209 PCBs in Different Species from the German Environmental Specimen Bank – Concentration Levels and Pattern of PCBs

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1 Introduction

Twenty years ago, polychlorinated biphenyls (PCBs) were listed as persistent organic pollutants (POPs) under the Stockholm Convention and the parties committed to cease their production and use. Today, the implementation process targets remaining stocks and residues of technical PCB mixtures. However, it is now known that some PCBs can also be newly formed during production processes or in products and released from there into the environment. Such PCBs that are not produced by purpose but formed unintentionally are referred to here as non-technical PCBs.

Examples for the environmental relevance of non-technical PCBs from recent years are e.g. high concentrations in environmental samples from the contamination of dyes and pigments Furthermore, there are indications for the long-range transport potential of dichlorinated PCB 11, which was detected in environmental samples from Arctic regions. In addition, PCB profiles in environmental samples show levels of the indicator PCB 52 that are significantly higher than would be expected based on the composition of the technical mixtures 1. Furthermore, the congeners PCB 35 and PCB 77 as well as the highly chlorinated PCBs 206 to 209 were found as typical non-technical PCBs in various dye and pigment samples. In addition to possible direct exposure of consumers, there is a risk that these substances may be found in waste and recycled products such as recycled paper. Another source for the formation and release of non-technical PCBs is the use of the crosslinker bis-(2,4-dichlorobenzoyl)-peroxide in the production of silicone rubber. Typical impurities formed in the product include PCB 47, PCB 51 and PCB 68. Although the potential for PCB formation from this process was known for a long time, production plants using this process were still operated for a long time. When particle emissions from a plant in North Rhine-Westphalia (Germany) were investigated, it became apparent that environmental pollution occurred due to this process 2. In addition, other studies have also documented outgassing of these PCB congeners from finished products, which can lead to problematic indoor air pollution 3.

Looking on all 209 PCBs, the aim of this study is to clarify whether and to what extent non-technical PCBs have already been released into the environment from products or production processes in Germany (quantities and congeners). Biota and non-biota samples from typical ecosystems types in the terrestrial, riverine and limnic compartment of the German Environmental Specimen Bank were used to investigate the distribution, potential pathways as well as potential sinks of the 209 PCBs.

2 Materials and Methods

Samples For this study limnic (bream muscle and liver, soft body of quagga and zebra mussel, suspended particulate matter (SPM)), marine (eelpout muscle, soft body of blue mussel, herring gull eggs) and terrestrial samples (coniferous shoots, deciduous tree leaves, earthworm, deer liver, soil) – in total 81 samples – from the German Environmental Specimen Bank were chosen. Biota samples have been collected annually since the late 1980s by the ESB Project Team, Trier University, Germany, suspended particular matter by the German Federal Institute of Hydrology (BfG), Koblenz, Germany (since 2016). Soil sampling was performed by Fraunhofer Institute for Molecular Biology and Applied Ecology (Fraunhofer IME), Department Environmental Specimen Bank, Schmallenberg, Germany. Sampled material was processed, cryomilled and archived in sub-samples at temperatures below -150°C by Fraunhofer IME. Sampling and processing were performed under well-defined and reproducible conditions according to standard operating procedures [4]. Sampling areas covered different ecosystem types: agrarian ecosystems, ecosystems close to conurbations, forestry ecosystems, marine ecosystems, nearly natural terrestrial ecosystems and freshwater ecosystems (see table 1 for details).

Analysis of all 209 PCBs. Typical sample intakes for the analysis are presented in table 1. Samples were spiked with a mixture of 35 $^{13}C_{12}$-quantification standards (Mono- to DecaCB) before extraction. Extraction was carried out by means of Soxhlet extraction using an appropriate mixture of organic solvents depending on the single matrix (including toluene, hexane or dichloromethane). Clean-up was performed by column chromatography using a combination of sulphuric acid treated silica and activated alumina. An additional set of 7 $^{13}C_{12}$-labelled PCBs (Di- to NonaCBs, except HeptaCBs) was added to the cleaned extract as recovery standards.

The following HRGC separation was performed on an HT8-PCB 60m x 0.25 mm x 0.25 µm GC-column using Thermo DFS and Waters Autospec high resolution mass spectrometers at mass resolution R ≥ 10.000. With the chosen setup, a separation of about 180 signals of constant data quality is possible. Quantification was performed using the isotope dilution method resulting in the quantification of 155 individually separated PCB-congeners, 20 co-eluting pairs of PCB congeners and two data sets each for three resp. four co-eluting PCBs.

QA/QC measures consisted e.g. in monitoring the quantification standard recovery rates (acceptance 60-120%), as well as blanks and control samples. The limits of quantification were calculated based on an approach according to EN1948-4 using the average laboratory blank level plus 5-fold standard deviation. Further details of the method and quality criteria are described elsewhere [5].

Table 1: Samples of the German Specimen Bank in this study

Compartment	Ecosystem type	Specimen	Number of sampling areas	Year of sampling
Terrestrial	Agrarian	Deer (liver)	2	2019
		Earthworm (body without gut content)	2	2019
		Spruce (shoots)	2	2019
		Beech (leaves)	2	2019
		Soil (organic layer or topsoil)	2	2018 or 2019
		Bream (muscle)	1	2019
		Bream (liver)	1	2019
		Zebra mussel	1	2019
	Conurbations	Deer (liver)	2	2020
		Earthworm (body without gut content)	2	2019 or 2020
		Spruce (shoots)	2	2018 or 2021
		Lombardy poplar (leaves)	2	2020
		Soil (organic layer or topsoil)	3	2018
	Forestry	Earthworm (body without gut content)	1	2013
		Spruce (shoots)	2	2019
		Beech (leaves)	2	2019
		Soil (organic layer or topsoil)	1	2018
	Nearly natural terrestrial	Deer (liver)	1	2020
		Spruce (shoots)	3	2020
		Beech (leaves)	3	2020
		Soil (organic layer or topsoil)	3	2014 or 2018
	Not classified	Spruce (shoots)	1	2018
Freshwater		Bream (muscle)	7	2019 or 2020
		Bream (liver)	7	2019 or 2020
		Zebra mussel	3	2019 or 2020
		Quagga mussel	5	2019 or 2020
		Suspended particulate matter (SPM)	8	2015 or 2019
Marine		Eelpout (muscle)	3	2021
		Blue mussel (soft body tissue)	3	2019 or 2020
		Herring gull (egg)	3	2021

3 Results and Discussion

Mean concentrations of non-technical PCBs as defined in this study (see also table 2 for details) are shown in figure 1. Concentrations of non-technical PCBs are highest in liver of bream, followed by herring gull eggs. In general, concentrations of non-technical PCBs seem to be higher in limnic ecosystems than in marine or terrestrial ecosystems. Looking at the share of non-technical PCBs in the total concentration of all PCBs (table 3), the limnic ecosystems show higher shares, whereas terrestrial and marine ecosystems seem to show quite similar shares (with the exception of earthworms). Looking on differences between the "non-living" environmental samples (soil and suspended particulate matter) versus the "living" environmental samples it seems that in limnic ecosystems the share of non-technical PCBs in all PCBs is equal (fish) or higher (mussels) for the "living" species. In terrestrial ecosystems this share is rather more equal or lower (exception: earthworm).

Table 2: Non-technical PCBs as defined in this study

Group	IUPAC-Code	Structure	Remark
DiCB	PCB 11	3,3'-Dichlorobiphenyl	
TriCB	PCB 35	3,3',4-Trichlorobiphenyl	
TetraCB	PCB 47	2,2',4,4'-Tetrachlorobiphenyl	Co-elution with PCB 48, PCB 65, PCB 75
	PCB 51	2,2',4,6'-Tetrachlorobiphenyl	
	PCB 52	2,2',5,5'-Tetrachlorobiphenyl	Co-elution with PCB 69

	PCB 68	2,3',4,5'-Tetrachlorobiphenyl	
	PCB 77	3,3',4,4'- Tetrachlorobiphenyl	
NonaCB	PCB 206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	
	PCB 207	2,2',3,3',4,4',5,6,6'- Nonachlorobiphenyl	
	PCB 208	2,2',3,3',4,5,5',6,6'- Nonachlorobiphenyl	
DecaCB	PCB 209	2,2',3,3',4,4',5,5',6,6'- Decachlorobiphenyl	

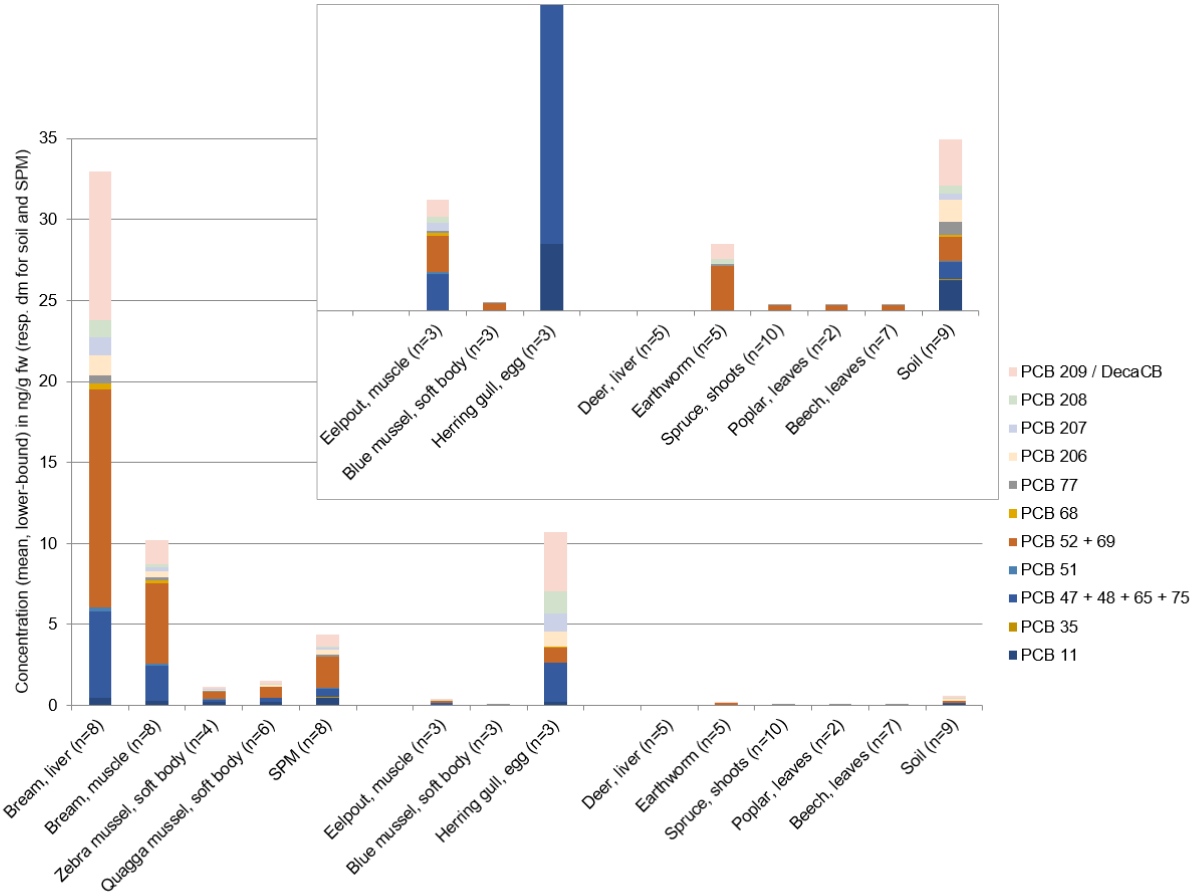

Figure 1: Concentrations (mean, lower-bound) of non-technical PCBs for different sample species (in ng/g dry matter for soil and suspended particulate matter resp. ng/g fresh weight for all other species)

Looking at the pattern of non-technical PCBs, all congeners given in table 2 were found in the fish, mussel and SPM samples from German limnic environments. In marine and terrestrial samples, only some of these PCBs could be quantified. PCB 52 (as co-elution with PCB 69) is the predominant congener in most samples analysed, with the exception of eggs from herring gull, deer liver and soil samples, where PCB 209 has the highest concentrations of the non-technical PCBs. This seems conclusive considering that herring gulls feed on terrestrial food sources in the coastal area before and during the breeding season and only switch to food from the marine food web after the chicks have hatched. PCB 47 (co-elution with three other PCB-congeners), PCB 209, PCB 77 and PCB 11 complement the profiles of non-technical PCBs in varying proportions.

Table 3: Share of non-technical PCBs (sum, lower-bound value) in all 209 PCBs (sum, lower-bound values)

Limnic ecosystems					Marine ecosystems			Terrestrial ecosystems					
Bream, liver (n=8)	Bream, muscle (n=8)	Zebra mussel (n=4)	Quagga mussel (n=6)	Suspended particulate matter (n=8)	Eelpout, muscle (n=3)	Blue mussel(n=3)	Herring gull. egg (n=3)	Deer, liver (n=5)	Earthworm (n=5)	Spruce shoots (n=10)	Lombardy poplar, leaves (n=2)	Beech leaves (n=7)	Soil (n=9)
2,9%	2,8%	5,2%	3,5%	2,8%	1,2%	1,1%	0,9%	0,1%	4,6%	2,2%	0,8%	1,6%	2,0%

4 Conclusions

Marine, limnic and terrestrial ecosystems in Germany are exposed to non-technical PCBs from the use of products or production processes, since they were detected in all environmental samples of this study, whereas the frequency of occurrence, concentrations and patterns varied between samples. Sources, pathways and / or sinks vary between the compartments (marine, limnic, and terrestrial) and further investigations are needed to understand their environmental fate and transport. The results shown here are to be regarded as a screening study due to the small number of samples, but impressively demonstrate the need for further investigations of non-technical PCBs, which may be in the shadow of the indicator compounds without justification.

5 Acknowledgments

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6 References

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