

Between Underground and the Deep Blue Sea: Contamination of Mine Water Effluents by Polychlorinated Biphenyls (PCBs)

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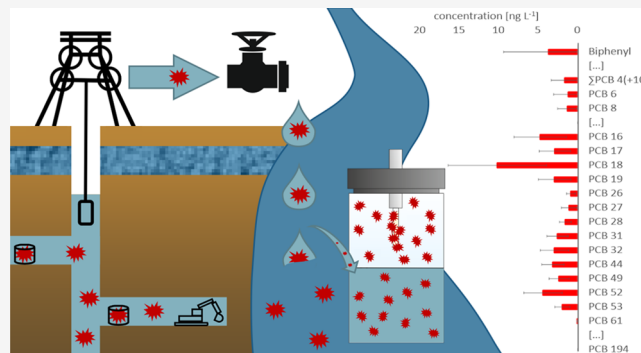
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ABSTRACT: Polychlorinated biphenyls (PCBs) were used as industrial chemicals due to their beneficial physicochemical properties in many applications until the recognition of their adverse effects. Although being banned for decades, PCBs are still ubiquitous in the environment due to their congener-specific high persistence and their ongoing remobilization from contaminated sites. While mining influenced water (MIW) was generally known to be a potential source of PCB contamination, hardly anything was known about concentrations, congener patterns, or PCB loads. For further elucidation of environmental risks, 14 MIW samples from five mine water effluents were analyzed for a set of 58 PCB congeners and biphenyl by a specifically optimized SPME-GC-MS method (LOD 0.004–0.58 ng L⁻¹). As a result, 53 mono- to heptachlorinated congeners could be detected in concentrations of 0.01–25.9 ng L⁻¹ per congener, of which mainly tri- but also di- and tetrachlorinated PCBs were identified in higher concentrations. Total PCB concentrations (0.02–0.12 mg m⁻³) and annual loads (0.1–0.7 kg PCBs a⁻¹ per mine) show the relevance of MIW as an additional point source for PCB release to the environment. Implementation of water treatment is recommended to achieve a decrease in these contaminant loads in agreement with worldwide efforts to eliminate PCBs.

KEYWORDS: persistent organic pollutants (POPs), legacy contaminants, solid-phase microextraction (SPME), PCB congeners, Clophen, planetary boundaries, novel entities, sustainable development goals (SDGs)



INTRODUCTION

Persistence, mobility with widespread distributions, and potential effects on earth-system processes were identified as key criteria raising major concern for substances if introduced to the environment.^{1,2} All of this is true for the group of polychlorinated biphenyls (PCBs), former industrial chemicals, which belong to the group of persistent organic pollutants (POPs) that have been banned worldwide by the Stockholm Convention since 2001³ but are still ubiquitously found in the environment, including the deep sea.^{4–7} As bioaccumulative substances, they concentrate in the adipose tissue of organisms and can harm entire marine predatory populations, even leading to their extinction.^{8–11} PCBs are discussed to be high-impact POPs based on hazard and production volumes^{12,13} for which an environmentally sound management is requested by 2028.^{14,15} Due to fire protection regulations, PCBs were also used in mining activities according to local health and safety regulations. Electrical equipment containing PCBs was used in both open-cast mining and underground. PCBs are found in transformers, drums that used transformer oil, in capacitors, and in ballasts for fluorescent lamps.¹⁶ Typical places of use are transformer stations, mine cars, electric locomotives, extraction machines, and conveyor belts.¹⁶ Because of leak accidents and

leaving behind entire machinery, mines can be polluted with PCBs until today. This has been reported by mine operators, authorities, and public media, but to the best of our knowledge, peer-reviewed studies have still been lacking until now. As a result of precipitation or groundwater inflow, mine workings are constantly subjected to water flow. Rising water levels during mine flooding can result in the release of PCBs from abandoned machinery and contaminated surrounding areas. Consequently, PCBs either get dissolved in mine water or are sorbed to and transported with suspended matter. This mining influenced water (MIW) is permanently pumped and discharged to surface waters to prevent flooding of active mines, or to prevent its uncontrolled surface discharge, or entry to groundwater in abandoned mines.^{17,18} Due to high dissolved salt and metal concentrations or rather reductive conditions, the composition of MIW can be extreme compared to that of

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surface water, which can cause adverse environmental effects in receiving water courses.¹⁹ Surveys of mine water and surface water in the vicinity of MIW discharges have been initiated by authorities and revealed low concentrations of dissolved indicator PCBs, reported in non-English gray literature such as reports and expert opinions.^{20,21} Although mainly technical mixtures with lower chlorination degrees have been used in mines, PCB analyses in the previously mentioned reports have been mainly limited to the six indicator PCBs. Analysis of these PCBs was based on either indirect determination of concentrations in rivers near discharge points²⁰ or highly laborious solvent extraction from 100 L samples.²¹ The use of miniaturized and solvent-free solid-phase microextraction (SPME)^{22–25} seems promising for PCB extraction from MIW. Coupled with gas chromatography-mass spectrometry (GC-MS), it can provide simple and fast extraction and analysis. However, because sample matrix can play a particular role in extraction by SPME, the analysis of PCBs in MIW can be highly challenging due to matrix effects caused by pH, dissolved salts, metals, sulfate, and suspended matter, which are specific to different mines.^{18,26} Although previously used for the analysis of PCBs,^{27–30} SPME was not yet applied for the detection of PCBs in MIW. Generally, peer-reviewed studies that related PCBs to mining investigated river water³¹ and sediments³² near mine water discharges. Therefore, data on PCB concentrations in MIW are still missing in the scientific literature. Furthermore, data on the occurrence of additional PCB congeners, their concentrations, relative patterns, and loads in MIW are still lacking. Consequently, the aims of the present study were (i) to optimize an SPME method with regard to low detection and quantification limits (LOD/LOQ) that can be applied to the analysis of PCB congeners in MIW and MIW-influenced streams; (ii) to elucidate total PCB concentrations in discharged MIW and to estimate their total annual loads; and (iii) to elucidate congener-specific PCB patterns in discharged MIW with respect to different mines as well as time-dependent changes within specific mines. Hence, the presence of biphenyl and 58 selected PCB congeners was investigated at five different sites, of which three were sampled four times within 2 years.

MATERIALS AND METHODS

Chemicals. Congener selection for PCB analysis was based on a prescreening of MIW on PCB-specific masses and chlorine patterns combined with the comparison of relative retention times (RTs) given in the literature. Standards of biphenyl and 58 PCB congeners were purchased (neat, purities $\geq 96.9\%$, Dr. Ehrenstorfer brand, LGC, U.K.) and prepared as stock solutions of single substances in methanol and mixed to working solutions. For the internal standard (IS) mix, biphenyl-*d*₁₀ (neat, purity $\geq 96.5\%$, LGC), deuterated PCB congeners (neat, purity $\geq 97\%$, CDN Isotopes, Pointe Claire, Canada), and ¹³C labeled PCB congeners (purity $\geq 98\%$ in nonane, redissolved in methanol, Wellington Laboratories, Canada) were combined and diluted in methanol. Further details can be found in the [Supporting Information](#) (SI), before Table S1.

HS-SPME-GC-MS Method Optimization. Following previously reported SPME methods for the analysis of PCBs,^{27–30} we have made efforts on further optimization and refinement that aimed at the specific MIW matrix and specific congener composition, available fiber coatings including newly produced fiber types, and further on the

optimization of extraction yields regarding extraction parameters as given below. For optimization, we relied on basic descriptions in the literature^{25,33,34} as well as experience from our own previous research.^{35–38} With sufficient volatilization of target analytes under elevated temperatures, the extraction of analytes from the gas phase above the aqueous sample by headspace (HS)-SPME is advantageous over direct immersion (DI)-SPME, where the fiber is in direct contact with the aqueous sample. Extraction by HS-SPME better preserves the fiber from wear and aging and reduces the parallel extraction of matrix components, which can further lead to a better signal-to-noise ratio. Therefore, method development for the simultaneous extraction of biphenyl and 58 PCBs included the optimization of HS-SPME extraction parameters, i.e., fiber coating (seven different fiber types, see below), extraction temperature (40–90 °C in 10 K steps), extraction time (10–50 min in 10 min steps), intensity of sample stirring during extraction (250–700 rpm, six intensities), desorption time (1–3 min), and fiber cleaning time (0–21 min in 3 min steps). These were modified aiming at extraction efficiency, considering the highly varying physicochemical properties of all PCBs but with a focus on low-chlorinated PCBs and biphenyl. Investigated fibers (Supelco/Merck, Darmstadt, Germany) were 50/30 μm mixed phase of divinylbenzene, carboxen, and polydimethylsiloxane (DVB/CAR/PDMS); 7 and 100 μm PDMS; 65 μm mixed phase of DVB/PDMS as both StableFlex and nitinol core fiber; and 85 μm polyacrylate (PA). The following procedure gives the optimized conditions for lower-chlorinated PCBs (biphenyl and mono- to trichlorinated congeners): samples were equilibrated in the agitator at 75 °C for 11 min at 500 rpm and afterward extracted in the agitator for 30 min with a 65 μm nitinol core fiber with DVB/PDMS coating. Subsequently, the fiber was transferred to the injector of the GC-MS system, where it was thermally desorbed for 3 min at 240 °C. For higher-chlorinated PCBs (tetra- to octachlorinated congeners), the samples were equilibrated and extracted at 80 °C with a 100 μm PDMS fiber. Information on quality assurance and quality control is given in the [SI](#) before Table S1.

Analyte correction of PCBs by IS, both for correction of instrumental variations and for calculation of total PCB concentrations, was investigated using 11 deuterated or ¹³C labeled congeners in solutions with varying matrices (e.g., salt, organic matter) to consider the widely varying compositions of MIW. The more similar the retention time of the IS-PCBs was to that of the PCBs, the better the correction. Therefore, the closest IS-PCB was always chosen as the IS for the MIW analysis ([Tables S1 and S2](#)). Additional details on instruments, IS recovery rates, and chromatographic and mass spectrometric details are given in [Tables S1–S4](#).

Information about the Mines and PCB Usage. All five mines are abandoned collieries that used longwall mining techniques. Walsum, Zollverein, and Stinnes are located in the Ruhr hard coal mining area (North Rhine-Westphalia, NRW, Germany), while Reden and Camphausen are in the Saar area (Saarland, Germany). Although the mines have had different operators throughout their history, their mining techniques and utilization of PCBs are comparable. These underground mines used inflammable PCBs, in later years mainly Clophen A30 and A40, in transformers and predominantly as hydraulic fluids in machinery²¹ until the 1980s, when they were banned. Leaks and spills allowed hydraulic fluids to enter the voids, and

during mine flooding, they were flushed out by the rising mine water.

Mine Water Analysis. Details on MIW sampling are provided in the SI before Table S1. For the PCB analysis of MIW, 10 mL of unfiltered, homogenized discharged mine water was added to 20 mL amber glass vials. For precautionary reasons, the preparation of sample vials took place in an anaerobic chamber (glovebox, Mecaplex, Grenchen, Switzerland) with a N₂/CO₂ atmosphere (ratio 80:20, “Foodpack 3”, Praxair, Germany) to provide anoxic conditions. Because water from mines is often lacking oxygen content, samples were prepared under anoxic conditions to avoid disturbing the composition of the MIW. The samples were each spiked with 2 μ L of IS-solution using an automated glass microliter syringe (eVoL Dispensing System, Thermo Fisher Scientific). The vials were sealed with magnetic screw caps with PTFE septa (CS-Chromatographie Service GmbH, Langerwehe, Germany) for use with the autosampler. Samples were prepared in duplicate for each MIW sample. Calibration samples were prepared in duplicate for a 12-point calibration of biphenyl and 58 PCBs (0.01–200 ng L⁻¹) in 0.01 mol of CaCl₂ L⁻¹ solution and were also spiked with 2 μ L of IS-solution. Analytes were extracted by SPME fiber from the gaseous phase (“headspace”) above aqueous MIW samples (HS-SPME). Concentrations of PCB congeners are provided as total concentrations (i.e., as the sum of freely dissolved and adsorbed species) after the correction of freely dissolved concentrations by IS as previously described.^{36,39,40} Briefly, the area of analytes in external calibration samples and in environmental samples is corrected by the respective IS with similar physicochemical characteristics. With these IS, matrix influences within samples as well as potential matrix differences between calibration samples and environmental samples are considered. Concentrations are then calculated based on linear calibration curves from external calibration samples. The procedure is provided in full detail in Böhm et al. (2017).³⁶ Selection of suitable IS for the present study, as well as conditions for extraction and analysis, is described in the [HS-SPME-GC-MS Method Optimization](#) section. The adjusted oven method intended for the separation of overlaying PCBs was used to specify overlaying PCBs 4 and 10 in samples from the five sites. Additionally, blank samples were prepared to check for potential carryover and to be used for the calculation of congener-specific limits of quantification (LOQ) and limits of detection (LOD). To determine extraction efficiency, we spiked MIW from three sites with PCB congeners that were not detected in these mines. Spiked samples were measured after 4 days of shaking. Congener profiles were explored by principal component analysis (PCA), cosine theta analysis, and cluster analysis. Results from PCA and cosine theta analysis were inconclusive; therefore, only cluster analysis is further considered. Additional details on material and methods can be found in the SI, as referenced throughout the article.

RESULTS AND DISCUSSION

Optimization of the HS-SPME-GC-MS Method. The seven SPME fibers tested for the simultaneous extraction of biphenyl and 58 PCBs differed greatly in their sensitivity depending on the physicochemical properties of the analytes ([Figures S1–S3](#)). Both 65 μ m PDMS/DVB fibers performed best with low-chlorinated PCBs but showed increasingly poor extraction properties with increasing chlorination levels. The PDMS/DVB fiber with the StableFlex core consistently had

slightly better recovery than the PDMS/DVB fiber with nitinol core, but extractions with the nitinol core fiber were subject to less variation. For the most common SPME fiber (PDMS 100 μ m), the extracted amount of biphenyl, mono-, and dichlorinated PCBs was insufficient. However, the recovery of tetra- and higher-chlorinated PCBs was best with this fiber. Contrary to the other fibers, its performance increased with increasing chlorination of the PCBs. The 7 μ m PDMS fiber had by far the lowest extraction rates, especially in the low-chlorinated range. Both the 85 μ m PA and the 50/30 μ m DVB/CAR/PDMS had their maximum at single- to double-chlorinated PCBs, with the PA-fiber performing multiple times better than the DVB/CAR/PDMS fiber ([Figure S1](#)). Expectedly, the extraction temperature had a major effect on the extraction yields, with optimum temperatures between 60 and 90 °C for individual analytes and extreme differences, especially for penta- to octachlorinated biphenyls ([Figure S2](#)). Increased stirring speed during extraction yields higher extraction amounts or shorter extraction times. To reduce the mechanical load of the agitator and the fiber, a rotation frequency of 500 rpm was seen as optimal based on comparative measurements ([Figure S3](#)). The choice of a thermal desorption temperature (240 °C) well below the maximum operating temperature specified by the manufacturer (270/280 °C) substantially reduced fiber wear while still ensuring adequate thermal desorption of the PCBs. A thermal desorption time of 3 min was sufficient for thermodesorption of analytes from the fiber and short enough to prevent relevant diffusion on the GC column and to ensure narrow chromatographic peaks. All PCBs with the same degree of chlorination could be chromatographically separated (except for $\sum$ PCB 4+10 and $\sum$ PCB 20+21+33), considering a reasonable analysis time of $\approx$ 40 min. The measurement of the most relevant PCBs in MIW is feasible also for higher-chlorinated congeners using only the 65 μ m PDMS/DVB nitinol core fiber at 75 °C. However, the additional measurement with the 100 μ m PDMS fiber at 80 °C allows a more sensitive analysis for higher-chlorinated congeners (especially above PCB 101). Fiber selection and optimization of extraction parameters resulted in very low congener-specific LODs and LOQs for the set of investigated PCBs (0.004–0.58 and 0.01–1.9 ng L⁻¹, respectively, [Table S5](#)). The mean extraction efficiency of the selected PCB congeners was 74–87% ([Table S6](#)).

PCB Contamination in Discharged Mine Water. The results from the investigated discharged MIW samples demonstrate the wide occurrence of PCB congeners: up to 53 of the 58 tested PCB congeners could be identified and quantified ([Table 1](#)). For $\sum$ PCB 4+10, an additional chromatographic separation revealed that PCB 4 is predominant compared to PCB 10 in all tested MIW samples. Therefore, the expression $\sum$ PCB 4(+10) is further used. PCB concentrations of individual congeners of up to 25.9 ng L⁻¹ were found in the 14 investigated MIW samples from five sites. In these samples, mainly di-, tri-, and tetrachlorinated PCBs could be identified. The MIW from different sites varies not only in their biphenyl and PCB concentrations but also in their relative congener composition. This is shown, e.g., by PCB 16, which is the PCB with the second highest concentration in the Walsum, Zollverein, and Stinnes MIW, but the fourth highest in Camphausen, and only the 12th highest in Reden. The highest congener concentration was found for PCB 18 in all mines (2.5–25.9 ng L⁻¹). PCBs 16, 17, 19, 28, 31, 32, 44, 49, 52, and 53 are usually present in the discharged mine water of

Table 1. Concentrations of Biphenyl and 53 PCB Congeners in MIW from Five Different Sites [ng L⁻¹]^{a,b,c}

PCB congener	Walsum	Zollverein	Stinnes	Reden	Camphausen	LOD
Biphenyl (bp)	1.35–3.05	0.25–0.80	11.5–19.2	0.24	0.23	0.06
PCB 1	0.04–0.08	0.01–0.23	0.08–0.12	<LOD	<LOD	0.004
PCB 2	<LOD	<LOD	<LOD–0.06	<LOD	<LOD	0.04
PCB 3	0.06	0.06	0.06–0.15	<LOD	0.06	0.03
ΣPCB 4(+10) ^d	0.72–1.64	4.64–5.65	0.65–1.10	0.66	0.37	0.06
PCB 5	0.11	0.11	<LOD–0.11	0.11	0.11	0.07
PCB 6	0.31	4.34–6.07	0.31	0.31	<LOD	0.2
PCB 7	<LOD–0.07	<LOD–0.23	<LOD–0.07	<LOD	<LOD	0.004
PCB 8	0.55–1.47	3.28–4.10	0.55–1.56	0.55	<LOD	0.3
PCB 9	0.05–0.14	0.05–0.39	0.05–0.15	<LOD	<LOD	0.03
PCB 11	0.30–0.45	1.38–1.88	0.15–0.60	0.73	0.54	0.09
PCB 13	<LOD	<LOD–0.96	<LOD	<LOD	3.34	0.6
PCB 15	0.34	0.82–1.36	0.34–0.78	<LOD	0.34	0.2
PCB 16	2.73–4.96	10.55–12.24	2.12–4.51	1.86	3.63	0.7
PCB 17	0.86–1.62	5.42–7.59	0.63–1.85	3.61	1.95	0.06
PCB 18	3.43–17.6	19.0–25.9	2.54–5.09	10.3	7.41	0.02
PCB 19	1.19–2.70	6.32–7.41	0.82–1.38	2.68	1.98	0.01
ΣPCB 20+21+33 ^d	0.20–0.31	0.24–0.70	0.19–0.78	0.04	0.12	0.01
PCB 24	0.05–0.09	0.18–0.21	0.03–0.17	0.02	0.04	0.004
PCB 26	0.14–0.23	1.19–2.30	0.14–0.60	1.28	0.90	0.008
PCB 27	<LOD–0.59	1.50–2.17	<LOD–0.59	2.67	0.59	0.4
PCB 28	0.49–1.11	2.14–3.65	0.30–1.92	1.87	1.65	0.004
PCB 31	1.38–2.00	3.41–6.59	0.45–2.12	2.96	2.98	0.02
PCB 32	0.93–1.55	4.86–7.16	0.37–1.58	3.73	3.01	0.2
PCB 38	<LOD	<LOD	<LOD–0.69	<LOD	<LOD	0.2
PCB 44	1.30–4.51	3.06–4.33	0.62–2.18	3.31	5.38	0.03
PCB 49	0.65–1.96	2.06–4.41	0.26–1.34	3.72	3.39	0.02
PCB 52	1.27–3.93	3.50–6.48	0.64–2.03	7.32	6.69	0.02
PCB 53	0.49–2.20	2.05–3.47	0.39–0.93	3.07	2.31	0.007
PCB 61	0.03	0.03	0.03–0.27	<LOD	<LOD	0.02
PCB 62	<LOD–0.01	<LOD	0.01–0.05	<LOD	<LOD	0.005
PCB 65	<LOD	0.01	<LOD–0.06	0.03	<LOD	0.01
PCB 77	<LOD–0.38	<LOD	0.38–1.41	<LOD	<LOD	0.2
PCB 85	<LOD–0.16	<LOD–0.16	<LOD–0.32	0.16	0.16	0.1
PCB 99	0.07–0.20	0.07	0.07–0.28	0.15	0.25	0.04
PCB 101	0.08–0.36	0.16–0.25	0.08–0.41	0.32	0.55	0.05
PCB 105	<LOD–0.43	<LOD	0.43	<LOD	0.43	0.3
PCB 110	0.22–0.72	0.22	0.22–0.61	0.48	0.83	0.1
PCB 116	0.09–0.26	0.09	0.09–0.32	0.09	0.25	0.06
PCB 118	<LOD–0.36	<LOD	0.36	0.36	0.36	0.2
PCB 128	<LOD–0.52	<LOD	<LOD–0.52	<LOD	<LOD	0.3
PCB 138	<LOD–0.51	<LOD	0.51	<LOD	0.51	0.3
PCB 146	<LOD–0.36	<LOD–2.5	<LOD–0.36	<LOD	<LOD	0.2
PCB 149	<LOD–0.24	0.24–1.59	0.24–1.07	0.24	0.24	0.1
PCB 153	<LOD–0.41	<LOD–0.41	<LOD–0.41	<LOD	0.41	0.3
PCB 156	<LOD–0.48	<LOD	0.48–1.00	<LOD	<LOD	0.3
PCB 167	<LOD–0.47	<LOD	0.47	<LOD	<LOD	0.3
PCB 170	<LOD–0.58	<LOD	0.58	<LOD	<LOD	0.4
PCB 180	<LOD–0.53	<LOD	0.53	0.53	0.53	0.3
PCB 183	<LOD–0.51	<LOD	0.51	0.51	0.51	0.3
PCB 187	<LOD–0.53	<LOD	0.53	<LOD	<LOD	0.3
ΣPCB _{53+bp}	21.7–59.5	82.6–121	30.5–57.4	53.9	52.1	
ΣPCB ₅₃	20.4–56.4	82.1–120	19.0–42.9	53.7	51.8	
ΣPCB _{i+118}	2.5–6.7	5.8–10.8	2.8–6.2	10.4	10.7	
ΣPCB _{top11}	14.0–20.9	62.4–88.2	9.5–24.9	44.4	40.4	

^aConcentrations from Walsum, Zollverein, and Stinnes are each given as min–max values from four sampling campaigns. Individual replicates are provided in Table S7. ^bInvestigated PCBs 12, 14, 30, 189, and 194 remained <LOD for all mines. For the calculation of sum PCB concentrations, zero was assumed for congeners <LOD, whereas congeners <LOQ were included with $0.5 \times \text{LOQ}$ in the calculations and given in the table with its value written in *italics*. ^cΣPCB_{53+bp} as the sum of all detected PCB congeners and biphenyl, ΣPCB₅₃ as the sum of all detected PCB congeners without biphenyl, ΣPCB_{i+118} as the sum of the six indicator PCBs and PCB 118, ΣPCB_{top11} as the sum of the 11 most abundant PCB congeners in all tested mines. ^dCongeners without chromatographic baseline separation.

every mine with the highest concentrations of detected congeners. Higher biphenyl concentrations are evident in the Stinnes MIW compared to those of the other mines. A possible explanation might be the presence of dehalogenating microorganisms such as *Dehalococcoides* that might have degraded PCB congeners into biphenyl.⁴¹ However, microbiological analysis was not performed in the present study. For the three NRW mines, where PCB concentrations were determined over a period of 26 months (Table S7), congener-specific PCB concentrations and sum concentrations varied during the investigated time frame. In general, PCB concentrations at all mines are in a range of ± 0 –200% fluctuation of the mean concentration within the investigated time frame of 26 months. The fluctuation of the concentrations does not indicate a trend of either increasing or decreasing concentrations.

Based on the chlorine pattern and PCB-specific molecule masses, full scan measurements revealed at least nine additional congeners (two tri- and seven tetrachlorinated PCBs) that did not match the analytical standards available in the present study (Table S8). Because the intensity of peaks can be highly different between congeners of identical chlorination degrees and concentrations, no valid information on concentrations can be given for these “unknown” congeners. However, based on a rough comparison of GC-MS data, estimated concentrations are in a range of 0.04–0.27 to 0.48–4.36 ng L⁻¹ (background on calculation is given in the SI in addition to Table S8). This demonstrates that the absolute PCB concentrations are higher than the sums given in Table 1.

To facilitate future analyses, the most abundant PCB congeners with the highest concentrations in all discharged MIWs were identified. The four PCBs 18, 19, 31, and 52 ($\sum\text{PCB}_{\text{top4}}$) occur in all waters within the top 10 groups of congeners with the highest concentrations. Together, they can explain 23–45% of the total PCB concentrations or 37–58% if biphenyl is included in the group. Because of differences in relative congener abundance, it is reasonable to consider the top 15 groups of congeners with the highest concentrations. In this case, 11 out of 15 congeners were identified in all five MIWs, which can explain 47–83% of total PCB concentrations or 68–83% if biphenyl is included in the group. This group of 11 PCB congeners ($\sum\text{PCB}_{\text{top11}}$) includes the $\sum\text{PCB}_{\text{top4}}$ and additionally PCBs 16, 17, 28, 32, 44, 49, and 53. Only two of these congeners, PCBs 28 and 52, belong to the group of indicator PCBs. The prevalence of these specific congeners in all investigated discharged MIW samples strongly suggests that they are characteristic of the current PCB cocktail discharged from the West German hard coal mines. Consequently, these nine congeners should be included in monitoring programs to consider “mining-specific” congeners. However, if detected in the environment, it must be considered that these congeners can originate as well from sources other than mining because low-chlorinated Clophen mixtures were also used in other applications. Nevertheless, it should be elucidated in upcoming investigations if the relative ratios of these congeners could serve as a natural tracer or fingerprint for PCBs in discharged MIW.

Distribution of congeners in the water phase of flooded mines is affected by their different water solubilities and sorption behavior. Generally, water solubility decreases with increasing degree of chlorination, whereas adsorption increases with increasing degree of chlorination. Consequently, higher-chlorinated PCBs will occur in lower freely dissolved

concentrations than lower-chlorinated congeners but can be translocated within mines and to receiving waters adsorbed to suspended particles in higher concentrations. The concentration of higher-chlorinated congeners in discharged MIW is therefore also dependent on sedimentation rates or rather the turbulence in mines that is influenced by flooding and pumping. However, for mines with reported predominant usage of lower-chlorinated technical PCB mixtures, higher concentrations of highly chlorinated PCBs (PCB 101, 118, 138, 153) are then unexpected to occur in MIW anyway. These influences are in agreement with the results of the present study where the lower-chlorinated PCBs were found at much higher concentrations. Comparison of total PCB concentrations from the present study with concentrations of the six indicator PCBs, PCB 118, and $\sum\text{PCB}_{4+10}$ from a previous report and an expert opinion is limited because of methodical differences (determination of freely dissolved PCB concentrations by passive samplers in rivers after discharge points and calculation of MIW concentrations under consideration of river background concentrations,²⁰ or determination of freely dissolved PCB concentrations by liquid–liquid extraction from filtered 100 L MIW samples²¹). Accordingly, total PCB concentrations in the present study derived directly from the unfiltered MIW are generally higher depending on specific congeners. We consider the SPME method to be perfectly applicable in terms of the invested resource consumption (labor and laboratory consumables) as well as sensitivity to effort. However, no differentiation between freely dissolved congeners and congeners sorbed to suspended matter is reflected by the SPME extraction. Due to the IS correction of extracted congener concentrations, total concentrations of PCB congeners result from the SPME method.^{36,39,40} However, we consider this as a further advantage because total PCB concentrations are essential for the consideration of PCB loads discharged to receiving rivers.

Considerations on Potential Sources of Discharged Mine Water PCB Congeners. Based on historical data on production and usage, it is expected that the technical PCB mixtures that were applied at the sites of the investigated MIW were Clophen mixtures. Clophen mixtures are characterized by their average degree of chlorination with a slight variation in composition of the individual commercial types.^{42–44} According to expert reports, both high-chlorinated PCBs and low-chlorinated PCBs were used.^{45–48} A recent expert report states that mostly insulating oils with low-chlorinated PCBs (i.e., Clophen A30 and A40) were used.²¹ This is strengthened by the congeners found in discharged MIW that are in good agreement with the congeners that are described to be part of Clophen A30 and A40 mixtures.^{42,44} PCBs with highest concentrations in the investigated MIW are also strongly represented in A30 and A40 Clophen mixes, with PCB 18 occurring only in Clophen A30 and A40, but not in higher-chlorinated mixtures. Further, PCBs with lowest concentrations in the MIW were not found in the two Clophen mixes or only in very small amounts (Figures S4–S11). A cluster analysis showed that the five MIW samples and the two technical PCB mixtures can be grouped into two clusters (Table S9 and Figure S12). The congener patterns of the NRW mines show more similarity with Clophen A30, while the Saarland mines show more similarity with Clophen A40. As the coal mines in these two regions were operated by two different companies, this suggests that they used different PCB mixtures. However, an exact match of environmental samples

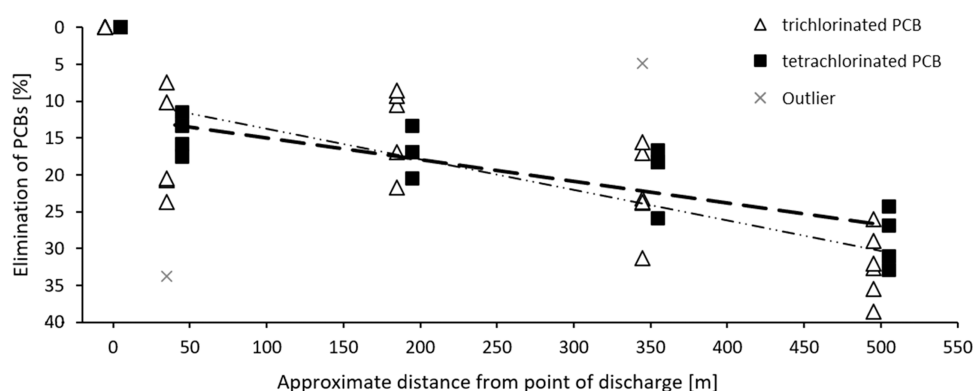


Figure 1. PCB elimination along the course of the constructed wetland at the Reden site. Elimination is exemplarily shown for the 11 most abundant PCBs ($\sum\text{PCB}_{\text{top11}}$). Each symbol at a specific distance represents an individual PCB congener. Symbols for tri- and tetrachlorinated PCBs have been set slightly off for better visibility. Dashed lines (fine: trichlorinated; bold: tetrachlorinated) are meant as guidance, not to express a linear correlation.

Table 2. Annual PCB Loads Calculated from Congener Concentrations and Discharge Rates of the Investigated Mines

	Walsum	Zollverein	Stinnes	Reden	Camphausen
$\sum\text{PCB}_{\text{S3+bp}}$ (Table 1) [ng L^{-1}]	21.7–59.5	82.6–121	30.5–57.4	53.9	52.1
$\sum\text{PCB}_{\text{S3}}$ (Table 1) [ng L^{-1}]	20.4–56.4	82.1–120	19.0–42.9	53.7	51.8
discharged mine water [$\text{mio m}^3 \text{ a}^{-1}$]	4.8 ^a	4.4 ^a	7.0 ^a	12.0 ^b	1.7 ^c
annual loads $\sum\text{PCB}_{\text{S3+bp}}$ [kg]	0.10–0.29	0.36–0.53	0.21–0.40	0.65	0.09
annual loads $\sum\text{PCB}_{\text{S3}}$ [kg]	0.10–0.27	0.36–0.53	0.13–0.30	0.64	0.09
$\sum\text{PCB}_{\text{S3+bp}}$ [kg mio m^{-3}]	0.02–0.06	0.08–0.12	0.03–0.06	0.05	0.05
$\sum\text{PCB}_{\text{S3}}$ [kg mio m^{-3}]	0.02–0.06	0.08–0.12	0.02–0.04	0.05	0.05

^aData from 2021, according to personal communication with employees of LANUV NRW. ^bData from 2019.⁵⁴ ^cData from 2013.⁵⁵

with technical PCB mixtures is unlikely, not least due to different congener characteristics regarding solubility, adsorption, and molecular breakdown. And so, our findings do not suggest that higher-chlorinated Clophen mixtures could not have been used in the mines as well (sorption and dissolution processes were discussed in the previous chapter). The various environmental conditions in the mines could also be decisive for a diverse congener composition. During a period of more than 40 years between the last PCB application and the current study, sorption and transfer processes most likely influenced the PCB composition. All of this can have an effect on the congener pattern, as the discharged MIW does not necessarily represent homogeneous aliquots of the entire system.⁴⁹ Furthermore, higher-chlorinated PCBs can turn into lower-chlorinated PCBs due to dechlorination processes.⁴² The microbial dehalogenation pathway depends on many factors, but there is a tendency to dechlorinate *meta* and/or *para* chlorines.⁵⁰ As a result, higher-chlorinated PCBs are degraded over time to form lower-chlorinated PCBs. This might be supported by the results of the present study, as the analyzed MIW contains higher levels of, for example, PCB 18 than expected from low-chlorinated Clophen mixtures. PCB 18 can (among others) arise from PCB 52 and 49, which in turn can arise from PCB 101—all congeners that occur in higher proportions in Clophen mixtures and tested MIW (Table 1). However, congeners that are not expected to occur at all in Clophen mixtures also appear, such as PCB 11. Consequently, two hypotheses can be considered relevant to explain its occurrence: PCB 11 can result from the dechlorination of higher-chlorinated congeners, e.g., from PCB 101 via PCBs 52 and 70 and further PCBs 26 and 35 (all of which were detected or suspected in the MIW, Tables 1 and S8), but could also

occur as a result of water contact with painted surfaces since PCB 11 plays a particular role in organic paint production.^{51,52} Compared to the congener distribution in Clophen mixtures, divergent congener distribution in the MIW also gives a further hint on predominant reduction of non-ortho and mono-ortho PCBs (e.g., PCB 28), whereas di-ortho PCBs occur in higher concentrations. Premising the same chlorination degree, di-ortho PCBs are assumed to be less toxic than non-ortho or mono-ortho chlorinated PCBs but are discussed in terms of lower degradation and increased bioaccumulation.^{50,53}

Natural Attenuation at the Reden Site. Discharged mine water from the Reden mine flows through a constructed wetland, causing natural attenuation along this system. In this artificially created stream, the Nebelbach, partitioning and degradation processes decrease the PCB load until it is discharged into the receiving water course (Figure 1).

The selected tetrachlorinated PCBs are eliminated faster than the trichlorinated PCBs, with the elimination rates converging at the end of the water course. A steady decrease in concentration (24–42%, mean value = 32% after 500 m) was observed for each PCB. Simultaneously, an absolute increase in biphenyl concentrations could be detected. With an annual load of 0.44 kg after 500 m instead of 0.64 kg at the discharge point, this prevents a considerable proportion of PCBs from entering the receiving water course. Elimination routes were not investigated but are assumed to include bioaccumulation by aquatic organisms such as fish in addition to sorption processes in and volatilization from the constructed wetland. Despite relevant reduction, the process is not dimensioned to achieve full elimination of PCBs. For further evaluation, elimination pathways, such as volatilization, sorption, bioaccumulation, and degradation, must be validated and

quantified. However, except in the case of the dechlorination of PCBs, elimination by volatilization, sorption, or bioaccumulation merely represents a shift of the problem to other systems.

PCB Loads from Mines. In addition to the PCB concentrations, the discharge rates need to be considered for an accurate assessment of risks. Although individual congener concentrations are in the pg–ng L^{−1} range, high PCB loads can be anticipated to be continuously released into the environment worldwide. This can be expected due to the summation of congeners and due to the large daily discharge volumes of mines (average of 3–23 m³ mine water min^{−1} per mine for mines of the present study; Table 2) as well as due to the large number of mines with PCB potentials worldwide.

From the five investigated mines, a total annual load of approximately 1–2 kg of PCBs is discharged to receiving surface waters. In addition to volatilization and atmospheric transport, subsequent transport to the sea is expected, especially for the lower-chlorinated PCBs. Compared to penta- or hexachlorinated indicator PCBs, they have a higher water solubility and a lower affinity for sorption to sediments and suspended matter. Two of the largest mine operators in Germany report a total annual mine water make of more than 134 mio m³.^{56,57} Based on these data and the average PCB concentration of the five investigated mines, this would result in an extrapolated annual load of approximately 6–9 kg PCBs. Such quantities are to be seen relative to the background of further inputs from a wide variety of sources, some of which are diffuse. For example, urban emissions of the six indicator PCBs alone from the City of Zurich to the atmosphere were estimated to be approximately 16 kg a^{−1} (median) based on data from 2010/2011 (summer/winter).⁵⁸ Emissions for the City of Toronto were estimated to be 16–190 kg a^{−1} for five congeners (PCB_i except PCB 138).⁵⁹ A recent study shows that total PCB emissions from India can be as high as 38 Mg a^{−1} from all sources and notes that unintentional PCB emissions (mainly from industry) are steadily increasing.⁶⁰ A previous report by the OSPAR commission (2000) estimated that 3–7 Mg a^{−1} of PCBs are discharged into the North Sea via wet deposition.⁶¹ These quantities might be lower today because PCB loads emitted to environmental systems were expected to further decline.^{7,62} Calculating the share of PCBs originating from MIW on total calculated loads is hampered by the different congener patterns of MIW PCBs because the investigation of low-chlorinated PCBs is mostly lacking in monitoring programs and most research studies. In addition to determining water concentrations, the measurement of air concentrations seems necessary, especially for the low-chlorinated PCBs, because their volatilization can be assumed to be higher compared to higher-chlorinated PCBs. This is of special relevance also in terms of changing climatic patterns, which is expected to highly influence the distribution of PCBs between environmental compartments, with further consequences for their long-range transport.⁶³

Appraisal of Environmental Challenges by PCB-Contaminated Mine Water Effluents. Following the global ban on PCBs, decreasing PCB emissions and environmental concentrations have been reported, with some observations of current stagnations.^{7,62,64} Although PCB loads from the mines investigated in the present study are comparatively smaller than loads emitted from other sources, a high relevance of this source type exists for several reasons. In Germany, legislation and administrative arrangements have been put in place to reduce the PCB burden from mining.²¹ Therefore, the

concentrations and loads reported in the present study are expected to be lower than elsewhere. Due to lack of or unavailable data on the situation in other regions together with the widespread use of PCBs in mining, MIW is very likely an underestimated source of PCB contamination worldwide. In this context, the United Nations Environmental Programme (UNEP) explicitly addressed the need to avoid PCB releases from mines to the environment and to protect groundwater according to the United Nations Sustainable Development Goal (SDG) No. 6 (Clean Water and Sanitation).^{14,65} Fresh water is a scarce and valuable resource that should be protected from PCBs and further pollutants, not least because water resources will become even scarcer in many areas in the course of global change.⁶⁶ For Germany, it has been reported that discharged mine water can account for up to 20% of the total amount of PCBs in rivers.⁶⁷ Taking into account periods of drought with low water levels resulting from global change, the relative proportion of MIW will increase further. This will likely be intensified with regard to increased secondary emissions of PCBs from their environmental reservoirs affecting their transport, bioaccumulation, and toxicity.^{68,69} But also, intense rainfalls and subsequent flooding pose a risk, especially in the course of global change, because PCBs will be transferred to floodplains and taken up by livestock.⁷⁰ Yet, PCBs are already having a severe negative effect on humans^{71–75} and the environment.^{5–10,76} Because the PCB loads calculated in our present study consist mainly of lower-chlorinated PCBs and not of indicator PCBs, the results highlight an additional load of PCBs that has not yet been reflected in global balancing and monitoring programs and potentially highlight an additional risk because data on health implications of lower-chlorinated PCBs are still scarce.

Countries that became parties of the Stockholm Convention are obliged to phase out the use of PCBs in equipment by 2025 and to ensure the elimination of PCBs by 2028, which includes ensuring the environmentally sound waste management of PCB-containing liquids and PCB-contaminated equipment,^{15,77} which is required for materials with a PCB content of >0.005% (50 mg kg^{−1}).^{77,78} This is applicable for at least some of the investigated mines.²¹ Permanent storage in facilities located underground such as mines is in general agreement with the Basel Convention.^{79,80} However, materials would then have to be stored in secure containers, and tunnels should be located in geological formations below zones of available groundwater or in formations that are completely isolated by impermeable rock or clay layers from water-bearing zones.⁸⁰ Either to secure safe storage or to prevent further harm by the contamination of surface waters, there is a need for action. Because mine water is discharged into surface waters by point sources, the elimination of PCBs from MIW can be implemented more easily compared with diffuse sources. However, average volumes of discharged mine water, such as 3–23 m³ min^{−1} per mine (Table 2), pose a particular challenge to elimination technologies that are already discussed for the elimination of chlorinated organic pollutants.^{37,81–86}

CONCLUSIONS

MIW is a globally underestimated point source of PCBs. With the SPME method applied in the current study, a highly recommendable method is at hand for the determination of PCB-contaminated discharged MIW, as well as for the evaluation of elimination methods. Concentrations of individ-

ual PCB congeners as high as 25.9 ng L⁻¹ were detected. Our results further showed that a focus on the analysis of indicator PCBs is inappropriate for discharged MIW. In this context, we suggest to include the most abundant congeners from our study (PCB_{top11} or at least PCB_{top4}) in future investigations on PCB concentrations in MIW as well as in investigations of MIW-associated PCBs in surface waters. The high share of lower-chlorinated PCBs in discharged MIW highlights additional PCB loads that should be considered in future monitoring programs. Concentrations in the ng L⁻¹ range combined with annual discharge volumes in the range of m³ per mine can easily sum up to annual loads in the kg range of total PCBs per mine (in our case, 0.1–0.7 kg PCBs a⁻¹ per mine). Constructed wetlands, as shown by the example of the Reden site, have the potential to at least reduce the PCB loads discharged into the sea until techniques aiming at full elimination of PCBs can be applied on a large scale.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestwater.3c00179>.

Additional details on materials and methods, including mine water sampling, quality assurance and quality control, information on PCB analytes and internal standards, details on instrumental analysis, congener-specific LODs and LOQs, extraction efficiency, and optimization of the HS-SPME-GC-MS method (Tables S1–S6, Figures S1–S3); as well as additional data on congener concentrations for specific sampling events (Table S7), estimation on further identified congeners (Table S8), comparison of PCB congeners in discharged MIW with PCB congeners in Clophen A30/A40 (Figures S4–S11), and cluster analysis of MIW samples and technical mixtures (Table S9 and Figure S12) (PDF)

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Author Contributions

L.B. conceived and designed the study. L.B. and R.-A.D. supervised the study. K.W. and C.W. conducted the sampling. K.W. performed the organic trace analysis and performed the data analysis. K.W. wrote the first version of the manuscript. The manuscript was written through contributions of all authors. All authors edited the manuscript. All authors have given approval to the final version of the manuscript. CRediT: **Katrin Wiltshka** data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, validation, visualization, writing-original draft, writing-review & editing; **Christian Wolkersdorfer** data curation, formal analysis, visualization, writing-review & editing; **Rolf-Alexander Düring** funding acquisition, project administration, resources, supervision, writing-review & editing; **Leonard Böhm** conceptualization, formal analysis, funding acquisition, methodology, project administration, resources, supervision, validation, visualization, writing-review & editing.

Notes

The authors declare no competing financial interest.

The title contains a play on words with the phrase “between the devil and the deep blue sea”, which means that one has to choose between two equally unpleasant courses of action.

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■ REFERENCES

- (1) Steffen, W.; Richardson, K.; Rockström, J.; Cornell, S. E.; Fetzer, I.; Bennett, E. M.; Biggs, R.; Carpenter, S. R.; Vries, W.; de Wit, C. A.; de Folke, C.; Gerten, D.; Heinke, J.; Mace, G. M.; Persson, L. M.; Ramanathan, V.; Reyers, B.; Sörlin, S. Sustainability. Planetary boundaries: guiding human development on a changing planet. *Science* **2015**, 347 (6223), No. 1259855.
- (2) Persson, L.; Carney Almroth, B. M.; Collins, C. D.; Cornell, S.; Wit, C. A.; de Diamond, M. L.; Fantke, P.; Hassellöv, M.; Macleod, M.; Ryberg, M. W.; Søgaard Jørgensen, P.; Villarrubia-Gómez, P.; Wang, Z.; Hauschild, M. Z. Outside the Safe Operating Space of the Planetary Boundary for Novel Entities. *Environ. Sci. Technol.* **2022**, 56 (3), 1510–1521.
- (3) *Stockholm Convention on Persistent Organic Pollutants*; POP-convention: United Nations, 22 May 2001.
- (4) Li, Y.-F.; Harner, T.; Liu, L.; Zhang, Z.; Ren, N.-Q.; Jia, H.; Ma, J.; Sverko, E. Polychlorinated biphenyls in global air and surface soil:

- distributions, air-soil exchange, and fractionation effect. *Environ. Sci. Technol.* **2010**, *44* (8), 2784–2790.
- (5) Ubl, S.; Scheringer, M.; Stohl, A.; Burkhardt, J. F.; Hungerbühler, K. Primary source regions of polychlorinated biphenyls (PCBs) measured in the Arctic. *Atmos. Environ.* **2012**, *62*, 391–399.
- (6) Sanganyado, E.; Chingono, K. E.; Gwenzi, W.; Chaukura, N.; Liu, W. Organic pollutants in deep sea: Occurrence, fate, and ecological implications. *Water Res.* **2021**, *205*, No. 117658.
- (7) Kuepper, N. D.; Böhm, L.; Braun, C.; Bustamante, P.; Düring, R.-A.; Libertelli, M. M.; Quillfeldt, P. Persistent organic pollutants and mercury in a colony of Antarctic seabirds: higher concentrations in 1998, 2001, and 2003 compared to 2014 to 2016. *Polar Biol.* **2022**, *45* (7), 1229–1245.
- (8) Jensen, S.; Johnels, A. G.; Olsson, M.; Otterlind, G. DDT and PCB in marine animals from Swedish waters. *Nature* **1969**, *224* (5216), 247–250.
- (9) Stuart-Smith, S. J.; Jepson, P. D. Persistent threats need persistent counteraction: Responding to PCB pollution in marine mammals. *Mar. Policy* **2017**, *84*, 69–75.
- (10) Desforges, J.-P.; Hall, A.; McConnell, B.; Rosing-Asvid, A.; Barber, J. L.; Brownlow, A.; Guise, S. de.; Eulaers, I.; Jepson, P. D.; Letcher, R. J.; Levin, M.; Ross, P. S.; Samarra, F.; Vikingson, G.; Sonne, C.; Dietz, R. Predicting global killer whale population collapse from PCB pollution. *Science* **2018**, *361* (6409), 1373–1376.
- (11) Ngoubeyou, P. S. K.; Wolkersdorfer, C.; Ndibewu, P. P.; Augustyn, W. Toxicity of polychlorinated biphenyls in aquatic environments – A review. *Aquat. Toxicol.* **2022**, *251*, No. 106284.
- (12) Breivik, K.; Sweetman, A.; Pacyna, J.; Jones, K. Towards a global historical emission inventory for selected PCB congeners – a mass balance approach: 1. Global production and consumption. *Sci. Total Environ.* **2002**, *290* (1–3), 181–198.
- (13) Li, L.; Chen, C.; Li, D.; Breivik, K.; Abbasi, G.; Li, Y.-F. What do we know about the production and release of persistent organic pollutants in the global environment? *Environ. Sci.: Adv.* **2023**, *2*, 55–68.
- (14) United Nations Environment Programme (UNEP). PCB a forgotten legacy? [https://wedocs.unep.org/bitstream/handle/20.500.11822/20786/PCB%20Brochure%20\(2017\).pdf?sequence=1&isAllowed=y](https://wedocs.unep.org/bitstream/handle/20.500.11822/20786/PCB%20Brochure%20(2017).pdf?sequence=1&isAllowed=y) (accessed 2023-10-01).
- (15) Melymuk, L.; Blumenthal, J.; Sáňka, O.; Shu-Yin, A.; Singla, V.; Šebková, K.; Pullen Fedinick, K.; Diamond, M. L. Persistent Problem: Global Challenges to Managing PCBs. *Environ. Sci. Technol.* **2022**, *56* (12), 9029–9040.
- (16) Bench, D. W. PCBs, Mining, and water pollution. Mine Design, Operations & Closure Conference, Polson, Montana, April 27–May 1, 2003; pp 1–12.
- (17) Raghavendra, N. S.; Deka, P. C. Sustainable Development and Management of Groundwater Resources in Mining Affected Areas: A Review. *Procedia Earth Planet. Sci.* **2015**, *11*, 598–604.
- (18) Wolkersdorfer, C. *Mine Water Treatment – Active and Passive Methods*, 1st ed.; Springer: Berlin, 2022.
- (19) Wolkersdorfer, C.; Mugova, E. Effects of Mining on Surface Water. In *Encyclopedia of Inland Waters*, Second ed.; Mehner, T.; Tockner, K., Eds.; Elsevier: Amsterdam, Netherlands, 2022; pp 170–188.
- (20) LANUV. Belastungen von Oberflächengewässern und von aktiven Grubenwasserleitungen mit bergbaubürtigen PCB (und PCB-Ersatzstoffen), 2018. https://www.lanuv.nrw.de/fileadmin/lanuv/wasser/pdf/2018-12-05_Bericht_LANUV_PCB_Grubenwasser.pdf (accessed 2023-10-01).
- (21) Schwarzbauer, J.; Denneborg, M. Gutachten zur Prüfung möglicher Umweltauswirkungen des Einsatzes von Abfall- und Reststoffen zur Bruch-Hohlraumverfüllung in Steinkohlenbergwerken in Nordrhein-Westfalen, Teil 2. Detailbericht 6: Risikoanalyse PCB und weitere organische Stoffe, 2018. http://www.umweltauswirkungen-utv.de/gutachten_2/final/Detailbericht_6.pdf (accessed 2023-10-01).
- (22) Arthur, C. L.; Pawliszyn, J. Solid phase microextraction with thermal desorption using fused silica optical fibers. *Anal. Chem.* **1990**, *62* (19), 2145–2148.
- (23) Zhang, Z.; Pawliszyn, J. Headspace solid-phase microextraction. *Anal. Chem.* **1993**, *65* (14), 1843–1852.
- (24) Mayer, P.; Tolls, J.; Hermens, J. L. M.; Mackay, D. Equilibrium sampling devices. *Environ. Sci. Technol.* **2003**, *37* (9), 184A–191A.
- (25) Pawliszyn, J. *Handbook of Solid Phase Microextraction*; Elsevier: London, Waltham, MA, 2012.
- (26) Banks, D.; Younger, P. L.; Arnesen, R.-T.; Iversen, E. R.; Banks, S. B. Mine-water chemistry: the good, the bad and the ugly. *Environ. Geol.* **1997**, *32* (3), 157–174.
- (27) Potter, D. W.; Pawliszyn, J. Rapid determination of polyaromatic hydrocarbons and polychlorinated biphenyls in water using solid-phase microextraction and GC/MS. *Environ. Sci. Technol.* **1994**, *28* (2), 298–305.
- (28) Llompart, M.; Li, K.; Fingas, M. Solid-phase microextraction and headspace solid-phase microextraction for the determination of polychlorinated biphenyls in water samples. *Anal. Chem.* **1998**, *70* (13), 2510–2515.
- (29) Derouiche, A.; Driss, M. R.; Morizur, J.-P.; Taphanel, M.-H. Simultaneous analysis of polychlorinated biphenyls and organochlorine pesticides in water by headspace solid-phase microextraction with gas chromatography-tandem mass spectrometry. *J. Chromatogr. A* **2007**, *1138* (1–2), 231–243.
- (30) Hawthorne, S. B.; Grabanski, C. B.; Miller, D. J. Solid-phase-microextraction measurement of 62 polychlorinated biphenyl congeners in milliliter sediment pore water samples and determination of K_{DOC} values. *Anal. Chem.* **2009**, *81* (16), 6936–6943.
- (31) Ouyang, Z.; Gao, L.; Yao, S. Concentrations, Possible Sources and Influence Factors of Dissolved Polychlorinated Biphenyls in the Water of Yangzhuang Coal Mining Subsidence Area, China. *Water Resour.* **2019**, *46* (2), 278–285.
- (32) Ohlemacher, S.; Post, C.; Baier, K. Mining Related PCB in Wetland Sediments of the River Lippe (North Rhine-Westphalia, Germany). In *Water resources management and sustainability*; Kumar, P.; Nigam, G. K.; Sinha, M. K.; Singh, A., Eds.; Advances in Geographical and Environmental Sciences; Springer: Singapore, 2022; pp 59–72.
- (33) Risticvic, S.; Lord, H.; Górecki, T.; Arthur, C. L.; Pawliszyn, J. Protocol for solid-phase microextraction method development. *Nat. Protoc.* **2010**, *5* (1), 122–139.
- (34) ASTM D7363-13A(2021)e1. *Standard Test Method for Determination of Parent and Alkyl Polycyclic Aromatics in Sediment Pore Water Using Solid-Phase Microextraction and Gas Chromatography/Mass Spectrometry in Selected Ion Monitoring Mode*; ASTM International: West Conshohocken, PA, 2021. DOI: 10.1520/D7363-13AR21E01.
- (35) Böhm, L.; Schlechtriem, C.; Düring, R.-A. Sorption of Highly Hydrophobic Organic Chemicals to Organic Matter Relevant for Fish Bioconcentration Studies. *Environ. Sci. Technol.* **2016**, *50* (15), 8316–8323.
- (36) Böhm, L.; Düring, R.-A.; Bruckert, H.-J.; Schlechtriem, C. Can solid-phase microextraction replace solvent extraction for water analysis in fish bioconcentration studies with highly hydrophobic organic chemicals? *Environ. Toxicol. Chem.* **2017**, *36* (11), 2887–2894.
- (37) Wiltshcka, K.; Neumann, L.; Werheid, M.; Bunge, M.; Düring, R.-A.; Mackenzie, K.; Böhm, L. Hydrodechlorination of hexachlorobenzene in a miniaturized nano-Pd(0) reaction system combined with the simultaneous extraction of all dechlorination products. *Appl. Catal., B* **2020**, *275*, No. 119100.
- (38) Böhm, L.; Grančić, P.; Scholtzová, E.; Heyde, B. J.; Düring, R.-A.; Siemens, J.; Gerzabek, M. H.; Tunega, D. Adsorption of the hydrophobic organic pollutant hexachlorobenzene to phyllosilicate minerals. *Environ. Sci. Pollut. Res.* **2023**, *30* (13), 36824–36837.
- (39) Poerschmann, J.; Zhang, Z.; Kopinke, F.-D.; Pawliszyn, J. Solid Phase Microextraction for Determining the Distribution of Chemicals in Aqueous Matrices. *Anal. Chem.* **1997**, *69* (4), 597–600.
- (40) Bondarenko, S.; Gan, J. Simultaneous measurement of free and total concentrations of hydrophobic compounds. *Environ. Sci. Technol.* **2009**, *43* (10), 3772–3777.

- (41) Smidt, H.; Vos, W. M. de. Anaerobic microbial dehalogenation. *Annu. Rev. Microbiol.* **2004**, *58*, 43–73.
- (42) Schulte, E.; Malisch, R. Berechnung der wahren PCB-Gehalte in Umweltproben. *Z. Anal. Chem.* **1983**, *314* (6), 545–551.
- (43) de Voogt, P.; Brinkman, U. Chapter 1 – Production, properties and usage of polychlorinated biphenyls. In *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products (Second ed.)*; Topics in Environmental Health; Kimbrough, R. D.; Jensen, A. A., Eds.; Elsevier: Amsterdam, 1989; pp 3–45.
- (44) Schulz, D. E.; Petrick, G.; Duinker, J. C. Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. *Environ. Sci. Technol.* **1989**, *23* (7), 852–859.
- (45) Gutachten zur Prüfung möglicher Umweltauswirkungen des Einsatzes von Abfall- und Reststoffen zur Bruch-Hohlraumverfüllung in Steinkohlebergwerken in Nordrhein-Westfalen. Detailbericht 6: Risikoanalyse PCB und weitere organische Stoffe, 2017. http://www.umweltauswirkungen-utv.de/gutachten_1_Apr_2017/Versatzgutachten_April_2017.pdf (accessed 2023-10-01).
- (46) Lorenz, H.; Neumeier, G. Polychlorierte Biphenyle (PCB). Ein gemeinsamer Bericht des Bundesgesundheitsamtes und des Umweltbundesamtes; BGA-Schriften 1983/4; MMV Medizin Verl.: München, 1983.
- (47) Engel, W.; Kihl, H. Schwerentflammbare und gesundheitsunschädliche Hydraulikflüssigkeiten des Typs HFD für den Bergbau. *Glückauf* **1987**, *123* (22), 1423–1426.
- (48) Reichel, J. Schwerentflammbare Druckflüssigkeiten für hydraulische Bergwerksmaschinen. *Glückauf* **1973**, *109* (17), 871–877.
- (49) Mugova, E.; Wolkersdorfer, C. Density stratification and double-diffusive convection in mine pools of flooded underground mines – A review. *Water Res.* **2022**, *214*, No. 118033.
- (50) Wiegel, J.; Wu, Q. Microbial reductive dehalogenation of polychlorinated biphenyls. *FEMS Microbiol. Ecol.* **2000**, *32* (1), 1–15.
- (51) Rodenburg, L. A.; Guo, J.; Du, S.; Cavallo, G. J. Evidence for unique and ubiquitous environmental sources of 3,3'-dichlorobiphenyl (PCB 11). *Environ. Sci. Technol.* **2010**, *44* (8), 2816–2821.
- (52) Mastin, J.; Harner, T.; Schuster, J. K.; South, L. A review of PCB-11 and other unintentionally produced PCB congeners in outdoor air. *Atmos. Pollut. Res.* **2022**, *13* (4), No. 101364.
- (53) Passatore, L.; Rossetti, S.; Juwarkar, A. A.; Massacci, A. Phytoremediation and bioremediation of polychlorinated biphenyls (PCBs): state of knowledge and research perspectives. *J. Hazard. Mater.* **2014**, *278*, 189–202.
- (54) Ministry for the Environment and Consumer Protection of Saarland. Transfer of the findings from the NRW report on PCBs and other substances to Saarland (orig.: Übertragung der Erkenntnisse aus dem NRW Gutachten bzgl. PCB und weiterer Stoffe auf das Saarland); PCB SAAR/19281/DE/LL, 2019. https://www.saarland.de/SharedDocs/Downloads/DE/muklav/wasser/grubenwasser/dl_gutachten_erkennnisse_nrw_pcb_muv.pdf?__blob=publicationFile&v=5 (accessed 2023-10-01).
- (55) RAG Aktiengesellschaft. Grubenwasserkonzept Saar, 2014. https://www.bergbau-unser-erbe.de/fileadmin/user_upload/Grubenwasserkonzept_Saar.pdf (accessed 2023-10-01).
- (56) RAG Aktiengesellschaft. Wasserhaltungskonzept. <https://www.rag.de/ewigkeitsaufgaben/wasserhaltung> (accessed 2023-10-01).
- (57) Wismut GmbH. Die Wasserbehandlungsanlagen der Wismut. <https://www.wismut.de/de/download.php?download=WBA+%C3%9Cbersicht+2021.pdf> (accessed 2023-10-01).
- (58) Bogdal, C.; Müller, C. E.; Buser, A. M.; Wang, Z.; Scheringer, M.; Gerecke, A. C.; Schmid, P.; Zennegg, M.; Macleod, M.; Hungerbühler, K. Emissions of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans during 2010 and 2011 in Zurich, Switzerland. *Environ. Sci. Technol.* **2014**, *48* (1), 482–490.
- (59) Diamond, M. L.; Melymuk, L.; Csiszar, S. A.; Robson, M. Estimation of PCB Stocks, emissions, and urban fate: Will our policies reduce concentrations and exposure? *Environ. Sci. Technol.* **2010**, *44* (8), 2777–2783.
- (60) Parmar, J.; Qureshi, A. Accounting of the Use and Emissions of Polychlorinated Biphenyl Compounds (PCBs) in India, 1951–2100. *Environ. Sci. Technol.* **2023**, *57* (12), 4763–4774.
- (61) OSPAR Commission. Region 2. Greater North Sea; Quality status report 2000. https://qsr2010.ospar.org/media/assessments/QSR_2000_Region_IL.pdf (accessed 2023-10-01).
- (62) Schuster, J. K.; Gioia, R.; Breivik, K.; Steinnes, E.; Scheringer, M.; Jones, K. C. Trends in European background air reflect reductions in primary emissions of PCBs and PBDEs. *Environ. Sci. Technol.* **2010**, *44* (17), 6760–6766.
- (63) Wagner, C. C.; Amos, H. M.; Thackray, C. P.; Zhang, Y.; Lundgren, E. W.; Forget, G.; Friedman, C. L.; Selin, N. E.; Lohmann, R.; Sunderland, E. M. A Global 3-D Ocean Model for PCBs: Benchmark Compounds for Understanding the Impacts of Global Change on Neutral Persistent Organic Pollutants. *Global Biogeochem. Cycles* **2019**, *33* (3), 469–481.
- (64) Vorkamp, K.; Rigét, F. F.; Bossi, R.; Dietz, R. Temporal trends of hexabromocyclododecane, polybrominated diphenyl ethers and polychlorinated biphenyls in ringed seals from East Greenland. *Environ. Sci. Technol.* **2011**, *45* (4), 1243–1249.
- (65) United Nations Environment Programme (UNEP). Terminal Evaluation of the UN Environment Project “Best Practices for PCB Management in the Mining Sector of South America” (GEF ID:3814): Final Report. https://wedocs.unep.org/bitstream/handle/20.500.11822/30613/3814_2019_te_unep_gef_regional_msp_pcb_South_America.pdf (accessed 2023-10-01).
- (66) Gosling, S. N.; Arnell, N. W. A global assessment of the impact of climate change on water scarcity. *Clim. Change* **2016**, *134* (3), 371–385.
- (67) Rahm, H.; Plantikow, K.; Spira, D.; Reifferscheid, G.; Schäfer, S. Neues Leben ohne Grubenwasser? Auswirkungen der Beendigung des Steinkohlebergbaus auf die Gewässerqualität in NRW. *Mitt. Umweltchem. Ökotox.* **2019**, *25* (3), 67–71.
- (68) Ma, J.; Hung, H.; Macdonald, R. W. The influence of global climate change on the environmental fate of persistent organic pollutants: A review with emphasis on the Northern Hemisphere and the Arctic as a receptor. *Global Planet. Change* **2016**, *146*, 89–108.
- (69) Borgå, K.; McKinney, M. A.; Routti, H.; Fernie, K. J.; Giebichenstein, J.; Hallanger, I.; Muir, D. C. G. The influence of global climate change on accumulation and toxicity of persistent organic pollutants and chemicals of emerging concern in Arctic food webs. *Environ. Sci.: Processes Impacts* **2022**, *24* (10), 1544–1576.
- (70) Weber, R.; Herold, C.; Hollert, H.; Kamphues, J.; Blepp, M.; Ballschmiter, K. Reviewing the relevance of dioxin and PCB sources for food from animal origin and the need for their inventory, control and management. *Environ. Sci. Eur.* **2018**, *30* (1), No. 42.
- (71) Fiedler, H. Global and local disposition of PCB. In *PCBs – Recent Advances in the Environmental Toxicology and Health Effects*; University Press of Kentucky: KY, 2001; pp 11–15.
- (72) Faroon, O. M.; Keith, S.; Jones, D.; Rosa, C. de. Carcinogenic effects of polychlorinated biphenyls. *Toxicol. Ind. Health* **2001**, *17* (2), 41–62.
- (73) Gore, A. C.; Wu, T. J.; Oung, T.; Lee, J. B.; Woller, M. J. A Novel Mechanism for Endocrine-Disrupting Effects of Polychlorinated Biphenyls: Direct Effects on Gonadotropin-Releasing Hormone Neurons. *J. Neuroendocrinol.* **2002**, *14* (10), 814–823.
- (74) Schettgen, T.; Alt, A.; Schikowsky, C.; Esser, A.; Kraus, T. Human biomonitoring of polychlorinated biphenyls (PCBs) in plasma of former underground miners in Germany – A case-control study. *Int. J. Hyg. Environ. Health* **2018**, *221* (7), 1007–1011.
- (75) Esser, A.; Schettgen, T.; Kraus, T. Assessment of a potential PCB exposure among (former) underground miners by hydraulic fluids. *J. Toxicol. Environ. Health, Part A* **2020**, *83* (6), 219–232.
- (76) Vorkamp, K.; Rigét, F. F. A review of new and current-use contaminants in the Arctic environment: evidence of long-range transport and indications of bioaccumulation. *Chemosphere* **2014**, *111*, 379–395.

(77) United Nations Environment Programme (UNEP). Report on progress towards the elimination of polychlorinated biphenyls (UNEP/POPS/COP.9/INF/10). Secretariat of the Basel, Rotterdam and Stockholm conventions, United Nations Environment Programme, Geneva. <https://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-COP.9-INF.10.English.pdf> (accessed 2023-10-01).

(78) United Nations Environment Programme (UNEP). *Stockholm convention on persistent organic pollutants (POPs), Text and Annexes revised in 2019, 2020*. <https://www.pops.int/Portals/0/download.aspx?d=UNEP-POPS-COP-CONVTEXT-2021.English.pdf> (accessed 2023-10-01).

(79) United Nations Environment Programme (UNEP). Basel Convention Technical Guidelines. Technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with polychlorinated biphenyls, polychlorinated terphenyls, polychlorinated naphthalenes or polybrominated biphenyls including hexabromobiphenyl (PCBs, PCTs, PCNs or PBBs, including HBB): UNEP/CHW.13/6/Add.4/Rev.1. <https://www.brsmeas.org/2017COPs/MeetingDocuments/tabid/5385/language/en-US/Default.aspx> (accessed 2023-10-01).

(80) United Nations Environment Programme (UNEP). Basel Convention Technical Guidelines. General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (General POPs): UNEP/CHW.14/7/Add.1/Rev.1. <https://www.brsmeas.org/2017COPs/MeetingDocuments/tabid/5385/language/en-US/Default.aspx> (accessed 2023-10-01).

(81) Payne, R. B.; May, H. D.; Sowers, K. R. Enhanced reductive dechlorination of polychlorinated biphenyl impacted sediment by bioaugmentation with a dehalorespiring bacterium. *Environ. Sci. Technol.* **2011**, 45 (20), 8772–8779.

(82) Yu, H.; Feng, C.; Liu, X.; Yi, X.; Ren, Y.; Wei, C. Enhanced anaerobic dechlorination of polychlorinated biphenyl in sediments by bioanode stimulation. *Environ. Pollut.* **2016**, 211, 81–89.

(83) Abel, S.; Akkanen, J. Novel, Activated Carbon-Based Material for in-Situ Remediation of Contaminated Sediments. *Environ. Sci. Technol.* **2019**, 53 (6), 3217–3224.

(84) Balasubramani, A.; Rifai, H. S. Efficacy of carbon-based materials for remediating polychlorinated biphenyls (PCBs) in sediment. *Sci. Total Environ.* **2018**, 644, 398–405.

(85) Payne, R. B.; Ghosh, U.; May, H. D.; Marshall, C. W.; Sowers, K. R. A Pilot-Scale Field Study: In Situ Treatment of PCB-Impacted Sediments with Bioamended Activated Carbon. *Environ. Sci. Technol.* **2019**, 53 (5), 2626–2634.

(86) Schüth, C.; Reinhard, M. Hydrodechlorination and hydrogenation of aromatic compounds over palladium on alumina in hydrogen-saturated water. *Appl. Catal., B* **1998**, 18, 215–221.