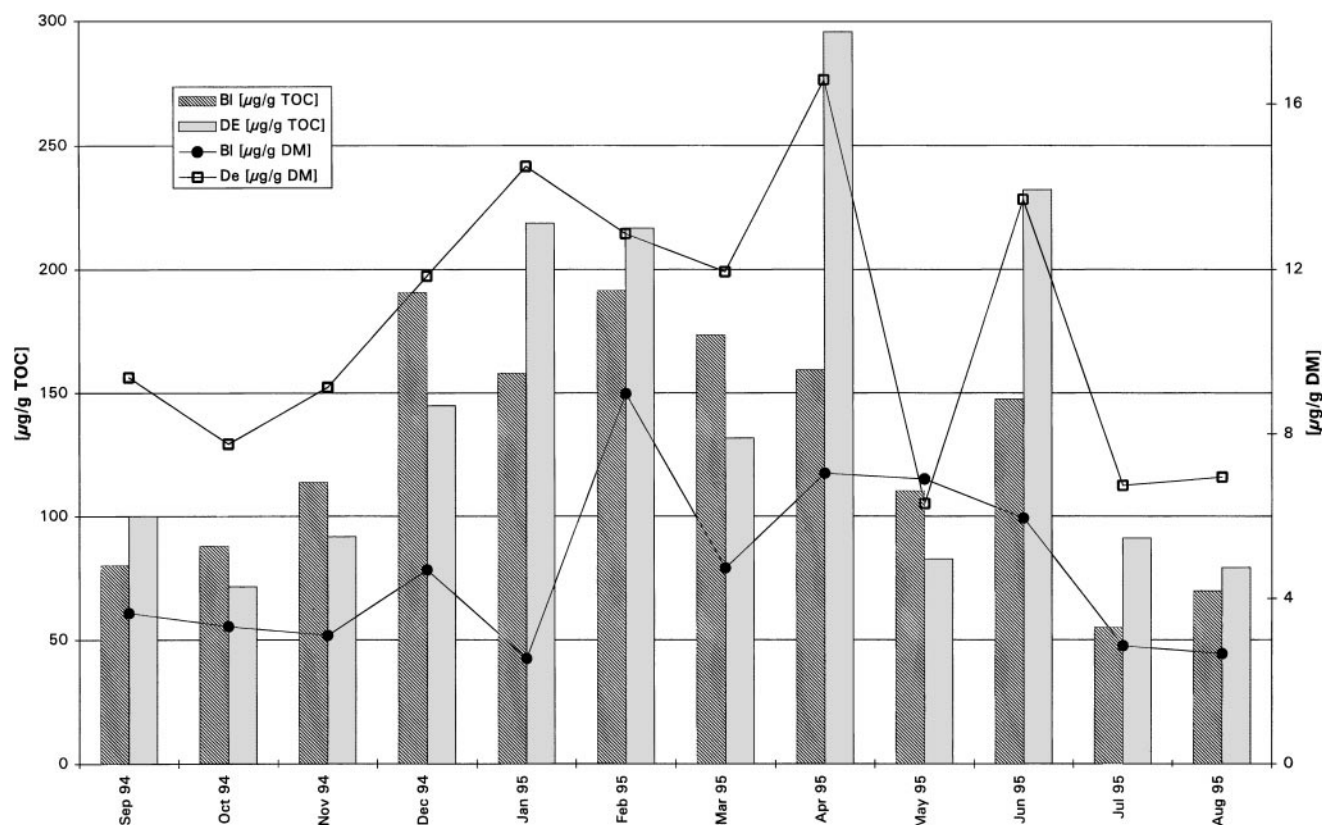


Fig. 4. Sum of PAHs in SPM of the sampling sites Hamburg (BI) and Dessau (De) related to TOC and DM

sources, which means it may be assumed in this case that in addition to terrestrial plants there is also a small input of petroleum. CPI values at Dessau showed a distinct seasonal dependence, the maximum being reached in October, at 4.75, and the minimum in April, at 2.39. Obviously, less petroleum is discharged into the Mulde in summer and autumn. By contrast, the CPI values in Hamburg were near the mean value throughout the year, indicating a more even input of anthropogenic and biogenic n-alkanes.

Summarizing the above, it can be said that input of aliphatic hydrocarbons at Hamburg has different sources. The most important source throughout the year is biogenic, resulting from terrestrial plant components. Depending on the season (May through October), C-17 and C-15 inputs are also recorded, which are due to aquatic organisms. CPI values indicate that a small proportion is also due to fossil fuel input. The mean CPI value at Hamburg was approximately 5% higher than that measured in suspended matter at Dessau. Absolute n-alkane levels related to DM were on average 67% lower than at Dessau; related to TOC content, they were 34% lower.

Alkane input at Dessau also came from different sources. Similar to Hamburg, the CPI values indicate slightly lower inputs of high-boiling n-alkanes, with n-alkanes from terrestrial plants prevailing from C-20 upward. Contrary to Hamburg, high concentrations were found in the range of low-boiling n-alkanes from C-12 to C-16, with a maximum at C-12. They are due to light oil input (heating oil or diesel fuel), which constituted 25% on average of the total n-alkane concentration. A constant concentration of this light oil over the entire sampling period indicates that it originates from a point source,

not from temporally and spatially diffuse events. Taking into account the monthly SPM levels and river discharge, particulate-bound n-alkane loads of approximately 0.55 t/a were determined for the Mulde and 13.4 t/a for the Elbe.

Input of PAHs

Concentrations of PAHs related to DM in samples of the River Elbe are given in Table 1, of the River Mulde in Table 2, a graph of total PAHs (related to DM and TOC) is given in Figure 4. At Hamburg, the average concentration of total PAHs was 4.7 µg/g DM. The lowest concentration was measured in January, at 2.54 µg/g, the highest one in February, at 8.98 µg/g DM. Related to TOC, the average PAH level was 128 µg/g, the minimum of 55 µg/g having been measured in July, the maximum of 191 µg/g again in February. At Dessau, the average PAH load was 10.6 µg/g DM, the minimum was 6.3 µg/g DM in May, the maximum 16.6 µg/g DM in April. The lowest concentration related to TOC was 71 µg/g in October, the highest one was 296 µg/g in April. The average PAH level of 146 µg/g TOC at Dessau was about 15% higher than at Hamburg. Considering the mean values of single compounds for Dessau, it is found that naphthalene alone accounts for about 25% of total PAHs. Such high concentrations, which are unusual for particulate matter and sediments, are probably due to a naphthalene-specific input source. Of the other PAH, the highest concentrations in both samples are found for fluoranthene, followed by pyrene (with few exceptions). Another unusual feature of the samples from Dessau is the high phenanthrene concentrations, which ex-

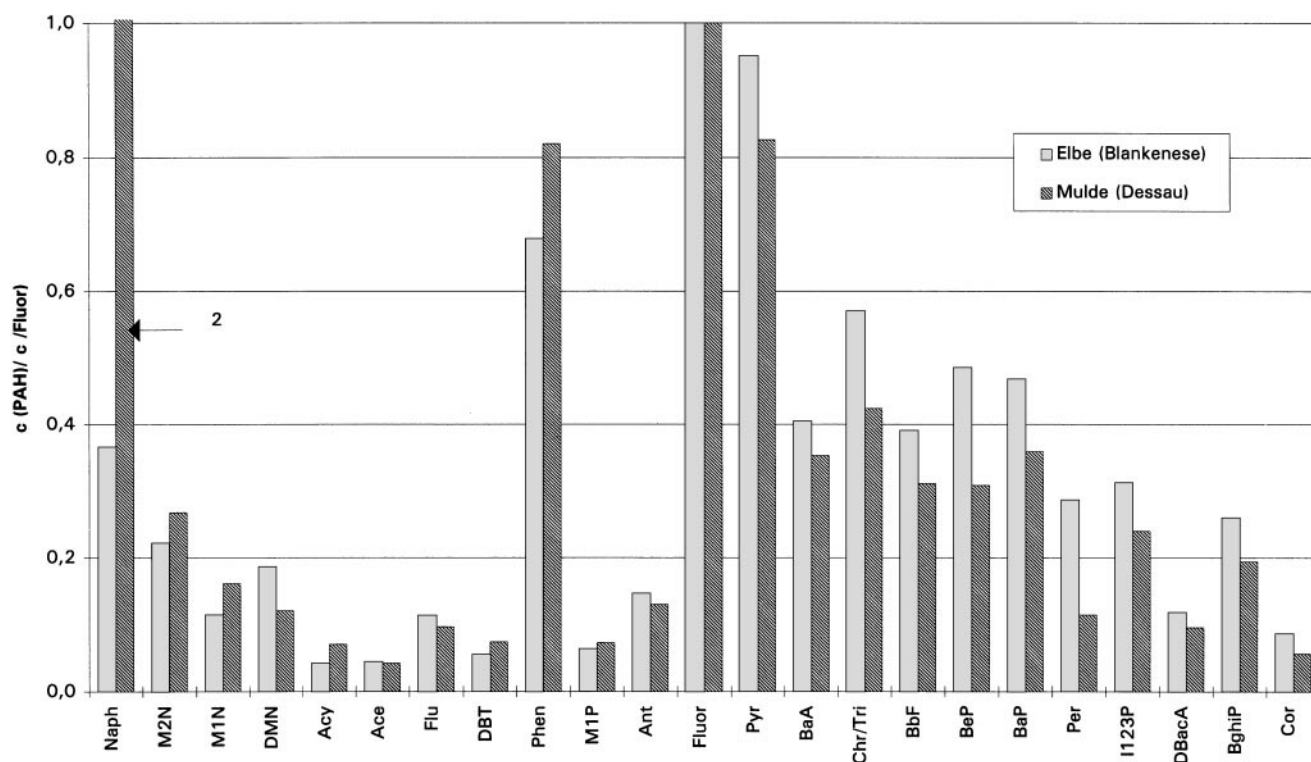


Fig. 5. Comparison of mean PAH concentrations, standardized to fluoranthene

ceeded the pyrene levels in December, January, April, May, and June.

To compare the PAH patterns of samples from the two stations, the concentrations of single compounds were normalized to fluoranthene. Figure 5 shows a comparison of the (average) relative PAH concentrations. The samples from Hamburg clearly have considerably higher relative concentrations of higher fused ring systems. The relative concentrations of four- to seven-ring systems at Hamburg, shown as percentages of the PAH levels in Dessau samples, were approximately 30% higher on average (Figure 6). The relative concentrations of coronene and benzo[*a*]pyrene were about 50% higher than in Dessau. The perylene concentration was even 150% higher. In Dessau, by contrast, relative concentrations of naphthalene, 1- and 2-methylnaphthalene, acenaphthylene, dibenzothiophene, phenanthrene, and 1-methylphenanthrene were higher. The existence of high concentrations, relative to fluoranthene, of two- and three-ring systems including the alkylated homologs in the Dessau samples, confirms findings of higher petroleum input in the River Mulde as compared to the Elbe because naphthalene and phenanthrene, together with their alkylated homologs, have the highest concentration levels in petroleum, while higher-fused PAHs result mainly from combustion processes. Dimethylnaphthalene would be expected to show a similar behavior as the other naphthalenes in the Mulde. As in the case of perylene in the Elbe, 2,6-dimethylnaphthalene may originate from a point source.

The normalized concentrations show that, with respect to naphthalene, acenaphthylene, dibenzothiophene, phenanthrene, benzo[*b*]fluoranthene, perylene, benzo[*e*]pyrene, benzo[*g,h,i*]perylene, and coronene, the relative differences between the samples from Hamburg and Dessau, throughout the sampling

period corresponded to the PAH pattern expressed by the mean values in Figure 5 without any exception. Therefore, these compounds may be considered significant criteria distinguishing the PAH patterns at Dessau and Hamburg.

Particle-bound PAH transported by the Mulde was approximately 0.14 t/a, compared to 4.1 t/a in the Elbe at Hamburg. These estimates correspond to literature data of PAH input into the North Sea by the River Elbe (Theobald *et al.* 1995). Having analyzed water samples (including SPM) of the River Elbe at Stade, the authors of that study calculated an annual input of 5 t of the 16 US EPA PAHs for 1991. Taking into account the fact that 80–90% of the PAHs in the total water body is adsorbed to SPM, the estimates are even closer.

Input of CHs

Concentrations of CHs related to DM in samples of the River Elbe are given in Table 1, of the River Mulde in Table 2, a graph of total CHs is given in Figure 7 (related to DM and TOC). Table 3 shows that the sum of quantified CHs at Hamburg was 0.20 $\mu\text{g/g}$ DM on an annual average, with levels ranging from 0.10 $\mu\text{g/g}$ DM in January to 0.34 $\mu\text{g/g}$ DM in February. Related to TOC, the mean concentration was 5.4 $\mu\text{g/g}$. The maximum of 7.6 $\mu\text{g/g}$ TOC was measured in April, the minimum of 2.6 $\mu\text{g/g}$ TOC in July. The levels related to TOC again show an annual pattern, as in the case of n-alkanes and PAH: the highest concentrations were measured in the autumn and winter months, while concentrations in spring and summer were clearly lower. At Dessau, CH levels ranged from 0.81 $\mu\text{g/g}$ DM in August to 2.1 $\mu\text{g/g}$ DM in September and from 9.2 $\mu\text{g/g}$ TOC in August to 27.3 $\mu\text{g/g}$ TOC in April. Mean concentrations, at 1.32 $\mu\text{g/g}$ DM

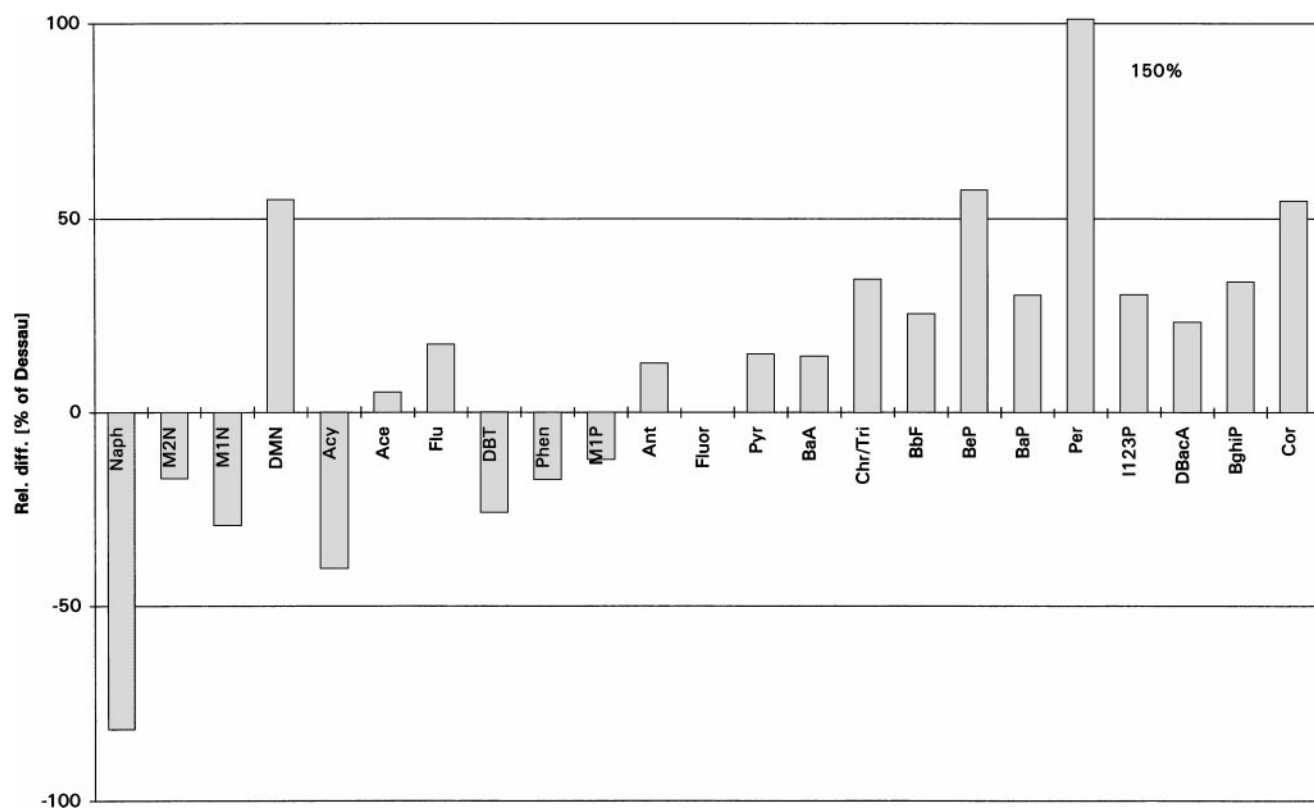


Fig. 6. Relative differences of standardized PAH concentrations between the Rivers Elbe and Mulde

and 17.1 $\mu\text{g/g}$ TOC, exceeded levels at Hamburg by the factor 6.6 (DM) and 3.2 (TOC).

Among the CHs, the comparatively high pesticide levels (DDT, HCB, HCH) of the Dessau samples were striking. Levels of γ -HCH exceeded those at Hamburg by a factor of 6, α -HCH levels by a factor of 3. HCB, at 39.4 ng/g DM, had the highest levels among CHs in the samples from Hamburg, but this level was exceeded by about a factor of 3 in the River Mulde. The biggest differences were found for DDT and its metabolites, DDD and DDE. For DDT in the River Mulde, the maximum concentration was 69 ng/g DM (in September), and the maximum of 69 ng/g DM in Hamburg was determined in June. On average, the DDT, DDD, and DDE levels in the Mulde exceeded those at Hamburg by factors of 11, 16, and 23, respectively. As in the case of HCH, the proportions of these three compounds differed clearly. At Dessau, DDT had the highest concentration throughout the sampling period, but DDD had the highest concentrations in the Hamburg samples, except for the months of February, March, April, and June. Use of DDT in Germany has been banned since 1972, so possible sources of contamination may be former production and storage sites as well as agricultural land that has been treated with DDT in East Germany until 1988 and from which DDT is now being washed out. With respect to pesticides, the large differences in concentration patterns and levels indicate a clearly different input pattern. By contrast, PCB levels in SPM were about equal, although the pattern of PCB congeners also showed differences.

Table 4 shows a comparison of the average CH loads determined for Hamburg with other SPM investigations in the Elbe River. Since the data presented there are the results of

studies made in other years and at different sampling locations, a comparison can only be used as a plausibility check. Taking into account variations in the monthly concentrations of SPM samples from Hamburg (Table 1), it is clearly seen that there is good correspondence in the orders of magnitude, the closest similarities being observed, as expected, at adjacent sampling stations (Hetlingen, Hamburg).

During the sampling period, particle-bound CH loads in the River Elbe at Hamburg were approximately 176 kg/a and in the River Mulde at Dessau 15.5 kg/a. These estimations again showed good agreement with calculations of the ARGE Elbe (Bergemann unpublished data).

Cluster Analysis

To determine specific local and seasonal similarities (or differences) in the pollutant patterns, cluster analyses of all 24 samples were carried out jointly for samples from Hamburg and Dessau. To that end, the pollutant patterns of the individual samples were compared with each other. The substance groups of PAHs (23 compounds), CHs (15 compounds), and n-alkanes (21 compounds) were investigated separately. Figure 8 shows the dendrograms of these evaluations. It should be noted that the variables in all cluster analyses has been standardized (see Eq. 2), and cluster formation thus has been independent of absolute concentrations.

To determine relative similarities or changes of single compounds, related to the other compounds, cluster analyses were performed separately for samples from Hamburg and

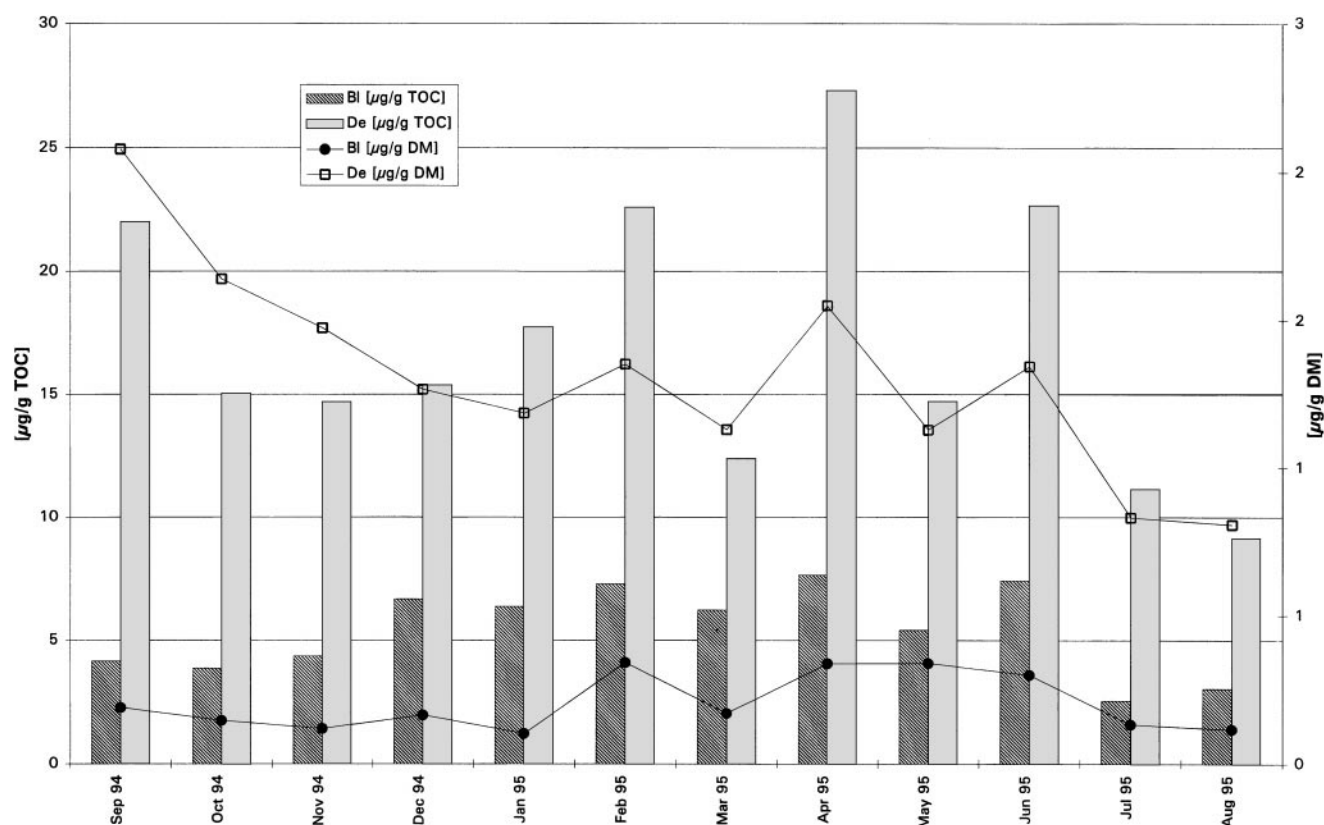


Fig. 7. Sum of CHs in SPM of the sampling sites Hamburg (BI) and Dessau (De) related to TOC and DM

Table 4. Comparison of CH concentrations (ng/g DM) with literature data

Reference:	This Study	Knauth <i>et al.</i> (1993)	Knauth <i>et al.</i> (1993)	Knauth <i>et al.</i> (1993)	Duinker <i>et al.</i> (1982)	Knauth <i>et al.</i> (1993)	Knauth <i>et al.</i> (1993)	Knauth <i>et al.</i> (1993)
River km:	634	607	607	644	654	692	692	692
Sample. site:	Blankenese	Oortkaten	Oortkaten	Hetlingen	Stade	Brunsbüttel	Brunsbüttel	Brunsbüttel
Year	94/95	1987	1988	1988	1976	1989	1990	1991
α -HCH	21.1				9.0	1.6		<0.5
γ -HCH	18.2	19.1	19.0	11.6	8.0	3.6		0.6
HCB	39.4	345.2	258.0	59.5	70.0	34.0	50.4	11
DDE	9.5	36.4	45.4	14.7		4.1	7.8	1.6
DDD	19.8	152.9	102.3	58.0	50.0	21.0	27.3	12
DDT	21.5	69.4	1.7	7.7	16.0	6.1	8.6	<0.5
PCB 28	3.5					2.2	3.2	<0.5
PCB 52	13.4				8.0	2.0	2.4	0.6
PCB 101	3.4				7.3	3.9	5.1	3
PCB 118	1.4							
PCB 153	18.1	26.0	24.0	14.5	13.7	6.3	10.1	3.8
PCB 105	2.4							
PCB 138	20.4	33.6	21.0	8.4	12.8	7.6	9.2	2.4
PCB 156	2.8							
PCB 180	11.4				95.8	2.9	3.6	2.2

Dessau. In the analyses, the seasonal patterns of the individual compounds were compared with each other. These analyses were also performed separately within the individual substance groups (Figures 9 and 10). Here, too, the variables were standardized, so that only differences/similarities in the patterns, not in absolute concentrations, were evaluated.

Site-Specific and Seasonal Pollutant Patterns: At an Euclidean distance of 31 distance units (DU), PAHs clearly showed a separation into two clusters, each cluster consisting exclusively of samples from the same measuring station (Figure 8, PAH). At an Euclidean distance of 2.5 DU, three subclusters for Hamburg and three subclusters for Dessau can be distinguished. Among

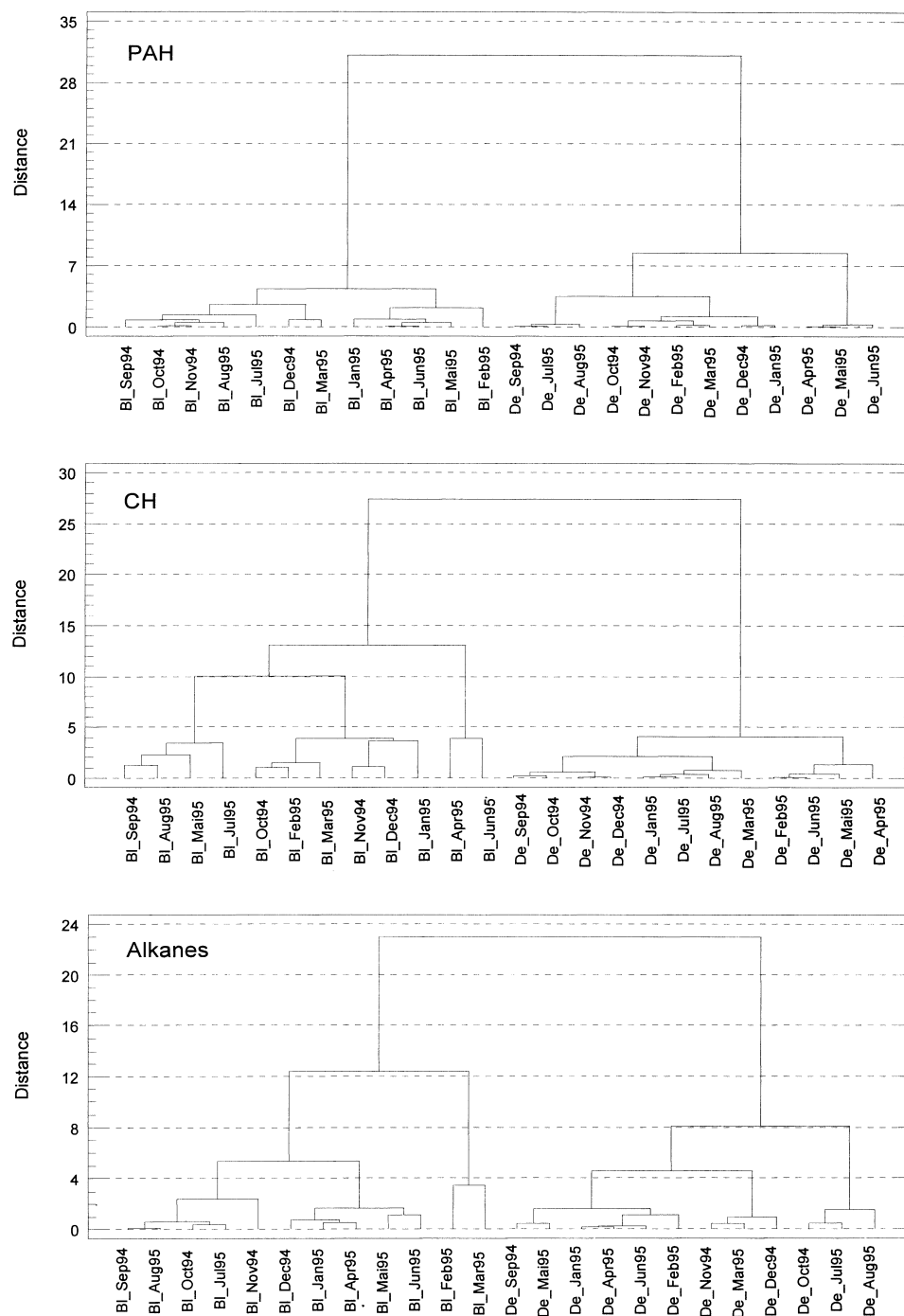


Fig. 8. Dendrograms for patterns of PAHs (top), CHs (middle), and the n-alkanes C-12 to C-20, as well as pristane and phytane (bottom) from SPM samples of the River Elbe at Hamburg (BI) and the River Mulde at Dessau (De) covering the period from September 1994 to August 1995 (complete linkage, Euclidean distance)

this subdivision, with the exception of cluster 2, groups of consecutive months are formed. Changes in the PAH pattern thus occurred relatively slowly and continuously in the course of the sampling period. It is interesting to note that the clusters 1 and 4 contained samples taken in consecutive years. For Hamburg, these were samples from July and August 1995, followed by samples from September to November 1994. At Dessau, samples from August and July 1995 were found together with a sample from September 1994. This allows the conclusion that PAH input, despite its anthropogenic origin, shows a certain constancy in its seasonal cycle. Clustering of BI_Dec94 and BI_Mar95 (cluster 2) is attributable mainly to

increased perylene and dimethylnaphthalene inputs as well as to markedly lower inputs of fluoranthene in those months.

Also for CH, significant differences were observed in the pollutant patterns of samples from Dessau and Hamburg. The Euclidean distance between the two clusters was approximately 27 DU, while a division into further clusters took place at approximately 13 DU for Hamburg, and about 4 DU for Dessau (Figure 8, CH). Similarities among the samples from Dessau thus are clearly higher than among those from Hamburg. Assuming a distance level of 8 DU for Hamburg and a distance level of 1.5 DU for Dessau, two times three clusters are also obtained in this case. Here, too, seasonal clustering is found,

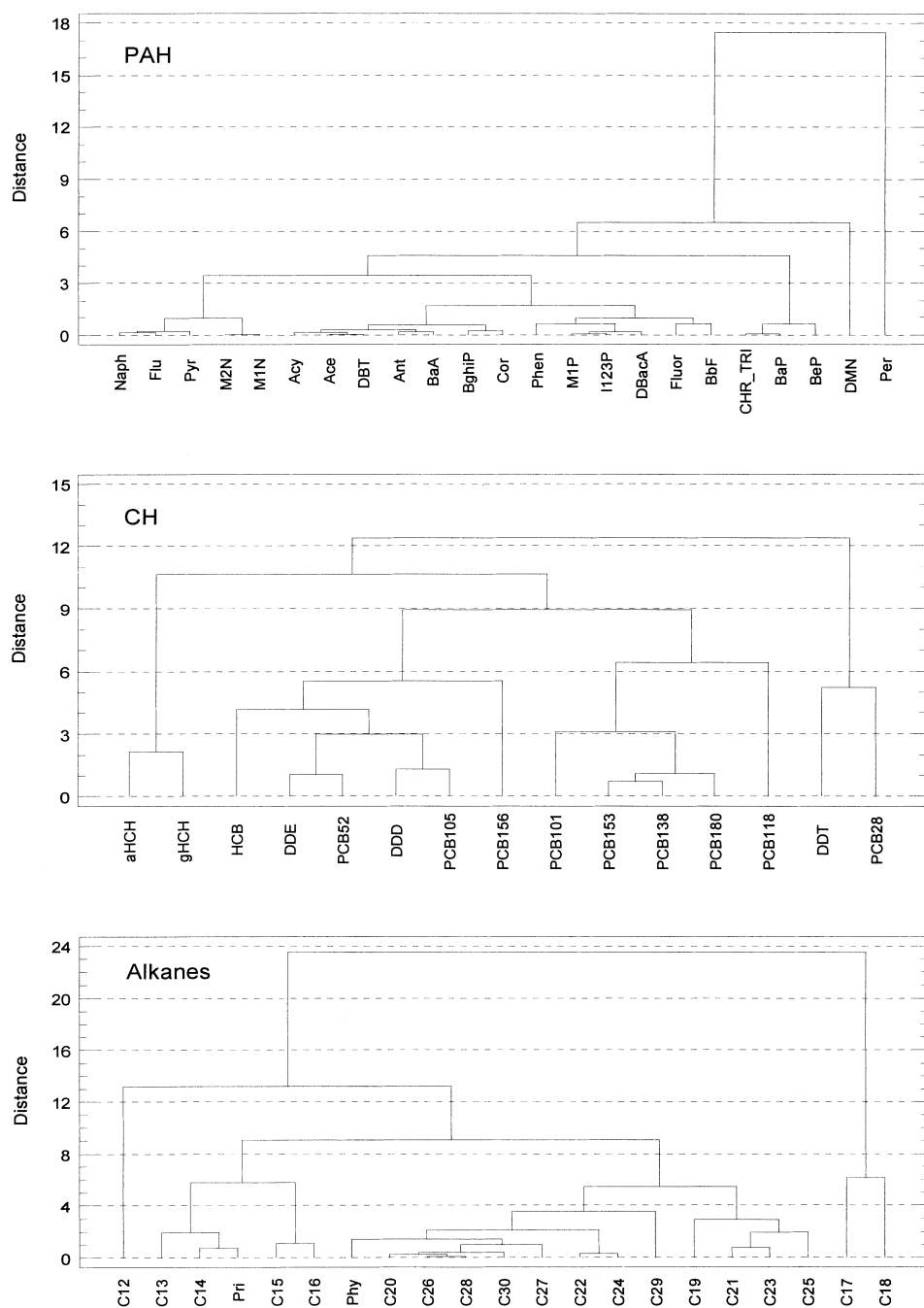


Fig. 9. River Elbe—dendrograms for single compounds of PAHs (top), CHs (middle), and n-alkanes (bottom) in SPM samples from September 1994 to August 1995 (complete linkage, Eukclidean distance)

which is not as marked as in the case of PAHs, with the samples from Dessau showing a lower variance. Cluster 1 of the Hamburg samples again shows a group of samples taken in consecutive years. This indicates a conservative input behavior.

For alkanes, unlike PAHs and CHs, a clear discrimination of two site-specific clusters was only possible after a selection had been made of n-alkanes C-12 to C-20, including pristane and phytane (Figure 8, n-alkanes). At a Eukclidean distance of 4 DU, six clusters were found, which once more indicated a seasonal correlation for Hamburg. This appears plausible in view of the dominance of biogenic n-alkanes. At Dessau, the situation was different because not only biogenic n-alkanes but also anthropogenic n-alkanes have an important influence on the alkane pattern. Cluster 6, which covers July and August, was due to the

low levels of low-boiling n-alkanes. Possible causes are either reduced input of light oil or higher evaporation, especially of low-boiling n-alkanes, during the summer months. In a cluster analysis of the n-alkanes C-12 to C-30, the largest difference (formation of two clusters with a Eukclidean distance of approximately 24 DU) was found for De_Jan95, De_Jun95, De_Feb95, and De_Apr95 and the other samples (Figure 8, n-alkanes). These four samples had the highest levels of the low-boiling n-alkanes C-12 to C-14. The next clustering was made for BI_Jul95, BI_Aug95, and BI_Sep94 and the other samples. These samples had the highest relative concentrations of C-17 (algal bloom). A separation of the samples from Hamburg and Dessau, with the exception of De_Oct95 and DeNov95, is only made at the next hierarchical level.

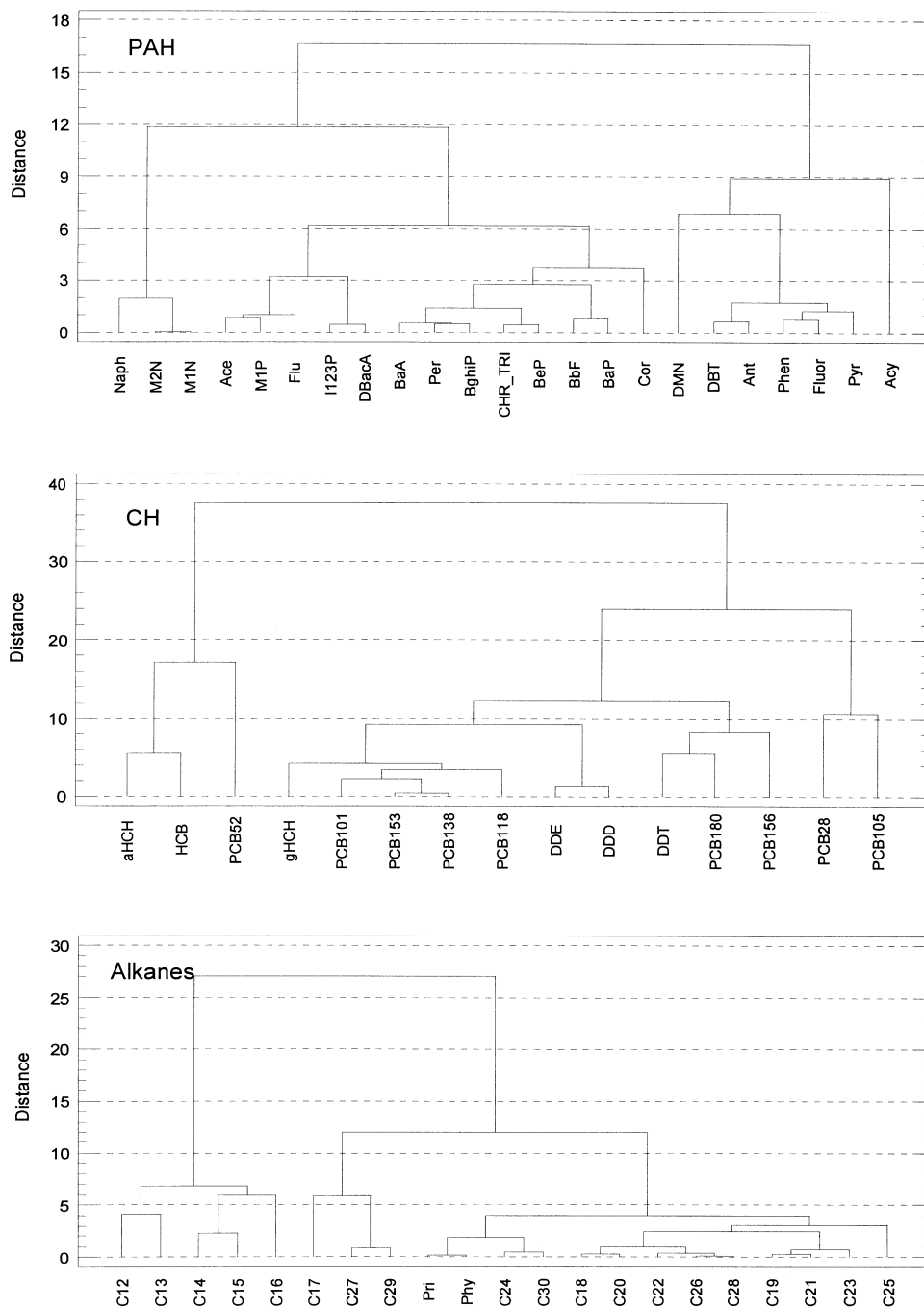


Fig. 10. River Mulde—dendrograms for single compounds of PAHs (top), CHs (middle) and n-alkanes (bottom) in SPM samples from September 1994 to August 1995 (complete linkage, Euclidean distance)

Clustering of Single Compounds: Figure 9 shows, with respect to the samples from Hamburg, that perylene and dimethylnaphthalene showed the largest relative changes in the seasonal cycle, related to the patterns of the other PAHs. By contrast, the largest similarities were observed for mono-methylated naphthalenes. At a Euclidean distance of 1.5 DU, a total of six clusters was formed; the relative composition of the PAH in the individual clusters showed major similarities during the sampling period. Because of the constancy of their patterns, such clusters are good indicator compounds that, through relative pattern changes, are capable of indicating PAH input from other sources (provided such inputs have different patterns). At Dessau, a subdivision into six subclusters was made at about 5

DU. The relative composition of PAH within the individual clusters showed a clearly lower constancy than that of the Hamburg samples (Figures 9 and 10). PAH input obviously had different sources, which weighted differently during the sampling period. Like the Hamburg samples, the largest similarities in the Dessau samples were found for methylated naphthalenes. These findings, like the invariant behavior of perylene and 2,6-dimethylnaphthalene at Hamburg, were confirmed by correlation analyses, which explains why they form separate clusters.

For CHs at Hamburg, the first separation of DDT and PCB 28 from the other CHs was found at 12 DU, followed by a cluster of α - and γ -HCH at 10 DU (Figure 9). The next separation (8 DU) produced two clusters, one of which consisted of PCB

Table 5. Correlation matrix for the sum contents of n-alkanes, PAHs, CHs, and general hydrographic parameters. Correlation coefficients (r) and significance levels (p) for SPM of the sampling site Hamburg are shown on the right side of the diagonal, values for Dessau are presented on the left side of the diagonal

	AH/DM	AH/TOC	PAH/DM	PAH/TOC	CH/DM	CH/TOC	TOC	SPM	Discharge
AH/DM									
r		0.521	0.933	0.281	0.963	0.482	0.705	-0.198	0.780
p		0.083	0.000	0.379	0.000	0.113	0.010	0.537	0.003
AH/TOC									
r	0.692		0.723	0.909	0.579	0.917	-0.228	-0.704	0.737
p	0.013		0.008	0.000	0.048	0.000	0.476	0.011	0.006
PAH/DM									
r	0.361	0.847		0.587	0.945	0.711	0.468	-0.405	0.874
p	0.250	0.001		0.045	0.010	0.125	0.192	0.000	
PAH/TOC									
r	0.127	0.774	0.943		0.392	0.914	-0.414	-0.752	0.621
p	0.695	0.003	0.000		0.207	0.000	0.181	0.005	0.031
CH/DM									
r	0.428	0.299	0.244	0.131		0.634	0.621	-0.356	0.839
p	0.165	0.345	0.445	0.685		0.027	0.031	0.255	0.001
CH/TOC									
r	0.149	0.637	0.734	0.789	0.649		-0.195	-0.779	0.782
p	0.645	0.026	0.007	0.002	0.022		0.543	0.003	0.003
TOC									
r	0.369	-0.405	-0.635	-0.829	0.230	-0.575		0.339	0.292
p	0.239	0.192	0.027	0.001	0.472	0.051		0.281	0.357
SPM									
r	0.100	-0.367	-0.633	-0.638	0.101	-0.425	0.663		-0.349
p	0.770	0.267	0.037	0.035	0.767	0.193	0.026		0.266
Discharge									
r	0.297	0.314	0.302	0.211	0.540	0.447	-0.016	0.077	
p	0.349	0.320	0.341	0.511	0.070	0.145	0.960	0.822	

exclusively, and the other of the DDT metabolites DDE and DDD, as well as of HCB and three PCBs. It is clearly seen that the seasonal cycle of pesticides differs from that of PCB, indicating different sources, which appears plausible considering the different applications of these CHs. At Dessau, a higher variance among the single compounds was observed (Figure 10), similar to that observed for PAH. Again, it may be assumed that the different CHs have diffuse sources, which had different impacts during the sampling period. High similarities were found at Dessau for DDE and DDD (2 DU), as well as one cluster consisting of PCB 101, 118, 138, and 153 (4 DU). A cluster of four PCBs was also found at Hamburg at a Euclidean distance of about 4 DU. In this case, it was a combination of PCB 101, 138, 153, and 180. As in the case of PAH, these clusters of four PCBs each may indicate input changes, which are reflected in changes of the relative PCB patterns.

Alkanes at Dessau showed significant clustering of the low-boiling n-alkanes C-12 to C-16 and of the other n-alkanes at 27 DU (Figure 10). From evaluations discussed above, it is known that this is due to light oil input into the Mulde river throughout the sampling period. Separation of these anthropogenic n-alkanes from the other n-alkanes again indicates that these are attributable to a different source. Alkanes C-17 to C-30 split up into further clusters at a Euclidean distance of 1.5 DU. These clusters consisted exclusively of odd-numbered and even-numbered n-alkanes (including pristane and phytane), respectively, again confirming the conclusion that odd-numbered, primarily biogenic n-alkanes have sources that differ from those of even-numbered n-alkanes. At Hamburg, one cluster was found that showed high similarities of the even-

numbered n-alkanes C-20 to C-30 and phytane (2.5 DU, Figure 9). Another cluster of odd-numbered n-alkanes C-19 to C-25 was found at 3 DU, and the other n-alkanes could not be allocated to any particular input source.

Correlation Analysis

Correlation analyses were performed in order to examine linear dependencies of contaminant concentrations and several hydrographic parameters. Table 5 contains the correlation coefficients r and the significance level p for each variable examined. The significance level p was computed on the basis of the t-test for a statistic certainty of 95%. Correlation coefficients greater than 0.5 together with p values smaller than 0.05 indicate a significant interdependency of the variables examined, whereas p values equal to or greater than 0.05 indicate that there is no significant correlation between the variables.

The contaminant levels of n-alkanes, PAHs, and CHs, in the form of sum contents, were compared to the levels of TOC (weight %), SPM (mg L^{-1}), temperature ($^{\circ}\text{C}$), and water discharge ($\text{m}^3 \text{s}^{-1}$). The comparisons were made for contaminant levels per DM ($\mu\text{g/g}$) on the one hand, and for contaminant levels per TOC ($\mu\text{g/g}$) on the other. Table 5 shows the correlation coefficients and significance levels for Hamburg to the right of the diagonal line and for Dessau to the left of the diagonal line. All parameters for which significant correlations were determined are printed in boldface.

Contaminant Sum Contents: At Hamburg, linear significant dependencies were found among the individual substance groups. The highest correlation coefficients between substance groups were found when comparing the concentrations per DM. In the case of n-alkanes, this was $r = 0.963$ for correlations with CHs, and $r = 0.933$ for correlations with PAHs. PAHs, in correlations with CHs had a coefficient of $r = 0.945$. At Dessau, significant correlations were found when comparing contaminant levels per TOC: $r = 0.774$ for n-alkanes and PAHs, $r = 0.637$ for n-alkanes and CHs, and $r = 0.789$ for PAHs and CHs.

Water Discharge: Dependencies were found between the contaminant levels (per TOC) and discharge volumes (n-alkanes $r = 0.780$, PAHs $r = 0.874$, CHs $r = 0.839$). Possible causes are runoff of surface depositions, which are transported into the rivers by rain and melted snow, mainly during late winter and in spring. An other reason can be the resuspension of contaminated sediments. At Dessau, a correlation between contaminant levels and discharge volumes can only be seen as a tendency, without having significance.

TOC: At Hamburg, a correlation of n-alkanes with the level of TOC of the SPM samples was found, which was not the case with PAH. According to (Bouloubassi and Saliot 1993), the decoupling of PAHs and n-alkanes is attributable to primarily biogenic input sources of n-alkanes, and almost exclusively anthropogenic input sources of PAHs. At Dessau, neither n-alkanes nor PAHs were found to correlate with TOC, which may indicate that here the n-alkanes, because of a high anthropogenic proportion, resemble the PAHs in their behavior.

SPM and Temperature: At Hamburg, negative correlations of the contaminant levels were found with the SPM contents (n-alkanes $r = -0.704$, PAHs $r = -0.752$, CHs $r = -0.779$) and temperature (n-alkanes $r = -0.721$, PAHs $r = -0.807$, CHs $r = -0.643$). Temperature and SPM contents showed a positive correlation ($r = 0.669$). High contaminant concentrations thus were determined at low SPM levels and low temperatures.

This may be mere coincidence, indicating that reduced bioproduction during the cold season leads to a low SPM level and that increased contaminant input is taking place during this time, which appears plausible at least for PAHs stemming from combustion. Studies of n-alkanes and PAHs in the total water body (aqueous phase and SPM) (Theobald *et al.* 1995) as well as of PAHs in the aqueous phase (Umweltbehörde 1995) of the Elbe River in fact showed basically higher concentrations during the winter months.

Nevertheless, causal links between these correlations cannot be excluded. Investigations of the distribution equilibrium of organic compounds between the particulate and liquid phases revealed a significant inverse relationship of adsorption rates and the SPM content (Heemken 1997). This effect is caused by increasing concentrations of dissolved organic carbon (DOC) in dependence of the SPM content. This increased DOC (humic substances) effects enhanced the solubility of the compounds in form of colloids, which leads to decreased enrichment rates in the particulate phase.

Correlations of Single Compounds: As expected, correlations of single compounds in the substance groups studied confirm the results of the cluster analyses. Compounds characterized by short Eukclidean distances in the dendrograms (Figures 9 and 10) had significant correlations among each other. For example, the 1- and 2-methylnaphthalenes, which clustered at Eukclidean distances < 0.1 DU in the samples from Dessau and Hamburg, both have correlation coefficients of 0.999. Fluoranthene and benzo[*b*]fluoranthene, with a distance of 0.8 DU, had a correlation of 0.972. Correlations of dimethylnaphthalene with the other PAHs (6 DU) ranged from 0.7 to 0.85. By contrast, perylene, which constituted a separate cluster at Hamburg, showed no significant correlation with any of the other PAHs. At Hamburg, correlation analyses of the single compounds with the sum of the PAHs quantified showed the highest correlation coefficients for acenaphthene ($r = 0.995$), anthracene ($r = 0.995$), dibenzothiophene ($r = 0.997$), dibenzo[*a,c*]anthracene ($r = 0.991$), and indeno[1,2,3]pyrene ($r = 0.991$). At Dessau, the highest correlation coefficients were found for fluorene ($r = 0.977$), 1-methylnaphthalene ($r = 0.967$), anthracene ($r = 0.959$), 1-methylphenanthrene ($r = 0.969$), and perylene ($r = 0.936$). Owing to their high correlation coefficients, these PAH are suitable as guiding parameters for monitoring the sum of PAHs in the areas examined. The lowest coefficients were determined for perylene ($r = 0.441$) at Hamburg and for dimethylnaphthalene and acenaphthylene at Dessau, which again confirms findings from cluster analysis.

SPM as Indicators of Pollutant Loads

Adsorption of organic compounds to SPM is influenced by a number of factors, the most important one being the chemical/physical properties of the substance groups concerned. Within a particular substance group, the adsorption rates can vary considerably. Figure 11 shows the partitioning of n-alkanes, PAHs, and CHs between aqueous and particulate phases (water samples of the River Elbe at Hamburg, November 1995, SPM content approximately 20 mg/L). For this investigation, separation of SPM was performed by centrifugation. For experimental details concerning the sampling see Heemken *et al.* (1998), for extraction of water samples see Theobald *et al.* (1990).

Alkanes showed a slightly alternating pattern, with biogenic (odd-numbered) n-alkanes being slightly more concentrated in SPM. The particle-bound n-alkanes amounted to 70%. PAHs showed a drastic shift in their phase distribution from two-ring systems up to seven-ring systems. Naphthalene and the methylnaphthalenes were dissolved in the aqueous phase at about 80%, but the higher fused PAHs showed the strongest enrichment in the particulate phase (up to 80%). Similar results were found by Weber and Ernst (1983) for PAHs in the Weser estuary, where association rates of five-ring PAHs reached to 90%. Also, PCBs showed a slight trend toward higher adsorption rates, which in this case depended on the degree of chlorination (Duinker 1986). The adsorption rates ranged from 60 to 80% (the concentration of PCB 156 in the aqueous phase was below the detection limit). By contrast, HCHs are dissolved nearly completely in the aqueous phase despite their K_{ow} values, which are comparable to those of methylnaphthalene (log K_{ow} about 3.8) (de Bruijn *et al.* 1989; Sangster 1989). This

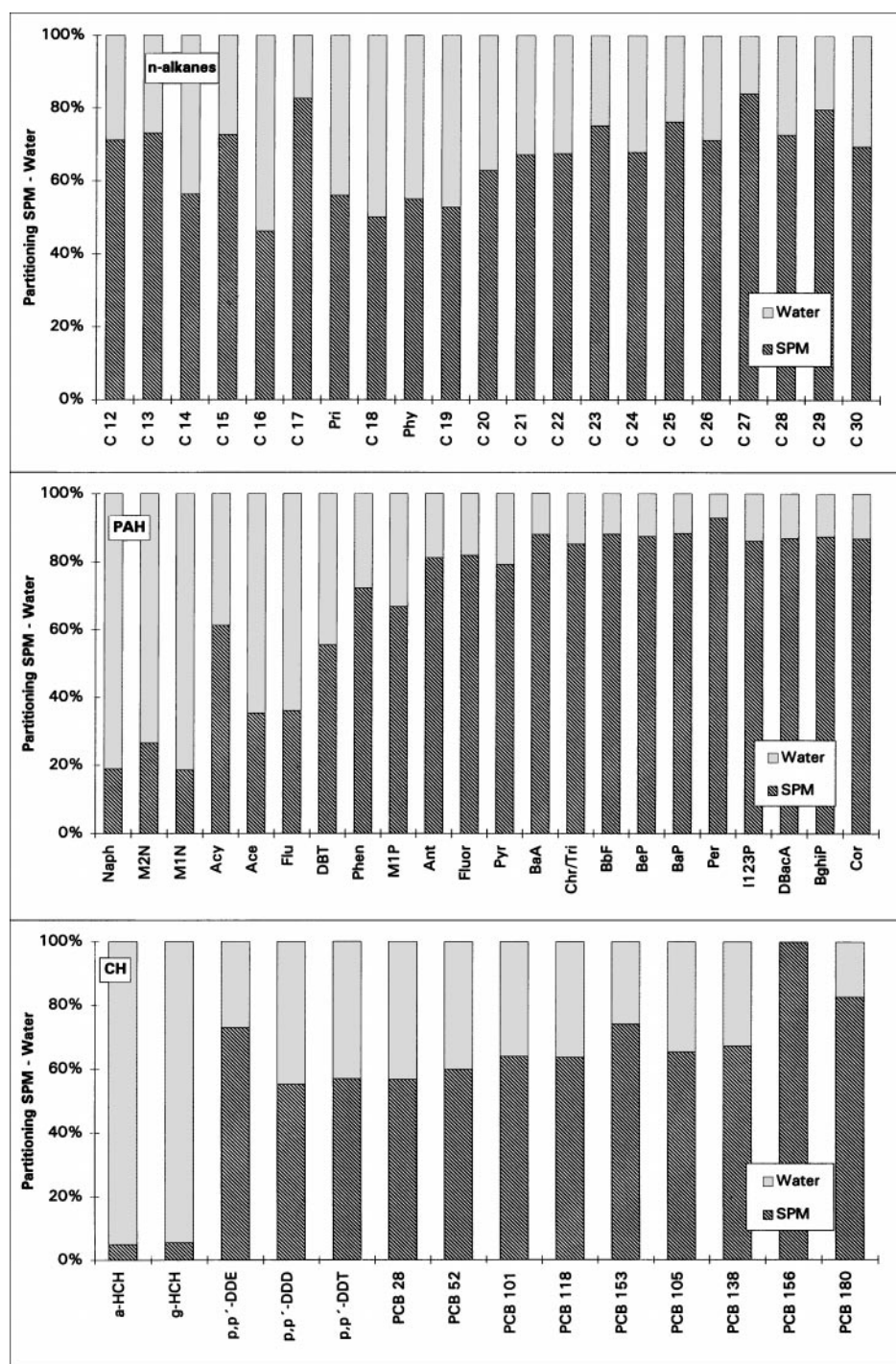


Fig. 11. Partitioning of n-alkanes (top), PAHs (middle), and CHs (bottom) between SPM and aqueous phase in water samples of the River Elbe (Hamburg, November 1995)

finding was confirmed by several investigations (Duinker and Hillebrand 1979; Weber and Saliot 1983). Another factor influencing the enrichment of organic trace substances is the amount of TOC in SPM. In SPM from the River Mulde at Dessau, which had markedly higher pollutant levels, the TOC levels on average were about 4 weight % higher than in SPM from the River Elbe at Hamburg. The TOC content thus is an important value in the context of pollutant levels.

Therefore, in evaluations of water quality on the basis of SPM analysis, the distribution of pollutants among the different

compartments and the relationships of these partitioning processes (SPM content, temperature, TOC, etc.) must be taken into account. In the example of Dessau, it becomes clear that naphthalene concentrations, which are very high in SPM samples anyway, are many times higher in the water column. The same is true for HCHs. For the evaluation of pollutant loads of the total water body (as a sum of aqueous and particulate phases), as well as in comparisons between the pollutant patterns derived from SPM analyses and those of potential input source, the distribution between the aqueous and particulate

phases has to be studied in detail for the individual compounds. In this context, it should be investigated to what extent the trapped SPM is representative for the entire (not sedimented) SPM inventory.

Conclusions

Pollutant Loads

Taking into account the average monthly SPM levels and water discharge, the particle-bound pollutant loads calculated for the River Mulde at Dessau were 0.55 t/a n-alkanes, 0.14 t/a PAHs, and 15.5 kg/a CHs in the sampling period from September 1994 to August 1995. The particle-bound pollutant loads in the River Elbe at Hamburg were 13.4 t/a n-alkanes, 4.1 t/a PAHs, and 176 kg/a CHs. Although processes like sedimentation and resuspension of SPM had not been considered in these estimations, plausibility checks of the PAH and CH levels of the Elbe with literature data showed good agreement.

Alkanes

Input of n-alkanes at sampling sites Hamburg and Dessau had different sources. At Hamburg, n-alkane input was primarily biogenic, consisting of terrestrial plant components and, depending on the season, C-17 and C-15 input due to aquatic organisms. Only a small proportion of n-alkane input at Hamburg was attributable to petroleum sources. At Dessau, the results showed input of light oil throughout the sampling period, constituting approximately 25% of the total n-alkane concentration. Input of high-boiling petroleum components was found to be about 5% lower than in the Elbe River, and again the share of long-chain hydrocarbons from C-20 consisted mainly of biogenic, terrestrial n-alkanes.

PAHs

SPM in the River Mulde had unusual high concentrations of naphthalene; it was probably due to a specific naphthalene input source. A comparison of the fluoranthene-standardized PAH concentrations from both stations clearly showed that higher fused ring systems, which mainly stem from combustion processes (four- to six-ring systems), had considerably higher relative concentrations in SPM from the River Elbe than from the River Mulde, where higher relative concentrations of the two- and three-ring systems naphthalene, 1- and 2-methylnaphthalene, acenaphthylene, dibenzothiophene, phenanthrene, and 1-methylphenanthrene were measured. These high concentrations of two- and three-ring systems in the samples from Dessau confirm findings that petroleum input is higher in the River Mulde than in the River Elbe.

CHs

SPM samples from the River Mulde had comparatively high pesticide levels. Concentrations of γ -HCH exceeded those in the River Elbe approximately by a factor of 6, α -HCH by about

a factor of 3. Concentrations of HCB, which in the samples in the River Elbe had the highest concentrations of all CHs, were found to be higher by about a factor of 3 in the River Mulde. The largest differences were found for DDT and its metabolites DDD and DDE. The maximum DDT load in the River Mulde was 840 ng/g DM, and the maximum in the River Elbe was 69 ng/g DM. On average, concentrations of DDT, DDD, and DDE in the Mulde were about 10, 15, and 25 times higher, respectively, than in the River Elbe. By contrast, the PCB levels in solid particulate matter from the Rivers Mulde and Elbe were about equal, although there were differences in the pattern of PCB congeners.

Cluster Analysis

A hierarchical cluster analysis was performed that showed that, with a high significance, the pollutant patterns of PAHs and CHs were sampling site-specific both in the Rivers Elbe and Mulde throughout the sampling period. By contrast, for n-alkanes only the C-12 to C-20 range could be clearly allocated to the sampling sites. In all cases, clustering of mostly consecutive months indicated continuous, slow changes of input, which moreover showed a certain constancy with respect to annual cycles. It would be promising, therefore, to prepare site-specific pollutant patterns to be able to record changes in the pollution situation on the basis of selected single compounds. Moreover, a comparison of additional sampling stations on the River Elbe and its tributaries appears useful in order to estimate the impacts of different input sources on the basis of similarities or differences in the pollutant patterns.

Correlation Analysis

The correlation analysis showed a number of linear dependencies of the pollutant summary parameters among each other and with general hydrographic parameters like temperature, SPM content, and water discharge. It will have to be clarified whether there are any causal links or whether this is mere coincidence.

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