PERSISTENT CHLORINATED HYDROCARBONS (PCHC), SOURCE-ORIENTED MONITORING IN AQUATIC MEDIA 5. POLYCHLORINATED BIPHENYLS (PCBs)

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SUMMARY

In the FRG, the synthesis of PCBs was done from 1950 till 1983 in the Bayer AG in Leverkusen. In the former GDR at the Deutsche Solvay-Werke in Westeregeln, 1,000 tons were synthesized from 1955 till 1964, and in the former USSR from 1930 till 1993 at the plants Orgselko in Dzerdzinsk and Orgsynthesis in Novomoskowsk 58,000 tons, in the former ČSSR in the enterprise Chemko in Strážské in Eastern Slovakia from 1959 till 1984 2,1482 tons (about 1,600 tons of PCB wastes), in Poland in the electrochemical factory in Zalkovice Bedzinske from 1966 till 1970 and after 1974 in Zaklady Azotowe Tarnow-Mosice in Tarnow not more than 17,500 tons. Publications about PCB production data in western European countries are not known.

The most important basis of this paper are the primary data from about 20 official institutions about the content of PCBs (Σ cong. 28, 52, 101 = LPCB, Σ cong. 138, 153, 180 = HPCB; Σ LPCB, HPCB = sPCB) in suspended matter, sediment and fishes from several fresh waters in the Czech Republic, the FRG, and Poland. These data, partly reaching from 1984 till 2004, were statistically calculated and evaluated in tables or pictures as spatial profiles (e.g. rivers Elbe, Rhine, Lippe, and Mosel) or time series. By doing so, it could be found that the sPCB values sometimes were present in surprisingly high amounts at some, mostly industrial sampling points till 2000. being remarkable at the river Elbe, the vicinity of the Škoda enterprise in Mlada Boleslav, the chemical enterprise Spolchemie at the Elbe tributary Bilina in Ústí n. L., at the Niederrhein, the sampling point in Hitdorf, influenced by the Bayer-Werke, and in the river Lippe at Marl/Hüls. In the Berlin waters, up to now high sPCB can be found in the Unterspree, which may be connected with the huge building activities in the city centre. On the contrary, e. g. in the river Odre, in Brandenburg-Mecklenburg waters, in the lakes in the east of Berlin, in Bavarian rivers and lakes, but also e.g. in lake Constance, and at the Hochrhein on the industrial enterprise Grenzach, in the year 2000 very low sPCB values were found, together with high HPCB shares. The PCBs must be evaluated in another way than e. g. DDT and HCH, since PCB aggregates were in use until recently. In the Regulation (EC) no. 850/2004, Article 9 „Monitoring“ is said: „The commission should establish approximate programs and mechanisms, consistent with the state of the art, for the regular provision of comparable monitoring data on the presence of PCB in the environment.“ This is the aim of this paper.

KEYWORDS: high PCB values in the vicinity of industry in the rivers Elbe and Niederrhein, and in the Berlin Spree.

INTRODUCTION

PCBs are a group of 209 individual compounds, produced in various industrial mixtures by introducing elementary chlorine in various degrees into biphenyl. By doing so, a chemically stable/inert, heat-resistant, non-flammable mixture is formed, with particularly useful dielectric properties. Consequently, it was used worldwide as a dielectric in electrical components, mainly transformers and capacitors („closed systems“), and as an additive in hydraulic, cutting and lubricating oils in „partially closed applications“. Other uses of PCB included „open applications“ in solvents, adhesives, casting waxes, surface coatings, plasticisers like PVC, rubber seals etc. The commercial use of PCBs began in 1929 in the USA, and the production is believed to have finally ceased in the mid eighties, except of the Soviet Union. At that time, approximately 1.5 million tons were produced for all applications worldwide (excluding the Soviet Union), of which a significant portion is still in use [1].

PCBs rarely cause acute toxic effects, but most of the effects observed are the result of a repetitive or chronic exposure. There is growing evidence linking PCBs to reproductive and immuno-toxic effects in wildlife. Effects on the liver, skin, immune system, reproductive system, gastrointestinal tract, and thyroid gland of laboratory rats have less been observed, and the compounds are classified as probable human cancer promoters [1].

For the toxicological assessment of the PCBs, some further aspects have to be considered:

- despite purification by neutralisation and distillation, the technical end products still contain contaminations, among others polychlorinated naphthalenes (PCNs) and polychlorinated dibenzofurans (PCDFs) [2]
- in the combustion from PCB-containing materials at temperatures < 1000 °C, PCDFs are formed
- mainly the higher chlorinated PCBs have an extremely high persistence, especially in abiotic matrices like aquatic sediment, and they are extremely bioaccumulative; due to the high persistence in the case of accidents, or in the vicinity of production devices, highly contaminated areas may arise (hot spots).

With the analytical techniques available for routine investigations, it is not possible to measure all 130 congeners determined so far from the theoretically possible 209. The data material used here mainly comes from institutions of the federal states, and there, the six DIN or Ballschmiter congeners 28, 52, 101, 138, 153, and 180 have been determined. These are the quantitatively most important congeners of the industrial PCB mixtures. The lower-chlorinated PCBs 28 and 52 are mainly part of hydraulic fluids e.g. in mining [3]. The six DIN congeners are not the most toxic ones, these are – due to their structural properties – the coplanar PCBs. They are not considered here, because only monitoring aspects are looked at.

The six DIN congeners differ in the number of Cl atoms within the molecule, and the resulting water solubility, bioaccumulation and persistence are given in Table 1.

The differences in water solubility, persistence and bioaccumulation give way for the interpretation of the results, explained in the chapter MATERIALS AND METHODS.

TABLE 1 - Basic ecological-chemical data for the six guiding congeners of PCB according to [4, 5].

Chemical or chemical class (abbreviation) [CAS Nr.]	WS µg/L (20 °C)	log K_{ow}	half-life or persistence in sediment ($t_{1/2}$ years)	Bioaccumulation factor		
				organism	BCF_W	BCF_L
2,4,4’-trichlorobiphenyl (PCB 28) [7012-37-5]	407	5.67	0.8–2.5	fish (5 % lipids) *Mytilus edulis*	20,800 5,500	417,000 458,000
2,2’,5,5’-tetrachlorobiphenyl (PCB 52)) [35693-99-3]	121	6.36	1.4–10	*Mytilus edulis* Zebra fish	19,000 83,500	1,710,000 2,860,000
2,2’,4,5,5’-pentachlorobiphenyl (PCB 101) [37680-73-2]	13	6.86		*Mytilus edulis* Zebra fish	126,000 295,000	10,500,000 10,000,000
2,2’,3,4,4’,5-hexachlorobiphenyl (PCB 138) [35065-28-2]		7.44	19–25	*Mytilus edulis* Zebra fish	282,000 764,400	23,500,000 26,180,000
2,2’,4,4’,5,5’-hexachlorobiphenyl (PCB 153) [35065-27-1]	1.3	7.23	19–25	Zebra fish	448,000	15,350,000
2,2’,3,4,4’,5,5’-heptachlorpbiphenyl (PCB 180) [35065-29-3]	2.9	7.36	25	fish (5 % lipids)	1,150000	22,900,000

WS = water solubility

There are only little data worldwide available as to the technical syntheses and further processing of PCBs. According to [6], in the USA from 1930 till 1977 600,000 tons of PCBs were produced, the maximum production was in 1970 with 40,000 tons. About 56 % were used in the electrical industry, 30 % as softeners and 12 % in hydraulic fluids and lubricating oils. The maximum of the yearly world production was reached in 1970 with 100,000 tons, with 40 % of this amount from the USA and 12 % from Japan. In the FRG, the synthesis of PCBs was done from 1950 till 1983 [7], in the Bayer-Werke Leverkusen, 30,000-33,000 tons were used for transformers. In the GDR at the Deutsche Solvay-Werke in Westeregeln, 1,000 tons of PCBs were synthesized from 1955 till 1964 [8]. In 1964, the factory was totally destroyed by a fire. From 1972 till 1985, 13,515 tons were imported and mostly filled into capacitors at Isokond Berlin as well as Elektronikon Gera [9].

According to [10, 11], in the former USSR PCBs were produced from 1930 to 1993 at the plants Orgstelko in Dzerdzinsk and Orgsynthesis in Novomoskowsk under three brand names:

Sovol, a mixture of tetra- and penta-chlorinated PCBs, used as a plasticizer in paints and varnishes, total production from 1939 till 1993 52,500 tons

Svotol, a mixture from Sovol with 1,2,4-trichlorobenzene, especially in the ratio 9:1, named Svotol 10, used in transformers, total production from 1939 till 1990: 57,700 tons

TCB, mixed isomers of trichlorobiphenyl, used in capacitors from 1968 till 1990, 70 000 tons.

Detailled data for the PCB production in the former ČSSR are available from [12]. The PCB synthesis was performed in the enterprise Chemko in Strážské, Michalovice district in Eastern Slovakia from 1959 till 1984. 21,482 tons of the mixture (about 1,600 tons of PCB wastes) were produced and used under the name *Delor* (Delotherm, Hydrodelor). 9,869 tons were exported, mainly into the former GDR. 11,613 tons were used in the ČSSR/ CSFR, in the paint factory Barvy a Laky in Uherské Hradiště, and as a dielectric fluid in power capacitors in the Czech electrochemical factory ZEZ in Žamberk. The PCB formulations Hydrodelor and Delotherm were especially designed for hydraulic equipment and heat exchange.

Chlorofen, the first Polish PCB mixture, was produced in the electrochemical factory in Zabkovice Bedzinske between 1966 and 1970 [13, 14]. It was used only as a component of transporting belts to make them non-flammable. The production did not exceed 1,000 tons. The manufacture of *Tarnol*, the second mixture, was probably started in 1974 at Zaklady Azotowe Tarnow-Mosice in Tarnow. Presumably, it was produced as a dielectric fluid for transformers. Altogether 17,500 tons of PCBs were used in Poland. In Romania, PCBs were produced in the factory Oltchim in Rm. Valcea [15].

These data and facts concerning the production and use of PCBs in eastern European countries were presented here, not least because similar data are hardly available for western European countries. It is known that France, Spain and Italy have produced and processed PCBs, but detailed data are not to be found in scientific literature.

A state influence on production and use of PCBs is much more difficult, as for e.g. DDT. This compound has only one outstanding property – the insecticidal effect. The range of technical properties of PCBs have been mentioned at the beginning. A detailed description would be much more comprehensive, it is given in a lot of publications, e.g. at [1, 2, 6]. Therefore, there are many *national* and *EU laws* and *guidelines* as well as their updates. Some of them are mentioned in the following, and detailed information can be get from [1]. In the PCB-, PCT-, VC-Verbotsordnung from 1989 [16], production, use, and offering for sale of PCBs were prohibited, and till 1999 in the FRG all devices with PCBs should be phased out. This year attracts attention by maxima of sPCB in aquatic media. This decree was then covered by the Chemikalien-Verbotsverordnung from 1993, and its changes, specifying this circumstance [17].

The Stockholm Convention [18] calls for urgent global actions to reduce releases of persistent organic pollutants (POPs), initially beginning with 12 identified POPs, among them the PCBs, with the goal of their continuing minimization till ultimate elimination. The continued use of electrical equipment containing PCBs until 2025 under restrictions is regulated there. The Regulation (EC) No. 850/ 2004 (19) in its Annex I contains a list of substances subjected to prohibition, and for PCBs the passage: „Without prejudice to Directive 96/56/EC articles already in use at the time of entry into force of this Regulation are allowed to be used.“ Special importance in this connection has Article 9 „Monitoring“, in which is said: „The Commission and the Member States shall establish, in close cooperation, appropriate programs and mechanisms, consistent with the state of the art, for the regular provision of comparable monitoring data on the presence of . . . PCB as identified in Annex III in the environment.

This is *the aim of this paper.*

MATERIALS AND METHODS

The primary data mostly come from publications or personal communications of IKSE Magdeburg [20], ARGE ELBE Hamburg [21-23], CHMU Prague [24], LAU Halle/ Saale [25], SENSTADT Berlin [26], FIA Berlin [27], LAU Brandenburg [28], SVLA Potsdam [29], IKSR Koblenz [30, 31], CLUA/CVUA Freiburg [32], CLUA Karlsruhe [33], HLUG Wiesbaden [3], HLVA Darmstadt/Kassel [34], CLUA Speyer [35], LÖBF/LAfAO NRW Kirchundem-Albaum [36], LAU NRW Essen [37], LUA Erlangen [38], LUA Oberschleißheim [39], BLfW München [40], as well as from the publications [41-52]. The meaning of the short names is described in the chapter REFERENCES. Obtaining, processing of the data and analytical details may be taken from the single publications. The data are obtained according basically to uniform and standardised methods, i. e. they are comparable.

The primary data have been arranged according to sampling points, statistically evaluated and summarized to annual distance profiles (e. g. river Rhine from Konstanz to the mouth), or time series at certain sampling points (e.g. 1984–2003 at km 16.5 Berlin Teltowkanal), shown in graphs or tables.

As can be gathered from Table 1, the six DIN congeners partly very much differ in their persistence, increasing with the rising number of Cl atoms, as does the bioaccumulation tendency. The water solubility strongly decreases in the same direction. These parameters influence not only the PCB content in the matrices, but also the congener distribution pattern, that is why the data are divided as follows:

sPCB = Σ cong. 28, 52, 101, 138, 153, 180 = sum PCBs

LPCB = Σ cong. 28, 52, 101 = lower chlorinated PCBs

HPCB = Σ cong. 138, 153, 180 = higher chlorinated PCBs

The composition of the PCB formulations reaching the water depends on the emittent. E. g., in breams from the river Saar near Völklingen in 1986, the highest LPCB values in fishes were found with 16 % HPCB share in sPCB [46]. According to [3, 53, 54], LPCBs, mainly PCB 28 and 53, were especially used as hydraulic fluids in the mining industry. This source of input, however, was restricted to mining only till the eighties, than substitutes have been used (e. g. Ugilec).

The decrease of the lower persistent LPCB shares in the course of time series can be seen in Figure 1. In contrast to DDT and especially HCH, which often reflected continuous decreases, the PCB decreases and the increases of HPCB shares were mostly discontinuously. This could be explained with continuous PCB immissions from diffuse sources. Looking at longer periods of time (e. g. in the Berlin Teltowkanal from 1984 till 2003), both processes – the decrease of the sPCB contents and the increase of the HPCB shares – are to be seen. The (however short) time series at the Untere Havel in Brandenburg better reflects the decrease of the LPCB shares in favour of HPCB, supported by the lack of new immissions.

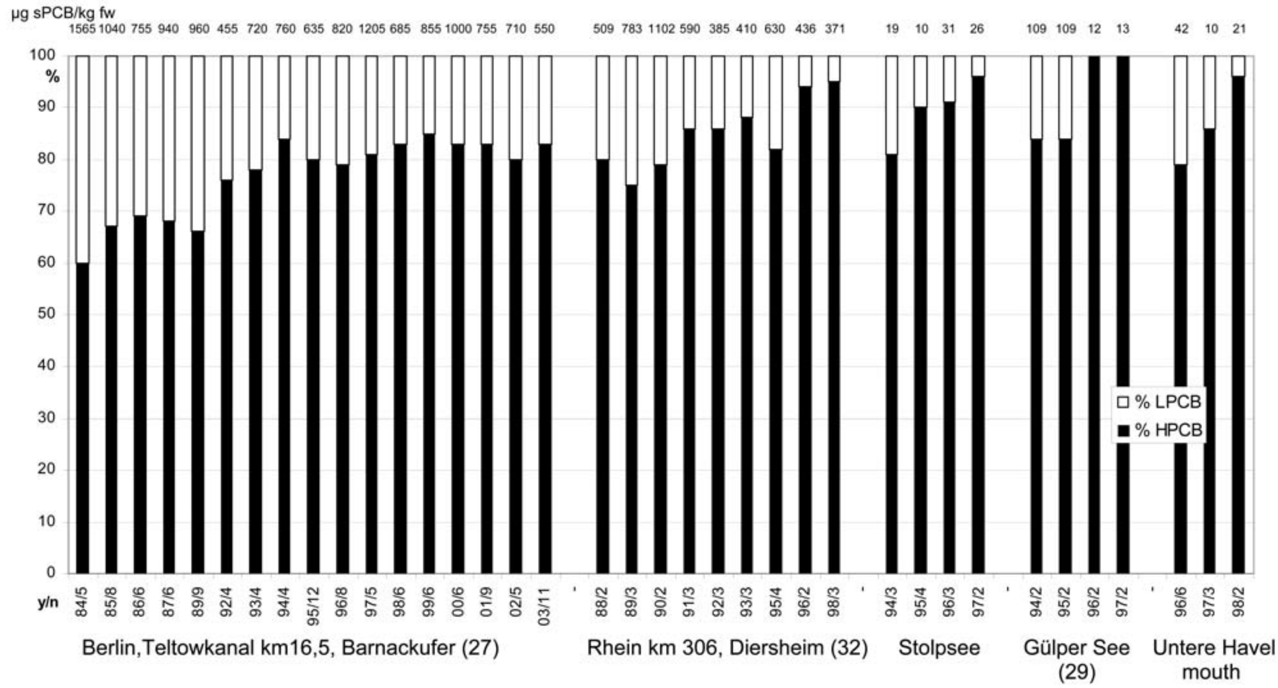


FIGURE 1 - PCB congener profiles in eels from different waters, time series. Arithmetic means of n specimen with > 10 % fat/sampling point/year, according to primary data from [27, 29, 32].

Figure 2 shows the PCB congener profiles in the sediment of some European rivers. The matrix sediment, like suspended matter, is especially suited for such reflections, because the distributions are only little influenced by metabolism, as they are in fishes. Furthermore, here samples were selected from the years 1998–2000, i. e. a relatively short period of time. In the left part of the graph (Elbe tributary Bilina till Schmilka at the river Elbe), comparatively high LPCB shares can be seen. In this part of the river Elbe, there are the chemical factories at Pardubice (VCHZ, Vály, km -228), Kolín (Lysá, km -150,7), Neratovice (Spolana, Obříství km -115) and Ústí n. L. (Spolchemie), which, partly until the nineties, discharged their waste into the river. The main sources of PCBs were the Škoda car factory of Mladá Boleslav and an industrial dump site upstream of Mladá Boleslav [20]. Especially these chemical factories, but also corresponding enterprises at the rivers Lippe and Rhine are marked by high LPCB shares. The causes for the profile at the sampling point Gorsdorf at the Schwarze Elster in Saxony-Anhalt could not be cleared up so far; but the river flows through a brown coal-mining area. The sampling points in Duisburg-Walsum, Vltava Zelčín, and Tabor are marked by heavy industry and combustion processes, which also led to PCB emissions, with LPCB probably playing, however, only a minor role because of their low stability.

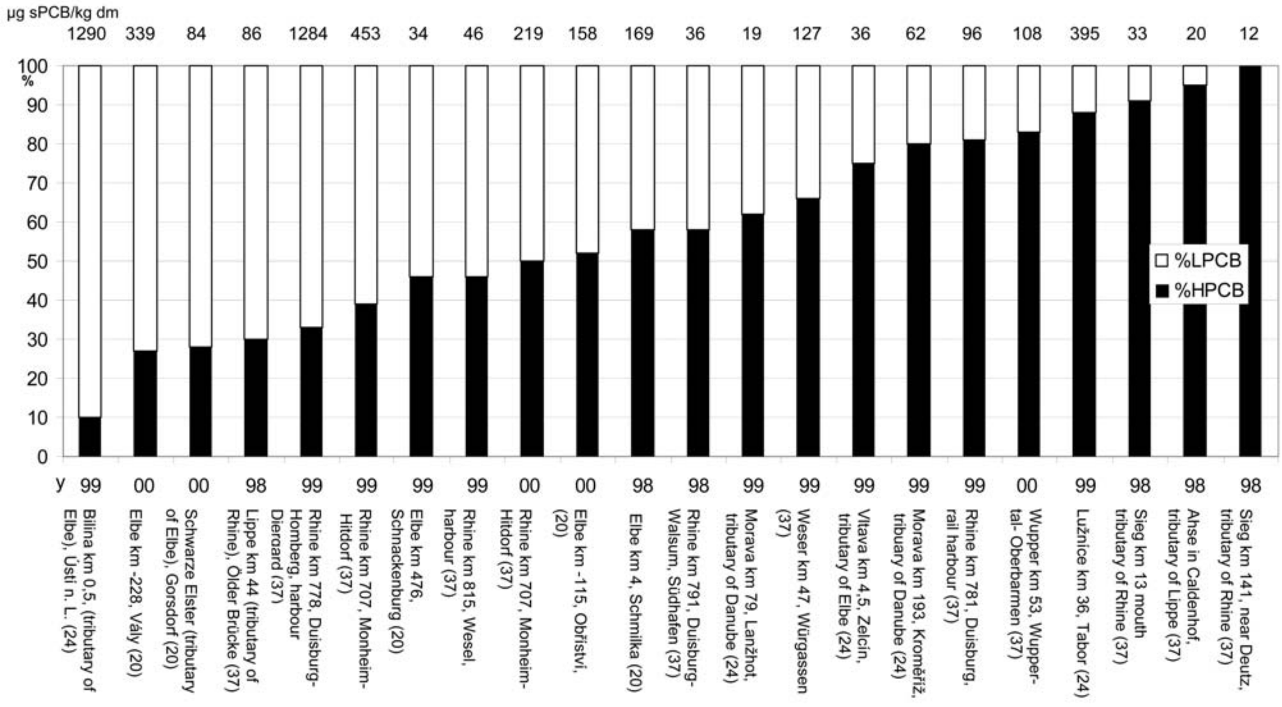


FIGURE 2 - PCB congener profiles in the sediment of some Central European rivers, 1998 – 2000 (Primary data from [20, 24, 37]).

From the congener profile pattern, hints may be derived to the sources of PCBs. But this must be done carefully, because,

- these sources may be manifold and diffuse, and
- mainly occur in fishes metabolism, first of all for the LPCB.

The comparatively less complicated interpretations described for DDT [55], HCH [56], and chlorobenzenes [57], turn out not to be so easy for the PCBs.

RESULTS AND DISCUSSION

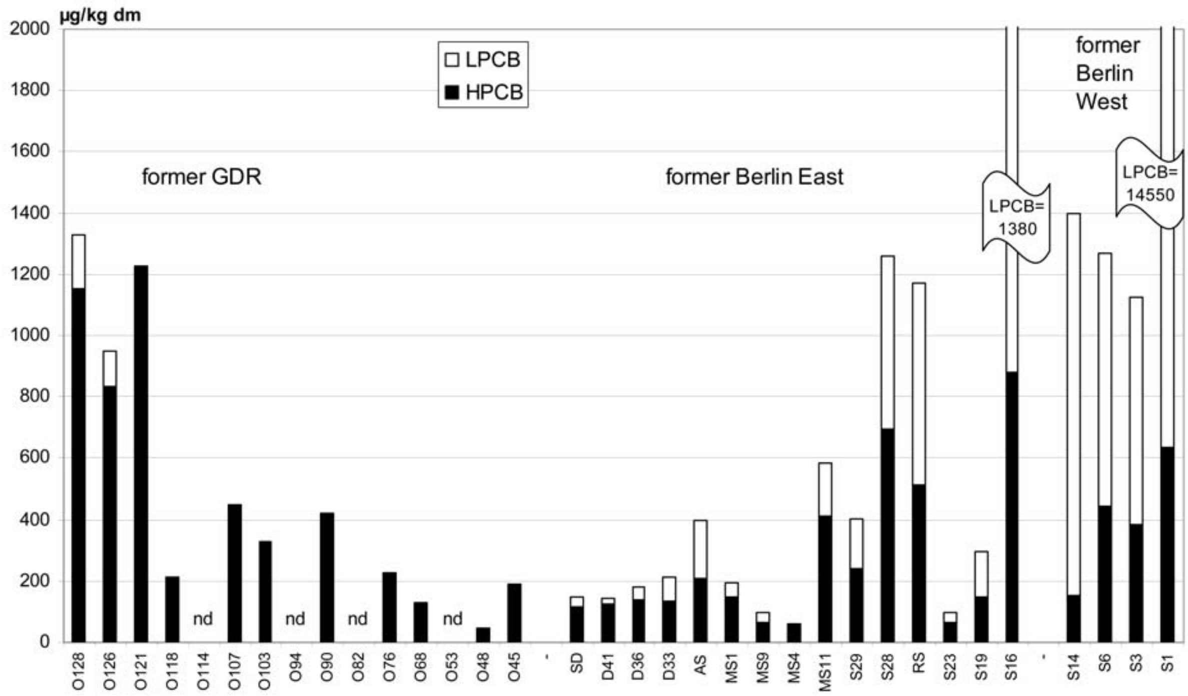
In this chapter, data and facts are evaluated as described above about PCBs in sediment, suspended matter and indicator fishes from the river Odre, the Odre-Spree system, Berlin waters, the river Elbe and some tributaries, as well as the river Rhine and tributaries in Baden-Württemberg, Hessen, Rhineland-Palatinate and Northrhine-Westphalia. The results from single publications were also considered for the discussion of the waters.

The river Odre, Odre-Spree system and waters in Berlin-Brandenburg

The Odre river is the main sink of wastewaters from provinces adjacent to the Odre bed, and also from provinces of the Odre river catchment area. Not quite unexpected, the PCBs play only a minor role as contaminants [58]. Also the flood in summer 1997 had only a minor influence on the load of the sediments in the area of estuary and the lower course of the Odre. In comparison with the state of 1995, after the flood in both arms of the river Odre the amount of PCBs slightly increased [59]. The single data for PCB in eels from the Odre near Schwedt and Hohenwutzen [28] were compared in the tables with the analogous data from other rivers, and confirm this assessment.

Additionally to the assessments published earlier concerning PCB loads in the Odre-Spree system [8], Figure 3 reflects corresponding measurements in sediment from the mouth of the Odre-Spree-Canal into the Odre in Eisenhüttenstadt, via this channel to the Berlin Seddinsee, the rivers Dahme, Müggelspree and Spree upto their mouths into the river Havel in Spandau.

The course of the Odre-Spree system leads through previously highly industrialised regions, e.g. in Eisenhüttenstadt, the Eisenhüttenkombinat EKO with high sPCB contents consisting mainly of HPCB, through forests and rural areas with only low sPCB contents, the cable factory Oberspree (KWO), where the sPCB maxima consist to about the half of LPCB up to the extreme values at Humboldt harbour and the Unterspree, where LPCB clearly pre-dominate. Especially the latter points to recent PCB inputs, which may be conceivable in the former Berlin West around 1990.



O: Oder-Spree-Kanal, SD: lake Seddinsee, Dkm: river Dahme, AS: river Alte Spree Köpenick, MSkm: river Müggelspree, Skm: river Spree, RS: lake Rummelsburger See

O128 Eisenhüttenstadt (EH) Unterer Hafen, O126 EH Straßenbrücke, O121 EH Eisenhüttenkombinat (EKO), O118 above EH, O114 Rautenkranz forest, O107 mouth Brieskower Kanal, O103 Kleiner Müllroser See mouth, O94 Wolfsbruch forest, O90 Kersdorfer See mouth, O82 Dehmsee mouth, O76 Fürstenwalde harbour, tyre factory, O68 Sluice Große Tränke, O53 below electricity line, O48 Sluice Wernsdorf, O45 Seddiner Hütte, SD lake Seddinsee, D41 Langer See western top, D36 river Dahme, shipyard, D33 river Dahme Lange Brücke, AS Alte Spree Köpenick, MS11 lake Hubertussee Köpenick, MS9 river Müggelspree, MS4 lake Großer Müggelsee northwestern shore, MS1 ORWO chemical plant, S29 lake Oberspree Kabelwerke main building, S28 Treskowbrücke, RS lake Rummelsburger See glass factory, S23 river Oberspree landing place Treptow park, S19 river Oberspree Schillingbrücke, S16 river Stadtspree Bode-Museum, S14 river Stadtspree congress hall, S6 river Unterspree sluice Charlottenburg, S3 river Unterspree power station Reuter, S1 mouth Alte Spree Spandau

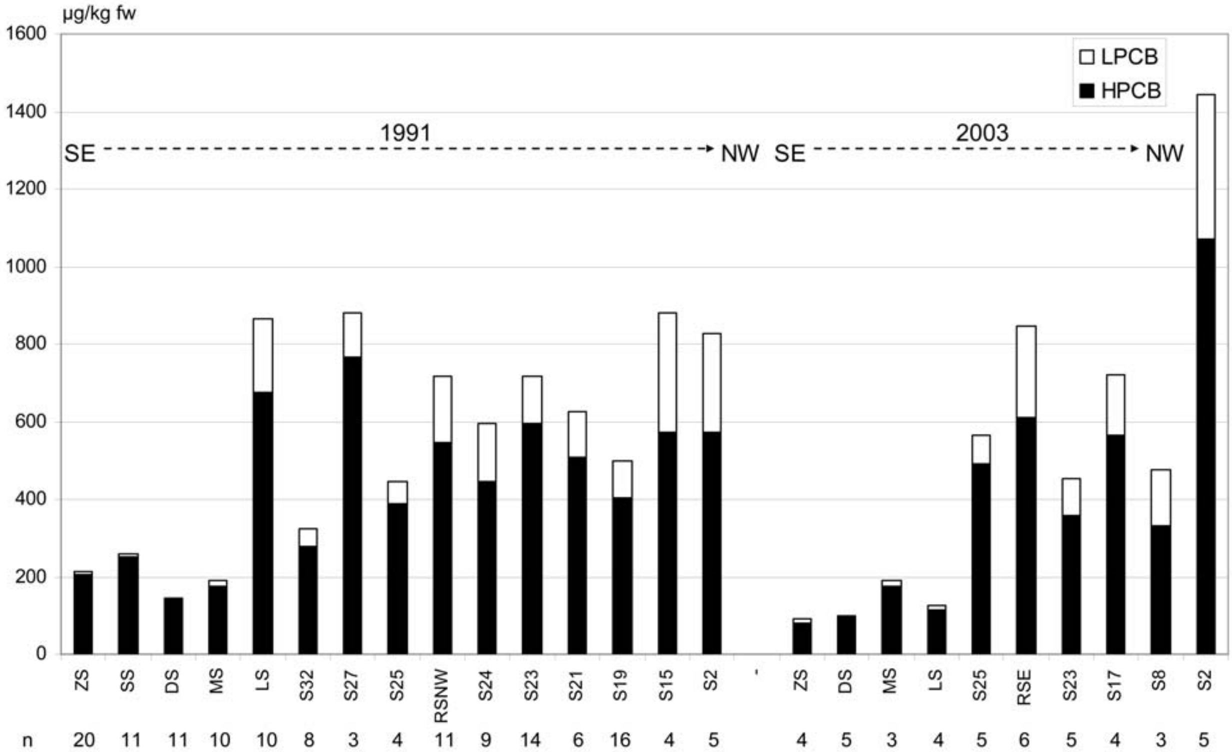
FIGURE 3 - PCB congener profiles Odre-Spree system sediment from Eisenhüttenstadt to the mouth of the river Spree in Spandau (Spatial profile 1990/91, data from single measurements from SENSTADT [26] and [41]).

As can be seen in Figure 4, the lakes in the southeast of Berlin were only slightly contaminated with PCB in 1991, and contents further declined till 2003. An exception was the lake Langer See at the entrance to the Teltowkanal, where in 1991 high PCB values were measured with high percentages of LPCB, pointing to recent immissions. The situation was similar in the river Spree at km 27, the entrance to the Britzer Zweigkanal. The high LPCB shares start from lake Rummelsburger See, where there were comprehensive building activities. The by far highest sPCB contents were measured in 2003 at the Unterspree, at power plant Kraftwerk Reuter. The LPCB shares were also considerable, so recent immissions can be assumed. The same observations were made in the sediment samples in Figure 3. It can, therefore, be concluded that PCBs in Berlin waters are of current interest, many years after their prohibition.

In the following Figures 5 and 6, time series are presented for the course of the PCB content in eels from different Berlin waters, and they are partly very different.

In Figure 5, declining curves for PCB may only be observed for lake Seddinsee and Castle Charlottenburg in 2000. First of all, at the Unterhavel, Alte Spree Spandau, the PCB markedly increase since 1998, probably due to the building activities at the sluice Charlottenburg. This tendency continues in the Oberhavel, and following a broadening of the river at the Jürgenlanke, an enhanced sedimentation is found.

In Figure 6, at first, the time series reflect declines of the sPCB content in indicator organisms, combined with a decrease of LPCB shares, at Barnackufer till 1992 and in lake Griebnitzsee till 1995. Both data mark the building activities in the Teltowkanal at the border Treptow-Rudow, the former border between Berlin East and West. From then on, the maxima and minima alternate at the two localities. In contrast to the analogous data in the rivers Stadtspree and Unterspree and continuing in the Unterhavel, from 1984 till 2003, a decline of the sPCB and the LPCB shares can be registered. The building activities at the Teltowkanal are serious, and reach the extent of the activities from lake Rummelsburger See, Tiergarten and sluice Charlottenburg.



Sampling points: ZS lake Zeuthener See, SS lake Seddinsee, DS lake Dämeritzsee, MS lake Großer Müggelsee, LS lake Langer See entrance Teltowkanal, S river Spree km: 32 Straßenbahnbrücke Köpenick, S 27 mouth Britzer Zweigkanal, S25 above lake Rummelsburger See, S24 canal thermal power station, RS lake Rummelsburger See NW shore, RSE lake Rummelsburger See end, S24 Liebesinsel, S23 below lake Rummelsburger See, S23 Abteiinsel, S21 Oberbaumbrücke, S19 Jannowitzbrücke, S17 Bodemuseum, S15 entrance Humboldthafen, S8 Schloß Charlottenburg, S2 Unterspree, power station Reuter

FIGURE 4 - PCB congener profiles in eels from the Odre-Spree system in Berlin, spatial profiles from the years 1991 and 2003 (Arithmetic means from n samples with > 10 % fat/sampling point, according to primary data from FiA Berlin [27]).

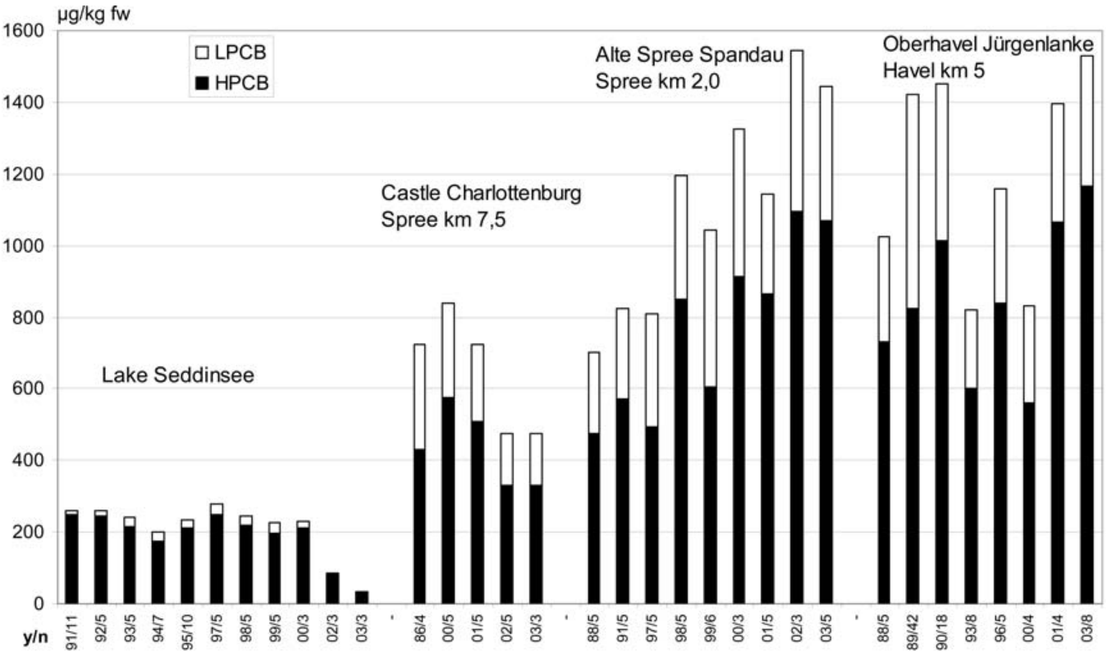


FIGURE 5 - PCB congener profiles in eels at selected sampling points in Berlin waters, time series (Arithmetic means from n samples with > 10 % fat/year, according to primary data from FiA Berlin [27]).

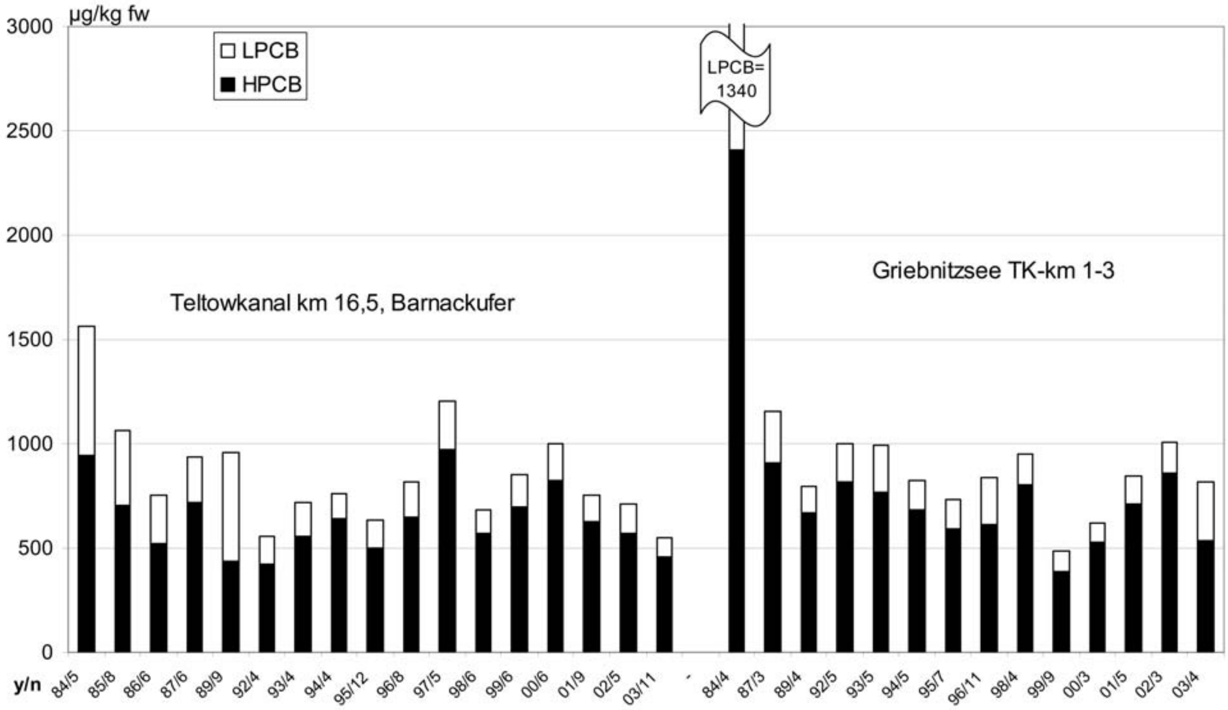


FIGURE 6 - PCB congener profiles in eels from Berlin Teltowkanal and lake Griebnitzsee, time series (Arithmetic means from n samples with > 10 % fat/year, according to primary data from FiA Berlin [27]).

The partly high sPCB contents in the sediment of Berlin water are also confirmed by [45, 51], with only low tendency to temporal declines in suspended matter found by [43, 44]. In the Mecklenburg lakes, in 1990 only very low sPCB contents could be measured in breams (*Abramis brama*), in the range of 3–5 µg/kg fw, with HPCB shares between 80 and 90 %. Only in the lake Zierker See near Neustrelitz, the corresponding values were about 13 µg sPCB/ kg and the HPCB shares at 66 % [42].

The river Elbe and some tributaries

The role of the chemical industry and the Škoda factory in Mladá Boleslav for the PCB content in the sediment of the river Elbe in the Czech Republic has already been mentioned at the beginning, in the explanations of Figure 2. The industrial density in this part of the Elbe is very high, and comparable to that of river Rhine. In Figure 7, the spatial profile of the river Elbe in 1999, the role of the industry can be seen very clearly, too. The outstanding value of 1290 sPCB/kg dm reflects the importance of the emittent Spolchemie. Also the extremely high share of LPCB of 90 % is remarkable. A similar high sPCB value in sediment from 1999 was measured in the river Rhine, km 778.0 in Duisburg-Homberg, Hafen Diergard with 1284 µg sPCB/kg with a LPCB share of 67 % [37]. The high values from Vály (VCHZ Pardubice), Lysá (Kolín) and Obříství (Spolana Neratovice) are characterised by LPCB shares of below 50 %. From Děčín downstream, a decrease of the sPCB values may be observed; the very high sPCB value is due to the activities of Spolchemie. The sPCB values in sediment of the rivers Mulde near Dessau, Schwarze Elster near Gorsdorf and Saale near Rosenburg are less remarkable.

In Figure 8, the spatial profiles of PCB in eels from the river Elbe on the area of the FRG are shown. Especially for 1999, from Prossen near the border to the Czech Republic, till Wahrenberg, a clear decline can be observed, until in the Hamburg city area, km 620, a new clear PCB peaks appears, which can also be seen in the spatial profile in 1994/95.

The two time series for the sampling points at the river Elbe in Figure 9 hardly show any decline. The course of the curves is very inhomogeneous. The maxima for 1996, which may be seen at all localities in the river Elbe till Hamburg, and which have high shares of LPCB, obviously may be due to new immissions. Similarly striking are the maxima in 2004.

In the river Mulde, the sPCB values at first increase from 1995 to 2000, but then almost continuously decline till 2004. The high contents which are characteristic for the other chloroorganics like DDT, HCH, and chlorobenzene, and which may be explained by the former production in Bitterfeld, cannot be seen here – PCBs have never been produced in Bitterfeld.

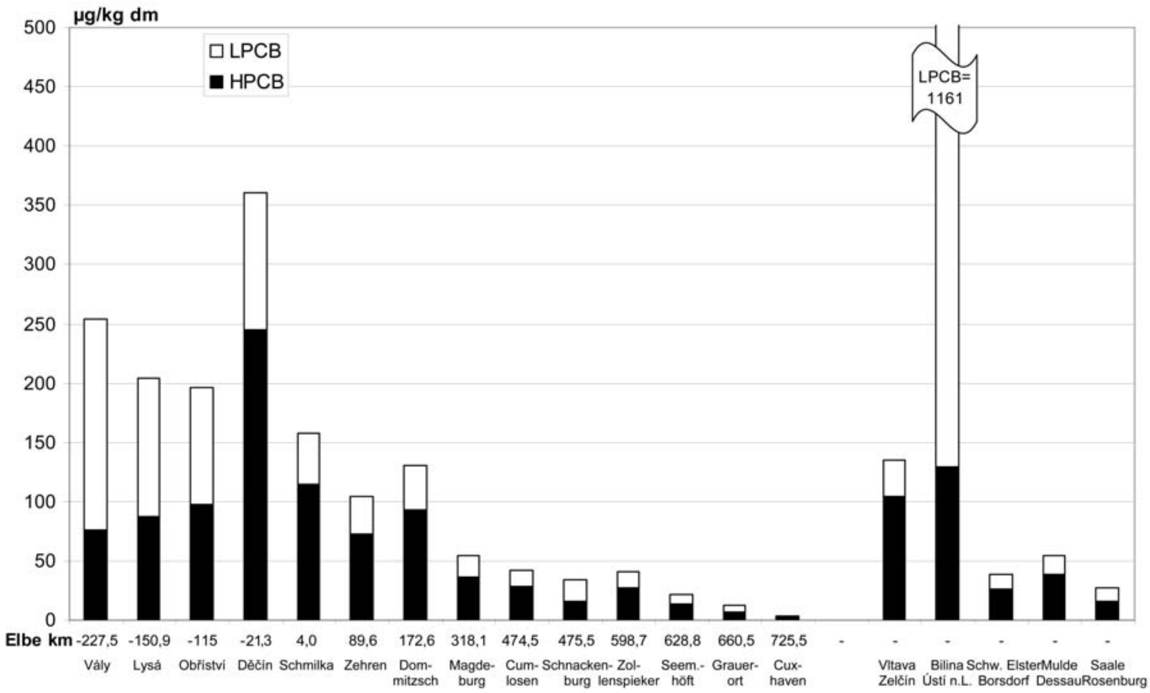


FIGURE 7 - PCB congener profiles in sediment of the river Elbe and some tributaries, spatial profile 1999 (Single annual data from IKSE [20], ARGE ELBE [21], and ČHMU [24]).

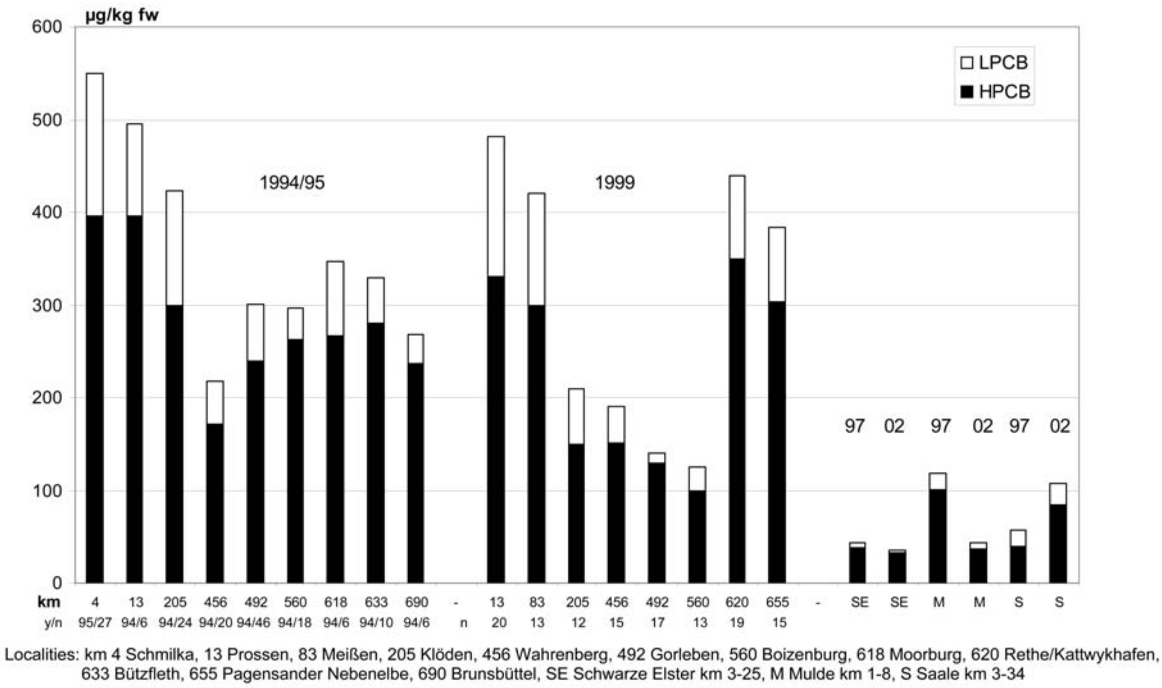


FIGURE 8 - PCB congener profiles in eels from the river Elbe, spatial profiles 1994/95, 1999 and time series from the tributaries Schwarze Elster, Mulde, and Saale (Arithmetic means of n samples with > 10 % fat/sampling point, according to primary data of ARGE ELBE [21, 22]).

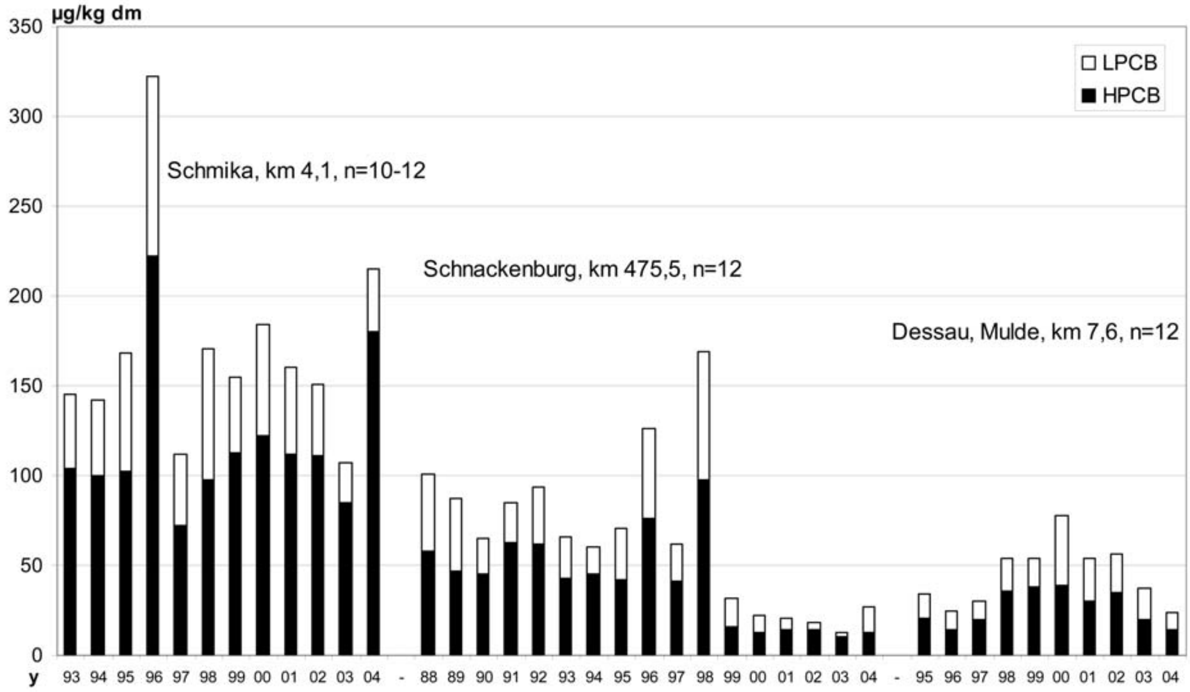


FIGURE 9 - PCB congener profiles in sediment of the rivers Elbe and Mulde, time series (Arithmetic means of n monthly samples/year, according to primary data of ARGE ELBE [21] and LAU Halle [25]).

Summarizing can be said that the very high PCB loads described by [46, 48] for the river Elbe on the area of the former FRG have decreased, as can also to be read in [49, 50]. The high PCB values in the Czech Republic, which continue on a slightly lower level at the sampling points in the FRG near the border, are due to immissions from the enterprise Spolchemie in Ústí n. L.

River Rhine and tributaries

In the Figures 10–12, spatial profiles are given for PCB in eels from the river Rhine from Konstanz till Emmerich for the years 1990/92, 1995 and 2000; the sampling points for the three Figures may be taken from Table 2. For 1990/92, the maximum values may be seen quite easily in the vicinity of the industrial sites at Rheinfelden, Grenzach, Gimbsheim (below Gernsheim), Hitdorf, Duisburg-Walsum and Emmerich (Figure 10). In 1995, from these sampling points remain only Grenzach (at a considerably lower level), Hitdorf (higher, compared with 1992) and Duisburg-Walsum (Figure 11). In 2000, there is no more increase of the PCB contents in Grenzach, the maximum value is found in Hitdorf, but on a lower level than 1995. In 1990/92, 1995, and 2000, there are remarkable peaks in Gambsheim and Koblenz with no explanation.

For most of the sampling points in Figures 10–12, a decrease of the sPCB may be registered in the periods of observation. In Figure 13, this tendency continues, sometimes even more clearly, but the period of sampling was prolonged, and, in the Hoch- and Oberrhein, fish samples were taken also in the eighties. In most cases, the time series show declining curves with increasing HPCB shares, in Grißheim this process proceeds almost continuously, whereas Koblenz is an exception, as the series has no trend.

TABLE 2 - Sampling points for fishes at river Rhine.

km 3 Konstanz, 34 Dissenhofen, 51 Rheinau, 91 Rekingen (CH), 139 Schwörstadt, 154 Rheinfelden, 160 Grenzach, 180 Istein, 210 Grißheim, 240 Sasbach, 255 Taubergießen, 256 Taubergießen Altrhein, 277 Ichenheim, 306 Diersheim, 309 Gambsheim (F), 321 Greffern, 366 Wörth, 377 Insel Rott, 387 Lingenfeld Altrhein, 394 Berghausen, 419 Rheingöntheim-Rehbachmündung, 432 Mannheim-Sandhofen, 437 Bobenheim-Roxheim, 440 Lampertheimer Altrhein – Fretter Loch, 464 Stockstadt, 469 Gimbsheim, 474 Erfelder Altrhein, 478 Schusterwörther Altrhein, 490 Bodenheim, 492 Ginsheimer Altrhein, 498 Mainz-Kastel, 512 Eltville, 525 Rüdesheim, 531 Bingerbrück, 556 St. Goar, 590 Koblenz, 608 Neuwied, 630 Linz, 642 Bad Honnef, 665 Niederkassel, 705 Hitdorf, 755 Düsseldorf-Kaiserswerth, 792 Duisburg-Walsum, 848 Emmerich

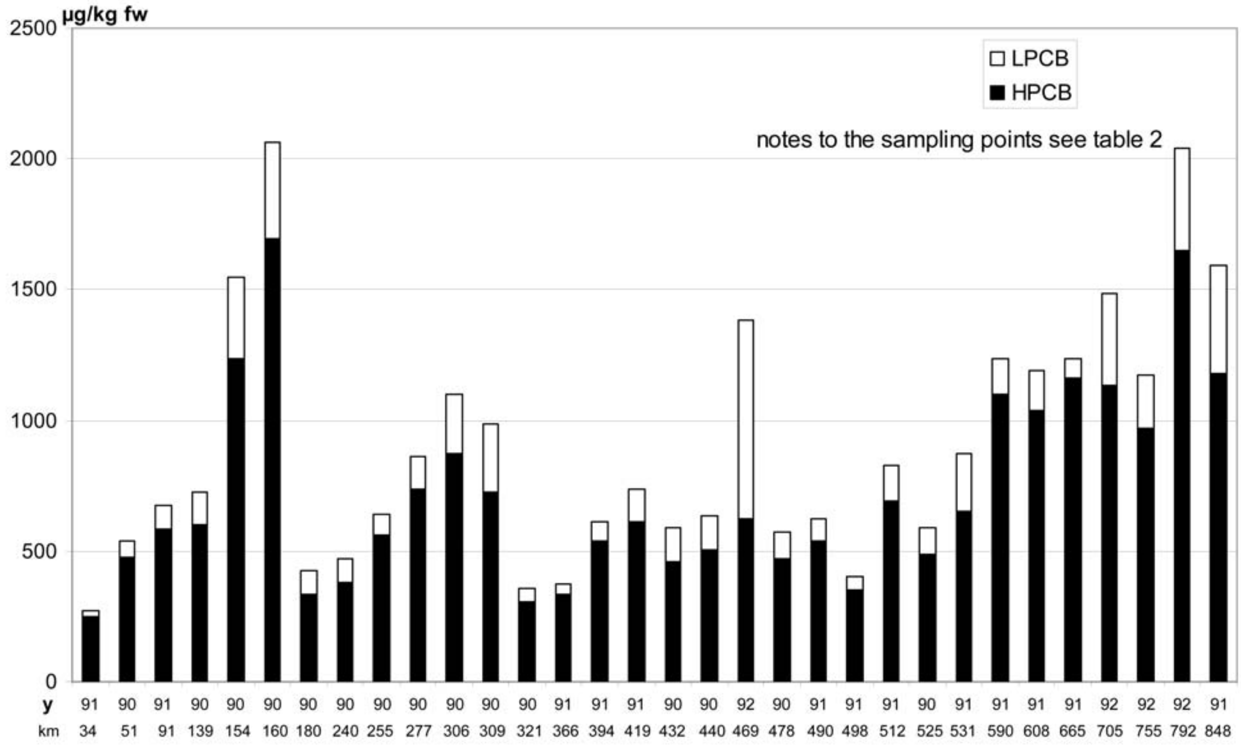


FIGURE 10 - PCB congener profiles in eels from the river Rhine, spatial profile 1990/92 taken from [52] (Arithmetic means of 3-5 samples with > 10 % fat/sampling point/year).

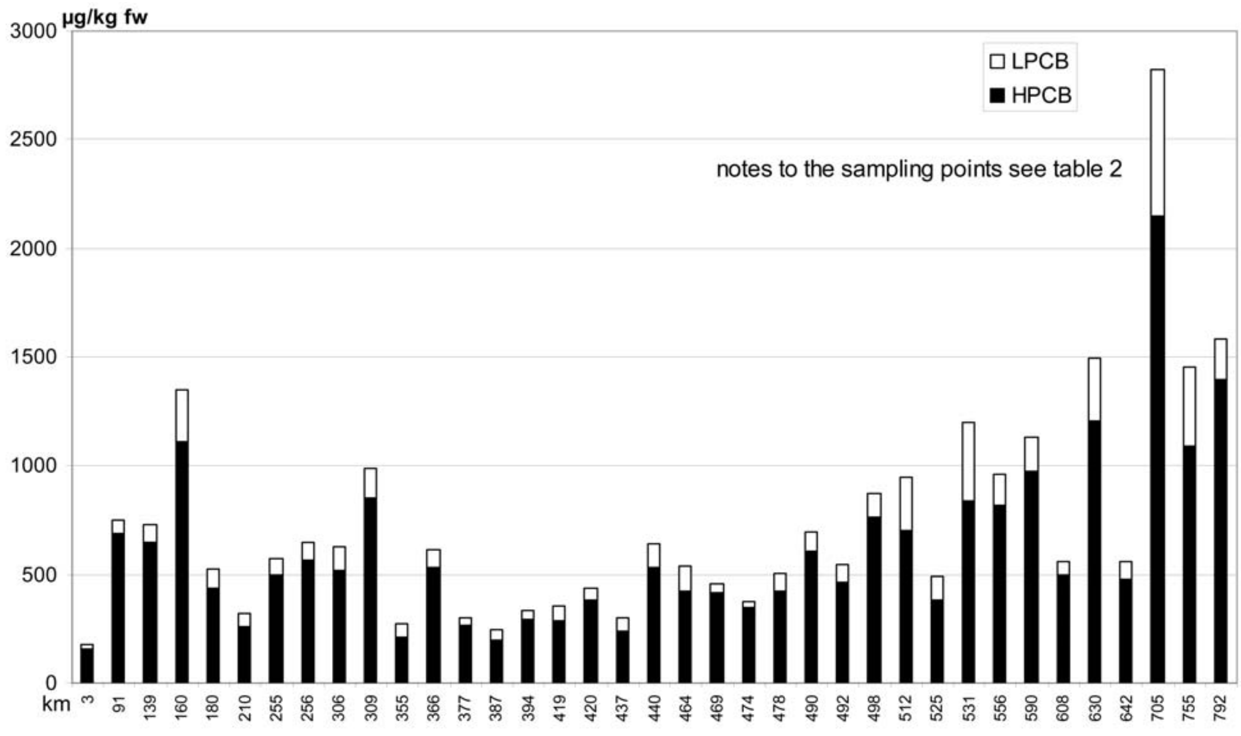


FIGURE 11 - PCB congener profiles in eels from the river Rhine, spatial profile 1995 taken from [52] (Arithmetic means of 3-5 samples with > 10 % fat/sampling point/year).

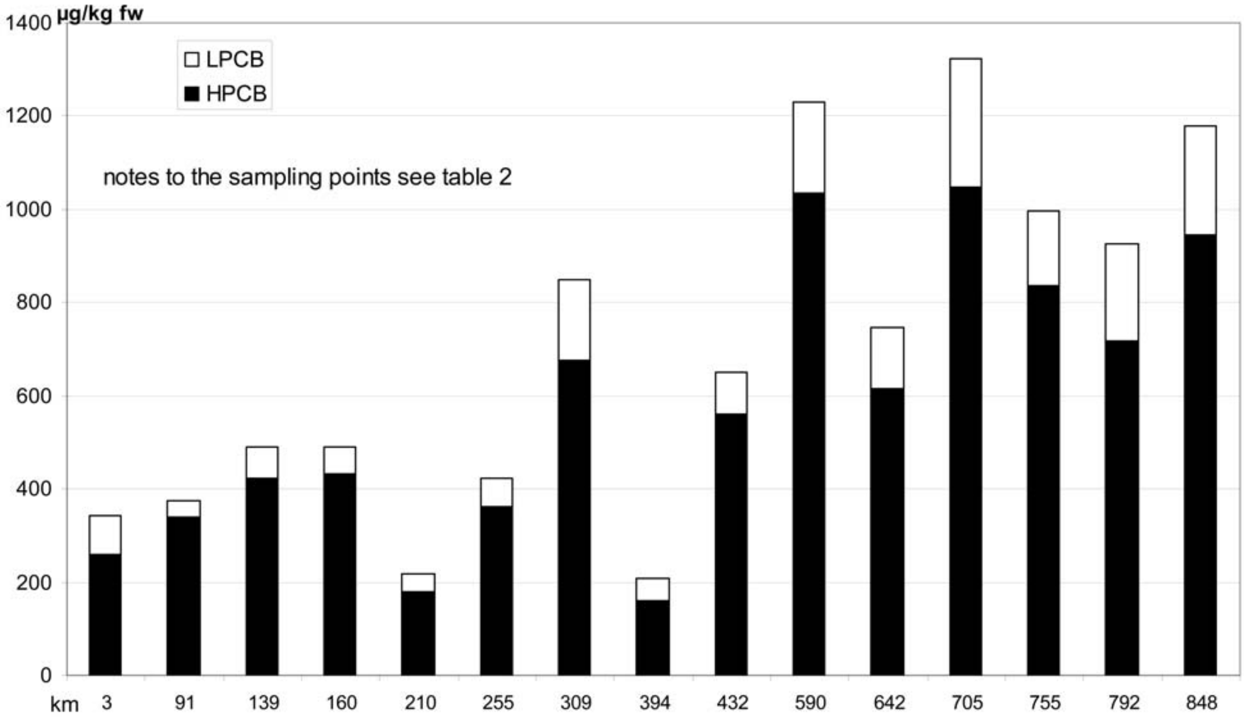


FIGURE 12 - PCB congener profiles in eels from river Rhine, spatial profile 2000 taken from [52] (Arithmetic means of 10-15 samples with > 10 % fat/sampling point).

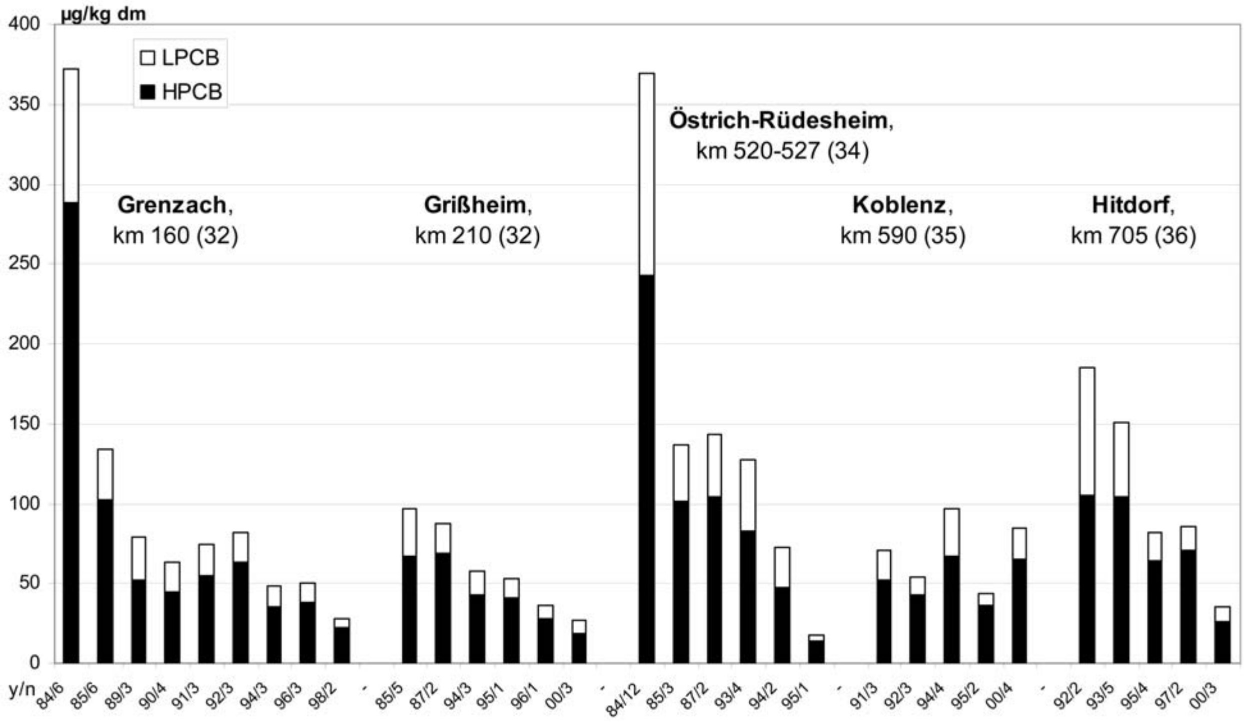


FIGURE 13 - PCB congener profiles in roaches (*Rutilus rutilus*) from river Rhine, time series (Arithmetic means of n specimen/sampling point/year, according to primary data from CLUA/ CVUA Freiburg [32], HLVA Darmstadt [34], CLUA Speyer [35] and LÖBF/LAfAO NRW [36]).

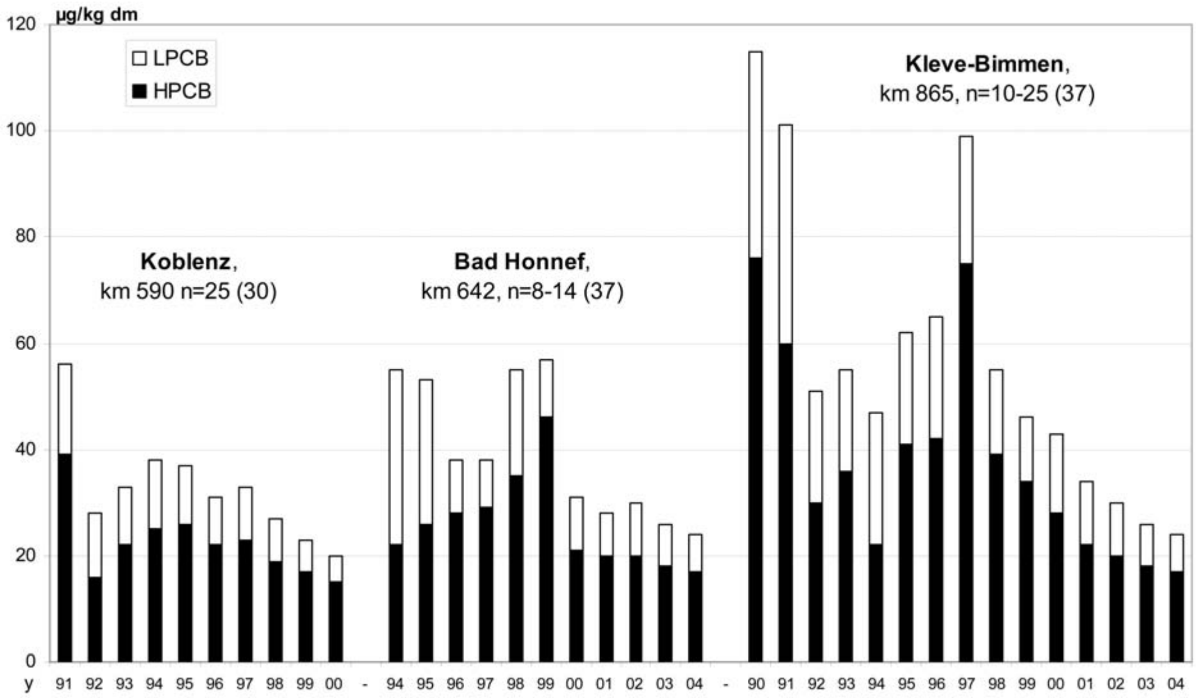


FIGURE 14 - PCB congener profiles in suspended matter from river Rhine, time series (Arithmetic means of n samples/sampling point/year, according to primary data from IKSR [30] and LAU NRW [37]).

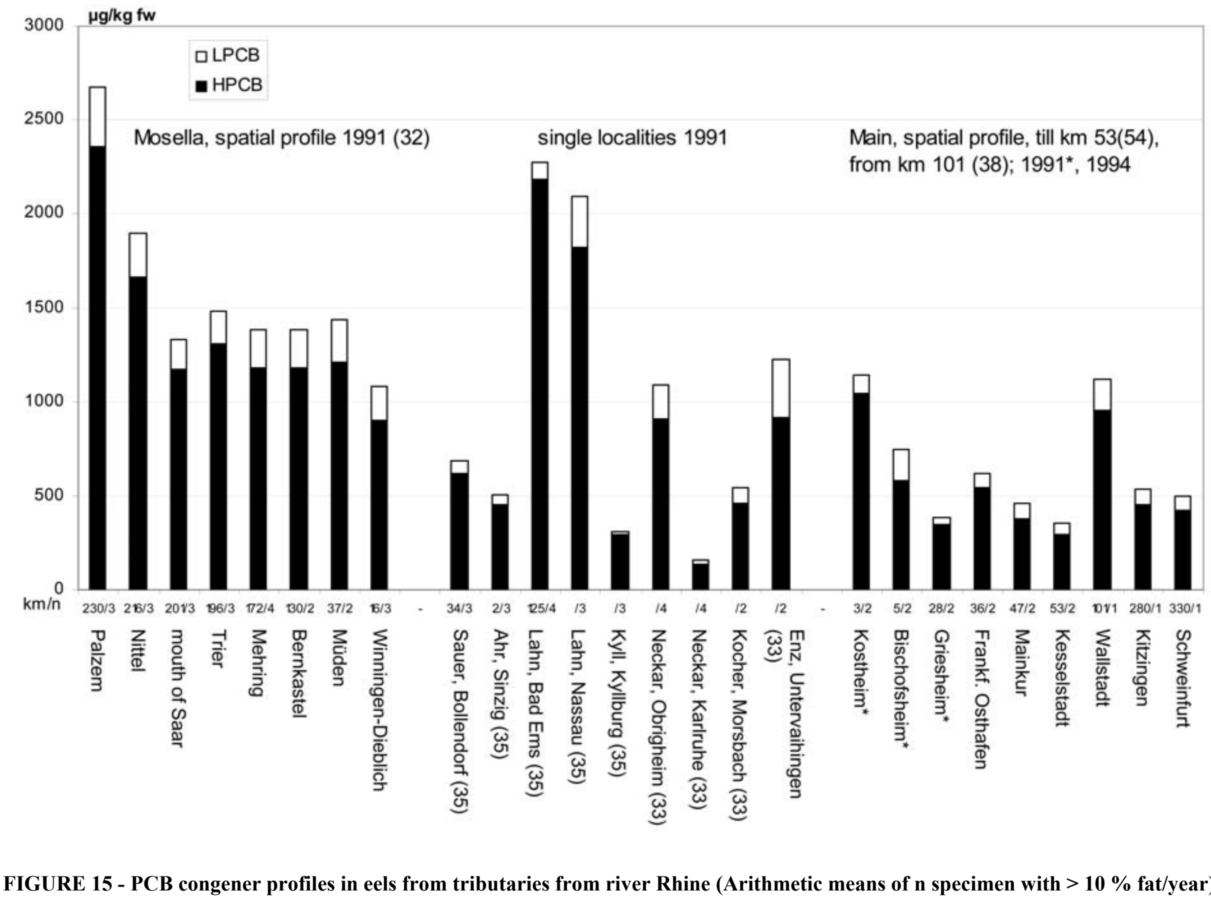


FIGURE 15 - PCB congener profiles in eels from tributaries from river Rhine (Arithmetic means of n specimen with > 10 % fat/year).

Looking at the whole time of observation, for all three localities in Figure 14, decreases of the sPCB contents can be registered; the values for Kleve-Bimmen being higher. The decrease in Koblenz proceeds almost continuously, the shares of HPCB continuously increase. The average HPCB shares amount to 65 % in Kleve Bimmen (90–04), 67 % in Bad Honnef (94–04), and 71 % in Koblenz (91–00).

In Figure 15, spatial profiles for the PCB contents in eels from the rivers Moselle (1991) and Main from Bavaria (1994) till Hesse (1991), as well as single sampling points in the rivers Sauer, Ahr, Lahn, Kyll, Neckar, Kocher, and Enz, are presented. On the river Moselle, downstream from Palzem, the first sampling point after the french border, till Trier there is a clear decrease of the sPCB contents, which may be due to imports. From the tributaries, extremely high sPCB levels are striking in the river Lahn. The lowest values for eels were measured in the Neckar near Karlsruhe.

In Figure 16, time series are presented for PCBs in particulate matter from four rivers in Northrhine-Westfalia, which are very different concerning the height of their sPCB contents and the congener profiles, and, therefore, point to different emittents. The course of the time series all show declining curves, especially striking for the river Lippe near Wesel. At this river, there are also the lowest HPCB shares, being 48 %, on average of the 7 years. The river Ruhr near Duisburg has some particulate matter with higher PCB and HPCB shares of 70 %. The lower contaminated particulate matter from the rivers Sieg near Bonn, and Erft near Neuss, have HPCB shares all above 80 %.

In Figure 17, a spatial profile of the PCB content in sediment from the river Lippe in NRW is shown, as well as time series for two localities from this river, at the bank, where the chemical enterprises Du Pont des Nemours, Hüls AG Marl and BASF power station Marl GmbH (Sickingsmühlenbach) were or have been active. The spatial profile for 2000 shows clear maxima at km 41.2 Wulthener bridge below Hüls-West and km 46.9 Lipprahmsdorfer bridge. Furthermore, the sPCB values are accompanied by the highest LPCB shares. From the time series can be seen that the same is true for the Lipprahmsdorfer bridge for the years 89–03. HPCB shares above 50 % appear as late as in Munthe, km 106.8. From km 121.9 at the weir in Hamm, the HPCB were predominantly, and LPCB are present only in traces.

In Figure 18, the PCB contents in suspended matter of different waters from Hesse are presented, covering also some municipal and industrial sewage plants. The highest sPCB value comes from the Schwarzbach-Ried near Trebur-Astheim, the continuation of Darmbach-Landgraben. These values approximately correspond to those from the central sewage plant in Darmstadt, and the outflow from Merck, Darmstadt. Also the sPCB contents from one of the two main sewage plants from Frankfurt/Main in Sindlingen are relatively high. Most striking are the analogous values from the sewage plant outflow of the enterprise Clariant, Werk Griesheim, not only because of the sPCB values, but mostly because of the extremely high shares of LPCB. The same phenomenon – high sPCB values and ex-

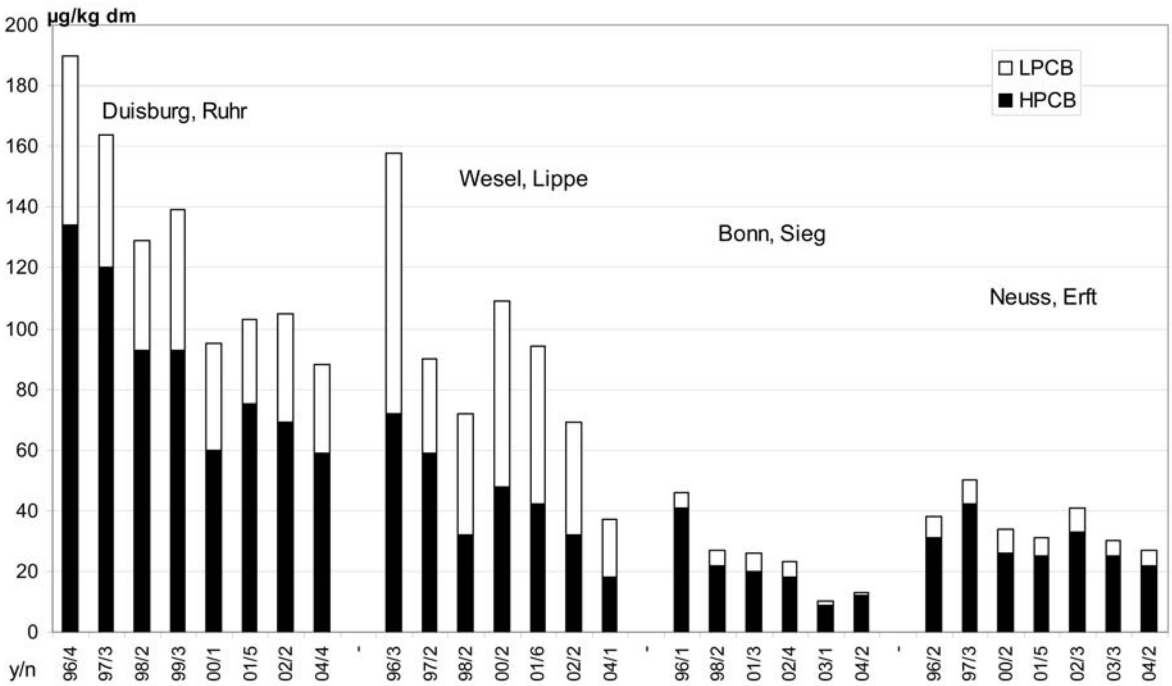


FIGURE 16 - PCB congener profiles in particulate matter from rivers in NRW, time series (Arithmetic means from n monthly samples/year from LUA NRW [37]).

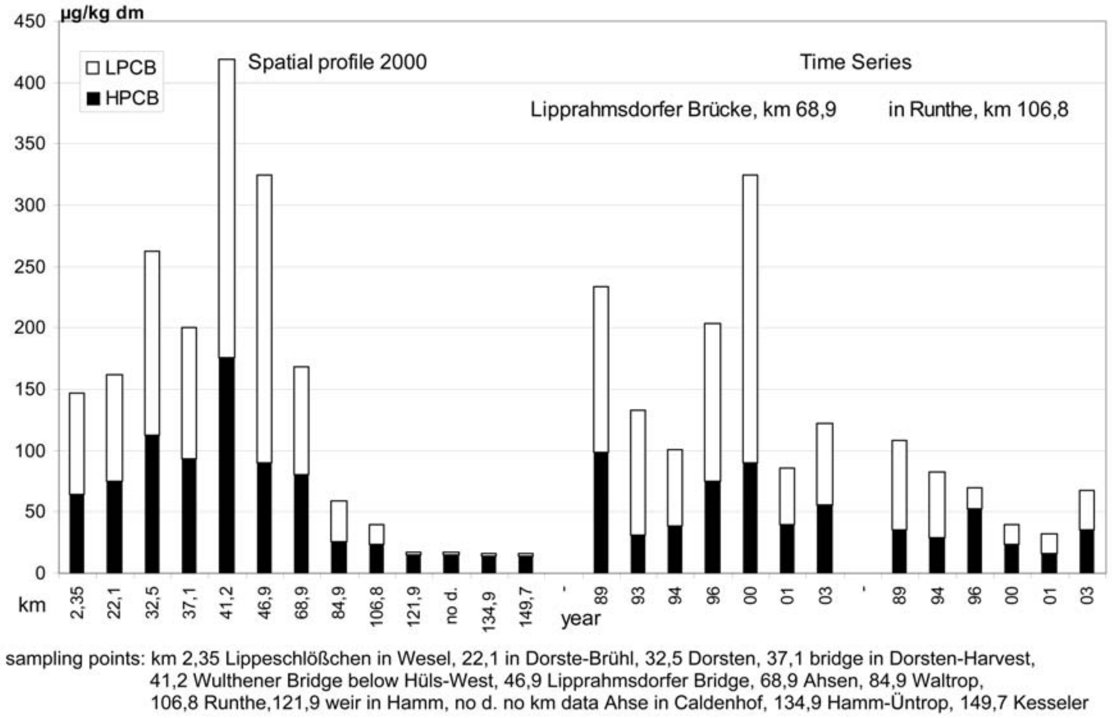


FIGURE 17 - PCB congener profiles in sediment of river Lippe (Annual single values from LAU NRW [37]).

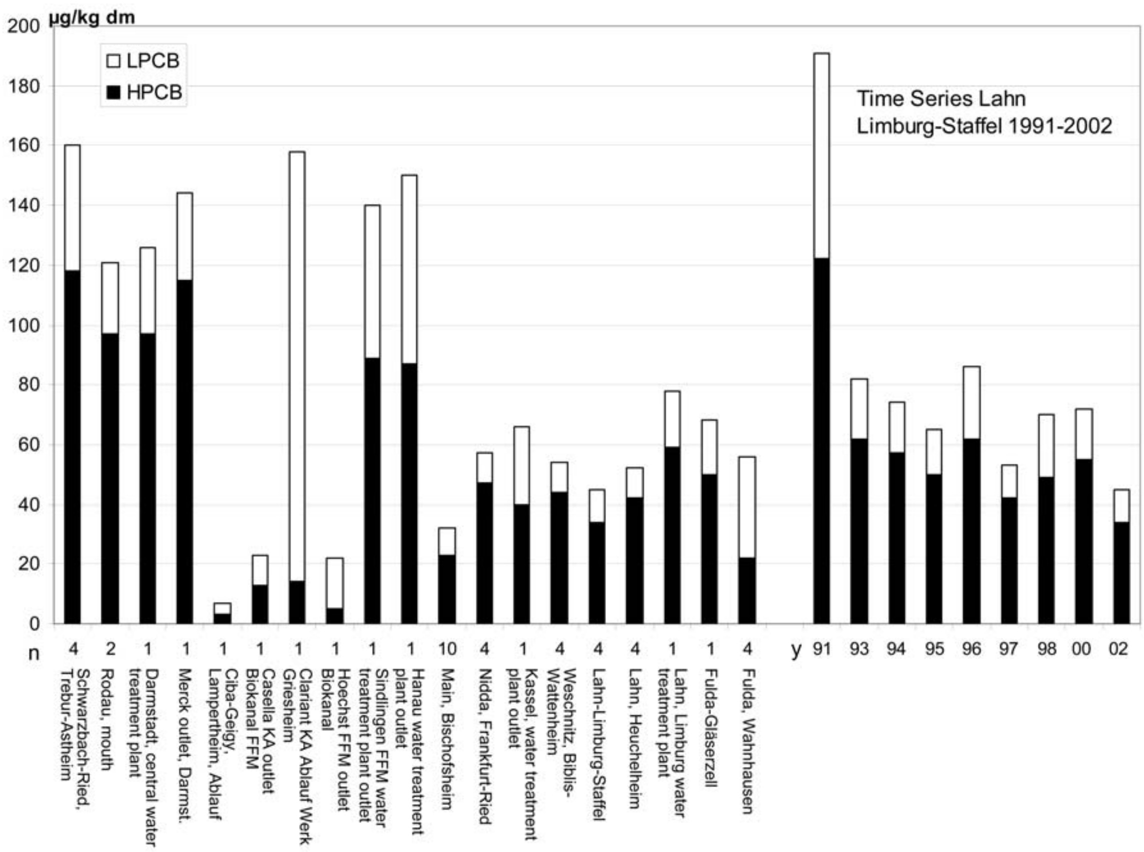


FIGURE 18 - PCB congener profiles in particulate matter in surface waters in Hesse in 2002 and time series Lahn, Limburg-Staffel 1991-2002 (Single samples or arithmetic means of n samples /year, according to annual data from HLUG [34]).

tremely low HPCB shares – were also observed in the sludge from the sewage plant outflow of the Clariant enterprise, Griesheim [34]. The time series, also presented in Figure 18, from the locality Lahn, Limburg-Staffel, reflects a declining curve with a rare continuity, not only in the decrease of the sPCB values from 191 µg/kg dm in 1991 to 45 µg/kg dm in 2002, but also the HPCB shares in the same period increase from 64 to 78 %.

Altogether, concerning the PCB data from the river Rhine and tributaries, may be said that the emitters could mostly be identified using the monitoring method used here, and, mostly, are chemical enterprises near Grenzach, Lampertheim, Biebesheim, Ingelheim and Hitdorf, the area of Frankfurt/M., Darmstadt, and Hüls (Lippe).

Regional comparisons of the PCB loads

In Table 3, some examples for sPCB contents in eels from different waters are given for the years 1984–86, 1992–96, 1996–98 and 2000–2003, with the aim of highlighting peculiarities. The first value, which is, at the same time, the highest sPCB value, originates from the Berlin Schlachtensee in 1985, a district of Berlin remote from industry. But the special characteristic of the lake is the position near the busy urban motorway Avus, and vehicles were the emitters. Among the high sPCB are also often the sampling points Hitdorf, Grenzach, Frankfurt/M., Stockstadt, and Lampertheim, i. e. sites near chemical industries. From 1995 on, again Berlin sampling points are among the highest – now without the Avus, and the old cars were sorted out. It is the Unterspree with high sPCB values and HPCB shares < 75 %, probably due to the building activities in the Tiergarten and at the sluice Charlottenburg. Furthermore, the Kleiner and Großer Wannsee with high sPCB values and high HPCB shares, all > 75 %, must be mentioned, but the origin could not have been cleared up so far.

The low sPCB data all come from Bavaria (Altmühl, Riegsee, Inn), Brandenburg (Gülper See, Unterhavel, Havel mouth, Odre near Hohenwutzen), the lakes in the east of Berlin (Dämeritzsee, Zeuthener See), or other low-contaminated waters like the Seerhein (Konstanz), Dümmer See or the river Saale. Altogether, the examples given here should demonstrate, how the elements of monitoring – the height of sPCB connected with the percentage of HPCB – can be used for the characterisation of the emitters.

TABLE 3 - Range of PCB contents in eels with > 10 % fat from waters in the FRG from 1984–1986, 1992–1996, 1996–1998, and 2000–2003 (Data from [21-23, 27-29, 31-36, 38-40, 46]).

y	n	Sampling point	sLPCB	sHPCB	sPCB	%HPCB	source
		1984–1986					
85	6	Berlin, Schlachtensee	510	3160	**3670**	*86*	27
86	5	Frankfurt/M. Osthafen, Main km 33–35	410	1535	**1865**	*78*	34
85	2	Biebesheimer Rhein, Stockstadt, Rh km 464	330	1235	**1565**	*79*	34
85	3	Lampertheimer Altrhein, Rh km 440	255	1375	**1330**	*81*	34
84	2	Sulz, Neckar	130	1120	**1250**	*80*	33
85	8	Berlin, Teltowkanal, Barnackufer, km 16,5	350	710	**1060**	*67*	27
85	3	Möhrendorf, Pegnitz	240	595	**835**	*71*	38
84	4	Giersheim, Main km 28	140	480	**640**	*75*	34
84	4	Erfelder Altrhein, Rh km 474	110	525	**635**	*83*	34
86	4	Rothenburg o. d. Tauber, Tauber	75	545	**620**	*88*	38
86	5	Weisweil, Rh km 248	75	390	**465**	*84*	32
86	4	Thann, Altmühl	30	260	**290**	*89*	40
86	2	Riegsee	40	145	**185**	*78*	39
86	19	Dümmer See	5	60	**65**	*90*	46
		1992–1994					
94	4	Hitdorf, Rh km 705	755	2270	**3025**	*75*	36
92	2	Grenzach, Rh km 160	135	2540	**2675**	*95*	32
92	3	Cramberg, Lahn	450	2210	**2660**	*98*	35
92	3	Linz, Rh km 630	410	1735	**2145**	*81*	35
92	5	Duisburg-Walsum, Rh km 772	325	1705	**2030**	*84*	36
93	3	Trier, Mosel km 196	390	1560	**1950**	*80*	35
92	2	Frankfurt/M. Osthafen, Main km 33–35	215	1230	**1445**	*85*	34
92	5	Berlin, Gr. Wannsee	260	925	**1185**	*78*	27
92	6	Besigheim, Enz	110	800	**910**	*88*	33
94	2	Biebesheimer Rhein, Stockstadt, Rh km 464	85	705	**790**	*89*	34
94	2	Kirchheim, Neckar	90	600	**690**	*87*	33
94	3	Bollendorf, Sauer	85	520	**605**	*86*	35
94	6	Prossen, Elbe km 13	100	395	**495**	*80*	21
94	19	Berlin, Gr. Müggelsee	45	385	**430**	*90*	21
94	4	Rosenbach, Vils	10	395	**405**	*98*	38
93	4	Fürstenwalde, Oder-Spree-Kanal	50	325	**375**	*87*	41
94	4	Donau km 2452–2453	35	325	**360**	*90*	39
92	3	Istein, Rh km 180	60	275	**335**	*82*	32
94	4	Wasserburg, Inn	45	215	**260**	*83*	39
94	20	Wahrenberg, Elbe km 458	45	170	**215**	*79*	21
94	3	Ketzin, Havel	20	95	**115**	*76*	29
94	4	Havelberg, Gülper See	20	90	**110**	*82*	29

TABLE 3 – continued.

y	n	Sampling point	sLPCB	sHPCB	sPCB	%HPCB	source
		1995–1998					
95	3	Hitdorf, Rh km 705	680	2145	**2825**	*76*	36
98	3	Berlin, Unterspree km 6, Schleuse Charlottenburg	495	1140	**1625**	*69*	27
98	3	Lahnstein, Lahn	230	1365	**1595**	*86*	35
95	2	Linz, Rh km 630	285	1210	**1495**	*81*	35
95	4	Grenzach, Rh km 160	245	1110	**1355**	*83*	32
98	5	Berlin, Unterspree, km 2, Kraftwerk Reuter	345	850	**1195**	*71*	27
95	4	Gambsheim, Rh km 309	140	850	**990**	*86*	32
95	5	Mainz-Kastel, Rh km 498	105	765	**870**	*88*	35
95	8	Lampertheimer Altrhein, Rh km 440	110	535	**645**	*83*	34
97	2	Main bei Lohr	5	600	**605**	*99*	38
96	3	Baunach, Unterfranken	145	360	**505**	*71*	38
98	2	Fränkische Saale	30	240	**270**	*83*	38
98	11	Schmilka, Elbe, km 4	65	200	**265**	*75*	21
98	30	Gorleben, Elbe, km 492	25	205	**230**	*89*	21
96	5	Schwedt, Oder, km595	30	175	**205**	*85*	28
97	5	Berlin, Gr. Müggelsee	10	150	**160**	*93*	27
96	3	Konstanz, Seerhein, km 3	20	125	**145**	*86*	32
97	5	Mulde, km 1–8	20	100	**120**	*85*	22
96	3	Hohenwutzen, Oder km 634	15	85	**100**	*83*	28
97	14	Saale, km 3–34	20	40	**60**	*60*	22
98	2	Havelmündung	5	15	**20**	*75*	23
		2000–2003					
03	4	Berlin, Kleiner Wannsee/Pohlesee	235	1285	**1520**	*84*	27
00	5	Berlin, Großer Wannsee	330	1150	**1480**	*78*	27
03	5	Berlin, Unterspree, km 2,0, Kraftwerk Reuter	375	1070	**1445**	*74*	27
00	15	Hitdorf, Rh km 705	280	1045	**1325**	*78*	33
00	14	Koblenz, Rh km 590	195	1005	**1230**	*84*	33
00	15	Emmerich, Rh km 848	235	945	**1180**	*80*	33
00	15	Duisburg-Walsum, Rh km 792	205	720	**925**	*78*	33
00	5	Berlin, Stadtspree, km 7,5, Schloß Charlottenburg	265	575	**840**	*67*	27
00	2	Main zwischen Eibelstadt und Winterhausen	135	715	**850**	*85*	38
01	6	Berlin, Rummselburger See	235	610	**845**	*72*	27
00	14	Gambsheim, Rh km 309	175	650	**825**	*79*	31
03	4	Berlin, Stadtspree, km 16,5 Bodemuseum	155	565	**720**	*78*	27
00	12	Mannheim-Sandhofen, Rh km 309	90	560	**650**	*86*	31
00	13	Grenzach, Rh km 160	55	435	**490**	*89*	31
01	3	Main bei Lohr	80	370	**450**	*82*	38
01	3	Main bei Haßfurth	45	345	**390**	*88*	38
00	14	Konstanz, Seerhein, Rh km 3	15	145	**160**	*92*	31
03	5	Berlin, Dämeritzsee	5	95	**100**	*95*	27
03	4	Berlin, Zeuthener See	10	80	**90**	*89*	27

ABBREVIATIONS

BCF_L	lipid-normalized bioaccumulation factor
EH	Eisenhüttenstadt
HPCB	Σ cong. 138, 153, 180
KA	sewage plant
K_{ow}	octanol/water partition coefficient
KWO	Kabelwerk Oberspreee (cable factory)
LPCB	Σ congeners 28, 52, and 101
NRW	Northrhine-Westfalia
sPCB	sum of PCB congeners 28, 52, 101, 138, 153, and 180
$t_{1/2}$	half-life
TK	Teltowkanal (canal in Berlin)
WS	water solubility

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