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Biomonitoring of polychlorinated biphenyls in Bavaria/Germany—long-term observations and standardization

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Abstract
In the 1980s, it was demonstrated that semi-volatile organic compounds (SVOCs) like polychlorinated biphenyls (PCBs) accumulate in plant leaves. Plants are at the base of the food chain, and therefore a starting point for transfer of PCBs to animals and related human exposure. For two decades, the Environment Agency of the German federal state of Bavaria (LfU) has been operating long-term monitoring stations to measure the impact of organic air pollutants. Standardized ryegrass, curly kale, and spruce needles are used as bioindicators for the atmospheric entries of PCBs into vegetation. From the end of 1990s to 2009, there was a marked decline in the concentrations of indicator PCBs (i-PCBs) and a minor decline in PCB-TEQ levels. After 2009, the concentrations leveled off. In rural areas, the median concentrations of Σ6 i-PCB in ryegrass and curly kale were about 3 and 4 μg/kg dm in 2000, and have been about 0.5 and 1 μg/kg dm since 2009, respectively. Concentrations in spruce needles fell from 0.9 to 0.4 μg/kg dm. Median PCB-TEQ concentrations in the bioindicator plants ranged from 0.05 to 0.23 ng/kg dm between 2002 and 2009 and from 0.15 to 0.05 ng/kg dm after 2009. Indicator PCB and PCB-TEQ concentrations were several times higher at the urban station in Munich than at the rural areas, reflecting the emissions from in-use PCB stocks in the building sector. The likely reason of the slower decrease of PCB-TEQ compared to i-PCBs is the formation of PCB-126 by dechlorination of industrial PCBs in open applications.

Keywords PCB · Dl-PCB · Biomonitoring · Bioindicator plant · Time series · Buildings · Sealant · Paint · PCB-126 · Dechlorination

Introduction

Polychlorinated biphenyls (PCBs) are a group of man-made chemicals with a global former production volume of 1.3–2 million t (Breivik et al. 2002; Fiedler 2001). Dioxin-like PCBs (dl-PCBs) are of particular toxicological concern. The TEQ-reservoir (toxicity equivalent concentration) of worldwide-produced PCBs was estimated to be 11,000 to 16,000 kg PCB-TEQ$_{(1998)}$ (Weber et al. 2008). Analytical data, established after 1995 in different European countries, have revealed that the TEQ levels of dl-PCBs in food of animal origin are equal to or even higher than the TEQ levels of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) (Kerst et al. 2004; Malisch and Dilara 2007; Santillo et al. 2003). A considerable part of the European population may still exceed the tolerable weekly intake for dioxin-like contaminants of 14 pg TEQ/kg bw (body weight) established by the European Scientific Committee on Food (SCF) (EFSA 2012; SCF 2001). The levels of PCBs in human milk exceed the EFSA and WHO recommendations by a factor of more than 10 (UNEP 2013; Van den Berg et al. 2017).

Although PCB production was discontinued in western countries during the 1970s and 1980s (Breivik et al. 2002) and PCBs were completely banned by the Stockholm Convention in 2004 (Stockholm Convention 2004); they are one of the most common and widely dispersed persistent organic pollutants (POPs) in the environment and in human milk (UNEP 2013). There are still important sources of PCB

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emissions in the cities of Western Europe and North America (Gingrich et al. 2001; Harner et al. 2004; Gasic et al. 2010; Diefenbacher et al. 2015).

PCBs were produced for open and closed applications (Breivik et al. 2007; Jartun et al. 2009) for a wide range of uses (IARC 2016). One fifth of worldwide PCB production was used in open applications (Breivik et al. 2007), mainly in building sealants and paint. In comparison to PCBs in closed applications, they are more easily released into the environment. It is estimated that a considerable share of these open applications is still in use today (Gluege et al. 2017; Weber et al. 2015). Only in the last decade, PCBs in buildings and constructions have been identified as a major source of the present PCB emission and present environmental PCB contamination (Weber et al. 2015; Kohler et al. 2005; Jamshidi et al. 2007; Robson et al. 2010; Weber and Herold 2015; Diefenbacher et al. 2016).

PCBs are of high concern because of their toxicity, persistence, bioaccumulative properties, and long-range atmospheric transport. PCBs are carcinogenic and endocrine disrupting chemicals (EDCs) (European Commission 2016; Hotchkiss et al. 2008; IARC 2016). EDCs interfere with the body's endocrine (hormone) system and have harmful effects on human and animal health, even at very low exposure levels. Hormones act in very small amounts and at precise moments in time to regulate the body's development, growth, reproduction, metabolism, immunity, and behavior. Exposure to EDCs of children in the womb can have life-long effects and can even have consequences on the next generation (European Commission 2016; Hotchkiss et al. 2008). Studies from several industrial countries have shown that prenatal PCB exposure is associated with neurobehavioral and developmental deficits and lower IQ during childhood, even at PCB levels found in the general population (Longnecker et al. 2003). Humans who are exposed to PCBs are at increased risk of infections, reduced cognitive function accompanied by adverse behavioral effects, hypothyroidism, infertility, ischemic heart disease, hypertension, diabetes, liver disease, asthma, arthritis, and cancer (Carpenter 2006; IARC 2016; Lauby-Secretan et al. 2013). In 2013, PCBs have been listed as category 1 carcinogen (Lauby-Secretan et al. 2013; IARC 2016).

PCBs are ubiquitous in the food chain. Consumption of contaminated food of animal origin is a major pathway for the exposure of the population to PCBs in industrialized countries (WHO 1998). Terrestrial animals take up PCBs with contaminated plants and soil during grazing and foraging (Weber et al. 2015, 2017). In the aquatic environment, fish, mussels, and marine mammals are also impacted from PCB contamination (Assmuth and Jalonen 2005; Geyer et al. 1984; Guhl et al. 2014; Stuart-Smith and Jepson 2017).

Although the emissions of PCBs into the environment declined in the last decades, exceedances of EU-maximum levels in feed and food still occur. Therefore, there is a need for detailed studies to prevent further dispersion to the environment contributing to feed and food and finally to human exposure (Assmuth and Jalonen 2005; Guhl et al. 2014; Santillo et al. 2003; Weber et al. 2015, 2017).

For more than 20 years, the Bavarian Environment Agency (Bayerisches Landesamt für Umwelt; LfU) has been operating a biomonitoring network to assess the air quality. Plants are used as bioindicators for air pollution as vegetation integrates contamination over time. During that period biological measuring techniques for the determination and evaluation of concentrations of air pollutants on plants (bioindication) were developed, continuously improved, and integrated in German technical guidelines (VDI 2007; VDI 2008; VDI 2016). The standardization of methods is an essential step in order to obtain comparable results across sites and over time. Bavaria is a German federal state with abundant biomass including forests, grass, and agricultural land with related adsorption capacity.

The major aims of the immission monitoring with bioindicators are (Peichl 1997, 2001):

- The determination of background contamination levels and trends, as a basis for evaluation and early detection of pollution and pollution trends.
- The survey of (potentially) polluted areas and emission sources.
- The development of scientific and technical guidelines for environmental policy measures.
- The assessment of human exposure via the route plant → feed → foods of animal origin.

In this study, the results of PCB monitoring in standardized cultures of ryegrass, curly kale, and spruce needles from around 2000 to 2015 are presented and discussed.

Materials and methods

Biomonitoring of pollutants at monitoring stations in Bavaria

In the course of the last two decades, the LfU's monitoring network has covered a total of 10 permanent observation stations (POSs) (hexagonal marks in Fig. 1) for monitoring the immission of PCDD/Fs, PCBs, PAHs, and heavy metals with the bioindicator plants ryegrass and curly kale with approx. Two thousand samples measured. Currently, seven POSs are operated. The POSs are mainly characterized by air masses from the rural background. The POS in Munich is an exception, being the only location in an urban environment.

Since the 1970s, the LfU is operating a spruce needle monitoring network throughout Bavaria. Since 1999, PCBs are

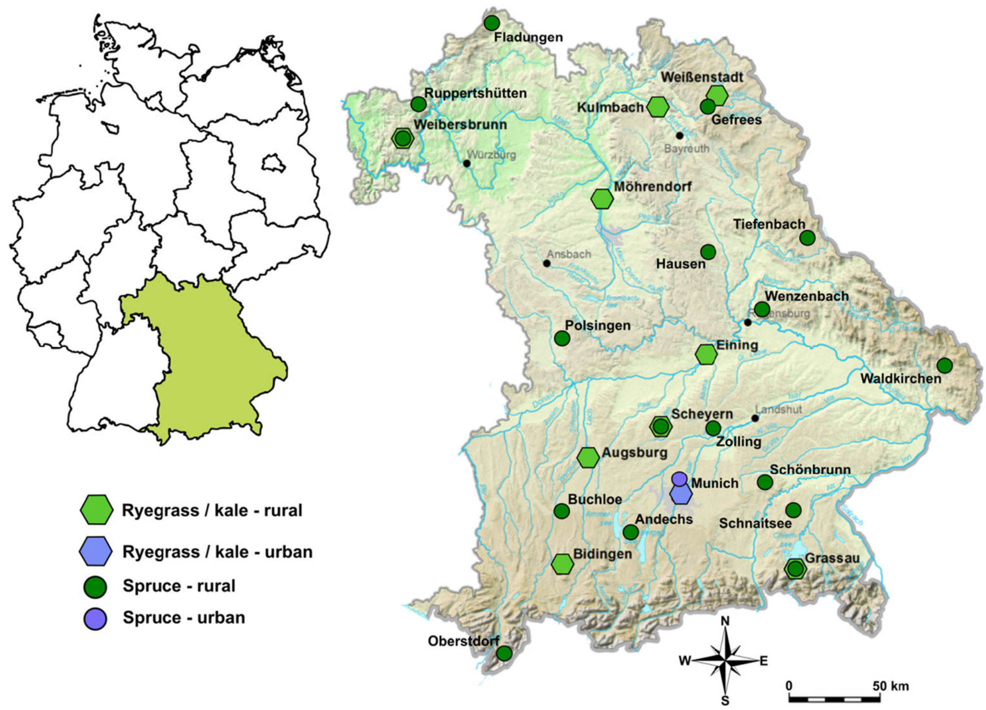

Fig. 1 Locations of the Bavarian permanent observation stations (POSs) for biomonitoring (hexagonal marks) and the monitoring network with spruce needles (filled circles) in Bavaria/Germany

measured. Data from 18 selected locations (17 rural and one urban site) are presented in this paper (filled circles in Fig. 1).

Sampling methods

Depending on the time of year, ryegrass, curly kale, and spruce needles were used to monitor the accumulation of the six indicator PCB congeners (i-PCB; PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, and PCB-180) and the twelve dioxin-like PCB congeners (dl-PCBs; PCB-77, PCB-81, PCB-126, PCB-169, PCB-105, PCB-114, PCB-118, PCB-123, PCB-156, PCB-157, PCB-167, and PCB-189).

For the biomonitoring, standardized methods were used including ryegrass (VDI 3957 Blatt 2) (VDI 2016) and curly kale cultures (VDI 3957 Blatt 3) (VDI 2008). All plants grow in a controlled substrate, without contact to the ground, at a height of 1.5 m. This guarantees the exclusive input of pollutants through the air as well as the best possible comparability between different locations.

The exposure time of ryegrass cultures (*Lolium multiflorum* Lam. ssp. italicum) is 4 weeks. Five exposure series are applied consecutively from May to September. At the same time, four–six cultures per site are exposed. Of the five exposure series, series 1–3 are combined to a pool sample. Thus, three data sets (May–July, August, and September) are available for ryegrass per site per year.

The exposure of the curly kale cultures takes place once a year over a period of 8 weeks, from October to November. At each site, four curly kale plants are exposed and sampled.

A standardized sampling procedure for "passive" biomonitoring with spruce needles has been used according to VDI guideline 3957, Blatt 11 (VDI 2007) at the respective stations of the Bavarian spruce-net.

Monitoring with spruce needles takes place at irregular intervals, with two sampling dates of needles from the same generation, during autumn and the consecutive spring. At the monitoring area, a certain amount of spruce shoots of the top crown area of three–five trees is sampled in autumn and at the same location in the following spring. For analysis only, the needles of the most recent needle year (first needle year) of spruce shoots are used. The top crown area of solitary trees or groves is chosen to ensure the best exposure to the wind.

The harvested sample material is packaged in aluminum foil and stored in air-tight PE bags. The samples are transported cooled (< 4 °C) and stored at − 18 °C until their preparation and analysis.

Laboratory analysis

The homogenized and freeze-dried samples are spiked with all 6 $^{13}C_{12}$-labeled i-PCBs and all 12 dl-PCB congeners before extraction. The sample materials are extracted by Soxhlet extraction with toluene for 24 h. A multistage liquid chromatographic for clean-up and separation of the PCB from the organic matrix is carried out. First, a multi-layer column with acidic and basic silica gel is applied followed by an alumina B column. I-PCBs and dl-PCBs/PCDD/F are analyzed separately (details of the procedures are described in LfU 2006). PCBs including dl-PCBs are measured with high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) (resolution = > 10,000). The limit of determination for the 18 PCB congeners (6 i-PCBs + 12 dl-PCBs) was 0.2 ng kg^{-1} dm for i-PCBs and mono-ortho dl-PCBs and 0.05 ng kg^{-1} dm for the non-ortho dl-PCBs. Measured concentrations were referred to 100% dry substance. For the calculation of PCB concentrations, the six Ballschmiter indicator congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, and PCB-180) (i-PCBs) are used. These six congeners are the most abundant congeners in technical PCB mixtures and thus are also marker congeners in the environment. Therefore, their sum can be regarded as a proxy to represent the level of PCB contamination. Toxic equivalent (TEQ) values for dioxin-like (dl-) PCBs were calculated according to WHO (2005) Toxic Equivalency Factor (TEF)-values (Van den Berg et al. 2006). The results of the long-term environmental monitoring are presented as the sum of the 6 i-PCBs and PCB-TEQ (WHO 2005 TEFs). Also, PCDD/PCDFs are measured but are not included in the current publication, focusing on PCBs.

Quality assurance and quality control

The laboratory is accredited for PCB and PCDD/F analysis according to DIN EN ISO/IEC 17025 by the German national accreditation body (DAkkS). The laboratory is participating every year in interlaboratory comparison tests for different matrices. Furthermore, an internal reference material (sewage sludge, later fly ash) is analyzed monthly to assure constant analytical quality and a maximum uncertainty of the PCB-TEQ value (and PCDD/F-TEQ) of 25% and of the sum of i-PCB concentrations of 20% over the whole long monitoring period. Additionally, the certified sediment reference material NWDX-3 has been analyzed and in recent years, the fortified cod liver oil EDF-5462 is used. Materials used for extraction and clean-up (e.g., silica gel and sodium sulfate) are heated to 500 to 600 °C before use to minimize PCB laboratory blanks. Each batch of a solvent is analyzed for possible PCB (and PCDD/F) blank values before first use. Laboratory blank samples are processed and analyzed in parallel to samples at least monthly. In few cases of implausible results (e.g., unexpected congener distribution), sample processing and analysis is repeated with residue material.

Results and discussion

Biomonitoring stations in Bavaria

The immission-induced pollutant input to an ecosystem can be evaluated by the accumulation in indicator plants. The standardization of biomonitoring methods is an essential step in order to obtain comparable results across sites and over time. The Bavarian LfU participated in the development/refining of VDI guidelines.

For about 20 years, the Bavarian LfU has been using the standardized cultures of ryegrass and curly kale for biomonitoring of PCBs, PCDD/Fs, PAHs, and heavy metals. Ten permanent observation stations have been operated at urban and rural areas (Fig. 1).

From 1992 to 2013, 536 spruce needle samples from 144 selected locations of the Bavarian spruce monitoring net were analyzed for PCDD/Fs. Since 1999, PCBs have been measured additionally. Data from 18 locations (Fig. 1) are evaluated in the following chapters.

The biomonitoring measurement using ryegrass and curly kale cultures are considered "active biomonitoring." The plants are grown under controlled conditions in a greenhouse, followed by the exposure period in the environment at the chosen locations.

The standardized sampling procedure for biomonitoring with spruce needles is considered "passive biomonitoring" since the samples are taken from spruce trees growing in their natural environment.

Time series of Σ6 i-PCBs in bioindicator plants

Indicator PCBs have been determined in ryegrass, curly kale, and spruce needles since 2000, 1997, and 1999, respectively, following standardized exposure and sampling methods (VDI 2007, VDI 2008, and VDI 2016).

The Σ6 i-PCBs for rural locations in Bavaria and for Munich are shown in Fig. 2. All values of rural sites are combined in a box plot for each exposure period. The green boxes represent data within the 25th and 75th quartile, the median value is shown as a black bar within the boxes, the 90th and 10th quantile are represented by the vertical lines and outliers are shown as black dots. The urban location (Munich), on the other hand, is included with individual values in the figures (blue-filled triangles).

Concentrations in the urban station Munich are markedly higher compared to background locations (see below and Figs. 2 and 3). In all bioindicators, a clear decrease of the i-PCB concentrations can be seen at rural sites until the year 2009. In the years after 2009, levels did not show a further decrease (Fig. 2).

From 2000 to 2009, median i-PCB concentrations in ryegrass dropped by 88% (from 4.04 to 0.47 μg/kg dm, start and end points of the regression curve) in rural locations and by 79% (from 11.20 to 2.31 μg/kg dm) in Munich.

There were particularly high PCB levels in Munich in August 2000 and August 2001, which were mainly caused by the low-chlorinated i-PCBs (PCB-28, PCB-52, and PCB-101). These values are likely to origin from releases from point sources of closed applications (capacitors/transformers or hydraulic oil) containing lower-chlorinated PCB mixtures

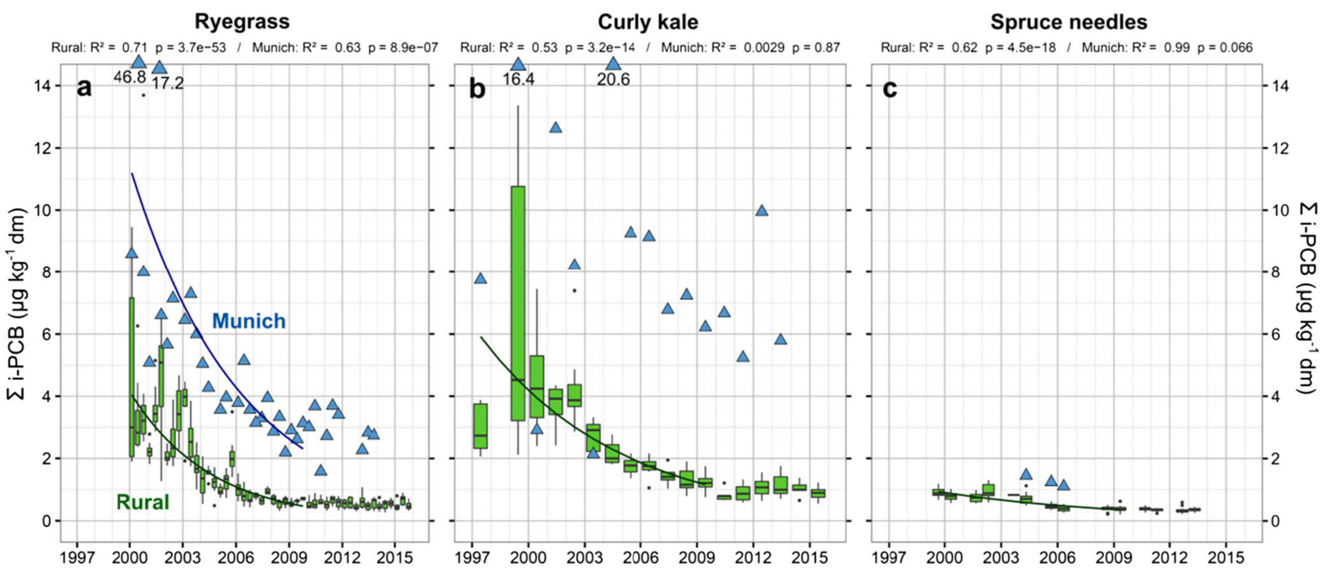

Fig. 2 Time series of i-PCB concentrations in ryegrass (**a**), curly kale (**b**), and spruce needles (**c**) in rural locations (green boxplots) and in Munich (blue triangles); trend lines are shown for significant trends

like Clophen A30 and A40, which relate to non-environmentally sound management of such equipment or oils. The management of PCBs in closed applications was largely concluded in Germany in the 1990s and early 2000. After 2001, none of the sampling stations particularly high levels of lower-chlorinated i-PCBs were detected.

In curly kale, median i-PCB concentrations declined by 80% (from 5.92 to 1.17 μg/kg dm) between 1997 and 2009 in the rural background. However, no significant decline could be observed at the urban site in Munich (Fig. 2). High levels in 1999 and 2004 in Munich, however, were mainly caused by the higher-chlorinated i-PCBs.

Median concentrations of i-PCBs in rural spruce needles decreased by 63% (from 1.0 to 0.37 μg/kg dm) between 1999 and 2009.

PCB congener patterns in the environment and inverse seasonal trends to PCDD/F emissions provide evidence that the source of PCBs are technical PCB mixtures and not emissions from combustion processes (Takasuga 2001; LfU 2006).

To determine possible trends in the time series, exponential regressions were calculated, as well as their coefficient of determination (R^2) and their probability value (p). The exponential model was chosen, as a decrease in PCB air concentrations is expected to follow an exponential behavior (Jones

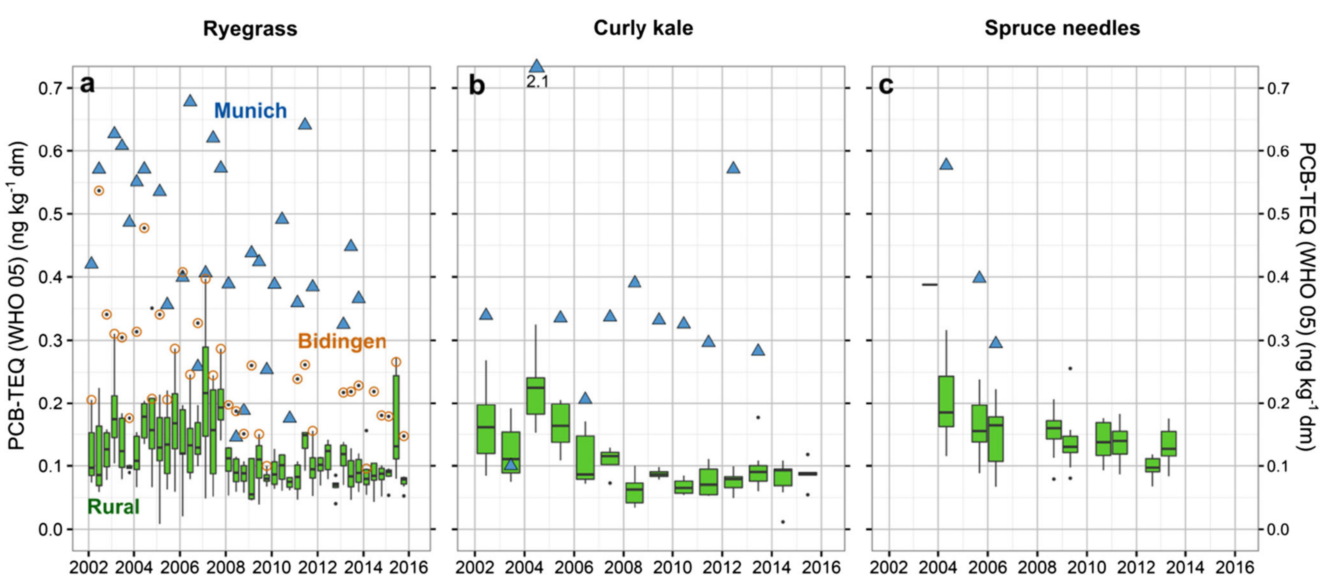

Fig. 3 Time series of the PCB-TEQ in ryegrass (**a**), curly kale (**b**), and spruce needles (**c**) in rural locations (green boxplots) and in Munich (blue triangles); Bidingen (orange circles in (**a**))

and De Voogt 1999) and for significant trends, the regression curves are integrated into the figures. However, it is clear that the underlying phase out of PCBs does not necessarily follow an exponential trend. The phase out of closed application has a certain deadline (2010 for EU member states and 2025 for Stockholm Convention). Reductions in PCB release until 2009 may be a result of the national implementation of the EU Directive 96/59/EC from 1996 on the disposal of polychlorinated biphenyls and polychlorinated terphenyls (PCB/PCT). This PCB/PCT Directive required an inventory of all equipment with more than 5 l of PCB containing fluids and disposal of those PCBs by the end of 2010 at the latest. Some peak emissions of the low-chlorinated industrial PCB mixtures used mainly in capacitors were detected in the urban station in Munich in ryegrass and curly kale (2000, 2001, 2004, and 2006 when the management of closed applications was finalized in Germany). No peak emissions of low-chlorinated PCB mixtures have been detected afterwards. Another relevant release potentially not managed within this deadline are the approximately 10,000 t of PCBs used in small capacitors in West Germany, mainly in fluorescent lamps. Small capacitors may progressively have reached the end of their operational life and might contribute to an exponential decrease. Still PCB releases from shredder plants are high, indicating that small condensers still contribute to current PCB release.

Emissions from open PCB applications are related to the quantities of PCBs that are present in buildings and other construction (e.g., metal constructions with PVC coatings or paint in swimming pools or road marking). Exponential decrease of emissions might reflect the exponential declining number of PCB-contaminated buildings/constructions as a result of refurbishment and demolition over time (Gluege et al. 2017). However, decline due to German government subsidy programs for basic renovation and energy-oriented modernization of buildings would not follow an exponential curve.

Since 2009, no significant decrease can be observed for the i-PCBs at any of the sites. In the three bioindicators, the values have now settled at median levels of about 0.54 μg/kg dm for ryegrass, 0.99 μg/kg dm for curly kale, and 0.36 μg/kg dm for spruce needles. This continuous input into the bioindicators shows that PCB sources with ongoing release are still present today. Concentrations at rural sites all over Bavaria are generally quite similar. This may be an indication that there is a large number of relatively weak PCB sources distributed all over the country like open applications in the building sector and possibly metal utility poles or old road marking but also reservoirs from disposed PCBs containing waste including contaminated building debris.

During the entire observation period, the values from the long-term observation station in Munich were higher by a factor of 4 in ryegrass and higher by a factor of 5 in curly kale (Fig. 2). For spruce needles, data from Munich is only available for three consecutive years (2004–2006), and concentrations of i-PCBs at the urban site were two to three times higher than at the rural locations. Higher PCB levels for Munich compared to the rural areas are consistent with the data from other European countries and from North America, which show that cities are sources of PCB emissions and that there is an urban–rural gradient in PCB air concentrations (Csiszar et al. 2013; Harner et al. 2004; Jamshidi et al. 2007; Gasic et al. 2010; Khairy et al. 2015). This is also in agreement with the observation that at least in industrial countries today, still primary sources are dominating for air contamination compared to secondary sources such as re-emission from soils (Csiszar et al. 2013; Jamshidi et al. 2007; Schuster et al. 2010).

A decreasing trend is, however, also seen in the environment including industrial countries (Breivik et al. 2007; Schuster et al. 2010). That the peak emission in industrial countries to the environment have occurred in the 1970s at the time of the use of open PCB applications (also short-term open applications like cutting oils, lubricants, or impregnated paper in addition to long-term open applications like sealants and paints) have also been documented by a long-term study of PCBs in soils amended with sewage sludge (Umlauf et al. 2004, 2011).

Time series of PCB-TEQ

Analyses of ryegrass and curly kale for dl-PCBs started in 2002 in the permanent observation stations and 1 year later in the spruce monitoring net. Time series of PCB-TEQ (2005) for Munich and the rural sites are shown in Fig. 3. During the observation period, the PCB-TEQ concentrations in the three bioindicator plants were at comparable levels. In Munich, PCB-TEQ values are significantly higher compared to the rural background, namely by a factor of 4 on average in ryegrass and curly kale, and by a factor of about 2.5 in spruce needles.

PCB-TEQ concentrations in ryegrass do not show a significant declining trend, both in rural locations and at the urban site. Nevertheless, median concentrations at rural sites are lower in the years after 2008 (range 0.06 to 0.15 ng PCB-TEQ/kg dm) than in the years before (range 0.09 to 0.22 ng PCB-TEQ/kg dm). The levels in grass could still be relevant for human exposure via milk/meat products (BfR 2003).

Among the rural observation stations is a single location (Bidingen) with constantly increased PCB-TEQ values (orange circles in Fig. 3). However, i-PCBs are not significantly elevated in ryegrass and curly kale at the same location. Here, a local dl-PCB source seems to be present.

PCB-TEQ concentrations in curly kale at rural locations show a declining trend between 2002 and 2015 (decline by 44% from 0.16 to 0.09 ng PCB-TEQ/kg dm; median values from 2002 and 2015, respectively) but no decline can be seen at the urban site.

PCB-TEQ concentrations in spruce needles declined significantly between 2004 and 2013 by 42% (from 0.19 to 0.13 ng PCB-TEQ/kg dm; median values from spring 2004 to spring 2013, respectively).

As for i-PCBs and also for the PCB-TEQ, no decline can be seen since 2008 in ryegrass, curly kale, and spruce needles at rural locations. In the period 2008 to 2015, the median PCB-TEQ concentration was at 0.09 ng PCB-TEQ/kg dm for ryegrass, 0.08 ng PCB-TEQ/kg dm for curly kale, and 0.13 ng PCB-TEQ/kg dm for spruce needles (2008 to 2013).

PCB-TEQ concentrations in the bioindicators did not drop by the same amount as did i-PCB concentrations. For the urban site, a significant decline of the PCB-TEQ cannot be observed.

Ratio of higher- to lower-chlorinated i-PCBs in ryegrass

In ryegrass, the decline for the three lower-chlorinated i-PCB congeners was stronger than for the higher-chlorinated i-PCBs. Figure 4 shows the temporal behavior of the ratio of the high-chlorinated i-PCBs (sum of PCB-138, PCB-153, and PCB-180) to low-chlorinated i-PCBs (sum of PCB-28, PCB-52, and PCB-101) (Cl-ratio) for the three different exposure series (May–July, August and September). The boxplots include all monitoring stations. In Fig. 4, an increase of the Cl-ratio is clearly visible for August. For the other exposure series, an increase is also visible, but less pronounced. To make the increase of the Cl-ratio clearly visible, linear regressions are depicted for the different exposure series in Fig. 4. As visible from the coefficients of determination (R^2), the linear regressions do only represent a smaller part of the data. Nevertheless, they indicate the increasing Cl-ratio.

The more pronounced decrease of lower-chlorinated PCBs, compared to higher-chlorinated PCBs, has two likely reasons: Firstly, closed PCB applications often contained lower-chlorinated PCB mixtures, such as Clophen A30 or Clophen A40, whereas open PCB applications almost always contain the higher-chlorinated mixtures Clophen A50 (sealants) or Clophen A60 (paint). In Germany, approx. two thirds of the used PCBs (60,000 t) had been related to closed applications mainly in transformers, capacitors, and hydraulic oils (Detzel et al. 1998; Knetsch 2012). The major disposal management of closed applications was conducted from the 1980s to early 2000. Transformers and capacitors were not always properly handled and disposed, 30 to 50% were not appropriately managed (Detzel et al. 1998). This resulted in a considerable release to the environment and to landfills (Detzel et al. 1998). Therefore, it can be expected that the release of lower-chlorinated i-PCBs is markedly reduced after phase-out of open PCB applications, whereas emissions of higher-chlorinated PCBs from open applications is not. This is also supported by the occurrence of extremely high levels of low-chlorinated i-PCB in bioindicators in Munich in 2000 and 2001. No occurrence of elevated concentrations of low-chlorinated i-PCB was detected since then.

Secondly, the congener profile of emissions from open applications (partly also containing Clophen A40) should move towards higher-chlorinated PCBs with exposure time, because lower-chlorinated congeners evaporate more easily and the surface layer of open applications gets depleted of lower-chlorinated PCBs.

Both effects might play a role in the increased ratio of higher- to lower-chlorinated i-PCBs.

Also, within single sampling years, some variation of the ratio of higher-chlorinated i-PCBs to lower-chlorinated i-PCBs can be observed. The ratio is in average somewhat higher for the measurements in August compared to September and May–July (see regression lines in Fig. 4).

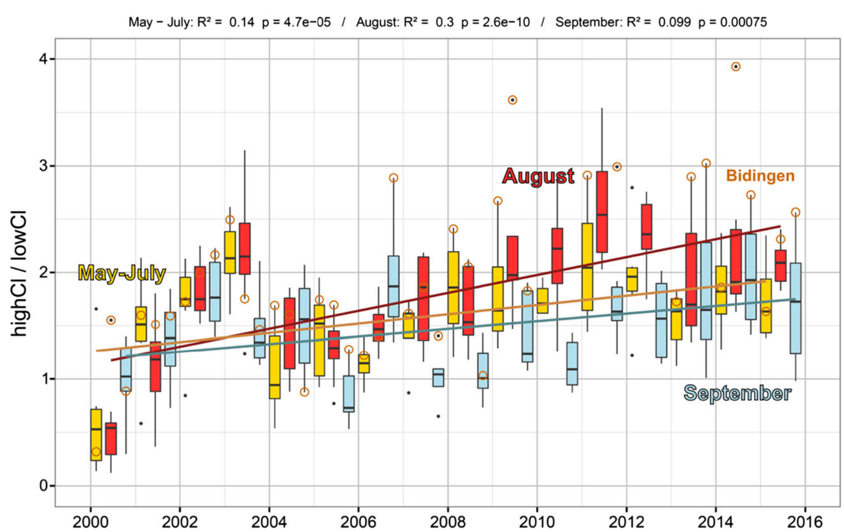

Fig. 4 Time series of the ratio higher-chlorinated i-PCBs to lower-chlorinated i-PCBs at all permanent observation stations in Bavaria/Germany; measurements in May–July (yellow boxplots), August (red boxplots), and September (blue boxplots); orange circles for Bidingen

These differences are probably triggered by the higher average temperatures in August compared to May–July and September. In ambient air, the high-chlorinated PCB show a stronger increase in the gas phase with increasing temperatures compared to the low-chlorinated congeners, which show a less strong increase (Falconer and Bidleman 1994).

Ratio of PCB-126-TEQ to higher-chlorinated i-PCBs

As described above, the PCB-TEQ did not decrease in a similar manner like the i-PCBs over time (Figs. 2 and 3). Just like the Cl-ratio, also the ratio of PCB-126 (dominating the PCB-TEQ) to high-chlorinated i-PCBs increases over time (Fig. 5). Since PCB-126 and the PCB-TEQ are considerably relevant for the contamination of meat, eggs, and feed (Weber et al. 2014, 2015), this observation shall be shortly discussed.

Different time trends for i-PCBs and dl-PCBs/PCB-126 could be an indication of different sources. For example, PCDDs/Fs and dl-PCBs are both formed during combustion processes (Sakurai et al. 2003) in addition to the release from technical PCB mixtures. However, PCDD/F concentrations in bioindicator plants increase during the heating period in autumn and winter (LfU 2006) and PCB-TEQ/PCB-126 concentrations do not show this behavior. In addition, PCDD/F immission is highest in winter and lowest in summer, whereas dl-PCB/PCB-126 and PCB-TEQ air concentrations show the same seasonal trend as the indicator PCBs, with the highest values in summer and the lowest in winter in Bavaria (LfU 2006). Therefore, also for dl-PCB, the main sources of emission are likely to be industrially produced PCB mixtures. The most reasonable explanation for the slower decrease of PCB-TEQ compared to the decrease of i-PCB (Figs. 2, 3, and 5) in the last 20 years, is a slow dechlorination of higher-chlorinated PCBs from open applications (mainly from Clophen A 60 and partly from A 50), resulting in the formation of PCB-126 (responsible for > 90% of PCB-TEQ) and other dl-PCBs (Miao et al. 1999). UV dechlorination of PCBs takes place with a preference in ortho-position. With coplanar PCB, the UV-degradation rate is reduced (Barr et al. 1997, Miao et al. 1999, Chang et al. 2003).

This is also evident from analyzing original Clophen A60 mixtures and Clophen A60-based paints applied decades ago. In the original Clophen A60 mixtures, PCB-126 is not detected (< 0.2 μg PCB-126-TEQ/g i-PCB) (Takasuga et al. 2006). In Clophen A60-based paints (indoor painting of a cow stable in Switzerland) exposed for several years to ambient conditions, PCB-126 was detected in relevant concentrations (1.1 and 2.5 μg PCB-126-TEQ/g i-PCB) (Weber et al. 2015; Zennegg et al. 2014). Furthermore, in Clophen A60-based swimming pool paints with long-term exposure to direct sun light, high PCB-126 levels were detected (22.5 μg PCB-126-TEQ/g i-PCB) (Weber et al. 2015). Therefore, the slight degradation/dechlorination of highy chlorinated PCB mixtures from open applications (paint and sealants) and associated formation of PCB-126 is likely the main driver for the lower decrease of PCB-TEQ compared to the decrease of i-PCBs (Figs. 2, 3, and 5).

Conclusions

A long-term biomonitoring of PCBs (and other environmental pollutants) has been established in Bavaria/Germany with the standardized indicator plants, ryegrass, curly kale, and spruce needles.

Since the beginning of the biomonitoring of PCBs at the end of the 1990s, a general reduction in the entries of PCBs was observed. However, during the last decade, the concentrations reached a low but constant plateau. In particular, the indicator PCBs, dominated by the three higher-chlorinated congeners (PCB-138, PCB-153, and PCB-180), show this behavior and point towards ongoing sources from the field of open applications in the building sector. Indicator PCBs and PCB-TEQ concentrations were several times higher at the urban station (Munich) than at the rural areas, also reflecting the emissions from in-use PCB stocks in the building sector.

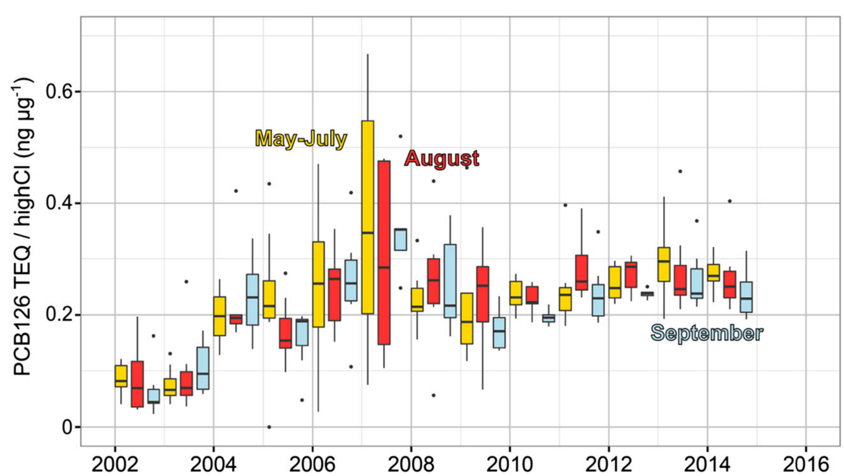

Fig. 5 Time trend of the ratio PCB-126 to high-chlorinated i-PCBs in ryegrass at all permanent observation stations in Bavaria/Germany; measurements in May–July (yellow boxplots), August (red boxplots), and September (blue boxplots)

Also, disposed or recycled PCB containing waste, e.g., from the construction sector likely contribute to emissions.

Besides these primary PCB sources, also secondary sources, like re-emission from the soil, contribute to an extended lifetime of PCB in air. However, the effect of re-emissions is considered to be of minor importance compared to primary sources at least in industrial countries (Csiszar et al. 2013; Jamshidi et al. 2007; Schuster et al. 2010).

Dioxin-like PCBs have not decreased in a similar manner and nowadays show only slightly smaller entries than at the beginning of the monitoring. The PCB-TEQ concentration in grass (around 0.1 ng TEQ/kg dm) could still be relevant for human exposure via milk products and meat (BfR 2003).

The reason for this less pronounced decline is most probably the formation of PCB-126 due to photolytic dechlorination of higher-chlorinated congeners. This process is likely to occur in the remaining PCBs from open applications in the construction sector, which are often highly chlorinated mixtures (Clophen A60 and A50) and partly exposed to solar radiation.

It is evident that even decades after the ban on the use of PCBs and the management of PCBs in closed applications, there are still relevant sources for PCBs for the environment and human exposure. Therefore, the control of PCB stockpiles and in particular of PCBs in the construction sector still remains important.

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