Part C PRESENT AND FUTURE QUALITY OF SEDIMENTS IN THE RHINE CATCHMENT AREA - PAHS, PCBS

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1 Introduction

The current Dutch chemical criteria for relocation of dredged material in the North Sea (table D 5-2) include besides metals a number of organic substances: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), several pesticides and hexachlorobenzene. With regard to the present regulation of organic contaminants, PAHs and PCBs are of concern, i.e. that concentrations of these substances frequently exceeded the Sea/Slufter limits (for relocation in the North Sea) in dredged material from the eastern parts of the port of Rotterdam.

For that reason, PAHs and PCBs were selected for the following investigation of point and diffuse sources in the Rhine catchment area, focussing on the relevant pathways with the aim to estimate their contribution to the contamination of the sediments in the port of Rotterdam. The methodology generally is comparable to the one applied to metals: (i) immission analysis, (ii) emission analysis/MONERIS, (iii) scenarios.

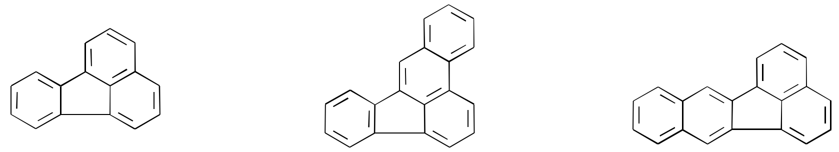
In the following two chapters a short introduction to PAHs and PCBs and their fate in the environment is given.

1.1 Compounds of interest

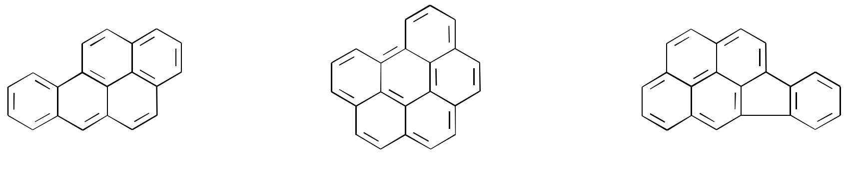
Polyaromatic hydrocarbons (PAHs)

A few PAHs, especially naphtalene, are produced technically, e.g. by distillation from coal tar. However, combustion of fossil fuels and related processes are responsible for the majority of PAH releases to the environment (residential heating, traffic, coke production etc.). Additional inputs to the environment occur from wood preservation with products derived from mineral oil or coal tar. Natural sources such as volcanoes and fires are to be neglected in comparison to anthropogenic sources, at least for Europe.

PAHs are a class of chemical compounds comprising different structures. Common to all these compounds is a condensed aromatic ring structure. Benzo(a)pyrene and benzo(b)fluoranthene are known to be carcinogens. Single PAHs are measured and the results most often are given as sum 6 PAHs (Borneff PAHs), sum 10 PAHs (VROM PAHs) or sum 16 PAHs (US-EPA PAHs). Individual PAHs included in the sum parameters are listed in appendix 1.1 and structures of selected PAHs are depicted in figure 1-1.



fluoranthene benzo(b)fluoranthene benzo(k)fluoranthene



benzo(a)pyrene benzo(ghi)perylene indeno(1,2,3-cd)pyrene

Figure 1-1: Structures of selected PAHs

Compared with other PAHs, most data, e.g. on emissions, are available for benzo(a)pyrene (BaP). For atmospheric emissions, relative BaP portions of sum 6 PAHs (5 %) and of total PAHs (1 %) were estimated (UBA, 1998a).

Polychlorinated biphenyls (PCBs)

From the beginning of the commercial production of PCBs in 1929, they were used in open applications as well as in closed systems:

- Open applications: e.g. as lubricants and in the paper and plastics production
- Closed systems: e.g. as dielectrics in capacitors and transformers, as hydraulic oil in mining

During the last 20 years PCB releases to the environment decreased, mainly due to the out-phasing of open applications and stricter regulations on their utilisation in closed systems. Emissions of PCBs are expected to continue at a lower level, e.g. due to scrap metal utilisation of electrical appliances with small capacitors.

PCBs are produced commercially by direct chlorination of biphenyl which results in possible 209 different compounds (congeners). Non-ortho or mono-ortho substituted PCBs, often referred to as coplanar PCBs, are classified as especially toxic due to their dioxin-like mode of action (Ahlborg et al., 1994).

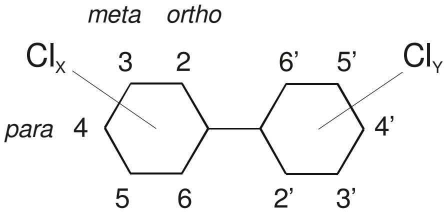


Figure 1-2: PCBs - numbering of chlorine substitution at the biphenyl molecule

Most often single PCBs (main components) are measured and the results given as:

- PCBs (sum 6): PCB 28, 52, 101, 138, 153, 180 (according to IUPAC)
- PCBs (sum 7): PCB 28, 52, 101, 118, 138, 153, 180 (according to IUPAC)

PCB 118 is the only coplanar congener comprised in the above given sum parameters. PCB congeners are numbered according to IUPAC, a higher number reflecting a higher degree of chlorination.

Annema et al. (RIVM, 1995) estimated that PCBs (sum 6) represent about 20 % of total PCBs. This value was derived as an average of technical PCB mixtures and PCB concentrations in soil samples.

1.2 Fate in the environment

The fate of PAHs and PCBs, released to the environment, depends on their physico-chemical properties among other parameters. PAHs and PCBs are classified as persistent organic pollutants (POPs). Although classified as 'persistent', degradation has to be taken into account, at least for atmospheric processes. For degradation in the atmosphere the reaction with OH radicals is assumed to be the main mechanism in the gas phase. Photolysis is considered to be important for some compounds as BaP as well. The degradation in water, soil and sediment is determined by different processes as biodegradation, hydrolysis and photolysis.

Table 1-1 gives an overview of estimated half-lifes in different environmental compartments for PAHs and PCBs (Mackay et al., 1992a, 1992b). Half-lifes generally increase for the different compartments in the order: air < water < soil < sediment. In case of PAHs, incorporated into soot particles in near-source areas, atmospheric half-lifes can be longer. Degradation of PCBs generally decreases with increasing degree of chlorination.

Table 1-1: Half-lifes of PAHs and PCBs in different environmental compartments

	Air class	Water class	Soil class	Sediment class
Fluoranthene	4	6	8	9
Benzo(a)pyrene	4	6	8	9
Dichloro-PCB	4	7	8	8
Heptachloro-PCB	7	9	9	9

Class	Mean half-life / hours	Range / hours
4	170 (~1 week)	100-300
5	550 (~3 weeks)	300-1,000
6	1,700 (~ 2 months)	1,000-3,000
7	5,500 (~8 months)	3,000-10,000
8	17,000 (~2 years)	10,000-30,000
9	55,000 (~ 6 years)	> 30,000

PAHs and PCBs are non-polar compounds with low water solubilities and comparably high octanol-water partitioning coefficients (log P_{OW}), which is reflected in their tendency to accumulate in soils, sediments and organisms. In surface waters with typical concentrations of 10 mg/L suspended particulate matter (SPM), compounds with log $P_{OW} > 5$ occur only to a small extent in the aquatic phase but are mainly bound to SPM.

PCBs with increasing degree of chlorination and PAH with increasing molecular weight (increasing number of ring systems) show an increasing octanol-water partitioning coefficient (log P_{OW}) and decreasing vapour pressure:

- PCB 28: log P_{OW} 5.6, vapour pressure 30 mPa (25 °C)
- PCB 180: log P_{OW} 7.2, vapour pressure 0.08 mPa (25 °C)
- PAHs (more than four ring systems): log $P_{OW} > 6$, vapour pressure < 0.005 mPa (25 °C)

The transport of PAHs and PCBs can follow a multi-media pathway (e.g. atmospheric and riverine transport). The residence time in the atmosphere for PAHs and PCBs is mainly affected by wet scavenging via precipitation, dry deposition of particles, or air-surface exchange. For near-source areas, particle deposition of PCBs appears to be the most important mechanism whereas in areas remote from sources PCBs are expected to prevail in the gas phase (table 1-2, Shatelov et al., 1999).

Table 1-2: PCB fractions sorbed on atmospheric aerosol particles at 10 °C

PCB	28	52	101	118	138	153	180
Aerosol fraction / %	0.4	1	5	13	26	21	61

In contrast to the PCBs, higher molecular weight PAHs as BaP are expected to be mainly bound to aerosol particles (Shatelov et al., 1999):

- BaP:	gas fraction approx. 10 %
- PAH (5 or more ring systems) as BbFl, BkFl and Ind:	gas fraction < 10 %

Berdowski et al. (1993) estimated that about 50 % of the total mass of BaP emitted in Europe is bound to (or incorporated in) in particles larger than 20 µm. This is one reason why atmospheric deposition rates near PAH sources are distinctly higher than in areas remote from sources. Calculations for the atmospheric transport of BaP indicated that 80 % of European BaP emissions are being deposited in Europe itself.

PCBs have a ‘multi-hop’ nature, i.e. for PCBs re-emissions from soil and water occur which explains their long-range transport to remote areas as the Arctic region.

1.3 Modelling approach

From the discussion in the preceding chapters it is apparent that individual PAHs or PCBs have differing physical and chemical properties, which determine their transport and fate in the environment. For that reason, individual compounds were selected for modelling, which are representative to some extent for the each class of compounds:

- PAHs: fluoranthene (Fl), benzo(b)fluoranthene (BbFl), benzo(a)pyrene (BaP)
- PCBs: 52, 138, 180 (according to IUPAC)

The modelling approach comprised basically the following four steps:

1. Immission analysis: estimation of point and diffuse loads (chapter 2)
2. Check for significance of certain pathways by regression analysis (2.4)
    - estimated diffuse loads and paved urban areas
    - estimated point loads and population connected to wastewater treatment plants
3. Emission analysis (MONERIS) for source apportionment (chapter 3)
4. Scenarios modelled with MONERIS and driven by reduction coefficients for the individual pathways (chapter 5)

All four steps of the modelling approach were carried out for the Rhine catchment area upstream Bimmen/Lobith, the Dutch/German border. Subsequently the results of the scenario analysis were used to forecast the future quality of sediments in the eastern parts of the port of Rotterdam.

2 Immission analysis

A description of the method using immission (observed load) data for the separation of point and diffuse sources is given in chapter B 2.1 (metals). This method was up to now primarily used for estimating the share of point and diffuse sources at the load for nutrients (Behrendt, 1993 & 1994; Behrendt et al., 1999 & 2000; Braun, 1994) and heavy metals (Behrendt, 1993; Vink et al., 1999). An application to organic chemicals was till now lacking.

2.1 Database - monitoring data

Data sets comprising PAH and PCB concentrations in suspended particulate matter (SPM), SPM concentrations and discharge data for several monitoring stations were kindly provided by the International Commission for the Protection of the Rhine (ICPR, 2000), Rheinguetestelle Worms (Diehl, 2000) and other institutions[1]. However, consistent data sets for the immission analysis of the selected PAHs and PCBs could only be obtained for the time period 1991 - 1996 for the following monitoring stations:

- Lauterbourg (Rhine), no data for 1991 - 1992
- Koblenz (Mosel)
- Koblenz (Rhine)
- Bad Honnef (Rhine), no data for 1991
- Bimmen (Rhine)
- Lobith (Rhine)

2.2 Analysis of trends

The requirement for the application of the immission analysis is that for each individual monitoring station approximately 50 to 100 data sets for concentrations and discharge are available. Consequently the analysis can only be carried out for longer time periods of about 4 to 5 years with monitoring/sampling intervals of two weeks. Another precondition for the application of the method is that the point source discharges of substances remain unchanged within the time period investigated.

Thus, to achieve a low uncertainty of results, the data sets for the whole period 1991 – 1996 should be taken for one analysis. However, if during that period a large change in point loads (contribution of point sources to total loads) occurred, the results would be misleading for the period 1994-1996, which will be used for emission analysis in chapter 3.

Trends in concentrations of PAHs and PCBs in suspended particulate matter (SPM) or total loads, as discussed in chapter 4.1, do not necessarily reveal changes in point loads. For this reason, prior to the immission analysis, a trend analyses was conducted applying a discharge windows technique (Behrendt, 1997) to compare similar discharge regimes. Particularly windows in low and high discharge ranges are useful to detect trends; low discharges being more influenced by point sources and high discharges mainly dominated by diffuse sources. As

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[1] Landesanstalt fuer Umweltschutz Baden-Wuertemberg, Landesumweltamt Nordrhein-Westfalen, Bayerisches Landesamt fuer Wasserwirtschaft.

a measure for the selection of the windows, the mean discharge (Q_M) for the whole time series was used. Based on these value, two discharge windows were applied: a low discharge window ($Q < 2/3\ Q_M$) and a high discharge window ($Q > 4/3\ Q_M$). Changes of the average PAH and PCB concentrations at low discharge and high discharge conditions in the period 1990 and 1996 for four different Rhine stations is given in figures 2-1 and 2-2.

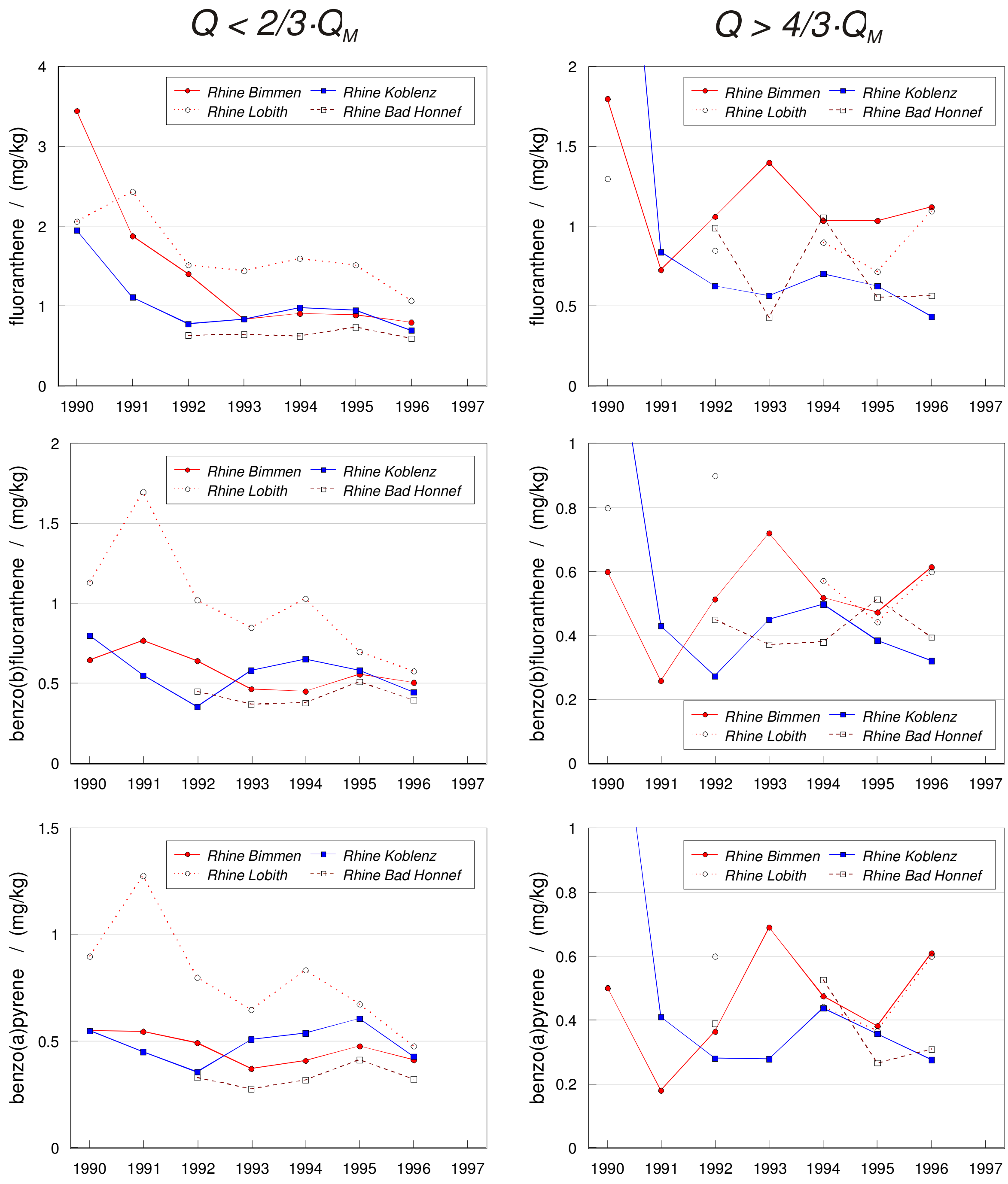
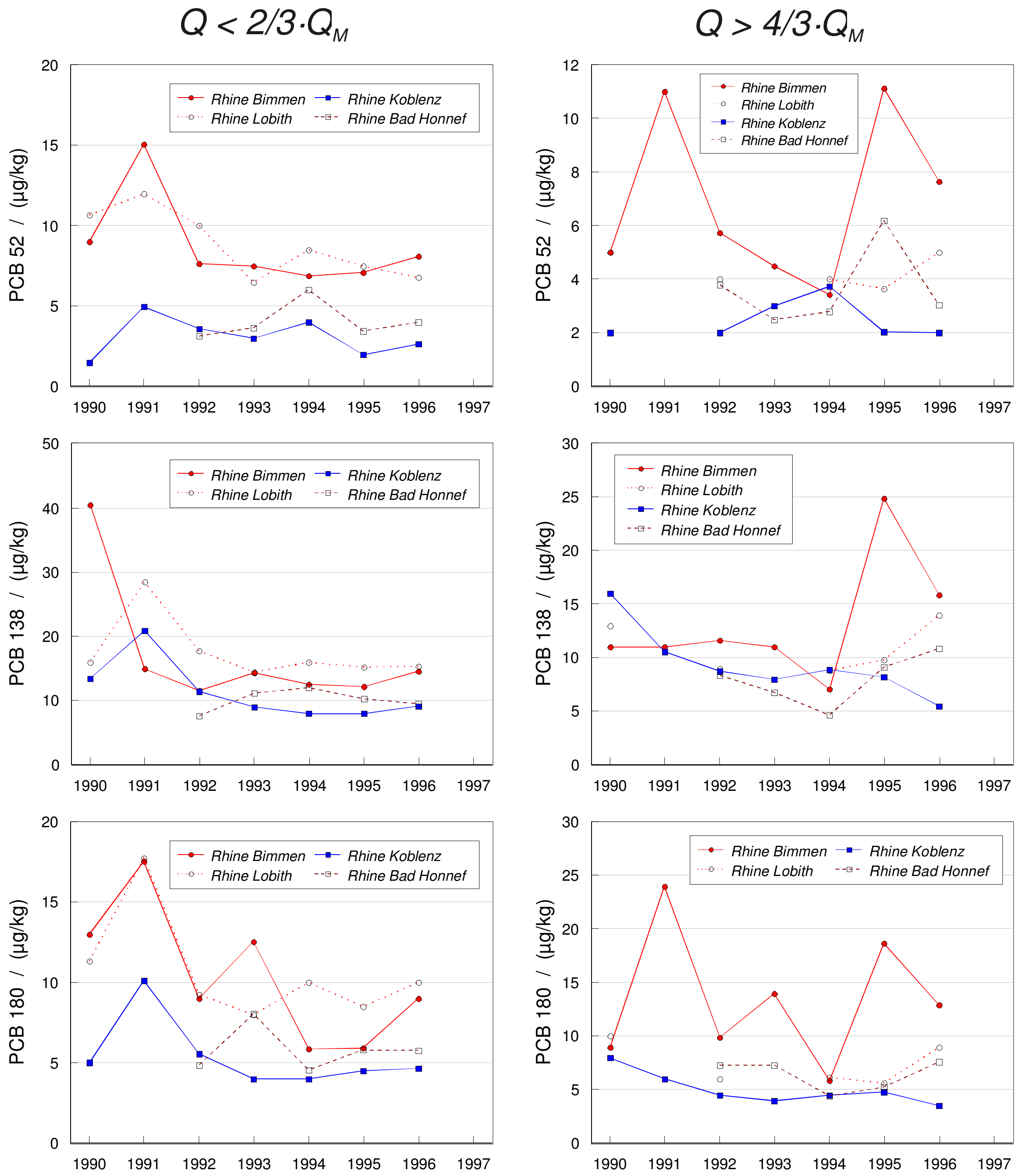


Figure 2-1: Change of the average PAH concentrations at low ($Q<2/3\ Q_M$) and high flow ($Q>4/3Q_M$) conditions for different Rhine stations in the time period from 1990 to 1996

At low discharge conditions, the selected PAHs and PCBs show higher concentrations in suspended particulate matter in the period 1990-1992 than in the following years for most of the

Rhine stations depicted in figures 2-1 and 2-2, thus indicating a possible decrease of PAH and PCB inputs from point sources from the beginning of the nineties until 1996.



$Q < 2/3 \cdot Q_M$ $Q > 4/3 \cdot Q_M$

Figure 2-2: Change of the average concentrations of selected PCBs at low ($Q<2/3\ Q_M$) and high flow ($Q>4/3Q_M$) conditions for different Rhine stations in the time period from 1990 to 1996

Therefore the whole time period was separated into two periods (1991-1993 and 1994-1996) for the immission analysis. The available number of data sets for both periods is then within the lower limit for this kind of analysis. However, accepting a higher uncertainty, especially for the period 1990-1993 (smaller number of data sets than for 1994-1996), seems more reasonable than conducting the immission analysis for the whole period 1991-1996. Including the years before 1993 into a joint analysis, the results for the last years would be skewed towards a too high share of point sources at the observed loads.

2.3 Separation of point and diffuse loads

Tables 2-1 and 2-2 present the results of the immission analysis for the investigated monitoring stations. The tables include the calculated total loads for suspended particulate matter (SPM), PAHs and PCBs for both time periods (1990-1993, 1994-1996) as well as the estimated point loads of PAHs and PCBs.

Table 2-1: Total loads and loads from point sources for the PAHs at different monitoring stations along the Rhine in the period 1991-1993 and 1994-1996

period	station	SPM	fluoranthene			benzo(b)fluoranthene			benzo(a)pyrene		
		total load 10^3 t/yr	total load kg/yr	point load kg/yr	relative point load %	total load kg/yr	point load kg/yr	relative point load %	total load kg/yr	point load kg/yr	relative point load %
91-93	Bimmen	2627	2922	862	29.5	1553	509	32.8	1310	359	27.4
94-96	Bimmen	3392	3137	436	13.9	1594	228	14.3	1382	212	15.3
91-93	Lobith	1619	1830	1149	62.8	1352	648	48.0	990	590	59.6
94-96	Lobith	3361	3073	391	12.7	1857	220	11.9	1506	189	12.6
91-93	Lob/Bimmen	2123	2376	1006	42.3	1452	579	39.8	1150	475	41.3
94-96	Lob/Bimmen	3377	3105	414	13.3	1726	224	13.0	1444	200	13.9
94-96	Bad Honnef	2382	2085	209	10.0	1193	123	10.3	1025	102	9.9
91-93	Koblenz	1486	1282	217	16.9	738	77	10.4	598	62	10.3
94-96	Koblenz	1986	1707	167	9.8	1099	119	10.8	1041	112	10.7
91-93	Koblenz (M)	223	464	22	4.8	261	13	4.8	198	10	4.9
94-96	Koblenz (M)	427	767	26	3.3	446	16	3.5	454	14	3.1
91-93	Koblenz	1263	818	195	23.8	477	64	13.4	400	52	13.0
94-96	Koblenz	1559	940	141	15.0	653	103	15.8	588	97	16.6
94-96	Lauterbourg	879	381	55	14.5	193	32	16.5	206	32	15.4

Table 2-2: Total loads and loads from point sources for the PCBs at different monitoring stations along the Rhine in the period 1991-1993 and 1994-1996

period	station	SPM	PCB 52			PCB 138			PCB 180		
		total load 10^3 t/yr	total load g/yr	point load g/yr	relative point load %	total load g/yr	point load g/yr	relative point load %	total load g/yr	point load g/yr	relative point load %
91-93	Bimmen	2627	22148	6188	27.9	37795	4881	12.9	44885	2994	6.7
94-96	Bimmen	3392	29741	3333	11.2	42070	4926	11.7	31414	3991	12.7
91-93	Lobith	1619	9997	6019	60.2	21246	10050	47.3	12355	5293	42.8
94-96	Lobith	3361	16585	2610	15.7	35109	4710	13.4	22984	3029	13.2
91-93	Lob/Bimmen	2123	16073	6104	38.0	29520	7465	25.3	28620	4143	14.5
94-96	Lob/Bimmen	3377	23163	2972	12.8	38589	4818	12.5	27199	3510	12.9
94-96	Bad Honnef	2382	13003	1575	12.1	23162	3033	13.1	14483	2214	15.3
91-93	Koblenz	1486	4537	1343	29.6	18702	6387	34.2	10367	1850	17.8
94-96	Koblenz	1986	5731	804	14.0	16601	2416	14.6	9551	1360	14.2
91-93	Koblenz (M)	223	1305	107	8.2	5370	314	5.8	3372	204	6.1
94-96	Koblenz (M)	427	1355	49	3.7	4151	250	6.0	2690	146	5.4
91-93	Koblenz	1263	3233	1236	38.2	13331	6073	45.6	6995	1646	23.5
94-96	Koblenz	1559	4376	754	17.2	12450	2166	17.4	6860	1214	17.7
94-96	Lauterbourg	879	2349	256	10.9	5544	940	16.9	3383	395	11.7

A significant decrease of absolute point loads of PAHs and PCBs can be observed at least for the downstream stations Bimmen/Lobith from the first period (1991-1993) to the second period (1994-1996). The estimated relative point loads of PAHs and PCBs (12-14 %) at Bimmen/Lobith for the period 1994-1996 have high inherent uncertainties due to the small number of data used for the analysis; mainly indicating that point sources contributed to total loads only to a minor amount. Moreover, comparing relative point loads for both periods, it has to be taken into account that calculated total loads of SPM, PAHs and PCBs are higher in the second period as in the period 1991-1993. This is caused by two large flood events with high transports of suspended solids and adsorbed substances in the period 1994-1996. Because the total loads of PAHs and PCBs are in the second time period higher compared with the first period, the respective relative contributions of point loads to total loads are lower.

2.4 Significance of certain pathways (regression analysis)

The immission analysis alone gives only a separation of the total load of a substance into portions caused by diffuse and point sources. The significance of certain sources/pathways for contaminants can be investigated by regression analysis. Significant inputs from wastewater treatment plants (WWTPs, point sources) should be related to point loads. Significant inputs related to diffuse sources could be expected to be related to:

- urban areas: diffuse loads from paved areas (e.g. after atmospheric deposition of PAHs and PCBs), which discharge via combined and separate sewer systems into rivers;
- erosion: diffuse loads from agricultural areas (PAHs and PCBs bound to particles in agricultural top soils enter rivers after rain events).

The regression analyses were calculated for the Rhine catchment area, summing up the following parameters (taken from Behrendt, 2000) (i) number of population connected to WWTPs, (ii) paved urban area and (iii) erosion from agricultural soils in downstream direction and correlating them with estimated point and diffuse loads derived in chapter 2.3.

The results of the regression analyses for WWTPs (number of population connected to WWTPs) and point loads as well as for paved urban area and diffuse loads are given in figure 2-3 (PAHs) and figure 2-4 (PCBs).

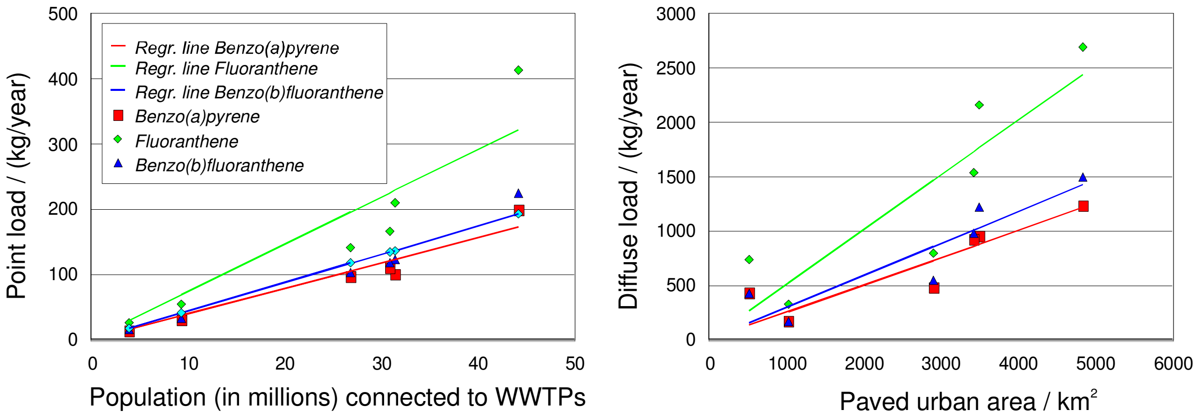


Figure 2-3: Dependencies of the point load of PAHs on the population number connected to WWTPs and of the diffuse load on the paved urban area in the basins upstream the monitoring stations in the period 1994-1996.

Point loads of PAHs and PCBs are significantly correlated with WWTPs. For benzo(a)pyrene, benzo(b)fluoranthene and PCB 138 the regression coefficient explains about 94% of the total variance, for PCB 180 and fluoranthene the regression coefficient is 84% and for PCB 52 73%. But even the latter is significant at a level of 10% uncertainty.

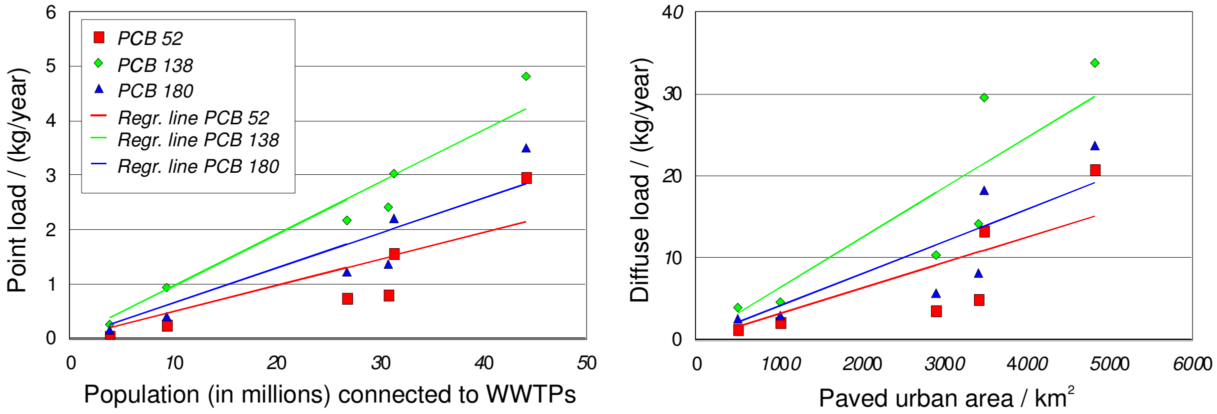


Figure 2-10: Dependencies of the point load of PCBs on the population number connected to WWTPs and of the diffuse load on the paved urban area in the basins upstream the monitoring stations in the period 1994-1996.

Diffuse loads are significantly correlated with paved urban areas. The estimated regression coefficients for PAHs and PCBs were in the range 73 % to 82 % with the exception of PCB 52 (66 %). Results for the regression analysis for erosion and diffuse loads (not shown) gave no significant correlation (regression coefficients for PAHs and PCBs in the range of 40 % to 55 %).

A combined approach (paved urban areas and erosion, multiple linear regression) for the diffuse loads was also tested. For all investigated substances the regression coefficients were only 1 % to 3 % higher than for the regression between diffuse loads and paved urban areas.

This pure statistical analysis show that there this is a strong indication that WWTPs are a major source for point loads and paved urban areas a major source/pathway for diffuse loads of PAHs and PCBs in the Rhine, erosion playing a minor role.

3 Modelling of point and diffuse sources in the Rhine catchment area

3.1 Emission analysis (MONERIS) - Rhine basin upstream Bimmen/Lobith

The emission analysis of PAHs and PCBs followed the same approach as applied for the heavy metals (chapter B 3.1). However, MONERIS (Modelling Nutrient Emissions in River Systems) was adapted for the specific requirements for modelling emissions of PAHs and PCBs. Figure 3-1 gives a general overview of pathways/ processes selected in this analysis. Certain pathways as groundwater, drainage and surface runoff comprising transport in the dissolved phase could be neglected as PAHs and PCBs are mainly transported bound to particles in terrestrial compartments (compare figure B 3-1, pathways for heavy metals). Concerning point sources, discharges from wastewater treatment plants (WWTPs) were taken into account whereas inputs from industry were not included (see below). The calculation of pathways/processes for inputs from WWTPs and paved urban areas was adapted.

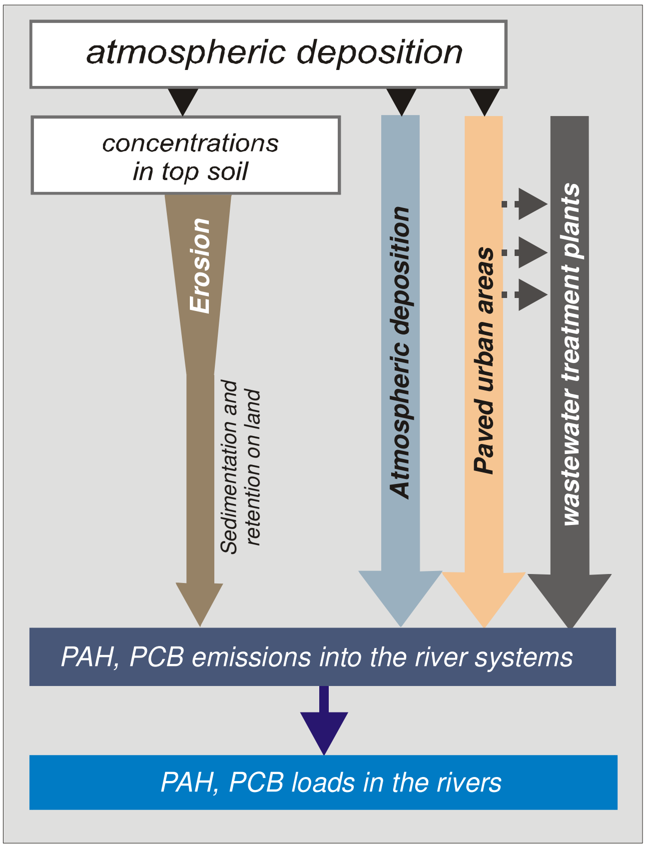


Figure 3-1: Pathways and processes in MONERIS modified for PAHs and PCBs

The emission analysis was carried out for the Rhine catchment area downstream to Bimmen/Lobith for the present state and the results compared to measured loads (calculated from monitoring data) for the period 1994 to 1996, which also served as the basis for the scenario calculations in chapter 5.

In the following, assumptions for the main input parameters for individual PAHs and PCBs, required for the different pathways and processes in MONERIS, are derived which are summarised in chapter 3.1.7.

3.1.1 Industry - emissions to water

On a European scale, inventories of emissions to water are planned but not yet realised. Such an emission inventory has been proposed as extension to CORINAIR and shall include metals as well as PAHs (EEA, 1998).

In contrast to metals, for the Rhine catchment area inventories of point sources are reported only as overall estimates for total PCB emissions from industrial point sources including municipal wastewater treatment plants (ICPR, 1999): 3300 kg (1985), < 230 kg/year (1992), < 24 kg/year (1996). For 1996 a portion of approximately 13% (< 3kg/year), originating from industrial point sources is stated. As this is negligible compared to averaged annual loads of sum 6 PCBs (> 100 kg/year) at Bimmen/Lobith (appendix 4.1b) and no information on individual industrial point sources were available, this pathway was not included.

Estimates for industrial point sources for PAHs in the Rhine catchment area were not available with the exception of the Netherlands (chapter 3.3); this pathway could not be included.

3.1.2 Wastewater treatment plants

In the case of metals, inputs from wastewater treatment plants (WWTPs) were modelled on the basis of inhabitant specific emission factors (chapter B 3.1.2) by using information on individual WWTPs as connected number of inhabitants, treatment efficiencies etc. For PAHs and PCBs this approach had to be modified. Input parameters were atmospheric deposition of PAHs and PCBs on paved urban areas (see chapter 3.1.3) as well as inhabitant specific emission factors in the case of PCBs (domestic wastewater). Mass balances for PAHs and PCBs in WWTPs in the Rhine basin upstream Bimmen/Lobith were checked, incorporating average estimated concentrations in influents and effluents of WWTPs and in sewage sludge, sludge volumes and elimination rates in WWTPs. The modified approach is illustrated in figure 3-2.

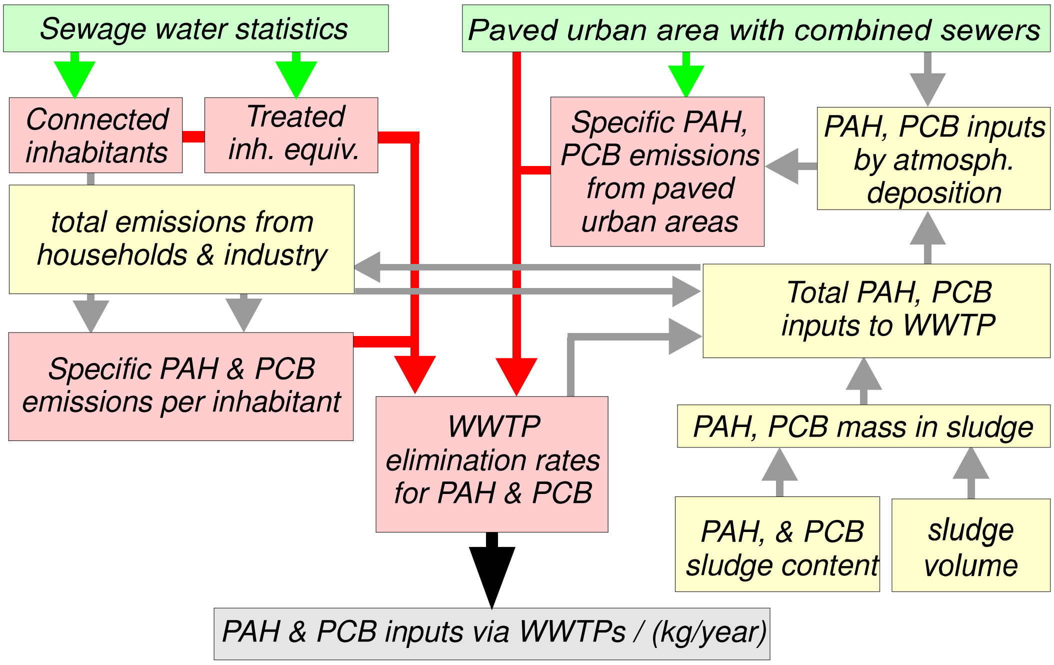


Figure 3-2: Model for the calculation of PAH and PCB inputs by wastewater treatment plants

In Germany an estimated amount of 2.8 million tons (dry weight) of sewage sludge is stemming from WWTPs per year. The average concentration of PAHs (sum 16) in sewage sludge is approximately 6 mg/kg, resulting in a total amount of about 20 tonnes PAHs per year in sewage sludge in Germany (UBA, 1998b).

Data on PAH and PCB concentrations in effluents of WWTPs are scarce (appendices 3.1.2a-b) and often, especially in the case of PCBs, below the limit of determination. For that reason concentrations of PAHs and PCBs in sewage sludge seemed to be more reliable and were evaluated for checking the mass balances for PAHs and PCBs in WWTPs.

PAH concentrations in sewage sludge of 53 WWTPs in Germany (appendix 3.1.2c) showed no significant differences with regard to a subset of data for WWTPs located at the Rhine (appendix 3.1.2d) and were comparable to the results of other studies (LAU Hessen, 1989 & 1997). There was no correlation of PAH (sum 16) concentrations with the size of WWTPs; and WWTPs for both municipal and industrial wastewater showed comparable PAH concentrations in sewage sludge as WWTPs only with municipal waste water (UBA, 1998b).

PCB concentrations in sewage sludge are given in appendix 3.1.2e (LAU Hessen, 1989) and were comparable to results for four WWTPs in 1994 (LAU Hessen, 2000). Sewage sludge from industrial WWTPs showed no increased PCB levels compared to municipal WWTPs (LAU Hessen, 1989). Somers et al. (1994) estimated that sum 7 PCBs contribute approximately 20 % to total PCB concentrations in influents and effluents of WWTPs.

The elimination of PAHs and PCBs in WWTPs, in the range of approximately 90 % or higher, is mainly due to their enrichment in sewage sludge with a very minor contribution by degradation in the case of PAHs. In WWTPs most PAHs, i.e. PAHs with higher molecular weight (more than 3 ring systems), are degraded only to a very limited extent. The lowest degradation rates have been observed for benzo(a)pyrene (UBA, 1998b). PCBs should be expected to be even more persistent.

For the estimation of PAH and PCB inputs from WWTPs average elimination rates in WWTPs were assumed:

- Fluoranthene (90 %), benzo(b)fluoranthene (90 %), benzo(a)pyrene (90 %)
- PCB 52 (90 %), PCB 138 (95 %), PCB 180 (95 %)

These are in agreement with data on PAH and PCB concentrations in influents and effluents of WWTPs (appendices 3.1.2a-b).

In case of PCBs, inputs to WWTPs via atmospheric deposition to paved urban areas could only partly explain the estimated PCB concentrations in sewage sludge. In order to balance PCB mass flows in WWTPs in the Rhine basin, other PCB inputs to WWTPs, e.g. inhabitant specific emissions from households, had to be assumed. In order to make the mass balance correct we calculated the following inhabitant (Inh.) specific emission factors:

- PCB 52 (1.6 $\mu g \cdot Inh.^{-1} \cdot d^{-1}$), PCB 138 (6.0 $\mu g \cdot Inh.^{-1} \cdot d^{-1}$), PCB 180 (3.0 $\mu g \cdot Inh.^{-1} \cdot d^{-1}$), or
- PCB 52 (0.58 $mg \cdot Inh.^{-1} \cdot yr$), PCB 138 (2.2 $mg \cdot Inh.^{-1} \cdot yr$), PCB 180 (1.1 $mg \cdot Inh.^{-1} \cdot yr$),

being equivalent to approximately 36 $mg \cdot Inh.^{-1} \cdot yr$ total PCBs.

A possible source for PCBs in domestic wastewater can be recycled paper products (e.g. toilet paper), as shown by Welling et al. (1992) who found concentrations of 0.08-4 µg/g total PCBs (as Arochlor 1242) in recycled paper products from Germany.

Emission factors from literature, based on concentrations in household wastewater in the Netherlands, are significantly lower than our assumptions: 9 $mg \cdot Inh.^{-1} \cdot yr$ total PCBs (STORA, 1985), 1.8 $mg \cdot Inh.^{-1} \cdot yr$ total PCBs (RIZA, 1992). This difference cannot be explained and would need further analysis.

3.1.3 Atmospheric deposition

PAHs and PCBs emitted to the atmosphere can reach the Rhine and its tributaries by direct deposition which is calculated, as in the case of metals, by multiplying deposition rates with the total surface water area in a specific region. Indirect inputs of PAHs and PCBs can reach the river system after deposition on rural areas (via erosion, chapter 3.1.4) and after deposition on paved urban areas (chapter 3.1.5).

While a number of data sets are available for PAH and PCB concentrations in the atmosphere, only a few deposition data are available. Pacyna (1999) reviewed atmospheric deposition data, and data on BbFl and BaP for Germany are given in appendices 3.1.3a-b.

Van Jarsfeld et al. (1996) calculated for Germany a total deposition of BaP of 160,000 tonnes/year equivalent to $1.2 \cdot 10^6$ $ng \cdot m^{-2} \cdot day^{-1}$. Obviously the authors accidentally stated 160,000 tonnes/year instead of 160,000 kg/year, comparing the number from the table with their deposition map. However 160 tonnes/year of BaP deposition in Germany still exceeds the estimated BaP emissions to atmosphere in Germany by a factor of more than 10 (compare appendix 5.1a). For that reason these estimations were not taken into account. TNO (1995) estimated an atmospheric deposition of 4.1 tonnes/year BaP for the Netherlands which is equivalent to an average deposition flux of 305 $ng \cdot m^{-2} \cdot day^{-1}$.

Deposition fluxes of PAHs in urban areas are distinctly higher than in regions remote from main sources (compare chapter 1.3, appendices 3.1.3a-b). For that reason, for PAHs, different deposition rates for paved urban areas and non-urban areas including surface waters were assumed:

§ Urban areas: Fl (2300 $ng \cdot m^{-2} \cdot day^{-1}$), BbFl (850 $ng \cdot m^{-2} \cdot day^{-1}$), BaP (820 $ng \cdot m^{-2} \cdot day^{-1}$)

§ Non-urban areas: Fl (140 $ng \cdot m^{-2} \cdot day^{-1}$), BbFl (52 $ng \cdot m^{-2} \cdot day^{-1}$), BaP (49 $ng \cdot m^{-2} \cdot day^{-1}$)

BaP deposition in Germany, according to the assumed deposition fluxes, is in the same range as estimates for BaP emissions in Germany (14 tonnes/year BaP, appendix 5.1.a). Deposition fluxes for Fl and BbFl were estimated relative to the assumed deposition flux of BaP according to PAH pattern in measured deposition data (Pacyna, 1999) and recalculated deposition fluxes for individual PAHs for the Netherlands (TNO, 1995, modelled data).

Atmospheric deposition data for PCBs were not available for Germany. From Pacyna (1999) wet deposition (incl. dry deposition) data, given as pg/L precipitation, were taken and recalculated to deposition fluxes. For four different coastal sampling stations in Sweden (1990-1996, *n*=72, sampling times 5-21 days) the aggregated data for PCBs (sum 6) are:
min.: 0.6 $ng \cdot m^{-2} \cdot day^{-1}$, mean: 2.2 $ng \cdot m^{-2} \cdot day^{-1}$, max.: 7.3 $ng \cdot m^{-2} \cdot day^{-1}$.

Annema et al. assumed mean deposition fluxes of total PCBs on the Netherlands (RIVM, 1995). The data for deposition over land were already corrected for re-emission fluxes into the atmosphere:

- Total PCBs: 0.2 $g \cdot ha^{-1} \cdot year^{-1}$ in 1990 and 0.1 $g \cdot ha^{-1} \cdot year^{-1}$ in 2000, being equivalent to
- Sum 6 PCBs: 13.7 $ng \cdot m^{-2} \cdot day^{-1}$ in 1990 and 6.8 $ng \cdot m^{-2} \cdot day^{-1}$ in 2000.

TNO (1995) estimated that approximately 50 % of the PCBs deposited from atmosphere on the Netherlands is stemming from Germany which is based on higher emission estimates for Germany than for the Netherlands (compare appendix 5.1d).

In contrast to PAHs, PCBs tend to prevail in the gas phase in the atmosphere (chapter 1.2) and less steep gradients between urban and remote areas can be assumed than for PAHs. For that reason and because of the lack of suitable data sets on atmospheric deposition, uniform deposition rates for individual PCBs in the Rhine catchment area were estimated (urban and non-urban areas incl. surface waters):

§ PCB 52 (5.5 $ng \cdot m^{-2} \cdot day^{-1}$), PCB 138 (9.3 $ng \cdot m^{-2} \cdot day^{-1}$), PCB 180 (6.1 $ng \cdot m^{-2} \cdot day^{-1}$).

Deposition of total PCBs in Germany, according to the assumed deposition fluxes, is approximately 21 tonnes/year which is in agreement with estimated emissions of total PCBs to atmosphere in Germany (1990: 43 tonnes/year, 2000: 19 tonnes/year, appendix 5.1c). This estimation assumes that sum 6 PCBs contribute 25% to total PCBs in atmospheric deposition (TNO, 1995). The calculation of deposition rates for individual PCBs was based on PCB pattern (appendix 3.1.3c) in atmospheric deposition data from Pacyna (1999).

3.1.4 Erosion

The inputs of PAHs and PCBs via erosion were calculated analogous as described for the metals (chapter B 3.1.5). The only difference is that for PAHs and PCBs no specific enrichment ratios could be calculated. The enrichment ratio for particulate phosphorus was used instead. The approach is illustrated in figure 3-3.

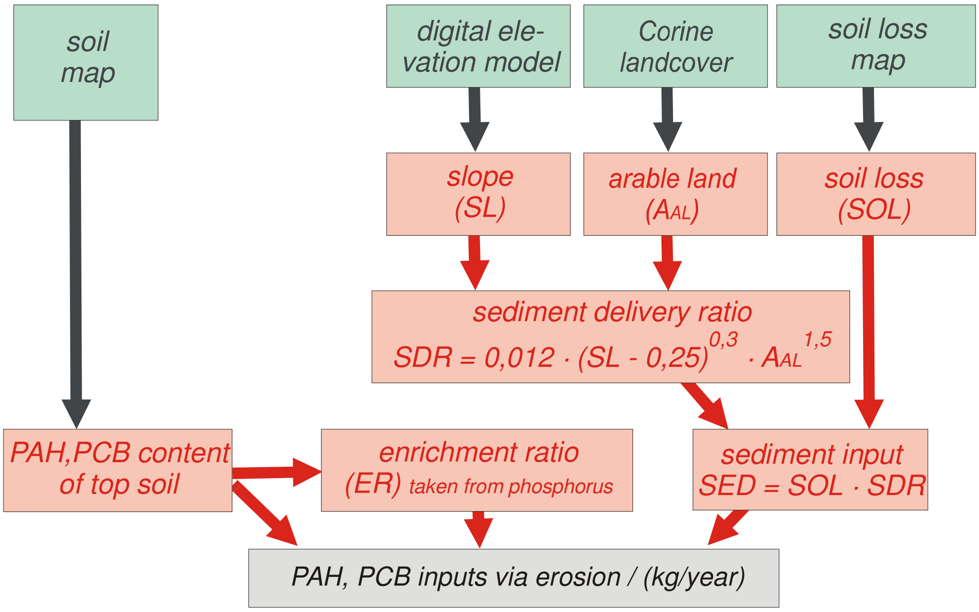


Figure 3-3: Model for the calculation of PAH and PCB inputs by erosion

PAH and PCB concentrations in top soils, needed as input parameter, differ considerably and generally show higher levels in urban compared to rural areas. Highest PAH concentrations were found in the neighbourhood of point sources as coking plants or in soils located adjacent to roads with high traffic.

Erosion mainly takes place in agricultural areas, especially at soils not or only partly covered by vegetation (arable land as crop fields, vineyards etc.). Therefore mainly data for arable land in rural areas were taken into account.

In contrast to metals, data on PAHs and PCBs in top soils are only available for a few states in Germany. Data on PCBs are even less consistent than data on PAHs. A comprehensive overview of PAH and PCB contents in top soils in several states of Germany is given in LABO (1998). Availability of data for PAHs was in the order BaP > sum 16 PAHs > sum 6 PAHs > BbFl > Fl. For PCBs, with a few exceptions, only data for sum 6 PCBs could be gathered.

An overview of aggregated data on BaP (50 percentiles, 90 percentiles) is given in appendix 3.1.4a. BaP data sets of different states in Germany (LABO, 1998; LAU Saarland, 1999) showed a variability in the range of:

Agricultural soils (crops etc.), rural regions

- 7 – 25 µg/kg dw BaP (50 percentiles)
- 20 – 91 µg/kg dw BaP (90 percentiles)

Agricultural soils (crops etc. or not specified), medium to high density of population

- 19 – 360 µg/kg dw BaP (50 percentiles)
- 57 – 1260 µg/kg dw BaP (90 percentiles)

Uniform concentrations for individual PAHs in agricultural top soils were assumed to estimate PAH inputs to the Rhine system via erosion:

§ Fl (45 µg/kg dw), BbFl (50 µg/kg dw), BaP (25 µg/kg dw).

The ratios of the concentrations of the individual PAHs are in agreement with PAH pattern in agricultural top soils, derived from data from LABO (1998) and Saar (1999):
Contribution to sum 6 PAHs: Fl (22 %), B(b)Fl (24 %), BaP (12 %).

For PCBs an overview of aggregated data (50 percentiles, 90 percentiles) is given in appendix 3.1.4b. Data sets of different states in Germany (LABO, 1998; Saar, 1999) showed a variability in the range of:

Agricultural soils (crops etc.), rural regions

- <1 – 4.5 µg/kg dw sum 6 PCBs (50 percentiles)
- <1 – 23 µg/kg dw sum 6 PCBs (90 percentiles)

Agricultural soils (crops etc. or pasture), medium to high density of population

- 1 – 20 µg/kg dw sum 6 PCBs (50 percentiles)
- 12.6 – 154 µg/kg dw sum 6 PCBs (90 percentiles)

RIVM (1995) estimated mean PCB concentrations in Dutch top soils as 2.45 µg/kg dw sum 6 PCBs. The data, derived from top soils in 13 agricultural regions in the Netherlands, are in agreement with the before discussed German data.

For the modelling of PCB inputs to the Rhine system via erosion we assumed a uniform average PCB (sum 6) concentration in agricultural top soils as 2.5 µg/kg dw sum 6 PCBs, being equivalent to:

§ PCB 52 (0.2 µg/kg dw), PCB 138 (0.6 µg/kg dw), PCB 180 (0.35 µg/kg dw)

Average concentrations for individual PCBs in top soils were calculated according to the PCB pattern derived from PCB concentrations in top soils in the Netherlands (RIVM, 1995, appendix 3.1.4c).

For both PAHs and PCBs a gradient in top soil concentrations from regions with high density of population to areas remote from emission sources is observed (appendices 3.1.4a-b). Therefore a factor of 5 lower PAH and PCB concentrations for soils in remote areas were assumed compared to the assumed mean concentrations in agricultural top soils.

3.1.5 Urban areas

PAHs and PCBs are deposited from atmosphere to paved urban areas and can enter surface waters via runoff. The related pathways comprise sewers without wastewater treatment (SWW), separate sewer (SS) systems for waste water and runoff, overflows (CSO) from combined sewer systems (CSS) as well as inputs from areas without sewer systems. The inputs from urban areas to surface waters were modelled according to the scheme depicted in figure 3-4. Inputs from wastewater treatment plants were already accounted for in chapter 3.1.2. Atmospheric deposition rates for individual PAHs and PCBs in urban areas were applied as estimated in chapter 3.1.3.

Input data as paved urban area or number of population connected to different sewer systems were available in MONERIS and were modelled for PAHs and PCBs analogous to the approach for metals (chapter B 3.1.8).

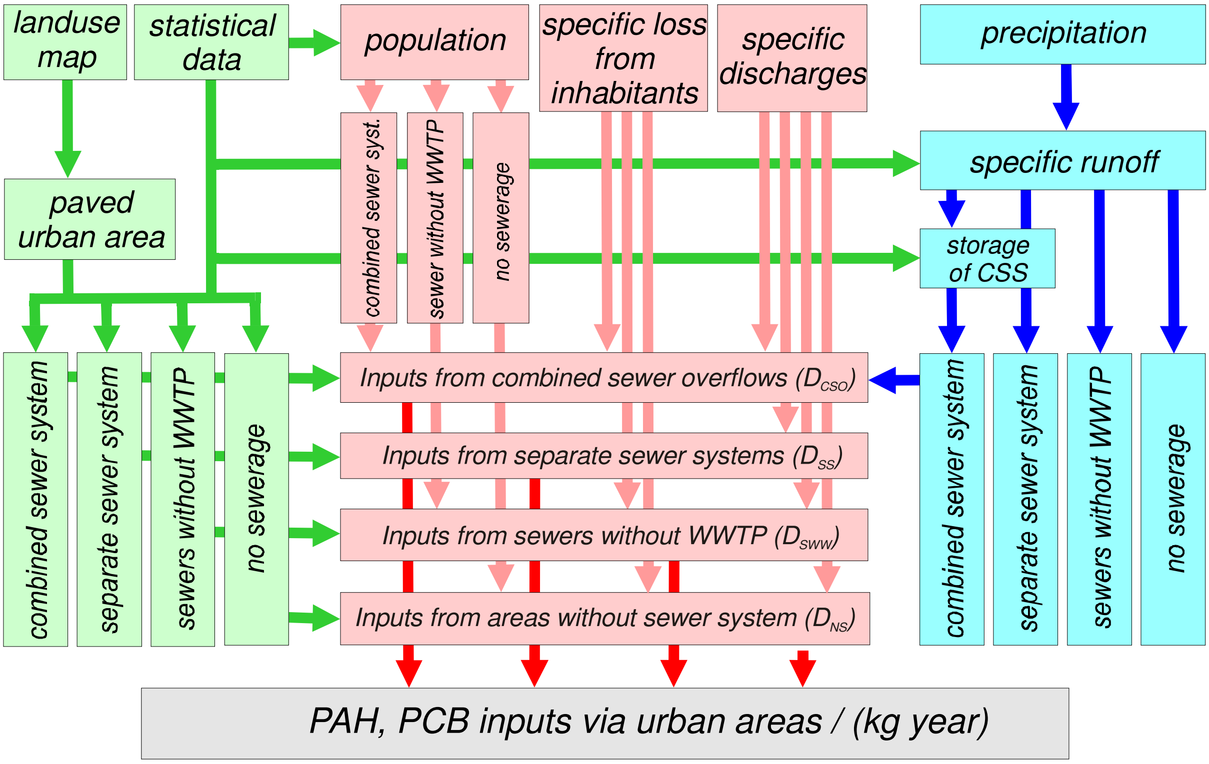


Figure 3-4: Model for the calculation of PAH and PCB inputs from paved urban areas

3.1.6 Shipping

Initially, PAH inputs to the Rhine system upstream Bimmen/Lobith were modelled with MONERIS, taking the pathways/processes into account as discussed in the previous chapters. The results of modelled PAH loads were significantly lower than the observed loads (calculated from monitoring data). For Bimmen/Lobith the difference of modelled and observed loads (9.2 tonnes/year sum 6 PAHs, 1992-1996) was approximately 3 tonnes/year sum 6 PAHs.

This difference might be explained by inputs from shipping. Releases from ships could stem e.g. from ship coatings, bilge waters and spills. Hulls of inland vessels have been coated with coal tar, having high PAH contents (up to 30 %, VROM, 1994). From the coated underwater surface of the hulls, PAHs were released to surface waters. Costs for alternative coatings for ships are higher than for coal tar, but alternative products have been available since several years. E.g., bitumen/epoxy coatings have approximately two orders of magnitude lower PAH contents in comparison to coal tar (RIZA, 1997a). The use of coal tar as ship coating in the Netherlands has been regulated by a law act in 1997 and was expected to be out-phased until 2000 (RIZA, 1997a). To our knowledge the use of coal tar as ship coating has not been regulated in Germany but inquiries at German shipyards confirmed that coal tar recently has not commonly be used any more.

Coal tar has as well be used for wood impregnation, e.g. for woods in constructions in inland waterways. PAH emissions from coal tar impregnated wood to Dutch surface waters were estimated as 1.6 tonnes/year in 1993 (RIZA, 1997b).

RIZA (1997a) estimated inputs from shipping in the Netherlands as:

- 1993: 11 tonnes/year sum 6 PAHs
- 2000: 0.8 tonnes/year sum 6 PAHs

Taking into account these estimations and considering the number of inland ships in the Netherlands (approx. 5,500; RIZA, 1997a) and the number of commercial ships in the Rhine catchment (approx. 10,000; CCNR, 1997), it seems to be reasonable that for the modelled period 1994-1996 approximately 3 tonnes/year sum 6 PAHs originated from shipping.

3.1.7 Summarised PAH and PCB specific coefficients

Specific coefficients for individual PAHs and PCBs used as parameters for modelling inputs from diffuse and point sources in the Rhine basin upstream Bimmen/Lobith for the time period 1994-1996, which have been derived in the preceding chapters, are summarised in table 3-1.

Table 3-1: Coefficients used for the modelling of PAH and PCB inputs by using MONERIS

		Fl	BbFl	BaP	PCB 52	PCB 138	PCB 180
emissions paved urban areas	g/(ha yr)	8.4	3.1	3.0	0.020	0.034	0.022
atmospheric deposition	ng/(m^2 d)	2300	850	820	5.5	9.3	6.1
soil content (agricultural soil)	µg/kg	45	50	25	0.20	0.60	0.35
soil content (remote areas)	µg/kg	9.0	10	5.0	0.04	0.12	0.07
atmospheric deposition to surface water	g/(ha yr)	0.50	0.19	0.18	0.020	0.034	0.022
	ng(/m^2 d)	140	52	49	5.5	9.3	6.1
household emissions	mg/(Inh. d)	0	0	0	0.0016	0.0060	0.0030
shipping	kg/yr	600	600	400	0	0	0
WWTP elimination rate	%	90	90	90	90	95	95

3.2 Results of the emission analysis - Rhine basin upstream Bimmen/Lobith

The results of the emission analysis for individual PAHs and PCBs for the time period 1994-1996 are listed in appendices 3.2a-f, giving the contribution of the different pathways/processes to loads at selected stations along the Rhine and its tributaries. Modelled loads (MONERIS) were compared with observed loads (calculated from monitoring data), which is visualised for Benzo(a)pyrene and PCB 138 in figures 3-5 and 3-6.

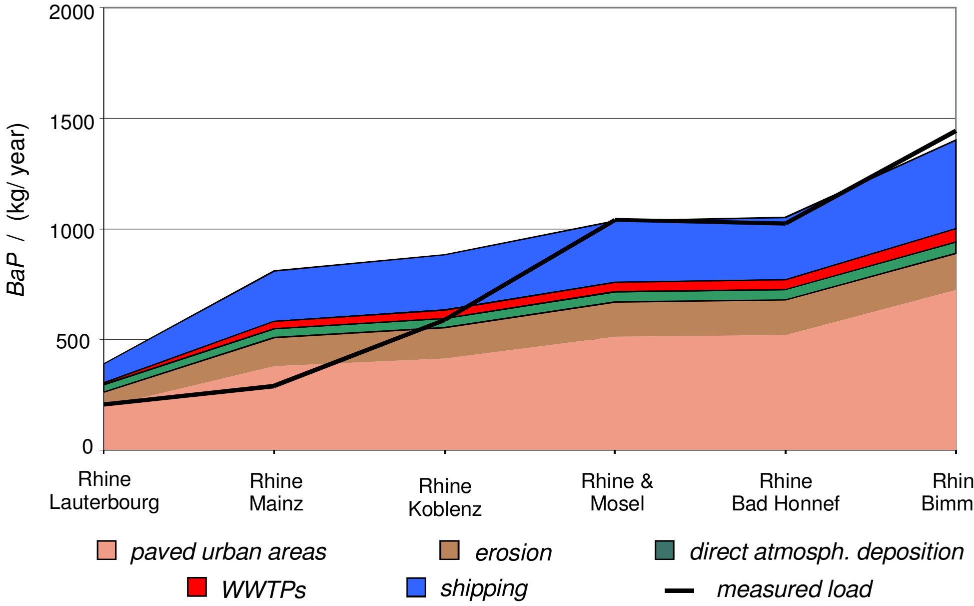


Figure 3-5: Comparison of calculated and measured BaP load from Lauterbourg to Bimmen/Lobith

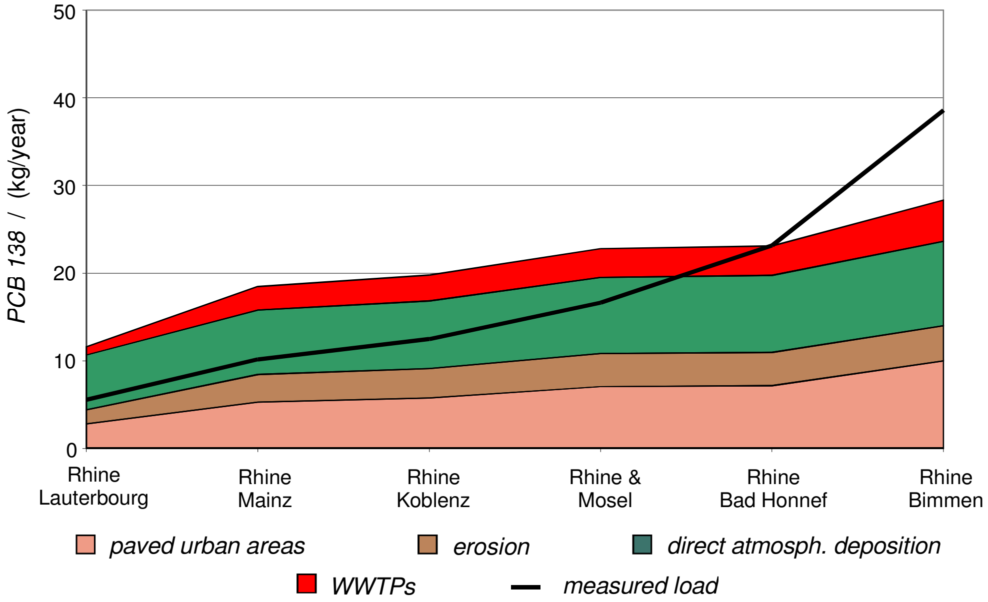


Figure 3-6: Comparison of calculated and measured PCB 138 load from Lauterbourg to Bimmen/Lobith

Obviously deviations exist between modelled and observed PAH and PCB loads. Generally, observed loads, calculated from monitoring data, have an inherent uncertainty due to the sampling/data frequency of 2-4 weeks and the variability of loads in time (compare loads at Bimmen and Lobith in appendices 4.1c-d). In addition, retention processes of suspended particulate matter, being the 'carrier for PAHs and PCBs' in the Rhine system were not taken into account and are expected to occur mainly in the upper Rhine, e.g. in Lake Constance (Bodensee), or in weirs and locks of the Rhine and its tributaries. This can explain the overestimation in modelled loads upstream of Koblenz.

The contributions of the different pathways/processes in the Rhine basin to modelled annual loads of PAHs and PCBs at Bimmen/Lobith are depicted in figures 3-7 and 3-8.

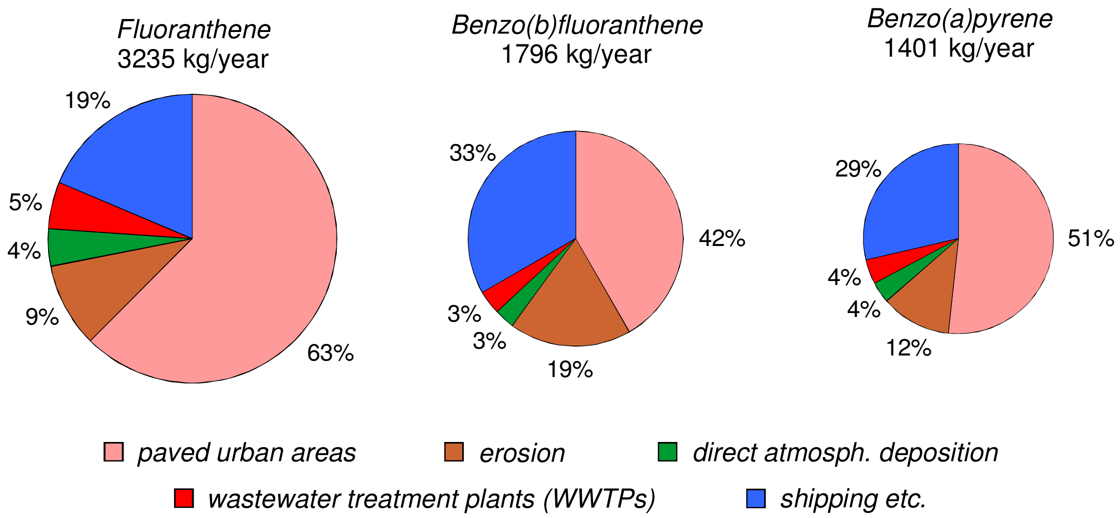


Figure 3-7: Sources of PAH loads for the Rhine basins upstream Bimmen/Lobith for the period 1994-1996

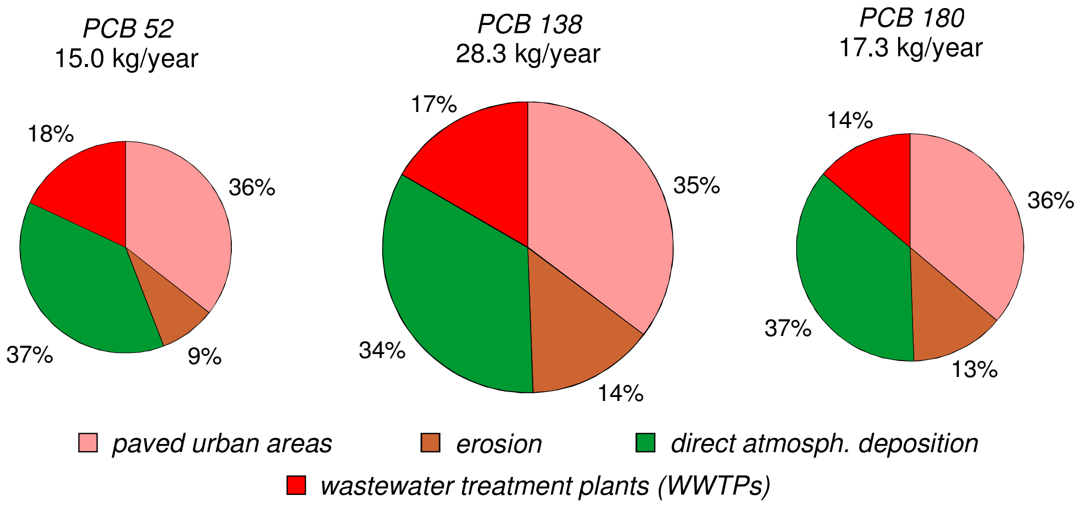


Figure 3-8: Sources of PCB loads for the Rhine basins upstream Bimmen/Lobith for the period 1994-1996

Largest contributions to the total loads of PAHs are inputs from paved urban areas (approx. 40-60 %, runoff after atmospheric deposition) followed by shipping and other unknown sources (approx. 20-30 %, compare chapter 3.1.6). In the case of PCBs, largest contributions to total loads are paved urban areas (approx. 35 %) and direct atmospheric deposition to surface waters (approx. 35 %). The relatively high contributions of PCB inputs from wastewater treatment plants (WWTPs) compared to PAHs are mainly due to the assumed inhabitant specific emission coefficients for PCBs (recycled paper products, chapter 3.1.2).

A more detailed discussion of the different paths/processes related to sources and possible reduction measures is given in the scenarios chapter (chapter 5).

3.3 Emissions in the Netherlands

In the preceding chapter the results of the emission analysis for PAHs and PCBs in the Rhine basin upstream Bimmen/Lobith were presented. In order to evaluate the impact of PAH and PCB loads in the Rhine on the quality of sediments in the eastern parts of the port of Rotterdam, emissions in the Dutch part of the Rhine basin have to be considered as well.

In the case of metals, inputs via different pathways/processes to the Rhine system in the Netherlands have been estimated by ICPR (1999). For PAHs and PCBs no comparable information could be gathered. Available emission estimates for PAHs and PCBs in the Dutch part of the Rhine catchment area and in the port of Rotterdam are summarised and compared to observed annual loads in the Rhine at Bimmen/Lobith in table 3-2.

Table 3-2: Emission estimates for PAHs and PCBs in the Netherlands and comparison with loads at Bimmen/Lobith

region	Rhine catchment, Netherlands		Rhine catchment, Netherlands		Port of Rotterdam			Rhine catchment	
source	industry	industry	industry	WWTPs	shipyards	industry	industry	load Bimmen/Lobith	
reference	RIZA (2000)		ICPR (1999)		RMPM (2000a)			this study: app. 4.1c	
	Σ 6 PAHs	PCBs	PCBs	PCBs	PAHs	PAHs	PCBs	Σ 6 PAHs	Σ 6 PCBs
	t/yr	kg/yr	kg/yr	kg/yr	t/yr	t/yr	kg/yr	t/yr	kg/yr
1994	0.02	<0.0001			0.20	0.02	<0.0001	10.3	128
1995	0.02	<0.0001			0.02	0.02	<0.0001	11.8	349
1996	0.03	<0.0001			0.02	0.03	<0.0001	5.7	100
1994-1996	0.02	<0.0001	<0.0001	0.596	0.08	0.02	<0.0001	9.2	192

PAH inputs from industry in the Dutch part of the Rhine catchment seem to originate mainly from the port of Rotterdam area and appear to be negligible (approximately 0.2 % of observed PAH loads at Bimmen/Lobith). Emission from shipyards in the port of Rotterdam, given in table 3-2, are terrestrial inputs. The portion, entering surface waters is unknown. Major contributions to PAH emissions in the port of Rotterdam were assumed to stem from shipping (Boderie & Sonneveldt, 1996). Inputs from shipping, related to the density of vessel traffic, can be expected to occur in the whole navigable part of the Rhine system (compare chapter 3.1.6).

PCB inputs from WWTPs and industry in the Dutch part of the Rhine catchment and in the port of Rotterdam, given in table 3-2, appear to be negligible compared to mean annual PCB loads at Bimmen/Lobith.

In the Dutch part of the Rhine catchment, erosion is not expected to be a major pathway as shown for the metals in comparison to drainage and groundwater. However inputs from drainage or groundwater are due to transport in the dissolved phase, which can be neglected for PAHs and PCBs. PAH and PCB inputs from urban areas and via atmospheric deposition should be roughly related to population and area.

The ICPR redefined the Dutch part of the Rhine catchment (ICPR, 1999). Area and population relative to the whole Rhine catchment area are (old/new definition): inhabitants (7 % / 21 %), area (5 % / 15 %). The new definition of the ICPR comprises more than half of the total area of the Netherlands as Rhine catchment area. Only part of it can be expected to contribute to emissions related to sediments in the port of Rotterdam.

Summarising, one can conclude that for our modelling purposes, the Dutch part of the Rhine catchment can be neglected in a first effort.

4 Trends in the quality of suspended particulate matter in the Rhine and link to the quality of dredged material in Rotterdam

The results of the emission analysis, carried out for the Rhine basin upstream Bimmen/Lobith (chapter 3), were taken as a basis for the scenario analysis and for the forecasts of the future quality of sediments/dredged material in the eastern parts of the Port of Rotterdam (chapter 5).

In the following, PAH and PCB concentrations in suspended particulate matter (SPM) in the Rhine are compared with PAH and PCB concentrations in sediments/dredged material in the port of Rotterdam for the period 1990-1998.

4.1 Trends in quality of suspended particulate matter in the Rhine

Averaged annual concentrations for a number of monitoring stations along the Rhine are depicted for sum 6 PAHs in figure 4-1 and for sum 6 PCBs in figure 4-2. Following the Rhine river in downstream direction, for both PAHs and PCBs, concentrations in suspended particulate matter (SPM) are generally increasing. A general trend over time for the period 1990-1999 is not obvious. It has to be assumed that uncertainties in the estimation of averaged annual concentrations are high because of a low sampling frequency (two or four weeks). The data for Bimmen and Lobith differ largely which probably is due to a distinct variability in time and space for PAH and PCB concentrations in SPM. In the case of Bimmen and Lobith, both stations are only approximately three kilometres apart, but the stations are located at different sides of the river and the frequency of sampling differs as well for some years.

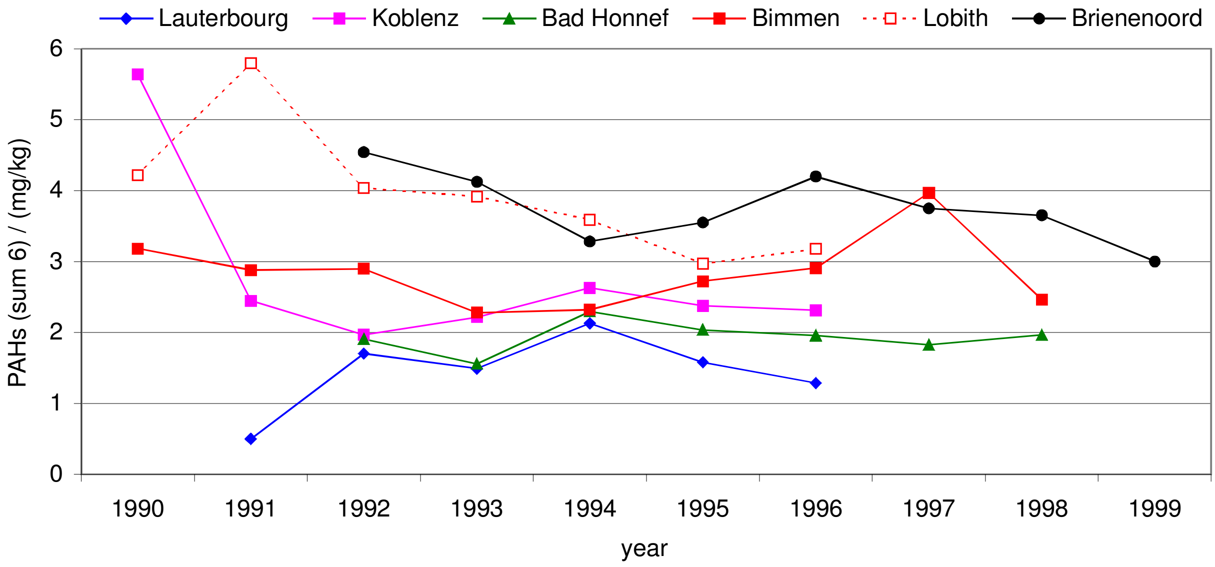


Figure 4-1: Averaged annual concentrations of sum 6 PAHs in SPM along the Rhine river

Looking at trends for averaged annual loads gives more or less the same picture as for the averaged annual concentrations. Annual loads were calculated from PAH (sum 6) and PCB (sum 6) concentrations in SPM respectively and the corresponding concentrations of SPM (mg/L) and discharges and are given in appendices 4.1a-b.

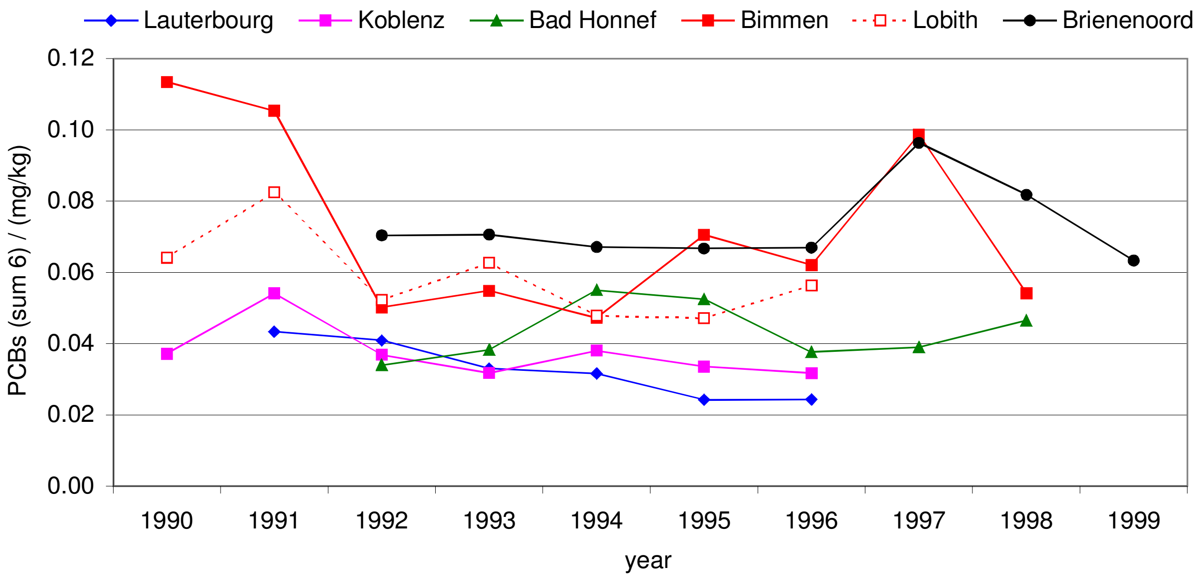


Figure 4-2: Averaged annual concentrations of sum 6 PCBs in SPM along the Rhine river

Loads of individual PAHs and PCBs, selected for immission and emission analysis, follow the course of the sum parameters for the different monitoring stations over time (appendices 4.1c-d).

The downstream transport of SPM, and thus PAHs and PCBs bound to SPM as well, is intensified by high water discharges due to re-erosion of sediments. For that reason averaged annual data on concentrations or loads depend on the discharge regimes in the individual years, i.e. the occurrence of periods with high discharges (flood events). These events are covered only partly by the samples from the monitoring stations which adds to the observed variance over time and between monitoring stations. Summarising, it can be stated that from the available data no clear trend over time is recognizable for concentrations or loads for PAHs and PCBs for the period investigated.

4.2 Trends in the quality of dredged material in comparison to suspended particulate matter at Lobith/Bimmen

The quality of sediments/dredged material in/from the western parts of the port of Rotterdam is mainly influenced by marine SPM. The following comparison of the quality of dredged material from the port of Rotterdam and SPM of the Rhine focuses on the eastern parts of the port, mainly influenced by SPM-bound PAHs and PCBs originating from the Rhine catchment area.

With regard to the Sea/Slufter limits for relocation of dredged material in the North Sea, concentrations of organic contaminants are normalised (standardised) towards the content of organic matter in the sediments/dredged material (RMPM, 2000b). Organic matter contents of sediments are measured with the so-called bichromat-method whereas the organic matter content of SPM from the Rhine monitoring stations is analysed as total organic carbon; thus concentrations of PAHs and PCBs standardised on the organic matter content of the sediments and SPM respectively cannot be compared. Evaluating trends in the quality of sediments/dredged material in/from the port of Rotterdam, concentrations are standardised and are corrected (weighted) towards average dredged volumes of the specific port areas (RMPM, 1998).

In order to compare the quality of dredged material and SPM from the Rhine river, data on concentrations of PAHs and PCBs (RMPM, 1999) were recalculated for the eastern part of the port of Rotterdam as

- averaged annual concentrations,
- averaged annual concentrations corrected to dredge volumes,
- averaged annual standardised concentrations, corrected to dredged volumes

and compared with not standardised averaged annual concentrations in SPM at Bimmen and Lobith (figure 4-3 and 4-4).

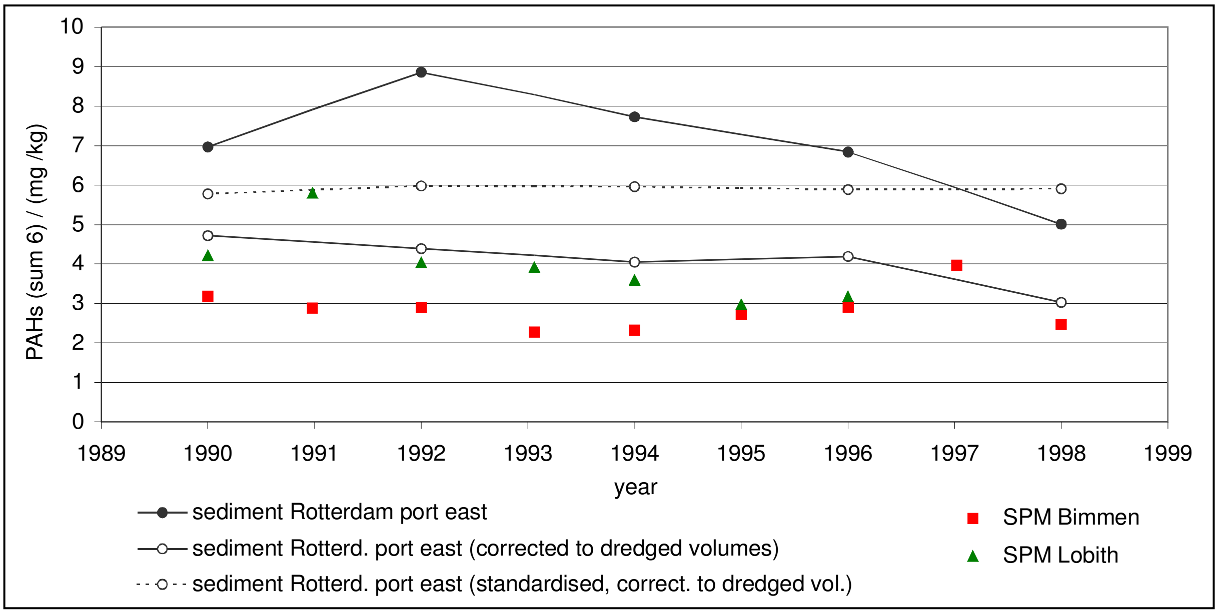


Figure 4-3: Averaged annual concentrations of sum 6 PAHs in Rotterdam port sediments and SPM at Lobith/Bimmen

PAHs (sum 6, not standardised) show a slightly decreasing trend in sediments of the eastern part of the port of Rotterdam whereas the standardised concentrations remain more or less on the same level (figure 4-3). For concentrations of PCBs (sum 6) a somewhat higher fluctuation between the years can be observed. The increase from 1996 to 1998 in concentrations indicates that the time period seems to be too short to state a significant trend yet (figure 4-4).

Concentrations of individual PAHs and PCBs, selected for immission and emission analysis, in the sediments follow the course of the sum parameters (appendices 4.2a-b).

Comparing concentrations of PAHs and PCBs in sediments in the Port of Rotterdam with concentrations in SPM of the Rhine at Bimmen/Lobith, it has to be considered that uncertainties in mean concentrations in SPM are expected to be relatively high due to small numbers of samples per year (e.g. PAHs, 1996: sediments Rotterdam east (*n*=107), SPM Bimmen (*n*=25), SPM Lobith (*n*=14).

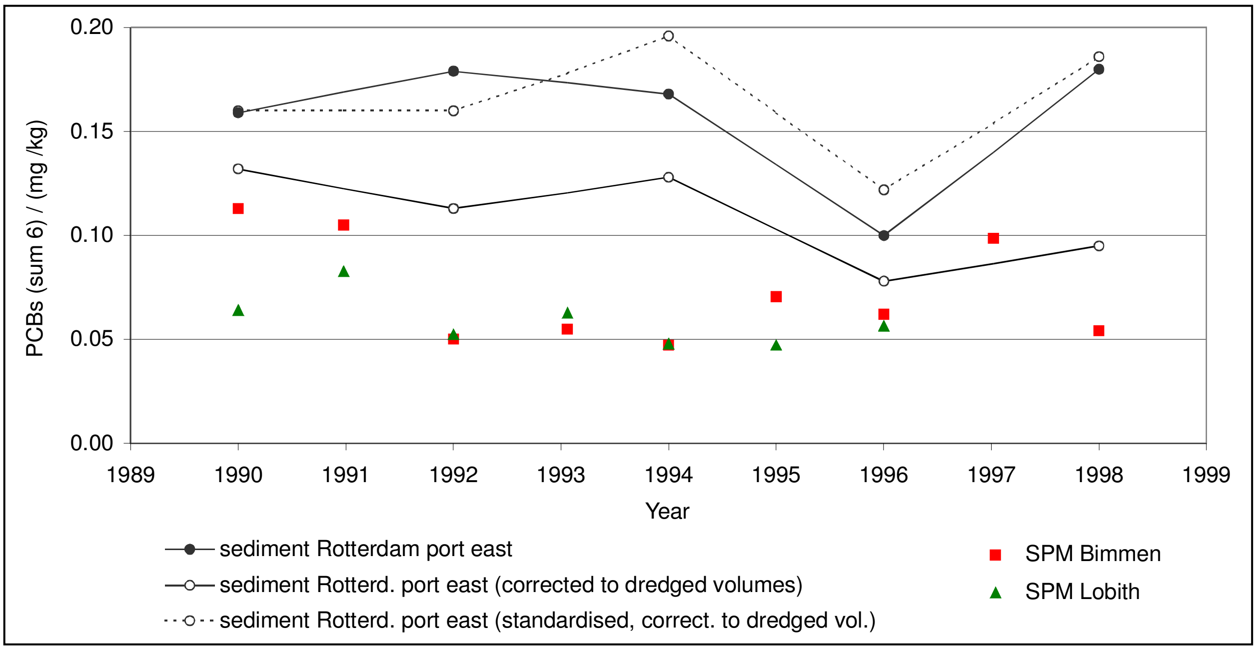


Figure 4-4: Averaged annual concentrations of sum 6 PCBs in Rotterdam port sediments and SPM at Lobith/Bimmen

As standardised concentrations for sediments and SPM cannot be compared, as discussed before, the most appropriate comparison is taking the not standardised concentrations, corrected (weighted) to average dredged volumes in the case of Rotterdam port sediments. For both PAHs and PCBs, these concentrations in SPM and sediments are on about the same levels, sediment concentrations generally being slightly higher than concentrations in SPM.

4.3 Link between suspended particulate matter in the Rhine and dredged material in the port of Rotterdam

Retention or loss processes, as described for metals in chapter B 4.4.1, are known to play an important role for PAHs and PCBs as these are transported in rivers mainly bound to particles and thus are subject to sedimentation and re-erosion in rivers. Retention functions, as calculated for metals could not be derived for PAHs and PCBs due to an insufficient number of monitoring data, not covering a large enough period of time and different discharge regimes.

For that reason, for the scenarios in the next chapter, the estimated changes in loads of PAHs and PCBs at Bimmen/Lobith were directly extrapolated on future concentrations in sediments/dredged material in the port of Rotterdam, neglecting retention or loss processes.

Inputs from emissions in the Netherlands, as discussed in chapter 3.3, are expected to be minor and were not taken into account.

5 Scenarios of future development in the Rhine catchment area and impact on dredged material quality in Rotterdam

The scenario analysis for PAHs and PCBs utilised the MONERIS approach as described in chapter 3 and generally followed the same scenarios as applied for the metals. It is based on the current state (1994-1996), estimating changes until 2015:

Ø ‘Business as Usual’ (*BAU*) scenarios: only measures are taken into account that have already been agreed on or are 'in the pipeline', i.e. their implementation can most probably be expected.

Ø ‘Green Environment’ (*Green*) scenarios: Additional measures are taken into account that might be realised but largely depend on upcoming policies.

General assumptions for both scenarios are:

- Suspended particulate matter concentrations, discharge and retention characteristics of the Rhine system remain unchanged.
- Parameters like population, traffic and paved urban areas do not change.

5.1 Assumptions for the scenario analysis

For the different pathways considered in MONERIS, changes in input parameters or reduction coefficients respectively were estimated according to measures related to the *BAU* and *Green* scenarios.

Industry - emissions to water

PAH and PCB emissions from industry (discharges to water) in the Rhine basin are assumed to stay negligible compared to the total loads at Bimmen/Lobith (compare chapters 3.1.1 and 3.3).

Wastewater treatment

For household emissions of PCBs (chapter 3.1.2) reductions of 25 % (*BAU*) and 50 % (*Green*) were assumed. Microfiltration or ultrafiltration techniques as possible measures could decrease concentrations of suspended solids in effluents of wastewater treatment plants (WWTPs) below 1 mg/L (Scharringhausen, 1990). As PAHs and PCBs are mainly bound to suspended solids this would achieve a further reduction of PCB and PAH inputs from WWTPs. However the implementation of filtration techniques would imply high costs and was therefore not taken into account.

Atmospheric deposition

The reduction coefficients for PAHs and PCBs were estimated from source-specific emission inventories and source-specific measures. The estimated reduction coefficients were applied for the direct atmospheric deposition to surface waters as well as for the atmospheric deposition to paved urban areas.

Emission estimates were submitted from a number of European countries according to a nomenclature of emission sources to OSPARCOM, HELCOM and the convention on LRTAP. These data were intended as well to serve as a preparatory step towards the preparation of the European CORINAIR emission inventory. An overview on the current activities on emission inventories was presented during a WMO/EMEP/UNEP workshop by Breivik et al. (1999).

Berdowski et al. (UBA, 1997) set up an European atmospheric emission inventory of heavy metals and persistent organic pollutants (POPs) for the year 1990 using the above mentioned data sets. For the countries, sources or compounds lacking in official submissions, default emission estimates were prepared in order to complete the inventory.

Estimated PAH emissions

Emissions of PAHs in Germany for 1994 and estimated reduction potentials are given by UBA (1998a) and listed for benzo(a)pyrene (BaP) in appendix 5.1a. These data were chosen as a basis for the estimation of reduction coefficients as it was the most recent and most detailed information available. Another argument is that Germany contributes about 64 % to the total Rhine catchment area, however keeping in mind the transboundary atmospheric transport of these substances.

Emission inventories differ in the absolute values as well as with regard to the estimated emission patterns (contribution of different sources). Berdowski et al. (UBA, 1997) have estimated uncertainties to be within factors ±2-5. Appendix 5.1b gives a comparison of emissions of different sources for Germany, the Netherlands and Europe.

Generally, including Europe-wide estimates, major contributions are due to residential heating, production processes in the steel and non-ferrous metal industries and wood impregnation with tar-oil. Contributions of combustion processes in large plants as power plants are negligible due to efficient flue gas cleaning techniques.

In comparison to Germany, Dutch BaP emissions seem to be overestimated. The relative contributions of power plants, residential heating and traffic are comparable and/or plausible. Neither the similar contribution of steel and non-ferrous metal industries nor the extremely different contributions from wood impregnation can be explained.

Reduction potentials for PAHs

A detailed description of possible reduction measures for the different emission sectors is given in UBA (1998a). The main reduction potentials are:

- Production processes: at present in Germany production processes generally already fulfil the quality targets (TA Luft, see chapter D3.2.1). In appendix 5.1a the reduction potential is stated assuming the application of best available technique (referring to 1997).
- Residential heating: in appendix 5.1a reduction potentials are given, assuming the replacement of older combustion/heating systems by BAT (best available technique) equipment. Due to increased efficiency of the combustion processes / heat generation fuel consumption decreases.
  Additional possible measures are: (1) better insulation of buildings resulting in an reduction potential up to 50 % (Feist, 1993), (2) substitution of wood, brown coal (incl. briquettes) and hard coal briquettes with fuels having lower emission factors as gas or light fuel oil. The only regulation in Germany with regard to these additional measures is the “Wärmeschutzverordnung” requiring an improved insulation of buildings.

Assumptions for scenarios (PAHs)

For the ‘Green Environment’ scenario all previously discussed measures are taken into account without the additional measures on residential heating systems representing an additional reduction potential. Considering that the implementation of BAT (best available techniques) to production processes until 2015 is rather questionable and that comparable measures would have to be undertaken as well by neighbouring countries (transboundary atmospheric transport), the following assumptions for the scenarios are made:

§ *BAU*: 10 % reduction of BaP emissions to air

§ *Green*: 20 % reduction of BaP emissions to air

For the *BAU* scenarios, this is in agreement with estimates from the European Commission. For Germany a slight decrease of BaP emissions until 2010 is expected whereas the total BaP emissions in the investigated 15 member states of the EU are likely to increase moderately (EEA, 1999).

Estimated PCB emissions

PCB emissions to air in Germany were estimated by UBA (1997) and RIVM (1995). The estimates for the different emission sectors are given in appendix 5.1c for the years 1980, 1990 and 2000.

During the last 20 years PCB emissions to air drastically decreased, mainly due to the out-phasing of open applications and stricter regulations on the utilisation in closed systems (electrical transformers and capacitors, as hydraulic oil in mining).

Previous reduction measures in Germany focussed on the substitution of PCBs in large transformers and capacitors, the collection of PCB containing waste oil, and controlled disposal, e.g. by incineration. Until 1994 in the majority of large transformers PCB had been substituted and it was estimated that until 1999 all PCB containing large transformers and capacitors should have been out of operation (UBA, 1998a).

Small PCB-containing capacitors were found in about 20% of electrical appliances used in households in 1996 (UBA, 1998a). Primarily it has to be ensured that electrical appliances are separated from domestic waste before disposal or incineration.

In the case of scrap metal utilisation, measures like draining off motor and transmission oils from wrecked cars and separation of PCB-containing capacitors from electrical appliances could reduce the release of PCBs from scrap metal utilisation by a factor of 10.

PCBs have been used for open applications, e.g. in building materials as sealing masses and paints. The separation of these materials before disposal would be desirable but for practical reason this is hardly achievable.

In 1984 PCB-containing hydraulic oils in mining were substituted by “UGILEC”, primarily consisting of tetrachlorobenzyltoluenes. It was assumed that most of the until 1984 in mining used PCBs (approx. 12,500 tonnes) have been released. The amount of these PCBs entering environmental compartments as ground water or surface waters are currently not known.

Restrictive measures for the manufacture and use of PCBs led to a significant reduction of emissions in the Netherlands and other European countries. Appendix 5.1d summarises emission estimates in comparison for Germany, The Netherlands and other European countries.

Due to the high emission loads in the past to air and water PCBs accumulated in soils and sediments. With an expected further decrease of PCB emissions, re-emissions from soil and water (see appendices 5.1c-d) will gain importance.

Assumptions for scenarios (PCBs)

As a basis for emissions in the time period 1994-1996, used as starting point for the scenarios, PCB emissions to air of 30 tonnes per year in Germany are assumed. Due to current and planned regulations a further large reduction of PCB emissions stemming from electrical equipment can be expected. Major uncertainties for future PCB emissions to air are:

- uncertainty of PCB emissions due to combustion and production processes
- future fate of PCB used in mining as hydraulic oil
- uncertainty of PCB re-emissions (the estimations for re-emissions in appendices 5.1c-d were derived from modelling and are not verified by measurements yet)
- concerning the long-range atmospheric transport of PCB, a further decrease of PCB concentrations in the atmosphere can not be achieved by measures only on the national but on the international level

The following assumptions for PCB emissions to air for the scenarios until 2015 are used:

§ *BAU*: reduction rate relative to 1994-96 of 33 %

§ *Green*: approx. 2 tonnes per year, reduction rate relative to 1994-96 of 67 %

Erosion

For the *Green* scenarios it was estimated that by erosion reducing measures (BBodschG, German law of soil protection, see chapter D3.2.2) in the upstream parts of the Rhine basin with high erosion rates diffuse inputs by erosion can be reduced by 25 %. The concentrations of PAHs and PCBs were assumed to be unchanged until 2015.

Urban areas

For the atmospheric deposition of PAHs and PCBs on paved urban areas the same reduction coefficients as for the direct atmospheric deposition to surface waters were applied. In the *Green* scenarios a decoupling (15 %) of paved areas from sewer systems was assumed. In addition the enlargement of storage basins for rainwater to 100 % (23 m^3/ha urban area) was taken into account for both separate and combined sewer systems.

Shipping

The assumed inputs of PAHs by shipping (ship coatings, bilge waters, spills) for the present state have a high uncertainty as discussed in chapter 3.1.6. PAH inputs stemming from ship coatings are expected to decrease drastically due to substitution of PAH rich coatings by alternative products (RIZA, 1997a). We assumed reductions (best guess) for PAH inputs from shipping: 25 % (*BAU*) and 50 % (*Green*).

Summarised input parameters for BAU and Green Scenarios

Summarised input parameters or reduction coefficients for the scenario analysis utilising MONERIS are summarised in table 5-1.

Table 5-1: Input parameters/reduction coefficients for scenarios

		Fl	BbFl	BaP	PCB 52	PCB 138	PCB 180
emissions paved urban areas	g/(ha yr)	8.4	3.1	3.0	0.020	0.034	0.022
atmospheric deposition	ng/(m^2 d)	2300	850	820	5.5	9.3	6.1
reduction BAU	%	**10**	**10**	**10**	**33**	**33**	**33**
reduction Green	%	**20**	**20**	**20**	**67**	**67**	**67**
soil content (agricultural soil)	µg/kg	45	50	25	0.20	0.60	0.35
reduction BAU	%	0	0	0	0	0	0
reduction Green	%	**25**	**25**	**25**	**25**	**25**	**25**
soil content (remote areas)	µg/kg	9.0	10	5.0	0.04	0.12	0.07
reduction BAU	%	0	0	0	0	0	0
reduction Green	%	0	0	0	0	0	0
atmospheric deposition to surface water	g/(ha yr)	0.50	0.19	0.18	0.020	0.034	0.022
	ng/(m^2 d)	140	52	49	5.5	9.3	6.1
reduction BAU	%	**10**	**10**	**10**	**33**	**33**	**33**
reduction Green	%	**20**	**20**	**20**	**67**	**67**	**67**
household emissions	mg/(Inh. d)	0	0	0	0.0016	0.0060	0.0030
reduction BAU	%				**25**	**25**	**25**
reduction Green	%				**50**	**50**	**50**
shipping	kg/yr	600	600	400	0	0	0
reduction BAU	%	**25**	**25**	**25**			
reduction Green	%	**50**	**50**	**50**			
WWTP elimination rate	%	90	90	90	90	95	95
decoupling paved areas BAU	%	0	0	0	0	0	0
decoupling paved areas Greer	%	**15**	**15**	**15**	**15**	**15**	**15**
rain water storage BAU	%	no change					
rainwater storage Green	%	**100**	**100**	**100**	**100**	**100**	**100**

5.2 Scenario results

The results from the scenario analysis for individual PAHs and PCBs until 2015 are listed in appendices 3.2a-f, stating the contributions of the different pathways/processes to loads at selected stations along the Rhine and its tributaries for the *BAU* and *Green* scenarios. Forecasted reductions for individual loads of PAHs (Fl, BbFl, BaP) at Bimmen/Lobith are in the range 12-13 % (*BAU*) and 29-33 % (*Green*) and for PCBs (52, 138, 180) in the range 27-30 % (*BAU*) and 58-60 % (*Green*). Taking benzo(a)pyrene and PCB 138 as examples, the results for the present state, the *BAU* and *Green* scenarios for the inputs in the Rhine catchment upstream Bimmen/Lobith are depicted in figures 5-1 and 5-2.

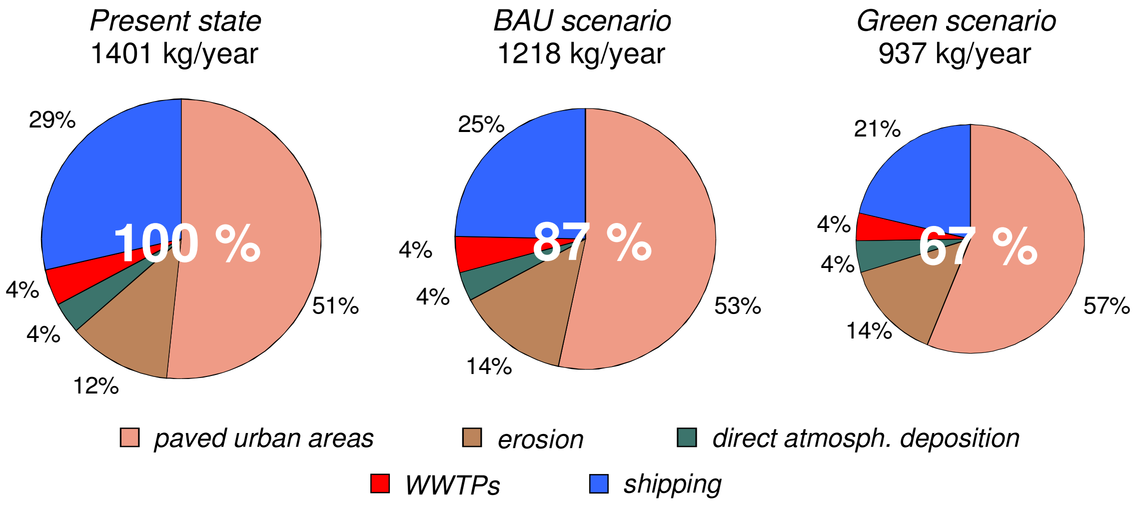


Figure 5-1: Results of scenario analysis for benzo(a)pyrene inputs in the Rhine upstream Bimmen/Lobith

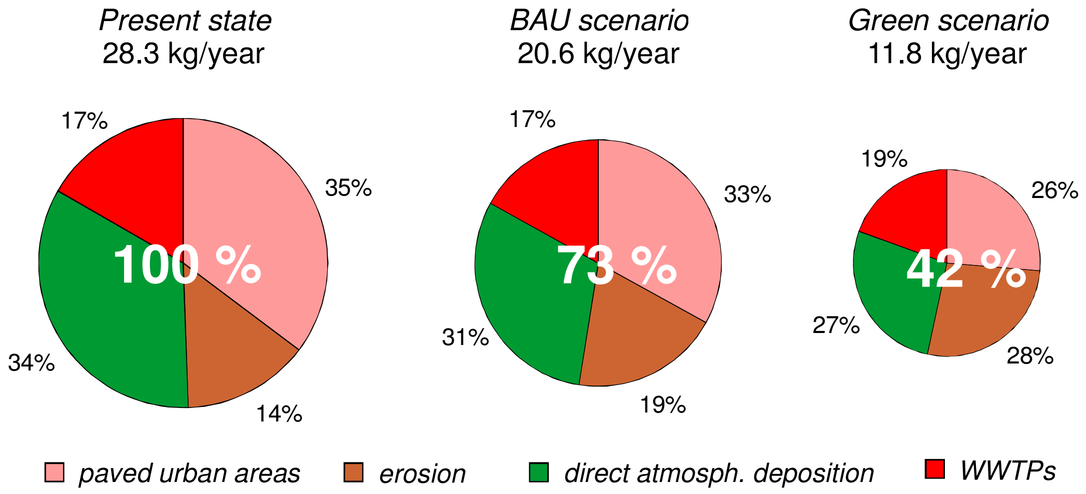


Figure 5-2: Results of scenario analysis for PCB 138 inputs in the Rhine upstream Bimmen/Lobith

In the scenarios for PAHs, reductions are mainly achieved by reduced inputs from shipping and paved urban areas. The estimations for inputs from shipping, in the scenarios as well as for the present state itself, have high uncertainties (chapter 3.1.6). Decreasing inputs from urban areas account for a reduction of total inputs of individual PAHs in the range of 4-6 % (*BAU*) and 9-14% (*Green*). This is mainly due to reduced atmospheric deposition rates to paved areas. An additional, but comparably lower, net reduction (< 1 %) results from decreased, direct atmospheric deposition to surface waters. Measures reducing erosion decrease total inputs in the Green scenarios by less than 4 %. The decoupling of paved urban areas and the enlargement of rainwater storage basins for separate and combined sewer systems achieve additional net reductions of approximately 7 % of total PAH inputs (Green scenarios).

In the scenarios for PCBs, reductions of inputs are mainly achieved by reduced atmospheric deposition, directly to surface waters as well as indirectly via runoff from paved urban areas. Both pathways have approximately the same share in the total reduction of PCB inputs. Measures reducing erosion decrease total inputs in the Green scenarios by less than 3 %. The decoupling of paved urban areas and the enlargement of rainwater storage basins for separate and combined sewer systems achieve additional net reductions of approximately 3 % of total PCB inputs (Green scenarios).

Forecast of dredged material quality in the eastern parts of the port of Rotterdam

For the forecast of dredged material quality in the port of Rotterdam the estimated changes in loads of PAHs and PCBs at Bimmen/Lobith were directly extrapolated on the concentrations in dredged material in the eastern parts of the port of Rotterdam (compare chapter 4.3).

PAH and PCB concentrations (RMPM, 1999), describing the present state, were recalculated from three sampling campaigns (315 samples) in the period 1994-1998. Mean individual PAH and PCB concentrations were derived after standardising to 10 % organic matter and weighting according to long-term mean dredged volumes at the individual sampling sites. For individual PAHs and PCBs the quality of dredged material (Present state, *BAU*, *Green*) is compared with the Dutch criteria for dredged materials (Sea/Slufter limits, target levels) in table 5-1.

Table 5-1: Sediments in the eastern part of the port of Rotterdam: Comparison of mean concentrations for the present state, BAU and Green scenarios with Sea/Slufter limits and target levels for PAHs and PCBs

	sea/slufter limit	target level	*BAU* reduction	*Green* reduction	*Present* 94-98	*BAU* 2015	*Green* 2015
	mg/kg dw 1)	mg/kg dw 1)	%	%	mg/kg dw 2)	mg/kg dw 2)	mg/kg dw 2)
naphtalene 3)	0.8		13	30	0.45	0.40	0.32
phenanthrene 3)	0.8		13	30	**1.20**	**1.05**	**0.84**
anthracene 3)	0.8		13	30	0.59	0.51	0.41
fluoranthene	2.0		11.9	28.6	**2.02**	1.78	1.44
benz(a)anthracene 3)	0.8		13	30	**0.85**	0.74	0.60
chrysene 3)	0.8		13	30	**1.17**	**1.01**	**0.82**
benzo(b)fluoranthene	(0.8)		13.2	32.0	1.08	0.94	0.73
benzo(k)fluoranthene 3)	0.8		13	30	0.42	0.36	0.29
benzo(a)pyrene	0.8		13.1	33.1	**0.88**	0.76	0.59
benzo(ghi)perylene 3)	0.8		13	30	0.76	0.66	0.53
indeno(1,2,3-cd-)perylene 3)	0.8		13	30	0.76	0.66	0.53
sum 10 PAH		*1*			*9.10*	*8.88*	*7.11*
PCB 28 3)	0.03	0.001	30	60	**0.037**	0.026	0.015
PCB 52	0.03	0.001	29.5	60.4	0.024	0.017	0.010
PCB 101 3)	0.03	0.004	30	60	0.027	0.019	0.011
PCB 118 3)	0.03	0.004	30	60	0.017	0.012	0.007
PCB 138	0.03	0.004	27.2	58.3	0.027	0.020	0.011
PCB 153 3)	0.03	0.004	30	60	**0.033**	0.023	0.013
PCB 180	0.03	0.004	27.9	59.3	0.016	0.012	0.006
sum 7 PCBs		*0.02*			*0.182*	*0.127*	*0.073*

1) standardised to 10% organic matter

2) standardised to 10 % organic matter and corrected/weighted to long-term mean dredged volumes

3) not modelled by MONERIS, assumed reductions for *BAU* and *Green* scenarios

Mean concentrations exceeding Sea/Slufter limits are given as bold numbers.

In the *Green* scenarios mean concentrations of PAHs and PCBs are expected to decrease below the Sea/Slufter limits with the exception of phenanthrene and chrysene. However, target levels will be still exceeded for PAHs as well as for PCBs.

Mean concentrations are no suitable yardstick for discussing dredged volumes to be disposed in the Slufter. Concentrations of PAHs and PCBs, as other contaminants, show a high variability in different sections of the port. If at least one parameter, e.g. one single PAH, exceeds the Sea/Slufter limit at a specific site, the dredged material has to be disposed in the Slufter.

Thus, the local variability of PAH and PCB concentrations has to be taken into account, estimating future amounts of dredged material to be disposed in the Slufter. Assuming for the eastern parts of the port of Rotterdam the same local variability of concentrations at the sampling sites and the same mean dredged volumes for the *BAU* and *Green* scenarios as for the present state, table 5-2 gives a rough estimation.

Table 5-2: Volumes of dredged material from the eastern part of the port of Rotterdam to be disposed in the Slufter according to present criteria (Sea/Slufter limits) for individual PAHs and PCBs (Present state, BAU and Green Scenarios)

	Volumes of dredged material exceeding sea/slufter limit for PAHs or PCBs		
	Present 1994-1998 %	*BAU* 2015 %	*Green* 2015 %
PAHs	78	62	43
PCBs	45	26	11

6 Summary and conclusions

At present, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are of concern in dredged material in the eastern parts of the port of Rotterdam which are mainly influenced by contaminated suspended particulate matter (SPM), originating from the Rhine basin. From the volumes dredged in the eastern parts of the port, currently approximately 80% exceed the so-called Sea/Slufter limits for PAHs and approximately 45% in the case of PCBs. This dredged material has to be stored in a confined disposal site, the Slufter.

The inputs from PAHs and PCBs from point and diffuse sources in the Rhine catchment area were quantified and linked to the quality of sediments/dredged material in the eastern parts of the port of Rotterdam. At present, direct inputs of PAHs and PCBs to the Rhine system from industry are negligible compared to inputs from diffuse sources.

In the case of PAHs, primary sources are emissions to the atmosphere from combustion of fossil fuels as well as inputs from shipping (PAH releases from ship coatings, bilge waters and spills). Largest contributions (approx. 40-60 % for individual PAHs) to total PAH loads in the Rhine are inputs from urban areas. PAHs enter the Rhine system via runoff from paved areas after atmospheric deposition. Erosion from top soils in agricultural areas contribute 9-19%, direct atmospheric deposition to surface waters 3-4 % and inputs from wastewater treatment plants 3-5 % to the total PAH loads in the Rhine. The estimated inputs from shipping activities (19-33 % for individual PAHs) have high uncertainties.

The use of PCBs in open applications (lubricants, additives in paper and plastic production) as well as the use in closed systems (dielectrics in capacitors and large transformers, hydraulic oil in mining) has been out-phased or widely restricted. This resulted in a large decrease of new PCB emissions during the last 20 years. Future primary emissions at a comparably low level are expected e.g. from incineration or scrap metal utilisation from small electrical appliances still containing PCBs. Due to the persistence of PCBs, the atmospheric transport of PCBs will continue to be a major pathway, re-emissions from soil and water gaining in importance.

Largest contributions to total PCB loads in the Rhine are paved urban areas (approx. 35 %) and direct atmospheric deposition to surface waters (approx. 35 %). Erosion from top soils in agricultural areas contribute 9-14 % and inputs from wastewater treatment plants 14-18 % to the total PCB loads in the Rhine.

Summarising, it can be stated that inputs of PAHs and PCBs to the Rhine system are dominated by diffuse sources; the main inputs originating from the Rhine basin upstream Bimmen/Lobith (Dutch/German border). The PAH and PCB concentrations in SPM at Bimmen/Lobith correspond to the contamination of sediments in the eastern parts of the Port of Rotterdam.

In order to forecast the future quality of sediments/dredged material in the eastern parts of the port of Rotterdam, two types of scenarios were modelled. They are based on no change in hydrological and (socio-)economic conditions (population, traffic, paved urban areas etc.), estimating changes until 2015:

Ø Business as usual (*BAU*) scenarios: only measures were taken into account that have already agreed on or are 'in the pipeline', i.e. their implementation can most probably can be expected.

Ø Green Environment (*Green*) scenarios: Additional measures were taken into account that might be realised but largely depend on upcoming policy choices.

In the scenarios for PAHs, reductions are mainly achieved by reduced inputs from shipping and paved urban areas. The estimations for inputs from shipping, in the scenarios as well as for the present state itself, have high uncertainties. Decreasing inputs from urban areas account for a reduction of total inputs of individual PAHs in the range of 4-6 % (*BAU*) and 9-14% (*Green*). This is mainly due to reduced atmospheric deposition rates to paved areas. An additional, but comparably lower, net reduction (< 1 %) results from decreased, direct atmospheric deposition to surface waters. Primary sources for PAH emissions to atmosphere, having the highest reduction potentials, are residential combustion of fossil fuels (domestic heating) and to a smaller extent production processes as coke production, steel and non-ferrous metal industry. Measures reducing erosion decrease total inputs in the Green scenarios by less than 4 %. The decoupling of paved urban areas and the enlargement of rainwater storage basins for separate and combined sewer systems achieve additional net reductions of approximately 7 % of total PAH inputs (Green scenarios).

In the scenarios for PCBs, reductions of inputs are mainly achieved by reduced atmospheric deposition, directly to surface waters as well as indirectly via runoff from paved urban areas. Both pathways have approximately the same share in the total reduction of PCB inputs. Measures reducing erosion decrease total inputs in the Green scenarios by less than 3 %. The decoupling of paved urban areas and the enlargement of rainwater storage basins for separate and combined sewer systems achieve additional net reductions of approximately 3 % of total PCB inputs (Green scenarios).

An issue of special importance for PCBs is the 'historic' contamination of sediments in the Rhine basin. As new inputs of PCBs will continue to decrease, the relative contribution of 'historically' contaminated sediments to PCB loads in the Rhine will gain in importance. This process is governed by re-erosion during high water discharges, by relocation of dredged material stemming from weirs and locks in the upper Rhine or tributaries of the Rhine and related retention and loss processes. As the described processes were not accounted for in the emission analysis, the forecasts in the scenarios for PCBs might be too optimistic.

For the forecast of dredged material quality in the port of Rotterdam, the estimated changes in PAH and PCB loads in the Rhine until 2015 were directly extrapolated to future changes in concentrations in sediments of the eastern parts of the port of Rotterdam. In order to estimate future amounts of dredged material to be disposed in the Slufter, the following assumptions were made:

- The relative local variability of PAH and PCB concentrations in different sections of the eastern parts of the port of Rotterdam will remain unchanged (compared to the present state);
- the mean volumes of sediments to be dredged in different sections of the Port of Rotterdam will remain unchanged.

The estimations are based on the current criteria, Sea/Slufter limits, and are summarised in table 6-1:

Table 6-1: Present and estimated future quality of sediments in the eastern parts of the port of Rotterdam with regard to current Dutch criteria.

	Volumes of dredged material exceeding sea/slufter limit for PAHs or PCBs		
	Present 1994-1998 %	*BAU* 2015 %	*Green* 2015 %
PAHs	78	62	43
PCBs	45	26	11

A sustainable situation which would allow the complete relocation of dredged material to the North Sea according to the current Dutch criteria (Sea/Slufter) limits is, based on our assumptions, not expected to be achieved until 2015. In addition, mean concentrations of PAHs and PCBs in sediments of the eastern parts of the port of Rotterdam will continue to exceed defined target levels. This indicates the need for further efforts in the Rhine catchment area, beyond reduction measures already accounted for in the *BAU* and even in the *Green* scenarios.

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List of abbreviations

BaP	benzo(a)pyrene
BAT	best available technique
BbFl	benzo(b)fluoranthene
BghiPe	benzo(ghi)perylene
BkFl	benzo(k)fluoranthe
CSO	overflows from combined sewer systems
CSS	combined sewer system
d	day
dw	dry weight
EMEP	European Monitoring and Evaluation Programme
Fl	fluoranthene
ha	hectare (10,000 m^2)
HELCOM	Helsinki Commission
Ind	indeno(1,2,3-cd)pyrene
Inh.	inhabitant
IUPAC	International Union of Pure and Applied Chemistry
LRTAP	Long-range Transboundary Air Pollution
OSPARCOM	Oslo and Paris Commission
PAHs	Polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyls
Pow	octanol-water partitioning coefficient
SPM	suspended particulate matter
SS	separate sewer
SWW	sewers without wastewater treatment
t	metric ton(nes)
UNEP	United Nations Environment Programme
US-EPA	Environmental Protection Agency of the United States
VROM	Ministry of Housing, Spatial Planning and the Environment in the Netherlands
WMO	World Meteorological Organization
WWTP	Wastewater treatment plant
yr	year