Trends of persistent organic pollutants in suspended matter of the River Rhine

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Abstract

Recently amended EU water policies call for an adequate monitoring of the chemical status of sediments and suspended matter (SM) in rivers. In this study we focus on long-term time series of particle-bound hexachlorobenzene (HCB) and selected polychlorinated biphenyls (PCB-138 and PCB-153) that were monitored bi-weekly to monthly at 8 stations in the River Rhine catchment. Our aims are (1) to detect trends in the concentration series HCB, PCB-138 and PCB-153, (2) to estimate the uncertainty of loads caused by SM collection techniques and load calculation procedures, and (3) to detect trends in the subsequently calculated annual load series.

HCB concentration in SM for the period 1995 to 2008 significantly ($p < 0.01$) decreased at 6 out of 8 monitoring stations. Decreasing PCB-138 and PCB-153 concentrations are significant at 6 out of 8, and 7 out of 8 monitoring stations, respectively.

A two-way ANOVA that tested the effect of two collection techniques and four load calculation procedure on annual loads indicates homogeneity of the methods at 4 out of 5 monitoring stations. Only, at Weil the loads of HCB, PCB-138 and PCB-153 are significantly effected by the collection technique.

The trend analysis of an extended series (1985 to 2007) of annual HCB loads at Koblenz showed a significant decrease from about 110 kg year^{-1} to ca. 15 to 23 kg year^{-1}, however, in the shorter period (1995 to 2007) only at 2 out of 8 monitoring stations decreasing trends of annual contaminant load could be detected.

We conclude that any of the tested load calculation procedures can be applied, as loads do no differ systematically. Although a high uncertainty in load estimation exists (e.g. maximum percentage error of $E = [18.1, 122.5]\%$ for HCB), the monitoring program at the Rhine is adequate for analyzing the long term chemical status of SM.

Keywords particle-bound load, suspended matter quality, environmental monitoring, organochlorine compounds, polychlorinated biphenyls

1 Introduction

Recently implemented European water policies call on the EU member states to establish effective monitoring programs for the detection of the long term status of "priority substances" in sediments of water bodies (EU Water Framework Directive, 2000/60/EC). Furthermore, member states should develop harmonized methodologies to measure the loss of priority substances that are accumulated in river sediments.

The focus in this study is on the long term trend (1995-2007) of suspended matter quality of the River Rhine with respect to both concentration and load of particle-bound micro-pollutants. Three organic micro-pollutants were selected in this study, i.e. hexachlorobenzene (HCB), which is classified as a "hazardous priority substance" and two congeners of polychlorinated biphenyls (PCB-138 and PCB-153), that are relevant pollutants of sediments in the River Rhine (ICPR, 2009). HCB and PCBs are known to be adsorptive to sediments, bio-accumulative, hardly biodegradable and thus persistent in the environment (Table 1).

The key questions of our study are:

1. Are there detectable trends in monthly concentrations of particle-bound HCB and PCB concentrations in the Rhine?
2. How do sampling techniques of suspended matter and various load estimation procedures effect the results of calculated annual micro-pollutant loads (uncertainty assessment)?
3. If emissions have stopped, are there significant trends in particle-bound micro-pollutant loads?

In this study, we apply for the first time a long-term trend analysis of HCB, PCB-138, and PCB-153 concentrations in suspended matter at the river Rhine, which is of transboundary interest. We analyze the effects on estimated annual particle-bound loads (L) of HCB, PCB-138 and PCB-153, when two different data sets of suspended sediment concentrations (S) in combination of four different calculation methods are used for load estimation. The major foci are on determining systematic errors and quantifying the random error that is introduced due to the aforementioned data sets and calculation methods, which has not been done for particle-bound loads, hitherto.

The calculated annual loads that include uncertainty bounds can further be used as a reference data set for e.g. the comparison of the output of hydrodynamic reactive transport models. With such models, process based scenario assessment (i.e. climate change driven long-term trends of particle-bound contaminant transport; dredging activities; efficiency of decontamination actions) can be conducted, provided that model simulations are within the uncertainty bounds of historic observations.

1.1 Uncertainty in suspended matter quality data

Monitoring of suspended matter quality and the consequent estimation of particle-bound micro-pollutant loads is subjected to several sources of uncertainty (Rode and Suhr, 2007) that comprise systematic and random structures. A water-quality monitoring station should be located at the longitudinal axis of a river in order to obtain a representative response of water quality and suspended matter quality caused by the entire catchment. However, local effects such as point source inputs, dead zones or incomplete mixing of large rivers downstream of tributaries may lead to a systematic over- or under-sampling of suspended matter and its associated micro-pollutants. As both occurs in large rivers, a cross sectional and vertical profile of suspended sediments (Horowitz *et al.*, 1990), the number of sampling points and the sampling depth at a specific sampling location may influence systematically the results of investigations on the quality of suspended matter.

The techniques for the collection of suspended matter for the subsequent chemical analysis may influence both the outcome of analytical results as well as calculated micro-pollutant loads. Two techniques for the separation of the sediment and water phases, i.e. centrifugation and sedimentation, are common in existing monitoring programs (ISO 5667-17, 2008; DVWK, 1999). Centrifuges are used for quasi-instantaneous or short-integral sampling over a period of up to 12 hours. Hence, the chemical status of suspended matter can be monitored for a specific date and repeated measurements with centrifuges can be used to track the chemograph of micro-pollutants during short periods (e.g. flood events). However, as this sampling technique is expensive, instantaneous samples are taken in existing monitoring programs only with a low temporal frequency (i.e. bi-weekly to monthly). The temporal frequency of sampling may lead to both random and systematic errors (i.e. underestimation) of suspended matter quality parameters, as several studies show this effect for solute concentrations and suspended matter (e.g. Littlewood *et al.*, 1998; LAWA, 2003; Webb *et al.*, 1997; Johnes, 2007; Moatar and Meybeck, 2005). As particle bound load is associated with erosive flood events - between 5% and 11% of the annual load of HCB, and 16% to 36% of the annual load of PCB-153 can be discharged during those events at Koblenz (Breitung, 1999) - a time proportional sampling strategy with instantaneous samplers (bi-weekly or monthly) may undersample the chemical status and thus particle-bound load. Passive collectors such as sedimentation tanks or floating collectors (Reinemann and Schemmer, 1994) are able to continuously collect suspended matter, but composite or mixed samples are inherently produced. Hence, it is practically not possible to identify single events in the analytical outcome. Furthermore, systematic errors occur, when mixed samples are used for load estimation. In cases of positively correlated discharge (Q) and concentration (c) of a substance, loads are systematically underestimated. The reverse is true for inversely correlated Q-c systems (BfG, 1997; LAWA, 2003). However, due to the hysteresis effect - i.e. c differs in the rising and falling limb of a flood wave, although Q is the same, relations between Q and c can be complex. Passive samplers are usually installed to collect suspended matter for periods of weeks or months.

Apart from the temporal frequency of sampling techniques, the methods differ in terms of separation efficiency and selectivity of sampled particle sizes. A comparison of instantaneously taken suspended matter samples with a centrifuge, a floating collector and filters at the river Elbe showed significant differences in median particle size as well as concentrations of particle-bound PCB-15 and HCB. Highest values for median particle size as well as adsorbed organic micro-pollutants were found when a floating collector was used for sampling (BfG, 2005).

Furthermore, the sample technique may contaminate or alter the chemical status of collected suspended matter. Horowitz *et al.* (1989) investigated the impact of several centrifuges on trace metal concentration in suspended matter. Higher trace metal concentrations due to attrition could be attributed to some of the employed centrifuges. Furthermore, concentrations of nutrients and organic compounds that are easily biodegradable may decrease when suspended matter is collected with passive samplers. This is due to the relatively long storage time of samples within the collectors of several days to weeks. Additional sources of uncertainty are conservation, transport and analytical errors of suspended matter samples.

1.2 Emission history and recent suspended-solids quality trends

The worldwide production of PCB dates back to the early 1930s, and peak production was between the 1960s and 1970s (Sanders *et al.*, 1994; Breivik *et al.*, 2002). PCBs were industrially used as plasticizers, flame retardant and dielectric fluids in transformers, capacitors and coolants. The largest producer of PCB in Western Germany was the Bayer AG with an estimated total production of ca. 159,062 t (Breivik *et al.*, 2002). The production of PCB in Western Germany declined in the 1970s and ended in 1983. The production, trade and use of PCB was finally banned according to a national directive (*PCB-Verbotsverordnung*) in 1989. However, as PCBs were widely used, they are ubiquitous micro-pollutants in the Rhine basin.

The major worldwide use of HCB has been as a fungicide applied to seeds, particularly cereal grains. It also has been used as a wood preservative, in pyrotechnic compositions and in the manufacture of dyes, polyvinyl chloride and synthetic rubber (Barber *et al.*, 2005). Within the Rhine catchment, one major historic point source of HCB could be identified at Rheinfelden in the area of the High Rhine. At this site, HCB first originated as a by-product from the production of pentachlorophenol (PCP) from the 1970s to 1980s in a chemical plant. The HCB-contaminated wastewater of this plant was discharged into the Rhine. The heavy pollution of the Rhine in the 1970s first became apparent when elevated HCB concentrations of up to 150 mg HCB kg^{-1} fat in eels (*Anguilla anguilla* L.) were found in 1975. The concentrations of HCB in Rhine water at Basel, which is located ca. 15 km downstream of Rheinfelden, during the mid-1970s were in the order of 40 to 100 ng L^{-1} according to a monitoring program that was conducted by the water supplier of the city of Basel. The average daily emission of HCB in 1981 was estimated by environmental agencies in the order of 10 kg day^{-1}. The PCP production stopped in 1985, but HCB still was formed as a by-product during the manufacturing of chlorosilanes at Rheinfelden. Until 1986, the HCB contaminated residues from the chlorosilanes production were hydrolyzed with water and emitted into the Rhine without any treatment. Since 1993, the emission of HCB at this site was reduced to practically zero. Although other producers and potential emitters of HCB were likely within the Rhine basin, no other relevant point source was identified by environmental agencies.

Although the primary sources (i.e. direct or point sources where effluents are emitted into the river) for HCB and PCB emissions into the Rhine have stopped since the early 1990s, secondary sources such as re-mobilizable contaminated sediments within the streams and at river banks are supposed to be the major cause for ongoing micropollutant load along the Rhine.

2 Materials and Methods

2.1 Station data

An extensive dataset was compiled for this study from several existing hydrological and environmental monitoring programs. First, average daily discharge (Q) data from 12 gages at the Rhine and its tributaries were used. Second, records of daily bulk-samples of suspended sediment concentration (S_{B}) were taken from 6 monitoring stations. Furthermore, bi-weekly to monthly data from 8 chemical monitoring stations on suspended sediment concentration (S_{C}) and micro-pollutants concentration in suspended matter (c) were used for this study. These samples were collected with centrifuges at each station (Fig. 1). The dataset covers the period from 1995 to 2008 and load calculations could be done for the period 1995 to 2007.

An extended time series (1985-2007) for calculating loads of HCB could be compiled with data by Keller (1994) for the station at Koblenz (Rhine).

2.1.1 Water level and discharge

A network of gages throughout Germany is operated by the environmental agencies of the German Federal States as well as the German Waterways and Shipping Administration. Water levels are recorded digitally every 15 minutes at these gages. Discharge is measured regularly to obtain water level - discharge curves and tables. Hourly discharge records are computed based on these water level - discharge curves. Both, average daily water levels and average daily discharge is then computed from the hourly records.

Prior to the calculation of particle-bound pollutant loads (L), the daily Q-data need to be preprocessed to either fill incomplete series or to account for local effects at several gages. As the discharge at the mouth of the river Neckar (i.e. gage Heidelberg) is influenced by backwater of the river Rhine during low flows and data gaps exist, the Q-series of gage Heidelberg was completed with records of the neighboring upstream gage Rockenau (ca. 34.6 km apart, see Table 2). Eq. 1 was used to calculate discharge when $Q_{d,\text{Heidelberg}} < 224$ m^{3}s^{-1}.

$$\hat{Q}_{d,\text{Heidelberg}} = Q_{d,\text{Rockenau}} \tag{1}$$

To complete the data series when $Q_{d,\text{Heidelberg}} \geq 224$ m^{3}s^{-1}, Eq. 2 was used:

$$\hat{Q}_{d,\text{Heidelberg}} = 35.6 + 1.09 \times Q_{d,\text{Rockenau}}. \tag{2}$$

The linear regression (Eq. 2) accounts for $R^2 = 98.5\%$. Furthermore, data gaps of the series of gage Alken (mouth of river Mosel) needed to be filled by means of linear regression with daily discharge from the upstream gage Cochem (ca. 27.7 km apart). As inconsistencies in the correlation of discharge between these two gages were obvious (data not shown), two separate equations were used to fill the data gaps of Alken. Equation 3 was used for all discharge data before 1. January 2006 and accounts for $R^2 = 99.9\%$:

$$\hat{Q}_{d,\text{Alken}} = 1.11 \times Q_{d,\text{Cochem}}. \tag{3}$$

All records since 1. January 2006 were calculated according to Eq. 4, that explains $R^2 = 99.6\%$ of the total variance:

$$\hat{Q}_{d,\text{Alken}} = 5.87 + 0.97 \times Q_{d,\text{Cochem}}. \tag{4}$$

There is no nearby gage for discharge at the suspended matter quality station Koblenz (Rhein), which is located upstream of the Mosel confluence. Hence, discharge of the upstream gage Kaub and the gage Kalkofen (tributary Lahn) were summated on a daily basis to yield discharge for Koblenz (Eq. 5):

$$\hat{Q}_{d,\text{Koblenz}} = Q_{d,\text{Kaub}} + Q_{d,\text{Kalkofen}}. \tag{5}$$

There is one gage and a monitoring station for suspended matter quality located at Mainz downstream of the mouth of the river Main. The river junction is located at the right bank of the river Rhine. As the suspended matter quality station is located in a short distance on the left bank of River Rhine, the mixing-length is too short for a complete mixing of suspended matter from both rivers. In other words, the monitoring station at Mainz only samples the chemical status of suspended matter of Rhine water prior to a mixing with suspended matter of the waters of the Main. Therefore, the discharge of Mainz was lowered by subtracting the daily discharge from Mainz with the daily discharge of Raunheim, where the final gage of the Main is located (Eq. 6).

$$\hat{Q}_{d,\mathrm{Mainz}} = Q_{d,\mathrm{Mainz}} - Q_{d,\mathrm{Raunheim}} \tag{6}$$

For the remaining suspended matter quality stations data from their corresponding gages and suspended sediment concentration stations were taken as provided in Table 2.

2.1.2 Suspended sediment concentration

The Federal Institute of Hydrology (*Bundesanstalt für Gewässerkunde*, BfG) in cooperation with the local boards of the German Waterways and Shipping Administration maintain a nationwide network of S_B-measurements at 67 stations in German waterways. Bulk water samples of 5 L are taken on every working-day at a single point within the cross-section of a river according to DVWK (1986). The samples are then filtered, dried and the filter residues are gravimetrically determined to yield S_B. The data are archived in relational databases and data gaps are filled through linear interpolation (Vetter, 2001).

2.1.3 Suspended matter quality data

Monitoring of the quality of suspended matter started in 1985 at the BfG in Koblenz. At that time, several hundreds of liter of river water were taken as bulk samples on a weekly basis and transferred into sedimentation balloons (Keller, 1994). The settled solids were then dried and analyzed for chlororganic compounds.

Monitoring programs throughout the Rhine and its tributaries were established in 1990 on an international level (International Commission for the Protection of the River Rhine, ICPR) and in 1992 on a national German level (*Deutsches Untersuchungsprogramm Rhein*). Since then, the quality of suspended matter is instantaneously monitored on a regular basis and sampling is conducted in either monthly or bi-weekly intervals depending on the station. The data were formerly printed in hardcopies (*Zahlentafeln des Rheins*) and are available in digital format through the Internet since the early 2000s.

Suspended matter is instantaneously collected with centrifuges at each monitoring station along the Rhine. As the separation rate of centrifuges accounts for up to 98% for dewatering suspended matter (Breitung, 1997), which was measured using filtered samples in the in-flow and out-flow device of the centrifuge, the suspened sediment concentration (S_{C}) can be derived using the recorded in-flow of the centrifuge and the mass of dry matter of centrifuge residues.

The centrifuge residues are dried through lyophilization for preservation prior to the analysis as bulk samples at certified laboratories. The further preparation and analysis of the dried samples is conducted in accordance to standard procedures for HCB (DIN 38407-3), PCB (DIN 38414-20; DIN 38407-3) and other organic or inorganic constituents. The limit of quantification (LOQ) for HCB and PCB ranges between 2 - 3 μg kg^{-1}, and 1 - 2 μg kg^{-1} respectively. In this study, we used half the value of LOQ for load calculation of a corresponding compound when analytical results were below LOQ.

2.2 Quantitative analysis

Based on the aforementioned datasets, monthly concentrations of HCB and PCB were calculated, as well as annual loads for each suspended matter quality station. The computation was done with the software package R, Version 2.9 (R Development Core Team, 2006).

2.2.1 Load calculation methods

Load is the mass flux of a constituent that is transported by flowing water through a cross section of a river (Eq. 7).

$$L = \int c(t)\ Q(t)\ S(t)\ \mathrm{d}t \tag{7}$$

Load is indicated by L, c is the micro-pollutant concentration in bulk suspended matter at sampling time t, Q is discharge, and S denotes the concentration of suspended sediments in the water. As the continuous variables $c(t)$ and $S(t)$ are sampled at discrete time steps (centrifuge and bulk samples, respectively), Eq. 7 can not be solved analytically. Therefore several equations were developed to approximate annual loads (LAWA, 2003; Quilbé *et al.*, 2006). The commonly used approximation also referred to as the standard procedure in suspended matter monitoring programs is given by Eq. 8. The flow adjusted method (also known as flow correction method, Eq. 9) normalizes mean flow at the sampling dates to mean flow for the entire year. While Eq. 8 and 9 require complete triplets of $c(t)$, $Q(t)$, and $S(t)$ data, the average method can be applied for incomplete data sets (Eq. 10). The linear interpolation method (Eq. 11) was suggested by Kronvang *et al.* (2004) for the calculation of dissolved nutrient loads.

$$\begin{aligned}
L_1 &= k_1\ \frac{1}{n}\sum_{t=1}^{n} c_t \cdot Q_t \cdot S_t && (8)\\
L_2 &= L_1\ \left(\frac{1}{365}\sum_{d=1}^{365} Q_d\right)\ /\ \left(\frac{1}{n}\sum_{t=1}^{n} Q_t\right) && (9)\\
L_3 &= k_1\ \ \frac{1}{n}\sum_{t=1}^{n} c_t\ \ \frac{1}{365}\sum_{d=1}^{365} Q_d\ \ \frac{1}{m}\sum_{j=1}^{m} S_j && (10)\\
L_4 &= k_2 \sum_{d=1}^{365} \hat{c}_d\ Q_d\ S_d && (11)
\end{aligned}$$

The conversion factors are given by $k_1 = 365 \cdot 60^2 \cdot 24 \cdot 10^{-9} = 0.031356$, and $k_2 = 86.4$ to yield L in g year^{-1}. Prior to applying Eq. 11, the daily concentrations $\hat{c}_d$ have to be calculated by linear interpolation according to (Eq. 12):

$$\hat{c}_d = \hat{c}(t) = c_0 + \frac{c_1 - c_0}{\Delta t}(t - t_0)\,, \tag{12}$$

with $t_o < t < t_1$ and $\Delta t = t_1 - t_0$.

As can be seen from Eq. 9, $L_1 = L_2$, if the mean discharge at the sampling dates equals the annual mean of the discharge. However, if mean discharge is undersampled (oversampled), the flow corrected load L_2 will be higher (lower) than the load of L_1.

A further method that is denoted as the regression method or rating curve method (Horowitz, 2003; Quilbé *et al.*, 2006), where gaps of $c(t)$ and $S(t)$ are filled by regression with $Q(t)$, exists in the literature (e.g. LAWA, 2003). However, in this study the application of the regression method was not useful: Although a high correlation (Fig. 2) measured as Spearman's correlation coefficient (r_S) is present for $S(t)$ and $Q(t)$ ($r_\mathrm{S} = 0.77$, $p < 0.01$), $c(t)$ and $Q(t)$ were almost not correlated (HCB: $r_\mathrm{S} = -0.09$, $p = 0.051$, PCB-138: $r_\mathrm{S} = -0.32$, $p < 0.01$, PCB-153: $r_\mathrm{S} = -0.33$, $p < 0.01$). It should be noted, that concentrations of PCB-138 and PCB-153 are associated with each other ($r_\mathrm{S} = -0.86$, $p < 0.01$, Fig. 2), which indicates similar sources and environmental behavior of these congeners. In this study, we used both datasets of S_B and S_C to calculate particle-bound loads according to Eqs. 8 to 11.

2.2.2 Uncertainty assessment - systematic vs. random errors

It is not clear whether the sampling techniques for suspended sediments and the various load calculation methods produce systematically different loads. Consequently, we tested the effect on particle-bound load conducting a two-way analysis of variance (two-way ANOVA) without interaction using a 2 × 4 layout for each monitoring station. The first factor (F_1) comprises the different sampling techniques for suspended sediment concentration (S_B and S_C), the second factor (F_2) comprises the four different load calculation methods ($L_1, \ldots, L_4$, Eqs. 8 to 11).

Furthermore, a derivative of the maximum percentage error (E in %, Eq. 13) was calculated separately for each station, micro-pollutant and year. This was done when the two-way ANOVA found no systematic impact of one of the aforementioned factors.

$$E = 100\ (L_{\mathrm{MX}} - L_{\mathrm{MN}})\ /\ \bar{L} \tag{13}$$

The maximum (L_{MX}), minimum (L_{MN}) and mean ($\bar{L}$) load from Eqs. 8 to 11 were used as inputs for the corresponding year.

2.2.3 Mann-Kendall trend test and Sen's slope

We used the non-parametric Mann-Kendall trend test (Kendall, 1975; Hipel and McLoed, 1994) for the detection of significant trends. A sequence of equidistant measurements in time is hereby tested for randomness (H_0) against the alternative hypothesis (H_1) that the data follow a monotonic trend. Furthermore, Kendall's-τ for the estimation of the strength of a trend was calculated for the monthly concentration series as well as the annual load series of HCB, PCB-138 and PCB-153. The Mann-Kendall trend test is robust to outliers and has no assumptions to the data distribution. However, the power of the Mann-Kendall trend test decreases when a seasonality (e.g. annual cycle) is present within the data. This is not the case for the concentrations of HCB, PCB-138 and PCB-153 in suspended matter in our dataset.

If significant trends were found, the non-parametric slope (b_{Sen}) according to Sen (1968) was calculated to yield a comparable measure for the increase or decrease of concentrations and loads across the different monitoring stations. Median b_{Sen} and it's 95%-confidence intervall is presented throughout this paper. The Mann-Kendall trend test, Kendall's-τ and b_{Sen} were computed with the R packages *Kendall* and *zyp*.

3 Results and Discussions

3.1 Trend detection in particle-bound micro-pollutant concentrations

3.1.1 HCB

Figure 3 depicts the temporal courses of monthly particle-bound HCB concentrations at various Rhine stations. Obviously, the chemographs show a high variability with single extreme values as e.g. at Karlsruhe with up to 340 μg kg^{-1} in 1999. The environmental objective for HCB ($c \leq 40$ μg kg^{-1}), that was introduced by the ICPR, is only steadily achieved in the upstream stretch of the river Rhine at Weil. Concentrations monitored at Karlsruhe and Mainz often exceed this objective.

For each station, significant ($p < 0.05$) decreasing trends were detected according to the Mann-Kendall test (Table 3). However, the association with time is modest and ranges from $\tau = -0.130$ at Mainz to $\tau = -0.454$ at Bimmen. It is worth noting that only weak decreasing trends exist for HCB in the period 1995 to 2008 although known primary sources stopped their emissions by 1993.

3.1.2 PCB-138

Except for Karlsruhe, where no trend could be detected, significant decreasing trends in PCB-138 concentrations are present at every Rhine station (Table 4). The association of PCB-138 concentrations with time is modest, as indicated by the range of $\tau = -0.182$ for Weil and $\tau = -0.399$ for Bad Honnef as well as by the high variability within the series (Fig. 4).

3.1.3 PCB-153

Similar to HCB, the ICPR introduced an environmental objective for PCB-153 ($c \leq 4$ μg kg^{-1}). As given by Fig. 5, this objective is frequently exceeded at every station along the Rhine. The temporal behavior of PCB-153 is similar to PCB-138 (Table 5). The decreasing trends are highly significant ($p < 0.01$), except for Karlsruhe where no trend was detectable.

3.2 Uncertainty assessment of load calculation procedures

3.2.1 HCB

Neither the sampling technique for suspended sediments nor the calculation method for load significantly impacts the results for annual HCB load at the Rhine stations according to the two-way ANOVA (non-significant results are not shown), which is also indicated by the overlapping symbols in the time-series (Fig. 7).

There is one exception: At Weil, the factor sampling technique for S (F_1) is significant ($F(1, 96) = 39.24$, $p < 0.01$), but the various load calculation methods do not lead to significant differences ($F(3, 96) = 0.22$, $p = 0.88$). At Weil, when S_{B} samples were used for load calculation instead of S_{C}, the particle-bound loads of HCB almost tripled (Fig. 7). This may be attributed to the fact that S_{B}-measurements at Weil differ to other monitoring stations. Since 1994, at Weil samples are taken automatically with pumps at four points within a cross-section. The inlet pipes are installed at about 1 m height above the river bed. In contrast, at other stations bulk samples are taken at one point close to the water surface. As a depth profile of S exists, where S is positively related with depth, the sampling strategy at Weil systematically produces higher concentrations of suspended sediments and, thus, particle-bound loads.

The magnitude of E for HCB is remarkable. It varies upon the stations and the individual years, e.g. $E = 18.1\%$ at Koblenz in 2006 to $E = 122.5\%$ at Karlsruhe in 1999.

3.2.2 PCB-138

Similar results as compared to HCB are obtained for PCB-138 (Fig. 8). No significant effects on PCB-138 loads could be detected for neither of the two factors except for Weil, where F_1 is highly significant ($F(1,96) = 74.3, p < 0.01$). This can be attributed to the same cause as described in Sect. 3.2.1.

E ranges from $E = 10.8\%$ for Koblenz in 1996 (Fig. 8) to $E = 98.7\%$ at Mainz in 1998. The higher uncertainties at Weil ($E = 214\%$ in 2005) can be attributed to the systematic differences caused by the suspended matter sampling techniques as explained in Sect. 3.2.1. In 1999, there was a flood event within the Rhine basin, that in return leads to higher uncertainty in calculated loadings of particle-bound PCB-138 at Weil ($E = 116\%$), Karlsruhe ($E = 124\%$), Mainz ($E = 71\%$), Koblenz ($E = 72\%$), and Bimmen ($E = 93\%$). However, as the uncertainty is high in years without flood events as well, the magnitude of E is only weekly associated with floods.

3.2.3 PCB-153

For PCB-153, the factor sampling technique for suspended matter is also significant at Weil ($F(1,96) = 100.4, p < 0.01$), whereas F_2 is not a significant factor. At the other stations, no significant effects on load based on F_1 and F_2 could be detected.

The general findings for E of PCB-153 are similar as compared to E of PCB-138. Minimum and maximum E were found at Koblenz ($E = 8.3\%$ in 2000) and Mainz ($E = 95\%$ in 2002), respectively. Although in the flood year 1999 higher uncertainty bounds are present at Karlsruhe, Mainz, Koblenz, Bad Honnef and Bimmen (Fig. 9), remarkably high uncertainty is also present in years when flood events are absent.

3.3 Trend detection in particle-bound micro-pollutant loads

3.3.1 HCB

Prior to the trend analysis of particle bound HCB-loads at multiple stations, the extended series of the station Koblenz was analyzed (Fig. 6). The annual loads for HCB decreased significantly ($\tau = -0.657$, $p \leq 0.001$) from ca. 110 kg year^{-1} in 1985 to about 15 to 23 kg year^{-1} in 2007. Contrarily, in the shorter time series of Koblenz (1995-2007, Fig. 7) no significant trend could be detected (Table 6). The recent magnitude of HCB load at the Rhine is higher as compared to reports from other rivers in the literature: e.g. for the Ebro River an annual load of HCB of 11 kg year^{-1} comprising both the solute and the particulate phase for the period 2002 to 2003 was reported by Gómez-Gutiérrez *et al.* (2006). An annual input of HCB for the period 1998 to 1999 from Rivers into the lagoon of Venice was estimated to 0.924 kg year^{-1} (Bettiol *et al.*, 2005). Furthermore, the magnitude of HCB reduction at the Rhine by a factor of 10 in the period of 1985 to 2007 is in agreement with e.g. reports from sedimentary core studies from the St. Lawrence River (Barber *et al.*, 2005).

The time-series (1995-2007) of Bad Honnef and Bimmen show significantly decreasing trends (Table 6). The reduction of HCB load expressed as Sen's slope and its 95%-confidence interval at Bimmen is stronger ($b_{\text{Sen}} = -7.1$ $[-12.8, -1.9]$ kg year^{-1}) as compared to Bad Honnef ($b_{\text{Sen}} = -4.5$ $[-9.7, -1.3]$ kg year^{-1}). However, at the majority of suspended matter quality stations of the Rhine, no decreasing trend could be detected.

3.3.2 PCB-138

Although significant decreasing trends were detected in the PCB-138 monthly concentration series at several monitoring stations, hardly any trends could be detected in the series of annual loadings (Fig. 8). Only at Bad Honnef and Bimmen significant reductions of PCB-138 loads are present (Table 7) with $b_{\text{Sen}} = -2.5$ $[-6.5, -0.6]$ kg year^{-1} for Bad Honnef, and $b_{\text{Sen}} = -2.1$ $[-8.9, -0.7]$ kg year^{-1} for Bimmen.

3.3.3 PCB-153

Similar to the trend behavior of PCB-138-loads, there are only significant trends present at Bad Honnef and Bimmen (Table 8). Even the magnitude of decrease (Bad Honnef: $b_{\mathrm{Sen}} = -2.6[-8.0, -0.8]$ kg year^{-1}; Bimmen: $b_{\mathrm{Sen}} = -2.5[-10.5, -0.9]$ kg year^{-1}) is similar to PCB-138, which is a further indication that both PCB congeners are associated in suspended matter.

3.4 Longitudinal profiles of loads

As the time series (1995-2007) of the investigated particle-bound micro-pollutant loads are almost stationary, the calculation of a long term average longitudinal profile is appropriate. Such profiles are useful for detecting potential sources or sinks of particle-bound micro-pollutants along the longitudinal river axis. Due to the averaging, single events will be smoothed, which is advantageous in light of the limited number of data.

HCB loads increase between Weil and Karlsruhe from ~ 2 kg year^{-1} to a level of ca. 25 kg year^{-1} (Fig. 10 A). In the stretch of the river Rhine between Karlsruhe and Bad Honnef, there is hardly any significant change in average annual loads. The inputs of HCB by the tributaries Neckar (ca. 0.6 kg year^{-1}), Main (ca.0.8 kg year^{-1}) and Mosel (ca. 0.4 kg year^{-1}) are negligible. However, a further rise of HCB load (ca. 27 kg year^{-1}) is visible between Bad Honnef and Bimmen, which coincides with higher uncertainties of the long term average HCB load at Bimmen. It is likely that further HCB input comes from the river Lippe, which drains parts of the industrialized Ruhrgebiet.

Clearly, the Upper Rhine (approx. Rhine-km 200 to Rhine-km 400) can be identified as one major area of secondary sources for HCB. In this river section, 10 barrages are present that act as sinks for sediments. The contaminated suspended matter and river sediments caused by the historic emissions of the chemical plant located at Rheinfelden are prone to deposit at these sedimentation areas. As regular dredging activities to facilitate the maintenance of the barrages as well as natural flood events occur, these areas of barrages are assumed to act as secondary sources (ICPR, 2009).

As opposed to the longitudinal profile of HCB, the Upper Rhine is apparently not the major source for PCB-138 and PCB-153 contamination. There is hardly any increase between Weil and Karlsruhe in neither of the loads of PCB-138 and PCB-153, respectively (Fig. 10 B & C). The rise of PCB-138 and PCB-153 loads between Karlsruhe und Mainz corresponds well with inputs from the tributaries Neckar (ca. 4.2 kg year^{-1} for PCB-138, and ca. 3.4 kg year^{-1} for PCB-153) as well as the river Main (ca. 1.8 kg year^{-1} for PCB-138, and ca. 2.0 kg year^{-1} for PCB-153). The tributary Mosel further increases the loads of PCB-138 (ca. 3.5 kg year^{-1}) and PCB-153 load (ca. 5.0 kg year^{-1}) of the river Rhine, as indicated by the rising limb between Koblenz and Bad Honnef (Fig. 10). The long term average annual load at Bimmen for PCB-138 and PCB-153 account for ca. 35 kg year^{-1} and ca. 37 kg year^{-1}, respectively.

4 Conclusions

As the monitoring program in order to assess the chemical status of suspended matter at the river Rhine started in the 1990s and, thus, after peak emissions, when organochlorine compounds and PCBs were already banned, only modest reduction in concentrations and hardly any significant trends in particle-bound micro-pollutant loads could be detected at the Rhine for the period 1995 to 2007. As environmental objectives are not approached, hitherto, the quality of suspended solids with respect to HCB and PCBs is still a cause for concern.

Only in the extended series, that covers the period from 1985 to 2007 at station Koblenz, a significant decreasing trend in HCB load with a remarkable reduction is present. However, during the recent 13 years the levels of loads stagnate for HCB, PCB-138 and PCB-153.

Secondary sources, such as sedimentation areas in dead zones, barrages, harbours, of the Rhine are the cause for ongoing particle-bound micro-pollutant load. The river stretch of the Upper Rhine is known as such a secondary source for HCB where contaminated sediments are regularly re-mobilized due to natural floods or dredging activities (ICPR, 2009; Gölz, 2008).

Load calculation of particle-bound micro-pollutants such as PCBs and organochlorine compounds is faced with high uncertainty, though systematic errors are hardly present. Consequently, for most of the Rhine stations, either one of the four load calculation methods can be applied as well as either one of the two different data sets of S_{B} and S_{C} can be used for the estimation of annual particle-bound pollutant load. We conclude that the ICPR monitoring program is adequate for analyzing the long term chemical status of suspended matter with respect to PCBs and HCB. However, the standard monitoring program (i.e. bi-weekly to monthly instantaneous samples) should be extended to higher temporal sampling frequencies when either flood events or dredging activities occur in the Rhine basin.

Further research is needed to explore and identify the contaminated areas, to estimate the pollutant reservoir of these sediments and to consequently project the long-term behavior of these micro pollutants under climate change conditions as well as the efficiency of decontamination strategies with the support of hydrodynamic reactive transport models.

Acknowledgment This research has been carried out in the project 5.01 "Climate projections for sediment balances and risks due to cohesive sediments" within the departmental research program "KLIWAS – Impacts of climate change on waterways and navigation" that is financed by the German Federal Ministry of Transport, Building and Urban Development. We are grateful to Dr. Martin Keller for his valuable comments on an earlier draft of this paper.

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Table 1: Physico-chemical characteristics of HCB, PCB-138 and PCB-153. Data were taken from Delle Site (2001); Djohan *et al.* (2005); Mackay *et al.* (2006).

Parameter	Unit	HCB	PCB-138	PCB-153
Molecular weight		284.782	360.878	360.878
Water solubility	mg L^{-1}	0.005	0.0015 - 0.0023	0.00115
Octanol water partition coefficient ($\log K_{\mathrm{OW}}$)	$\log(\mathrm{L\ L^{-1}})$	5.1 - 6.1	6.42 - 7.25	6.34 - 8.35
Distribution coefficient ($\log K_{\mathrm{D}}$)	$\log(\mathrm{L\ kg^{-1}})$	3.3 - 3.5	5.3 - 5.9	4.0 - 5.9
Bioconcentration factor ($\log \mathrm{BCF}$)	$\log \mathrm{BCF}$	3.1 - 6.0	4.79 - 5.96	4.48 - 6.78

Table 2: Names of the suspended matter quality stations (S_C & c) and their river kilometer index (RKMI). Each line gives the corresponding discharge gage (Q) and station for daily suspended sediment concentration (S_B), which data were additionally used for particle-bound load calculation. If not mentioned otherwise, RKMI refers to the River Rhine.

S_C & c	Q	S_B
Weil (km 164.3)	Basel (km 164.3)	Weil (km 173)
Karlsruhe-Iffezheim (km 333.9)	Plittersdorf (km 340.2)	Plittersdorf (km 339.8)
Mannheim (Neckar-km 3.0)	Heidelberg (Neckar-km 26.1), Rockenau (Neckar-km 60.7)	-
Mainz (km 498.5)	Mainz (km 498), Raunheim (Main-km 12.2)	Nierstein (km 480.6)
Koblenz (km 590.3)	Kaub (km 546), Kalkofen (Lahn-km 106.4)	St. Goar (km 557)
Koblenz (Mosel-km 2.0)	Alken (Mosel-km 23.9), Cochem (Mosel-km 51.6)	Brodenbach (Mosel-km 27.2)
Bad Honnef (km 645.8)	Bonn (km 646)	-
Bimmen (km 865.0)	Rees (km 837)	Emmerich (km 851.9)

Table 3: Results of the Mann-Kendall trend test for monthly, particle-bound HCB concentrations in suspended solids (1995-2008). τ, p-value, b_{Sen}, and n denote Kendall's-τ, its level of significance, and Sen's slope with its 95%-confidence intervall, and the number of data pairs. Italics denote significant ($p < 0.05$) and bold letters indicate very significant ($p < 0.01$) trends.

Station	τ	p-value	b_{Sen} (ng kg^{-1} year^{-1})	n
Weil	-0.303	< **0.01**	-11 [-15,-7]	156
Karlsruhe	-0.193	< **0.01**	-35 [-58,-15]	135
Mainz	-0.130	*0.02*	-19 [-37,-2]	150
Koblenz	-0.147	*0.01*	-11 [-20,-3]	156
Bad Honnef	-0.345	< **0.01**	-34 [-48,-22]	133
Bimmen	-0.454	< **0.01**	-50 [-61,-38]	141

Table 4: Results of the Mann-Kendall trend test for monthly, particle-bound PCB-138 concentrations in suspended solids (1995-2008). Same notation as Table 3

Station	τ	p-value	b_{Sen} (ng kg^{-1} year^{-1})	n
Weil	-0.182	< **0.01**	-5 [-7,-2]	156
Karlsruhe	-0.082	0.16	-3 [-8,1]	136
Mainz	-0.121	*0.03*	-5 [-10,0]	150
Koblenz	-0.322	< **0.01**	-7 [-10,-5]	156
Bad Honnef	-0.399	< **0.01**	-13 [-16,-10]	131
Bimmen	-0.346	< **0.01**	-16 [-21,-12]	139

Table 5: Results of the Mann-Kendall trend test for monthly, particle-bound PCB-153 concentrations in suspended solids (1995-2008). Same notation as Table 3

Station	τ	p-value	b_{Sen} (ng kg^{-1} year^{-1})	n
Weil	-0.264	$<$ **0.01**	-5 [-6,-3]	156
Karlsruhe	0.012	0.84	0 [-4,5]	136
Mainz	-0.267	$<$ **0.01**	-11 [-16,-7]	150
Koblenz	-0.361	$<$ **0.01**	-9 [-12,-7]	156
Bad Honnef	-0.469	$<$ **0.01**	-16 [-20,-12]	130
Bimmen	-0.472	$<$ **0.01**	-24 [-29,-19]	139

Table 6: Results of the Mann-Kendall trend test for annual particle-bound HCB loads (1995-2007). τ, p-value, and n denote Kendall's-τ, the level of significance, and the number of years, respectively. Italics denote $p < 0.05$ and bold letters $p < 0.01$.

Station	τ	p-value	n
Weil	-0.256	0.25	13
Karlsruhe	-0.309	0.21	11
Mannheim (Neckar)	-0.121	0.63	12
Bischofsheim (Main)	-0.333	0.73	4
Mainz	-0.179	0.43	13
Koblenz (Rhein)	-0.333	0.13	13
Koblenz (Mosel)	-0.205	0.36	13
Bad Honnef	-0.576	$<$ **0.01**	12
Bimmen	-0.576	$<$ **0.01**	12

Table 7: Results of the Mann-Kendall trend test for particle-bound PCB-138 load (1995-2007). Same notation as Table 6.

Station	τ	p-value	n
Weil	-0.051	0.86	13
Karlsruhe	-0.055	0.88	11
Mannheim (Neckar)	-0.303	0.19	12
Bischofsheim (Main)	-0.389	0.18	9
Mainz	-0.154	0.50	13
Koblenz (Rhein)	-0.385	0.08	13
Koblenz (Mosel)	-0.385	0.08	13
Bad Honnef	-0.545	*0.02*	12
Bimmen	-0.564	$<$ **0.01**	13

Table 8: Results of the Mann-Kendall trend test for particle-bound PCB-153 load (1995-2007). Same notation as Table 6.

Station	τ	p-value	n
Weil	-0.128	0.58	13
Karlsruhe	-0.055	0.88	11
Mannheim (Neckar)	-0.121	0.63	12
Bischofsheim (Main)	-0.389	0.18	9
Mainz	-0.205	0.36	13
Koblenz (Rhein)	-0.359	0.10	13
Koblenz (Mosel)	-0.385	0.08	13
Bad Honnef	-0.606	$<$ **0.01**	12
Bimmen	-0.590	$<$ **0.01**	13

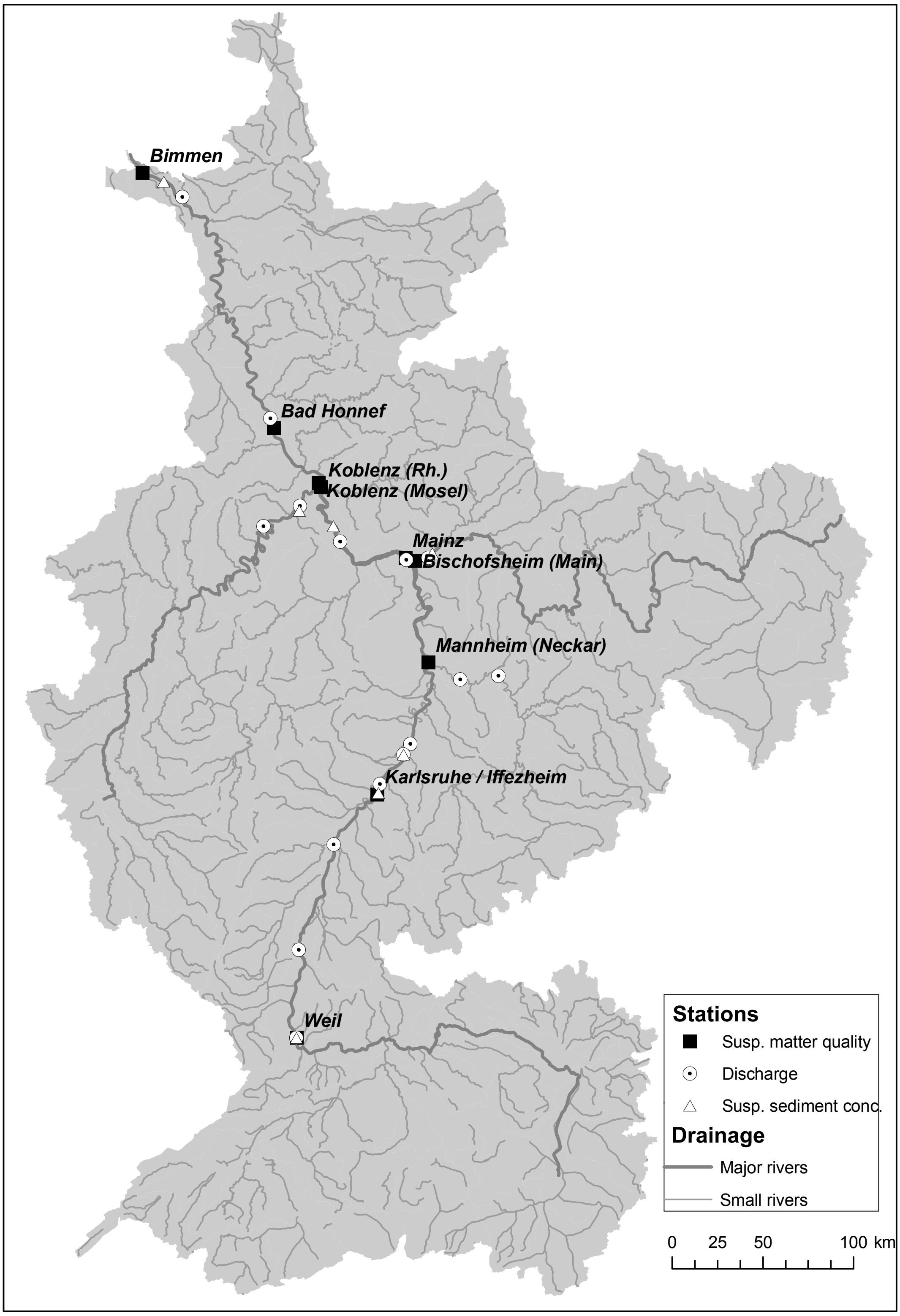


Figure 1: Rhine basin and locations of monitoring stations for suspended matter quality, suspended sediment concentration and discharge.

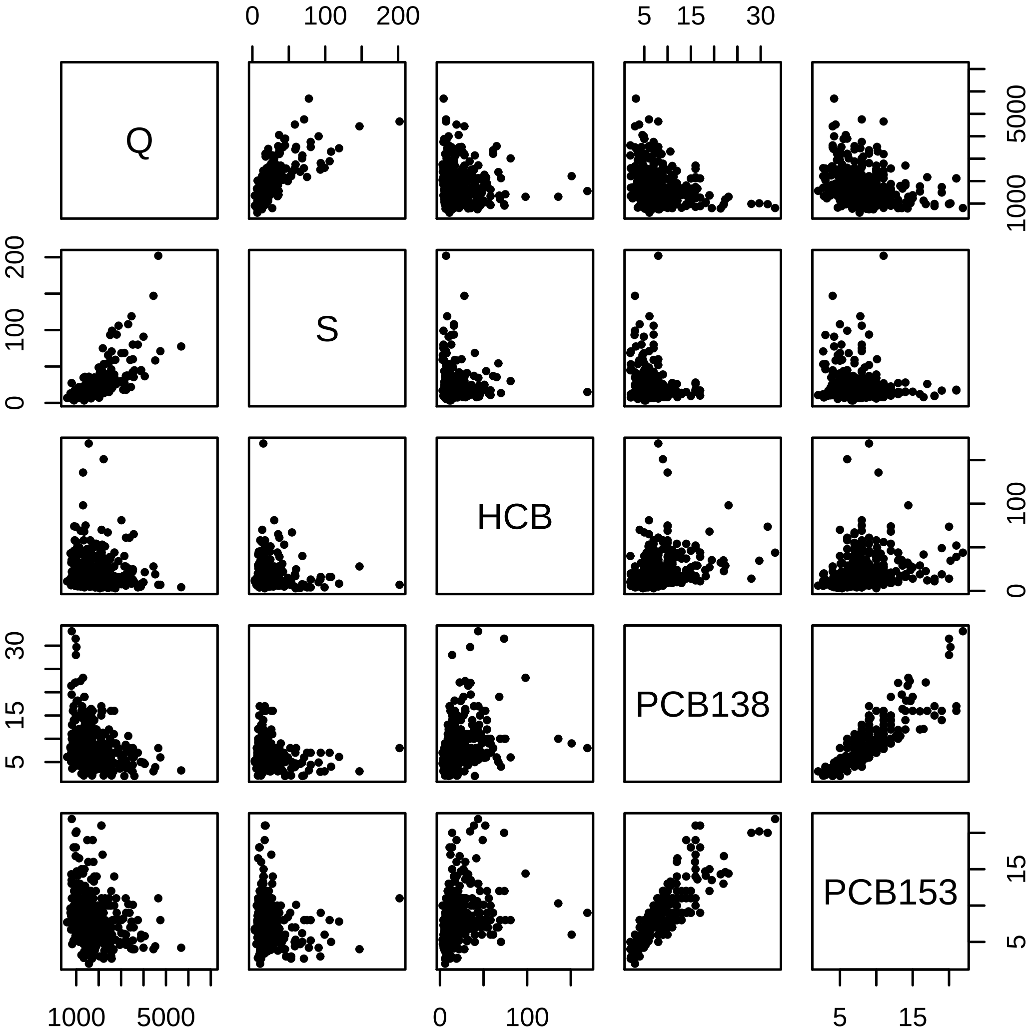


Figure 2: Scatterplots of the investigated variables discharge (Q in m^3 s^{-1}), suspended sediments concentration (S in mg L^{-1}), HCB, PCB-138, and PCB-154 (in μg kg^{-1}) at Koblenz (1990-2008).

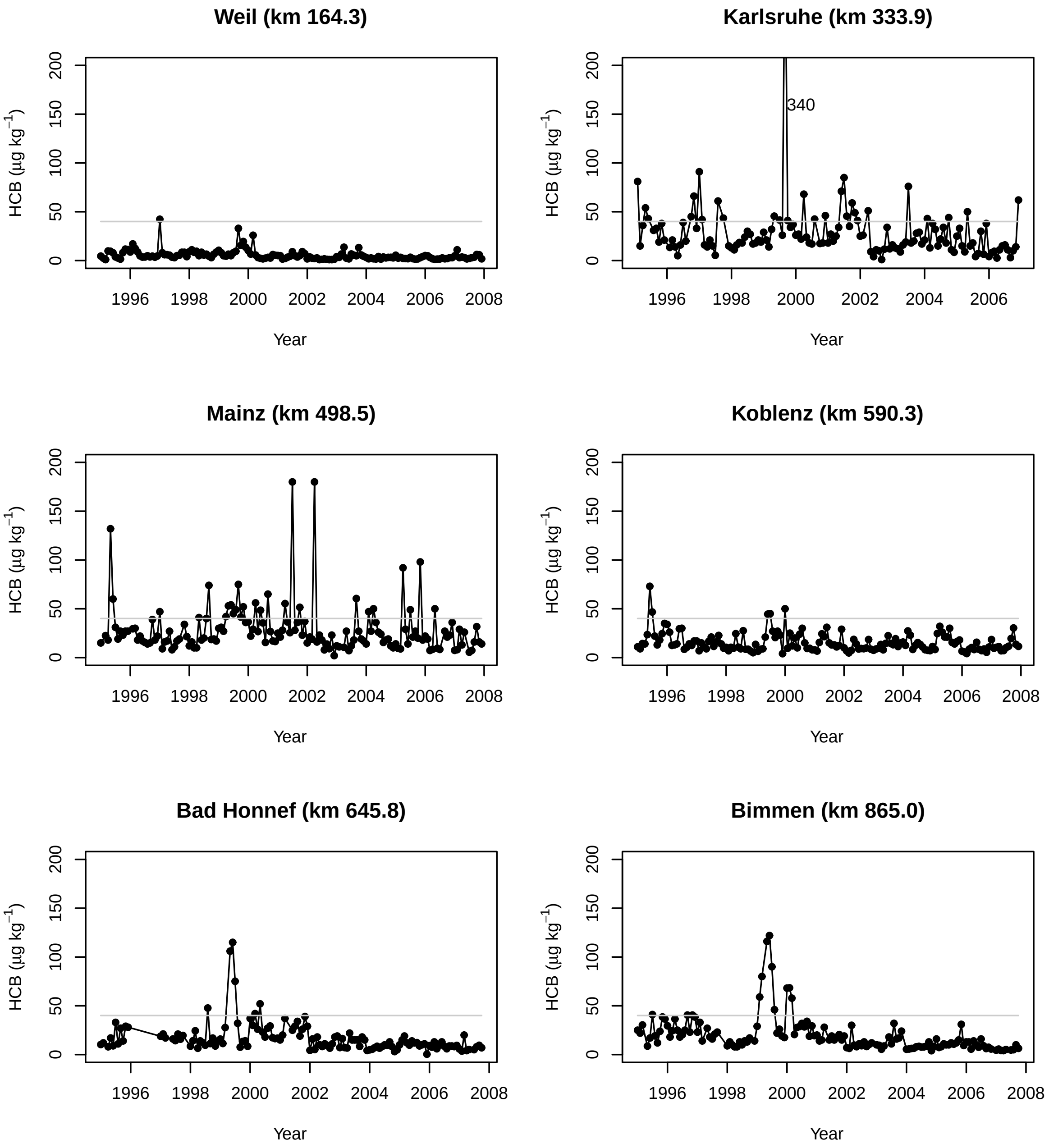


Figure 3: Monthly concentration of HCB in suspended matter (μg kg^{-1}) at the Rhine (1995-2008). Grey line indicates the ICPR environmental objective for HCB of $c \leq 40$ g kg^{-1}.

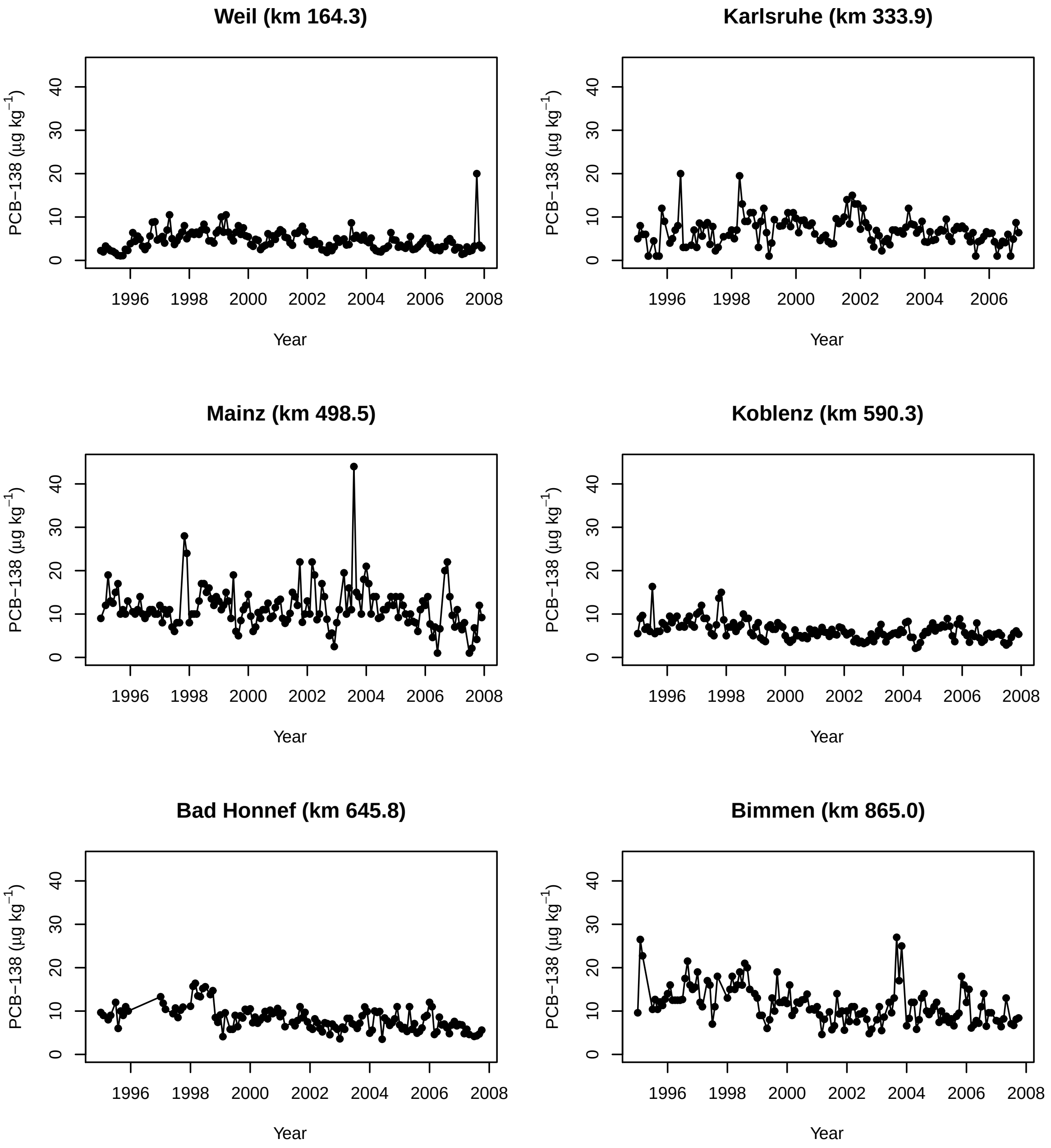
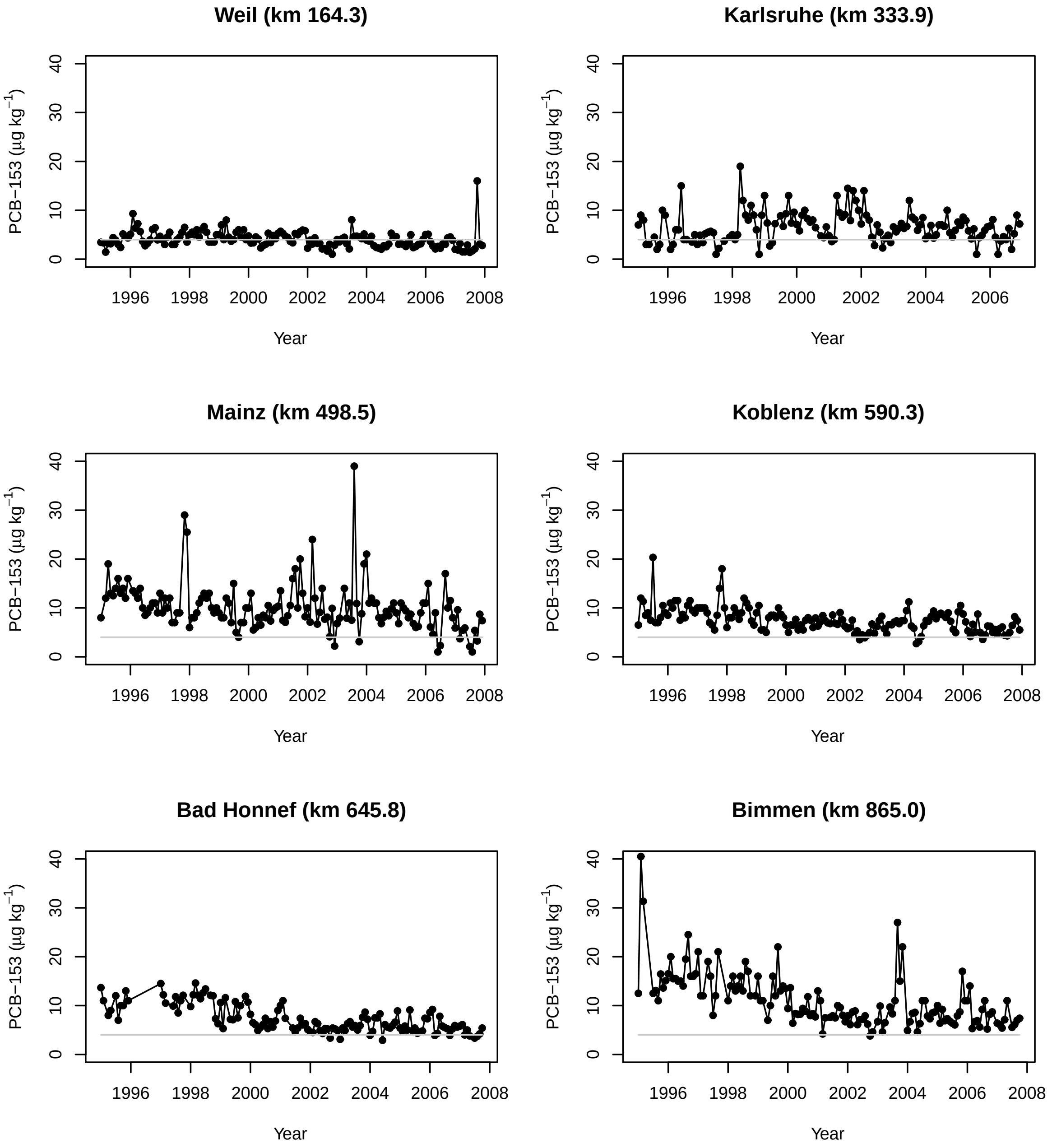


Figure 4: Monthly concentration of PCB-138 in suspended matter (μg kg^{-1}) at the Rhine (1995-2008).



Weil (km 164.3)

Karlsruhe (km 333.9)

Mainz (km 498.5)

Koblenz (km 590.3)

Bad Honnef (km 645.8)

Bimmen (km 865.0)

Figure 5: Monthly concentration of PCB-153 in suspended matter (μg kg^{-1}) at the Rhine (1995-2008). Grey line indicates the ICPR environmental objective for PCB-153 of $c \leq 4$ g kg^{-1}.

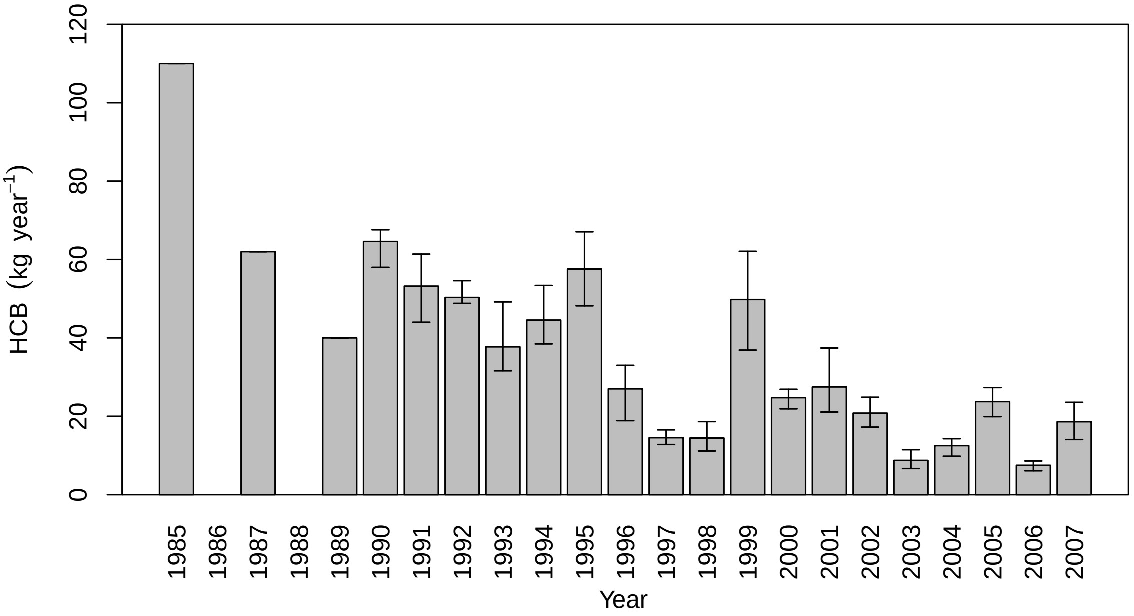


Figure 6: Trend of annual particle-bound HCB loads (kg years^{-}1) at station Koblenz (Rhein-km 590.3) for the period 1985-2007. Boxes indicate the mean annual load calculated with the various load estimation methods. Error bars indicate the range of the various calculated loads (see Sect. 2.2.1 for explanation).

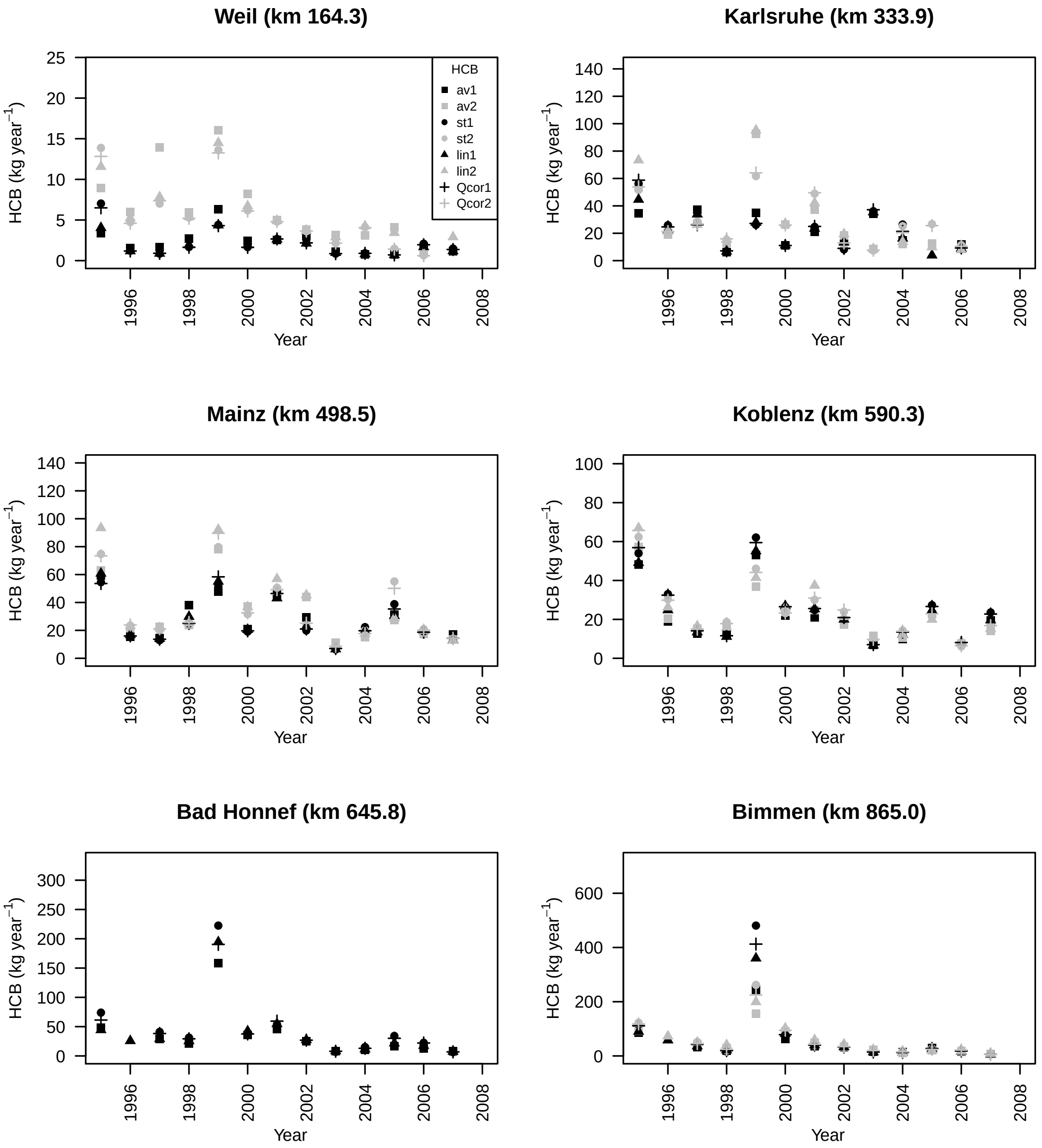


Figure 7: Annual loads of particle-bound HCB in the river Rhine (kg years^{-}1). av, st, lin, and Qcor denote the load calculation methods, i.e. average method, standard method, linear-interpolation method, and flow-corrected standard method. The concentration of suspended sediments was gravimetrically determined from centrifuge residues (1) and filter residues (2). Note that the scale of the y-axis differs among the plots.

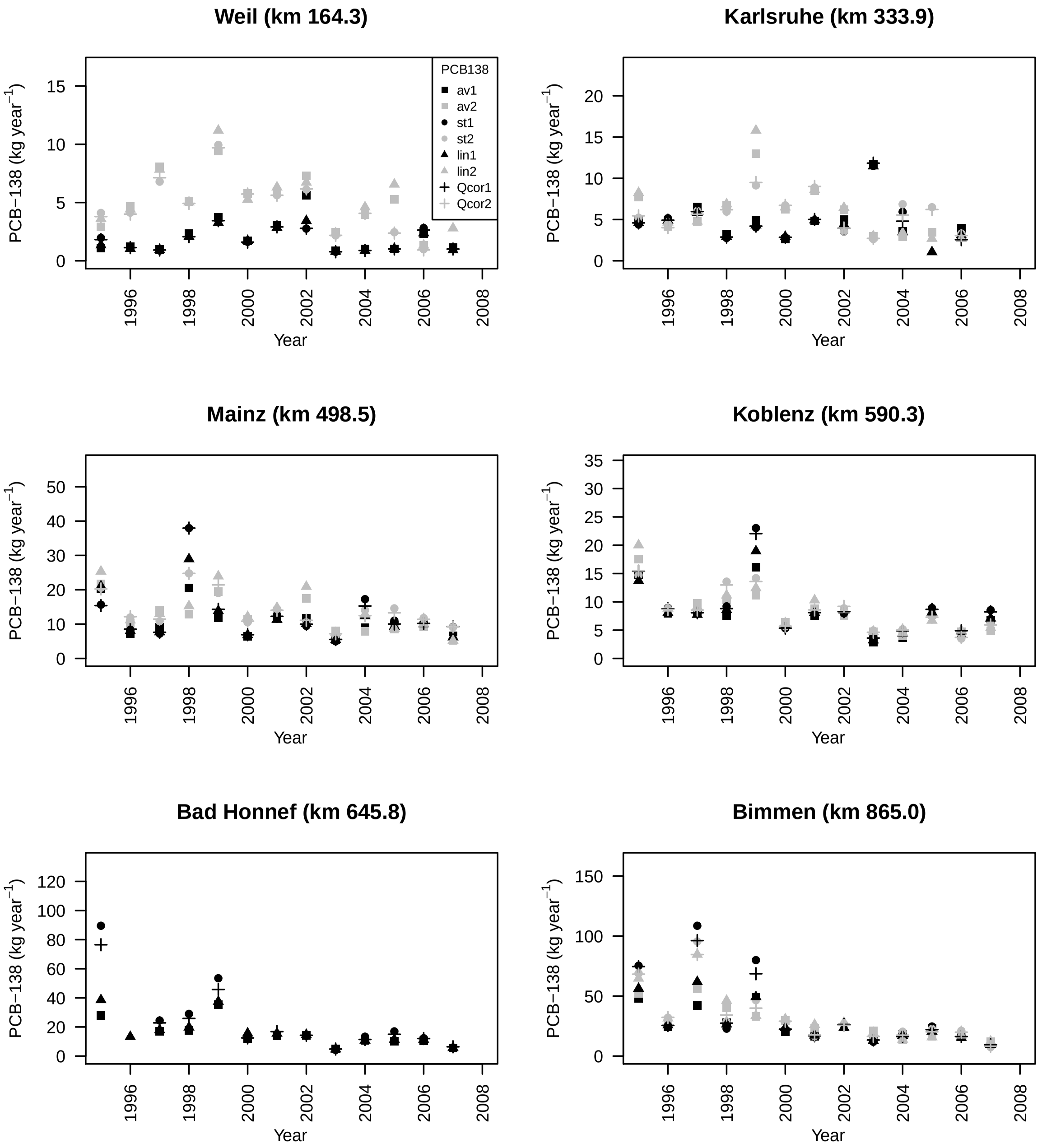


Figure 8: Annual loads of particle-bound PCB-138 (kg years^{-}1) in the Rhine. Same notation as Fig. 7.

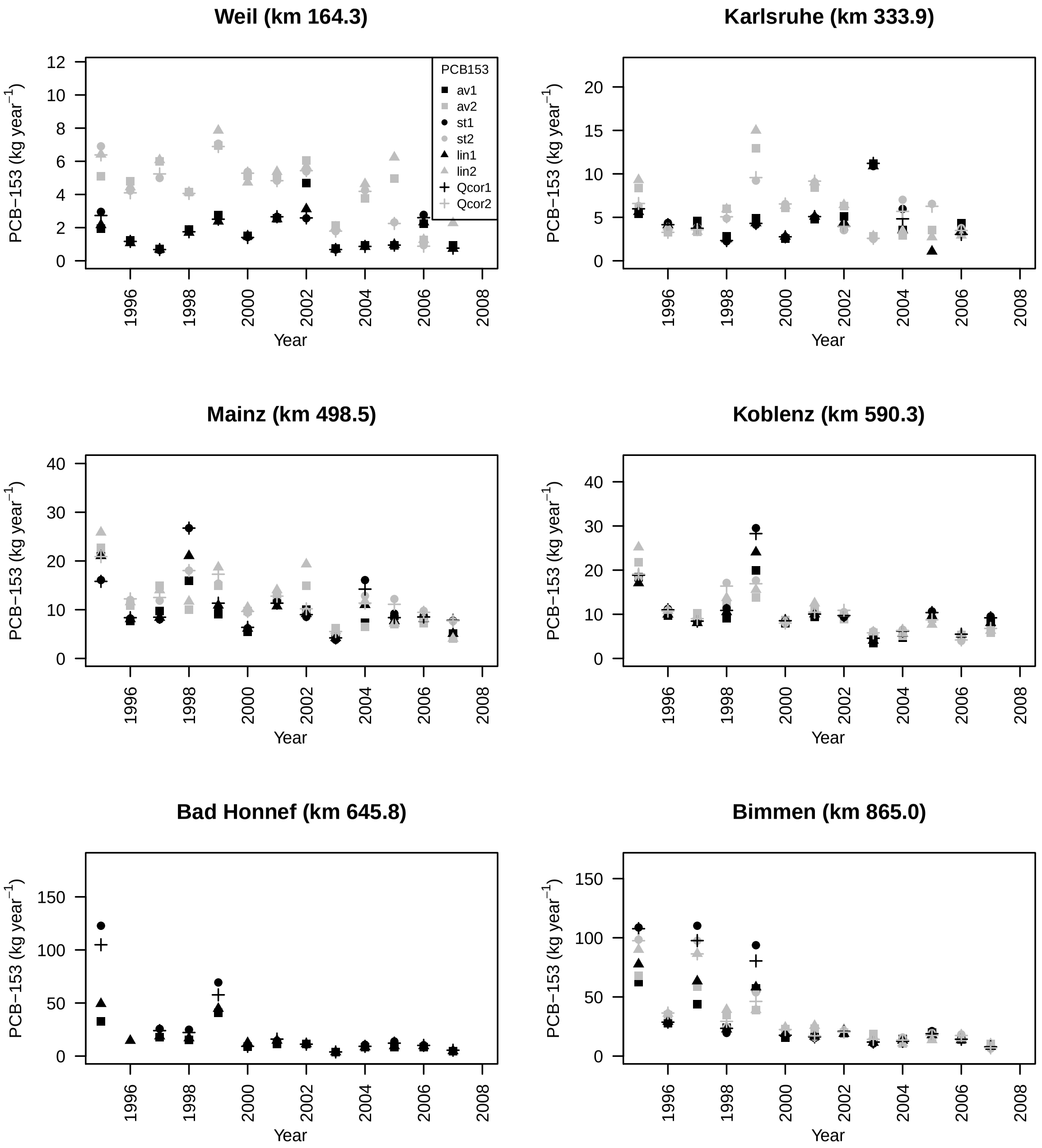


Figure 9: Annual loads of particle-bound PCB-153 (kg years^{-}1) in the Rhine. Same notation as Fig. 7.

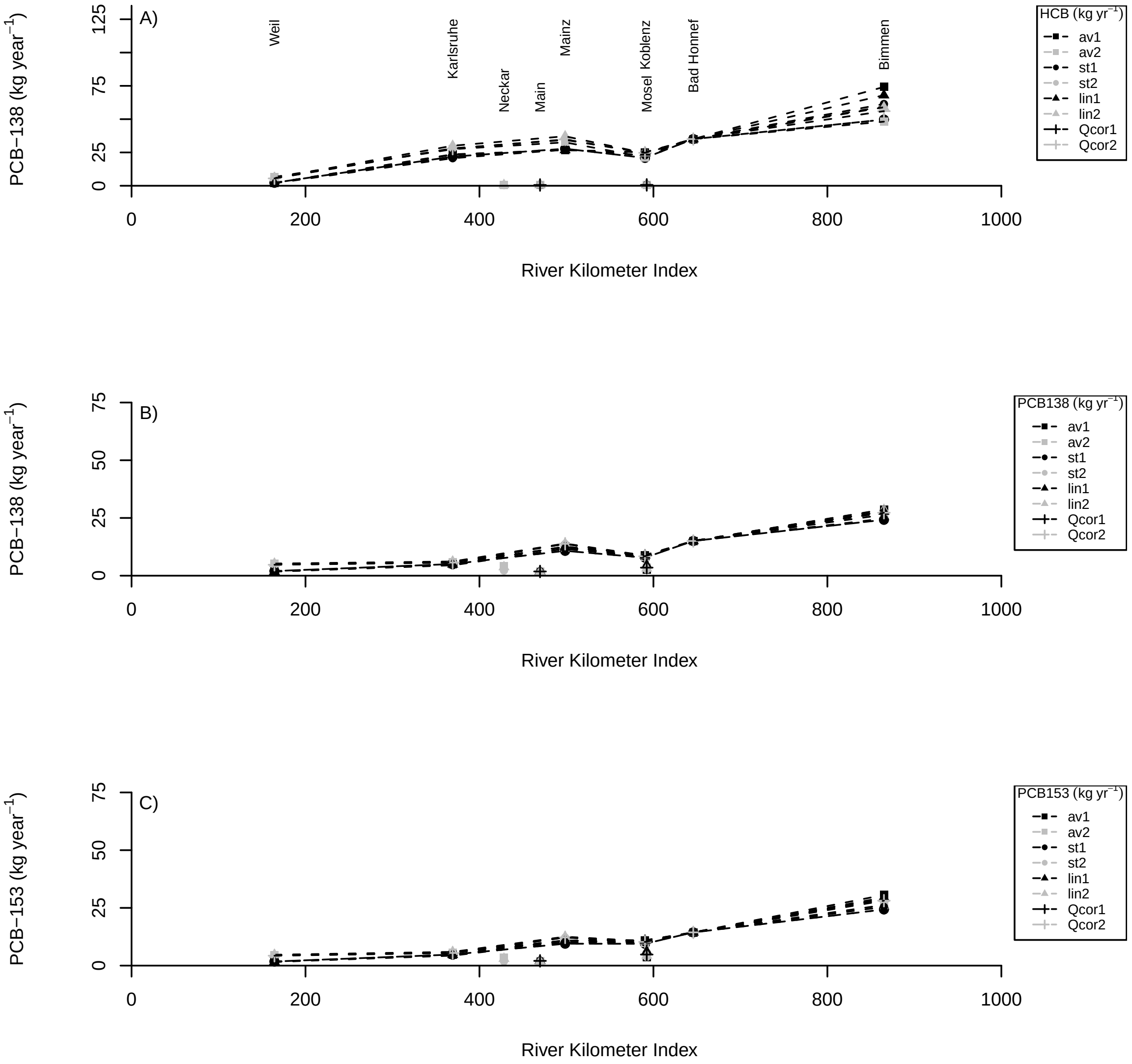


Figure 10: Longitudinal profile of particle-bounde, average annual A) HCB, B) PCB-138, and C) PCB-153 loads (1995-2007) of the River Rhine.