Justus-Liebig-Universität Gießen

Interdisziplinäres Forschungszentrum
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Institut für Bodenkunde und Bodenerhaltung

Von der Analytik bis zur Behandlung: Quantifizierung mit SPME-GC-MS und katalytischer Abbau mit palladiumbasierten Verfahren von PCB-Kongeneren in Grubenwässern

Kumulative Dissertation

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Hexagons are the Bestagons

(CGP Grey)

Ich habe diese Dissertation bewusst in deutscher Sprache verfasst. Zum Thema PCB-Konzentrationen in Grubenwässern gibt es kaum begutachtete Literatur, und die wenigen vorhandenen Fachartikel sind nicht immer für alle zugänglich. Zudem liegen bergbaubezogene Themen häufig im Aufgaben- oder Interessenbereich von Ingenieurbüros, Behörden oder Interessenverbänden, in denen nicht alle Mitglieder die englische Sprache sicher beherrschen. Mein Ziel war es daher, die Themen und Ergebnisse meiner Dissertation so niedrigschwellig wie möglich aufzubereiten, um sie möglichst vielen Menschen zugänglich zu machen.

Glück auf!

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Abkürzungsverzeichnis

$\sum PCB_{58}$	Summe der 58 PCB, die in dieser Studie quantifiziert wurden
$\sum PCB_{top11}$	Die 11 in größten Konzentrationen in Grubenwässern vorkommenden polychlorierten Biphenyle
A_{Pd}	Spezifische katalytische Aktivität von Palladium
B	Benzol
C	Kohlenstoff
$C_6H_5Na_3O_7 * 2\,H_2O$	Trinatriumcitrat Dihydrat
CAR	Carboxen
CB	Chlorbenzol
Cl	Chlor
DCB	Dichlorbenzol
DVB	Divinylbenzol
GC-MS	Gaschromatographie-Massenspektrometrie
H_2	Wasserstoffmolekül
HCB	Hexachlorbenzol
HS-SPME	Gasraum-Festphasenmikroextraktion (Headspace-solid-phase microextraction)
IS	Interner Standard
K	Kelvin
K_{OW}	*n*-Octanol-Wasser-Verteilungskoeffizient
LLE	Flüssig-Flüssig-Extraktion (liquid-liquid extraction)
LOD	Nachweisgrenze (limit of detection)
LOQ	Bestimmungsgrenze (limit of quantification)
Na_2SO_3	Natriumsulfit
MCB	Monochlorbenzol
mQ	“Milli-Q”, Reinstwasser
MIW	Bergbaubeeinflusstes Wasser (mining influenced water)
$NaHCO_3$	Natriumhydrogencarbonat
NRW	Nordrhein-Westfalen
PA	Polyacrylat
PCB	Polychlorinierte Biphenyle

PCB_{i+118}	Indikator-PCB inklusive PCB 118
PDMS	Polydimethylsiloxan
PeCB	Pentachlorbenzol
Pd	Palladium
Pd/Al_2O_3	Palladium auf einem Aluminiumoxidträger
PDMS	Polydimethylsiloxan
POP	Persistente organische Schadstoffe (persistent organic pollutants)
RT	Retentionszeit (retention time)
SDG	Ziele für nachhaltige Entwicklung (sustainable development goals)
Silgel	SilGel® 612 A/B
SPE	Festphasenextraktion (solid-phase extraction)
SPME	Festphasenmikroextraktion (solid-phase microextraction)
TeCB	Tetrachlorbenzol
TCB	Trichlorbenzol
UNEP	Umweltprogramm der Vereinten Nationen (United Nations Environment Programme)

Zusammenfassung

Über Jahrzehnte hinweg wurden persistente organische Schadstoffe (POPs) als Industriechemikalien produziert oder entstanden als Nebenprodukte bei Fertigungs- und Verbrennungsprozessen. Insbesondere Hexachlorbenzol (HCB) und polychlorierte Biphenyle (PCB) wurden vor ihrem Verbot durch die Stockholmer Konvention in zahlreichen landwirtschaftlichen und industriellen Anwendungen genutzt. Im Bergbau war der Einsatz von PCB zeitweise sogar gesetzlich vorgeschrieben. Die in technischen Gemischen eingesetzten PCB enthielten bis zu 130 verschiedene Verbindungen (Kongenere), die bis heute in Bergwerken und Grubenwässern aus alten Leckagen und zurückgelassener Ausrüstung nachweisbar sind.

Heutige Untersuchungen der PCB-Belastung von (Gruben-)Wässern fokussieren oft nur auf die sechs Indikator-PCB („Leit-Kongenere“) sowie PCB 118 (PCB_{i+118}), was häufig zu einer Unterschätzung der tatsächlichen PCB-Konzentrationen führt. Ziel dieser Studie war es, die Konzentrationen der am häufigsten vorkommenden PCB-Kongenere in Grubenwässern umfassend zu bestimmen und daraus die Gesamtfrachten abzuleiten, um Risiken für Mensch und Umwelt besser abschätzen zu können. Zusätzlich wurde ein ressourcenschonendes Konzept zur Reduktion von PCB angepasst und auf Effizienz geprüft. Ein innovativer Ansatz in der Wasseraufbereitung ist die katalytische Dechlorierung mit Palladium-(Pd-)Partikeln. Hierbei können POPs unter reduzierenden Bedingungen in Anwesenheit von Elektronendonatoren wie Wasserstoff dehalogeniert werden.

Für die Analyse der PCB-Kongenere wurde eine Festphasen-Mikroextraktionsmethode (SPME) in Kombination mit Gaschromatographie-Massenspektrometrie (GC-MS) optimiert, um PCB direkt aus unbehandeltem Grubenwasser lösungsmittelfrei zu extrahieren und empfindlich nachzuweisen. Zur Untersuchung der Dechlorierungsmechanismen und -pfade wurden zunächst Experimente mit HCB durchgeführt, da es strukturell ähnlich zu PCB ist, aber eine einfachere Molekülstruktur aufweist. Anschließend wurden die Versuche auf grubenwasserspezifische PCB übertragen und unter Laborbedingungen mit dispergierten Pd-Partikeln in Pufferlösung durchgeführt. Weitere Tests folgten mit Pd-Partikeln, die in Silikon eingebettet waren, um den Katalysator vor Katalysatorgiften zu schützen und die Tests direkt in unbehandeltem Grubenwasser durchzuführen.

Die SPME-Methode erwies sich als gut geeignet zur Quantifizierung von PCB in Grubenwässern. In den Wässern von fünf getesteten Gruben konnten über 50 PCB identifiziert werden. Angesichts der PCB-Konzentrationen von bis zu 120 ng L^{-1} und der erheblichen Wassermengen von bis zu 12 Millionen L a^{-1} pro Grube ergeben sich jährliche PCB-Frachten, die dringenden Handlungsbedarf signalisieren. Die Hydrodechlorierung mit Pd-Partikeln erwies sich als wirkungsvoll, um POPs innerhalb weniger Minuten in leichter abbaubare Strukturen umzuwandeln, mit spezifischen katalytischen Aktivitäten von bis zu 3350 L g^{-1} min^{-1}. Der Abbau von HCB erfolgte hauptsächlich durch die Substitution vicinaler Chloratome, beeinflusst durch einen induktiven Effekt. Bei PCB führte der zweite Phenylring zu bevorzugtem Abbau der meta-

und para-positionierten Chloratome, wodurch die Bildung toxischer, dioxinähnlicher PCB minimiert wurde. Die Dechlorierung von PCB konnte durch die Silikon-Einbettung der Pd-Katalysatoren auch in der katalysatorgiftreichen Grubenwassermatrix erfolgreich durchgeführt werden. Nach Anpassung und Skalierung bietet diese Technologie durchaus Potenzial zur großflächigen Behandlung von HCB und PCB kontaminierter Wässer.

Abstract

Over several decades, persistent organic pollutants (POPs) have been produced as industrial chemicals or emerged as byproducts from manufacturing and combustion processes. In particular, hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs) were widely used in agricultural and industrial applications until they were banned under the Stockholm Convention. In mining, PCB usage was at times even legally mandated. The technical mixtures used contained up to 130 different compounds (congeners) of this group, which can still be detected in mining sites and mine waters due to leakage and abandoned equipment from that era.

Current assessments of PCB contamination in (mine) waters often focus only on the six indicator PCBs ("marker congeners") and PCB 118 (PCB_{i+118}), which frequently leads to an underestimation of actual PCB concentrations. The aim of this study was to comprehensively determine the concentrations of the most common PCB congeners in mine waters and to derive the total loads, enabling a more accurate risk assessment for humans and the environment. Additionally, a resource-efficient PCB reduction concept was adapted and tested for efficacy. An innovative approach in water treatment is the catalytic dechlorination using palladium (Pd) particles. In this process, POPs can be dehalogenated under reducing conditions in the presence of electron donors, such as hydrogen.

For the analysis of PCB congeners, a solid-phase microextraction method (SPME) combined with gas chromatography-mass spectrometry (GC-MS) was optimized to sensitively detect PCBs directly from untreated mine water without solvents. To investigate the mechanisms and pathways of dechlorination, initial experiments were conducted with HCB due to its structural similarity to PCBs but simpler molecular structure. These tests were then extended to mine water-specific PCBs and conducted under laboratory conditions with dispersed Pd particles in buffer solution. Further tests followed with Pd particles embedded in silicone, to protect the catalyst from poisons, allowing testing directly in untreated mine water.

The SPME method was found to be well suited for the quantification of PCBs in mine waters. More than 50 PCBs were identified in the waters of five tested mines. Given the PCB concentrations of up to 120 ng L^{-1} and the large water volumes of up to 12 million L a^{-1} per mine, annual PCB loads indicate an urgent need for action. The hydrodechlorination with Pd particles proved effective for transforming POPs within minutes into more easily degradable structures, with specific catalytic activities of up to 3350 L g^{-1} min^{-1}. The degradation of HCB occurred mainly through the substitution of vicinal chlorines, influenced by an inductive effect. For PCBs, the second phenyl ring influenced preferential cleavage of meta- and para-positioned chlorines, which minimizes the formation of more toxic, dioxin-like PCBs. The dechlorination of PCBs was successfully carried out in the catalyst poison-rich mine water matrix by embedding the Pd catalysts in silicone. With proper adjustments and scaling, this technology offers considerable potential for the large-scale treatment of HCB and PCB contaminated waters.

1 Erweiterte Zusammenfassung

1.1 Einleitung

1.1.1 Allgemeine Einführung

Persistente organische Schadstoffe (persistent organic pollutants, POPs) stellen eine Klasse von Chemikalien dar, die weltweit erhebliche Gefahren für die Umwelt und die menschliche Gesundheit bergen [1]. Diese Substanzen wurden entweder gezielt als Pflanzenschutzmittel und Industriechemikalien produziert oder traten als Nebenprodukte bei industriellen Fertigungsprozessen auf, bevor sie schließlich global geächtet wurden [2]. Unter diesen gefährlichen Verbindungen sind insbesondere Hexachlorbenzol (HCB), ein früher weitverbreitetes Pestizid, sowie polychlorierte Biphenyle (PCB) hervorzuheben, die primär als Transformatorenöle und Dielektrika Verwendung fanden. PCB bestehen aus einer großen Bandbreite von theoretisch bis zu 209 Kongeneren; technische PCB-Mischungen enthielten meist zwischen 80 und 100 verschiedene Kongenere. In Deutschland und anderen Ländern war die Nutzung von PCB aufgrund ihrer Eigenschaft nicht brennbar zu sein zeitweise im Kohlebergbau gesetzlich vorgeschrieben.

Bislang gab es kaum Informationen zu PCB-Konzentrationen in Grubenwässern, obwohl Grubenwässer aufgrund ihrer hohen kontinuierlich anfallenden Volumina weltweit zu den größten Schadstoffströmen gehören [3]. Veröffentlichte Daten zu Konzentrationen stammen größtenteils aus behördlichen Berichten und Gutachten [4–11], extern begutachtete Publikationen sind selten. Die Untersuchung bergbaubeeinflusster Wässer (mining influenced water, MIW) war bisher durch die Komplexität der Probenvorbereitung und Analysen, und die begrenzte Empfindlichkeit bestehender Nachweismethoden erschwert.

Zur Entfernung von POPs aus wässrigen Lösungen stehen unterschiedliche Ansätze zur Verfügung. Ein Verfahren ist die Abtrennung und anschließende thermische Zerstörung der Schadstoffe [12]. Ein weiterer Ansatz fokussiert sich auf die chemische Umwandlung der POPs in weniger schädliche Verbindungen. Für diesen Zweck eignen sich insbesondere Palladium-(Pd)-Katalysatoren [13]. Die Reaktivität des Katalysators kann jedoch durch Katalysatorgifte erheblich beeinträchtigt werden, was die katalytische Effizienz verringern oder sogar vollständig aufheben kann [14]. Schutzmechanismen sind daher erforderlich, um eine Deaktivierung des Katalysators zu verhindern.

Ziel dieser Arbeit ist es, eine schnelle und effiziente Extraktionsmethode zu optimieren, um PCB in geringen Volumina von Grubenwasser zu quantifizieren. Dabei soll aufgezeigt werden, dass die PCB-Konzentrationen auch Jahrzehnte nach dem Verbot dieser Substanzen höher sein können als bisher angenommen, was Grubenwasser als relevante Quelle für PCB-Belastung bestätigt (Kapitel 2). Weiterhin wird das Reaktionsverhalten von HCB und weiteren Chlorbenzolen (CB) untersucht, um die Mechanismen, Reaktionswege und Zwischenprodukte der Dechlorierung chlorierter Substanzen mithilfe von Pd-Katalysatoren aufzuklären (Kapitel 3). Eine Einbettung der

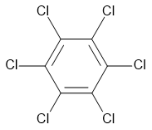
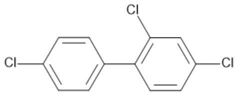
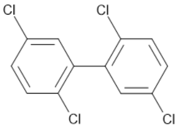
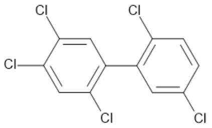
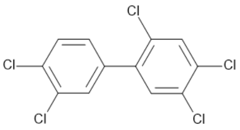
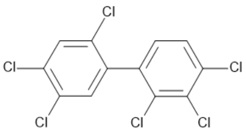
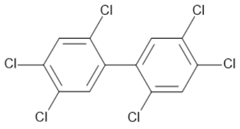
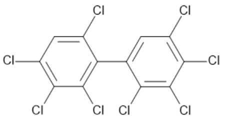
Katalysatoren in eine PDMS-Beschichtung ermöglicht deren Wiederverwendung und erhält die katalytische Aktivität, auch in der komplexen, katalysatorgiftreichen Grubenwassermatrix (Kapitel 4).

1.1.2 Persistente Organische Schadstoffe

POPs sind chemische Verbindungen, die in der Umwelt nur sehr langsam abgebaut werden und daher weltweit in besorgniserregend hohen Konzentrationen zu finden sind. Ursprünglich wurden POPs für industrielle, landwirtschaftliche und kommerzielle Zwecke synthetisiert und fanden Verwendung als Pestizide, Flammschutzmittel und in zahlreichen anderen Anwendungen. Neben gezielt hergestellten POPs entstanden einige dieser Substanzen jedoch auch als Nebenprodukte in Produktions- und Verbrennungsprozessen [15]. POPs zeichnen sich durch ihre chemische Stabilität und eine sehr hohe Persistenz in der Umwelt aus, die es ihnen ermöglicht, über Jahrzehnte hinweg nahezu unverändert zu bleiben. Diese Eigenschaften, zusammen mit ihrer Lipophilie, die sich in einem positiven, hohen dekadischen Logarithmus des Octanol-Wasser-Verteilungskoeffizienten (log K_{OW}) bemerkbar macht, tragen dazu bei, dass POPs in lebenden Organismen akkumulieren und sich in Nahrungsnetzen anreichern. Dabei werden sie von einem trophischen Level zum nächsten weitergegeben und dort oft in höheren Konzentrationen als ursprünglich aufgenommen gespeichert [16]. Auf diese Weise entfalten POPs signifikante toxische Effekte über alle Ebenen des Ökosystems hinweg – von Mikroorganismen bis hin zu Säugetieren, einschließlich des Menschen, bei dem sie mit endokrinen, immunologischen und krebserregenden Effekten in Verbindung stehen [1,17].

Angesichts ihrer weitreichenden Umweltschäden und schwerwiegenden Auswirkungen auf die Gesundheit wurde 2001 durch das Stockholmer Übereinkommen ein umfassendes internationales Gebot zur Substitution der gefährlichsten POPs beschlossen [2]. Das „Dreckige Dutzend“, eine Liste von ursprünglich zwölf chemischen Verbindungen oder Stoffgruppen, wurde als besonders bedenklich eingestuft. Diese Liste umfasste auch HCB und PCB (Tabelle 1). Seit der Einführung der ursprünglichen Liste des „dreckigen Dutzends“ wurden zahlreiche weitere Verbindungen identifiziert und dem Abkommen hinzugefügt, da sie ähnliche Gefährdungspotenziale für Umwelt und Gesundheit aufweisen [18]. Trotz weltweiter Regulierungen, die Produktion und Verwendung dieser Substanzen nahezu vollständig verbieten, sind POPs aufgrund ihrer physischen Eigenschaften weiterhin überall in der Umwelt nachweisbar. Selbst in sehr entlegenen Regionen, wie Wüsten, Polarregionen und Weltmeeren, können sie in relevanten Konzentrationen gemessen werden [19–23]. Diese weite Verbreitung und anhaltende Präsenz der POPs erklärt sich durch atmosphärische Transportmechanismen [24], die es ihnen ermöglichen, durch „global distillation“ (globale Destillation) oder „Fraktionierung“ in die Umwelt zu gelangen. Dieser Effekt führt dazu, dass POPs aus wärmeren Regionen in kältere Klimazonen transportiert werden [25]. Da POPs in warmen Regionen stärker volatilisiert werden, können sie in die Atmosphäre gelangen und sich im Verlauf wiederholt in kühleren Gebieten absetzen. Dieser

Tabelle 1. Übersicht zu Hexachlorbenzol und ausgewählten polychlorierten Biphenylen (PCB)

Struktur	Substanz	Anwendung	CAS-Nr.	log K_{OW}
	Hexachlorbenzol	Pestizid	118-74-1	5,73[a]
	PCB 28	Industriechemikalie	7012-37-5	5,60[b]
	PCB 52	Industriechemikalie	35693-99-3	5,88[b]
	PCB 101	Industriechemikalie	37680-73-2	6,32[b]
	PCB 118	Industriechemikalie	31508-00-6	6,72[b]
	PCB 138	Industriechemikalie	35065-28-2	6,75[b]
	PCB 153	Industriechemikalie	35065-27-1	6,76[b]
	PCB 180	Industriechemikalie	35065-29-3	7,28[b]

[a] log K_{OW}-Werte aus Bruijn et al. [26]; [b] log K_{OW}-Werte aus Wang et al. [27], als Maß für die Lipophilie.

Mechanismus, der auch als „Grashüpfereffekt“ (engl. grasshopper effect) bezeichnet wird (Abbildung 1), erlaubt es POPs, in einer Serie von „Sprüngen“ Distanzen von mehreren Tausend Kilometern zu überwinden und sogar die Polarregionen zu erreichen, wo sie schließlich akkumulieren [28,29]. Diese Effekte führen dazu, dass POPs aus ihren ursprünglichen Emissionsquellen remobilisiert und in andere Regionen transportiert werden, wo sie oft weiter die Umwelt und die Gesundheit gefährden.

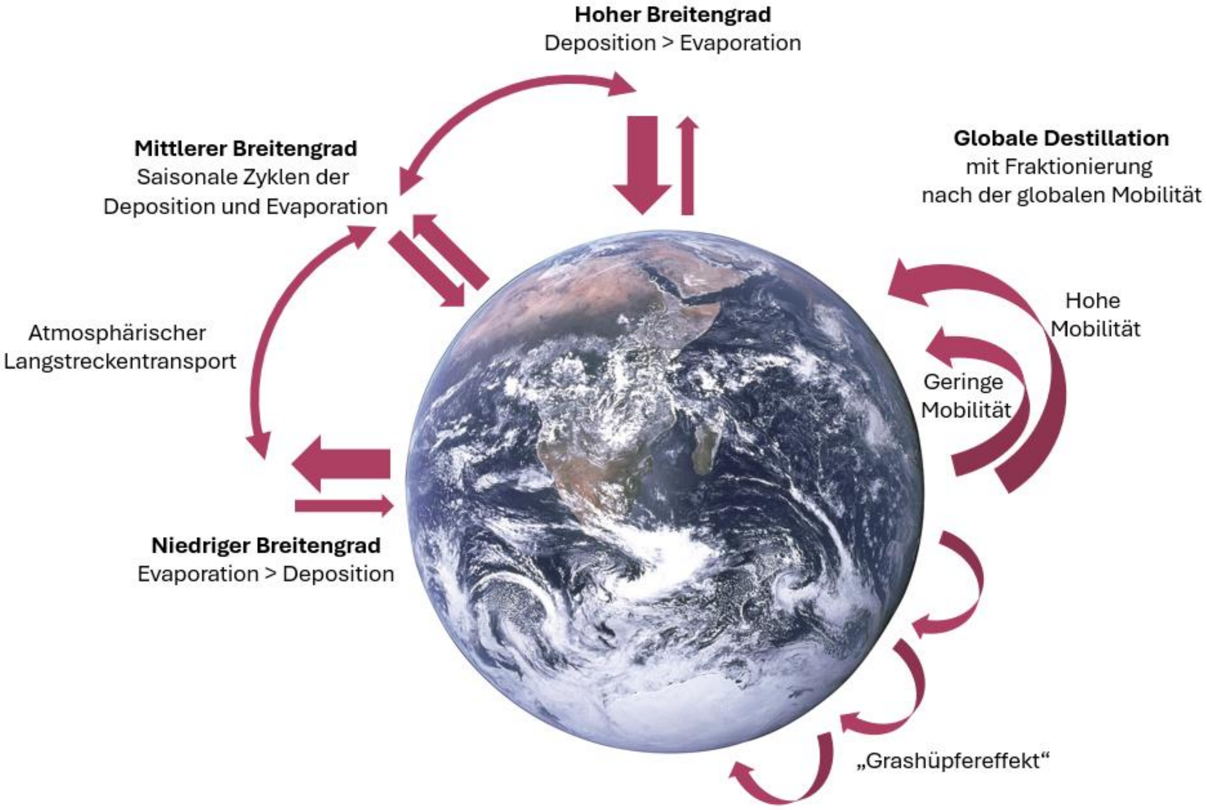


Abbildung 1. Schematische Darstellung der globalen Destillation und des „Grashüpfereffekts“, verändert nach Wania und Mackay [28] und Vallack et al. [30] (Bild: „The Blue Marble“; CC0 1.0 Universell).

Die toxischen Effekte von POPs wurden bereits weltweit durch Monitoringprogramme in den unterschiedlichsten Ökosystemen dokumentiert, die dabei helfen, das Ausmaß der Kontamination zu erfassen [31]. Unter den verschiedenen POPs nehmen PCB aufgrund ihrer vielseitigen industriellen Anwendungen und großen Produktionsmengen eine besondere Rolle ein. Die Charakteristika, Einsatzgebiete und Umweltprobleme dieser Stoffgruppe werden im folgenden Kapitel detailliert dargestellt.

1.1.2.1 Polychlorierte Biphenyle

PCB sind eine Gruppe von synthetischen organischen Verbindungen, die in der Mitte des 20. Jahrhunderts weltweit in großen Mengen produziert wurden und bis zu ihrem Verbot in zahlreichen industriellen und technischen Anwendungen weit verbreitet waren. PCB bestehen aus zwei verbundenen Benzolringen, deren Wasserstoffatome mit bis zu zehn Chloratomen in unterschiedlichen Positionen substituiert sein können. Diese Struktur führt dazu, dass PCB in bis zu 209 verschiedenen Varianten, den sogenannten Kongeneren, existieren, die sich in ihren chemischen und physikalischen Eigenschaften stark unterscheiden können [32]. Besonders hochchlorierte Kongenere sind dabei sehr stabil, was ihre Persistenz die und damit verbundenen Umweltprobleme verstärkt.

Ein Großteil der produzierten PCB wurde in Form von technischen Gemischen wie Clophen (Bayer, Deutschland), Aroclor (Monsanto, USA), Kanechlor (Kanegafuchi, Japan) oder Phenoclor (Prodolec, Frankreich) verwendet [33]. Sie bestanden jeweils aus PCB-Kongenermischungen mit festgelegten Chlorierungsgraden. So bezeichnete zum Beispiel „Clophen A50“ ein Gemisch mit etwa 50 % Chloranteil, während „Arochlor 1221“ etwa 21 % Chlor enthielt [34,35]. Diese Mischungen enthielten in der Regel 80 bis 100 der möglichen Kongenere, die eine für den jeweiligen Einsatzzweck optimale Balance aus chemischer Stabilität und spezifischen physikalischen Eigenschaften boten.

Die PCB-Industrie profitierte lange Zeit von der Annahme, dass PCB inert seien und keine negativen Auswirkungen auf die Umwelt hätten. Erst in den 1970er-Jahren wurde bekannt, dass PCB in der Umwelt sehr persistent sind, sich bioakkumulieren und in Nahrungsnetzen anreichern können. Nach dem Verbot von PCB im Rahmen des Stockholmer Übereinkommens wurden PCB weltweit aus dem Verkehr gezogen, aber viele Altlasten, etwa in Geräten und in kontaminierten Böden, bestehen bis heute fort und tragen zur aktuellen Umweltbelastung bei.

Trotz der Verbreitung und Risiken von PCB ist die Analyse aller 209 theoretisch möglichen Kongenere aufwendig. Deshalb hat sich international die Methode durchgesetzt, nur eine, idealerweise repräsentative, Untergruppe von sogenannten Indikator-Kongeneren (PCB_{i+118}) zu messen. Diese sechs bis sieben repräsentativen Kongenere (PCB 28, 52, 101, 118, 138, 153 und 180) ermöglichen eine vereinfachte Schätzung der Gesamtbelastung, indem ihre Summenkonzentration mit einem Multiplikationsfaktor von 5 zur Schätzung der Gesamtmenge herangezogen wird [36]. Diese Annäherungsmethode hat jedoch ihre Grenzen: In Fällen von hochchlorierten PCB-Kongeneren kann die Summe der Indikatoren die tatsächliche Belastung überschätzen, während sie bei niedrigchlorierten PCB-Kongeneren die PCB-Gesamtkonzentration oft unterschätzt. Eine vollständige Analyse aller 209 theoretisch möglichen PCB-Kongenere ist jedoch aufgrund des hohen Aufwands meist nicht praktikabel.

Insgesamt stellen PCB aufgrund ihrer Bioakkumulationseigenschaften und toxischen Effekte eine schwerwiegende Gefahr für die Umwelt und die menschliche Gesundheit dar. Die Langzeitstabilität und die nach wie vor bestehende Verbreitung in vielen Umweltmedien, darunter auch Trink- und Grundwasser in ehemals industriell genutzten Regionen, machen PCB zu einem zentralen Thema für das Umweltmanagement und die Schadstoffsanierung.

1.1.2.2 PCB in der Bergbauindustrie – Verwendung, Verbleib und Herausforderungen

Vor knapp 100 Jahren wurden PCB aufgrund ihrer vermeintlichen Unbedenklichkeit und Umweltfreundlichkeit als besonders vielversprechend angesehen. Sie wurden durch ihre Eigenschaften als nicht brennbare und nicht explosive Stoffe als Kühl- und Isolierflüssigkeit genutzt, weshalb sie vor allem in Kondensatoren, Transformatoren, und Vorschaltgeräten vorkamen [34]. In Ermangelung des Wissens über ihre schädlichen Auswirkungen wurde jedoch oftmals sorglos mit diesen Stoffen umgegangen. So wurden bei der Schließung von Gruben häufig PCB-haltige Ausrüstungen zurückgelassen, was im schlimmsten Fall zu einer Verunreinigung des Grundwassers führen konnte [37]. Ende der 1960er Jahre setzten die Hersteller verstärkt auf niedrigchlorierte PCB (in Deutschland A30 und A40), da diese als „umweltfreundlicher“ galten [38]. Bereits 1965 wies Monsanto darauf hin, dass PCB-Gemische aufgrund ihrer toxischen Eigenschaften auf geschlossene Systeme beschränkt werden sollten [39]. Trotz der späteren Reduktion der Verwendung von PCB in Kondensatoren, Transformatoren, Wärmeübertragungs- und Hydraulikflüssigkeiten in Bergmaschinen kam es weiterhin zu Leckagen [40]. In den USA wurden PCB und PCB-haltige Produkte frühzeitig verboten [41], während ihre Verwendung im deutschen Bergbau erst 1992 eingestellt wurde [42]. In Deutschland wurden etwa 12.000 t PCB-haltige Hydrauliköle verwendet. Lediglich 10 % davon wurden recycelt und 5 % entsorgt [4]. Der Rest verblieb in den Minen.

Diese zurückgelassenen PCB sind jedoch einem ständigen Wassereintrag ausgesetzt, da Grundwasser oder Niederschläge in die Schächte eindringen. Dies macht Arbeiten in aktiven Minen unmöglich und bedroht sowohl die Grundwasserqualität als auch die Stabilität des Schachtsystems und der darüberliegenden Umwelt [43]. Um dies zu verhindern, wird das Grubenwasser hochgepumpt und zur Verdünnung in Oberflächengewässer eingeleitet (Abbildung 2). Trotz ihrer geringen Löslichkeit werden bedeutsame Mengen an PCB vom Grubenwasser aufgenommen und, teils auch an Partikeln haftend, an die Oberfläche transportiert. Begutachtete Artikel zu den PCB-Konzentrationen in Grubenwässern und MIW fehlen jedoch. Ein möglicher Grund hierfür ist, dass die gefundenen PCB-Konzentrationen oft unterhalb der Bestimmungs- (LOQs) oder Nachweisgrenzen (LODs) liegen. Werte unterhalb des LOD bedeuten jedoch nicht zwangsläufig, dass keine bedenklichen Mengen an PCB vorhanden sind. Aufgrund der hohen Persistenz von PCB können diese selbst bei niedrigsten Konzentrationen über Jahrzehnte hinweg von Organismen aufgenommen werden. Ein bekanntes Beispiel ist der Schwertwal Lulu, dessen Tod 2017 ein internationales Medienecho auslöste [44]. Selbst Konzentrationen von 0,071–1,7 pg L^{-1} in den Ozeanen [45] können zu einer derartigen Anreicherung im Nahrungsnetz führen, dass im Fettgewebe eines Orcas eine PCB-Konzentration von 957 mg kg^{-1} nachgewiesen werden konnte [46]. Dieser Wert war über 100 Mal höher als der Grenzwert von 9 mg kg^{-1}, ab dem bekanntermaßen Gesundheitsschäden bei Meeressäugern auftreten [47]. Ein weiterer Grund für das Fehlen von Studien könnte der hohe Aufwand bei der Analyse von Grubenwasser auf PCB sein. Für aussagekräftige Messungen sind häufig 100-Liter-Proben für Extraktionen oder die

Verwendung von Passivsammlern über mehrere Wochen hinweg erforderlich [8]. Die Messmethoden für PCB sind also oft eingeschränkt, entweder durch hohe Nachweisgrenzen, wie im vorherigen Abschnitt erwähnt durch die Analyse auf lediglich PCB_{i+118}, oder durch den erheblichen Aufwand der Probenahme- und Extraktionsmethoden. Bisher fehlte eine geeignete Methode mit niedrigen Nachweisgrenzen, die eine umfassende Analyse möglichst vieler PCB-Verbindungen in Grubenwässern und MIW ermöglicht.

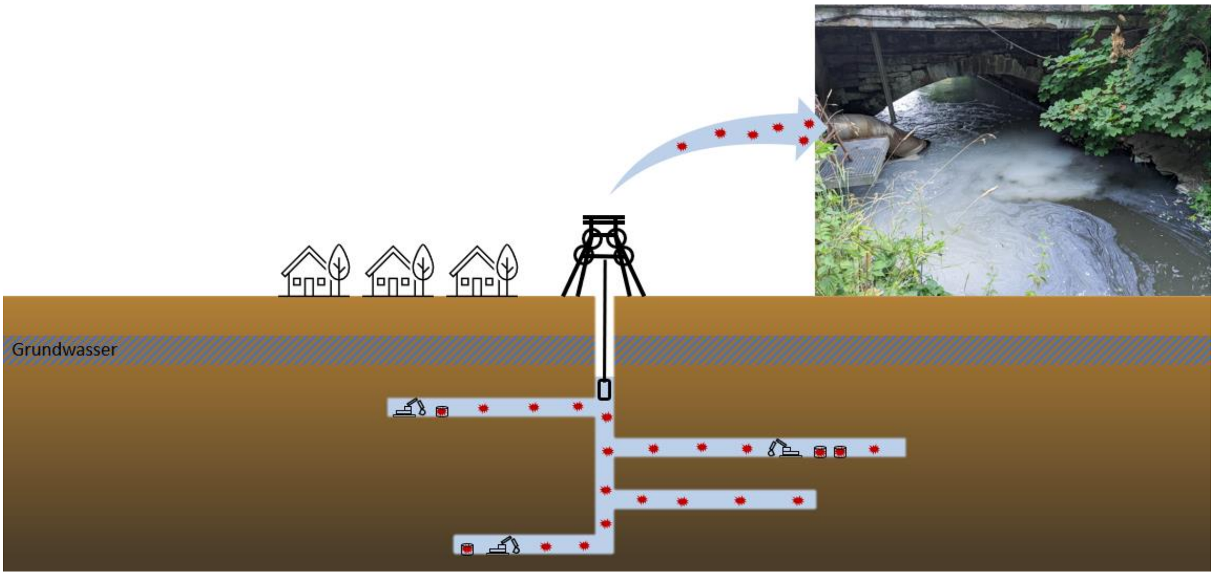


Abbildung 2. Schematische Darstellung der Grubenwasserhaltung mit daraus folgendem PCB-Eintrag in die Oberflächengewässer (Abbildung angelehnt an Wiltschka et al. [48], CC-BY 4.0.; Foto: K. Wiltschka, Grubenwassereinleitung in den Fischbach, Saarland).

Verbesserungsbedarf besteht jedoch nicht nur beim Nachweis von PCB in Grubenwässern, sondern auch beim Umgang mit diesen, um Mensch und Umwelt nicht weiter zu belasten. Da es sich bei Grubenwässern um Punktquellen handelt, bieten sich hier gezielte Verfahren zur Reduzierung der PCB-Konzentrationen an, bevor diese Stoffe weiter in der Umwelt verteilt werden.

1.1.3 Analytische Methoden

1.1.3.1 Festphasenmikroextraktion – Definition und Vorteile

Die Festphasenmikroextraktion (solid-phase microextraction, SPME) basiert auf der Verteilung der Analyten zwischen einer Probe und einer polymerbeschichteten Quarzfaser [49]. Sie ist eine lösungsmittelfreie, miniaturisierte Extraktionsmethode, und bietet damit eine vielversprechende Grundlage für die auf grüner Chemie basierenden Forschung [50]. Die Faser wird entweder direkt in die flüssige Probe eingetaucht („immersed“ SPME) oder in den Gasraum über der Probe („headspace“, HS-SPME) positioniert [49,51–54] (Abbildung 3), wobei Zweiteres die Lebensdauer der Faser erhöht [49]. Die Extraktion ist dabei nicht erschöpfend, allerdings werden die Analyten von der Faser annähernd vollständig in den Injektor übertragen. Die Auswahl der Polymerbeschichtung richtet sich nach den physikochemischen Eigenschaften der zu analysierende Stoffe. SPME wurde bereits für die Analyse von PCB eingesetzt [55–58], jedoch bisher nicht für deren Nachweis in kontaminierten Grubenwässern oder MIW.

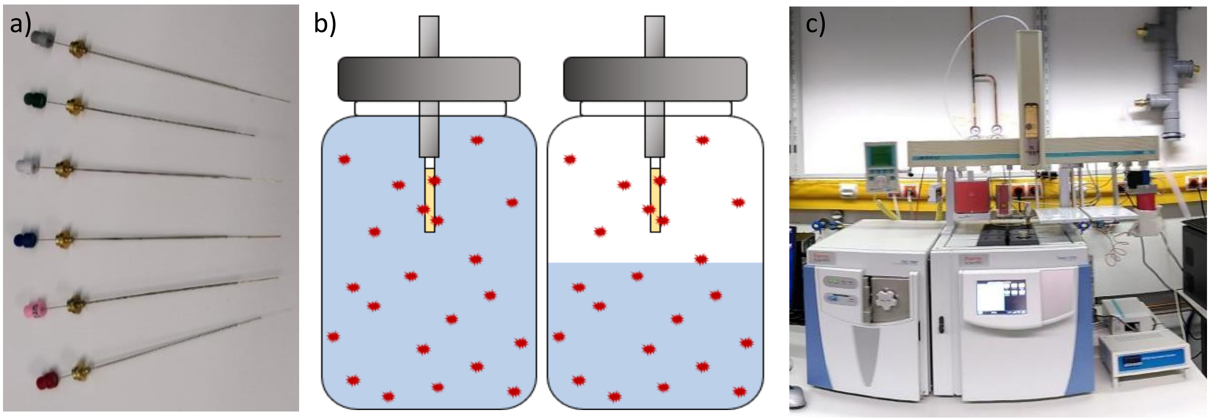


Abbildung 3. Schematische Darstellung von SPME. a) Verschiedene SPME-Fasern mit unterschiedlichen Beschichtungen und Beschichtungsmengen, erkennbar an der Kopffarbe; b) Gegenüberstellung von immersed SPME und HS-SPME; c) GC-MS mit einem Autosampler für SPME-Messungen.

Die Probenmatrix spielt bei der Extraktion eine entscheidende Rolle. Matrixkomponenten wie gelöste Salze und Metalle, der pH-Wert, sowie Schwebstoffe können zu Matrixeffekten führen, die die Analyse erschweren oder die Lebensdauer der Fasern verkürzen. Für solche komplexen Matrizes bietet die HS-SPME erhebliche Vorteile, da die Faser nicht direkt mit der Probenmatrix in Kontakt kommt, wodurch eine aufwendige Probenvorbereitung entfällt. Im Gegensatz zu anderen Methoden, die oft zwischen adsorbierten und frei gelösten Konzentrationen differenzieren, ermöglicht SPME die Bestimmung der PCB-Gesamtkonzentration in unbehandelten MIW-Proben, was durch den Einsatz eines geeigneten Internen Standards (IS) gewährleistet ist.

Die SPME bietet im Vergleich zur Festphasenextraktion (solid-phase extraction, SPE) und der Flüssig-Flüssig-Extraktion (liquid-liquid extraction, LLE) mehrere Vorteile, insbesondere hinsichtlich Umweltfreundlichkeit, Effizienz und Anwendungsmöglichkeiten. Ein großer Vorteil der SPME ist der Verzicht auf organische Lösungsmittel, die bei der LLE in großen Mengen und bei der SPE für die Konditionierung der Kartuschen und Elution der Analyten erforderlich sind [59,60]. Darüber hinaus ist die SPME weniger arbeitsintensiv, da sie ohne komplexe Vorbereitungsschritte wie Konditionierung, Waschen und Elution auskommt, die für die SPE typisch sind. Ein weiterer Vorteil der SPME ist ihre Vielseitigkeit. Mit HS-SPME können flüchtige Analyten effektiv extrahiert werden, die bei der LLE leicht verloren gehen. Im Vergleich zur SPE bietet die SPME zudem eine größere Optimierungsmöglichkeit durch eine große Auswahl an Polymerbeschichtungen, Möglichkeit zur Temperatureinstellung, Sammeldauer, Rotationsgeschwindigkeit und Desorptionszeit. Ein potenzieller Nachteil der SPME ist allerdings ihre begrenzte Kapazität, wodurch sie besser für Spurenanalyse geeignet ist. Allerdings ist dies bei Grubenwasser- und MIW-Proben meist unproblematisch, da hier ohnehin sehr geringe Analytkonzentrationen vorliegen. In Fällen höherer Analytkonzentrationen kann die SPE aufgrund ihrer größeren Beladungskapazität von Vorteil sein. Dennoch überwiegen die Effizienz und Vielseitigkeit der SPME in vielen Anwendungen, insbesondere bei komplexen Matrizes.

1.1.3.2 Gaschromatographie-Massenspektrometrie

Die Gaschromatographie-Massenspektrometrie (GC-MS) ist eine bewährte Methode zur qualitativen und quantitativen Analyse komplexer organischer Verbindungen. Die Probe wird in den Gaschromatographen eingeführt, wo sie verdampft und anhand ihrer physikochemischen Eigenschaften aufgetrennt wird [61]. Eine Kapillarsäule dient als stationäre Phase, während das Trägergas als mobile Phase dient. Anschließend gelangen die getrennten Substanzen in das Massenspektrometer, wo sie ionisiert und fragmentiert werden. Anhand der resultierenden Massenspektren und Zeiten (Retentionszeiten, RT), die sie von der Injektion bis zum MS brauchen, können die Analyten bestimmt werden. Dies macht die GC-MS zu einer unverzichtbaren Technik in der Umweltanalytik, beispielsweise bei der Untersuchung von Schadstoffen wie PCB. Gerade für Proben mit komplexen Matrizes wie Grubenwasser oder MIW ermöglicht die Methode die empfindliche und selektive Analyse von vielen PCB-Kongeneren in Spurenkonzentrationen. Neben ihrer Vielseitigkeit, die sich durch Anpassungsmöglichkeiten an unterschiedlichste Substanzen auszeichnet, bietet die GC-MS den Vorteil einer präzisen Identifikation und Quantifizierung. Herausforderungen bestehen allerdings bei thermolabilen Substanzen, die bei der Verdampfung zerfallen können [62]. Trotz dieser Einschränkung gilt die GC-MS als Standardmethode für die Analyse flüchtiger und semi-flüchtiger organischer Verbindungen und bleibt in der chemischen und Umweltanalytik von zentraler Bedeutung.

1.1.4 Verschiedene Verfahren zur Reduzierung von chlorierten Stoffen

POPs stellen eine erhebliche Gefahr für die Gesundheit von Mensch und Umwelt dar. Daher wurden zahlreiche Methoden entwickelt, um ihre Konzentrationen in der Umwelt du reduzieren. Eine relativ einfache und weit verbreitete Methode ist die Filtration von POPs und der Partikel, an die sie adsorbiert sind [63–66]. Häufig wird dabei Aktivkohle eingesetzt, die durch ihre feinkörnige Struktur und hohe Porosität eine große innere Oberfläche bietet. Vor allem dreifach- und vierfachchlorierte PCB sorbieren an Aktivkohle [67], wodurch ihre Bioverfügbarkeit stark reduziert wird [68]. Allerdings bleiben die adsorbierten POPs chemisch stabil und können prinzipiell wieder mobilisiert werden. Deshalb ist eine sichere Entsorgung, thermische Zerstörung oder die Kombination mit mikrobiellen Abbauverfahren notwendig, um die Schadstoffe langfristig zu eliminieren. Letzteres bietet den Vorteil, dass POPs adsorptiv akkumuliert und gleichzeitig biologisch abgebaut werden [69–71].

Die Nutzung von mit Biofilm überzogener Aktivkohle wurde bereits in den 1970er Jahren intensiv untersucht [72] und hat sich seither in der Abwasserbehandlung etabliert [73]. Mikroorganismen bauen die Schadstoffe entweder durch Umwandlung oder vollständige Entfernung ab [74]. Hochchlorierte POPs werden dabei zunächst unter anaeroben Bedingungen zu niedrigchlorierten Verbindungen dechloriert, die anschließend aerob weiter abgebaut werden können [75,76]. Der biologische Abbau von PCB ist jedoch zeitaufwändig und kann mehrere Monate in Anspruch nehmen [65,77]. Zudem ist es nicht immer möglich, alle PCB vollständig zu Biphenyl zu dechlorieren [78]. Ein weiteres Hindernis ist die Schaffung geeigneter Umweltbedingungen für die Mikroorganismen, was insbesondere bei stark kontaminierten Proben mit Mischbelastungen problematisch sein kann.

Ein weiteres passives Verfahren zur PCB-Entfernung ist die Phytoremediation. Dabei nutzen Pflanzen und Böden Sorption, Aufnahme (unterstützt durch pflanzliche Tenside [79]) oder mikrobiellen Abbau, um PCB zu entfernen [80–82]. Feuchtgebiete wurden bereits erfolgreich für die Behandlung von Regenwasser, kommunalem Abwasser und bergbaubedingten Abwässern eingesetzt. Aufgrund der hohen log K_{OW}-Werte der PCB ist die direkte Aufnahme von Pflanzen jedoch begrenzt [83], sodass der Beitrag der Phytoremediation in der Regel indirekt über die Stimulierung mikrobieller Aktivität erfolgt [84]. Der vollständige Abbau kann zudem viel Zeit erfordern [85].

Darüber hinaus ist die chemische Dechlorierung von PCB eine weitere Option, die jedoch oft hohe Temperaturen und Drücke erfordert [86]. Niedervalente Metalle wie Alkalimetalle in alkoholischen Lösungen oder Magnesium und Zink in sauren oder basischen Medien haben sich dabei als effektiv erwiesen [87,88]. Bei diesen Prozessen werden PCB durch aromatische nukleophile Substitution in weniger chlorierte Verbindungen umgewandelt [89]. Chemische Verfahren sind im Vergleich zu biologischen Methoden deutlich schneller (Minuten bis Stunden) [89–91], gehen jedoch mit hohen Kosten einher und werden deshalb meist gezielt für besonders belastete Proben eingesetzt.

1.1.4.1 Metallkatalysatoren: Lösungen für belastete Umweltproben

Um die theoretisch extremen Reaktionsbedingungen bei der Dechlorierung von POPs zu vermeiden, können Katalysatoren eingesetzt werden. Metallnanopartikel katalysieren dabei die Bildung von Wasserstoffradikalen aus Elektronendonatoren wie molekularem Wasserstoff (H_2). Diese Radikale ermöglichen die Substitution von Halogenatomen im POP-Molekül. Besonders häufig kommen Übergangsmetalle wie Nickel oder Pd zum Einsatz. Pd-Katalysatoren zeigen im Vergleich zu anderen Metallen eine höhere Aktivität und Selektivität sowie eine geringere Toxizität und verbesserte Stabilität unter Laborbedingungen. Daher gelten sie als vielversprechend für die Behandlung von PCB-kontaminierten (Ab-)Wasser und Boden-Wasser-Systemen [13,92–99].

Pd-katalysierte Hydrodechlorierungen zeichnen sich durch ihre Effizienz aus, da die Reaktionen oft bei Raumtemperatur und innerhalb von Minuten bis Stunden ablaufen [92,94,100]. Trotz dieser Vorteile können hohe Kosten für die Herstellung von Übergangsmetallkatalysatoren die Anwendung einschränken. Zudem sind viele Katalysatoren nicht wiederverwendbar, was die Wirtschaftlichkeit und Nachhaltigkeit der Verfahren beeinträchtigt. Auch eine Freisetzung von Metallnanopartikeln in die Umwelt könnte potenzielle Risiken bergen [101,102]. Ein weiteres Problem sind die sogenannten Katalysatorgifte, also Substanzen in den zu behandelnden Medien, die die Aktivität der Katalysatoren hemmen können [103].

Um diese Herausforderungen zu adressieren, können Metallnanopartikel in Silikon, wie zum Beispiel Polydimethylsiloxan (PDMS), eingebettet und als dünne Schicht auf Oberflächen in Reaktionsgefäßen aufgetragen werden. Solche Beschichtungen verhindern Agglomeration [104] und reduzieren die Exposition gegenüber katalytischen Giften, wodurch die Stabilität und Langlebigkeit der Katalysatoren verbessert wird [105]. Studien zeigen, dass Pd-PDMS-Verbundstoffe einen zuverlässigen Schutz vor ionischen Störsubstanzen bieten [14,105], allerdings geht dies mit einer leicht verringerten katalytischen Aktivität einher [105]. Eine hohe Stabilität der Katalysatoren ist jedoch entscheidend für nachhaltige Anwendungen.

Da die Strukturen von HCB und PCB ähnliche Eigenschaften aufweisen – HCB besteht aus einem chlorierten Benzolring, PCB bestehen aus zwei, über eine C-C-Bindung verknüpften, Benzolringen – wird angenommen, dass ihre Dechlorierungsmechanismen vergleichbar sind. Hochchlorierte PCB können jedoch durch partielle Dechlorierung toxischere, dioxinähnliche Zwischenprodukte bilden. Ein Verständnis der zugrundeliegenden Mechanismen ist daher entscheidend, um solche unerwünschten Produkte vorherzusagen, beziehungsweise im besten Fall auszuschließen.

1.1.5 Forschungsziele

Die Hauptziele dieser Dissertation lauten:

Eine hochaufgelöste Quantifizierung von PCB in Grubenwässern und darauf aufbauend eine Erarbeitung von Ansätzen zur Reduktion der PCB-Belastung vor der Einleitung in Oberflächengewässer.

Die Forschungsziele gliedern sich in drei zentrale Aspekte, die jeweils in einem eigenen Kapitel behandelt werden:

i) **Anpassung und Optimierung einer analytischen Methode:** Anpassung und Optimierung einer SPME-GC-MS-Methode zur effizienten Extraktion und Analyse von 58 PCB-Kongeneren aus Grubenwässern. Ziel ist es, präzise Gesamtkonzentrationen und jährliche Frachten von PCB zu berechnen (Kapitel 2)

ii) **Beschreibung der Dechlorierungsmechanismen:** Aufklärung der Dechlorierungsmechanismen, Reaktionspfade und Intermediate bei PCB-ähnlichen, aber strukturell einfacher aufgebauten Analyten, mittels Pd-Katalysatoren (Kapitel 3)

iii) **Entwicklung wiederverwendbarer geschützter Katalysatorensysteme:** Einbettung von Pd-Katalysatoren in eine PDMS-Schicht, um deren Wiederverwendbarkeit sicherzustellen und ihre Aktivität gegenüber Katalysatorgiften in komplexen Grubenwasser-Matrizes zu schützen (Kapitel 4)

Die Ergebnisse dieser Arbeit sollen bestehende Wissenslücken hinsichtlich der PCB-Belastung in Grubenwässern, MIW und anderen Umweltmedien schließen. Zudem wird ein Beitrag zur Entwicklung nachhaltiger Technologien geleistet, die es ermöglichen, auch nicht vorbehandelte, komplexe und mit halogenierten Stoffen belastete Wässer ressourcenschonend und effektiv zu reinigen. Diese Technologie könnte zukünftig dazu beitragen, den Eintrag toxischer Verbindungen in die Umwelt zu reduzieren. Diese strukturierte Vorgehensweise verbindet grundlagenwissenschaftliche Untersuchungen mit anwendungsorientierten Technologien und soll langfristig zur Lösung drängender Umweltprobleme beitragen.

1.2 Forschungsansatz – Methoden

1.2.1 Quantifizierung von PCB in Grubenwässern

Um die analytischen Herausforderungen bei der Spurenanalyse von PCB zu bewältigen und eine zuverlässige Methode zur Extraktion und Analyse zu entwickeln (i), wurden geeignete Extraktionsmethoden aus der Literatur ausgewählt und optimiert [55–58]. Der Schwerpunkt lag auf der Analyse von niedrigchlorierten PCB sowie Biphenyl, allerdings ist die Methode mit kleinen Änderungen auch für hochchlorierte PCB geeignet. Insgesamt wurden fünf verschiedene Grubenwässer an verschiedenen Standorten untersucht. Die Standorte Walsum und Zollverein (einschließlich Strang Stinnes) befinden sich im Steinkohlerevier des Ruhrgebiets (Nordrhein-Westfahlen (NRW), Deutschland), während die Zechen Reden und Camphausen im Saarland (Deutschland) liegen (Abbildung 4).

Die Grubenwässer in NRW wurden über einen Zeitraum von 26 Monaten an vier Terminen beprobt, um mögliche zeitliche Schwankungen der PCB-Konzentrationen zu erfassen. Am Standort Reden erfolgt vor der Ableitung des Grubenwassers über den Mosesgang in den Nebelbach eine thermische Nutzung. Der Nebelbach, ein künstlicher Bachlauf mit einer Länge von etwa 500 m, wird ausschließlich aus Grubenwasser gespeist. Zur Untersuchung des Remediationspotenzials des damit verbundenen Feuchtbiotops wurden Wasserproben entlang des Bachverlaufs entnommen.

Für die Handhabung organischer Verbindungen wurden Glasbehältnisse verwendet, um Adsorptionsverluste an Kunststoffoberflächen zu vermeiden. Die Probenahmeflaschen (0,5- oder 1-L-Schottflaschen, Duran®, mit Schraubverschlussdeckeln und PTFE-beschichteter Silikondichtung) wurden vor Gebrauch gründlich mit Aceton und Reinstwasser (mQ-Wasser) gereinigt. Vor der Probenahme im Saarland wurden die Flaschen dreimal mit dem jeweiligen Grubenwasser gespült, bevor die eigentliche Probe entnommen wurde. Um Kontakt mit Luftsauerstoff und eine mögliche Volatilisierung der PCB zu vermeiden, wurden die Probenflaschen vollständig befüllt. Die Proben wurden bis zur Analyse bei 4 °C gelagert, um chemische Umwandlungsprozesse zu minimieren.

Für die Messung wurde jeweils ein Aliquot von 10 mL der Grubenwasserproben in ein 20 mL-SPME-Fläschchen überführt und mit IS versetzt. Der IS enthielt sowohl vier deuterierte (B-d_{10}, PCB 3-d_5, PCB 9-d_5, PCB 18-d_5) als auch acht ^{13}C-markierte (^{13}C-PCB 9, ^{13}C-PCB 28, ^{13}C-

Abbildung 4. Übersicht der Probenahmestandorte für Grubenwasser. a) Übersicht der beprobten Zechengebiete in NRW und im Saarland (Deutschland); b) Standort Reden, Mosesgang (Foto: K. Wiltschka); c) Standort Zollverein, mit den Strängen Zollverein und Stinnes (Foto: M. Dittmar); d) Standort Camphausen, Einleitung in den Fischbach (Foto: K. Wiltschka).

PCB 52, ^{13}C-PCB 101, ^{13}C-PCB 118, ^{13}C-PCB 138, ^{13}C-PCB 153, ^{13}C-PCB 180) Isotope, um eine große Ähnlichkeit zwischen den jeweiligen Kongeneren und entsprechenden IS zu gewährleisten. Die Analyten wurden mit dem IS korrigiert, der die ähnlichste RT besaß. Die Arbeitsschritte erfolgten unter inertem Stickstoff-Kohlendioxid-Gemisch (80:20) in einer Anaerobbox, um

Sauerstoffeintrag zu vermeiden und Veränderungen in der Probenzusammensetzung zu verhindern.

Die Grundlagen der SPME-Methode wurden auf Basis mehrerer Studien zur PCB-Analytik [55–58] entwickelt. Da die Faserbeschichtungen kontinuierlich weiterentwickelt werden und die Extraktionseffizienz der Fasern stark von Matrixeigenschaften, Temperatur und weiteren Parametern abhängt, wurden die wichtigsten SPME-Bedingungen systematisch optimiert. Zu den untersuchten Parametern gehörten die Faserbeschichtung (sechs verschiedene Beschichtungstypen: 50/30 µm Divinylbenzol/Carboxen/PDMS (DVB/CAR/PDMS), 7 und 100 µm PDMS, 65 µm DVB/PDMS sowohl mit StableFlex™ als auch mit Nitinolkern, und 85 µm Polyacrylat (PA)), die Extraktionstemperatur (40–90 °C in 10 K-Schritten), die Equilibrierungsdauer (die Zeit, die die Probe braucht, um die gewünschte Extraktionstemperatur zu erreichen), die Extraktionszeit (10–50 min in 10 min-Schritten), die Durchmischungsintensität während der Extraktion (250–700 rpm, sechs Intensitäten), die Desorptionszeit (1–3 min) und die Faserreinigungszeit (0–21 min in 3 min-Schritten).

Die PCB-Analytik erfolgte mittels GC, gefolgt von MS. Dabei wurden die PCB zunächst nach ihren physikochemischen Eigenschaften chromatographisch getrennt und anschließend auf Basis ihres Masse-zu-Ladung-Verhältnisses detektiert. Zur Trennung wurde eine 60 m lange TraceGOLD TG-XLBMS Säule mit einem Durchmesser von 0,25 mm und einer Beschichtungsdicke von 0,25 µm verwendet, die aufgrund ihrer guten Trennleistung besonders für die PCB-Analyse geeignet ist. Basierend auf Literaturdaten zu Ofentemperaturprogrammen [55,57,58] wurde ein angepasstes Temperaturprogramm entwickelt, um möglichst viele der 58 analysierten PCB-Kongenere ($\sum PCB_{58}$) basisliniengetrennt zu separieren.

1.2.2 Dechlorierung von chlorierten organischen Verbindungen

Zur Untersuchung des Dechlorierungspotenzials von Metallkatalysatoren sowie der zugrunde liegenden Dechlorierungsmechanismen und -pfade (ii) wurde HCB, dessen Struktur PCB ähnelt, zusammen mit anderen Chlorbenzolen (CB) in umweltrelevanten Konzentrationen durch Pd(0)-Nanopartikel dechloriert. Um die Reaktionswege umfassend zu analysieren, war es notwendig, die Bildung und den Abbau potenzieller Zwischenprodukte zu verfolgen. Dabei stellt sich die Herausforderung, zu differenzieren, ob die Konzentration eines Zwischenproduktes auf eine hohe Entstehungsrate oder auf dessen Charakter als sogenanntes Dead-End-Produkt (chemische Verbindung, die keine weiteren Reaktionsprozesse eingeht) zurückzuführen ist. Aus diesem Grund wurden in den Dechlorierungsexperimenten zusätzlich die elf möglichen Dechlorierungsprodukte – Pentachlorbenzol (PeCB), drei Tetrachlorbenzole (TeCB), drei Trichlorbenzole (TCB), drei Dichlorbenzole (DCB) und Monochlorbenzol (MCB) – als Ausgangsverbindungen untersucht. Auch hier wurden mehrere Isotope als IS eingesetzt (^{13}C-HCB, ^{13}C-PeCB, ^{13}C-1,2,3,4-TeCB, ^{13}C-1,2,3-TCB, ^{13}C-1,4-DCB, ^{13}C-MCB und B-d_6), um die Genauigkeit der Analyse zu verbessern.

Um den Reaktionsverlauf bis zum Endprodukt Benzol (B) präzise zu verfolgen und Ressourcen effizient zu nutzen, wurden die Experimente direkt in den 20 mL-Fläschchen durchgeführt, die später für die Analyse verwendet wurden. Die Versuche fanden in einer anaeroben Umgebung statt, um eine Deaktivierung des Katalysators durch Luftsauerstoff zu verhindern. Zunächst wurden die Pd(0)-Dispersion und die Pufferlösung (9 g L^{-1} Natriumhydrogencarbonat, $NaHCO_3$, und 2.94 g L^{-1} Trinatriumcitrat Dihydrat, $C_6H_5Na_3O_7 * 2\ H_2O$) mit Wasserstoff (H_2) angereichert, um optimale Bedingungen für die Dechlorierung zu schaffen. Hierfür wurden die beiden Flüssigkeiten 30 min lang mit H_2 durchströmt. Danach wurden 10 mL einer Mischung aus Pufferlösung und Pd(0)-Dispersion in ein 20 mL-Fläschchen überführt. Um noch mehr Wasserstoff als Elektronendonatoren zur Verfügung zu stellen, wurde 1 mL des Gasraums mit einer Spritze durch 1 mL H_2 ersetzt. Nach der Zugabe von HCB oder einem anderen Chlorbenzol (3 µg L^{-1}, oder 6 µg L^{-1} für MCB) startete die Reaktion, und die Fläschchen wurden auf einem Horizontalschüttler zur besseren Durchmischung platziert.

Die Dechlorierung wurde nach definierten Zeitintervallen (1, 3, 6, 12, 30 oder 60 min) durch Zugabe eines Katalysatorgifts (Natriumsulfit, Na_2SO_3) gestoppt. Anschließend wurde IS hinzugefügt. Für die Zeitstufe „0 min“, sowie die Kalibrierstufen wurde das Katalysatorgift bereits zu Beginn zusammen mit der Pufferlösung in die Fläschchen gegeben, um eine identische Matrix ohne Dechlorierungsreaktion zu erhalten. Jedes Zeitintervall wurde in vierfacher Wiederholung durchgeführt. Die Proben wurden anschließend mittels SPME-GC-MS gemessen.

Die katalytische Hydrodechlorierung folgt einer Reaktion pseudoerster Ordnung. Die spezifische Pd-Aktivität des Nanokatalysators für die Substanz „*i*“ ($A_{Pd,i}$) wurde mit folgender Gleichung berechnet [100]:

$$A_{Pd,i}[L\ g^{-1}min^{-1}] = \frac{V_{Wasser}}{m_{Pd} \cdot \tau_{1/2}} = \frac{\ln\left(\frac{c_{t0,i}}{c_{tx,i}}\right)}{ln2 \cdot c_{Pd} \cdot (t_x - t_0)} \qquad (1)$$

Dabei stehen

- V_{Wasser} [L] für das Volumen der Reaktionslösung
- m_{Pd} und c_{Pd} für die Masse bzw. Konzentration des Pd-Katalysators
- $\tau_{1/2}$ für die Halbwertszeit des Reaktanten
- t_0 und t_x für die Start- bzw. Endzeit (wobei x = der Zeitpunkt der Katalysatorvergiftung, 1–60 min)
- c_{t0} und c_{tx} für die Konzentration der Substanz *i* zu den entsprechenden Zeitpunkten

1.2.3 Einbettung von Katalysatoren in eine Beschichtung

Um die spezifische katalytische Aktivität von Pd-Katalysatoren auch in Gegenwart katalysatorgiftreicher Grubenwässer aufrechtzuerhalten (iii), wurden Pd/Al_2O_3-Partikel in eine PDMS-Schicht eingebettet. Die Einbettung soll die Katalysatoren fixieren und gleichzeitig eine hohe katalytische Effizienz sicherstellen.

Zur Untersuchung der Dechlorierungsmechanismen und der katalytischen Aktivität wurden HCB-Dechlorierungsexperimente mit Pd(0)-Partikeln und vier grubenwasserspezifischen PCB-Kongeneren (PCB 4, 18, 28, 52) durchgeführt. Diese Experimente erlaubten sowohl die Überprüfung der Dechlorierungswege als auch die Quantifizierung der katalytischen Aktivitäten unter optimalen Bedingungen (dispergierter Katalysator in Pufferlösung). Es zeigte sich jedoch, dass dispergierte Pd(0)-Partikel ungeeignet für die Einbettung in eine PDMS-Schicht sind. Vorangegangene Untersuchungen haben gezeigt, dass Pd/Al_2O_3-Partikel im Vergleich zu anderen Pd-basierten Katalysatoren die katalytische Aktivität am effektivsten aufrechterhalten können [14]. Daher wurden diese Partikel für die Einbettung in die PDMS-Schicht verwendet.

Für die Beschichtung kam SilGel® 612 A/B (Silgel) zum Einsatz, das zur besseren Verarbeitbarkeit mit Hexan verdünnt wurde. Unterschiedliche Silgelmengen (75, 375 oder 750 mg) wurden mit 0,3 mg Pd/Al_2O_3-Partikeln in 20 mL-Fläschchen gegeben. Um eine gleichmäßige Beschichtung der Innenwände der Fläschchen zu erreichen, wurden diese in einen Überkopfschüttler (Abbildung 5) eingespannt und über Nacht rotiert, sodass das Hexan vollständig abdampfen konnte und sich ein dünner Silgel-Film auf der Innenseite bildete.

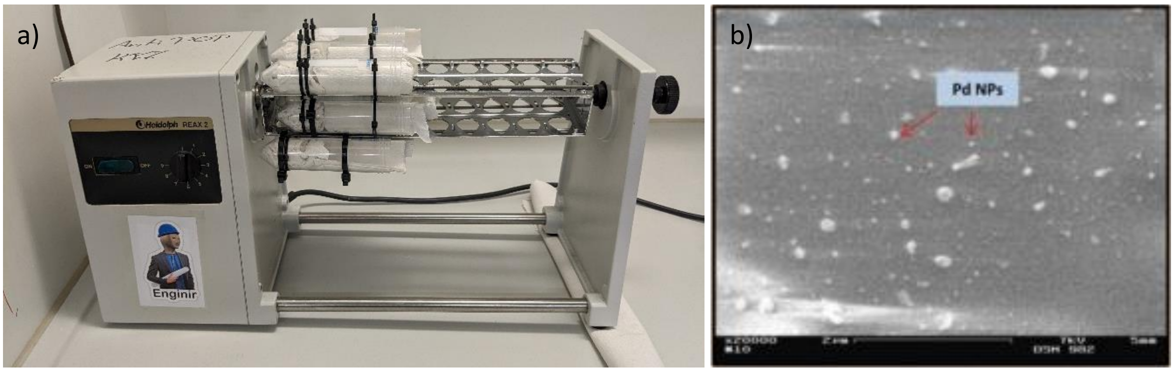


Abbildung 5. a) Überkopfschüttler für das Auftragen der Beschichtung an die Innenseiten der Fläschchen, b) In PDMS eingebettete Pd-Nanopartikel [105].

Die spezifischen katalytischen Aktivitäten der Katalysatoren wurden unter drei verschiedenen Bedingungen verglichen: dispergierte Pd(0)-Partikel, suspendierte Pd/Al_2O_3-Partikel und in PDMS eingebettete Pd/Al_2O_3-Partikel. Die Experimente wurden sowohl in einer Pufferlösung als auch in drei repräsentativen Grubenwässern (Walsum, Stinnes, Reden) durchgeführt. Der Abbruch der Dechlorierungsreaktion wurde bei dispergierten Katalysatoren durch Zugabe eines Katalysatorgifts erreicht, während er bei suspendierten und eingebetteten Katalysatoren durch Aliquotentnahme und anschließende Zugabe des Katalysatorgifts erfolgte. Während die dispergierten und suspendierten Katalysatoren für Reaktionszeiten von bis zu 60 min getestet wurden, wurden die eingebetteten Katalysatoren unter Langzeitbedingungen bis zu 48 Stunden untersucht. Diese Vorgehensweise erlaubte eine umfassende Bewertung der Stabilität und Effektivität der eingebetteten Katalysatoren im Vergleich zu den nicht eingebetteten Varianten.

1.3 Zusammenfassung der Ergebnisse

1.3.1 PCB-Belastung von Grubenwässern

Die getesteten SPME-Fasern zeigen deutliche Unterschiede in ihren Extraktionseigenschaften für PCB-Kongenere und Biphenyl. Für niedrigchlorierte PCB erwiesen sich zwei Fasern mit einer 65 µm PDMS/DVB-Beschichtung als besonders effizient. Dabei führte die Variante mit einem Nitinol-Kern (anstelle von StableFlex™) zu stabileren und weniger schwankenden Extraktionsraten. Mit steigendem Chlorierungsgrad nahm jedoch die Extraktionseffizienz ab. Eine Faser mit einer 100 µm-dicken PDMS-Beschichtung war am besten für hochchlorierte PCB geeignet, zeigte jedoch eine geringere Eignung für niedrigchlorierte Kongenere.

Die optimale Extraktionstemperatur variierte zwischen 60 °C und 90 °C. Niedrigchlorierte PCB und Biphenyl wurden bei niedrigeren Temperaturen effizienter extrahiert, während höherchlorierte PCB bei höheren Temperaturen eine bessere Extraktion zeigten. Die Zeit, die erforderlich war, um die Proben auf 95 % der Zieltemperatur zu bringen, betrug bis zu 8 min – ein kritischer Parameter angesichts der temperaturabhängigen Extraktionsleistung. Eine intensivere Durchmischung verkürzte die Extraktionszeit; jedoch brachten Intensitäten über 500 rpm keine weiteren Verbesserungen und könnten die Fasermechanik beeinträchtigen. Daher wurde eine Intensität von 500 rpm mit einer Extraktionszeit von 30 min gewählt. Die optimale Desorptionszeit wurde auf 3 min festgelegt, um die vollständige Freisetzung der Analyten von der Faser zu gewährleisten. Letztendlich wurden für die PCB-Extraktionen aus den Grubenwässern zwei verschiedene Methoden gewählt. Für eine optimale Extraktion von niedrigchlorierten PCB wurde eine PDMS/DVB-Faser bei 75 °C verwendet, während für hochchlorierte PCB eine PDMS-Faser bei 80 °C genutzt wurde. Durch diese Methodenoptimierungen konnten sehr niedrige LODs (0,004–0,58 ng L^{-1}) und LOQs (0,01–1,9 ng L^{-1}) erzielt werden.

Die PCB-Konzentrationen in den untersuchten Grubenwässern lagen zwischen 19,0 und 120 ng L^{-1}, wobei insbesondere di-, tri- und tetrachlorierte Kongenere nachgewiesen wurden. Die PCB-Zusammensetzung variierte je nach Herkunft der Grubenwässer, blieb jedoch innerhalb der einzelnen Gruben über den Beobachtungszeitraum von 26 Monaten konstant. PCB 18 war in allen Proben mit Konzentrationen von bis zu 25,9 ng L^{-1} am häufigsten vertreten. Von den PCB_{i+118} wurden lediglich PCB 28 und PCB 52 in relevanten Mengen gefunden. Die Summierung der PCB_{i+118}-Werte und deren Multiplikation mit einem Faktor von 5 lieferte für die saarländischen Grubenwässer akzeptable Ergebnisse, war jedoch für die Proben aus NRW ungeeignet (Tabelle 2). Besonders im Grubenwasser von Zollverein führte diese Methode aufgrund des hohen Anteils niedrigchlorierter PCB zu einer starken Unterschätzung der Gesamtkonzentration.

Zur besseren Charakterisierung der PCB-Belastung wurden elf häufig vorkommende Kongenere ($\sum PCB_{top11}$: PCB 16, 17, 18, 19, 28, 31, 32, 44, 49, 52 und 53) identifiziert, die in allen Gruben zu den häufigsten 15 PCB gehören. Ihr Anteil an der PCB-Gesamtmenge schwankte zwischen 37 % und 83 %, wodurch sie als geeigneteres Maß für die Belastung durch aus dem Bergbau stammende PCB-Kontamination betrachtet werden können.

Tabelle 2. Konzentrationen für PCB_{i+118}, PCB_{53} und entsprechende Multiplikationsfaktoren

Grube	$\sum PCB_{53}$	$\sum PCB_{i+118}$	Faktor
Walsum	20,4–56,4	2,5–6,7	8,2–8,4
Zollverein	82,1–120	5,8–10,8	11,1–14,2
Stinnes	19,0–42,9	2,8–6,2	6,8–6,9
Reden	53,7	10,4	5,2
Camphausen	51,8	10,7	4,8

Um die Gemeinsamkeiten und Unterschiede zwischen unterschiedlichen Grubenwässern zu verdeutlichen, sowie zwischen diesen Grubenwässern und verschiedenen Clophen-Mixturen, wurden die homologen PCB-Kongenere der Grubenwässer zusätzlich mit den homologen Kongeneren der Clophen-Mixturen A30, A40 und A50 verglichen (Abbildung 6). Die Ähnlichkeit vor allem zu Clophen A30, aber auch A40 ist dabei besonders deutlich. Clophen A50 weist dagegen eine ganz andere Zusammensetzung auf als die in den Grubenwässern gefundenen Kongenere. Dies bestätigt die Angaben aus älteren Berichten, dass in deutschen Steinkohlegruben vorwiegend A30 und A40 verwendet wurden [4].

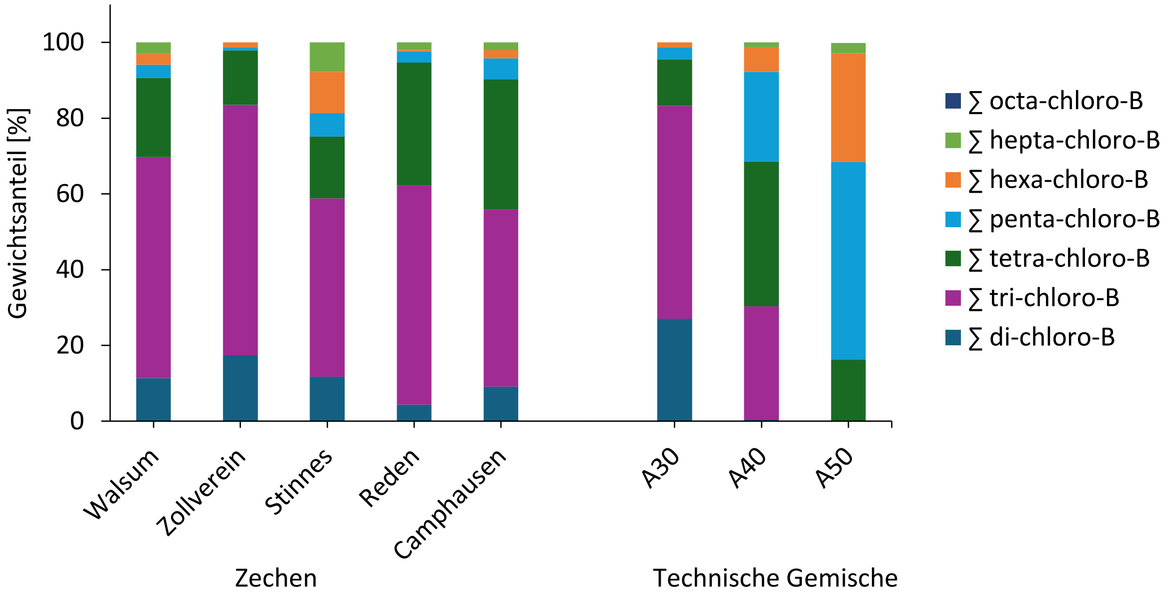


Abbildung 6. Vergleich der Verteilung der PCB-Homologe in Grubenwässern und technischen Gemischen.

Für eine fundierte Risikoabschätzung sind nicht nur die PCB-Konzentrationen, sondern auch die jährlichen Frachten entscheidend. Obwohl die Konzentrationen im Bereich von pg–ng L^{-1} liegen, führen die hohen Grubenwasservolumina (je Grube 1,7–12 Mio. m^3 a^{-1}) zu einer PCB-Fracht von 1–2 kg pro Jahr in die angrenzenden Oberflächengewässer. Zwei der größten Bergwerksbetreiber in Deutschland geben zusammengerechnet einen Gesamtgrubenwasserbestand von insgesamt mehr als 134 Mio. m^3 a^{-1} an [106,107]. Davon ausgehend, dass andere Grubenwasser ähnlich stark belastet sind wie die der fünf untersuchten Zechen, ergibt sich hochgerechnet eine potenzielle jährliche PCB-Fracht von ca. 6–9 kg. Jedoch müssen diese Mengen in Relation betrachtet werden. Im Vergleich dazu emittiert die Stadt Zürich etwa 16 kg PCB jährlich in die Atmosphäre [108], während für die Stadt Toronto die Schätzungen bis zu 190 kg betragen [109]. Dennoch dürfen diese PCB-Freisetzungen aus Grubenwässern nicht unterschätzt werden, da selbst geringe Mengen schwerwiegende Umweltwirkungen haben können.

Am Standort Reden fließt das Grubenwasser zunächst durch einen künstlichen Bachlauf, bevor es in einen Vorfluter gelangt. Hier führen Prozesse wie Partitionierung oder Degradation zu einer Abnahme der PCB-Konzentrationen (Abbildung 7).

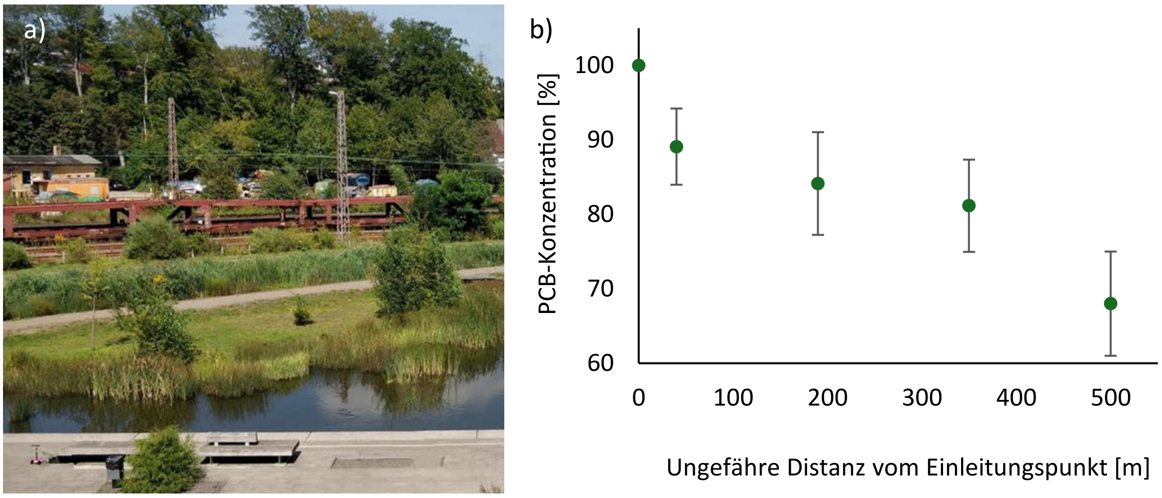


Abbildung 7. a) Ein Ausschnitt des künstlichen Bachlaufs in Reden; b) Konzentrationsverringerung der $\sum PCB_{top11}$ *entlang des künstlichen Bachlaufs am Standort Reden, die Fehlerbalken zeigen die relative Standardabweichung.*

Nach einer Strecke von 500 m haben sich die PCB-Konzentrationen im Durchschnitt um 32 % verringert. Dadurch wird die jährliche Fracht von 0,64 kg auf 0,44 kg gesenkt und ein wesentlicher Teil der PCB gelangt nicht in den Vorfluter. Dennoch ist eine vollständige Eliminierung der PCB auf diesem Wege nicht möglich. Zudem wird die PCB-Belastung lediglich in andere Umweltsysteme verlagert. Da der Austritt von Grubenwässern als Punktquellen gelten, bieten sie eine Möglichkeit für gezielte Behandlungsansätze, wie Dechlorierungsverfahren, bevor sich die PCB weiter in der Umwelt verteilen.

1.3.2 Aufklärung der Reaktionsmechanismen und -pfade bei der Dechlorierung von HCB mit Pd-Katalysatoren

Die Hydrodechlorierung von HCB und anderen CB wurde über einen Reaktionszeitraum von 60 min untersucht (Abbildung 8). Im Allgemeinen nahm die Reaktionsgeschwindigkeit mit abnehmendem Chlorierungsgrad der CB zu. Ausnahmen bildeten jedoch Verbindungen wie 1,2,4,5-TeCB oder 1,2,4-TCB, bei denen die Reaktion langsamer verlief. Für diese Verbindungen sowie für HCB wurde zudem eine anfängliche Verzögerung bei der Bildung von B beobachtet. Die Entstehung von Zwischenprodukten deutet auf einen schrittweisen Dechlorierungsprozess hin, bei dem jeweils ein Chloratom gegen ein Wasserstoffatom ausgetauscht wurde. Eine parallele

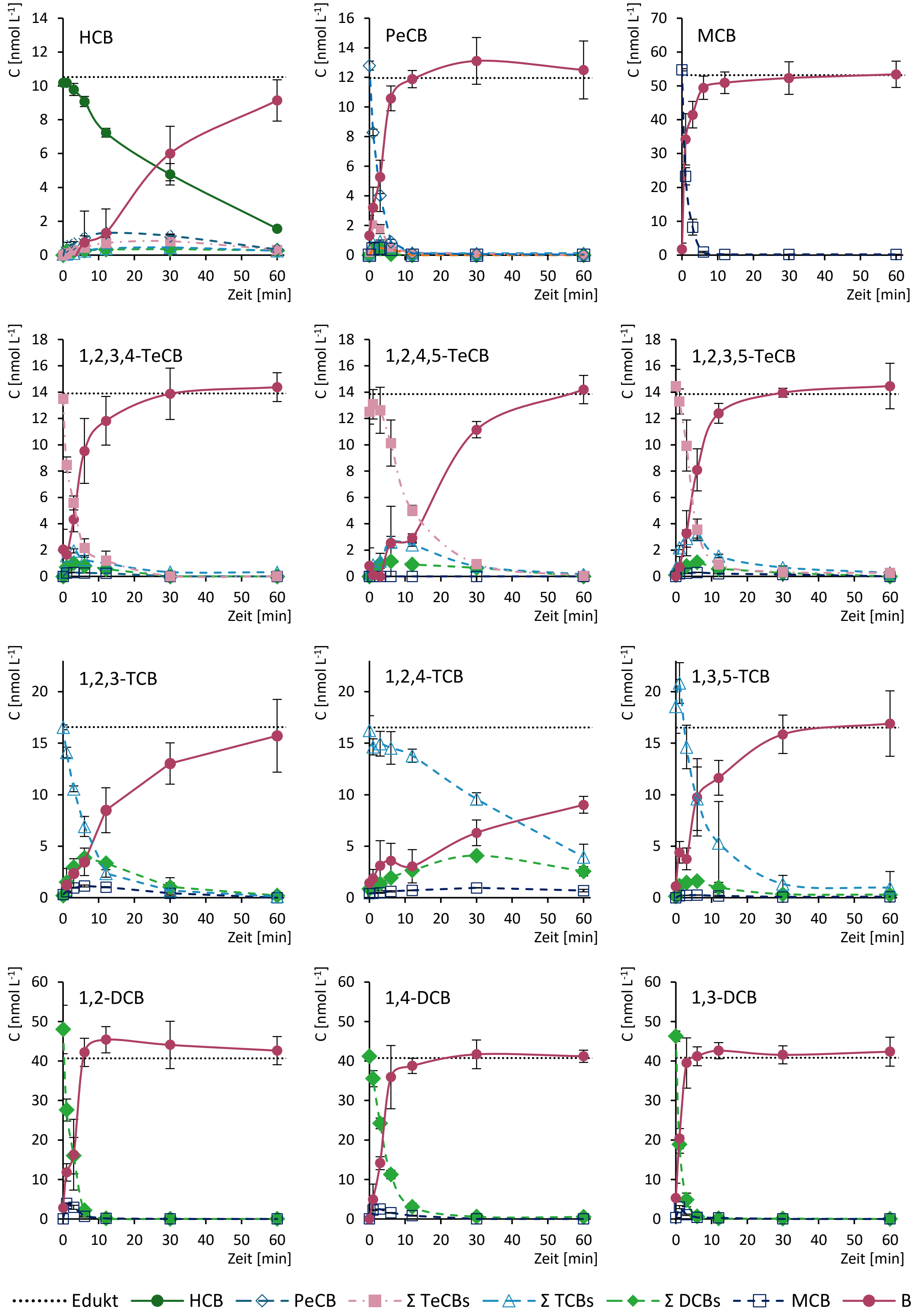


Abbildung 8. Dechlorierungsverläufe von allen CB. Auftretende Intermediate mit dem gleichen Chlorierungsgrad angegeben als Summe. Die Linien wurden inkludiert, um den Blick des Lesers zu führen. Grafik angelehnt an Wiltschka et al. (2020) [110].

direkte Dechlorierung zu B konnte jedoch nicht ausgeschlossen werden. Die Dechlorierung von POPs erfolgt überwiegend durch Wasserstoff- [111] oder Elektronentransfermechanismen [112]. In diesem Fall dominierte der Wasserstofftransfer, da im System durch Pd(0) aktivierter Wasserstoff vorlag, der elektrophil an den aromatischen Ring addiert werden konnte [113]. Adsorbierte polychlorierte aromatische Verbindungen neigten dazu, eine Doppelbindungscharakteristik in der Kohlenstoff-Chlor-Bindung (C=Cl) zu entwickeln [114]. Dies ermöglichte die Abspaltung mehrerer Chloratome ohne vorherige Desorption von der Katalysatoroberfläche. Elektrophile Substituenten entzogen dem aromatischen Ring Elektronen und beschleunigten die katalytische Hydrodechlorierung [115]. Die Stärke der C=Cl-Bindung war dabei von der Anzahl der Chloratome im Molekül abhängig. Die Elektronen wurden teilweise aus den d-Orbitalen entfernt, was zu einer zusätzlichen Stabilisierung führte. Dies begünstigte die Bildung zweier C=Cl-Bindungen und die Abspaltung von zwei Chloratomen ohne Desorption von der Katalysatoroberfläche [116].

Die Experimente zur Dechlorierung von CB identifizierten häufig auftretende Zwischenprodukte, darunter die Isomere 1,2,3,4-TeCB, 1,2,3-TCB und 1,2-DCB. Bevorzugt wurden dabei benachbarte (vicinale) Chloratome substituiert. Zwischenprodukte, die bei der Dechlorierung von HCB in größeren Mengen entstanden, zeigten selbst rasche Abbaureaktionen. Dies belegte, dass es sich nicht um Dead-End-Produkte handelte, sondern um bevorzugte Intermediate, aus denen der bevorzugte Abbauweg von HCB abgeleitet werden konnte (Abbildung 9).

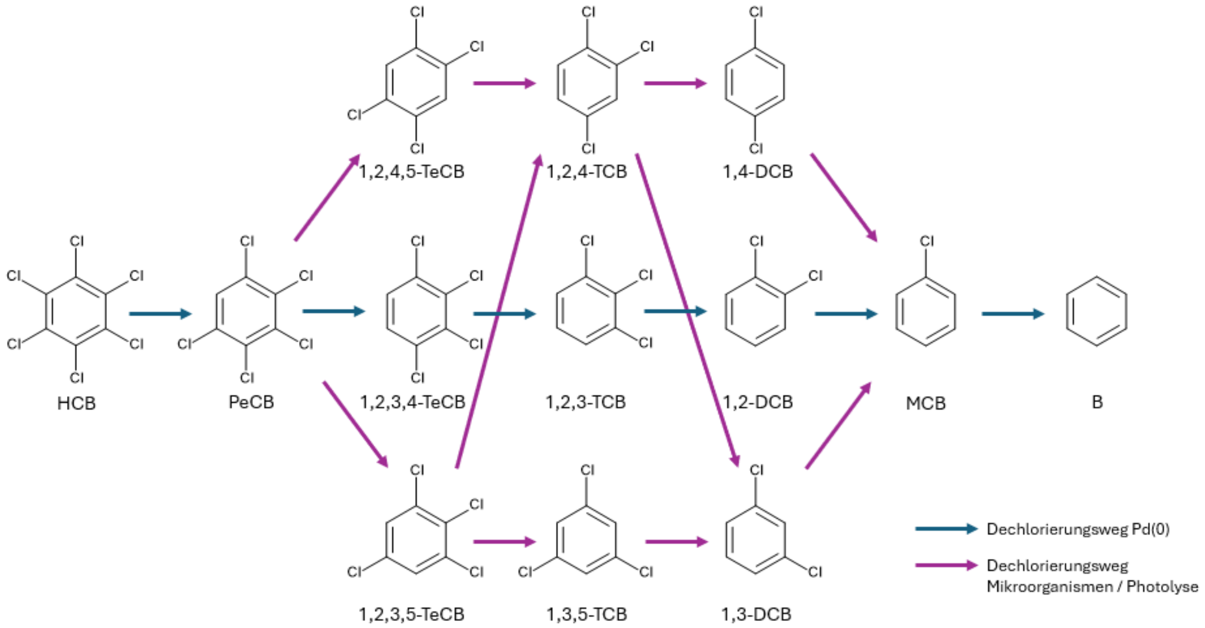


Abbildung 9. Dechlorierungswege von HCB. Blaue Pfeile = bevorzugter Abbauweg mithilfe von Pd(0)-Nanopartikeln; violette Pfeile = bevorzugter Abbauweg mithilfe von Mikroorganismen [76] oder Photolyse [117], angelehnt an Wiltschka et al. 2020 [110].

Ein Vergleich mit der mikrobiologischen [76] oder photolytischen Dechlorierung [117] zeigte, dass dort die Reaktionswege grundlegend anders verlaufen. Vicinalchlorierte CB stellen in diesen Prozessen energetisch ungünstigere Zwischenprodukte dar [118]. Eine mögliche Erklärung für die hier beobachteten Reaktionswege ist die Bildung einer „abschirmenden Wand“ aus negativen Teilladungen durch die elektronenziehende Wirkung der Chloratome. Diese Schutzwirkung nimmt mit der Entfernung zwischen benachbarten Chloratomen ab, wodurch die Substitution erleichtert wird (Abbildung 10). Bei PCB haben die Ortho-Substituenten durch den benachbarten Phenylring zusätzlichen Schutz. Dies erschwert die Substitution von Chloratomen an den Ortho-Positionen.

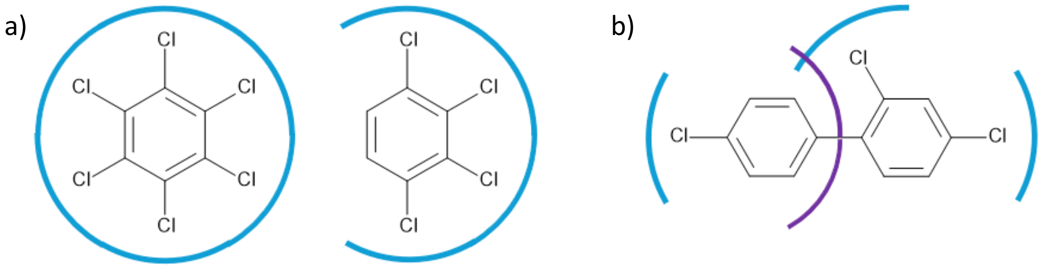


Abbildung 10. Schematische Darstellung zu den induktiven Effekten. a) Geschlossener Ring bei HCB, bei dem einzelne Chloratome nur schwer substituiert werden können. Bei 1,2,3,4-TeCB gibt es eine große Lücke, in der benachbarte Chloratome bevorzugt abgespalten werden. b) Zusätzlich zu dem induktiven Effekt der Chloratome (blau) wird ein abschirmender Effekt durch die Phenylringe (hier nur für den linken dargestellt, violett) vermutet.

Die Bildung von Zwischenprodukten ist von erheblicher Bedeutung für den Einsatz in Reinigungsanlagen. Reaktionen verlaufen häufig nicht vollständig, und Störungen im Reaktionssystem können verhindern, dass alle Verbindungen vollständig abgebaut werden. Während HCB und andere CB eine vergleichbare Toxizität aufweisen, können bei anderen Ausgangstoffen, wie hochchlorierten PCB, dioxin-ähnliche Verbindungen entstehen, deren Toxizität deutlich höher ist. Die Versuche mit HCB zeigten, dass vorzugsweise vicinale Chloratome substituiert werden. Bei PCB führt die sterische Hinderung durch den zusätzlichen Phenylring dazu, dass insbesondere Chloratome an meta- und para-Positionen bevorzugt abgespalten werden, was nicht zur Bildung von toxischeren Zwischenprodukten führt. Die spezifischen katalytischen Aktivitäten $A_{\mathrm{Pd,i}}$ der Pd(0)-Katalysatoren wurden gemäß Formel (1) berechnet und lagen im Bereich von 110–3380 L g^{-1} min^{-1}. Für HCB wurde eine Aktivität von 150 L g^{-1} min^{-1} (Tabelle 3).

Tabelle 3. Spezifische katalytische Aktivitäten der Pd(0)-Katalysatoren für die Dechlorierung von CB. Daten aus Wiltschka et al. 2020 [110]

Edukt	HCB	PeCB	TeCB	TCB	DCB	MCB
$A_{\mathrm{Pd,i}}$ [L g^{-1} min^{-1}]	150	2120	440–1160	110–770	1060–3380	3210

Die Ergebnisse zeigen, dass die katalytische Aktivität mit abnehmendem Chlorierungsgrad zunimmt. Die insgesamt hohen katalytischen Aktivitäten deuten darauf hin, dass Pd-Katalysatoren eine effektive Entfernung von POPs aus wässrigen Lösungen ermöglichen. Insbesondere bei Grubenwässern, die große Volumina aufweisen und meist niedrigchlorierte CB enthalten, erscheinen Pd-Katalysatoren unter Laborbedingungen besonders geeignet. Einschränkungen bestehen jedoch durch die Neigung dispergierter Pd(0)-Nanopartikel zur

Agglomeration oder Deaktivierung durch Katalysatorgifte [100,119]. Studien belegen, dass eine Einbettung in eine PDMS-Beschichtung die Aktivität von Pd-Katalysatoren zwar verringert, aber in Anwesenheit von Katalysatorgiften erhalten kann [14,105,120]. Das Potenzial von Pd-Katalysatoren sollte weiter erforscht werden, um ihre Anwendung auch unter realen Bedingungen, wie bei stark mit Katalysatorgiften belasteten Grubenwässern, zu optimieren.

1.3.3 Aufrechterhaltung der katalytischen Aktivität von Metallkatalysatoren in Anwesenheit von Katalysatorgiften

Die Hydrodechlorierung ausgewählter PCB durch dispergierte Pd(0)-Nanopartikel sowie die Bildung der Hauptintermediate und des Endprodukts B wurden über einen Zeitraum von 60 min untersucht (Abbildung 11). In einer reinen Pufferlösung konnte die Reaktion erfolgreich beobachtet werden. In Grubenwasser hingegen trat, wie erwartet, keine Reaktion auf, da die in der Lösung enthaltenen Katalysatorgifte die Katalysatoren deaktivierten.

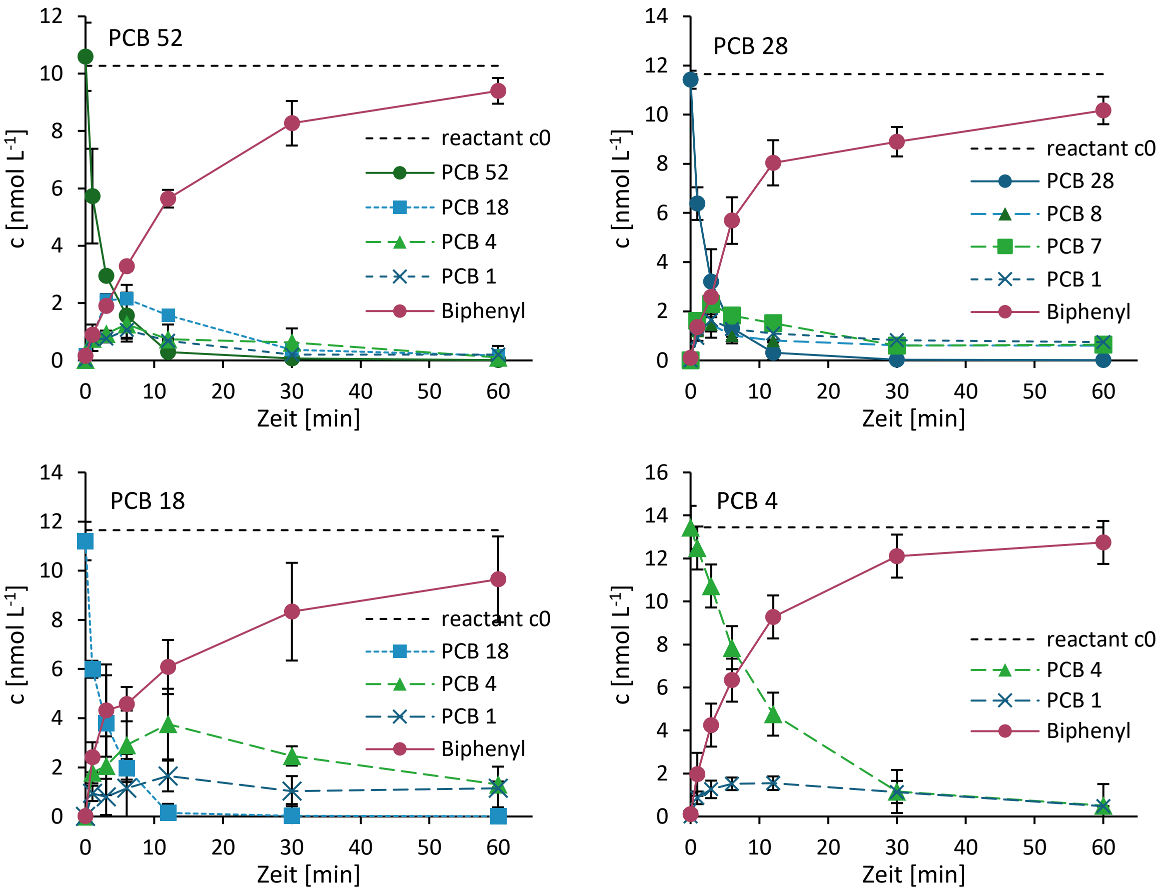


Abbildung 11. Dechlorierung ausgewählter PCB durch dispergierte Pd(0)-Nanopartikel. Zur besseren Übersicht werden nur die Hauptintermediate gezeigt. Die Linien sollen den Blick des Lesers führen. Abbildung entnommen aus Wiltschka et al. (2024) [121].

Ähnlich wie bei der Dechlorierung von HCB zeigte sich auch hier, dass bevorzugt Chloratome ohne benachbarte Substituenten ersetzt wurden, insbesondere solche in meta- oder para-Positionen.

Dies führte zur Bildung von Intermediaten, die hauptsächlich ortho-substituiert sind und daher nicht zu den dioxinähnlichen PCB gehören.

Die katalytischen Aktivitäten wurden zunächst für dispergierten Pd(0)-Nanopartikel sowie suspendierte und in PDMS eingebettete Pd/Al_2O_3-Partikel in Pufferlösung bestimmt. Ziel war es, die Unterschiede in der Aktivität zwischen den Katalysatoren zu quantifizieren und den Einfluss der PDMS-Beschichtung auf die Aktivität zu bewerten (Tabelle 4).

Tabelle 4. Spezifische katalytische Aktivitäten von Pd(0)- und Pd/Al_2O_3-Katalysatoren für die Dechlorierung ausgewählter PCB in Pufferlösung; disp = dispergiert, susp = suspendiert, eingeb = eingebettet. Daten aus Wiltschka et al. (2024) [121]

Edukt	Pd(0)	Pd/Al_2O_3	Pd/Al_2O_3
	$A_{\text{Pd,disp}}$ [L g^{-1} min^{-1}]	$A_{\text{Pd,susp}}$ [L g^{-1} min^{-1}]	$A_{\text{Pd,eingeb}}$ [mL g^{-1} min^{-1}]
PCB 52	2740 ± 190	860 ± 100	610 ± 90
PCB 28	3350 ± 300	1130 ± 110	830 ± 100
PCB 18	2600 ± 410	720 ± 30	610 ± 70
PCB 4	850 ± 20	260 ± 50	200 ± 30

Im Gegensatz zu HCB und CB nahmen die spezifischen katalytischen Aktivitäten nicht immer mit abnehmendem Chlorierungsgrad zu. PCB 4 zeigte stets die geringste katalytische Aktivität. Dies deutet darauf hin, dass die Dechlorierungsgeschwindigkeit eher von der Position der Chloratome abhängt als von ihrer Anzahl.

Die katalytischen Aktivitäten der dispergierten Pd(0)-Nanopartikel und der suspendierten Pd/Al_2O_3-Partikel waren in etwa vergleichbar. Allerdings wiesen die suspendierten Pd/Al_2O_3-Partikel durchgehend eine um den Faktor 3,0–3,6 niedrigere Aktivität auf. Dies ist darauf zurückzuführen, dass die dispergierten Pd(0)-Nanopartikel durch ihre bessere Verteilung in der Pufferlösung einen effizienteren Kontakt zu den PCB hatten. Trotz des Einsatzes eines Überkopfschüttlers war der Kontakt der suspendierten Partikel zu den PCB weniger effektiv. Zudem mussten die PCB bei diesen Partikeln erst die aktiven Stellen des Pd-Clusters erreichen, was zu einer langsameren Reaktion und geringeren spezifischen Aktivitäten führte.

Die zusätzliche Einbettung in eine PDMS-Schicht führte zu nochmals niedrigeren spezifischen Aktivitäten, die bis zu 1000-fach geringer waren als bei den suspendierten Pd/Al_2O_3-Partikeln. Hierbei mussten die PCB zunächst durch die Silikonschicht diffundieren, bevor sie die katalytisch aktiven Stellen des Pd/Al_2O_3-Clusters erreichen konnten. Zusätzlich war auch in diesem Fall Wasserstoff notwendig, um die Chloratome zu substituieren.

Unter natürlichen Bedingungen sind ideale Voraussetzungen für die Katalysatoren unwahrscheinlich. Die Aufbereitung von Grubenwässern, um Katalysatorgifte zu entfernen, ist ressourcenintensiv. Um die Leistungsfähigkeit der Katalysatoren unter realistischen Bedingungen zu bewerten, wurden verschiedene Grubenwässer als Reaktionsmatrix anstelle der Pufferlösung getestet. Die dispergierten Pd(0)- und die suspendierten Pd/Al_2O_3-Katalysatoren wurden durch die in den Grubenwässern enthaltenen Katalysatorgifte deaktiviert, wodurch keine nachweisbare Dechlorierung stattfand. Anders verhielt es sich mit den eingebetteten Pd/Al_2O_3-Partikeln. In zwei von drei untersuchten Grubenwässern konnten sie alle getesteten PCB dechlorieren. Allerdings waren die katalytischen Aktivitäten mit 20–210 mL g^{-1} min^{-1} nochmals deutlich geringer als in der Pufferlösung (200–830 mL g^{-1} min^{-1}). Im Stinnes-Grubenwasser, das die höchste Konzentration an Chlorid und Metallen aufwies, wurde jedoch keine Dechlorierung festgestellt.

Das getestete PCB 18 war auch das am häufigste in den Grubenwässern der Zechen Walsum, Zollverein, Stinnes, Reden und Camphausen vorkommende PCB. Diese Gruben erzeugen pro Minute etwa 1–10 m^3 min^{-1} Grubenwasser. Bei einer spezifischen katalytischen Aktivität von 100–170 mL g^{-1} min^{-1} für PCB 18 würde jede dieser Gruben 6–100 kg Pd/Al_2O_3-Katalysator benötigen, um das Grubenwasser zu reinigen – vorausgesetzt, die Grubenwässer enthalten nicht so viele Katalysatorgifte wie das Stinnes-Grubenwasser und die Katalysatoraktivität bleibt erhalten. Um die spezifische Katalysatoraktivität weiter zu steigern, könnte ein verbesserter Schutz vor Katalysatorgiften implementiert werden. Dies könnte beispielsweise durch die Verwendung einer dickeren PDMS-Schicht erreicht werden, oder durch eine zusätzliche PDMS-Schicht mit „Schwefel-Fängern" (wie Calciumoxid, Natriumhydroxid, oder Magnesiumdioxid) über der Pd/Al_2O_3-PDMS-Schicht, die nichtionische Gifte wie H_2S binden können [14,122].

1.4 Schlussfolgerungen und Ausblick

Eine SPME-GC-MS-Methode wurde erfolgreich optimiert, die sich sehr gut zur Quantifizierung von PCB in kleinen Mengen von unbehandelten Grubenwässern und MIW eignet. Die Konzentrationen einzelner PCB-Kongenere in den untersuchten Grubenwässern liegen bei bis zu 25,9 ng L^{-1}. Die PCB_{i+118} machen jedoch nur einen kleinen Anteil der am in größten Konzentrationen nachgewiesenen Kongenere aus. Die Analyse der PCB_{i+118}, einschließlich der Multiplikation mit einem Faktor 5, ist insbesondere für die Grubenwässer aus NRW ungeeignet, um die Gesamtkonzentrationen der PCB zu bestimmen. Bei bergbau- oder Clophen-A30-bedingten PCB-Kontaminationen sollte die Analyse generell auf die in dieser Studie definierten $\sum PCB_{top11}$ basieren.

Es ist problematisch, dass viele Analysen niedrigchlorierte PCB nicht berücksichtigen, da für eine präzise Bestimmung der PCB-Gesamtkonzentrationen größere Korrekturfaktoren erforderlich sind. Dies führt dazu, dass die tatsächlichen Mengen in globalen Bilanzierungs- und Überwachungsprogrammen systematisch unterschätzt werden. Obwohl die PCB-Konzentrationen im Bereich von ng L^{-1} liegen, summieren sie sich aufgrund der enormen Pumpvolumina zu Frachten im kg-Bereich.

Das Umweltprogramm der Vereinten Nationen (UNEP) betont die Notwendigkeit, PCB-Freisetzungen aus dem Bergbau zu verhindern [123]. Diese Forderung wird auch durch das UN-

Nachhaltigkeitsziel (SDG) Nr. 6 („Sauberes Wasser und Sanitäranlagen“) unterstützt. Süßwasser sollte als wertvolle Ressource behandelt und vor PCB sowie anderen Schadstoffen geschützt werden, insbesondere angesichts des Klimawandels und der Zunahme von Dürreperioden in vielen Regionen [124]. Grubenwässer sind lokale Schadstoffquellen, deren Schadstoffeintrag jedoch globale Auswirkungen hat. Künstlich angelegte Feuchtgebiete, wie im Beispiel Reden demonstriert, können dazu beitragen, Schadstoffe zu reduzieren und den Eintrag in natürliche Oberflächengewässer teilweise zu verhindern. Allerdings bieten sie keine vollständige Reduktion der PCB-Konzentrationen und keine Zerstörung der PCB-Kongenere. Dadurch wird die Problematik lediglich in andere Systeme verlagert, ohne sie endgültig zu lösen.

Im Gegensatz zu diffusen Schadstoffquellen können hier Reinigungsverfahren viel einfacher implementiert werden. Zur globalen Reduktion von POP-Konzentrationen stellt die hier eingesetzte Hydrodechlorierung mittels Pd-Katalysatoren eine vielversprechende Methode dar. Unter optimalen Bedingungen kann eine vollständige Dechlorierung innerhalb weniger Stunden oder sogar Minuten erfolgen, mit spezifischen katalytischen Aktivitäten von bis zu 3350 L g^{-1} min^{-1}. Bevorzugt entstehen vicinal-chlorierte oder ortho-chlorierte POPs, da sterische Hinderungen durch andere Chloratome oder den zweiten Phenylring eine Rolle spielen.

Dispergierte Pd(0)-Nanopartikel sind jedoch nicht wiederverwendbar und nicht vor in der Umwelt vorkommenden Katalysatorgiften geschützt. Die Einbettung des Katalysators ermöglichte hingegen nicht nur dessen Wiederverwendung, sondern auch die Dechlorierung von PCB in unbehandelten, katalysatorgift- und matrixreichen Grubenwässern. Obwohl die katalytische Aktivität durch diese Einbettung deutlich reduziert wurde, blieb sie ausreichend hoch, um weitere Forschungsarbeiten zur Optimierung zu rechtfertigen. Die katalytische Aktivität kann durch zusätzliche Schutzmaßnahmen weiter gesteigert werden, beispielsweise durch eine zusätzliche Schutzschicht mit „Schwefel-Fängern“. Dies würde den Katalysatorbedarf reduzieren und die Methode kostengünstiger machen. Weitere Anpassungen, wie eine Größenskalierung, die Vergrößerung der Kontaktfläche zwischen Beschichtung und Wasser oder geeignete Vorbehandlungen zur Vermeidung von Salz- und Metallablagerungen, könnten die Effizienz und Praktikabilität der Katalysator-PDMS-Beschichtung weiter erhöhen. Dieses System hat das Potenzial, als umweltentlastende Technologie auch außerhalb des Labors Anwendung zu finden.

Zukünftige Forschung sollte jedoch nicht nur den Katalysator selbst weiter optimieren, sondern auch die globalen PCB-Eintragsquellen besser untersuchen. Eine erweiterte Analyse von MIW aus Kohlenabbaugebieten in Großbritannien, Polen, den USA, China, Indien und Australien könnte zu einem umfassenderen Verständnis der PCB-Vorkommen weltweit beitragen und helfen, gezielte Maßnahmen zur Reduktion dieser Schadstoffe zu erarbeiten. Es ist entscheidend, geeignete Technologien zu entwickeln und anzuwenden, um die PCB-Frachten global zu reduzieren und somit unseren Planeten vor weiteren Umweltbelastungen zu schützen.

1.5 Literaturverzeichnis

[1] Alharbi, O.M., Basheer, A.A., Khattab, R.A., Ali, I. (2018), Health and environmental effects of persistent organic pollutants, Journal of Molecular Liquids 263 442–453. https://doi.org/10.1016/j.molliq.2018.05.029.

[2] Stockholm Convention, Stockholm Convention on Persistent Organic Pollutants: POP-convention, United Nations.

[3] C. Wolkersdorfer, Mine Water Treatment - Active and Passive Methods, 1st ed., Springer, Berlin, 2022.

[4] J. Schwarzbauer, M. Denneborg, 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.

[5] C. Klinger, M. Eckart, J. Löchte, Integration of Solid Matter Coupled Contaminant Transport into the 3D Reactive Transport Boxmodel by the Example of PCB in German Hard Coal Mining. In: Wolkersdorfer C, Sartz L, Sillanpää M, Häkkinen A (eds) IMWA 2017 - Mine Water & Circular Economy. vol I. Lappeenranta University of Technology, Lappeenranta, p 303-311.

[6] B. Jäger, P. Obermann, F.L. Wilke, (1990) Studie zur Eignung von Steinkohlebergwerken im rechtsrheinischen Ruhrkohlebezirk zur Untertageverbringung von Abfall- und Reststoffen, Report No LWA Studie 1990. Institut für Techn. Umweltschutz der Technischen Universität Berlin, Ruhr Universität Bochum, Institut für Bergbauwissenschaften, Bergbaukunde II der Technischen Universität Berlin, Düsseldorf, 628 p.

[7] U. S. Environmental Protection Agency, (2000) Abandoned Mine Site Characterization and Cleanup Handbook. vol EPA 910-B00-001. U.S. Environmental Protection Agency, Denver, San Francisco, Seattle.

[8] LANUV, Belastungen von Oberflächengewässern und von aktiven Grubenwassereinleitungen mit bergbaubürtigen PCB (und PCB-Ersatzstoffen), 2018.

[9] Weston Solutions Inc., (2018) Final Expanded Site Inspection Report Shaffer Equipment/Arbuckle Creek Area Site Minden, Fayette County, West Virginia, Report № EP-S3-15-02. U.S. Environmental Protection Agency Region III, Hazardous Site Cleanup Division, West Chester, 159 p.

[10] W. Merkel, O. Dördelmann, C. Mauer, U. Rieth, (2016) Gutachterlichen [sic!] Untersuchung / Recherche zu den technischen Möglichkeiten einer PCB-Elimination von Grubenwässern („PCB-Gutachten“), Report № 16/034.1 vom 21.04.2016. Ministerium für Klimaschutz, Umwelt, Landwirtschaft, Natur- und Verbraucherschutz des Landes Nordrhein-Westfalen, Mülheim an der Ruhr, 70 p.

[11] H. Rahm, K. Plantikow, D. Spira, G. Reifferscheid, S. Schäfer, Neues Leben ohne Grubenwasser?: Auswirkungen der Beendigung des Steinkohlebergbaus auf die Gewässerqualität in NRW. Mitt. Umweltchem. Ökotox., 2019.

[12] Yan, D., Peng, Z., Karstensen, K.H., Ding, Q., Wang, K., Wang, Z. (2014), Destruction of DDT wastes in two preheater/precalciner cement kilns in China, The Science of The Total Environment 476-477 250–257. https://doi.org/10.1016/j.scitotenv.2014.01.009.

[13] Schüth, C., Reinhard, M. (1998), Hydrodechlorination and hydrogenation of aromatic compounds over palladium on alumina in hydrogen-saturated water, Appl. Catal. B: Environ. (Applied Catalysis B: Environmental) 18 215–221. https://doi.org/10.1016/S0926-3373(98)00037-X.

[14] Comandella, D., Werheid, M., Kopinke, F.-D., Mackenzie, K. (2017), Optimization of PDMS-embedded palladium hydrodechlorination catalysts, Chemical Engineering Journal 319 21–30. https://doi.org/10.1016/j.cej.2017.02.155.

[15] Tuppurainen, K., Asikainen, A., Ruokojärvi, P., Ruuskanen, J. (2003), Perspectives on the formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during municipal solid waste (MSW) incineration and other combustion processes, Accounts of chemical research 36 652–658. https://doi.org/10.1021/ar020104.

[16] Kelly, B.C., Ikonomou, M.G., Blair, J.D., Morin, A.E., Gobas, F.A.P.C. (2007), Food web-specific biomagnification of persistent organic pollutants, Science 317 236–239. https://doi.org/10.1126/science.1138275.

[17] J. Mes, (1987). PCBs in human populations. In J. S. Waid (Ed.), PCBs and the Environment, 3, 39-63. Boca Raton, Fl: CRC Press.

[18] Stockholm Convention, (2020) Stockholm Convention on Persistent Organic Pollutants (POPs) - Text and Annexes, Report No. United Nations, Genf, 77 p.

[19] Garrison, V.H., Majewski, M.S., Foreman, W.T., Genualdi, S.A., Mohammed, A., Massey Simonich, S.L. (2014), Persistent organic contaminants in Saharan dust air masses in West Africa, Cape Verde and the eastern Caribbean, The Science of The Total Environment 468-469 530–543. https://doi.org/10.1016/j.scitotenv.2013.08.076.

[20] Li, Y.-F., Harner, T., Liu, L., Zhang, Z., Ren, N.-Q., Jia, H., Ma, J., Sverko, E. (2010), Polychlorinated biphenyls in global air and surface soil: distributions, air-soil exchange, and fractionation effect, Environ. Sci. Technol. 44 2784–2790. https://doi.org/10.1021/es901871e.

[21] Ubl, S., Scheringer, M., Stohl, A., Burkhart, J.F., Hungerbuhler, K. (2012), Primary source regions of polychlorinated biphenyls (PCBs) measured in the Arctic, Atmos. Environ. (Atmospheric Environment) 62 391–399. https://doi.org/10.1016/j.atmosenv.2012.07.061.

[22] Sanganyado, E., Chingono, K.E., Gwenzi, W., Chaukura, N., Liu, W. (2021), Organic pollutants in deep sea: Occurrence, fate, and ecological implications, Water research 205 117658. https://doi.org/10.1016/j.watres.2021.117658.

[23] Kuepper, N.D., Böhm, L., Braun, C., Bustamante, P., Düring, R.-A., Libertelli, M.M., Quillfeldt, P. (2022), 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. (Polar Biology) 45 1229–1245. https://doi.org/10.1007/s00300-022-03065-w.

[24] Beyer, A., Mackay, D., Matthies, M., Wania, F., Webster, E. (2000), Assessing Long-Range Transport Potential of Persistent Organic Pollutants, Environ. Sci. Technol. 34 699–703. https://doi.org/10.1021/es990207w.

[25] Lie, E., Bernhoft, A., Riget, F., Belikov, S.E., Boltunov, A.N., Derocher, A.E., Garner, G.W., Wiig, Ø., Skaare, J.U. (2003), Geographical distribution of organochlorine pesticides (OCPs) in polar bears (Ursus maritimus) in the Norwegian and Russian Arctic, Science of The Total Environment 306 159–170. https://doi.org/10.1016/S0048-9697(02)00490-4.

[26] Bruijn, J. de, Busser, F., Seinen, W., Hermens, J. (1989), Determination of octanol/water partition coefficients for hydrophobic organic chemicals with the “slow-stirring” method, Enviro Toxic and Chemistry 8 499–512. https://doi.org/10.1002/etc.5620080607.

[27] Wang, X., Tang, S., Liu, S., Cui, S., Wang, L. (2003), Molecular hologram derived quantitative structure-property relationships to predict physico-chemical properties of polychlorinated biphenyls, Chemosphere 51 617–632. https://doi.org/10.1016/S0045-6535(02)00839-1.

[28] Frank Wania, Mackay, D. (1993), Global Fractionation and Cold Condensation of Low Volatility Organochlorine Compounds in Polar Regions, Ambio 22 10–18.

[29] Goldberg, E.D. (1975), Synthetic organohalides in the sea, Proceedings of the Royal Society of London. Series B, Biological sciences 189 277–289. https://doi.org/10.1098/rspb.1975.0057.

[30] Vallack, H.W., Bakker, D.J., Brandt, I., Broström-Lundén, E., Brouwer, A., Bull, K.R., Gough, C., Guardans, R., Holoubek, I., Jansson, B., Koch, R., Kuylenstierna, J., Lecloux, A., Mackay, D., McCutcheon, P., Mocarelli, P., Taalman, R.D. (1998), Controlling persistent organic pollutants-what next?, Environmental toxicology and pharmacology 6 143–175. https://doi.org/10.1016/s1382-6689(98)00036-2.

[31] United Nations Environment Programme (UNEP), POPs GMP Reports: Various reports on POP Monitoring Programmes, https://www.unep.org/topics/chemicals-and-pollution-action/pollution-and-health/persistent-organic-pollutants-pops/pops, accessed 25 March 2024.

[32] Ballschmiter, K., Zell, M. (1980), Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography, Z. Anal. Chem. 302 20–31. https://doi.org/10.1007/BF00469758.

[33] H. Fiedler, Polychlorinated Biphenyls (PCB), Chapter 12. Polychlorinated biphenyls (PCBs): Uses and Environmental Releases. Bavarian Institute for Waste Research - BIfA GmbH, 1997.

[34] Bench, D.W., PCBs, MINING, AND WATER POLLUTION, in: Mine Design, Operations & Closure Conference, Polson, Montana, April 27-May 1, 2003, 2003, pp. 1–12.

[35] Albro, P.W., Parker, C.E. (1979), Comparison of the compositions of Aroclor 1242 and Aroclor 1016, Journal of chromatography 169 161–166. https://doi.org/10.1016/0021-9673(75)85041-2.

[36] Brenk F.-R., W.G.-J. (1985), Quantifizierung von polychlorierten Biphenylen (PCB) in Altöl, Erdöl und Kohle, Erdgas, Petrochemie 38(10) 469–470.

[37] G.M. Ferrel, (1987) West Virginia Ground-Water Quality. U S Geol Surv Open File Rep 87-0761:9.

[38] J. Reichel, (1973) Schwerentflammbare Druckflüssigkeiten für hydraulische Bergwerksmaschinen. Glückauf 109(17):871–877.

[39] Markowitz, G., Rosner, D. (2018), Monsanto, PCBs, and the creation of a "world-wide ecological problem", Journal of public health policy 39 463–540. https://doi.org/10.1057/s41271-018-0146-8.

[40] de Voogt, P., Brinkman, U., Chapter 1 - Production, properties and usage of polychlorinated biphenyls, in: R.D. Kimbrough, A.A. Jensen (Eds.), Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products (Second Edition) Topics in Environmental Health, Elsevier, Amsterdam, 1989, pp. 3–45.

[41] Markowitz, G. (2018), From Industrial Toxins to Worldwide Pollutants: A Brief History of Polychlorinated Biphenyls, Public health reports (Washington, D.C. 1974) 133 721–725. https://doi.org/10.1177/0033354918801578.

[42] ahu AG Wasser Boden Geomatik, (2017) Gutachten zur Prüfung möglicher Umweltauswirkungen des Einsatzes von Abfall- und Reststoffen zur Bruch-Hohlraumverfüllung in Steinkohlenbergwerken in Nordrhein-Westfalen, Report № Endbericht 2017. Ministerium für Klimaschutz, Umwelt, Landwirtschaft, Natur- und Verbraucherschutz des Landes Nordrhein-Westfalen & Ministerium für Wirtschaft, Energie, Industrie, Mittelstand und Handwerk des Landes Nordrhein-Westfalen, Aachen, 216 p.

[43] R. F. Bekendam, J. J. Pottgens (1996), Ground movements over the coal mines of southern Limburg, the Netherlands, and their relation to rising mine waters, International Journal of Rock Mechanics and Mining Sciences and Geomechanics Abstracts 8 377A.

[44] The Guardian, UK killer whale died with extreme levels of toxic pollutants (2017).

[45] Gioia, R., Nizzetto, L., Lohmann, R., Dachs, J., Temme, C., Jones, K.C. (2008), Polychlorinated Biphenyls (PCBs) in Air and Seawater of the Atlantic Ocean: Sources, Trends and Processes, Environ. Sci. Technol. 42 1416–1422. https://doi.org/10.1021/es071432d.

[46] BBC News, 'Shocking' levels of PCB chemicals in UK killer whale Lulu (2 May 2017).

[47] Kannan, K., Blankenship, A.L., Jones, P.D., Giesy, J.P. (2000), Toxicity Reference Values for the Toxic Effects of Polychlorinated Biphenyls to Aquatic Mammals, Human and Ecological Risk Assessment: An International Journal 6 181–201. https://doi.org/10.1080/10807030091124491.

[48] Wiltschka, K., Wolkersdorfer, C., Düring, R.-A., Böhm, L. (2023), Between Underground and the Deep Blue Sea: Contamination of Mine Water Effluents by Polychlorinated Biphenyls (PCBs), ACS EST Water 3 3474–3484. https://doi.org/10.1021/acsestwater.3c00179.

[49] Zhang, Z., Pawliszyn, J. (1993), Headspace solid-phase microextraction, Anal. Chem. 65 1843–1852. https://doi.org/10.1021/ac00062a008.

[50] Gałuszka, A., Migaszewski, Z., Namieśnik, J. (2013), The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, TrAC Trends in Analytical Chemistry 50 78–84. https://doi.org/10.1016/j.trac.2013.04.010.

[51] Arthur, C.L., Pawliszyn, J. (1990), Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem. 62 2145–2148. https://doi.org/10.1021/ac00218a019.

[52] Risticevic, S., Lord, H., Górecki, T., Arthur, C.L., Pawliszyn, J. (2010), Protocol for solid-phase microextraction method development, Nat Protoc 5 122–139. https://doi.org/10.1038/nprot.2009.179.

[53] Böhm, L., Düring, R.-A., Bruckert, H.-J., Schlechtriem, C. (2017), Can solid-phase microextraction replace solvent extraction for water analysis in fish bioconcentration studies with highly hydrophobic organic chemicals?, Environmental toxicology and chemistry 36 2887–2894. https://doi.org/10.1002/etc.3854.

[54] Piri-Moghadam, H., Ahmadi, F., PAWLISZYN, J. (2016), A critical review of solid phase microextraction for analysis of water samples, TrAC Trends in Analytical Chemistry 85 133–143. https://doi.org/10.1016/j.trac.2016.05.029.

[55] Potter, D.W., Pawliszyn, J. (1994), Rapid determination of polyaromatic hydrocarbons and polychlorinated biphenyls in water using solid-phase microextraction and GC/MS, Environ. Sci. Technol. 28 298–305. https://doi.org/10.1021/es00051a017.

[56] Llompart, M., Li, K., Fingas, M. (1998), Solid-phase microextraction and headspace solid-phase microextraction for the determination of polychlorinated biphenyls in water samples, Anal. Chem. 70 2510–2515. https://doi.org/10.1021/ac971332y.

[57] Derouiche, A., Driss, M.R., Morizur, J.-P., Taphanel, M.-H. (2007), Simultaneous analysis of polychlorinated biphenyls and organochlorine pesticides in water by headspace solid-phase microextraction with gas chromatography-tandem mass spectrometry, Journal of Chromatography A 1138 231–243. https://doi.org/10.1016/j.chroma.2006.10.064.

[58] Hawthorne, S.B., Grabanski, C.B., Miller, D.J. (2009), Solid-phase-microextraction measurement of 62 polychlorinated biphenyl congeners in milliliter sediment pore water samples and determination of K(DOC) values, Anal. Chem. 81 6936–6943. https://doi.org/10.1021/ac901001j.

[59] Cantwell, F.F., Losier, M., Chapter 11 Liquid—liquid extraction, in: Sampling and Sample Preparation for Field and Laboratory, Elsevier, 2002, pp. 297–340.

[60] Marcé, R.M., Borrull, F. (2000), Solid-phase extraction of polycyclic aromatic compounds, Journal of Chromatography A 885 273–290. https://doi.org/10.1016/S0021-9673(00)00428-3.

[61] Leemans, F.A.J.M., McCloskey, J.A. (1967), Combination gas chromatography-mass spectrometry, J Americ Oil Chem Soc 44 11–17. https://doi.org/10.1007/BF02908363.

[62] Poole, C.F., Poole, S.K., Chapter 9 Gas chromatography, in: Fundamentals and Applications of Chromatography and Related Differential Migration Methods - Fundamentals and Techniques, Elsevier, 1992, A393-A447.

[63] Abel, S., Akkanen, J. (2019), Novel, Activated Carbon-Based Material for in-Situ Remediation of Contaminated Sediments, Environ. Sci. Technol. 53 3217–3224. https://doi.org/10.1021/acs.est.8b06471.

[64] Balasubramani, A., Rifai, H.S. (2018), Efficacy of carbon-based materials for remediating polychlorinated biphenyls (PCBs) in sediment, Sci. Total. Environ. (Science of the Total Environment) 644 398–405. https://doi.org/10.1016/j.scitotenv.2018.06.360.

[65] Payne, R.B., May, H.D., Sowers, K.R. (2011), Enhanced reductive dechlorination of polychlorinated biphenyl impacted sediment by bioaugmentation with a dehalorespiring bacterium, Environ. Sci. Technol. 45 8772–8779. https://doi.org/10.1021/es201553c.

[66] Choi, Y., Cho, Y.-M., Luthy, R.G. (2014), In situ sequestration of hydrophobic organic contaminants in sediments under stagnant contact with activated carbon. 1. Column studies, Environmental science & technology 48 1835–1842. https://doi.org/10.1021/es403335g.

[67] Vasilyeva, G.K., Strijakova, E.R., Nikolaeva, S.N., Lebedev, A.T., Shea, P.J. (2010), Dynamics of PCB removal and detoxification in historically contaminated soils amended with activated carbon, Environmental pollution (Barking, Essex 1987) 158 770–777. https://doi.org/10.1016/j.envpol.2009.10.010.

[68] Denyes, M.J., Langlois, V.S., Rutter, A., Zeeb, B.A. (2012), The use of biochar to reduce soil PCB bioavailability to Cucurbita pepo and Eisenia fetida, The Science of The Total Environment 437 76–82. https://doi.org/10.1016/j.scitotenv.2012.07.081.

[69] B. Kjellerup, S. Edwards, Application of Biofilm Covered Activated Carbon Particles as a Microbial Inoculum Delivery System for Enhanced Bioaugmentation of PCBs in Contaminated Sediment. Technical Report, SERDP Project ER-2135, 2013.

[70] Payne, R.B., Ghosh, U., May, H.D., Marshall, C.W., Sowers, K.R. (2019), A Pilot-Scale Field Study: In Situ Treatment of PCB-Impacted Sediments with Bioamended Activated Carbon, Environ. Sci. Technol. 53 2626–2634. https://doi.org/10.1021/acs.est.8b05019.

[71] Mercier, A., Joulian, C., Michel, C., Auger, P., Coulon, S., Amalric, L., Morlay, C., Battaglia-Brunet, F. (2014), Evaluation of three activated carbons for combined adsorption and biodegradation of PCBs in aquatic sediment, Water research 59 304–315. https://doi.org/10.1016/j.watres.2014.04.021.

[72] Dussert, B.W., Tramposch, W.G. (1997), Impact of Support Media on the Biological Treatment of Ozonated Drinking Water, Ozone: Science & Engineering 19 97–108. https://doi.org/10.1080/01919519708547308.

[73] Tammaro, M., Salluzzo, A., Perfetto, R., Lancia, A. (2014), A comparative evaluation of biological activated carbon and activated sludge processes for the treatment of tannery wastewater, Journal of Environmental Chemical Engineering 2 1445–1455. https://doi.org/10.1016/j.jece.2014.07.004.

[74] Vidali, M. (2001), Bioremediation. An overview, Pure and Applied Chemistry 73 1163–1172. https://doi.org/10.1351/pac200173071163.

[75] Abramowicz, D.A. (1995), Aerobic and anaerobic PCB biodegradation in the environment, Environmental health perspectives 103 Suppl 5 97–99. https://doi.org/10.1289/ehp.95103s497.

[76] Field, J.A., Sierra-Alvarez, R. (2008), Microbial degradation of chlorinated benzenes, Biodegradation 19 463–480. https://doi.org/10.1007/s10532-007-9155-1.

[77] Yu, H., Feng, C., Liu, X., Yi, X., Ren, Y., Wei, C. (2016), Enhanced anaerobic dechlorination of polychlorinated biphenyl in sediments by bioanode stimulation, Environ. Pollut. (Environmental Pollution) 211 81–89. https://doi.org/10.1016/j.envpol.2015.12.039.

[78] Kumar, A., Bisht, B.S., Joshi, V.D., Dhewa, T. (2011), Review on Bioremediation of Polluted Environment: A Management Tool, International Journal of Environmental Sciences.

[79] Xia, H., Chi, X., Yan, Z., Cheng, W. (2009), Enhancing plant uptake of polychlorinated biphenyls and cadmium using tea saponin, Bioresource technology 100 4649–4653. https://doi.org/10.1016/j.biortech.2009.04.069.

[80] Carvalho, P., Arias, C., Brix, H. (2017), Constructed Wetlands for Water Treatment: New Developments, Water 9 397. https://doi.org/10.3390/w9060397.

[81] Haarstad, K., Bavor, H.J., Mæhlum, T. (2012), Organic and metallic pollutants in water treatment and natural wetlands: a review, Water Science and Technology 65 76–99. https://doi.org/10.2166/wst.2011.831.

[82] Singh, T., Singh, D.K. (2017), Phytoremediation of organochlorine pesticides: Concept, method, and recent developments, International journal of phytoremediation 19 834–843. https://doi.org/10.1080/15226514.2017.1290579.

[83] Ryan, J.A., Bell, R.M., Davidson, J.M., O'Connor, G.A. (1988), Plant uptake of non-ionic organic chemicals from soils, Chemosphere 17 2299–2323. https://doi.org/10.1016/0045-6535(88)90142-7.

[84] Passatore, L., Rossetti, S., Juwarkar, A.A., Massacci, A. (2014), Phytoremediation and bioremediation of polychlorinated biphenyls (PCBs): state of knowledge and research perspectives, Journal of hazardous materials 278 189–202. https://doi.org/10.1016/j.jhazmat.2014.05.051.

[85] Strek, H.J., Weber, J.B., Shea, P.J., Mrozek, E., Overcash, M.R. (1981), Reduction of polychlorinated biphenyl toxicity and uptake of carbon-14 activity by plants through the use of activated carbon, Journal of agricultural and food chemistry 29 288–293. https://doi.org/10.1021/jf00104a018.

[86] Jing, R., Fusi, S., Kjellerup, B. v. (2018), Remediation of Polychlorinated Biphenyls (PCBs) in Contaminated Soils and Sediment: State of Knowledge and Perspectives, Front. Environ. Sci. 6 183. https://doi.org/10.3389/fenvs.2018.00079.

[87] Krishnamurthy, S., Brown, H.C. (1980), Selective reductions. 27. Reaction of alkyl halides with representative complex metal hydrides and metal hydrides. Comparison of various hydride reducing agents, J. Org. Chem. 45 849–856. https://doi.org/10.1021/jo01293a018.

[88] Kulkarni, P.S., Crespo, J.G., Afonso, C.A.M. (2008), Dioxins sources and current remediation technologies--a review, Environment international 34 139–153. https://doi.org/10.1016/j.envint.2007.07.009.

[89] Mitoma, Y., Uda, T., Egashira, N., Simion, C., Tashiro, H., Tashiro, M., Fan, X. (2004), Approach to Highly Efficient Dechlorination of PCDDs, PCDFs, and Coplanar PCBs Using Metallic Calcium in Ethanol under Atmospheric Pressure at Room Temperature, Environ. Sci. Technol. 38 1216–1220. https://doi.org/10.1021/es034379b.

[90] Ryoo, K.-S., Byun, S.-H., Choi, J.-H., Hong, Y.-P., Ryu, Y.-T., Song, J.-S., Lee, D.-S., Lee, H.-S. (2007), Destruction and Removal of PCBs in Waste Transformer Oil by a Chemical Dechlorination Process, Bulletin of the Korean Chemical Society 28 520–528. https://doi.org/10.5012/bkcs.2007.28.4.520.

[91] DeVor, R., Carvalho-Knighton, K., Aitken, B., Maloney, P., Holland, E., Talalaj, L., Fidler, R., Elsheimer, S., Clausen, C.A., Geiger, C.L. (2008), Dechlorination comparison of mono-substituted PCBs with Mg/Pd in different solvent systems, Chemosphere 73 896–900. https://doi.org/10.1016/j.chemosphere.2008.07.006.

[92] Kopinke, F.-D., Mackenzie, K., Köhler, R. (2003), Catalytic hydrodechlorination of groundwater contaminants in water and in the gas phase using Pd/γ-Al2O3, Applied Catalysis B: Environmental 44 15–24. https://doi.org/10.1016/S0926-3373(03)00006-7.

[93] Choi, H., Al-Abed, S.R., Agarwal, S. (2009), Catalytic Role of Palladium and Relative Reactivity of Substituted Chlorines during Adsorption and Treatment of PCBs on Reactive Activated Carbon, Environ. Sci. Technol. 43 7510–7515. https://doi.org/10.1021/es901298b.

[94] Agarwal, S., Al-Abed, S.R., Dionysiou, D.D., Graybill, E. (2009), Reactivity of Substituted Chlorines and Ensuing Dechlorination Pathways of Select PCB Congeners with Pd/Mg Bimetallics, Environ. Sci. Technol. 43 915–921. https://doi.org/10.1021/es802538d.

[95] Bunge, M., Mackenzie, K., Sustainable Synthesis of Palladium(0) Nanocatalysts and their Potential for Organohalogen Compounds Detoxification, in: O.V. Singh (Ed.), Bio-nanoparticles: Biosynthesis and sustainable biotechnological implications, Wiley Blackwell, Hoboken, New Jersey, 2015, pp. 205–224.

[96] Zhang, J., Lei, C., Chen, W., Xie, Q., Guo, Q., Huang, B. (2021), Electrochemical-driven nanoparticulate catalysis for highly efficient dechlorination of chlorinated environmental pollutant, Journal of Catalysis 395 362–374. https://doi.org/10.1016/j.jcat.2021.01.032.

[97] Keane, M.A. (2011), Supported Transition Metal Catalysts for Hydrodechlorination Reactions, ChemCatChem 3 800–821. https://doi.org/10.1002/cctc.201000432.

[98] Chaplin, B.P., Reinhard, M., Schneider, W.F., Schüth, C., Shapley, J.R., Strathmann, T.J., Werth, C.J. (2012), Critical review of Pd-based catalytic treatment of priority contaminants in water, Environmental science & technology 46 3655–3670. https://doi.org/10.1021/es204087q.

[99] Olson, M.R., Blotevogel, J., Borch, T., Petersen, M.A., Royer, R.A., Sale, T.C. (2014), Long-term potential of in situ chemical reduction for treatment of polychlorinated biphenyls in soils, Chemosphere 114 144–149. https://doi.org/10.1016/j.chemosphere.2014.03.109.

[100] Mackenzie, K., Frenzel, H., Kopinke, F.-D. (2006), Hydrodehalogenation of halogenated hydrocarbons in water with Pd catalysts: Reaction rates and surface competition, Applied Catalysis B: Environmental 63 161–167. https://doi.org/10.1016/j.apcatb.2005.10.004.

[101] Zhang, F., Wang, Z., Peijnenburg, W.J.G.M., Vijver, M.G. (2022), Review and Prospects on the Ecotoxicity of Mixtures of Nanoparticles and Hybrid Nanomaterials, Environ. Sci. Technol. 56 15238–15250. https://doi.org/10.1021/acs.est.2c03333.

[102] Medici, S., Peana, M., Pelucelli, A., Zoroddu, M.A. (2021), An updated overview on metal nanoparticles toxicity, Seminars in Cancer Biology 76 17–26. https://doi.org/10.1016/j.semcancer.2021.06.020.

[103] Albers, P., Pietsch, J., Parker, S.F. (2001), Poisoning and deactivation of palladium catalysts, Journal of Molecular Catalysis A: Chemical 173 275–286. https://doi.org/10.1016/S1381-1169(01)00154-6.

[104] Hotze, E.M., Phenrat, T., Lowry, G. v. (2010), Nanoparticle Aggregation: Challenges to Understanding Transport and Reactivity in the Environment, Journal of Environment Quality 39 1909. https://doi.org/10.2134/jeq2009.0462.

[105] Comandella, D., Woszidlo, S., Georgi, A., Kopinke, F.-D., Mackenzie, K. (2016), Efforts for long-term protection of palladium hydrodechlorination catalysts, Applied Catalysis B: Environmental 186 204–211. https://doi.org/10.1016/j.apcatb.2015.12.043.

[106] Wismut GmbH, Die Wasserbehandlungsanlagen der Wismut, 2021, https://www.wismut.de/de/download.php?download=WBA+%C3%9Cbersicht+2021.pdf, accessed 9 December 2022.

[107] RAG Aktiengesellschaft, Wasserhaltungskonzept, https://www.rag.de/ewigkeitsaufgaben/wasserhaltung/, accessed 9 December 2022.

[108] Bogdal, C., Müller, C.E., Buser, A.M., Wang, Z., Scheringer, M., Gerecke, A.C., Schmid, P., Zennegg, M., Macleod, M., Hungerbühler, K. (2014), Emissions of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans during 2010 and 2011 in Zurich, Switzerland, Environ. Sci. Technol. 48 482–490. https://doi.org/10.1021/es4044352.

[109] Diamond, M.L., Melymuk, L., Csiszar, S.A., Robson, M. (2010), Estimation of PCB stocks, emissions, and urban fate: will our policies reduce concentrations and exposure?, Environ. Sci. Technol. 44 2777–2783. https://doi.org/10.1021/es9012036.

[110] Wiltschka, K., Neumann, L., Werheid, M., Bunge, M., Düring, R.-A., Mackenzie, K., Böhm, L. (2020), Hydrodechlorination of hexachlorobenzene in a miniaturized nano-Pd(0) reaction system combined with the simultaneous extraction of all dechlorination products, Appl. Catal. B: Environ. (Applied Catalysis B: Environmental) 275 119100. https://doi.org/10.1016/j.apcatb.2020.119100.

[111] Fueno, H., Tanaka, K., Sugawa, S. (2002), Theoretical study of the dechlorination reaction pathways of octachlorodibenzo-p-dioxin, Chemosphere 48 771–778. https://doi.org/10.1016/s0045-6535(02)00141-8.

[112] Arulmozhiraja, S., Morita, M. (2004), Electron Affinities and Reductive Dechlorination of Toxic Polychlorinated Dibenzofurans: A Density Functional Theory Study, J. Phys. Chem. A 108 3499–3508. https://doi.org/10.1021/jp037620h.

[113] Gao, X., Wang, W., Liu, X. (2008), Low-temperature dechlorination of hexachlorobenzene on solid supports and the pathway hypothesis, Chemosphere 71 1093–1099. https://doi.org/10.1016/j.chemosphere.2007.10.041.

[114] C.A. Coulson, Valence, 2nd ed., Oxford: University Press, London, 1965.

[115] M. Kraus, V. Bazant, Miami Beach, FL, Catalysis: Proceedings of the Fifth International Congress on Catalysis, 20-26, pp. 1073-1083. August 1972.

[116] Yakovlev, V.A., Simagina, V.I., Trukhan, S.N., Likholobov, V.A. (2000), Kinetic study of liquid-phase hydrodechlorination of hexachlorobenzene on Ni/C and 2%PdNi/C, Kinet Catal 41 25–32. https://doi.org/10.1007/BF02756136.

[117] Yamada, S., Naito, Y., Takada, M., Nakai, S., Hosomi, M. (2008), Photodegradation of hexachlorobenzene and theoretical prediction of its degradation pathways using quantum chemical calculation, Chemosphere 70 731–736. https://doi.org/10.1016/j.chemosphere.2007.06.039.

[118] Dolfing, J., Novak, I. (2015), The Gibbs free energy of formation of halogenated benzenes, benzoates and phenols and their potential role as electron acceptors in anaerobic environments, Biodegradation 26 15–27. https://doi.org/10.1007/s10532-014-9710-5.

[119] Korte, N., Zutman, J., Schlosser, R., Liang, L., Gu, B., Fernando, Q. (2000), Field application of palladized iron for the dechlorination of trichloroethene, Waste Management 20 687–694. https://doi.org/10.1016/S0956-053X(00)00037-4.

[120] Navon, R., Eldad, S., Mackenzie, K., Kopinke, F.-D. (2012), Protection of palladium catalysts for hydrodechlorination of chlorinated organic compounds in wastewaters, Applied Catalysis B: Environmental 119-120 241–247. https://doi.org/10.1016/j.apcatb.2012.03.002.

[121] K. Wiltschka, S. Bobric, R.-A. Düring, L. Böhm, Coating-Protected Pd/Al2O3 Catalysts for the Elimination of Polychlorinated Biphenyls (PCBs) from Mine Water Effluents: Manuscript submitted to *Applied Catalysis B: Environment and Energy*., 2024.

[122] Comandella, D., Ahn, M.H., Kim, H., Mackenzie, K. (2017), Enhanced protection of PDMS-embedded palladium catalysts by co-embedding of sulphide-scavengers, The Science of The Total Environment 601-602 658–668. https://doi.org/10.1016/j.scitotenv.2017.05.154.

[123] United Nations Environment Programme (UNEP), PCB a forgotten legacy?, 2017, https://wedocs.unep.org/bitstream/handle/20.500.11822/20786/PCB%20Brochure%20(2017).pdf?sequence=1&isAllowed=y.

[124] Gosling, S.N., Arnell, N.W. (2016), A global assessment of the impact of climate change on water scarcity, Clim. Change (Climatic Change) 134 371–385. https://doi.org/10.1007/s10584-013-0853-x.

2 Kontamination von Grubenwässern durch polychlorierte Biphenyle (PCB)

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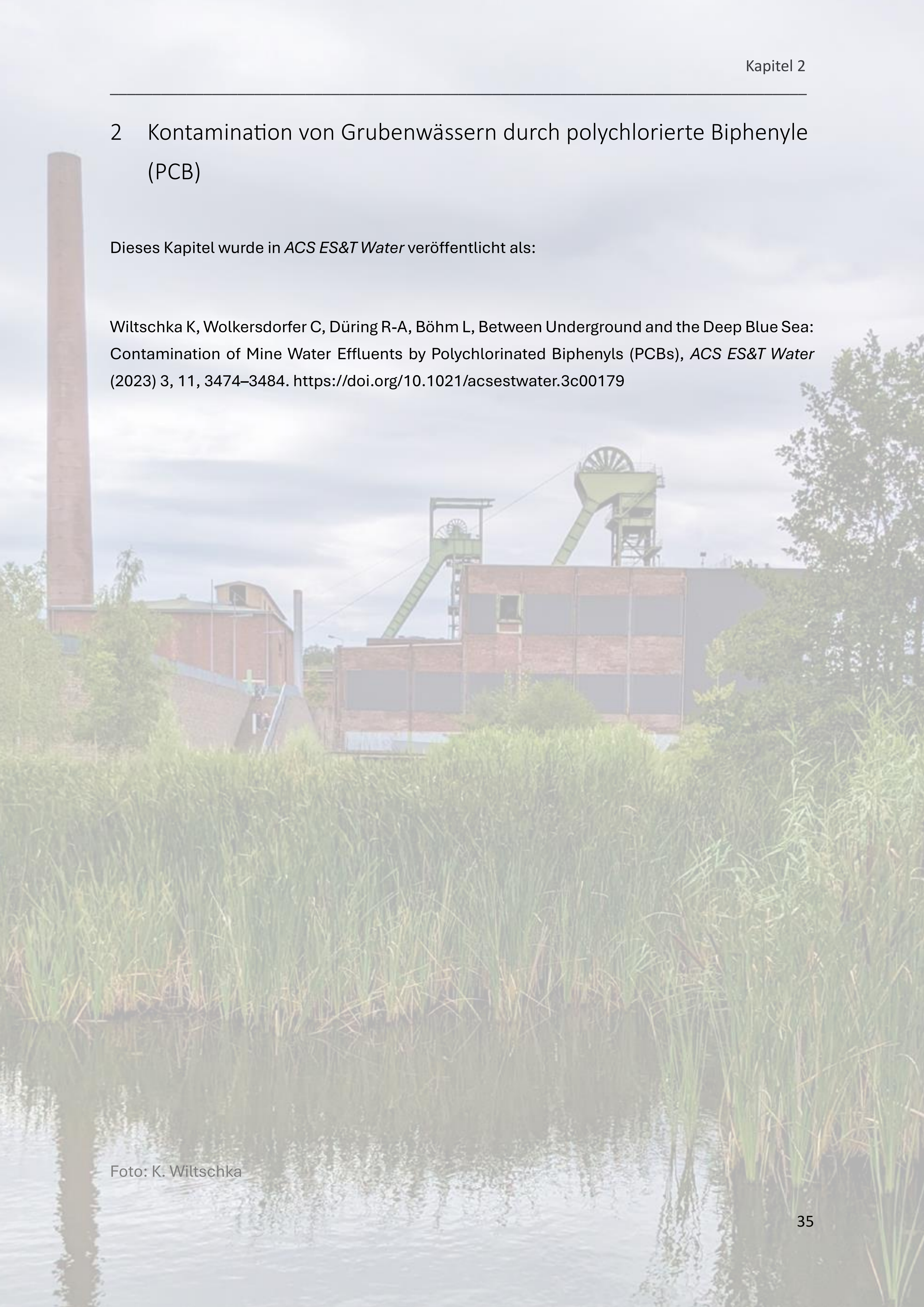

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Between Underground and the Deep Blue Sea: Contamination of Mine Water Effluents by Polychlorinated Biphenyls (PCBs)

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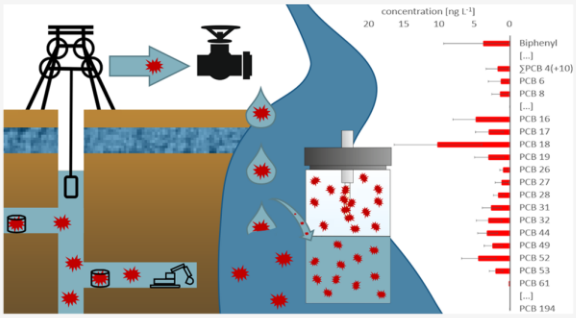
ABSTRACT: Polychlorinated biphenyls (PCBs) were used as industrial chemicals due to their beneficial physicochemical properties in many applications until the recognition of their adverse effects. Although being banned for decades, PCBs are still ubiquitous in the environment due to their congener-specific 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 2001[3] 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 conveyer 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 points[20] 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 water[31] and sediments[32] 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 ≥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 ≥96.5%, LGC), deuterated PCB congeners (neat, purity ≥97%, CDN Isotopes, Pointe Claire, Canada), and ^{13}C labeled PCB congeners (purity ≥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 ^{13}C 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 machinery[21] 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 N_2/CO_2 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 μL 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 $CaCl_2$ L^{-1} solution and were also spiked with 2 μL 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 μm 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 μm), 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 μm PDMS fiber had by far the lowest extraction rates, especially in the low-chlorinated range. Both the 85 μm PA and the 50/30 μm 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 ≈40 min. The measurement of the most relevant PCBs in MIW is feasible also for higher-chlorinated congeners using only the 65 μm PDMS/DVB nitinol core fiber at 75 °C. However, the additional measurement with the 100 μm 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
∑PCB 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
∑PCB 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
$\sum PCB_{53+bp}$	21.7−59.5	82.6−121	30.5−57.4	53.9	52.1	
$\sum PCB_{53}$	20.4−56.4	82.1−120	19.0−42.9	53.7	51.8	
$\sum PCB_{i+118}$	2.5−6.7	5.8−10.8	2.8−6.2	10.4	10.7	
$\sum PCB_{top11}$	14.0−20.9	62.4−88.2	9.5−24.9	44.4	40.4	

[a] Concentrations from Walsum, Zollverein, and Stinnes are each given as min−max values from four sampling campaigns. Individual replicates are provided in Table S7. [b] Investigated 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 × LOQ in the calculations and given in the table with its value written in *italics*. [c] $\sum PCB_{53+bp}$ as the sum of all detected PCB congeners and biphenyl, $\sum PCB_{53}$ as the sum of all detected PCB congeners without biphenyl, $\sum PCB_{i+118}$ as the sum of the six indicator PCBs and PCB 118, $\sum PCB_{top11}$ as the sum of the 11 most abundant PCB congeners in all tested mines. [d] Congeners 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 ($\sum PCB_{top4}$) 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 ($\sum PCB_{top11}$) includes the $\sum PCB_{top4}$ 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 $\sum$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 samples[21]). 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

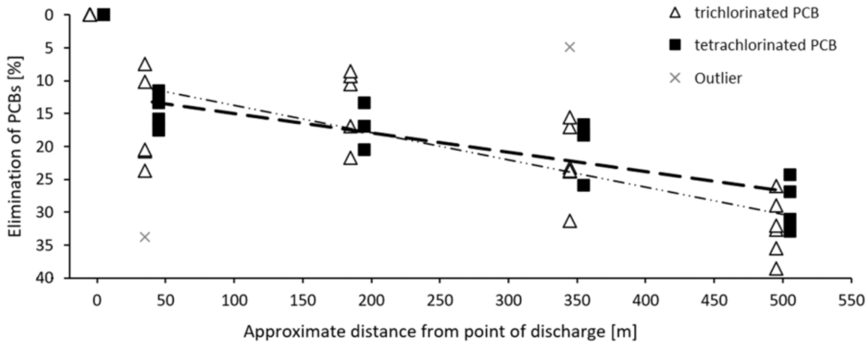

Figure 1. PCB elimination along the course of the constructed wetland at the Reden site. Elimination is exemplarily shown for the 11 most abundant PCBs ($\sum PCB_{top11}$). Each symbol at a specific distance represents an individual PCB congener. Symbols for tri- and tetrachlorinated PCBs have been 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
$\sum PCB_{53+bp}$ (Table 1) [ng L^{-1}]	21.7−59.5	82.6−121	30.5−57.4	53.9	52.1
$\sum PCB_{53}$ (Table 1) [ng L^{-1}]	20.4−56.4	82.1−120	19.0−42.9	53.7	51.8
discharged mine water [mio m^3 a^{-1}]	4.8[a]	4.4[a]	7.0[a]	12.0[b]	1.7[c]
annual loads $\sum PCB_{53+bp}$ [kg]	0.10−0.29	0.36−0.53	0.21−0.40	0.65	0.09
annual loads $\sum PCB_{53}$ [kg]	0.10−0.27	0.36−0.53	0.13−0.30	0.64	0.09
$\sum PCB_{53+bp}$ [kg mio m^{-3}]	0.02−0.06	0.08−0.12	0.03−0.06	0.05	0.05
$\sum PCB_{53}$ [kg mio m^{-3}]	0.02−0.06	0.08−0.12	0.02−0.04	0.05	0.05

[a]Data from 2021, according to personal communication with employees of LANUV NRW. [b]Data from 2019.[54] [c]Data 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

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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 m^3 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 m^3.[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 m^3 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-

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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 mio m^3 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

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 Wiltschka** 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 During** 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.; Burkhart, J. F.; Hungerbuhler, 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: Occurence, 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.; Víkingson, 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 (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 Grubenwassereinleitungen 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) Risticevic, 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) Wiltschka, 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.; Grančič, 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)*; PCBSAAR/19281/DE/LL, 2019. https://www.saarland.de/SharedDocs/Downloads/DE/mukmav/wasser/grubenwasser/dl_gutachten_erkenntnisse_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_II.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 Neurones. *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.

Supporting Information

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

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Summary: 18 pages including experimental and analytical details (9 tables and 12 figures).

Additional details on materials and methods

Chemicals

Neat PCBs were prepared as stock solutions of single substances in methanol (≥ 99.9%, p.a. quality, Carl Roth GmbH, Karlsruhe, Germany) (87–230 mg L^{-1}), and mixed group wise to concentrations of 10 and 15 mg L^{-1} in methanol. Stock solutions in methanol were stored in 20-mL screw neck vials (hydrolytic class 1) with screw caps with silicone/PTFE septa (Klaus Trott Chromatographie-Zubehör, Kriftel, Germany). Working solutions (mix of all investigated PCBs, 0.005–2000 µg L^{-1}) were stored in 1.5-mL Certan capillary bottles (Merck KGaA, Darmstadt, Germany). Method optimization experiments were prepared in a solution containing 0.01 mol $CaCl_2$ L^{-1} (purity ≥ 99%, p.a. quality, Carl Roth GmbH, Karlsruhe, Germany). All water used within the study was of ultrapure quality (ELGA PF2XXXXM1, Veolia Water Solutions & Technologies, High Wycombe, UK).

HS-SPME-GC-MS method optimization and mine water analysis

PCB analysis was carried out with a CombiPAL autosampler (CTC Analytics AG, Zwingen, Switzerland) equipped with a SPME fiber assembly, a Trace 1310 GC (Thermo Fisher Scientific, San Jose, CA, USA), and an ISQ 7000 MS (Thermo Fisher Scientific). The GC method was optimized for baseline separation of PCBs with the shortest possible GC runtime. Overlapping PCBs were individually identified with a separate GC method. Quantification was performed in selected ion monitoring (SIM) mode based on one quantifier and one qualifier ion.

Chromatographic separation was conducted on a fused silica capillary column (TG-XLBMS: 60 m, 0.25 mm inner diameter, 0.25 µm coating thickness; Thermo Fisher Scientific). Helium 5.0 (Praxair, Germany) was used as carrier gas at a constant flow rate of 1.0 mL min^{-1}. Oven programs are given in Table S4. The injector was programmed with a split flow of 30 mL min^{-1} after splitless thermodesorption of the fiber for 3 min at 210 °C. The transfer line to the MS was heated at 280 °C. Ionization of molecules was performed by electron impact ionization (70 eV) at 275 °C.

Mine water sampling

Mine water samples (1–2 L each) were collected from five different sites: the Walsum, Zollverein, and Stinnes mines (NRW) as well as from the Reden and Camphausen mines (Saarland). For the NRW mines, three further sampling campaigns were conducted after 9, 16 or 18, and 26 months (specific sampling times are provided in Table S7). At the Reden site, four additional samples were taken along an artificial stream that is fed exclusively by MIW to assess PCB elimination along the course of this constructed wetland. Samples from the Walsum, Zollverein, and Stinnes mines were taken by employees of the North Rhine-Westphalia State Office for Nature, Environment and Consumer Protection (LANUV NRW) and collected through sampling taps on delivery pipes. Information on materials and storage is given in the SI in the “Quality assurance and quality control” section below.

Quality assurance and quality control

The SPME fiber was thermally cleaned at 240 °C before extraction and after thermodesorption for 9 min in the needle heater in order to remove possible residues and to prevent carry-over of analytes between sampling events. Fibers were reused, but visually controlled for any changes and frequently rinsed/cleaned with methanol. The internal standard mix used allowed for the correction of potentially occurring variability in sensitivity of the SPME fiber and the GC-MS instrument. Blank samples (0.01 mol $CaCl_2$ L^{-1}) were measured as described in the main article to check for potential carry-over or impurities.

The glassware for mine water sampling was rinsed out with acetone, and then baked out at a minimum temperature of 140 °C. Blank samples were taken to check the sample vessels for any contamination before filling. All amber glass bottles were fully filled to avoid any remaining headspace, minimizing both exposure to atmospheric oxygen and volatilization losses of PCBs. For the mine water of the Reden and Camphausen mines, the bottles were rinsed with acetone and rinsed thrice with the respective mine water. These samples were taken at the end of the corresponding discharge pipes, thus contact with air could not be fully excluded. During sampling, care was taken to ensure that only glassware with the highest hydrolytic resistance was used (Schott Duran® bottles and screw caps with a PTFE coated silicone seal, Th. Geyer GmbH & Co., Renningen, Germany). After sampling, the bottles were stored at 4 °C until measurement.

Table S1. Retention times (RT) and ions used for identification and quantification of analytes and internal standards (IS). Analytes were corrected with their RT-nearest IS. For ^{13}C-PCB 9 and PCB 9-d_5, the correction by the ^{13}C-labeled PCB was consistently better. Trichlorobiphenyls had a second qualifier to improve their differentiation from sulfur component spectra that can occur in mine water.[1]

Substance	Purpose	RT [min]	Quantifier [m/z]	Qualifier 1 [m/z]	Qualifier 2 [m/z]
Biphenyl-d_{10}	IS	16.48	164	80	
Biphenyl	Analyte	16.58	154	76	
PCB 1	Analyte	18.88	188	152	
PCB 2	Analyte	20.51	188	152	
PCB 3-d_5	IS	20.76	193	157	
PCB 3	Analyte	20.81	188	152	
∑PCB 4(+10) [a,b]	Analyte	21.23	222	152	
PCB 9-d_5	IS	22.24	227	157	
^{13}C-PCB 9	IS	22.27	234	164	
PCB 9	Analyte	22.28	222	152	
PCB 7	Analyte	22.35	222	152	
PCB 6	Analyte	22.64	222	152	
PCB 5	Analyte	22.91	222	152	
PCB 8	Analyte	22.98	222	152	
PCB 19	Analyte	23.51	256	186	150
PCB 14	Analyte	23.56	222	152	
PCB 30	Analyte	23.90	256	186	150
PCB 18-d_5	IS	24.30	263	191	
PCB 11	Analyte	24.33	222	152	
PCB 18	Analyte	24.35	256	186	150
PCB 17	Analyte	24.47	256	186	150
PCB 12	Analyte	24.57	222	152	
PCB 13	Analyte	24.69	222	152	
PCB 27	Analyte	24.70	256	186	150
PCB 24	Analyte	24.83	256	186	150
PCB 16	Analyte	25.03	256	186	150
PCB 15	Analyte	25.05	222	152	
PCB 32	Analyte	25.13	256	186	150
PCB 26	Analyte	25.85	256	186	150
PCB 31	Analyte	26.25	256	186	150
PCB 53	Analyte	26.30	292	220	
^{13}C-PCB 28	IS	26.34	270	198	
PCB 28	Analyte	26.35	256	186	150
∑PCB 20+21+33 [a]	Analyte	26.48	256	186	150
^{13}C-PCB 52	IS	27.25	304	232	
PCB 52	Analyte	27.27	292	220	
PCB 49	Analyte	27.44	292	220	
PCB 65	Analyte	27.66	292	220	
PCB 38	Analyte	27.71	256	186	150
PCB 62	Analyte	27.71	292	220	
PCB 44	Analyte	27.94	292	220	
PCB 61	Analyte	29.22	292	220	
^{13}C-PCB 101	IS	30.14	338	266	
PCB 101	Analyte	30.15	326	254	
PCB 99	Analyte	30.35	326	254	
PCB 116	Analyte	31.09	326	254	
PCB 85	Analyte	31.28	326	254	
PCB 110	Analyte	31.42	326	254	
PCB 77	Analyte	31.84	292	220	
PCB 149	Analyte	32.00	360	290	
^{13}C-PCB 118	IS	32.42	338	266	

PCB 118	Analyte	32.43	326	254
PCB 146	Analyte	32.66	360	290
^{13}C-PCB 153	IS	32.87	372	302
PCB 153	Analyte	32.88	360	290
PCB 105	Analyte	33.30	326	254
^{13}C-PCB 138	IS	33.80	372	302
PCB 138	Analyte	33.81	360	290
PCB 187	Analyte	34.12	394	324
PCB 183	Analyte	34.31	394	324
PCB 128	Analyte	34.74	360	290
PCB 167	Analyte	34.86	360	290
PCB 156	Analyte	35.61	360	290
^{13}C-PCB 180	IS	35.83	406	336
PCB 180	Analyte	35.84	396	324
PCB 170	Analyte	36.77	394	324
PCB 189	Analyte	37.85	394	324
PCB 194	Analyte	38.63	430	358

[a] Congeners without chromatographic baseline separation.

[b] The RTs for PCB 4 and PCB 10 for the alternative temperature program of the GC oven (see Table S4b) are 35.00 and 35.06 min, respectively.

Table S2. Analytes and their respective internal standards (IS).

Analyte	IS	Analyte	IS
Biphenyl	Biphenyl-d_{10}	PCB 38	^{13}C-PCB 52
PCB 1	PCB 3-d_5	PCB 44	^{13}C-PCB 52
PCB 2	PCB 3-d_5	PCB 49	^{13}C-PCB 52
PCB 3	PCB 3-d_5	PCB 52	^{13}C-PCB 52
∑PCB 4(+10)	PCB 3-d_5	PCB 53	^{13}C-PCB 28
PCB 5	^{13}C-PCB 9	PCB 61	^{13}C-PCB 101
PCB 6	^{13}C-PCB 9	PCB 77	^{13}C-PCB 118
PCB 7	^{13}C-PCB 9	PCB 85	^{13}C-PCB 101
PCB 8	^{13}C-PCB 9	PCB 99	^{13}C-PCB 101
PCB 9	^{13}C-PCB 9	PCB 101	^{13}C-PCB 101
PCB 11	PCB 18-d_5	PCB 105	^{13}C-PCB 153
PCB 12	PCB 18-d_5	PCB 110	^{13}C-PCB 118
PCB 13	PCB 18-d_5	PCB 116	^{13}C-PCB 101
PCB 14	PCB 18-d_5	PCB 118	^{13}C-PCB 118
PCB 15	PCB 18-d_5	PCB 128	^{13}C-PCB 138
PCB 16	PCB 18-d_5	PCB 138	^{13}C-PCB 138
PCB 17	PCB 18-d_5	PCB 146	^{13}C-PCB 153
PCB 18	PCB 18-d_5	PCB 149	^{13}C-PCB 118
PCB 19	PCB 18-d_5	PCB 153	^{13}C-PCB 153
∑PCB 20+21+33	^{13}C-PCB 28	PCB 156	^{13}C-PCB 180
PCB 24	PCB 18-d_5	PCB 167	^{13}C-PCB 180
PCB 26	^{13}C-PCB 28	PCB 170	^{13}C-PCB 180
PCB 27	PCB 18-d_5	PCB 180	^{13}C-PCB 180
PCB 28	^{13}C-PCB 28	PCB 183	^{13}C-PCB 138
PCB 30	PCB 18-d_5	PCB 187	^{13}C-PCB 138
PCB 31	^{13}C-PCB 28	PCB 189	^{13}C-PCB 180
PCB 32	PCB 18-d_5	PCB194	^{13}C-PCB 180

Table S3. Recovery rates for the IS.

Internal Standards	Recovery rate [%]
Biphenyl-*d*$_{10}$	49–183
PCB 3-*d*$_5$	52–169
PCB 9-*d*$_5$	57–165
^{13}C-PCB 9	56–174
PCB 18-*d*$_5$	52–200
^{13}C-PCB 28	50–218
^{13}C-PCB 52	45–198
^{13}C-PCB 101	46–192
^{13}C-PCB 118	45–203
^{13}C-PCB 153	45–200
^{13}C-PCB 138	44–213
^{13}C-PCB 180	45–205

Table S4. Temperature program of the GC oven for conditions optimized (a) for baseline separation and runtime, and (b) for separation of PCBs 4 and 10. Total times: (a) 41 min and (b) 47 min.

(a)

Rate [°C min^{-1}]	Temperature [°C]	Hold time [min]
-	60	3.00
30	120	0.00
6	320	2.00

(b)

Rate [°C min^{-1}]	Temperature [°C]	Hold time [min]
-	35	3.00
30	120	0.00
2	200	1.00

Optimization of the HS-SPME-GC-MS method

Extraction yields for specific parameters such as SPME fiber (Figure S1), extraction temperature (Figure S2), as well as extraction time and shaking intensity (Figure S3) were compared for selected congeners. For each specific congener, the largest extraction yield per investigated parameter was set to 1 and the further extraction yields are given relative to the maximum. For Figure S1, exemplarily, the best extraction yield for PCB 28 was achieved with the 100 µm PDMS fiber and therefore set to 1.0. Extraction yields of PCB 28 with the further fibers were between 6 and 90 % of the 100 µm PDMS fiber and therefore given with relative intensities of 0.06–0.90.

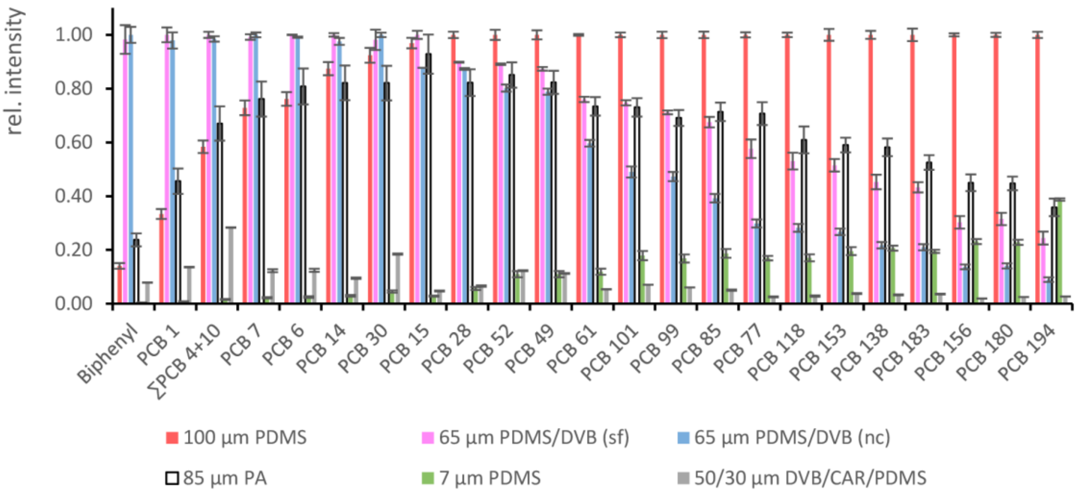

Figure S1. Extraction efficiency of tested SPME fibers (*n* = 2, error bars show standard deviation). Extraction conditions: 50 °C extraction temperature, 30 min extraction time, sf: StableFlex, nc: nitinol-core.

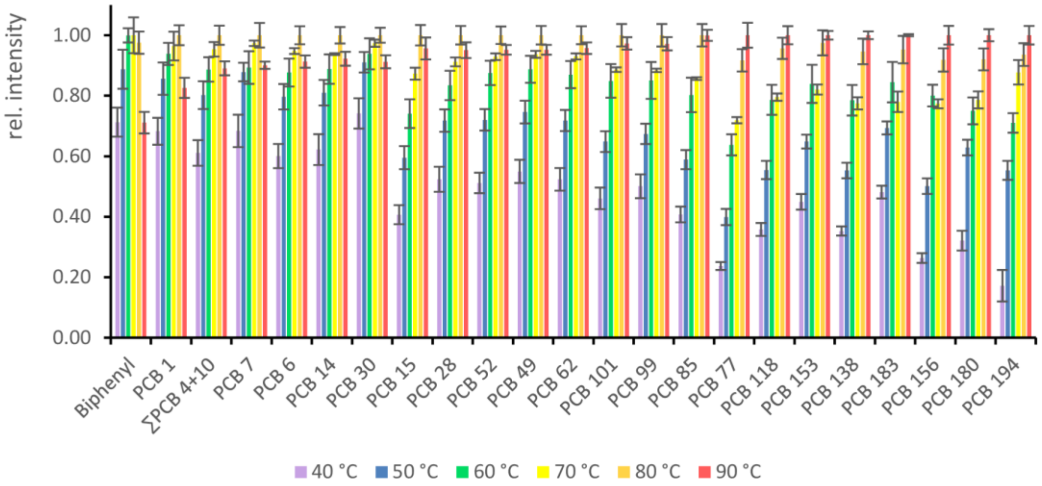

Figure S2. Extraction efficiency at selected extraction temperatures in the agitator (*n* = 3, error bars show standard deviation). Extraction conditions: 65 µm PDMS/DVB (nitinol-core) fiber, 30 min extraction time.

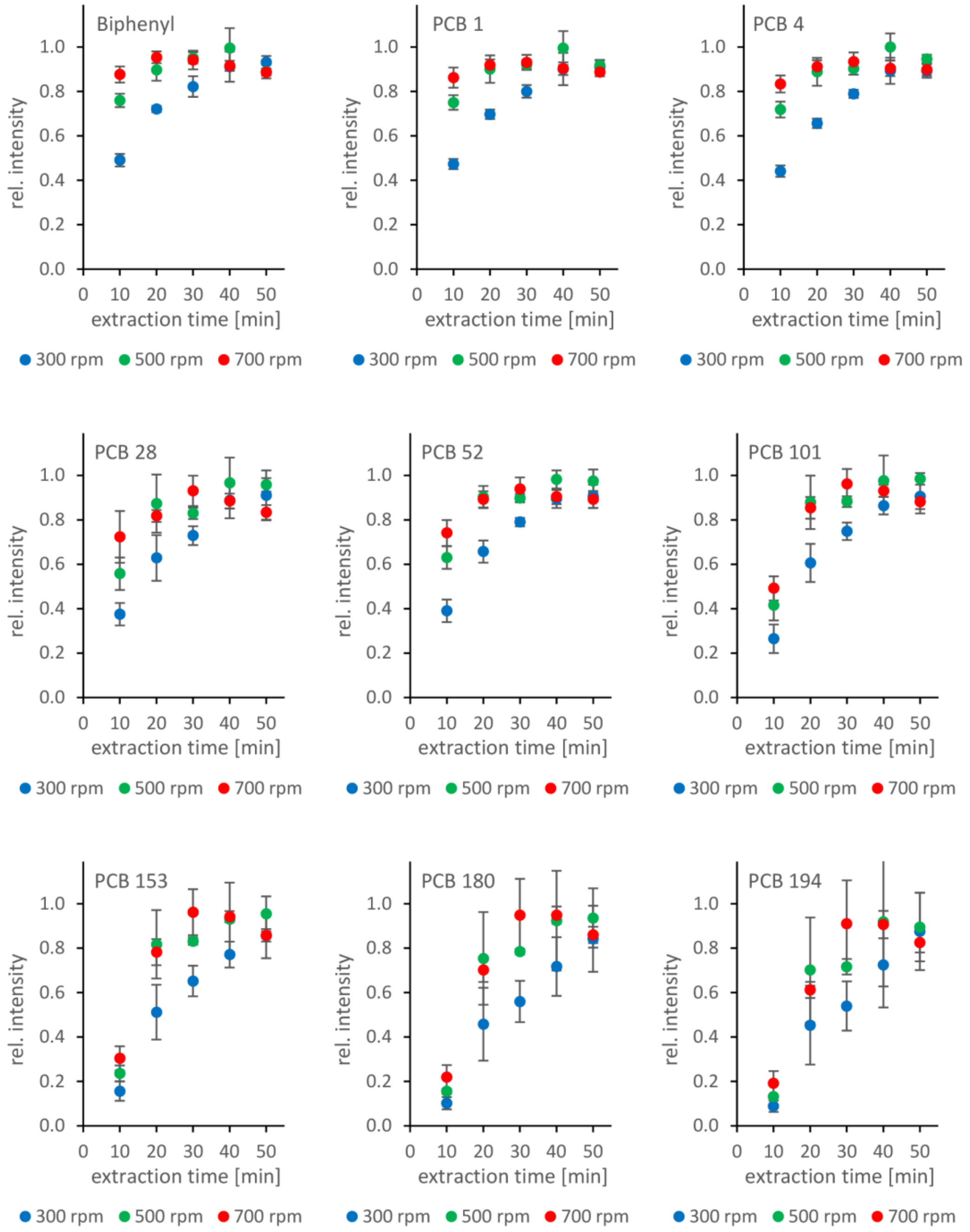

Figure S3. Extraction efficiency depending on extraction time and intensity of sample stirring during extraction (*n* = 5, error bars show standard deviation). For better overview, the tested stirring rates of 250, 400, and 600 rpm are not shown. Presented are nine congeners that were exemplarily selected depending on their chlorination degree with a focus on indicator PCBs. Extraction conditions: 65 µm PDMS/DVB (nitinol-core) fiber, 75 °C extraction temperature.

Determination of congener specific limits of detection (LOD) and limits of quantification (LOQ)

For determination of LODs and LOQs, the standard deviation of the signal generated by multiple blank measurements (*n* = 10) was divided by the slope of the calibration curve. The resulting noise concentrations were multiplied by 3 and 10 to obtain LOD and LOQ, respectively.[2,3] These calculations were performed for PCB analyses using both the PDMS/DVB (65 µm with nitinol-core) and PDMS (100 µm) SPME fibers. For biphenyl and mono- to trichlorinated PCBs the PDMS/DVB fiber was used, and for tetrachlorinated and higher PCBs the PDMS fiber was used.

Table S5. Congener specific LODs and LOQs as median (*n* = 10) in ng L^{-1} for mine water analysis.

	Analyte	LOD	LOQ
	Biphenyl	0.06	0.19
Mono	PCB 1	0.004	0.014
	PCB 2	0.04	0.13
	PCB 3	0.03	0.11
Di	∑ PCB 4(+10)	0.06	0.19
	PCB 5	0.07	0.22
	PCB 6	0.2	0.62
	PCB 7	0.04	0.14
	PCB 8	0.3	1.10
	PCB 9	0.03	0.10
	PCB 11	0.09	0.29
	PCB 12	0.004	0.014
	PCB 13	0.6	1.9
	PCB 14	0.08	0.27
	PCB 15	0.2	0.67
Tri	PCB 16	0.7	2.2
	PCB 17	0.06	0.20
	PCB 18	0.02	0.08
	PCB 19	0.01	0.043
	∑ PCB 20+21+33	0.01	0.035
	PCB 24	0.004	0.015
	PCB 26	0.008	0.028
	PCB 27	0.4	1.18
	PCB 28	0.04	0.15
	PCB 30	0.007	0.23
	PCB 31	0.02	0.058
	PCB 32	0.2	0.74
	PCB 38	0.2	0.55
Tetra	PCB 44	0.03	0.089
	PCB 49	0.02	0.062
	PCB 52	0.02	0.050
	PCB 53	0.007	0.023
	PCB 61	0.02	0.068
	PCB 62	0.005	0.016
	PCB 65	0.01	0.026
	PCB 77	0.2	0.75
Penta	PCB 85	0.1	0.32
	PCB 99	0.04	0.14
	PCB 101	0.05	0.16
	PCB 105	0.3	0.85
	PCB 110	0.1	0.43
	PCB 116	0.06	0.19
	PCB 118	0.2	0.71
Hexa	PCB 128	0.3	1.0
	PCB 138	0.3	1.0
	PCB 146	0.2	0.72
	PCB 149	0.1	0.48
	PCB 153	0.3	0.82
	PCB 156	0.3	0.91
	PCB 167	0.3	0.93
Hepta	PCB 170	0.4	1.2
	PCB 180	0.3	1.0
	PCB 183	0.3	1.0
	PCB 187	0.3	1.1
	PCB 189	0.3	1.0
Octa	PCB194	0.6	1.9

Efficiency of extraction from mine water

Recovery rates of PCB congeners were investigated to account for PCB losses during storage, i.e. between sampling and measurement of samples. Recovery rates were calculated based on spiked PCB concentrations that were measured four days after spiking. Native mine water samples were spiked with 10 ng L^{-1} with PCB congeners that were not found in the samples. External calibration samples were prepared before analysis, respectively.

Table S6. Recovery rates [%] for selected PCB congeners from different mine water samples.

	PCB 14	PCB 38	PCB 105	PCB 189	PCB 194
Walsum (April 22)	82.0	85.7	88.2	89.8	97.8
Zollverein (April 22)	78.4	78.5	68.9	72.1	77.4
Reden	79.5	75.6	65.7	69.5	86.0
mean recovery	80.0	79.9	74.3	77.1	87.1

Table S7. PCB concentrations [ng L^{-1}] in mine water from the three NRW mines over 26 months. Zero was assumed for congeners <LOD, congeners <LOQ were included with 0.5 × LOQ and written in *italics*.

	Walsum				Zollverein				Stinnes			
Analyte	FEB 2020	NOV 2020	JAN 2021	APR 2022	FEB 2020	NOV 2020	AUG 2021	APR 2022	FEB 2020	NOV 2020	AUG 2021	APR 2022
Biphenyl	3.05	2.92	1.35	2.30	0.37	0.49	0.25	0.80	14.50	14.71	11.54	19.18
PCB 1	0.08	0.06	0.04	0.07	0.19	0.19	*0.007*	0.23	0.12	0.09	0.08	0.11
PCB 2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	*0.06*	<LOD	<LOD	<LOD
PCB 3	*0.06*	*0.06*	*0.06*	*0.06*	*0.06*	*0.06*	*0.06*	*0.06*	0.11	*0.06*	*0.06*	0.15
∑ PCB 4(+10)	1.64	1.10	0.72	1.18	5.00	4.64	4.75	5.65	1.06	0.85	0.65	1.10
PCB 5	*0.11*	*0.11*	*0.11*	*0.11*	*0.11*	*0.11*	*0.11*	*0.11*	*0.11*	<LOD	<LOD	<LOD
PCB 6	*0.31*	*0.31*	*0.31*	*0.31*	4.51	4.34	4.69	6.07	*0.31*	*0.31*	*0.31*	*0.31*
PCB 7	*0.07*	*0.07*	<LOD	*0.07*	0.16	0.19	<LOD	0.23	*0.07*	<LOD	<LOD	*0.07*
PCB 8	1.47	1.22	*0.55*	1.34	3.58	3.28	3.67	4.10	1.52	*0.55*	*0.55*	1.56
PCB 9	0.14	*0.05*	*0.05*	*0.05*	0.39	0.34	*0.05*	0.39	0.15	*0.05*	*0.05*	0.14
PCB 11	0.50	0.36	0.30	0.45	1.58	1.38	1.60	1.88	0.60	*0.15*	*0.15*	0.38
PCB 12	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 13	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	*0.96*	<LOD	<LOD	<LOD	<LOD
PCB 14	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 15	*0.34*	*0.34*	*0.34*	*0.34*	0.93	0.82	1.04	1.36	0.78	*0.34*	*0.34*	*0.34*
PCB 16	4.96	3.50	2.73	3.98	12.24	10.55	10.91	11.21	4.51	2.52	2.12	3.56
PCB 17	1.62	1.18	0.86	1.59	6.27	5.42	6.46	7.59	1.85	0.68	0.63	1.24
PCB 18	17.57	5.09	3.43	4.40	20.99	19.00	21.75	25.91	5.09	2.78	2.54	4.31
PCB 19	2.70	1.82	1.19	1.96	6.85	6.32	7.04	7.41	1.38	1.05	0.82	1.37
∑ PCB 20+21+33	0.23	0.20	0.21	0.31	0.63	0.54	0.24	0.70	0.78	0.22	0.19	0.29
PCB 24	0.09	0.06	0.05	0.07	0.21	0.18	0.18	0.19	0.17	0.05	0.03	0.05
PCB 26	0.16	0.14	0.14	0.23	1.29	1.19	1.61	2.30	0.60	0.15	0.14	0.19
PCB 27	*0.59*	<LOD	<LOD	<LOD	1.63	1.50	1.77	2.17	*0.59*	<LOD	<LOD	<LOD
PCB 28	0.57	0.49	0.58	1.11	2.37	2.14	2.70	3.65	1.92	0.30	0.32	0.93
PCB 30	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB 31	1.00	0.89	0.92	1.63	3.76	3.41	4.85	6.59	2.12	0.45	0.53	1.16
PCB 32	1.51	1.21	0.93	1.55	5.24	4.86	6.14	7.16	1.58	*0.37*	*0.37*	0.98
PCB 38	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.69	*0.28*	<LOD	<LOD
PCB 44	4.51	1.58	1.30	1.55	3.50	3.06	3.60	4.33	2.18	0.62	0.70	1.20
PCB 49	1.96	0.67	0.65	0.87	2.37	2.06	3.05	4.41	1.34	0.26	0.32	0.67
PCB 52	3.93	1.50	1.27	1.62	3.85	3.50	4.77	6.48	2.03	0.64	0.73	1.28
PCB 53	2.20	0.66	0.49	0.65	2.22	2.05	2.83	3.47	0.93	0.45	0.39	0.64
PCB 61	*0.03*	*0.03*	*0.03*	*0.03*	*0.03*	*0.03*	*0.03*	*0.03*	0.27	0.08	*0.03*	*0.03*
PCB 62	0.008	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.05	0.02	*0.008*	*0.008*
PCB 65	<LOD	<LOD	<LOD	<LOD	*0.01*	*0.01*	*0.01*	*0.01*	0.06	*0.01*	*0.01*	<LOD
PCB 77	*0.38*	<LOD	*0.38*	<LOD	<LOD	<LOD	<LOD	<LOD	1.41	0.82	*0.38*	*0.38*
PCB 85	*0.16*	<LOD	<LOD	<LOD	*0.16*	*0.16*	*0.16*	<LOD	0.32	*0.16*	*0.16*	<LOD
PCB 99	0.20	*0.07*	*0.07*	*0.07*	*0.07*	*0.07*	*0.07*	*0.07*	0.28	*0.07*	*0.07*	*0.07*
PCB 101	0.36	*0.08*	*0.08*	*0.08*	0.21	0.16	0.21	0.25	0.41	*0.08*	*0.08*	*0.08*
PCB 105	*0.43*	<LOD	*0.43*	<LOD	<LOD	<LOD	<LOD	<LOD	*0.43*	*0.43*	*0.43*	*0.43*
PCB 110	0.72	*0.22*	*0.22*	*0.22*	*0.22*	*0.22*	*0.22*	*0.22*	0.61	*0.22*	*0.22*	*0.22*
PCB 116	0.26	*0.09*	*0.09*	*0.09*	*0.09*	*0.09*	*0.09*	*0.09*	0.32	*0.09*	*0.09*	*0.09*
PCB 118	*0.36*	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	*0.36*	*0.36*	*0.36*	*0.36*
PCB 128	*0.52*	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	*0.52*	*0.52*	*0.52*	<LOD
PCB 138	*0.51*	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	*0.51*	*0.51*	*0.51*	*0.51*
PCB 146	*0.36*	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.50	*0.36*	*0.36*	*0.36*	<LOD
PCB 149	*0.24*	<LOD	*0.24*	<LOD	*0.24*	*0.24*	*0.24*	1.59	*0.24*	1.07	*0.24*	*0.24*
PCB 153	*0.41*	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	*0.41*	*0.41*	*0.41*	*0.41*	<LOD
PCB 156	*0.48*	<LOD	*0.48*	<LOD	<LOD	<LOD	<LOD	<LOD	1.00	*0.48*	*0.48*	*0.48*
PCB 167	*0.47*	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	*0.47*	*0.47*	*0.47*	*0.47*
PCB 170	*0.58*	<LOD	*0.58*	<LOD	<LOD	<LOD	<LOD	<LOD	*0.58*	*0.58*	*0.58*	*0.58*
PCB 180	*0.53*	*0.53*	*0.53*	<LOD	<LOD	<LOD	<LOD	<LOD	*0.53*	*0.53*	*0.53*	*0.53*
PCB 183	*0.51*	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	*0.51*	*0.51*	*0.51*	*0.51*
PCB 187	*0.53*	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	*0.53*	*0.53*	*0.53*	*0.53*
PCB 189	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
PCB194	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
$\sum PCB_{53+bp}$	59.4	26.4	21.7	28.3	91.3	82.6	95.2	120.6	57.6	36.3	30.6	46.8
$\sum PCB_{53}$	56.4	23.7	20.4	26.0	91.0	82.1	94.9	119.8	43.1	21.6	19.0	27.6
$\sum PCB_{i+118}$	6.7	2.6	2.5	2.8	6.4	5.8	7.7	10.8	6.2	2.8	2.9	3.7
$\sum PCB_{top11}$	14.0	18.6	14.4	20.9	69.7	62.4	74.1	88.2	24.9	10.1	9.5	17.3

Table S8. Further PCBs that were identified in mine water based on specific masses [*m*/*z*], chlorine pattern, and peak area and height without available external standards. For rough estimation, assumed concentrations were estimated based on raw data that was corrected by the IS with nearest RT and by calibration curves of both sensitive and non-sensitive PCB congeners. The possible PCB number represents an educated guess based on a relative retention time [RT] comparison but is subject to uncertainty.

RT [min]	Chlorination degree	Possible PCB based on RT	Assumed concentrations [ng L^{-1}]
25.95	tri	25	0.04–4.36
26.81	tetra	45	0.19–3.22
27.02	tetra	46	0.04–0.48
27.57	tetra	47	0.09–2.43
28.53	tetra	42	0.27–4.52
28.62	tri	35	0.03–0.84
29.40	tetra	74	0.07–1.18
29.47	tetra	70	0.18–2.58
29.62	tetra	66	0.10–1.39

Figures S4–S11 provide the PCB congeners that were detected in the investigated MIW in comparison to congeners that are reported to occur in the technical Clophen mixtures A30 and A40, which are reported to have been used at the respective sites. This comparison does not aim at showing a perfect match between congener pattern in MIW and congener pattern in Clophen mixtures. Details and discussion on influencing factors such as e.g. solubility of congeners, adsorption, and molecule breakdown are given in the manuscript.

Nevertheless, this comparison gives a visually insight to both matches and discrepancies between PCB in MIW and Clophen mixtures. These data experimentally support the reported use of low-chlorine technical mixtures (such as Clophen A30 and A40), but also suggest the additional use of higher-chlorine technical mixtures in mines, as is most evident for the Stinnes mine (Figure S9).

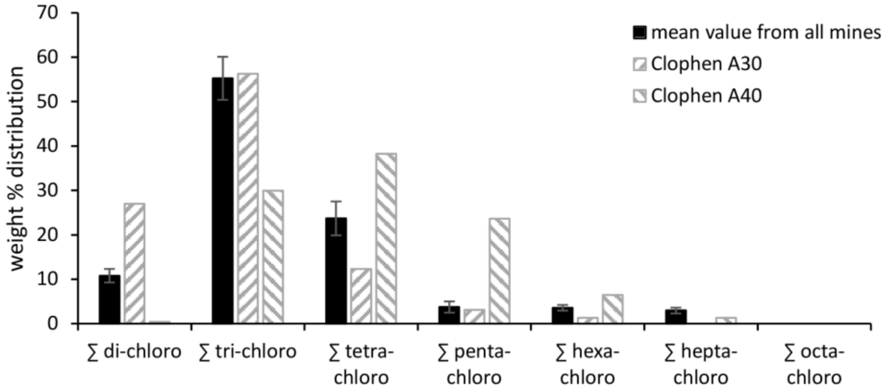

Figure S4. Comparison of homologue PCB congeners in discharged mine water from the present study with homologue congeners in Clophen A30 and Clophen A40.[4] For the provided mean value, mean values of the four sampling times (Walsum, Stinnes, Zollverein), and individual values (Reden, Camphausen) were used for calculation. Error bars show the standard deviation.

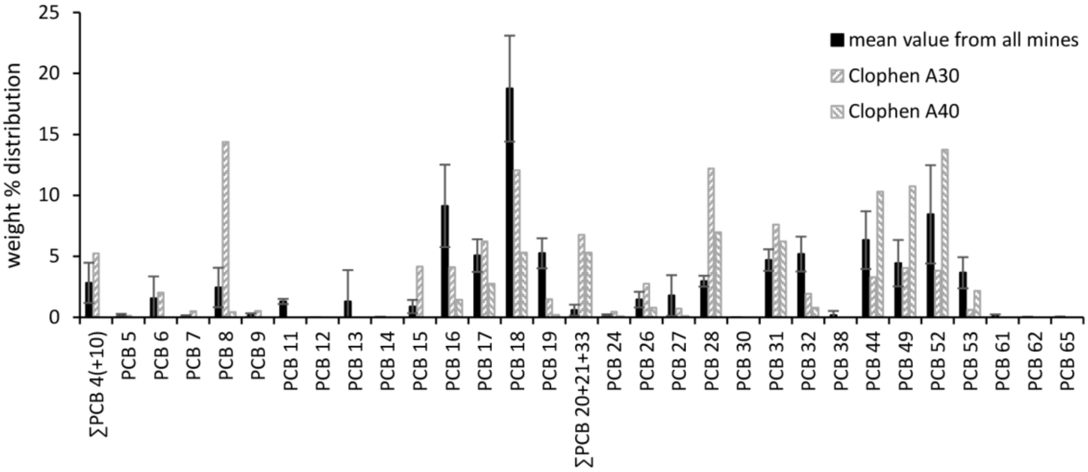

Figure S5. Comparison of PCB congeners in discharged mine water from the present study with congeners in Clophen A30 and Clophen A40.[4] Only congeners between PCB 4 and 65 are shown due to very low concentrations of higher chlorinated PCBs. For the provided mean value, mean values of the four sampling times (Walsum, Stinnes, Zollverein), and individual values (Reden, Camphausen) were used for calculation. Error bars show the standard deviation. Mine specific PCB profiles including congeners up to PCB 194 are provided in Figure S6–S11.

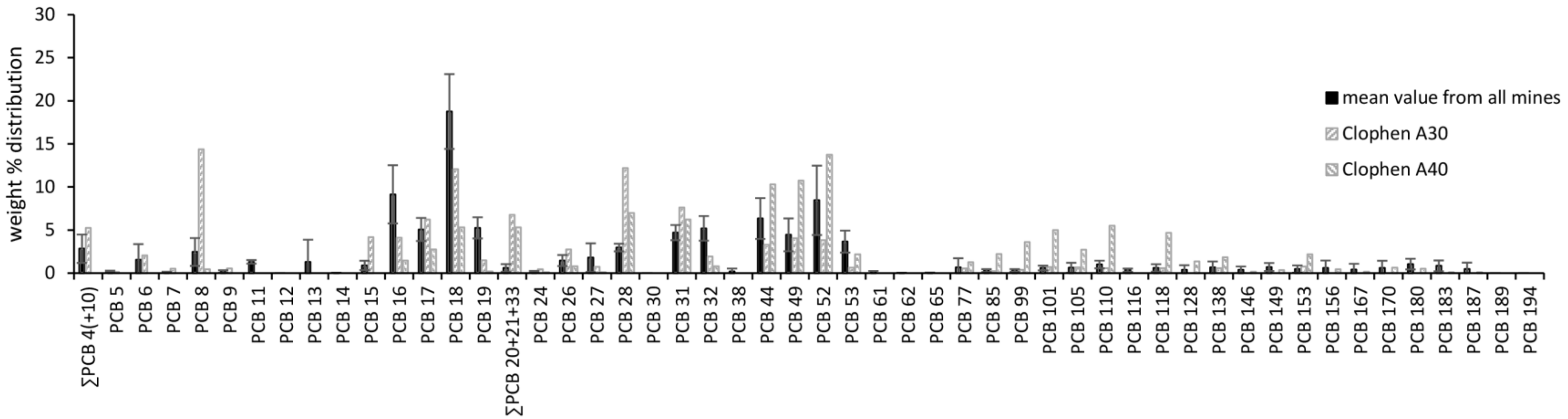

Figure S6. Comparison of PCB congeners in discharged mine water from the present study with congeners in Clophen A30 and Clophen A40.[4] For the provided mean value, mean values of the four sampling times (Walsum, Stinnes, Zollverein), and individual values (Reden, Camphausen) were used for calculation. Error bars show the standard deviation. This Figure corresponds to Figure S5 of the present study but includes additional PCB congeners detected.

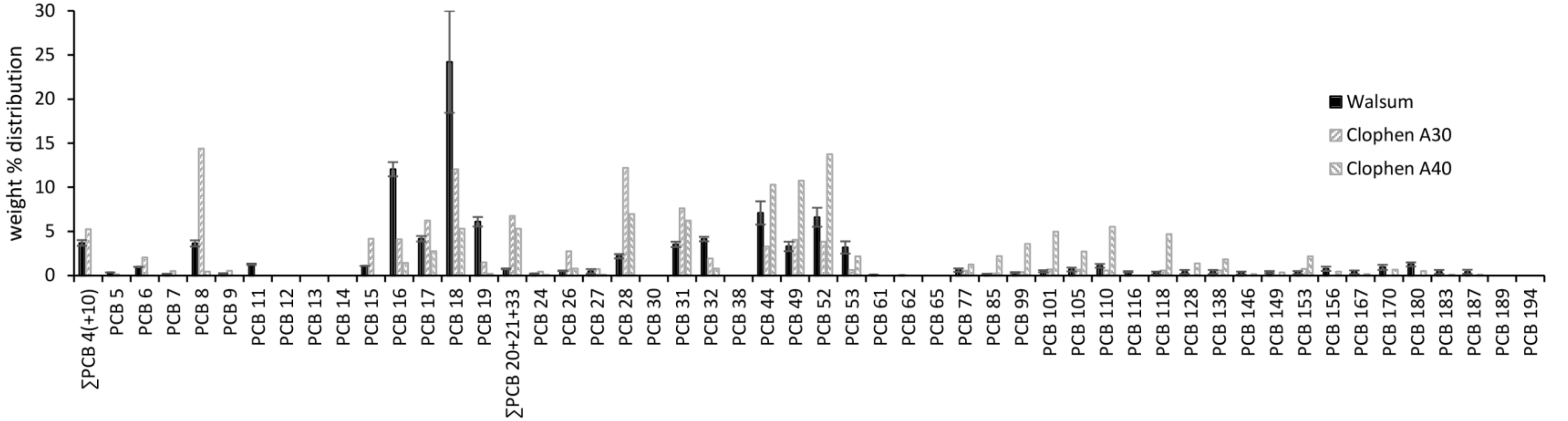

Figure S7. Comparison of PCB congeners in Walsum discharged mine water with congeners in Clophen A30 and Clophen A40.[4] Mean values of four sampling times are shown. Error bars show the standard deviation.

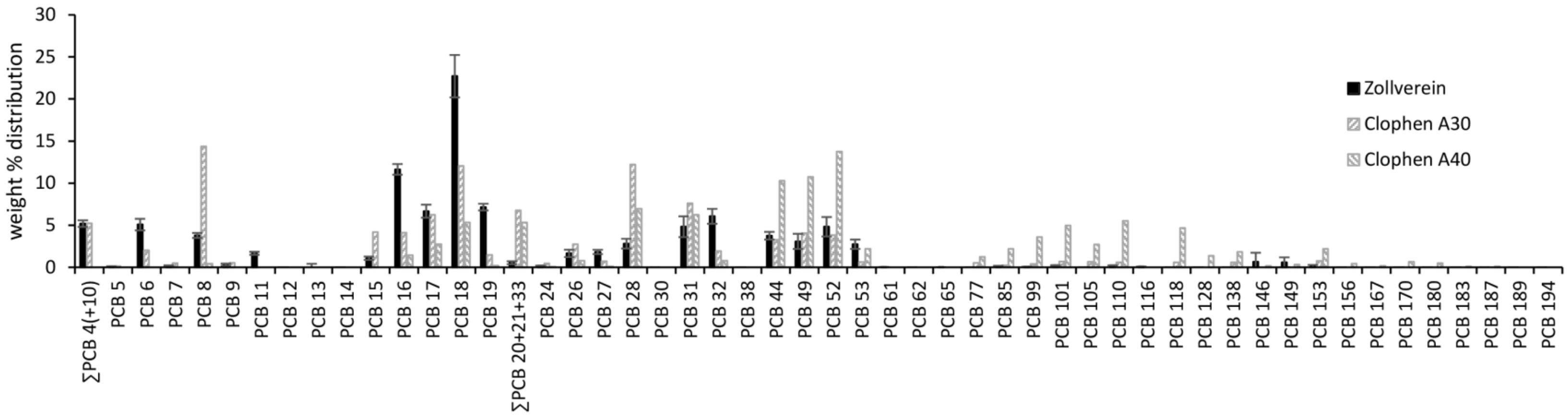

Figure S8. Comparison of PCB congeners in Zollverein discharged mine water with congeners in Clophen A30 and Clophen A40.[4] Mean values of four sampling times are shown. Error bars show the standard deviation.

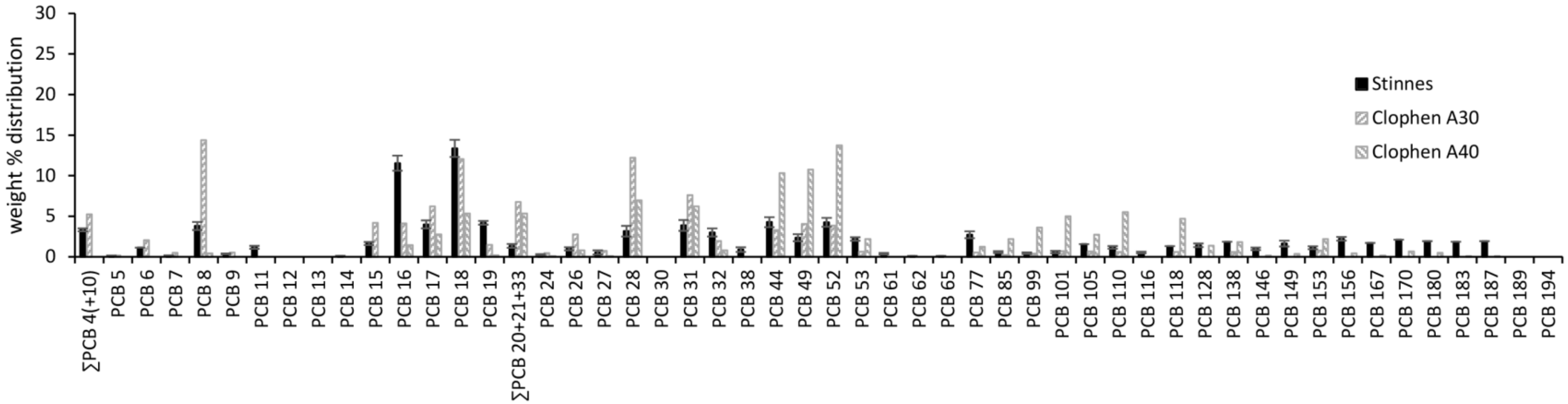

Figure S9. Comparison of PCB congeners in Stinnes discharged mine water with congeners in Clophen A30 and Clophen A40.[4] Mean values of four sampling times are shown. Error bars show the standard deviation.

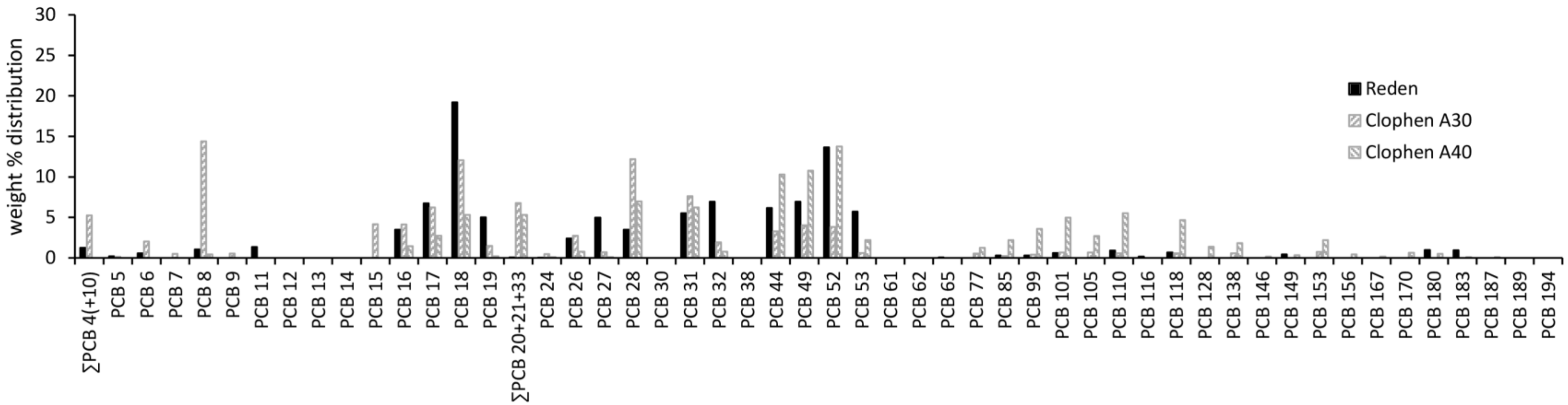

Figure S10. Comparison of PCB congeners in Reden discharged mine water with congeners in Clophen A30 and Clophen A40.[4]

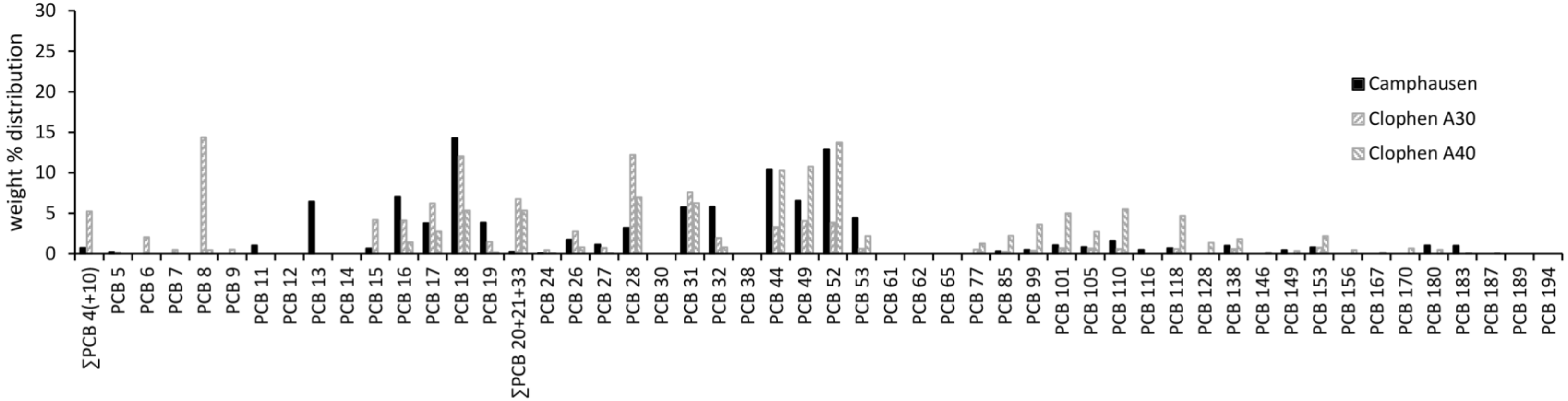

Figure S11. Comparison of PCB congeners in Camphausen discharged mine water with congeners in Clophen A30 and Clophen A40.[4]

Hierarchical clustering of the five mine water samples and the congener composition of Clophen A30 and A40.

Table S9. A *k*-means and hierarchical cluster analysis of the five mine water samples and the congener composition of Clophen A30 (CL30) and Clophen A40 (CL40) showed that they can be grouped into two clusters.

Congener Composition	Region	Cluster
Walsum	North Rhine-Westphalia	1
Zollverein	North Rhine-Westphalia	1
Stinnes	North Rhine-Westphalia	1
Reden	Saarland	2
Camphausen	Saarland	2
Clophen A30 (CL30)	–	1
Clophen A40 (CL40)	–	2

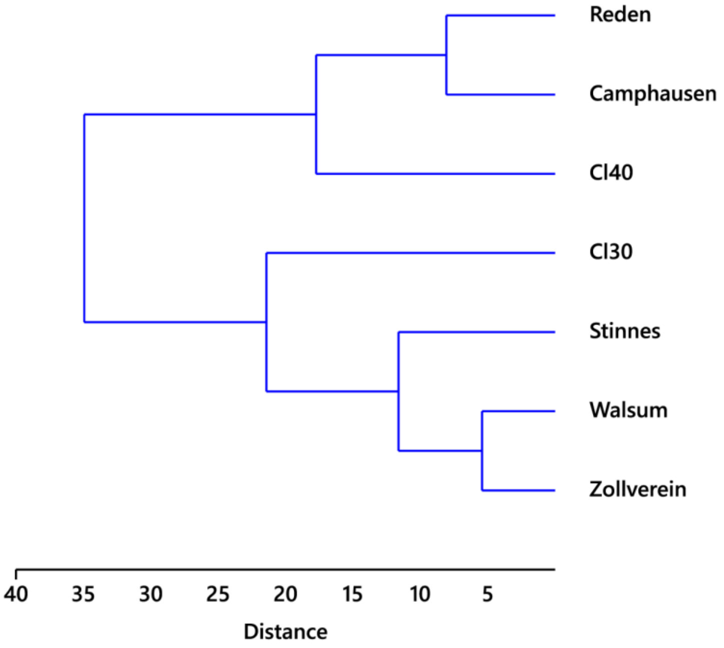

Figure S12. Hierarchical cluster using Ward's method. The five mine water samples and the two technical PCB mixtures can be divided into two clusters. One represents the Saarland mines (Reden, Camphausen), and the other the mines in North Rhine-Westphalia (Walsum, Zollverein, Stinnes). While the Saarland cluster indicates that the congener composition of Clophen A40 (Cl40) was used, the cluster in North Rhine-Westphalia is closer to Clophen A30 (Cl30).

Due to the small data set and possible degradation of PCBs to lower chlorinated PCBs, the statistical significance of these results needs to be determined with additional data in future studies.

References

(1) Bradt, P.; Mohler, F. L.; Dibeler, V. H. Mass spectrum of sulfur vapor. *J. Res. Natl. Bur. Stand.* **1956,** *57* (4), 223; DOI 10.6028/jres.057.027.

(2) Currie, L. A. Nomenclature in evaluation of analytical methods including detection and quantification capabilities (IUPAC Recommendations **1995**). *Pure Appl. Chem.***,** *67* (10), 1699–1723; DOI 10.1351/pac199567101699.

(3) Krupčík, J.; Májek, P.; Gorovenko, R.; Blaško, J.; Kubinec, R.; Sandra, P. Considerations on the determination of the limit of detection and the limit of quantification in one-dimensional and comprehensive two-dimensional gas chromatography. *J. Chromatogr. A* **2015,** *1396*, 117–130; DOI 10.1016/j.chroma.2015.03.084.

(4) 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; DOI 10.1021/es00065a015.

3 Hydrodechlorierung von Hexachlorbenzol und dessen Zwischenprodukten in einem miniaturisierten Nano-Pd(0)-Reaktionssystem

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Hydrodechlorination of hexachlorobenzene in a miniaturized nano-Pd(0) reaction system combined with the simultaneous extraction of all dechlorination products

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ABSTRACT

The persistent organic pollutant hexachlorobenzene (HCB) and all 11 further chlorobenzenes were hydrodechlorinated at environmentally relevant concentrations in miniaturized reaction systems, catalyzed by low concentrated Pd(0)-nanoparticles, to examine differences in dechlorination rates and pathways. Using solid-phase microextraction coupled to gas chromatography-mass spectrometry allowed the simultaneous extraction and detection of reactants, intermediate products and fully dechlorinated benzene, regardless of their different physicochemical properties. Dechlorination of HCB with formation of intermediates mainly proceeded via pentachlorobenzene, 1,2,3,4-tetrachlorobenzene, 1,2,3-trichlorobenzene, 1,2-dichlorobenzene, and monochlorobenzene to benzene. Specific catalytic activities of Pd(0)-nanoparticles (100–3400 $L\,g^{-1}\,min^{-1}$) differed depending on chlorination degree of chlorobenzenes and position of chlorine atoms. An inductive effect is assumed to favor a removal of the vicinal chlorine atom. The presented method permits the facile determination and comparison of nanomaterials' specific catalytic activities and allows the elucidation of dehalogenation pathways. It further enables to specifically examine formed intermediates to assess their toxicity and biodegradability.

1. Introduction

Persistent organic pollutants (POPs) are characterized by long lifetimes in the environment, possible long-range transport, a high potential for bioaccumulation and often also a negative impact on human health and the environment [1]. Hexachlorobenzene (HCB) belongs to this group of POPs and is part of the 'dirty dozen', initially 12 substances or substance groups that are globally banned by the 2001 Stockholm Convention on POPs of the United Nations Environment Program (UNEP) [2]. Furthermore, it is classified as persistent, bioaccumulative and toxic (PBT) substance according to the European Union's chemicals legislation and is suspected of being carcinogenic and teratogenic. It was used mainly as a fungicide or as disinfectant in agriculture, but also as a wood preservative. Due to its persistency and despite the global ban, HCB is still ubiquitous in the environment and consequently accumulates in food webs [3]. In the environment, HCB can be degraded by photolysis and chemical reactions with radicals [4], therefore methods based on irradiation for the degradation of chlorobenzenes are constantly further developed [5,6]. Microbial degradation of HCB in soils and sediments mainly occurs under anaerobic conditions, whereas less chlorinated compounds can be degraded also by oxidation [7]. The pathways for microbial and photolytic dechlorination are very similar. However, these degradation mechanisms occur in nature only to a limited extend, because chemical reduction can require high energy input and biodegradation is not efficient enough. The high catalytic activities of Pd nanoparticles indicate an enormous intrinsic potential for the transformation of contaminants [8]. Supported by their large specific surface area, catalytically active metal nanoparticles can be used to efficiently dechlorinate HCB and further halogenated organic

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pollutants even under moderate conditions [9–11]. In these reactions, metal nanoparticles catalyze the formation of activated hydrogen, which is able to perform the substitution of halogen atoms in the POP molecule [12], while hydrochloric acid (HCl) in case of dechlorination reactions is released. The presence of dissociated HX in higher concentrations in the near vicinity of Pd can lead to self-poisoning of the catalyst material. Sufficient amounts of aqueous solution or even addition of buffers offer a gradient for HX withdrawal from the active centers [9]. Furthermore, Pd (0) nanoparticles are sensitive to poisoning by matrix constituents (e.g., salts). A further disadvantage is that suitable separation and recycling processes still have to be developed [13]. Although the intrinsic activity of nanoparticles is mostly comparable to supported catalysts, the minimized mass transfer in aqueous media when using nanoparticles is beneficial. Catalysis promoted by Pd is seen as one of the most promising strategies to efficiently remove reducible contaminants in water treatment approaches [14]. Highest reaction rates are reached when using nanosized catalyst particles [9,15]. When applying nanosized catalysts, a suitable suspending agent is needed in order to prevent agglomeration of the particles, and an appropriate source of hydrogen. Hydrodehalogenation of higher halogenated substances using Pd catalysts can generally lead to fully dehalogenated products. However, it seems that a direct pathway, but also a successive stepwise dehalogenation pathway exist in parallel. If dehalogenation is not complete, less halogenated intermediate products can remain. Generally, they are recognized as less dangerous in the environment compared to the higher halogenated substances, especially due to an easier microbial transformation, a lower bioaccumulation potential and an often reduced toxicity [13]. However, specific transformation products can be formed that are more toxic compared to others or the parent compound itself. This is most obvious for the dechlorination of dioxins where formation of the highly toxic congener 2,3,7,8-tetrachlorodibenzo-*p*-dioxin has to be avoided [16]. Another example of highly undesired intermediates of a stepwise dechlorination is the formation of vinylchloride from polychlorinated ethenes [17]. For the group of chlorobenzenes, toxicity also varies between its representatives. Therefore, it is most helpful to know dehalogenation pathways in full detail. However, the analytical monitoring of intermediate steps within the dehalogenation process can be very laborious due to the highly varying characteristics of reactant, intermediate products, reaction rates and the final dehalogenation product. This can require the combination of various extraction methods, such as headspace extraction for (highly) volatile substances and solvent extraction with filtration and concentration of solvent extracts. With solid-phase microextraction (SPME), a technique is available that can facilitate the extraction of substances with varying physicochemical properties, usually when using multiple extraction phases. SPME is a solventless, miniaturized, equilibrium based, and mostly non-exhaustive extraction method, which is built on the partitioning of analytes between the sample and a polymer-coated quartz fiber that is introduced directly to the sample (immersed SPME) or to the headspace above the sample (HS-SPME) [18–21]. Depending on the type of commercially available fibers, different coating materials exist that provide targeted selectivity for matrix separation and the extraction of analytes. Using an appropriately equipped autosampler, samples can be extracted consecutively by the same fiber in an ‘agitator’, a device which can be programmed to specific stirring speed and extraction temperatures. After extraction, the fiber is transferred to the injection system of the gas chromatography-mass spectrometry (GC-MS) instrument, where the thermal desorption of analytes is performed before regular GC-MS analysis. Potential carry-over of analytes by the fiber between samples can be avoided when a conditioning station is used in which the fiber is additionally heated between sampling events. Quantification can be easily performed with external standard calibration and internal standards. Besides saving solvents, the use of SPME can significantly reduce labor time and allow extractions specific to individual research questions. However, method development can be extensive, because several parameters such as type of fiber coatings, extraction time, extraction temperature, stirring speed, and conditioning of the fiber have to be investigated [19–22]. For HCB and its transformation products as environmentally relevant target analytes an efficient monitoring in reaction approaches and natural matrices is necessary. Therefore, the aims of this study were (i) to establish a SPME method for the simultaneous extraction of HCB and all dechlorination products directly from a miniaturized reaction system, (ii) to elucidate the dechlorination pathways by tracking intermediate products and examining their dechlorination behavior, and (iii) to determine the specific catalytic activity of Pd(0) nanoparticles for the dechlorination of HCB and its transformation products. Hence, a SPME method was established for the examination of HCB dechlorination in the presence of low concentrations of Pd(0) nanoparticles in aqueous solution under anoxic conditions in a miniaturized reaction system with hydrogen as reducing agent. Furthermore, the intermediate steps of the dechlorination of HCB to benzene were investigated. HCB and all possible intermediates were used as individual reactants.

2. Materials and methods

2.1. Chemicals and catalysts

Molecular structures and physicochemical properties of the test substances HCB, pentachlorobenzene (PeCB), tetrachlorobenzene (TeCB) isomers (1,2,3,4-TeCB, 1,2,3,5-TeCB, and 1,2,4,5-TeCB), trichlorobenzene (TCB) isomers (1,2,3-TCB, 1,2,4-TCB, and 1,3,5-TCB), dichlorobenzene (DCB) isomers (1,2-DCB, 1,3-DCB, and 1,4-DCB), monochlorobenzene (MCB), and benzene (B) are summarized in Table S1 in the supporting information. All analytes were purchased as neat substances from Dr. Ehrenstorfer GmbH (Augsburg, Germany) (purities ≥ 98.0%), prepared as stock solutions of single substances in methanol ($123–1032\,mg\,L^{-1}$), and mixed to concentrations of 0.05, 0.5, and $5\,mg\,L^{-1}$ of each substance in methanol (methanol purity ≥ 99.9%, p.a. quality, Carl Roth GmbH, Karlsruhe, Germany) yielding working solutions for calibration. Stock solutions of single substances were diluted in methanol to concentrations of $10\,mg\,L^{-1}$ yielding working solutions for dechlorination experiments. Stock solutions in methanol were stored in screw top vials with Mininert valves (CZT analytical equipment, Kriftel, Germany), working solutions ($10\,mg\,L^{-1}$) were stored in Certan capillary bottles (LGC Standards GmbH, Wesel, Germany). For the internal standard mix, benzene-d_6 ($2000\,\mu g\,mL^{-1}$ in methanol, Dr. Ehrenstorfer) was combined with a mixture of ^{13}C labeled mono- to hexachlorobenzenes (mono-to-hexachlorobenzene solution [$^{13}C_6$, 99%] $500\,\mu g\,L^{-1}$ in toluene, CIL brand purchased from LGC Standards, Wesel, Germany) and diluted in methanol ($5\,mg\,L^{-1}$).

An aqueous working solution for dechlorination experiments was prepared with $9\,g\,L^{-1}$ $NaHCO_3$ for pH stabilization (purity ≥ 99.5%, p.a. quality, Carl Roth GmbH, Karlsruhe, Germany) [23] and $2.94\,g\,L^{-1}$ tri-sodium citrate dihydrate for nanoparticle stabilization (purity ≥ 99.0%, p.a. quality, Carl Roth GmbH, Karlsruhe, Germany) in a 1000-mL volumetric flask filled up with water [9].

The Pd nanoparticles utilized in dechlorination experiments were obtained by chemical reduction of the tetrachloropalladate complex with sodium borohydride as reducing agent [24]. Particles were suspended in an aqueous solution ($60\,mg\,L^{-1}$) containing citrate for stabilization purpose. The final colloid suspension contained finely dispersed spherical Pd nanoparticles with an average size of 3.9 nm (d50; transmission electron microscopy, TEM) and was electrostatically stabilized in a pH range of 8–9 (Figure S1). Immediately before the start of the experiment, the suspension was transferred via air cushion pipette into 20-mL vials and gassed with hydrogen for 30 min for the activation of the catalyst material [9].

A solution of sodium sulfite (Na_2SO_3) (purity ≥ 98.0%, p.a. quality, Carl Roth, Karlsruhe, Germany) was produced in a concentration of $60\,g\,L^{-1}$ in water, ensuring a 5-fold stoichiometric excess when added to end dechlorination reactions by catalyst poisoning.

All water used within the study was of ultrapure quality (Milli-Q Advantage A10 System, Millipore).

2.2. Preparation and design of experiments

The stabilization solution and nano-Pd suspension were flushed with hydrogen for 30 min. The containers were hermetically sealed by membranes (silicone/PTFE). The pure hydrogen was introduced with a sterile disposable needle (Sterican, Braun Melsungen AG, Melsungen, Germany). In order to prevent a potential contamination with particles or oil residues from the gas supply line, a syringe filter (Filtropur S 0.2, Sarstedt, Nümbrecht, Germany) was placed in line. Another sterile needle ensured that the previously contained air composition could escape. The resulting holes served later as a puncture site for the microliter glass syringe.

Dechlorination experiments described below were performed in an anaerobic chamber (glovebox, Mecaplex, Grenchen, Switzerland) with N_2/CO_2 atmosphere (ratio 80:20, 'Foodpack 3', Praxair, Germany), to provide anoxic conditions for reductive dechlorination experiments.

9.95 mL of the $NaHCO_3$ solution and 50 μL nano-Pd suspension were filled in 20-mL amber glass vials yielding an experimental concentration of 300 μg Pd L^{-1}. Vials were sealed with magnetic screw caps with PTFE septa for use with the autosampler (CS-Chromatographie Service GmbH, Langerwehe, Germany). Using a syringe, 1 mL of the gas phase was withdrawn and replaced with 1 mL hydrogen to provide a concentration of 10% hydrogen (v/v) in the N_2/CO_2 atmosphere of the samples. Through the remaining hole, the samples were each spiked with 3 μL HCB solution (or 3 μL of PeCB, 1,2,3,5-TeCB, 1,2,4,5-TeCB, 1,2,3,4-TeCB, 1,3,5-TCB, 1,2,4-TCB, 1,2,3-TCB; or 6 μL of 1,4-DCB, 1,3-DCB, 1,2-DCB, MCB solution, each 10 mg L^{-1}). An automated glass microliter syringe (eVol® Dispensing System, Thermo Fisher Scientific) was used for spiking to achieve a final concentration of 3 μg L^{-1} (or 6 μg L^{-1}) for the above listed reactants. After HCB was added to the Pd suspension, the system was shaken continuously at 300 rpm on a horizontal shaker (VWR International) throughout the reaction ensuring sufficient contact and distribution of reactants, nanocatalysts and hydrogen. All reactions were performed at room temperature (22 ± 1 °C). The dechlorination reaction was stopped after 1, 3, 6, 12, 30, and 60 min by adding 10 μL of a 60 g L^{-1} Na_2SO_3 solution as catalyst poison to the sample. Subsequently, 2 μL of internal standard solution was injected through the septa and the syringe holes in the caps were sealed with superglue (Ultra Gel, Pattex, Henkel, Düsseldorf, Germany). Samples were prepared in four replicates for each of the 6 reaction times.

Calibration samples were prepared in Pd solution to avoid matrix differences between calibration samples and dechlorination samples. Calibration samples were prepared in duplicates for a 7-point calibration of benzene and chlorobenzenes (0.01–3 μg L^{-1}). Reference samples (dechlorination time $t = 0$ min) were prepared with four replicates. In order to prevent dechlorination in calibration and reference samples, Na_2SO_3 was added to the Pd suspension before it was spiked with analytes (calibration or rather reactant solutions) and internal standards. All other steps were kept constant to the procedure described above. Additionally, duplicate blank samples were measured for the various media used (vials with 10 mL water, with 10 mL $NaHCO_3$ solution containing 10 μL Na_2SO_3, and with 9.95 mL $NaHCO_3$ solution containing 50 μL nano-Pd suspension and 10 μL Na_2SO_3). After the experiments, the samples were exported from the glovebox just before the measurement.

2.3. Instrumental analysis

Method development of the combined SPME-GC-MS method included optimization of SPME extraction based on previous work by Böhm et al. [21,22], i.e. the parameters fiber coating, extraction temperature, extraction time, thermodesorption temperature, as well as fiber cleaning time and temperature were modified with regard to the different physicochemical properties of benzene and the 12 chlorobenzenes. Simultaneous extraction of benzene and all chlorobenzenes was tested with five different fiber coatings or fiber types (Supelco, Sigma-Aldrich): 100 μm polydimethylsiloxane (PDMS); 65 μm mixed phase of divinylbenzene and PDMS (DVB/PDMS) as both StableFlex and fused silica fiber; 85 μm polyacrylate (PA); and 50/30 μm mixed phase of DVB, Carboxen and PDMS (DVB/CAR/PDMS). The GC method was optimized for a 60 m column with regard to a baseline separation of the two isomers 1,2,3,5-TeCB and 1,2,4,5-TeCB, which are often given as sum parameter in literature due to their similar chromatographic retention [25,26]. The following procedure gives the optimized conditions: Samples were extracted by automated HS-SPME on a CombiPAL autosampler (CTC-Analytics, Zwingen, Switzerland) equipped with a combined heating/shaking device ('agitator') and a separate fiber desorption oven ('needle heater') for the cleaning of SPME fibers between sampling events. Extraction was performed with a 65 μm fused silica fiber with DVB/PDMS coating (Supelco/Sigma-Aldrich 57345-U) for 20 min at 40 °C while shaking the sample at 250 rpm in the agitator. Prior to extraction, samples were left in the agitator for 5 min at 250 rpm to allow for an adaption to the extraction temperature by shaking and heating of the sample. After extraction, the fiber was directly transferred to the injector of the GC-MS system, where it was thermally desorbed for 3 min at 210 °C using a 1 mm SPME liner (Straight Inlet Liner, Restek, Bad Homburg, Germany) in splitless mode. Detailed parameters for GC–MS conditions as well as further procedures for quality assurance and quality control are given in Tables S2 and S3.

2.4. Data analysis

Raw data from GC–MS were processed with the software 'Xcalibur' (Thermo Fisher Scientific) combined with a manual verification of peak integration. Data for all analytes were corrected based on internal standards. The three isomers of DCB, TCB, and TeCB were corrected with one internal standard per degree of chlorination (Table S3). Quantification was performed by calibration with external standards. The four replicates per preset dechlorination time are given as mean value. Standard deviation of the mean value was calculated as the square root of the residual sum of squares divided by n with n as the number of replicates.

2.5. Calculation of specific Pd activity for catalytic hydrodechlorination

Empiric basis shows that the catalytic hydrodehalogenation of organic halogen compounds follows 'pseudo first-order' kinetics with respect to reactants. The specific Pd activity of the nanocatalyst in a dechlorination experiment with the substance 'i' ($A_{Pd,i}$) was calculated using the following equation [27]:

$$A_{Pd,i}\,[L\,g^{-1}\,min^{-1}] = \frac{V_{water}}{m_{Pd} \bullet \tau_{1/2}} = \frac{\ln\left(\frac{c_{t0,i}}{c_{tx,i}}\right)}{\ln 2 \bullet c_{Pd} \bullet (t_x - t_0)} \tag{1}$$

giving the water volume (V_{water} in [L]) contaminated with the substance '*i*' in a given concentration $c_{t0,i}$, which can be treated with the mass of catalyst applied (m_{Pd} in [g]) yielding a half-life of the reactant ($\tau_{1/2}$ in [min]); or rather with the concentration of the reactant ($c_{t0,i}$) and ($c_{tx,i}$) at the chosen start time (t_0) and end time (t_x) (where x is the specific time of catalyst poisoning, 1–60 min) of the dechlorination experiment, and the concentration of the catalyst applied (c_{Pd}). For reaching a given elimination goal, $A_{Pd,i}$ therewith allows to calculate how much Pd would be necessary to treat a certain volume of water in a certain time frame [13].

3. Results and discussion

3.1. Simultaneous extraction of analytes by SPME

The SPME fibers tested for the simultaneous extraction of HCB and all possible dechlorination products widely differed in their sensitivity depending on the physicochemical characteristics of the analytes. For the most commonly used SPME fiber (PDMS 100 µm), the amount of extracted benzene was not sufficient. This was the same for the 85 µm PA fiber, which is often used for more polar compounds. The DVB/CAR/PDMS fiber was very promising because the CAR phase led to a very sensitive extraction of benzene, MCB and DCBs. However, thermal desorption from the fiber was not sufficient for the higher chlorinated benzenes. This caused a carry-over effect that could not be eliminated by an increase in thermodesorption temperature or increased cleaning time in the needle heater. The amount of extracted benzene was much lower for the DVB/PDMS fiber, but was sufficient for a valid detection at low benzene concentrations (linear calibration curve down to 0.01 µg L^{-1}). Choosing a thermodesorption temperature (210 °C) significantly lower than the maximum operating temperature given by the manufacturer (270 °C) was crucial, since higher temperatures led to a slow but noticeable degradation of the DVB phase resulting in interferences with the detection of benzene. These interferences could be avoided at 210 °C, while ensuring sufficient thermal desorption of HCB.

Simultaneous extraction of HCB and all possible dechlorination products made it possible to follow the dechlorination reaction in terms of reactant reduction, appearance and disappearance of intermediate products, and formation of the final product benzene as a function of time and nanoparticle concentration. Therefore, dechlorination pathways could be derived.

3.2. Dechlorination of chlorobenzenes by Pd nanocatalysts

Hydrodechlorination of HCB and all further chlorobenzenes, as well as the formation of intermediate products and benzene as the fully dechlorinated product, was followed over time (Fig. 1). The individual intermediates of the dechlorination of HCB are shown in Fig. 2 including the differentiation between isomers formed. For all dechlorination experiments, the rate constant *k* value of pseudo first order kinetics for the disappearance of the reactant was calculated (Figure S2). Fig. 1 shows that the elimination of chlorobenzenes normally increases with decreasing chlorination degree. Nonetheless, intermediate products were detected, as Fig. 2 illustrates in more detail for HCB as parent compound. Slower abreaction of lower chlorinated intermediates that were expected to react more quickly than the higher chlorinated species is not fully understood and needs explanation. Fig. 1 also shows that in some cases benzene formation curves indicate a lag phase in the beginning, as for HCB itself, 1,2,4,5-TeCB and 1,2,4-TCB. In these cases, also the further reduction of intermediates seems slightly inhibited. Stepwise reduction of chlorobenzenes seems dominant while direct dechlorination to benzene or other less chlorinated chlorobenzenes in a single step, without detachment from the catalyst, cannot be ruled out as parallel reaction. However, the product pattern found during dechlorination suggests also preferred reaction pathways. Since benzene formation occurs for most reactants immediately after the reaction start, not only the consecutive pathway can be assumed, but in addition a multiplet mechanism as assumed by other studies [28–30]. For the dechlorination of POPs, electron transfer mode [31] and hydrogen transfer mode [32] are seen as the main dechlorination mechanisms. The latter mechanism is assumed to dominate in our experiments because Pd(0)-generated activated hydrogen is present in the system and consequently activated hydrogen is added electrophilically to the aromatic ring [33]. For adsorbed polychloroaromatic compounds, the interaction between the lone electron pairs of the chlorine atom and the π-cloud of the aromatic ring is discussed in such a way that the C−Cl bond reaches the character of a double bond [29] leading to the elimination of several chlorine atoms without desorption of the chloroaromatic substrate from the catalyst surface. The catalytic hydrodechlorination is accelerated by the electron-withdrawing substituents stabilizing this formal C=Cl double bond by withdrawing the electron density of the aromatic ring [30]. The C=Cl bond becomes more pronounced the more chlorine atoms are present in the ring. The electrons of chlorine and the aromatic ring are partially withdrawn from d-orbitals of the transition metal (Pd). This is assumed to cause additional stabilization, allowing the formation of two C=Cl bonds and the removal of two chlorine atoms without desorption of the chlorinated benzene from the catalyst surface [28]. It is unclear why in the HCB reaction the intermediates are existent for a longer time, whereas e.g. in the PeCB reaction, the dechlorination rate of the formed intermediates is higher. This may indicate that the catalyst is affected by HCB in a different way than in the presence of PeCB. It is possible that HCB is strongly stabilized in its adsorption so that competitors cannot replace it until most of the HCB is dechlorinated. Furthermore, faster reacting compounds such as DCBs should not or only minimally emerge in these experiments. If the intermediates remain adsorbed on the catalyst surface during dechlorination [28], and the C−Cl bonds are split one after the other, the intermediates only appear when the system is disturbed and therefore are able to desorb (e.g., by Na_2SO_3 as catalyst poison that reduces H_2 uptake of the catalyst and also modifies the catalyst surface by formation of PdS). Because number and positions of chlorine substituents and therewith electronic effects vary, chlorobenzenes can differ in their adsorption/desorption behavior on the catalyst surface, which could influence the amount of detected analytes and therewith interpretation of dechlorination pathways. However, these differences are taken into account by the use of internal standards, which allow the correction for influences of sorption on the amount of detected analytes. Although, based on the internal standards used, small deviations could occur for the isomers with the same chlorination degree, these differences are seen to be negligible [21]. Based on the experiments with the less chlorinated benzenes introduced as starting material, it was possible to identify the quantitatively most abundant intermediates formed in the individual dechlorination reactions. For the dechlorination of HCB to benzene, the intermediate products PeCB and mainly the isomers 1,2,3,4-TeCB, 1,2,3-TCB, and 1,2-DCB were detected, suggesting an attack of activated hydrogen on the vicinal chlorine atoms. When these intermediates were introduced as starting reactant, the same pattern was obtained. In addition, MCB could be detected as the last intermediate product of full dechlorination. Comparative dechlorination of all TeCB, TCB, and DCB isomers revealed that the most abundant isomers are those with the highest dechlorination rates as individuals. Instead of a relative enrichment of the non-vicinal chlorinated isomers which are slower dechlorinated, lower concentrations of these substances as intermediates were found. Consequently, this indicates that the vicinal chlorinated intermediates are representative for a vicinal dechlorination pathway. Based on these dechlorination experiments, the main gradational reaction pathways for the dechlorination of HCB using Pd(0) nanoparticles are proposed, of which the progressive vicinal substitution of Cl is the dominating hydrodechlorination route (Fig. 3).

This represents a fundamentally different reaction pathway than has been demonstrated in photolytic dechlorination (radical attack) [6] or microbiological dechlorination (reductive dechlorination) [7,34], where 1,2,3,4-TeCB, 1,2,3-TCB and 1,2-DCB were not formed at all or only in very small quantities. However, this is not unexpected, since these are different mechanisms that bring different reaction patterns. In addition, considering the Gibbs free energy values for the reductive dechlorination of chlorobenzenes, 1,2,3,4-TeCB, 1,2,3-TCB, and 1,2-DCB are the energetically unfavorable intermediate products [35], but these isomers are found as the relevant intermediate products within the present study. Surprisingly, the consecutive mechanism part of hydrodechlorination by Pd(0) is identical to the mechanochemical dechlorination by Mg/Al_2O_3 [36]. Non-hydrogenation active metals are another system with a different mechanism (single electron transfer), which makes it difficult to accomplish the aromatics dependent two-electron transition. Nevertheless, the mechanochemical reaction takes place, possibly due to the increased energy input in mechanochemical reactions [37].

Based on a statistical distribution of randomly attacked chlorine atoms, the formation of specific TeCB, TCB and DCB isomers is more

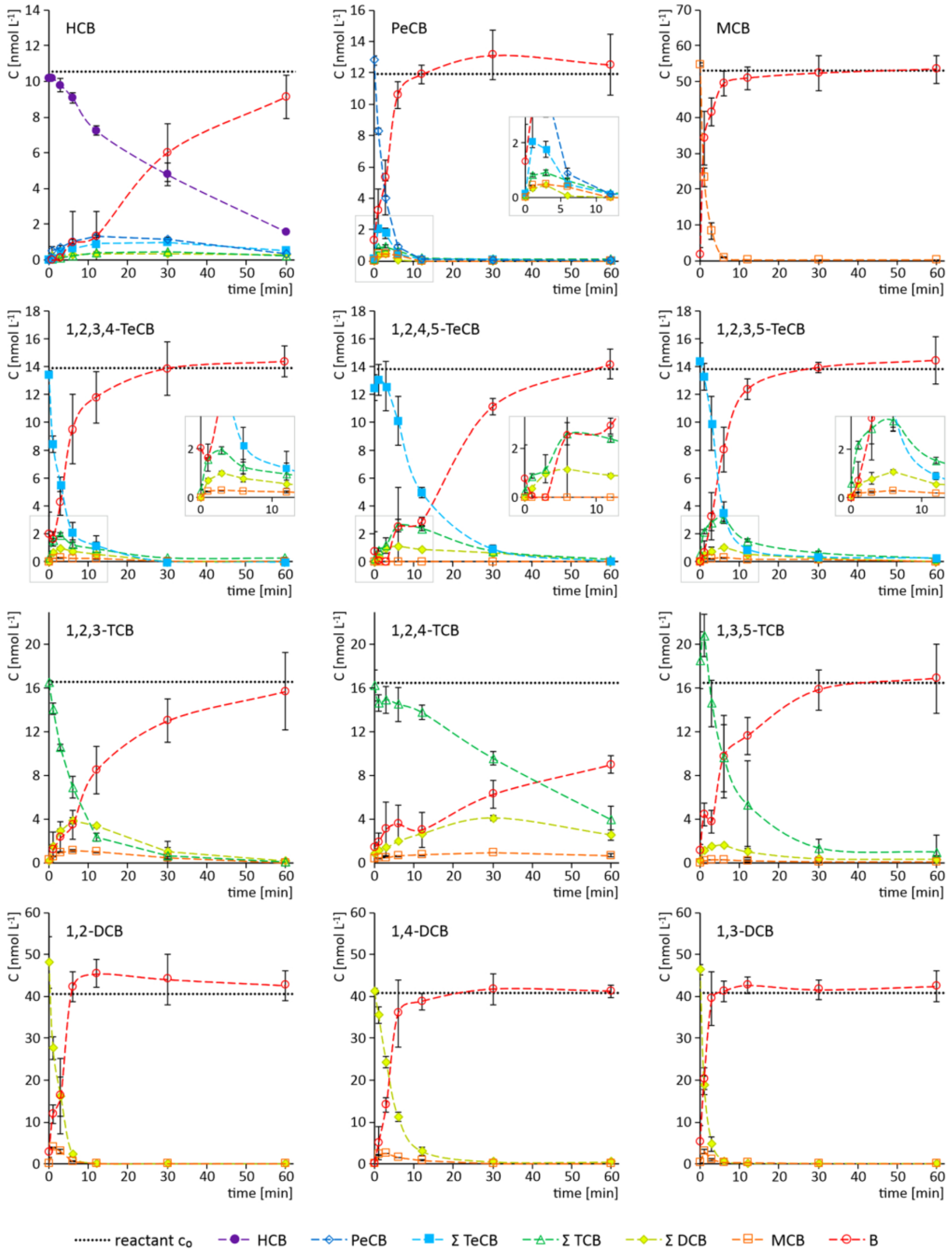

Fig. 1. Dechlorination of all chlorobenzenes used as reactants. Occurring intermediates with the same degree of chlorination are given as the sum of isomers for the sake of clarity. n = 4 replicates per time step ($c_{0,CBs}$ = 3 or 6 µg L^{-1}, c_{Pd} = 300 µg L^{-1} with d50 = 3.9 nm, c_{NaHCO3} = 9 g L^{-1}, $c_{Na\text{-}citrate}$ = 2.94 g L^{-1}).

likely. For example, assuming a dechlorination of PeCB by chance, the formation of 1,2,4,5-TeCB is less probable (20%) since specifically the 3-chloro position of PeCB has to be substituted by hydrogen, whereas the formation of the two further TeCB isomers is equally likely (40% each) because a substitution of the 1-chloro and 5-chloro or rather of the 2-chloro and the 4-chloro positions yield identical molecules, respectively. Similar differences exist as well for the formation of TCB and DCB isomers. However, actual occurrence and concentrations of isomers do not match a dechlorination by chance. Instead, the formation is interpreted with regard to energetically beneficial reactions. It is claimed that the transition states of PeCB, where the negative charge is on the carbon atom attached to the hydrogen atom, are the most stable resonance structures that appear in different positions relative to the hydrogen atom during the formation of the formal C═Cl bond [28]. In all other structures, the negative charge is located at the carbon atom bound to the negatively charged chlorine atom. Therefore, the formation of 1,2,3,5-TeCB, 1,3,5-TCB, and 1,3-DCB should be unlikely. This partially contradicts the data presented in the present study, where the

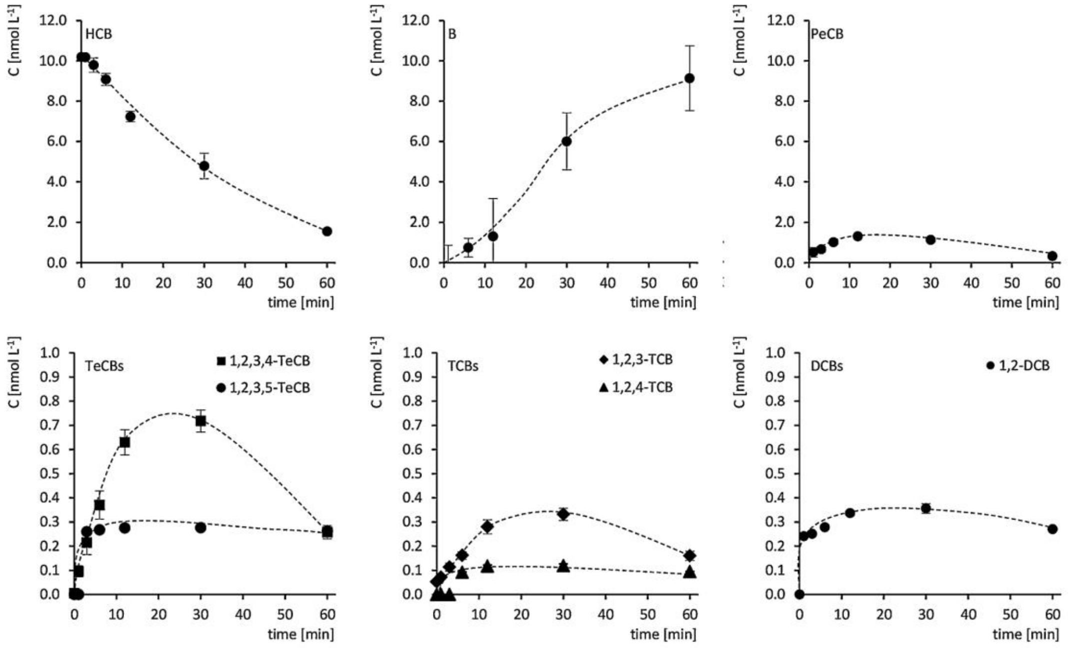

Fig. 2. Dechlorination of HCB and the formation of intermediate products and benzene over time. MCB was not detected. Error bars show sd, n = 4 per time step ($c_{0,CBs} = 3$ or $6\,\mu g\,L^{-1}$, $c_{Pd} = 300\,\mu g\,L^{-1}$ with d50 = 3.9 nm, $c_{NaHCO3} = 9\,g\,L^{-1}$, $c_{Na\text{-}citrate} = 2.94\,g\,L^{-1}$). The dotted lines are added to guide the eye.

formation of 1,2,3,5-TeCB was more comprehensive than the formation of 1,2,4,5-TeCB. One reason for this could be the addition of a catalyst poison to terminate dechlorination reactions that could influence the transition state at the decisive moment. However, other factors may also control the formation of specific intermediates, such as unfavorable steric conditions and their partial charges. They could serve as a 'shielding wall', promoting an inductive effect, which protects against dechlorination attacks. The partial charges can further explain the slower dechlorination of HCB compared to the less chlorinated benzenes (Fig. 1), and the different formation of TeCBs with the preference for 1,2,3,4-TeCB, a minor proportion of 1,2,3,5-TeCB, and a negligible formation of 1,2,4,5-TeCB. Since a chlorine atom is already substituted by hydrogen as in PeCB, the vicinal chlorine atom is next to be replaced due to a lower inductive effect. Both TeCBs have comparatively large gaps in their shielding wall, whereas for 1,2,4,5-TeCB the remaining chlorine atoms are distributed in such a way that the smallest possible attack surface is formed. The same applies more or less to the TCBs. The lack of three adjacent chlorine atoms in 1,2,3-TCB and two adjacent chlorine atoms in 1,2,4-TCB create a better contact surface (Fig. 4).

However, in addition to inductive effects, also the affinity of the reactants for adsorption to the catalyst has to be considered as influencing factor. Comparative studies on dechlorination reactions of PCB 21 catalyzed by nanoparticles show that the chlorine atoms that are para to the phenyl group are the ones first dechlorinated [38]. Further, it was shown for the dechlorination of 1,2,3,4-tetrachlorodibenzo-*p*-dioxin (TCDD) that the vicinal chlorine atom is preferably substituted

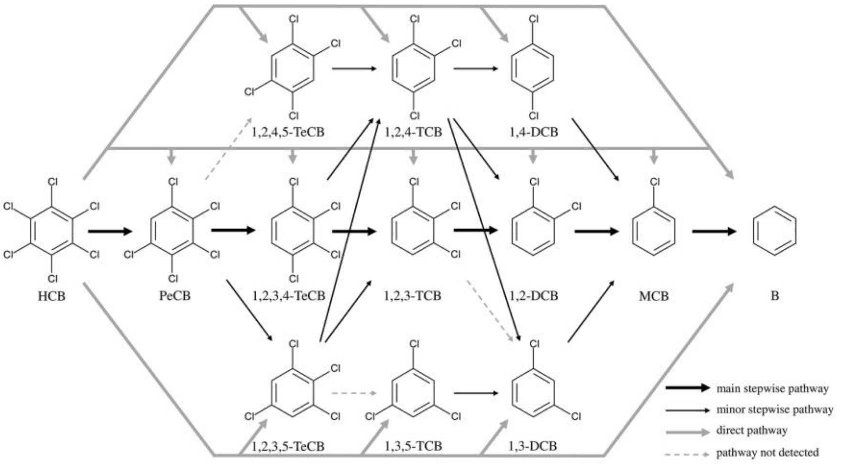

Fig. 3. Dechlorination of HCB using Pd(0) nanoparticles with proposed main stepwise reaction pathway (black bold), minor stepwise reaction pathways (black plain), direct reaction pathways (grey bold), and not detected reaction pathways (grey dotted).

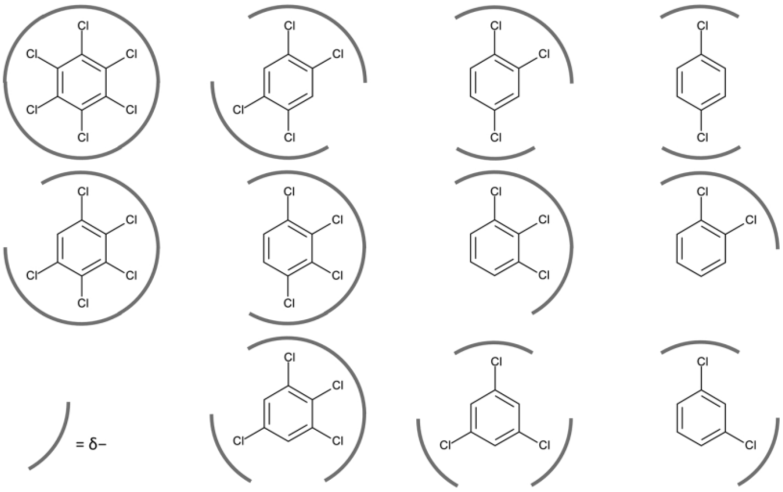

Fig. 4. Visualization of inductive effects for the dechlorination of chlorobenzenes.

and the formation of 2,3-substituted congeners could not be detected [16,39]. In contrast, in a catalyzed dechlorination using zinc nanoparticles, the vicinal chlorosubstituents of octachlorodibenzo-*p*-dioxin are not split off, and thus no 2,3,7,8-TCDD is formed [40]. This reinforces the assumption that different metal nanoparticles also induce different dechlorination steps. So far, it seems that Pd(0) nanoparticles preferably induce a dechlorination of the vicinal positioned chlorine, regardless of the chlorinated hydrocarbon reactant.

Test concentrations (3 µg L^{-1} for HCB, PeCB, TeCBs, TCBs, and 6 µg L^{-1} for DCBs and MCB) reflect environmentally relevant concentrations for the low water-soluble hydrophobic compounds. Commonly, dehalogenation of water pollutants means detoxification. Although, in terms of acute toxicity, the LC50 for fish can be higher for some intermediates compared to HCB. However, the persistent and bioaccumulative properties of HCB have to be taken into account as well. For organisms in the aquatic environment and human health, it is nevertheless regarded as beneficial when chlorobenzenes are dechlorinated because benzene and chlorinated benzenes with low substitution degree have a much better biodegradability compared to HCB [13,41]. The overall elimination rate of chlorinated benzenes and benzene in the environment is therefore accelerated. Toxicity can vary widely among isomers with the same degree of chlorination. While for the chlorobenzene isomers the differences in toxicity are comparatively small, the presented approach is nevertheless promising to investigate and predict the formation of highly toxic isomers after adaption of the method to further substances or substance groups. Regarding this, it is relevant to elucidate if further halogenated pollutants are primarily degraded by a vicinal dehalogenation pathway such as found for HCB, especially for the POPs where specific isomers show highly varying toxicity, persistence, bioaccumulation potential, and long range transport, e.g. polychlorinated dioxins and furans (PCDD/Fs), dioxin-like PCBs, or per- and polyfluorinated or -brominated compounds. The corresponding C−X bond strengths in halogenated hydrocarbons have been listed based on various studies [27]. For halobenzenes (iodobenzene, bromobenzene, chlorobenzene, and fluorobenzene) comparison works well due to the same structure and variation of the halogen substituent. With increasing electronegativity of the halogen, the C−X bond has an increased strength and correspondingly a lower specific catalyst activity results for hydrodehalogenation. Therefore, it can be assumed that hexaiodobenzene, hexabromobenzene, and hexafluorobenzene will be dehalogenated via both stepwise and multiplet mechanism just like HCB, except that the specific catalytic activity of Pd nanoparticles would most likely be lower for hexafluorobenzene and higher for hexaiodobenzene and hexabromobenzene. However, for larger substituents, such as bromine, the steric effects might have an increased influence, as well as their adsorption to the catalyst surface.

3.3. Catalytic activity of Pd nanocatalysts

The catalytic Pd activities for chlorobenzenes, calculated according to Eq. (1), are listed in Table 1. The specific catalytic activity of the Pd (0) particles for HCB was determined as A_{Pd} = 150 L g^{-1} min^{-1}. As a general tendency, for unsaturated substances, an increasing catalytic activity can be observed with decreasing degree of chlorination, which also correlates with increasing water solubility of the chlorobenzenes (Figure S3). However, some of the isomers show a deviation from this general tendency as can be seen for the TCBs in Table 1. As an explanation, the inductive effect can again be considered to affect the reactivity depending on the arrangement of the chlorine atoms. Other studies have already determined the activity of Pd(0) nanoparticles in further dehalogenation reactions. Several experiments were carried out in which halogenated hydrocarbons were degraded by Pd catalysts [27]. Because the type of catalyst particles differed from the ones used in the present study and the particle size was slightly larger, a much lower specific catalyst activity was detected for several substances [27], e.g. for MCB with a catalyst activity of 200 L g^{-1} min^{-1} compared to

Table 1
Specific catalytic activity of Pd(0) nanoparticles for the dechlorination of all chlorobenzenes ($c_{0,CBs}$ = 3 µg L^{-1}, c_{Pd} = 300 µg L^{-1} with d50 = 3.9 nm, c_{NaHCO3} = 9 g L^{-1}, $c_{Na\text{-}citrate}$ = 2.94 g L^{-1}).

Reactant	Pd activity A_{Pd}, L g^{-1} min^{-1}
HCB	150
PeCB	2120
1,2,3,4-TeCB	950
1,2,4,5-TeCB	440[a]
1,2,3,5-TeCB	1160
1,2,3-TCB	770
1,2,4-TCB	110[a]
1,3,5-TCB	440
1,2-DCB	2420[b]
1,4-DCB	1060[b]
1,3-DCB	3380[b]
MCB	3210[b]

[a] Problems with regard to measurement and reproducibility within the marked experiment.

[b] 6 µg L^{-1}.

3210 L g^{-1} min^{-1} under the here presented conditions. Considering the huge intrinsic Pd activity, the chosen reaction conditions represent a surplus of Pd(0) compared to the low contaminant concentrations, leading to a lower turnover compared to previous studies (e.g., 171 μmol MCB g^{-1} Pd(0) min^{-1} in the present study compared to 35.5 mmol MCB g^{-1} Pd min^{-1} [27]). Different from the conditions in the present study, previous studies on the dechlorination of HCB by Pd used bimetallic or carbon-supported nanoparticles and provided reactant concentrations that have been far above the pollutant's water solubility (e.g., from 0.5 mg L^{-1} in aqueous solution [42] to the g L^{-1} range of HCB provided in organic solvents [28,43–45]). The small reactant concentrations used in the present study rather refer to relevant aqueous environmental concentrations reflecting the water solubility of reactants (e.g., 6 μg L^{-1} for HCB). The resulting specific activity A_{Pd} given in Table 1 can be understood as a material property. Ideally, the catalyst shows its true catalyst activity for a broad contaminant concentration range. Thus, A_{Pd} reflects the volume of contaminated water that can be treated in a certain time frame with a certain amount of Pd, independent of the contaminant concentration as long as there are no negative effects (e.g., catalyst overload by the reactant). After all, the high catalytic activities indicate a relevant potential for the removal of contaminants. However, suspended Pd(0) nanoparticles are known to agglomerate and precipitate quite rapidly, adsorb to the surface of organic matter and are deactivated by a variety of catalyst-poisoning substances [27,46]. Therefore, long-term maintenance of the catalytic performance is challenging. But recent studies have shown that the catalytic activity of nanoparticles is lower but largely retained when embedded in a PDMS coating [23,47,48]. Thus, the high potential of Pd (0) nanoparticles should be further exploited and adjusted to state-of-the-art long-term protection approaches to develop specific applications for environmentally relevant challenges in water treatment.

4. Conclusions

The SPME method established for the simultaneous extraction of all chlorobenzenes and benzene in the ng L^{-1} to μg L^{-1} range was shown to be viable for analysis of such substance mixtures comprising a wide span of properties. The dehalogenation reactions in multi-analyte mixtures could be followed much faster than for single components and with high precision using the method presented in this study. For dechlorination of HCB and less chlorinated benzenes by Pd(0) nanoparticles, substitution of vicinal chlorine atoms by hydrogen was confirmed as preferred reaction pathway. Pd(0) nanoparticles showed high catalytic activity allowing treatment of HCB and intermediate products at environmental relevant concentrations with low Pd(0) concentrations in the μg L^{-1} range. Our method allowed to reach permissible concentrations within reaction times as short as one hour which is highly relevant in terms of resource efficiency. However, with regard to the applicability in terms of potential catalyst loss and poisoning, the use of suspended Pd(0) as performed in the present study is not directly transferable to the treatment of contaminated waters. We used this approach to demonstrate the potential to monitor dechlorination experiments by SPME, to allow an in-depth monitoring of reaction pathways, and to provide information on the potential of using Pd(0) for the dechlorination of environmental pollutants. With regard to future applications, Pd(0) particles should be introduced to protective films (e.g., PDMS) in order to prevent catalyst poisoning and loss of Pd. While this results in a reduction of the catalyst activity, it is still seen to be advantageous for environmental applications because the catalyst activity is so high that a certain reduction in activity is outweighed by the benefits of long-term activity protection of the catalysts. The specific Pd activity for the dechlorination of individual chlorobenzenes roughly increased with decreasing chlorination degree. For isomers with the same degree of chlorination, the Pd activity was higher when the inductive effect in the molecules was lower which led to the concept of the inductive effect as kind of shielding wall that limits the accessibility of the nanoparticles and explains the preferred formation of vicinal chlorinated isomers. The concept of the shielding wall can easily be applied to further halogenated compounds and prediction of their hydrodehalogenation behavior.

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CRediT authorship contribution statement

Katrin Wiltschka: Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Larissa Neumann:** Methodology. **Matthias Werheid:** Resources. **Michael Bunge:** Project administration, Funding acquisition. **Rolf-Alexander Düring:** Conceptualization, Resources, Project administration, Funding acquisition. **Katrin Mackenzie:** Writing - review & editing, Funding acquisition. **Leonard Böhm:** Conceptualization, Methodology, Validation, Formal analysis, Writing - original draft, Writing - review & editing, Visualization, Supervision.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcatb.2020.119100.

References

[1] J.L. Barber, A.J. Sweetman, D. van Wijk, K.C. Jones, Hexachlorobenzene in the global environment: emissions, levels, distribution, trends and processes, Sci. Total Environ. 349 (2005) 1–44.

[2] UNEP, Stockholm Convention on Persistent Organic Pollutants: United Nations Environment Program, (2001).

[3] K. Borgå, G.W. Gabrielsen, J.U. Skaare, Differences in contamination load between pelagic and sympagic invertebrates in the Arctic marginal ice zone: influence of habitat, diet and geography, Mar. Ecol. Prog. Ser. 235 (2002) 157–169.

[4] E.S.C. Kwok, R. Atkinson, Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: an update, Atmos. Environ. 29 (1995) 1685–1695.

[5] G.A. Epling, E.M. Florio, Borohydride-enhanced dechlorination of chlorobenzenes and toluenes, J. Chem. Soc. Perkin Trans. I 1 (1988) 703.

[6] S. Yamada, Y. Naito, M. Takada, S. Nakai, M. Hosomi, Photodegradation of hexachlorobenzene and theoretical prediction of its degradation pathways using quantum chemical calculation, Chemosphere 70 (2008) 731–736.

[7] J.A. Field, R. Sierra-Alvarez, Microbial degradation of chlorinated benzenes, Biodegradation 19 (2008) 463–480.

[8] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X. Xie, Z.F. Liu, Use of iron oxide nanomaterials in wastewater treatment: a review, Sci. Total Environ. 424 (2012) 1–10.

[9] H. Hildebrand, K. Mackenzie, F.-D. Kopinke, Highly active Pd-on-Magnetite nanocatalysts for aqueous phase hydrodechlorination reactions, Environ. Sci. Technol. 43 (2009) 3254–3259.

[10] S. De Corte, T. Hennebel, J.P. Fitts, T. Sabbe, V. Bliznuk, S. Verschuere, D. van der Lelie, W. Verstraete, N. Boon, Biosupported bimetallic Pd–Au nanocatalysts for dechlorination of environmental contaminants, Environ. Sci. Technol. 45 (2011) 8506–8513.

[11] F.-D. Kopinke, K. Mackenzie, R. Köhler, Catalytic hydrodechlorination of groundwater contaminants in water and in the gas phase using $Pd/\gamma\text{-}Al_2O_3$, Appl. Catal. B 44 (2003) 15–24.

[12] J. Padmanabhan, R. Parthasarathi, V. Subramanian, P.K. Chattaraj, Molecular structure, reactivity, and toxicity of the complete series of chlorinated benzenes, J. Phys. Chem. A 109 (2005) 11043–11049.

[13] M. Bunge, K. Mackenzie, Sustainable synthesis of palladium(0) nanocatalysts and their potential for organohalogen compounds detoxification, in: O.V. Singh (Ed.), Bio-Nanoparticles: Biosynthesis and Sustainable Biotechnological Implications, Wiley Blackwell, Hoboken, New Jersey, 2015, pp. 205–224.

[14] B.P. Chaplin, M. Reinhard, W.F. Schneider, C. Schüth, J.R. Shapley, T.J. Strathmann, C.J. Werth, Critical review of Pd-based catalytic treatment of priority contaminants in water, Environ. Sci. Technol. 46 (2012) 3655–3670.

[15] M.O. Nutt, J.B. Hughes, S.W. Michael, Designing Pd-on-Au bimetallic nanoparticle catalysts for trichloroethene hydrodechlorination, Environ. Sci. Technol. 39 (2005) 1346–1353.

[16] M. Schlüter, T. Hentzel, C. Suarez, M. Koch, W.G. Lorenz, L. Böhm, R.-A. Düring, K.A. Koinig, M. Bunge, Synthesis of novel palladium(0) nanocatalysts by microorganisms from heavy-metal-influenced high-alpine sites for dehalogenation of polychlorinated dioxins, Chemosphere 117 (2014) 462–470.

[17] B.S. Ballapragada, H.D. Stensel, J.A. Puhakka, J.F. Ferguson, Effect of hydrogen on reductive dechlorination of chlorinated ethenes, Environ. Sci. Technol. 31 (1997) 1728–1734.

[18] C.L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, Anal. Chem. 62 (1990) 2145–2148.

[19] S. Risticevic, H. Lord, T. Górecki, C.L. Arthur, J. Pawliszyn, Protocol for solid-phase microextraction method development, Nat. Protoc. 5 (2010) 122–139.

[20] H. Piri-Moghadam, F. Ahmadi, J. Pawliszyn, A critical review of solid phase microextraction for analysis of water samples, Trac Trends Anal. Chem. 85 (2016) 133–143.

[21] L. Böhm, R.-A. Düring, H.-J. Bruckert, C. Schlechtriem, Can solid-phase microextraction replace solvent extraction for water analysis in fish bioconcentration studies with highly hydrophobic organic chemicals? Environ. Toxicol. Chem. 36 (2017) 2887–2894.

[22] L. Böhm, C. Schlechtriem, R.-A. Düring, Sorption of highly hydrophobic organic chemicals to organic matter relevant for fish bioconcentration studies, Environ. Sci. Technol. 50 (2016) 8316–8323.

[23] D. Comandella, S. Woszidlo, A. Georgi, F.-D. Kopinke, K. Mackenzie, Efforts for long-term protection of palladium hydrodechlorination catalysts, Appl. Catal. B 186 (2016) 204–211.

[24] A.-K. Herrmann, P. Formanek, L. Borchardt, M. Klose, L. Giebeler, J. Eckert, S. Kaskel, N. Gaponik, A. Eychmüller, Multimetallic aerogels by template-free self-assembly of Au, Ag, Pt, and Pd nanoparticles, Chem. Mater. 26 (2014) 1074–1083.

[25] B.G. Oliver, K.D. Bothen, Determination of chlorobenzenes in water by capillary gas chromatography, Anal. Chem. 52 (1980) 2066–2069.

[26] I.M. Chen, F.C. Chang, Y.S. Wang, Correlation of gas chromatographic properties of chlorobenzenes and polychlorinated biphenyls with the occurrence of reductive dechlorination by untamed microorganisms, Chemosphere 45 (2001) 223–229.

[27] K. Mackenzie, H. Frenzel, F.-D. Kopinke, Hydrodehalogenation of halogenated hydrocarbons in water with Pd catalysts: reaction rates and surface competition, Appl. Catal. B 63 (2006) 161–167.

[28] V.A. Yakovlev, V.I. Simagina, S.N. Trukhan, V.A. Likholobov, Kinetic study of liquid-phase hydrodechlorination of hexachlorobenzene on Ni/C and 2%PdNi/C, React. Kinet. Catal. Lett. 41 (2000) 25–32.

[29] C.A. Coulson, Valence, 2nd ed., Oxford: University Press, London, 1965.

[30] M. Kraus, V. Bazant, Miami Beach, FL, Catalysis: Proceedings of the Fifth International Congress on Catalysis, 20-26 1972, pp. 1073–1083. August.

[31] S. Arulmozhiraja, M. Morita, Electron affinities and reductive dechlorination of toxic polychlorinated dibenzofurans: a density functional theory study, J. Phys. Chem. A 108 (2004) 3499–3508.

[32] H. Fueno, K. Tanaka, S. Sugawa, Theoretical study of the dechlorination reaction pathways of octachlorodibenzo-p-dioxin, Chemosphere 48 (2002) 771–778.

[33] X. Gao, W. Wang, X. Liu, Low-temperature dechlorination of hexachlorobenzene on solid supports and the pathway hypothesis, Chemosphere 71 (2008) 1093–1099.

[34] J.E. Beurskens, C.G. Dekker, H. van den Heuvel, M. Swart, J. de Wolf, J. Dolfing, Dechlorination of chlorinated benzenes by an anaerobic microbial consortium that selectively mediates the thermodynamic most favorable reactions, Environ. Sci. Technol. 28 (1994) 701–706.

[35] J. Dolfing, I. Novak, The Gibbs free energy of formation of halogenated benzenes, benzoates and phenols and their potential role as electron acceptors in anaerobic environments, Biodegradation 26 (2015) 15–27.

[36] Y. Ren, S. Kang, J. Zhu, Mechanochemical degradation of hexachlorobenzene using Mg/Al2O3 as additive, J. Mater. Cycles Waste Manag. 17 (2015) 607–615.

[37] J.L. Howard, Q. Cao, D.L. Browne, Mechanochemistry as an emerging tool for molecular synthesis: what can it offer? Chem. Sci. 9 (2018) 3080–3094.

[38] S. Agarwal, S.R. Al-Abed, D.D. Dionysiou, E. Graybill, Reactivity of substituted chlorines and ensuing dechlorination pathways of select PCB congeners with Pd/Mg bimetallics, Environ. Sci. Technol. 43 (2009) 915–921.

[39] J.-H. Kim, P.G. Tratnyek, Y.-S. Chang, Rapid dechlorination of polychlorinated dibenzo- p -dioxins by bimetallic and nanosized zerovalent Iron, Environ. Sci. Technol. 42 (2008) 4106–4112.

[40] V. Bokare, J.-L. Jung, Y.-Y. Chang, Y.-S. Chang, Reductive dechlorination of octachlorodibenzo-*p*-dioxin by nanosized zero-valent zinc: modeling of rate kinetics and congener profile, J. Hazard. Mater. 250-251 (2013) 397–402.

[41] J. Nowak, N.H. Kirsch, W. Hegemann, H.-J. Stan, Total reductive dechlorination of chlorobenzenes to benzene by a methanogenic mixed culture enriched from Saale river sediment, Appl. Microbiol. Biotechnol. 45 (1996) 700–709.

[42] J. Wan, Z. Li, X. Lu, S. Yuan, Remediation of a hexachlorobenzene-contaminated soil by surfactant-enhanced electrokinetics coupled with microscale Pd/Fe PRB, J. Hazard. Mater. 184 (2010) 184–190.

[43] V. Simagina, V. Likholobov, G. Bergeret, M.T. Gimenez, A. Renouprez, Catalytic hydrodechlorination of hexachlorobenzene on carbon supported Pd–Ni bimetallic catalysts, Appl. Catal. B 40 (2003) 293–304.

[44] Y.-h. Shih, Y.-C. Chen, M.-y. Chen, Y.-t. Tai, C.-P. Tso, Dechlorination of hexachlorobenzene by using nanoscale Fe and nanoscale Pd/Fe bimetallic particles, Colloids Surf. A Physicochem. Eng. Asp. 332 (2009) 84–89.

[45] S.V. Klokov, E.S. Lokteva, E.V. Golubina, K.I. Maslakov, A.V. Levanov, S.A. Chernyak, V.A. Likholobov, Effective Pd/C catalyst for chlorobenzene and hexachlorobenzene hydrodechlorination by direct pyrolysis of sawdust impregnated with palladium nitrate, Catal. Commun. 77 (2016) 37–41.

[46] N.E. Korte, J.L. Zutman, R.M. Schlosser, L. Liang, B. Gu, Q. Fernando, Field application of palladized iron for the dechlorination of trichloroethene, Waste Manag. 20 (2000) 687–694.

[47] R. Navon, S. Eldad, K. Mackenzie, F.-D. Kopinke, Protection of palladium catalysts for hydrodechlorination of chlorinated organic compounds in wastewaters, Appl. Catal. B 119-120 (2012) 241–247.

[48] D. Comandella, M.H. Ahn, H. Kim, K. Mackenzie, Enhanced protection of PDMS-embedded palladium catalysts by co-embedding of sulphide-scavengers, Sci. Total Environ. 601-602 (2017) 658–668.

Supporting Information

Hydrodechlorination of hexachlorobenzene in a miniaturized nano-Pd(0) reaction system combined with the simultaneous extraction of all dechlorination products

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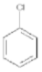
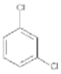
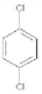
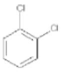
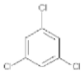
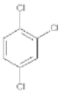
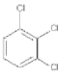
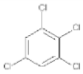
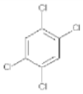
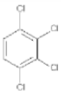
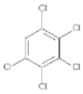
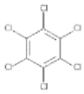
Summary: 7 pages including experimental and analytical details (3 tables and 3 figures).

S1

Table S1. Molecular structures and physicochemical parameters of the test substances.

Analyte	Molecular structure	Structure	CAS RN	Molar mass [g mol^{-1}]	Water solubility [mg L^{-1}] [a]	log K_{OW} [a]	Vapor pressure [mm Hg] [a]	log K_{AW} [b]
B		C_6H_6	71-43-2	78.115	1 790	2.13	94.8	-0.64
MCB		C_6H_5Cl	108-90-7	112.56	498	2.84	11.97	-0.90
1,3-DCB		$C_6H_4Cl_2$	541-73-1	147.00	125	3.53	2.15	-0.97
1,4-DCB		$C_6H_4Cl_2$	106-46-7	147.00	81.3	3.44	1.74	-1.01
1,2-DCB		$C_6H_4Cl_2$	95-50-1	147.00	156	3.43	1.36	-1.11
1,3,5-TCB		$C_6H_3Cl_3$	108-70-3	181.45	6.01	4.19	0.24	-1.11
1,2,4-TCB		$C_6H_3Cl_3$	120-82-1	181.45	49.0	4.02	0.46	-1.24
1,2,3-TCB		$C_6H_3Cl_3$	87-61-6	181.45	18.0	4.05	0.21	-1.29
1,2,3,5-TeCB		$C_6H_2Cl_4$	634-90-2	215.89	5.10	4.56	0.0553	-1.19
1,2,4,5-TeCB		$C_6H_2Cl_4$	95-94-3	215.89	0.60	4.64	0.0054	-1.39
1,2,3,4-TeCB		$C_6H_2Cl_4$	634-66-2	215.89	5.92	4.60	0.039	-1.51
PeCB		C_6HCl_5	608-93-5	250.34	0.83	5.17	0.00101	-1.54
HCB		C_6Cl_6	118-74-1	284.78	0.006	5.73	0.000018	-1.16

[a] physprop database syrres.com (at 25 °C) [1]; [b] calculated from Henry's Law Constants [atm m^3 mol^{-1}] given in [1].

Particle size distribution of Pd nanoparticles – Figure S1

Citrate stabilized Pd nanoparticles were synthesized by chemical reduction [2]. Therefore, a stock solution containing sodium borohydride was quickly added to a boiling solution containing the palladium precursor $PdCl_2 \cdot 2HCl$ and sodium citrate as stabilizer. The final product was a sol with a brown color. The suspensions were investigated with transmission electron microscopy (TEM) (Tecnai T20, equipped with a LaB_6-cathode, operated at 200 kV). The Pd nanoparticles were finely dispersed with a size of 3.9 nm (d50%) (Figure S1).

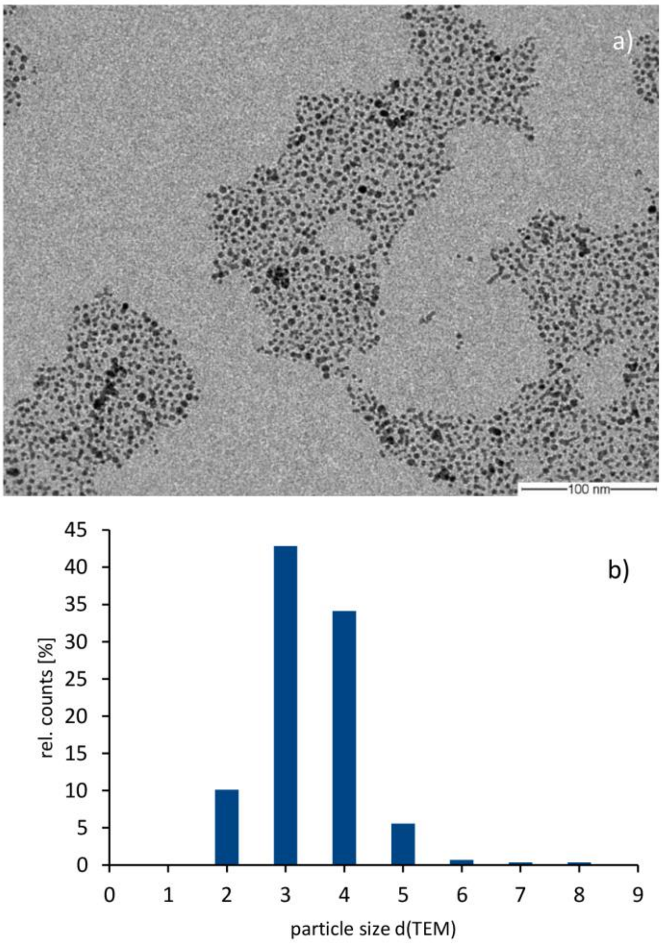


Figure S1. (a) Transmission electron microscopy (TEM) image of the citrate-stabilized Pd nanoparticles (magnification 43000 x), (b) particle size distribution of the Pd nanoparticles (dried, TEM, d50% = 3.9 nm).

Instrumental analysis / GC-MS parameters – Tables S2 and S3

A GC coupled to an ion trap MS (Trace GC Ultra/ITQ 900, Thermo Fisher Scientific) was used for separation and detection of analytes. The injector was programmed with a split flow of 30 mL min^{-1} after thermodesorption at 210 °C. The GC was equipped with a 60 m × 0.25 mm fused silica capillary column with 0.25 µm coating (TraceGOLD TG-XLBMS, Thermo Fisher Scientific). The temperature program of the GC oven is given in Table S2. Helium 5.0 was used as carrier gas with a flow rate of 1.0 mL min^{-1}. The transfer line to the MS was heated at 260 °C. The MS was used in selected ion storage (SIS) mode (designated as "selected ion monitoring", SIM, in Thermo Xcalibur software) with respective segments for the analytes. Detailed parameters for GC-MS conditions are given in Table S3. Ionization of molecules was performed by electron impact ionization (70 eV) at 200 °C.

Quality assurance and quality control

The SPME fiber was thermally cleaned at 210 °C before extraction and after thermodesorption for 4 min each in the needle heater in order to remove possible residues and to prevent carry-over of analytes between sampling events. Blank samples as described in the main article were measured to check for potential carry-over or impurities. Fibers were reused, but visually controlled for any changes and frequently rinsed/cleaned with methanol. The internal standard mix used allowed for the correction of potentially occurring variability in sensitivity of the SPME fiber and the GC-MS instrument.

In order to avoid agglomeration of nanoparticles, the entire equipment which came in contact with nanoparticles was washed before use with nitric acid (HNO_3, 33 %) and water. The 20-mL glass vials and screw caps were used out of the box and were not reused.

Table S2. Temperature program of the GC oven (total time 30.75 min).

Rate [°C min^{-1}]	Temperature [°C]	Hold time [min]
–	40	3.00
8.0	150	0.00
4.0	180	0.00
40.0	280	4.00

Table S3. Parameters for MS detection of analytes and internal standards in SIM mode.

Analyte	Structure	Molar mass [g mol^{-1}]	Retention time [a] [min]	Ion used for quantification [m/z]
B	C_6H_6	78.12	6.27	78
B-d_6	C_6D_6	84.15	6.21	84
MCB	C_6H_5Cl	112.56	10.72	112
^{13}C-MCB	$^{13}C_6\ H_5Cl$	118.52	10.72	118
1,3-DCB	$C_6\ H_4Cl_2$	147.00	14.71	146
1,4-DCB	$C_6\ H_4Cl_2$	147.00	14.96	146
^{13}C-1,4-DCB	$^{13}C_6\ H_4Cl_2$	152.96	14.95	152
1,2-DCB	$C_6\ H_4Cl_2$	147.00	15.33	146
1,3,5-TCB	$C_6\ H_3Cl_3$	181.45	17.64	182
1,2,4-TCB	$C_6\ H_3Cl_3$	181.45	18.65	182
1,2,3-TCB	$C_6\ H_3Cl_3$	181.45	19.35	182
^{13}C-1,2,3-TCB	$^{13}C_6\ H_3Cl_3$	187.41	19.34	188
1,2,4,5-TeCB	$C_6H_2Cl_4$	215.89	22.22	216
1,2,3,5-TeCB	$C_6H_2Cl_4$	215.89	22.32	216
1,2,3,4-TeCB	$C_6H_2Cl_4$	215.89	23.47	216
^{13}C-1,2,3,4-TeCB	$^{13}C_6H_2Cl_4$	221.85	23.46	222
PeCB	$C_6\ HCl_5$	250.34	26.18	250
^{13}C-PeCB	$^{13}C_6\ HCl_5$	256.30	26.18	256
HCB	C_6Cl_6	284.78	28.13	284
^{13}C-HCB	$^{13}C_6Cl_6$	290.74	28.12	290

[a] column: Thermo TG-XLBMS, 60 m x 0.25 mm x 0.25 µm; flow rate: 1.0 mL helium min^{-1}.

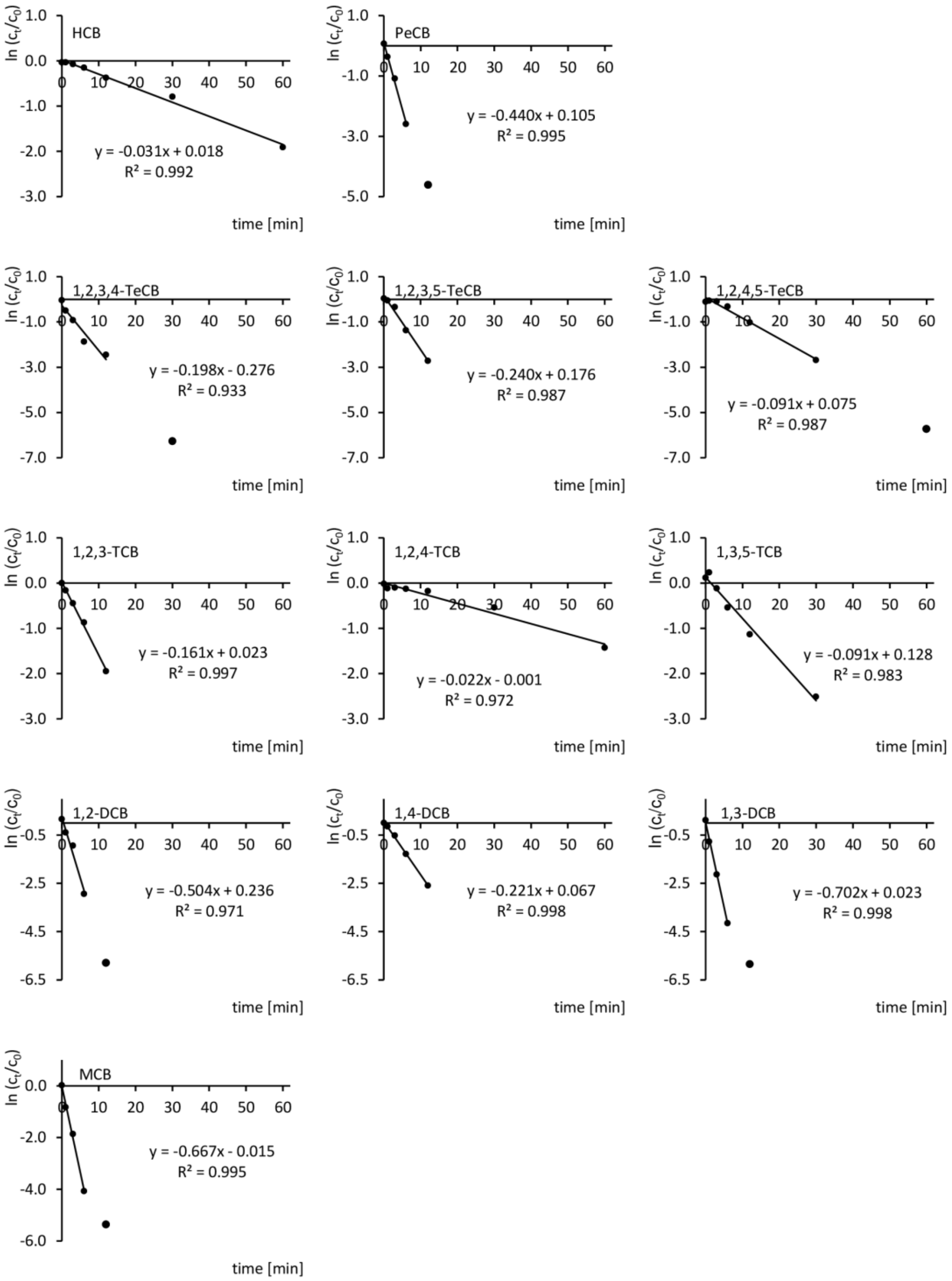


Figure S2. The rate constant *k* value of pseudo first order kinetics for dechlorination experiments.

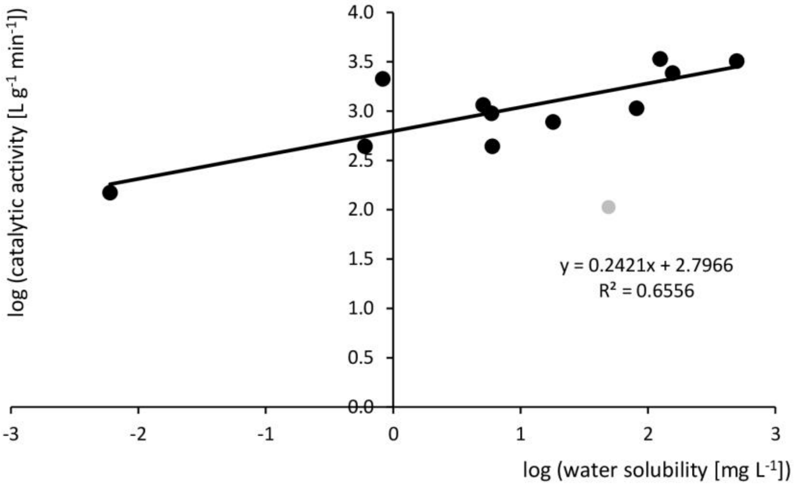


Figure S3. Relationship between specific catalytic activity for hydrodechlorination (L g^{-1} min^{-1}) and water solubility (mg L^{-1}) of chlorobenzenes. Water solubilities are derived from the SRC PhysProp Database [1]. The data point for 1,2,4-TCB (grey) was excluded based on a cook's distance > 4/n with n as the number of observations.

References

[1] SRC, *FatePointers Search Module*: *PHYSPROP database.* Data was accessed from the meanwhile inactive website *http://esc.syrres.com/fatepointer/search.asp*. The *PHYSPROP* database is still available as part of the US EPI Suite:
US EPA. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. United States Environmental Protection Agency (2017), Washington, DC, USA.

[2] A.-K. Herrmann, P. Formanek, L. Borchardt, M. Klose, L. Giebeler, J. Eckert, S. Kaskel, N. Gaponik, A. Eychmüller, Multimetallic Aerogels by Template-Free Self-Assembly of Au, Ag, Pt, and Pd Nanoparticles, Chem. Mater. 26 (2014) 1074–1083.

4 Beschichtungsgeschützte Pd/Al_2O_3-Katalysatoren zur Entfernung von polychlorierten Biphenylen (PCB) aus Grubenwässern

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Coating-Protected Pd/Al_2O_3 Catalysts for the Elimination of Polychlorinated Biphenyls (PCBs) from Mine Water Effluents

Katrin Wiltschka,*[a] Silviu Bobric[a], Rolf-Alexander Düring[a] and Leonard Böhm *[a]

Polychlorinated biphenyls (PCBs) are persistent, toxic, and bioaccumulative pollutants that are ubiquitous in the environment. To reduce existing as well as to prevent further environmental contamination and hazard, appropriate dechlorination techniques are crucial. This study investigates the catalytic efficiency of palladium (Pd) nanocatalysts for the dechlorination of PCBs for potential applications in real-world environmental waters, specifically mine water, which is one of the remaining point sources of PCB discharge to the environment. Elimination of the mine water specific PCBs 4, 18, 28, and 52 from three types of PCB-contaminated mine water was studied for dispersed Pd(0), suspended Pd/Al_2O_3, as well as Pd/Al_2O_3 catalysts incorporated into a polydimethylsiloxane (PDMS) coating. All PCB congeners that can occur as potential intemediate products were considered. The study provides new insights into the reaction pathways of PCB dechlorination, to the specific catalytic activity of Pd particles, and to their potential applications in matrix-rich waters. Results revealed specific catalytic activities for Pd of up to 3350 L g^{-1} min^{-1} in reference medium. Chlorine atoms in para position were preferentially dechlorinated, indicating steric hindrance of ortho dechlorination by the other phenyl ring. The catalytic activity of Pd decreased in the order dispersed Pd > suspended Pd/Al_2O_3 > embedded Pd/Al_2O_3 in reference buffer solution. In mine water, dispersed Pd(0) nanoparticles and suspended Pd/Al_2O_3 were mostly deactivated by the mine waters rich in catalyst poisons. Embedding of micro Pd/Al_2O_3 particles to PDMS coatings prevented the catalyst deactivation in two of the three investigated mine waters and ensured the dechlorination of PCBs with a catalyst activity of 20–210 L g^{-1} min^{-1} in the matrix rich mine water. Embedding of particles allows the catalysts to be handled in a resource-conserving manner maintaining their activity for an extended period of time. Scaling of the method for large-scale applications is possible and is discussed with regard to resource consumption of both catalysts and dechlorination time. Further increase of catalyst protection to enhance the catalytic activity is recommended, which is especially necessary for sulfide rich mine waters.

Environmental significance

Polychlorinated biphenyls (PCBs) are persistent organic pollutants that pose serious environmental and health risks. This study presents a resource-efficient method for the catalytic dechlorination of PCBs in contaminated waters, using Pd/Al_2O_3 particles embedded in polydimethylsiloxane (PDMS) coatings. By improving the efficiency and reusability of the catalyst, this approach addresses the challenge of persistent PCB contamination in aquatic environments. The findings contribute to advancing sustainable remediation technologies, reducing PCB levels in real-world waters, and offering a scalable solution for mitigating long-term environmental hazards associated with these toxic compounds.

1. Introduction

Chemical pollution of the environment by persistent organic pollutants (POPs) is a pressing topic that is seen to violate planetary boundaries and must be considered to preserve a safe operating space for humanity.[1] Polychlorinated biphenyls (PCBs) were one of the first 12 substances and groups of substances banned by the Stockholm Convention in 2001 and are seen as high-impact POPs based on hazard and production volumes.[2,3] They were produced industrially in large quantities until the 1980s. Worldwide production of PCBs reached approximately 1.3–2 million tons.[4,5] They were utilized as industrial chemicals due to their thermal and chemical stability, low flammability, and non-conductive properties. Additionally, PCBs were also used in mining due to their non-flammable properties. In Germany, they were even legally required in coal mines. Underground, they were primarily utilized in electronic equipment (capacitors, transformers and lamps).[6] Mines can still be contaminated with PCBs due to improper handling or accidents. To prevent flooding of active mines or to protect nearby groundwater, mine water is pumped out and discharged into surface waters for dilution. The annual load of PCBs discharged to rivers can be more than 640 g per mine, despite concentrations in the ng L^{-1} range.[7] Even though dilution in subsequent surface waters may be significant, even small amounts of PCBs can accumulate in food webs and have adverse effects on humans and the environment.[8–11] PCBs are often diffusely distributed due to decades of ubiquitous use, making their removal challenging. Point sources, as mine water effluents are, allow for easier application of methods to reduce contamination compared to diffuse sources. To achieve a lower-risk state of the environment, it is necessary to remove PCBs before they reach surface waters or the environment at large. Bioremediation, a natural process, involves the degradation or removal of pollutants by microorganisms or plants.[12] However, PCBs typically require up to several months for plants and/or microorganisms to dechlorinate,[13–15] and some PCBs cannot be fully biologically dechlorinated to biphenyl.[16] Another drawback of biological remediation is the requirement to establish a suitable environment for bacteria. This can be a problem in many field experiments because PCBs may be accompanied by other material contamination. Nanoparticle-catalyzed dehalogenation reactions with transition metals, particularly palladium (Pd), are a very promising alternative

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to other concepts.[17,18] In the presence of a hydrogen donor, such as molecular hydrogen (H_2), they exhibit high catalytic efficiency and fast reaction times,[19–21] making them suitable for the application of new environmentally friendly technologies.[22–25] The high cost of transition metal catalysts is a potential issue, but appropriate recycling processes can be employed.[26,27] However, the challenge of interfering substances (catalyst poisons) affecting the activity of the nanoparticles remains.[28,29] To counteract the loss of metal catalysts (and thereby environmental pollution), and to prevent the agglomeration of nanoparticles due to van der Waals forces or electrostatic attraction,[30] the nanocatalysts can be applied in coatings on surfaces in the reactor, e.g. in a polydimethylsiloxane (PDMS) coating,[31,32] where Pd/Al_2O_3 particles in particular have shown that their catalytic activity is still high even when embedded. Catalyst protection is of great interest for mine water treatment, because many mine waters are characterized by an extreme, catalyst-deactivating matrix.[33] Therefore, our overarching goal for this study was to advance dechlorination techniques with regard to catalyst protection to allow for the first time PCB dechlorination in untreated mine water. For the basic understanding of processes and influencing factors as well as with regard to performance maximization, comparison of catalysts, knowledge of the catalysts under optimal reaction conditions, knowledge of reaction pathways and intermediates, as well as knowledge on the degree of catalyst deactivation is crucial. Therefore, the aims of this study were (i) to clarify the dechlorination pathways by monitoring the formation of intermediate products, (ii) to incorporate the nanoparticles into a coating to improve stability and durability and (iii) to determine and compare the specific catalytic activity of dispersed, suspended, and embedded Pd particles, to provide insights into the potential of eco-friendly applied technology. Therefore, we performed dechlorination experiments in a miniaturized reaction system with the mine water relevant PCBs 1, 2, 3, 4, 18, 28, and 52 in the presence of low and thereby cost-efficient concentrations of finely dispersed pure Pd, as well as suspended and coating-embedded Pd/Al_2O_3 catalysts in both buffer solution and different mine waters.

2. Materials and methods

2.1 Chemicals and catalysts

Standards of biphenyl and PCB congeners (PCB 1–4, 6–9, 11, 15, 18, 26, 28, and 52) as well as PCB congeners 6 and 49, used as internal standards (IS), were purchased as neat substances from LGC Standards (Dr. Ehrenstorfer brand, purities ≥ 97.5%). Additionally, we purchased the isotopically labeled compounds biphenyl-d_{10} (LGC Standards, Dr. Ehrenstorfer brand, purities ≥ 96.5%) and the PCB congeners 3-d_5, 9-d_5, and 18-d_5 (CDN Isotopes Inc., Pointe Claire, QC, Canada, purities ≥ 96.5%) as neat substances for use as IS. PCBs 26 and 28 were used both as standard and as IS, depending on the specific experiment. Analytes and IS were diluted in methanol. More detailed information on preparation and usage of standards and IS can be found in the Supporting Information (SI) in Table S1,S2 and subsequent text.

The Pd(0) nanoparticles were producted by chemically reducing the tetrachloropalladate complex using sodium borohydride as the reducing agent,[34] stabilized in an aqueous citrate solution (60 mg L^{-1}). These spherical, finely dispersed Pd nanoparticles averaged 2.8 nm in diameter (d50%; transmission electron microscopy, TEM) and were electrostatically stabilized within a pH range of 8–9 (Figure S1). Just prior to the experiment, the Pd suspension was transferred to 20-mL vials using an air cushion pipette and purged with hydrogen for 30 min to activate the catalyst.

The following solutions were prepared based on previous studies.[35] For pH and nanoparticle stabilization during dechlorination experiments, an aqueous working solution (buffer solution) was prepared with 9 g L^{-1} sodium hydrogencarbonate ($NaHCO_3$) (purity ≥ 99.5%, p.a. quality, Carl Roth GmbH, Karlsruhe, Germany) and 2.94 g L^{-1} tri-sodium citrate dihydrate ($Na_3C_6H_5O_7*2H_2O$) (purity ≥ 99.0%, p.a. quality, Carl Roth GmbH, Karlsruhe, Germany) and water. A sodium sulfite (Na_2SO_3) solution (purity ≥ 98.0%, p.a. quality, Carl Roth, Karlsruhe, Germany) was prepared at a concentration of 60 g L^{-1} in water, to achieve a 20-fold stoichiometric excess when added to the reaction system to terminate the dechlorination reactions of dispersed and suspended catalysts by catalyst poisoning.

A Pd/Al_2O_3 catalyst, the commercially available egg-shell Pd on γ-Al_2O_3 with 0.5 wt% Pd (G-133 D, with a BET surface area of 160 m^2 g^{-1}) was purchased from Commercia, Germany. SilGel® 612 A/B (Silgel) for the coatings was purchased from Wacker Chemie, Germany.

The mine water samples were collected from three different sites as described in Wiltschka et al. 2023:[7] the Walsum and Stinnes mines (North Rhine-Westphalia, NRW, Germany) and the Reden mine (Saarland, Germany), all of which are abandoned hard coal collieries. Samples were stored at 4 °C in fully filled amber glass bottles (Schott Duran ® bottles and screw caps with a PTFE coated silicone seal, Th. Geyer GmbH & Co., Renningen, Germany) until experiments were carried out.

All water used within the study was of ultrapure quality (ELGA PF2XXXXM1, Veolia Water Solutions & Technologies, High Wycombe, United Kingdom).

2.2 Preparation and design of dechlorination experiments with finely dispersed colloidal nano-Pd(0)

The purpose of the experiments with the single substances PCB 4, 18, 28, and 52 was to clarify the dechlorination pathways by tracking their intermediate products. The dechlorination experiments with the single substances (PCB 1, 2, or 3) and the mixture of all three (PCB 1, 2, and 3) were designed to determine whether there are differences in the specific catalytic activities of the same analyte in the presence of other, similar substances due to a preference in dechlorination.

With the experimental design of Pd(0) based experiments, we followed our previous work.[35] To prepare the nano-Pd suspension and the buffer solution, they were flushed with hydrogen for 30 min in Schott bottles with screw caps with a PTFE coated silicone seal (Duran®, Th. Geyer GmbH & Co. Renningen, Germany). Pure hydrogen was introduced with a sterile disposable needle (Sterican, Braun Melsungen AG, Melsungen, Germany). A syringe filter (Filtropur S 0.2, Sarsted, Numbrecht, Germany) was placed in line, to prevent a potential contamination with particles or oil residues from the gas supply line. Another sterile needle ensured that the gas space could be exchanged.

The dechlorination experiments were performed under anoxic conditions. An anaerobic chamber (Glovebox, Mecaplex, Grenchen, Switzerland) with N_2/CO_2 atmosphere (ratio 80:20, 'Sanfresh 3', Praxair, Germany) was used for this purpose. Buffer solution (or mine water, respectively) (9.97 mL) and nano-Pd suspension (25 µL) were filled into 20 mL brown glass vials. This resulted in an experimental Pd concentration of 150 µg L^{-1}. The vials were sealed with screw caps containing PTFE septa. Through the septa, 1 mL of the gas phase was removed using a syringe with a cannula and replaced with 1 mL of hydrogen (10% hydrogen (v/v) in the N_2/CO_2 sample atmosphere). Through this hole, 3 µL of a PCB solution (PCB 1, 2, 3, 4, 18, 28, or 52, 10 mg L^{-1} each; or PCB 1+2+3, 3.33 mg L^{-1} each) was added to each of the samples to achieve concentrations of 3 µg L^{-1} in the reaction vessels. After PCB spiking, the dechlorination reaction started automatically. During reaction time, the reaction vessel was shaken continuously at 300 rpm on a horizontal shaker (VWR International). After specified times (1, 3, 6, 12, 30 and 60 min), the catalyst was inactivated with catalyst poison (10 µL Na_2SO_3 solution). After adding the appropriate IS mix (2 µL) through the septa holes, they were sealed with superglue (Pattex, Henkel, Düsseldorf, Germany). Samples were prepared in four replicates for each of the 6 reaction times. All steps were performed at room temperature (22 ± 1 °C). The same dechlorination experiments were performed with 3 different mine water instead of the buffer solution.

The same matrix was used for the calibration samples and the starting-point samples (0 min) as for the dechlorination samples (stabilization solution, Pd solution, catalyst poison solution, hydrogen). To prevent dechlorination, the catalyst poison was added before the corresponding PCB solutions. All other previously described steps remained unchanged. The 7-point calibration (0.01–3 µg L^{-1}) was performed in duplicate. Reference samples (dechlorination time t = 0 min) were prepared with four replicates. In addition, blank samples were measured for the different media used (ultrapure water, buffer solution containing 10 µL Na_2SO_3, as well as buffer solution containing 10 µL Na_2SO_3 and 25 µL nano-Pd suspension). After the experiments, the samples were removed from the glove box immediately before measurement.

2.3 Preparing the (Pd-)PDMS wall-coated reactors

The coating was produced following the procedure of Comandella et al.,[32] with adjustments. 5 mL Silgel were diluted with hexane at different ratios to test for easier handling, and 2.2 mL of the corresponding mix were poured into a 20-mL SPME vial; resulting in approximately 75, 375, or 750 mg Silgel in the vial. The different dilutions were necessary to achieve an appropriately consistent coating. For recovery experiments, the Silgel-hexane-mix was added to the vials without the addition of Pd/Al_2O_3.For dehalogenation experiments, Pd/Al_2O_3 was added before to the Silgel-hexane-mix, then together shortly dispersed via ultrasonication (10 min), resulting in 0.3 mg Pd/Al_2O_3 in the individual vial (this corresponds to the same amount of palladium as in the experiments with the finely dispersed particles in 2.2).

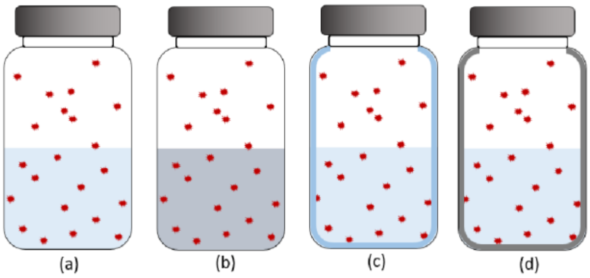

Fig. 1 Overview of the different experiment designs with Pd/Al_2O_3 catalysts, with (a) no PDMS coating and no catalysts – for quality control only; (b) no PDMS coating but with suspended catalysts – for comparison with dispersed nano-Pd(0) (chapter 2.2), and to determine the catalytic activity of suspended Pd/Al_2O_3 catalysts (chapter 2.5); (c) PDMS coating and no catalysts – for recovery rate experiments (chapter 2.6); and (d) PDMS-coated catalysts – to determine the catalytic activity of embedded Pd/Al_2O_3 catalysts (chapter 2.7). Red symbols = PCBs in liquid and gas phase.

The individual vials were then mounted horizontally on an overhead shaker (Reax 2, Heidolph, Schwalbach, Germany) and rotated overnight at the lowest speed. Prior to the experiments, the vials underwent a rinsing process with mQ water to eliminate any catalysts that were not embedded in the PDMS.

2.4 Experimental overview

The different experiments with Pd/Al_2O_3 catalysts are shown in Figure 1 to get a better overview of the several test design variations described in 2.5–2.7. Variants (b) and (d) were carried out with both buffer solution and mine water.

The following experiments aim to enable comparability of the various results. The experiment in Figure 1b is intended to show the difference between dispersed (the particles cannot sediment in the Earth's gravitational field) nano-Pd(0) and suspended (the particles can sediment in the Earth's gravitational field) Pd/Al_2O_3 catalysts; also to show the catalytic activity of non-embedded Pd/Al_2O_3 catalysts. Figure 1c shows the test setup with Silgel coating only, for determining recovery rates. And Figure 1d displays the experimental setup for Pd/Al_2O_3 catalysts embedded in Silgel. A comparison with the non-embedded variant (Figure 1b) enables an assessment of the amount of catalyst activity increase in mine water due to the coating.

2.5 Preparation and design of dechlorination experiments with suspended Pd/Al_2O_3 catalysts

These dehalogenation experiments were carried out to investigate the different performances of suspended and embedded Pd/Al_2O_3 catalysts. The Pd/Al_2O_3 catalyst was crushed by hand with mortar and pestle, and sieved using a stainless steel sieve (d ≤ 25 µm). In contrast to the previous procedure (chapter 2.2), the buffer solution and catalyst (0.3 mg) were added to the reaction vessels before rinsing with hydrogen. The experimental setup was as in chapter 2.2, except that the vials were mounted horizontally on an overhead shaker (Reax 2, Heidolph, Schwalbach, Germany) at 50 rpm during the dechlorination time. After the 6 different time points, an aliquot (8 mL) was transferred to another 20-mL glass vial containing 10 µL Na_2SO_3 (as a precautionary measure to deactivate any catalyst particles carried over). The remaining 2 mL were discarded. Finally, 2 µL of the IS mix was added to the solution.

For the calibration samples, vials were filled with 8 mL of buffer solution. All other previously described steps remained unchanged. The 7-point calibration (0.01–3 µg L^{-1}) was performed in duplicate.

2.6 Preliminary tests on recovery rates with Pd-PDMS wall-coated reactors

Pre-tests where used to determine if the coating absorbs the reactants, intermediates, and products, leading to incomplete transfer during aliquot transfer and resulting in inaccurate recovery rates. To conduct these tests, vials coated with PDMS were prepared in the same manner as for the dechlorination experiments (but without Pd particles) and filled (buffer solution, hydrogen, calibration, etc., see following section). Next, 3 µL of biphenyl or one of the PCB solutions (PCB 2, 4, 18, 52) was added. After rotating continuously at 50 rpm, an aliquot (8 mL) was taken at the different time points (1, 24, and 48 hours) and mixed with 2 µL of IS mix. Subsequently, a solvent extraction was performed: 5 mL hexane was added three times to the empty PDMS-coated vials and shaken for 10 min each time. The hexane from the various runs was collected, evaporated under a gentle stream of nitrogen, and mixed with 2 µL of IS mix. Recovery rates were then determined by summing the quantities extracted from the aqueous solution and from the PDMS coating. Each sample was prepared in triplicate for each of the three reaction times.

2.7 Preparation and design of dechlorination experiments with Pd/Al_2O_3-PDMS wall-coated reactors

The wall-coated vials were filled with 10 mL of buffer solution (or mine water, respectively) and flushed with hydrogen for 5 min. The subsequent dechlorination experiments were conducted in an anaerobic chamber. 1 mL of the gas phase was replaced with 1 mL of hydrogen. To initiate the reaction, 3 µL of a PCB solution (PCB 4, 18, 28, or 52, 10 mg L^{-1} each) was added. The vials were continuously rotated at 50 rpm. In contrast to the experiments with the suspension, the reaction could not be stopped by the addition of catalyst poison, because the embedding in PDMS protects the catalysts to a relevant extent. Therefore, an aliquot (8 mL) was taken at the different time points (1, 6, 24, and 48 hours) and transferred to a vial containing 10 µL Na_2SO_3 (in case Pd particles released from the coating were also transferred). The remaining 2 mL were discarded. Subsequently, 2 µL of the IS mix was added. To also analyze the analytes that remained in the coating, another solvent extraction was performed, as mentioned in chapter 2.5. Samples were prepared in triplicates for each of the four reaction times. All steps were carried out at room temperature (22 ± 1 °C).

2.8 Instrumental analysis

The PCB analysis followed the method described in our previous study.[7] Briefly, the extraction and analysis was carried out with a CombiPAL autosampler (CTC Analytics AG, Zwingen, Switzerland) equipped with a SPME fiber assembly, and a Trace 1310 gas chromatograph (GC) combined with an ISQ 7000 mass spectrometer (MS) (Thermo Fisher Scientific, San Jose, CA, USA). For all measurements, a SPME fiber coated with PDMS/DVB (65 µm, nitinol core) was used (Sigma-Aldrich, St. Louis, MO, USA). After the samples were pre-heated in the agitator for 11 minutes at 500 rpm and 75 °C, extraction was performed for 30 min under the same conditions. Afterwards, the fiber was thermally desorbed in splitless mode in the GC injector for 3 min at 240 °C (split flow during the remaining run: 30 mL min^{-1}). Chromatographic separation was conducted on a fused silica capillary column (TG-XLBMS: 60 m, 0.25 mm inner diameter, 0.25 µm coating thickness; Thermo Fisher Scientific). Helium 5.0 (Praxair, Germany) was used as carrier gas at a constant flow rate of 1.0 mL min^{-1}. The initial oven temperature was set to 60 °C and held for 3 min. The temperature was ramped to 120 °C at a rate of 30 °C min^{-1}. Then, it was ramped to 320 °C at a rate of 6 °C min^{-1} and held for 2 min. Parameters for MS detection of analytes and IS are provided in Table S3, considering sulfur component spectra that can occur in mine water.[33]

2.9 Data analysis

The raw data obtained from GC-MS was processed using 'Chromeleon 7.2.9' software (Thermo Fisher Scientific), and manually verified for peak integration. All analyte data were corrected based on the IS (Table S3). Provided concentrations refer to the mean value of the replicates of a specific dechlorination time. Standard deviation (sd), calculated as the square root of the residual sum of squares divided by *n*, where *n* is the number of replicates, is provided as measure of deviation.

2.10 Calculation of specific Pd activities for catalytic hydrodechlorination

Equation (1)[36] was used to calculate the specific Pd activity of the nanocatalyst ($A_{Pd,i}$) during a dechlorination experiment involving the substance *i*:

$$A_{Pd,i}\ [L\ g^{-1}\ min^{-1}] = \frac{V_{water}}{m_{Pd}\ \times\ \tau_{1/2}} = \frac{ln\ (\frac{c_{t0,i}}{c_{tx,i}})}{\ln 2\ \times\ c_{Pd} \times (t_x - t_0)} \qquad (1)$$

giving the water volume (V_{water} [L]) contaminated with the substance *i* at a given concentration $c_{t0,i}$, [µg L^{-1}] which can be treated with the mass of catalyst applied (m_{Pd} [g]) with a half-life of the reactant ($\tau_{1/2}$ [min]); or rather with the concentration of the reactant ($c_{t0,i}$) and ($c_{tx,i}$) [µg L^{-1}] at the chosen start time (t_0) and end time (t_x) [min] (where x is the specific time at which catalyst poisoning was done) of the dechlorination experiment, and the concentration of the applied catalyst (c_{Pd}) [g]. To achieve a given elimination goal, $A_{Pd,i}$ can be utilized to determine the necessary amount of Pd needed to treat a particular volume of water within a designated time frame.[26]

3. Results and discussion

3.1 Dechlorination of PCBs by finely dispersed Pd(0) nanocatalysts

The hydrodechlorination of the individual PCBs (PCB 1, 2, 3, 4, 18, 28, 52) and mixed PCBs (PCB 1+2+3), the formation of intermediate products and biphenyl as dechlorination product were observed over time in experiments with buffer solution and are shown graphically for selected congeners (Figure 2). Concentrations of all target compounds per specific dechlorination experiments are listed in Table S4–S8. The rate constants k_i values of the pseudo-first order kinetics for the educt elimination were determined for all dechlorination experiments (Figure S2). A single-step direct dechlorination to less chlorinated biphenyls or biphenyl without detachment from the catalyst may occur, as biphenyl formation begins immediately after the reaction starts for certain reactants. A multiplet mechanism has already been hypothesized in other studies for similar compounds.[35,37-39] However, the formation of intermediates shows that the polychlorinated biphenyls are reduced stepwise, at least partially and to a relevant extent. In any case, a preferred reaction path based on the product pattern found during dechlorination can be inferred. For POPs, the main dechlorination mechanisms are hydrogen transfer mode[40] and electron transfer mode.[41] In our experiments, the former mechanism is likely to occur because the Pd catalyst forms activated hydrogen, which can be added electrophilically to the aromatic rings.[42] Using mine water instead of buffer solution, no dechlorination of PCBs was observed in the experiments with finely dispersed Pd(0). This was not surprising, as the mine water can contain catalyst poisoning or inhabiting matrix (high levels of sulfur compounds, high salt content, high TOC[43]), which can lead to the inhibition or even deactivation of the exposed catalyst. The most frequently intermediates that were formed during the dechlorination are likely part of the main dechlorination pathway.[35] The formation of these intermediates is not caused by low catalytic activity or slower further transformation. Instead, a significant portion of the original reactant is converted into them. The main gradational reaction pathway was elucidated for the dechlorination of each individual PCB used. PCB 1 and biphenyl were formed in the experiments for all PCBs used as educts (PCB congeners 52, 28, 18, and 4). For PCB 52, the main further intermediate products for each degree of chlorination were PCB 18 and PCB 4; for PCB 28, the main further intermediate product was PCB 7; and for PCB 18, the main further intermediate product was PCB 4 (Figure 3). It can be concluded that primarily para-substituted chlorine atoms are replaced by hydrogen atoms, resulting in intermediates with ortho-substitution. In other words, para-substituted intermediates, such as PCB 15 from the dechlorination of PCB 28, are not formed at all. These findings confirm those of similar studies.[21,44–47] This reaction pathway is fundamentally different

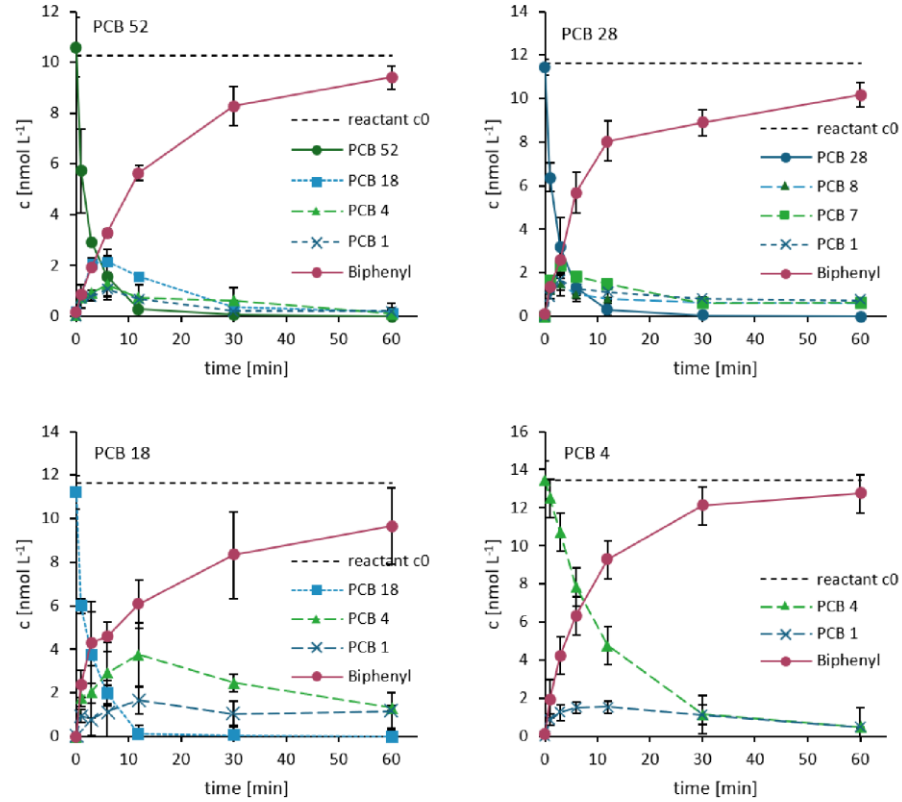

Fig. 2 Dechlorination of selected PCBs (PCB 52, 28, 18, 4) by finely dispersed Pd(0). For a better overview, only the formation of the main intermediate products and biphenyl are shown over time. The concentrations for all measured compounds is given in Tables S3–S6. Error bars show *sd*, number of replicates: $n = 4$ per time step ($c_{0,PCBs} = 3\ \mu\ L^{-1}$, $c_{Pd} = 150\ \mu g\ L^{-1}$ with d50% = 2.8 nm, $c_{NaHCO3} = 9\ g\ L^{-1}$, $c_{Na\text{-}citrate} = 2.94\ g\ L^{-1}$). The lines are provided to guide the eye.

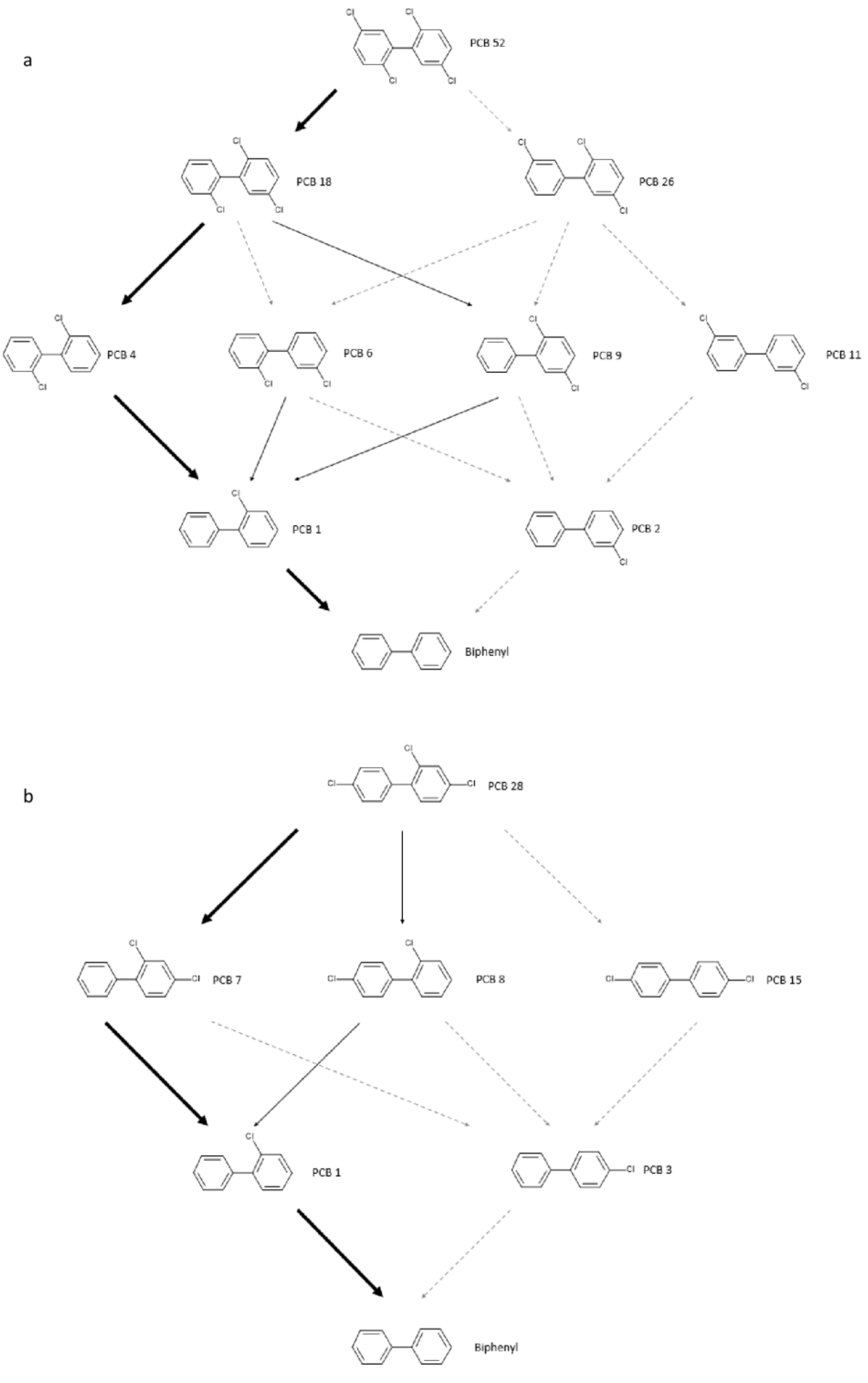

Fig. 3 Dechlorination pathway for selected PCBs. (a): summarized dechlorination pathways of PCBs 52, 18, and 4; (b): dechlorination pathway of PCB 28. The different lines refer to main dechlorination pathways (black bold), minor reaction pathways (black plain), and possible but not detected (or only detected to a small extent) reaction pathways (grey dotted). For reasons of clarity, possible direct pathways are not shown.

from microbiological dechlorination (reductive dechlorination)[48] or photolytic dechlorination (radical attack).[49] Such mechanisms do not form ortho-substituted PCBs, or only form them in very small quantities. However, this is not contradictory, given that distinct mechanisms result in varying reaction patterns.

The catalytic activity for each analyte is provided in Table 1. It is evident that the catalytic activity does not necessarily increase with decreasing chlorination degree. PCB 28 dechlorinates the fastest, while PCB 4 dechlorinates the slowest. This phenomenon was not observed for hexachlorobenzene, where elimination increased as the degree of chlorination decreased.[35] The difference between hexachlorobenzene and the other analytes lies in their molecular structure. When discussing PCBs, it is important to consider the steric hindrance caused by both the chlorine atoms[35] and the (chlorinated) phenyl ring. Here, PCB 4 has two ortho-substituted chlorine atoms that are shielded by each other and the nearby phenyl ring, while PCB 28 has only one ortho-substituted chlorine atom and two para-substituted chlorine atoms, resulting in no steric hindrance from either the other chlorine atoms or the other phenyl ring. The same applies to PCB 52, which has two ortho-substituted chlorine atoms and two meta-substituted chlorine atoms that can be easily exchanged for hydrogen atoms. The similarity in specific catalytic activities between PCB 52 and 18 is due to their very similar molecular structure. Both PCB 52 and 18 have a structure of twice ortho and twice meta, or rather twice ortho and once meta, respectively.

In both the experiments with individual substances (PCB 1, 2, 3) and the mixture (PCB 1-2-3), there were no differences in specific catalytic activities. Therefore, no preference for a particular analyte in the presence of several analytes could be determined (Table 1). The specific catalytic activity was not impaired even in the presence of substances with a lower steric hindrance. For instance, PCB 1, which has ortho substitution and higher steric hindrance, was dechlorinated at the same rate whether it was alone or in a mixture with PCB 2 (meta substituted, lower steric hindrance) and PCB 3 (para substituted, lowest steric hindrance).

Table 1 Mean values of specific catalytic activity of dispersed Pd(0) nanoparticles (d50% = 2.8 nm, $c_{0,PCBs}$ = 3 µg L^{-1}, c_{Pd} = 150 µg L^{-1}, c_{NaHCO3} = 9 g L^{-1}, $c_{Na\text{-}citrate}$ = 2.94 g L^{-1}). No dechlorination took place for the experiments with mine water instead of buffer solution as reaction matrix

Reactant (in buffer solution)	Pd activity A_{Pd} [L g^{-1} min^{-1}]
PCB 52	2740 ± 190
PCB 28	3350 ± 300
PCB 18	2600 ± 410
PCB 4	850 ± 20
PCB 3	3190 ± 160
PCB 2	2820 ± 90
PCB 1	990 ± 30
PCB 3 (mix PCB 1-2-3)	2940 ± 270
PCB 2 (mix PCB 1-2-3)	2650 ± 170
PCB 1 (mix PCB 1-2-3)	1160 ± 30

The specific activity A_{Pd} provided here has the advantage of being understood as a material property. This metric is independent of the contaminant concentration and reflects the amount of contaminated water that a specific amount of Pd can treat over a given period. Additionally, the concentrations tested here (3 µg L^{-1} for PCB 1, 2, 3, 4, 18, 28, and 52, and 1 µg L^{-1} for PCB 1, 2, 3 in mix) are environmentally relevant. Approximately one can say, compounds with a high degree of chlorination are more bioaccumulative and persistent than those with a low degree of chlorination.[50] Therefore, the dechlorination of such substances typically provides relief for both humans and the environment. The chlorination of PCBs plays a decisive role in their toxicity. Even PCBs with a medium degree of chlorination can be highly toxic due to the arrangement of the chlorine atoms. Dioxin-like PCBs have four to seven chlorine atoms, which are mainly para and meta substituted. Assuming that the environment is contaminated with highly chlorinated PCBs, remediation through microorganisms or UV light may result in the formation of dioxin-like PCBs as an intermediate product due to the affinity for splitting off ortho-substituted chlorine atoms.[48,49] However, treatment with Pd catalysts has shown that the para position is preferentially substituted,[44–46] and that the reaction pathway preferably does not involve dioxin-like PCBs.

3.2 Recovery rates of PCBs in Pd-PDMS wall coated reactors

To ensure the reusability of Pd/Al_2O_3 particles, which are difficult to recover by filtration when suspended, and to protect them from potential catalyst poisons in environmental media, it is beneficial to apply them in a thin PDMS layer to the inside of the reaction vessels. Preliminary tests were conducted to verify that the concentration was reduced due to dechlorination processes and not due to diffusion into the PDMS coating. The tests with selected PCB congeners, representative for the degrees of chlorination, showed evidence of a decreasing recovery rate for the thicker coatings and increasing degree of chlorination (Table 2).

The thicker the PDMS coating, the more the PCBs are captured. Biphenyl alone has a high recovery rate. This can be seen to be advantageous as the PCBs move into the coating towards the catalysts and faster dechlorination is encouraged, whereas biphenyl will partition out of the coating to a higher degree. A complete dechlorination produces the same amount of product (in mol) from the reactant. Therefore, since the degradation of the educt and the formation of biphenyl are related, the formation of biphenyl can also be used to determine the specific catalytic activity, by subtracting the amount of biphenyl from the amount of educt at the start time. However, caution is required here: In reactions that are slower or have many intermediates, the formation of the final product may be delayed. Therefore, the specific catalytic activity calculated based on the formation of the product is, at most, equal to and in most cases lower than the specific catalytic activity calculated from the decrease of the reactant. A PDMS mass of 75 mg per vial was chosen to allow for the indirect derivation of the reactants degradation rate from the formation rate of biphenyl as final dechlorination product.

Table 2 Recovery rates [%] of Biphenyl and chosen PCBs in Pd-PDMS wall coated reactors, n = 3 per time step. The results for different diffusion times (1, 24, and 48 h) were similar and therefore included to mean values (i.e., n = 9 per substance and treatment)

Analyte	Recovery rate [%] with 750 mg of PDMS	Recovery rate [%] with 375 mg of PDMS	Recovery rate [%] with 75 mg of PDMS
PCB 52	0	0	0
PCB 18	0	1 ± 4	1 ± 4
PCB 4	4 ± 4	6 ± 3	11 ± 4
PCB 2	11 ± 5	17 ± 5	24 ± 6
Biphenyl	67 ± 6	78 ± 6	96 ± 8

3.3 Dechlorination of PCBs by suspended and PDMS-embedded Pd/Al_2O_3 catalysts

The experiments with finely dispersed Pd(0) nanoparticles have already elucidated the preferred reaction pathway along with the corresponding intermediates (chapter 3.1). No other reaction pathway takes place with suspended or embedded Pd/Al_2O_3 catalysts (Figure 1b, 1d, Figure 4), only that dehalogenation proceeds more slowly. The focus here is on the special catalytic activity of the suspended and the embedded Al_2O_3 catalysts, both with buffer solution and with mine water as reaction matrices.

3.3.1 Performance of suspended and embedded Pd/Al2O3 catalysts with buffer solution matrix

In these experiments, the specific catalytic activities of the Pd/Al_2O_3 catalysts were determined under optimal matrix conditions without catalyst poisons. The rate constant *k* value of the pseudo-first order kinetics for the formation of the product (elimination of the educt) was determined for all dechlorination experiments (Figures S3–S4). The activity levels are comparable to those of similar substances.[36,51] The specific activity of the suspended Pd/Al_2O_3 particles is only one third of that of the dispersed Pd(0) particles. And for the PDMS-embedded Pd/Al_2O_3 particles it is a whole order of magnitude lower than for the suspended particles (Table 3), as analytes must first move through the silicone to the embedded catalysts. However, the difference in activity is only one order of magnitude lower, which emphasizes the benefits of Pd/Al_2O_3 catalysts over other Pd catalysts.[32] No differences were found in the ratio of specific activities of suspended and PDMS-embedded and Pd/Al_2O_3 catalysts among the individual PCBs (with ratios of 1.2–1.4 x 10^3). Therefore, it can be assumed that the degree of chlorination of the PCBs has no influence on the specific catalytic activity of embedded Pd/Al_2O_3 catalysts. Anyhow, differences could still occur with highly chlorinated PCBs. However, these promising results also have a limitation. It is unlikely that environmental media will provide ideal conditions for the catalysts, and purifying the media to the point where the catalyst activity is not affected is prohibitively expensive. The following step was therefore undertaken to test whether the protected catalyst can perform under extremely challenging, naturally occurring conditions.

Fig. 4 Reaction vials with an inner PDMS layer for the experiments with embedded Pd/Al_2O_3 catalysts. Left: pure PDMS without Pd/Al_2O_3; right: PDMS including Pd/Al_2O_3 (0.3 mg).

3.3.2 Performance of suspended and embedded Pd/Al2O3 catalysts with mine water matrix

In these experiments, the specific catalytic activities of the Pd/Al_2O_3 catalysts were determined under real conditions with catalyst poison rich matrices. As with the finely dispersed Pd(0) catalysts (chapter 3.1), no or only very slight dehalogenation occurred in the tests with suspended Pd/Al_2O_3 catalysts with mine water matrix. As in previous tests, the catalyst poisons contained in the mine water severely limit the activity, what was also the result in other studies. However, with catalysts embedded in the PDMS, dechlorination occurred for the first time using mine water as a matrix (Table 4), although the specific catalytic activity was much lower than in the buffer solution. The rate constant *k* values of the pseudo-first order kinetics of product formation (educt elimination) were determined for all dechlorination experiments (Figures S5–S6).

The activity of the catalyst is affected differently by the three mine waters, due to their different compositions (Table S9). The embedded catalysts perform about as well in the presence of Walsum mine water as in the presence of Reden mine water. The Stinnes mine water, which has a high concentration of chloride and metals, has the strongest inhibitory effect on the activity, therefore no dechlorination could be detected. The concentrations of reduced

Table 3 Mean values of specific Pd activity and their ratios for PCB reactants with suspended ($A_{Pd,susp}$) and PDMS-embedded ($A_{Pd,emb}$) Pd/Al_2O_3 catalysts for dechlorination in buffer solution matrix

Reactant	$A_{Pd,susp}$ ($L\ g^{-1}\ min^{-1}$)	$A_{Pd,emb}$ ($mL\ g^{-1}\ min^{-1}$)	A_{Pd}-ratios$_{(susp/emb)}$
PCB 52	860 ± 100	610 ± 90	1.4 x 10^3
PCB 28	1130 ± 110	830 ± 100	1.4 x 10^3
PCB 18	720 ± 30	610 ± 70	1.2 x 10^3
PCB 4	260 ± 50	200 ± 30	1.3 x 10^3

Table 4 Mean values of specific Pd activity for the dechlorination of chosen PCBs by PDMS-embedded Pd/Al_2O_3 catalysts with mine water matrix

Reactant	$A_{Pd,emb}$ (mL g^{-1} min^{-1}) 'Walsum'	$A_{Pd,emb}$ (mL g^{-1} min^{-1}) 'Reden'	$A_{Pd,emb}$ (mL g^{-1} min^{-1}) 'Stinnes'
PCB 52	100 ± 30	180 ± 10	-
PCB 28	120 ± 30	210 ± 70	-
PCB 18	100 ± 30	170 ± 50	-
PCB 4	20 ± 5	90 ± 30	-

S species, if present at all, are relatively low in the three mine waters compared to the corresponding sulfate concentration. The absence of high sulfide concentrations explains why the mine water does not rapidly deactivate the catalyst albeit protected, because PDMS protected catalysts remain vulnerable to non-ionic sulfide species.[52] PCB 18 is the congener with the highest concentration in German mine water,[7] making its catalyst activities (100–170 mL g^{-1} min^{-1}) of particular interest for further extrapolations. Mine water is pumped and discharged in high volumes, averaging 1–10 m^3 min^{-1} per mine. To completely dechlorinate this quantity within 1 min, it would require 6–100 kg (best to worst case) of Pd/Al_2O_3 catalyst. However, this amount could be reduced by increasing the contact time with the catalyst, for example, from 1 min to 1 h. In this case, only 0.1–1.7 kg of catalyst would be needed. In some cases, it may be necessary to consider whether a shorter contact time with a larger amount of catalyst or a longer contact time with a smaller amount of catalyst is more effective. When dealing with mine water and its significant and continuous volume flow, it is more practical to increase the amount of catalyst. Additionally, the activity of the incorporated catalysts could be enhanced. In the present study, a thin PDMS layer was selected to facilitate observation of the reaction process. Given the recent evidence of dechlorination in mine water, it is recommended to use a thicker PMDS layer to enhance catalyst protection against deactivation,[31] or, based on the findings with the Stinnes mine water, an additional layer of sulfide-scavengers[52] could be applied.

4. Conclusions

Palladium-catalyzed hydrodechlorination is a rapid and straightforward method for dechlorinating POPs like PCBs and transforming them into less hazardous and more readily degradable substances. This process consumes minimal energy and resources when conducted under environmental conditions. In the dechlorination process, chlorine atoms in the para and meta positions are preferentially substituted first, likely due to steric hindrance from the other phenyl ring. The reaction rate was determined by the positioning of the chlorine atoms and not by their number. The catalysts showed high catalytic activity at low concentrations (0.15 mg L^{-1}) and at ambient pressure and temperature, as well as at environmentally relevant concentrations in the µg L^{-1} range. All of the seven tested PCBs were dechlorinated within one hour in the presence of suspended Pd/Al_2O_3 particles in buffer solution, allowing for the tracking of intermediates and reaction pathways. However, suspended particles cannot be directly applied for the treatment of contaminated water: catalyst loss and inhibition by catalyst poisoning matrix are methodic limitations that prevent the intended scaling for environmental applications. Therefore, to prevent catalyst loss and protect against a wide range of catalyst poisons, Pd/Al_2O_3 particles were incorporated into a protective PDMS layer. The results showed that under optimal reaction conditions, the protection reduced catalyst activity, but the specific catalytic activity remained high enough to outweigh the disadvantages. The protective film not only facilitates dechlorination in "ideal" buffer solutions, but its strength is particularly evident in the treatment of matrix-rich waters, as demonstrated in this study even for highly matrix-rich mine water rich in catalyst poisons. As mine water remains one of the few point sources of PCBs, appropriate water treatment technologies are needed to prevent further PCB release to the environment. Although further optimization of reaction efficiency and application design is still needed before large-scale applicability, our results clearly demonstrate the potential and general feasibility of protected Pd nanocatalysts for the elimination of PCBs from matrix-rich waters.

Author contributions

Katrin Wiltschka: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – Original Draft, Writing – Review & Editing, Visualization, Funding acquisition. **Silviu Bobric:** Formal analysis, Investigation. **Rolf-Alexander Düring:** Resources, Writing – Review & Editing, Funding acquisition. **Leonard Böhm:** Conceptualization, Methodology, Validation, Resources, Writing – Review & Editing, Supervision, Funding acquisition.

Conflicts of interest

There are no conflicts to declare.

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References

1 L. Persson, B. M. Carney Almroth, C. D. Collins, S. Cornell, C. A. de Wit, M. L. Diamond, P. Fantke, M. Hassellöv, M. Macleod, M. W. Ryberg, P. Søgaard Jørgensen, P. Villarrubia-Gómez, Z. Wang and M. Z. Hauschild, Outside the Safe Operating Space of the Planetary Boundary for Novel Entities, *Environ. Sci. Technol.*, 2022, **56**, 1510–1521.

2 UNEP, *Stockholm Convention on Persistent Organic Pollutants: United Nations Environment Programm*, 2001.

3 L. Li, C. Chen, D. Li, K. Breivik, G. Abbasi and Y.-F. Li, What do we know about the production and release of persistent organic pollutants in the global environment?, *Environ. Sci.: Adv.*, 2023, **2**, 55–68.

4 H. Fiedler, *Global and local disposition of PCB. In: PCBs – recent advances in the environmental toxicology and health effects.*, University Press of Kentucky, Kentucky, pp 11–15, 2001.

5 K. Breivik, A. Sweetman, J. Pacyna and K. Jones, Towards a global historical emission inventory for selected PCB congeners — a mass balance approach: 2. Emissions, *Sci. Total Environ. (The Science of The Total Environment)*, 2002, **290**, 199–224.

6 D. W. Bench, in *Mine Design, Operations & Closure Conference, Polson, Montana, April 27-May 1, 2003*, 2003, pp. 1–12.

7 K. Wiltschka, C. Wolkersdorfer, R.-A. Düring and L. Böhm, Between Underground and the Deep Blue Sea: Contamination of Mine Water Effluents by Polychlorinated Biphenyls (PCBs), *ACS EST Water*, 2023, **3**, 3474–3484.

8 J.-P. Desforges, A. Hall, B. McConnell, A. Rosing-Asvid, J. L. Barber, A. Brownlow, S. de Guise, I. Eulaers, P. D. Jepson, R. J. Letcher, M. Levin, P. S. Ross, F. Samarra, G. Víkingson, C. Sonne and R. Dietz, Predicting global killer whale population collapse from PCB pollution, *Science*, 2018, **361**, 1373–1376.

9 R. Lohmann, B. Vrana, D. Muir, F. Smedes, J. Sobotka, E. Y. Zeng, L.-J. Bao, I. J. Allan, P. Astrahan, R. O. Barra, T. Bidleman, E. Dykyi, N. Estoppey, G. Fillmann, N. Greenwood, P. A. Helm, L. Jantunen, S. Kaserzon, J. V. Macías, K. A. Maruya, F. Molina, B. Newman, R. M. Prats, M. Tsapakis, M. Tysklind, B. L. van Drooge, C. J. Veal and C. S. Wong, Passive-Sampler-Derived PCB and OCP Concentrations in the Waters of the World–First Results from the AQUA-GAPS/MONET Network, *Environ. Sci. Technol.*, 2023, **57**, 9342–9352.

10 N. D. Kuepper, L. Böhm, C. Braun, P. Bustamante, R.-A. Düring, M. M. Libertelli and P. Quillfeldt, 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. (Polar Biology)*, 2022, **45**, 1229–1245.

11 L. Montano, C. Pironti, G. Pinto, M. Ricciardi, A. Buono, C. Brogna, M. Venier, M. Piscopo, A. Amoresano and O. Motta, Polychlorinated Biphenyls (PCBs) in the Environment: Occupational and Exposure Events, Effects on Human Health and Fertility, *Toxics*, 2022, **10**. DOI: 10.3390/toxics10070365.

12 M. Vidali, Bioremediation. An overview, *Pure and Applied Chemistry*, 2001, **73**, 1163–1172.

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

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

15 M. Mackova, T. Macek, J. Ocenaskova, J. Burkhard, K. Demnerova and J. Pazlarova, Biodegradation of polychlorinated biphenyls by plant cells, *International Biodeterioration & Biodegradation*, 1997, **39**, 317–325.

16 A. Kumar, B. S. Bisht, V. D. Joshi and T. Dhewa, Review on Bioremediation of Polluted Environment: A Management Tool, *International Journal of Environmental Sciences*, 2011.

17 B. P. Chaplin, M. Reinhard, W. F. Schneider, C. Schüth, J. R. Shapley, T. J. Strathmann and C. J. Werth, Critical review of Pd-based catalytic treatment of priority contaminants in water, *Environmental science & technology*, 2012, **46**, 3655–3670.

18 C. Schüth and M. Reinhard, Hydrodechlorination and hydrogenation of aromatic compounds over palladium on alumina in hydrogen-saturated water, *Applied Catalysis B: Environmental*, 1998, **18**, 215–221.

19 C. G. Schreier and M. Reinhard, Catalytic hydrodehalogenation of chlorinated ethylenes using palladium and hydrogen for the treatment of contaminated water, *Chemosphere*, 1995, **31**, 3475–3487.

20 F.-D. Kopinke, K. Mackenzie and R. Köhler, Catalytic hydrodechlorination of groundwater contaminants in water and in the gas phase using Pd/γ-Al2O3, *Applied Catalysis B: Environmental*, 2003, **44**, 15–24.

21 K. Johnson and M. Lu, Experimental study of catalytic hydrodechlorination (HDC) of Aroclor 1232, *Chemosphere*, 2024, **349**, 140987.

22 C. Schüth, S. Disser, F. Schüth and M. Reinhard, Tailoring catalysts for hydrodechlorinating chlorinated hydrocarbon contaminants in groundwater, *Applied Catalysis B: Environmental*, 2000, **28**, 147–152.

23 C. Schüth, N.-A. Kummer, C. Weidenthaler and H. Schad, Field application of a tailored catalyst for hydrodechlorinating chlorinated hydrocarbon contaminants in groundwater, *Applied Catalysis B: Environmental*, 2004, **52**, 197–203.

24 Y. Wang, D. Zhou, Y. Wang, L. Wang and L. Cang, Automatic pH control system enhances the dechlorination of 2,4,4‘-trichlorobiphenyl and extracted PCBs from contaminated soil by nanoscale Fe^0 and Pd/Fe^0, *Environ Sci Pollut Res*, 2012, **19**, 448–457.

25 P. Sun, L. Cheng, S. Gao, X. Weng and X. Dong, Industrial Chlorinated Organic Removal with Elimination of Secondary Pollution: A Perspective, *J. Phys. Chem. C*, 2023, **127**, 6610–6618.

26 M. Bunge and K. Mackenzie, in *Bio-nanoparticles*, ed. O. V. Singh, Wiley Blackwell, Hoboken, New Jersey, 2015, pp. 205–224.

27 M. Schlüter, T. Hentzel, C. Suarez, M. Koch, W. G. Lorenz, L. Böhm, R.-A. Düring, K. A. Koinig and M. Bunge, Synthesis of novel palladium(0) nanocatalysts by microorganisms from heavy-metal-influenced high-alpine sites for dehalogenation of polychlorinated dioxins, *Chemosphere*, 2014, **117**, 462–470.

28 Y. Si, Z.-Y. Guo, Y. Meng, H.-H. Li, L. Chen, A.-Y. Zhang, C.-H. Gu, W.-W. Li and H.-Q. Yu, Reusing Sulfur-Poisoned Palladium

Waste as a Highly Active, Nonradical Fenton-like Catalyst for Selective Degradation of Phenolic Pollutants, *Environ. Sci. Technol.*, 2022, **56**, 564–574.

29 G. Zhao, T. Liu, B. Wu, B. Chen and C. Chu, Constructing the Support as a Microreactor and Regenerator for Highly Active and In Situ Regenerative Hydrogenation Catalyst, *Adv Funct Materials*, 2021, **31**. DOI: 10.1002/adfm.202100971.

30 E. M. Hotze, T. Phenrat and G. v. Lowry, Nanoparticle Aggregation: Challenges to Understanding Transport and Reactivity in the Environment, *Journal of Environment Quality*, 2010, **39**, 1909.

31 D. Comandella, S. Woszidlo, A. Georgi, F.-D. Kopinke and K. Mackenzie, Efforts for long-term protection of palladium hydrodechlorination catalysts, *Applied Catalysis B: Environmental*, 2016, **186**, 204–211.

32 D. Comandella, M. Werheid, F.-D. Kopinke and K. Mackenzie, Optimization of PDMS-embedded palladium hydrodechlorination catalysts, *Chemical Engineering Journal*, 2017, **319**, 21–30.

33 P. Bradt, F. L. Mohler and V. H. Dibeler, Mass spectrum of sulfur vapor, *J. Res. Natl. Bur. Stand. (Journal of Research of the National Bureau of Standards)*, 1956, **57**, 223.

34 A.-K. Herrmann, P. Formanek, L. Borchardt, M. Klose, L. Giebeler, J. Eckert, S. Kaskel, N. Gaponik and A. Eychmüller, Multimetallic Aerogels by Template-Free Self-Assembly of Au, Ag, Pt, and Pd Nanoparticles, *Chem. Mater.*, 2014, **26**, 1074–1083.

35 K. Wiltschka, L. Neumann, M. Werheid, M. Bunge, R.-A. Düring, K. Mackenzie and L. Böhm, Hydrodechlorination of hexachlorobenzene in a miniaturized nano-Pd(0) reaction system combined with the simultaneous extraction of all dechlorination products, *Appl. Catal. B: Environ. (Applied Catalysis B: Environmental)*, 2020, **275**, 119100.

36 K. Mackenzie, H. Frenzel and F.-D. Kopinke, Hydrodehalogenation of halogenated hydrocarbons in water with Pd catalysts: Reaction rates and surface competition, *Applied Catalysis B: Environmental*, 2006, **63**, 161–167.

37 V. A. Yakovlev, V. I. Simagina, S. N. Trukhan and V. A. Likholobov, Kinetic study of liquid-phase hydrodechlorination of hexachlorobenzene on Ni/C and 2%PdNi/C, *Kinet Catal*, 2000, **41**, 25–32.

38 C. A. Coulson, *Valence. 2nd ed., Oxford: University Press, London*, 1965.

39 M. Kraus and V. Bazant, eds., *Catalysis. Proceedings of the Fifth Internat. Congress on Catalysis, Miami Beach, Fl., 20-26 Aug., 1972, pp. 1073-1083*, North-Holland Pub. Co.; American Elsevier Co, Amsterdam, New York, 1973, 5th.

40 H. Fueno, K. Tanaka and S. Sugawa, Theoretical study of the dechlorination reaction pathways of octachlorodibenzo-p-dioxin, *Chemosphere*, 2002, **48**, 771–778.

41 S. Arulmozhiraja and M. Morita, Electron Affinities and Reductive Dechlorination of Toxic Polychlorinated Dibenzofurans: A Density Functional Theory Study, *J. Phys. Chem. A*, 2004, **108**, 3499–3508.

42 X. Gao, W. Wang and X. Liu, Low-temperature dechlorination of hexachlorobenzene on solid supports and the pathway hypothesis, *Chemosphere*, 2008, **71**, 1093–1099.

43 D. Banks, P. L. Younger, R.-T. Arnesen, E. R. Iversen and S. B. Banks, Mine-water chemistry: the good, the bad and the ugly, *Environ. Geol. (Environmental Geology)*, 1997, **32**, 157–174.

44 R. LAPIERRE, Hydrodechlorination of polychlorinated biphenyl, *Journal of Catalysis*, 1978, **52**, 230–238.

45 S. Agarwal, S. R. Al-Abed, D. D. Dionysiou and E. Graybill, Reactivity of Substituted Chlorines and Ensuing Dechlorination Pathways of Select PCB Congeners with Pd/Mg Bimetallics, *Environ. Sci. Technol.*, 2009, **43**, 915–921.

46 K. Venkatachalam, X. Arzuaga, N. Chopra, V. G. Gavalas, J. Xu, D. Bhattacharyya, B. Hennig and L. G. Bachas, Reductive dechlorination of 3,3‘,4,4‘-tetrachlorobiphenyl (PCB77) using palladium or palladium/iron nanoparticles and assessment of the reduction in toxic potency in vascular endothelial cells, *Journal of hazardous materials*, 2008, **159**, 483–491.

47 G. v. Lowry and K. M. Johnson, Congener-specific dechlorination of dissolved PCBs by microscale and nanoscale zerovalent iron in a water/methanol solution, *Environ. Sci. Technol.*, 2004, **38**, 5208–5216.

48 J. A. Field and R. Sierra-Alvarez, Microbial transformation and degradation of polychlorinated biphenyls, *Environmental pollution (Barking, Essex : 1987)*, 2008, **155**, 1–12.

49 K. H. Wong and P. K. Wong, Degradation of Polychlorinated Biphenyls by UV-Catalyzed Photolysis, *Human and Ecological Risk Assessment: An International Journal*, 2006, **12**, 259–269.

50 D. Henschler, Toxicity of Chlorinated Organic Compounds: Effects of the Introduction of Chlorine in Organic Molecules, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 1920–1935.

51 H. Hildebrand, K. Mackenzie and F.-D. Kopinke, Highly Active Pd-on-Magnetite Nanocatalysts for Aqueous Phase Hydrodechlorination Reactions, *Environ. Sci. Technol.*, 2009, **43**, 3254–3259.

52 D. Comandella, M. H. Ahn, H. Kim and K. Mackenzie, Enhanced protection of PDMS-embedded palladium catalysts by co-embedding of sulphide-scavengers, *The Science of The Total Environment*, 2017, **601-602**, 658–668.

Supporting Information

Coating-Protected Pd/Al_2O_3 Catalysts for the Elimination of Polychlorinated Biphenyls (PCBs) from Mine Water Effluents

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Summary: 11 pages including experimental and analytical details (9 tables and 6 figures).

Additional Information on Materials and Methods

The neat PCB substances (PCB 1–4, 6–9, 11, 15, 18, 26, 28, 52) were prepared as stock solutions of single substances (114–150 mg L^{-1}) in methanol (≥ 99.9%, p.a. quality, Carl Roth GmbH, Karlsruhe, Germany) that were mixed to the working solutions (WS) 'WS 28' (Biphenyl, PCBs 1, 3, 7, 8, 15, and 28) and 'WS 4-18-52' (Biphenyl, PCBs 1, 2, 4, 6, 9, 11, 18, 26, and 52) with concentrations of 0.05, 0.5 and 5 mg L^{-1}. Educt stock solutions (ESS) of single substances (Biphenyl, PCBs 1, 2, 3, 4, 18, 28, and 52) and a mix of the three monochlorinated congeners (PCB 1, 2, 3) were diluted in methanol to concentrations of 10 and 3 mg L^{-1} each, respectively, yielding working solutions for dechlorination experiments. Working solutions were stored in Certan capillary bottles (LGC Standards GmbH, Wesel, Germany).

The analytes for the internal standards were mixed according to Table S1 in a concentration of 5 mg L^{-1}, and combined according to Table S2.

Table S1. Working solutions for analytes and their respective internal standards (IS), used for external calibration in dechlorination experiment measurements with PCBs 52, 18, or 4 (a: WS I) and PCB 28 (b: WS II).

a)	WS I ('4-18-52')	ISS I ('4-18-52')
	Analyte	IS
	Biphenyl	Biphenyl-d_{10}
	PCB 1	PCB 3-d_5
	PCB 2	PCB 3-d_5
	PCB 4	PCB 3-d_5
	PCB 6	PCB 9-d_5
	PCB 9	PCB 9-d_5
	PCB 11	PCB 18-d_5
	PCB 18	PCB 18-d_5
	PCB 26	PCB 28
	PCB 52	PCB 49

b)	WS II ('28')	ISS II ('28')
	Analyte	IS
	Biphenyl	Biphenyl-d_{10}
	PCB 1	PCB 3-d_5
	PCB 3	PCB 3-d_5
	PCB 7	PCB 9-d_5
	PCB 8	PCB 9-d_5
	PCB 15	PCB 26
	PCB 28	PCB 26

Table S2. Combination of educt stock solutions (ESS), working solutions (WS) and internal standard solutions (ISS).

ESS	WS	ISS
PCB 1	WS II	ISS II
PCB 2	WS II	ISS II
PCB 3	WS II	ISS II
PCB 1+2+3	WS II	ISS II
PCB 4	WS I	ISS I
PCB 18	WS I	ISS I
PCB 28	WS II	ISS II
PCB 52	WS I	ISS I

Particle size distribution of Pd(0) nanoparticles – Figure S1

The Pd nanoparticles were synthesized by chemical reduction.[1] A stock solution of sodium borohydride was added to a boiling solution with Pd precursor $PdCl_2$ x 2HCl and sodium citrate as stabilizer. The suspension was investigated with transmission electron microscopy (TEM) (JEOL JEM-1400 Plus microscope, operated at 120 kV). The Pd nanoparticles had a size of 2.8 nm (d50%) (Figure S1).

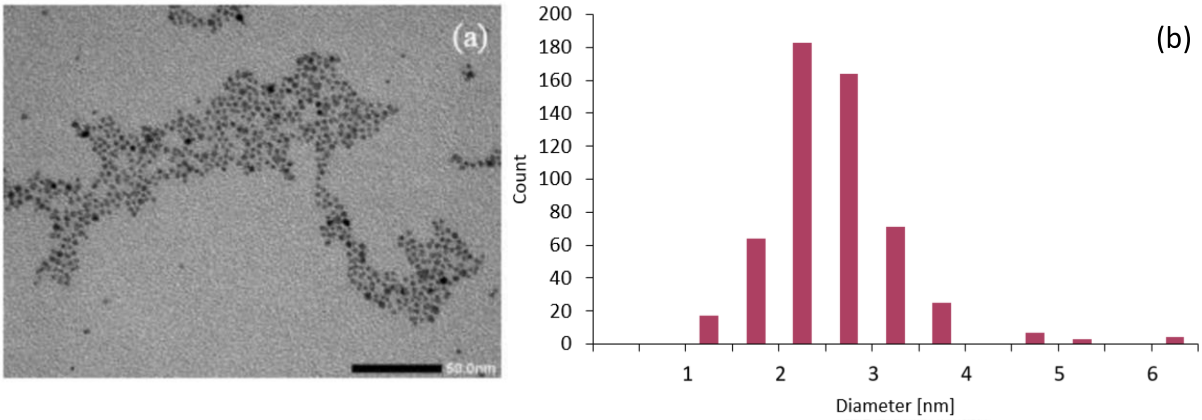

Figure S1. (a) TEM image of the citrate-stabilized Pd(0) nanoparticles, (b) particle size distribution of the Pd(0) nanoparticles (dried, TEM, d50% = 2.8 nm).

Quality assurance

To avoid agglomeration of suspended nanoparticles, the entire equipment which came in contact with nanoparticles, solutions and water was washed before use with nitric acid (HNO_3, 33 %), mQ water, and acetone. The 20-mL glass vials and screw caps were not reused.

Blanks, both with and without PDMS coating, were run to determine the sorption on glass walls/PDMS and to include this in the further calculations.

The mine water analyzed in this study has a background load of PCBs in the ng L^{-1} range. The additional amount of PCBs (µg L^{-1}) is high enough that the inherent background load only accounts for a maximum of 1% and is therefore not considered significant. However, the concentrations of the specific congeners used were determined for each mine water sample and included in the subsequent calculations.

Instrumental analysis / GC-MS parameters – Table S3

The MS was used in selected ion monitoring (SIM) mode with respective segments for the analytes. Detailed parameters for GC-MS conditions are given in Table S3.

Table S3. Parameters for MS detection of analytes and IS in SIM mode. Trichlorobiphenyls had an additional second qualifier in experiments with mine water to improve their differentiation from sulfur component spectra that can occur in mine water.[2]

Substance	Purpose	RT [min]	Quantifier [m/z]	Qualifier 1 [m/z]	Qualifier 2 [m/z]
Biphenyl-d_{10}	IS	16.48	164	80	
Biphenyl	Analyte	16.58	154	76	
PCB 1	Analyte	18.88	188	152	
PCB 2	Analyte	20.51	188	152	
PCB 3-d_5	IS	20.76	193	157	
PCB 3	Analyte	20.81	188	152	
PCB 4	Analyte	21.23	222	152	
PCB 9-d_5	IS	22.24	227	157	
PCB 9	Analyte	22.28	222	152	
PCB 7	Analyte	22.35	222	152	
PCB 6	Analyte	22.64	222	152	
PCB 18-d_5	IS	24.30	263	191	
PCB 11	Analyte	24.33	222	152	
PCB 18	Analyte	24.35	256	186	150
PCB 15	Analyte	25.05	222	152	
PCB 26	Analyte / IS	25.85	256	186	150
PCB 28	Analyte / IS	26.35	256	186	150
PCB 52	Analyte	27.27	292	220	
PCB 49	IS	27.44	292	220	

Table S4. Hydrodechlorination of PCB 52 with finely dispersed Pd(0) nanoparticles. Mean values [nmol L^{-1}] are provided for the PCB reactant, intermediate product PCB congeners, and biphenyl as product of complete hydrodechlorination. Number of replicates per reaction time: *n* = 4.

Time [min]	Biphenyl	PCB 1	PCB 2	PCB 4	PCB 6	PCB 9	PCB 11	PCB 18	PCB 26	PCB 52
0	0.16±0.06	0.01±0.02	0.01±0.00	0.02±0.03	0.00±0.00	0.01±0.07	0.01±0.02	0.20±0.14	0.01±0.02	10.59±1.19
1	0.89±0.11	0.74±0.10	0.66±0.01	0.76±0.14	0.01±0.01	0.22±0.14	0.10±0.04	0.79±0.46	0.00±0.04	5.73±1.65
3	1.90±0.07	0.76±0.13	0.66±0.01	0.93±0.11	0.01±0.01	0.43±0.09	0.10±0.02	2.10±0.21	0.01±0.02	2.95±0.06
6	3.28±0.16	1.06±0.41	0.69±0.02	1.26±0.47	0.00±0.03	0.42±0.23	0.10±0.05	2.15±0.49	0.02±0.05	1.56±0.80
12	5.64±0.31	0.69±0.02	0.68±0.00	0.74±0.03	0.01±0.00	0.24±0.04	0.10±0.01	1.58±0.12	0.01±0.02	0.29±0.96
30	8.27±0.78	0.20±0.40	0.20±0.03	0.63±0.49	0.00±0.02	0.22±0.05	0.10±0.02	0.37±0.26	0.00±0.03	0.00±0.51
60	9.40±0.45	0.20±0.31	0.06±0.01	0.10±0.22	0.00±0.01	0.18±0.18	0.10±0.01	0.17±0.09	0.01±0.01	0.01±0.13

Table S5. Hydrodechlorination of PCB 28 with finely dispersed Pd(0) nanoparticles. Mean values [nmol L^{-1}] are provided for the PCB reactant, intermediate product PCB congeners, and biphenyl as product of complete hydrodechlorination. Number of replicates per reaction time: *n* = 4.

Time [min]	Biphenyl	PCB 1	PCB 3	PCB 7	PCB 8	PCB 15	PCB 28
0	0.10±1.46	0.00±0.09	0.00±0.03	0.00±0.15	0.00±0.11	0.00±0.01	11.42±0.37
1	1.36±0.33	0.91±0.12	0.10±0.03	1.60±0.15	1.21±0.10	0.01±0.02	6.38±0.66
3	2.58±0.59	1.65±0.72	0.00±0.14	2.30±0.33	1.47±0.29	0.00±0.01	3.20±1.32
6	5.69±0.95	1.28±0.45	0.00±0.06	1.82±0.18	1.01±0.05	0.02±0.01	1.32±0.63
12	8.04±0.92	1.10±0.36	0.10±0.03	1.51±0.13	0.81±0.04	0.01±0.01	0.31±0.29
30	8.90±0.60	0.82±0.08	0.10±0.00	0.61±0.04	0.62±0.00	0.00±0.00	0.03±0.02
60	10.17±0.56	0.74±0.06	0.10±0.01	0.64±0.07	0.60±0.00	0.00±0.00	0.01±0.01

Table S6. Hydrodechlorination of PCB 18 with finely dispersed Pd(0) nanoparticles. Mean values [nmol L^{-1}] are provided for the PCB reactant, intermediate product PCB congeners, and biphenyl as product of complete hydrodechlorination. Number of replicates per reaction time: *n* = 4.

Time [min]	Biphenyl	PCB 1	PCB 2	PCB 4	PCB 6	PCB 9	PCB 18
0	0.01±0.01	0.00±0.01	0.00±0.02	0.00±0.05	0.00±0.01	0.00±0.02	11.21±0.78
1	2.41±0.61	0.94±0.31	0.17±0.09	1.78±0.43	0.00±0.03	0.38±0.07	5.99±0.35
3	4.31±1.88	0.80±0.74	0.18±0.07	2.06±1.20	0.01±0.05	0.50±0.46	3.79±1.96
6	4.57±0.70	1.14±1.20	0.16±0.06	2.90±1.41	0.01±0.03	0.82±0.24	1.97±0.57
12	6.08±1.10	1.65±0.63	0.21±0.12	3.76±1.44	0.01±0.02	0.90±0.19	0.14±0.37
30	8.33±1.99	1.03±0.61	0.11±0.02	2.46±0.39	0.00±0.02	0.49±0.31	0.03±0.47
60	9.65±1.75	1.15±0.88	0.10±0.01	1.31±0.12	0.01±0.01	0.36±0.42	0.01±0.36

Table S7. Hydrodechlorination of PCB 4 with finely dispersed Pd(0) nanoparticles. Mean values [nmol L^{-1}] are provided for the PCB reactant, intermediate product PCB congeners, and biphenyl as product of complete hydrodechlorination. Number of replicates per reaction time: *n* = 4.

Time [min]	Biphenyl	PCB 1	PCB 4
0	0.10±0.00	0.00±0.01	13.44±2.75
1	1.96±0.45	0.87±0.30	12.49±1.29
3	4.25±1.63	1.26±0.41	10.72±2.96
6	6.34±1.38	1.52±0.29	7.85±4.69
12	9.28±1.23	1.55±0.32	4.76±1.14
30	12.11±0.72	1.14±0.52	1.16±0.58
60	12.74±1.79	0.47±0.01	0.51±0.08

Table S8. Hydrodechlorination of PCB 1, 2, and 3 with finely dispersed Pd(0) nanoparticles. Mean values [nmol L^{-1}] are provided for the PCB reactant, intermediate product PCB congeners, and biphenyl as product of complete hydrodechlorination. Number of replicates per reaction time: *n* = 4.

Time [min]	Biphenyl	PCB 1	Biphenyl	PCB 2	Biphenyl	PCB 3
0	0.00±0.01	15.95±1.66	0.39±0.00	15.62±2.33	0.20±0.18	15.72±0.24
1	1.11±0.68	14.58±1.53	6.45±1.46	9.45±1.11	7.58±1.05	8.35±2.11
3	4.73±0.81	11.35±1.98	9.78±3.65	6.02±3.08	11.03±2.43	4.30±1.51
6	7.80±1.30	8.28±1.14	13.29±2.00	2.52±0.38	14.01±3.17	1.59±2.35
12	11.33±1.33	4.68±0.52	15.29±1.96	0.42±0.47	15.92±4.05	0.26±0.12
30	14.27±1.52	1.41±0.61	15.84±2.66	0.04±0.16	16.13±2.20	0.03±0.13
60	14.84±0.78	0.73±0.04	15.94±1.86	0.01±0.17	16.20±1.26	0.01±0.04

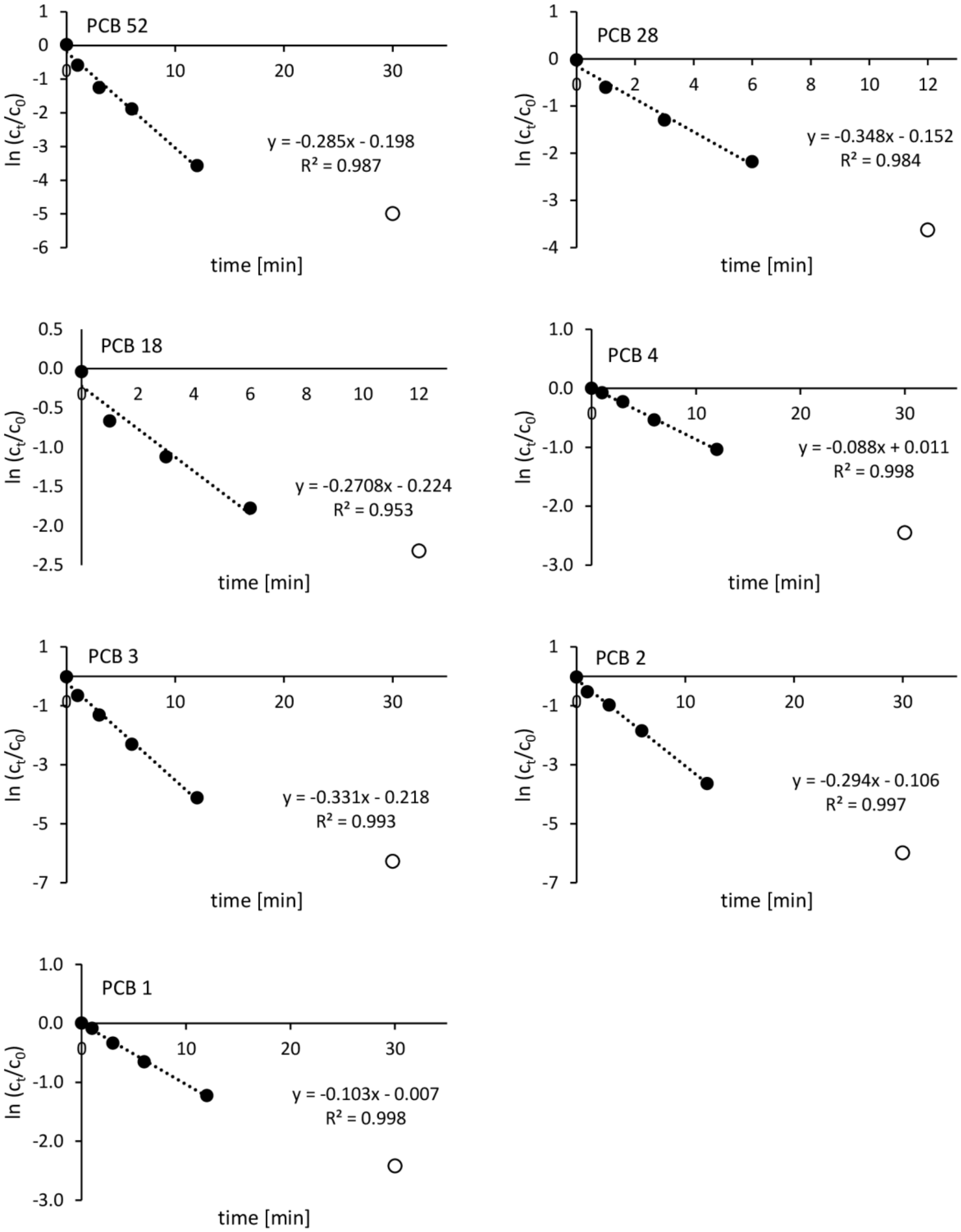

Figure S2. The rate constant *k* value of pseudo first order kinetics for dechlorination experiments with finely dispersed Pd(0) particles.

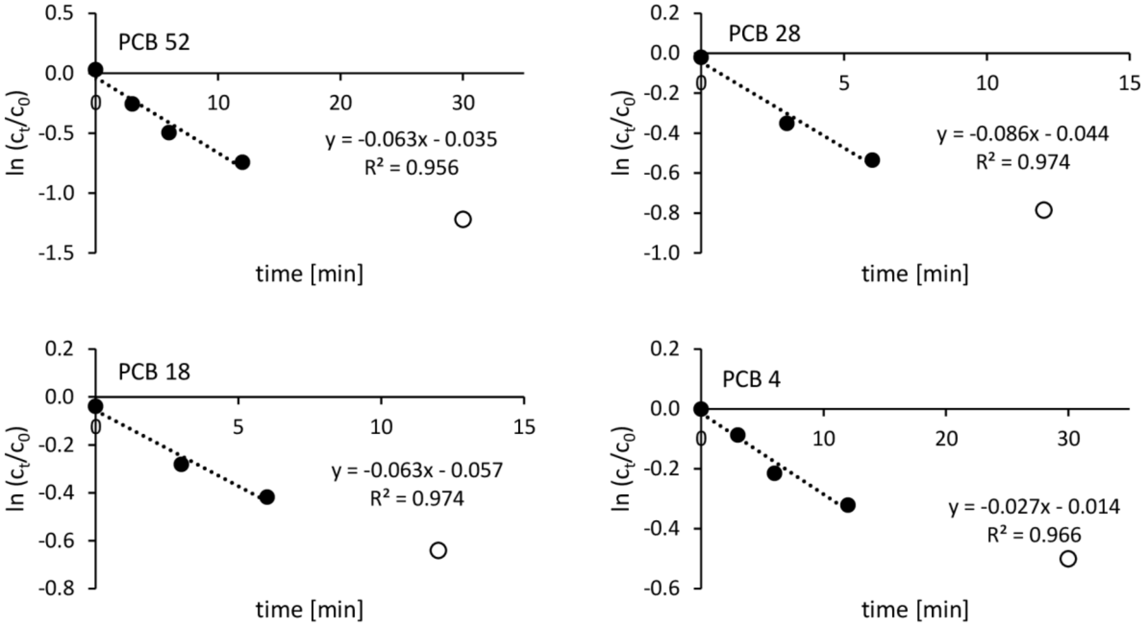

Figure S3. The rate constant *k* value of pseudo first order kinetics for dechlorination experiments with suspended Pd/Al_2O_3 particles in buffer solution.

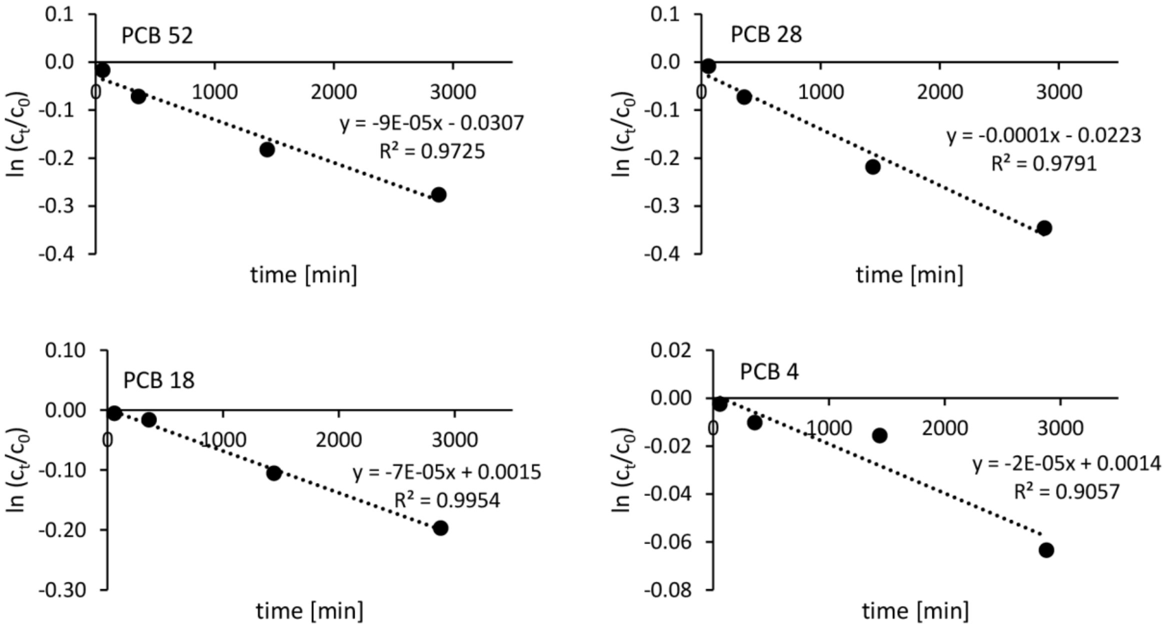

Figure S4. The rate constant *k* value of pseudo first order kinetics for dechlorination experiments with coating-protected (embedded) Pd/Al_2O_3 particles in buffer solution.

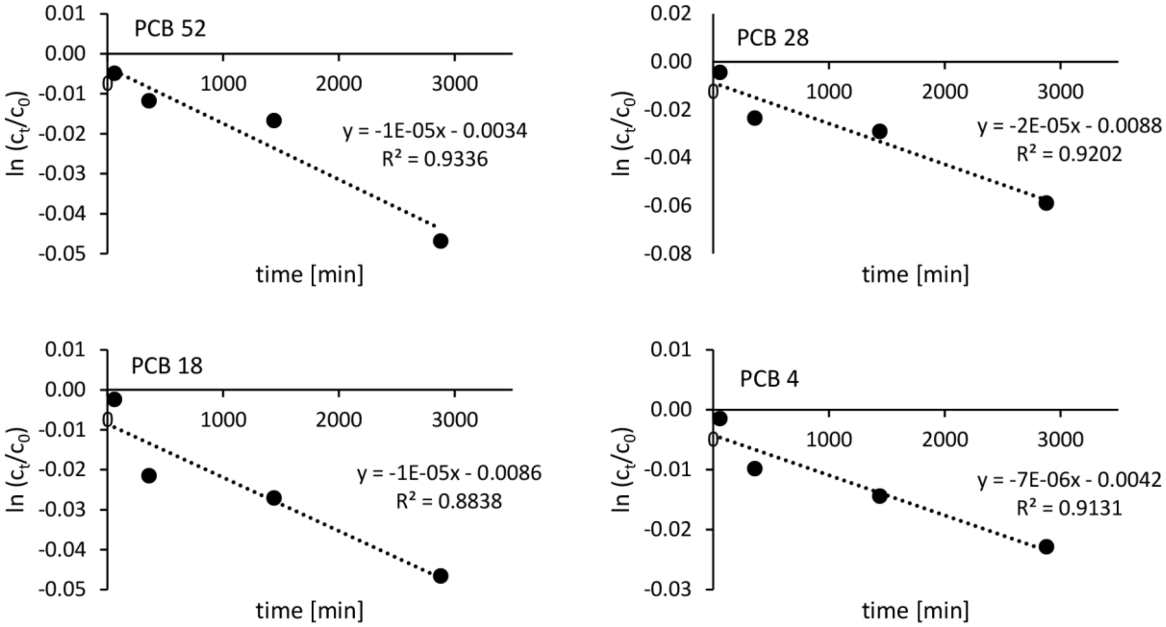

Figure S5. The rate constant *k* value of pseudo first order kinetics for dechlorination experiments with coating-protected (embedded) Pd/Al_2O_3 particles in Walsum mine water.

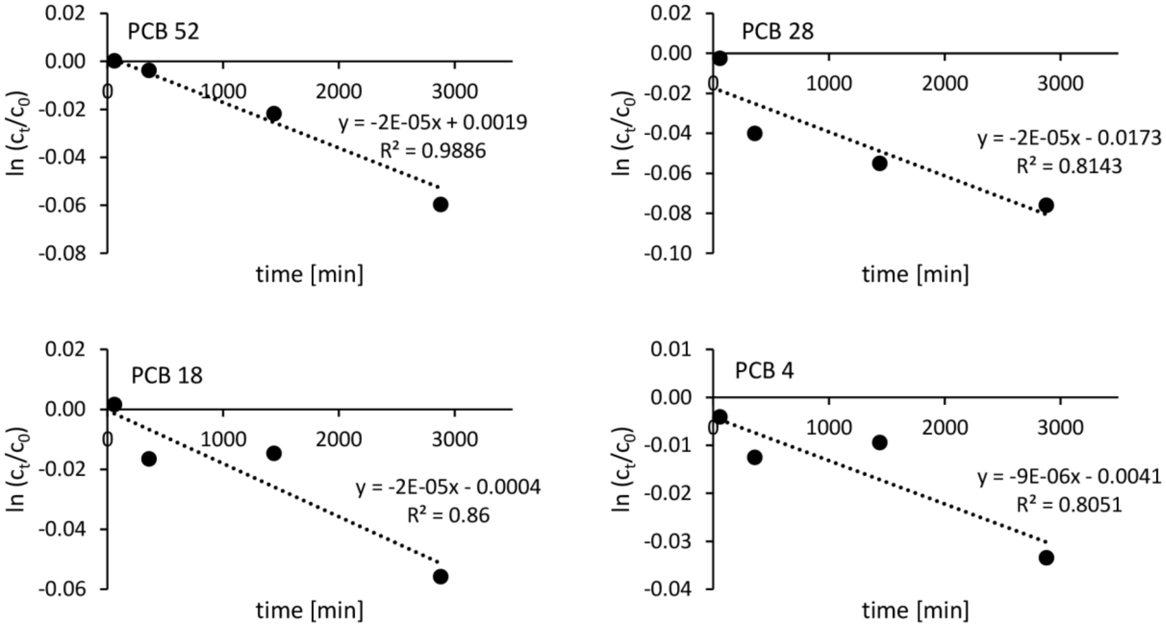

Figure S6. The rate constant *k* value of pseudo first order kinetics for dechlorination experiments with coating-protected (embedded) Pd/Al_2O_3 particles in Reden mine water.

Table S9. The used mine waters and their different inorganic compositions.

	Walsum	Reden	Stinnes
Chloride[a] [mg L^{-1}]	35,400	175	59,720
Nitrite[a] [mg L^{-1}]	< 0.4	0.21	< 0.4
Nitrate[a] [mg L^{-1}]	< 0.2	2.48	< 0.2
Sulfate[a] [mg L^{-1}]	564	160	< 0.5
Bromide[a] [mg L^{-1}]	< 0.4	< 0.4	< 0.4
Cd[b] [µg L^{-1}]	< 0.01	< 0.01	2.01
Cu[b] [µg L^{-1}]	94.8	19.5	116
Fe[b] [µg L^{-1}]	36.9	< 0.29	210
Mn[b] [µg L^{-1}]	1,396	1.31	2,314
Pb[b] [µg L^{-1}]	4.9	1.8	5.11

[a] determined with IC, photometry and AAS; [b] determined with ICP-MS.

References

1 A.-K. Herrmann, P. Formanek, L. Borchardt, M. Klose, L. Giebeler, J. Eckert, S. Kaskel, N. Gaponik, A. Eychmüller, Multimetallic Aerogels by Template-Free Self-Assembly of Au, Ag, Pt, and Pd Nanoparticles, Chem. Mater. 26 (2014) 1074–1083. https://doi.org/10.1021/cm4033258.

2 P. Bradt, F.L. Mohler, V.H. Dibeler, Mass spectrum of sulfur vapor, J. Res. Natl. Bur. Stand. (Journal of Research of the National Bureau of Standards) 57 (1956) 223. https://doi.org/10.6028/jres.057.027.

Liste der begutachteten Publikationen

Im Folgenden sind die Veröffentlichungen aufgeführt, die während der Promotionsphase erstellt wurden.

Wolkersdorfer C, Mahlangu OT, **Wiltschka K**, Böhm L, Analysis, Occurrence and Removal of Polychlorinated Biphenyls (PCBs) in Mine Water – A Review, Manuskript in Arbeit, wird eingereicht in *Environmental Sciences Europe*.

Beiträge der Autoren: **Christian Wolkersdorfer:** Konzeptualisierung, Schreiben – Originalentwurf, Schreiben – Überprüfung & Bearbeitung, Akquisition von Fördermitteln. **Oranso Themba Mahlangu:** Schreiben – Originalentwurf. **Katrin Wiltschka:** Schreiben – Überprüfung & Bearbeitung, Fördermittelakquise. **Leonard Böhm:** Schreiben – Überprüfung & Bearbeitung, Fördermittelakquise.

Tirpiz V, Lopez M-A, Krey T, Krüger C, Krüger-Zechlin V, Nagel M, **Wiltschka K**, Düring R-A, Wilke T, Ziegler M, Reichert J, Factors influencing the response of reef-building coral polyps to microplastics, Manuskript in Arbeit, wird eingereicht in *PLOS Biology*.

Beiträge der Autoren: **Vanessa Tirpitz**: Conceptualization, Methodology, Investigation, Formal analysis, Writing - Original Draft, Writing - Review & Editing, Visualisation. **Maria Antonieta Lopez**: Conceptualization, Investigation, Writing - Review & Editing. **Tim Krey**: Methodology, Investigation, Writing - Review & Editing. **Celine Krüger**: Methodology, Investigation, Writing - Review & Editing. **Verena Krüger-Zechlin**: Methodology, Investigation, Writing - Review & Editing. **Moritz Nagel**: Methodology, Investigation, Writing - Review & Editing. **Katrin Wiltschka**: Methodology, Investigation, Writing - Review & Editing. **Rolf-Alexander Düring**: Resources. **Thomas Wilke**: Resources, Writing - Review & Editing. **Maren Ziegler**: Resources, Writing - Review & Editing, Supervision. **Jessica Reichert**: Conceptualization, Methodology, Writing - Review & Editing, Supervision.

Wiltschka K, Bobric S, Düring R-A, Böhm L, Coating-Protected Pd/Al_2O_3 Catalysts for Elimination of Polychlorinated Biphenyls (PCBs) from Mine Water Effluents, Manuskript eingereicht in *RSC Advances*.

Beiträge der Autoren: **Katrin Wiltschka:** Konzeptualisierung, Methodik, Validierung, formale Analyse, Untersuchung, Schreiben – Originalentwurf, Schreiben – Überprüfung & Bearbeitung, Visualisierung, Akquisition von Fördermitteln. **Silviu Bobric:** Formale Analyse, Untersuchung. **Rolf-Alexander Düring:** Ressourcen, Schreiben – Überprüfung & Bearbeitung, Akquisition von Fördermitteln. **Leonard Böhm:** Konzeptualisierung, Methodik, Validierung, Ressourcen, Schreiben – Überprüfung & Bearbeitung, Betreuung, Fördermittelakquise.

Wiltschka K, Wolkersdorfer C, Düring R-A, Böhm L, Between Underground and the Deep Blue Sea: Contamination of Mine Water Effluents by Polychlorinated Biphenyls (PCBs), *ACS ES&T Water* (2023) 3474–3484. https://doi.org/10.1021/acsestwater.3c00179

Beiträge der Autoren: **Katrin Wiltschka:** Konzeptualisierung, Methodik, Validierung, Formale Analyse, Untersuchung, Schreiben – Originalentwurf, Schreiben – Überprüfung & Bearbeitung, Visualisierung, Akquisition von Fördermitteln. **Christian Wolkersdorfer:** Formale Analyse, Schreiben – Überprüfung & Bearbeitung. **Rolf-Alexander Düring:** Ressourcen, Schreiben – Überprüfung & Bearbeitung, Betreuung, Fördermittelakquise. **Leonard Böhm:** Konzeptualisierung, Ressourcen, Schreiben – Überprüfung & Bearbeitung, Betreuung, Fördermittelakquise.

Simon MP, Knuth D, Böhm L, **Wiltschka K**, Schatz M, Düring R-A, A miniaturized method for fast, simple, and sensitive pesticide analysis in soils, *Journal of Soils and Sediments* (2022) 496–508. https://doi.org/10.1007/s11368-021-03080-0

Beiträge der Autoren: **Marcel Pierre Simon:** Methodik, Validierung, formale Analyse, Untersuchung, Datenkuratierung, Schreiben – Originalentwurf, Schreiben – Überprüfung & Bearbeitung, Visualisierung. **Dennis Knuth:** Methodik, Validierung, formale Analyse, Untersuchung, Schreiben - Überarbeitung & Redaktion. **Leonard Böhm:** Methodik, Validierung, Untersuchung, Schreiben – Überprüfung & Bearbeitung. **Katrin Wiltschka:** Methodik, Validierung, formale Analyse, Untersuchung, Schreiben – Überprüfung & Bearbeitung. **Marlene Schatz**: Methodik, Validierung, Untersuchung, Schreiben – Überprüfung & Bearbeitung. **Rolf-Alexander Düring:** Konzeptualisierung, Methodik, Validierung, Untersuchung, Ressourcen, Schreiben – Überprüfung & Bearbeitung, Betreuung, Projektverwaltung, Fördermittelakquise.

Wiltschka 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, *Applied Catalysis B: Environmental* (2020) 119100. https://doi.org/10.1016/j.apcatb.2020.119100

Beiträge der Autoren: **Katrin Wiltschka:** Validierung, Formale Analyse, Untersuchung, Schreiben – Originalentwurf, Schreiben – Überprüfung & Bearbeitung, Visualisierung. **Larissa Neumann:** Methodik. **Matthias Werheid:** Ressourcen. **Michael Bunge:** Projektverwaltung, Fördermittelakquise. **Rolf-Alexander Düring:** Konzeption, Ressourcen, Projektadministration, Fördermittelakquise. **Leonard Böhm:** Konzeptualisierung, Methodik, Validierung, Formale Analyse, Schreiben – Originalentwurf, Schreiben – Überprüfung & Bearbeitung, Visualisierung, Betreuung.

Liste der Konferenzbeiträge als Erstautor

Wiltschka K, Bobric S, Düring R-A, Böhm L, **Hydrodechlorination of Mine Water-specific Polychlorinated Biphenyls (PCBs) Using Palladium Catalysts.** SETAC Europe Konferenz 2024, Sevilla, Spanien, Poster.

Wiltschka K, Wolkersdorfer C., Düring R-A, Böhm L, **Belastung von Grubenwässern durch polychlorierte Biphenyle (PCB).** kassel23 Tagung, Kassel, Deutschland, Präsentation (Preis für den besten Vortrag).

Wiltschka K, Bobric S, Düring R-A, Böhm L, **Hydrodechlorination of Mine Water-specific Polychlorinated Biphenyls (PCBs) Using Palladium Catalysts.** GGL Konferenz 2023, Gießen, Deutschland, Präsentation.

Wiltschka K, Bobric S, Düring R-A, Böhm L, **Hydrodechlorierung grubenwasserspezifischer polychlorierte Biphenyle (PCB) mithilfe von Palladiumkatalysatoren.** Umwelt 2023, Muttenz, Schweiz, Präsentation (Preis für den besten Vortrag).

Wiltschka K, Wolkersdorfer C, Düring R-A, Böhm L, **Contamination of Mine Water Effluents by Polychlorinated Biphenyls (PCBs).** SETAC Europe Konferenz 2023, Dublin, Irland, Präsentation.

Wiltschka K, Hamscher G, Düring R-A, Böhm L, **Polychlorinated Biphenyls in Mine Water – Miniaturized Approaches for Congener Specific Analysis and Palladium Catalyzed Dechlorination.** GGL Conference 2022, Gießen, Deutschland, Poster.

Wiltschka K, Düring R-A, Böhm L, **Polychlorierte Biphenyle (PCB) in Grubenwässern – kongenerspezifische Analyse mittels SPME-GC-MS.** Umwelt 2022, Emden, Deutschland, Präsentation.

Wiltschka K, Düring R-A, Böhm L, **Polychlorinated Biphenyls in Mine Water – Miniaturized Approaches for Congener Specific Analysis and Palladium Catalyzed Dechlorination.** SETAC Europe Konferenz 2022, Kopenhagen, Dänemark, Poster.

Wiltschka K, Hamscher G, Düring R-A, Böhm L, **Polychlorinated biphenyl (PCB) loads in mine water – congener specific analysis by SPME-GC-MS.** GGL Konferenz 2021, online, Präsentation.

Wiltschka K, Düring R-A, Böhm L, **Polychlorierte Biphenyle (PCB) in Grubenwässern – kongenerspezifische Analyse mittels SPME-GC-MS.** SETAC GLB Konferenz 2021, online, Schnappschuss-Präsentation.

Wiltschka K, Hamscher G, Düring R-A, Böhm L, **AntiPOP – Dechlorination of polychlorinated biphenyls in contaminated waters using palladium nanocatalysts.** GGL Konferenz 2020, online, Präsentation.

Wiltschka K, Bunge M, Düring R-A, Mackenzie K, Böhm L, **Dechlorierung von Hexachlorbenzol durch Palladium-Nanokatalysatoren – simultaner Nachweis aller Dechlorierungsprodukte aus einem miniaturisierten Reaktionssystem.** SETAC GLB Konferenz 2019, Landau, Deutschland, Poster.

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Eidesstattliche Erklärung

Erklärung gemäß der Promotionsordnung des Fachbereichs 09 vom 07. Juli 2004 § 17 (2)

Ich erkläre: Ich habe die vorgelegte Dissertation selbständig und ohne unerlaubte fremde Hilfe und nur mit den Hilfen angefertigt, die ich in der Dissertation angegeben habe. Alle Textstellen, die wörtlich oder sinngemäß aus veröffentlichten Schriften entnommen sind, und alle Angaben, die auf mündlichen Auskünften beruhen, sind als solche kenntlich gemacht. Bei den von mir durchgeführten und in der Dissertation erwähnten Untersuchungen habe ich die Grundsätze guter wissenschaftlicher Praxis, wie sie in der „Satzung der Justus-Liebig-Universität Gießen zur Sicherung guter wissenschaftlicher Praxis“ niedergelegt sind, eingehalten.

Katrin Valentina Wiltschka