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REVIEW **Open Access**

Analysis, occurrence and removal of polychlorinated biphenyls (PCBs) in mine water – A review

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Abstract

Background Polychlorinated biphenyls (PCBs) are persistent organic pollutants, and as such, they are subject to prohibition under the Stockholm Convention, due to their environmental and health effects. Despite their historical utilisation in mining operations, the presence of PCBs in mining influenced water (MIW) remains a subject that has not been adequately investigated. PCBs sorbed to suspended solids are often overlooked in conventional water analyses, contributing to misconceptions about their presence in the environment. Given their bioaccumulative and endocrine-disrupting properties, even minute amounts of PCBs in MIW pose substantial risks to ecosystems and human health.

Main body This review article describes the occurrence, environmental fate and treatment of PCBs in MIW and addresses critical knowledge gaps in the mining industry. Historical data demonstrate that PCBs were extensively utilised in mining applications, including dielectric fluids and hydraulic systems. Despite decades of regulatory oversight, residual PCBs persist in MIW, often at concentrations below DIN or ISO detection limits, yet they accumulate through the food web. The sampling challenges posed by the low solubility and sorption of PCBs to solids necessitate the employment of advanced analytical techniques. This study summarises the results of literature searches, laboratory analyses and discussions with international experts. There is still a global lack of monitoring and awareness of PCB contamination in MIW, with Germany being a notable exception. The study's primary sections address PCB detection methods, sampling techniques and environmental behaviour, emphasising the persistence and mobility of PCBs through adsorption and desorption processes. Treatment strategies encompass biodegradation, filtration, and thermal processes; however, the efficacy of these strategies is contingent on the specific characteristics of the site.

Conclusions PCBs in MIW pose a substantial environmental challenge and necessitate multidisciplinary efforts to monitor, understand and eliminate their adverse effects. This review is a comprehensive resource for researchers, regulators and industry representatives, facilitating science-based decisions to protect ecosystems and comply with international environmental standards. Continued research is essential to refine detection methods and develop innovative remediation technologies for PCBs.

Keywords Environmental fate, Stockholm convention, Legacy pollution, Mining, Persistent organic pollutants (POPs), Organohalogens, Environmental remediation, Water treatment, Nanoparticles

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Background

Polychlorinated biphenyls (PCBs) in mining influenced water (MIW) have long been ignored by the mining industry as their concentration was or still is often below the standard methods' detection limit in the water phase. Because mine water samples are usually filtered before analyses, the PCBs sorbed to the suspended solids (also referred to as suspended particulate matter, SPM) or the filter papers are often overlooked. Yet, PCBs are one of the world's most critical pollutants [69, 250]. They are banned by the Stockholm Convention [230] but are still present in the environment decades after their ban [169] or are unintentionally emitted from various sources [144, 169, 270]. To identify low PCB concentrations in MIW ("low" in this context refers to the pg to ng L^{-1} range), it is first necessary to understand the processes involved in sample extraction, analysis, and the concentration ranges of PCB in MIW. As PCBs bioaccumulate in the food web [29, 266], and because of their endocrine-disrupting behaviour [3] as well as their high persistence, even low concentrations of PCB in MIW cannot be disregarded because of their substantial environmental and health relevance. They must be removed from the ecosphere, as some marine top predators, for example, are already at risk of extinction [63]. This requirement is in line with the International Stockholm Convention, which requires its parties to take measures to eliminate or reduce the release of POPs into the environment [136, 230]. According to the Stockholm Convention, all PCB-containing equipment need to be phased out by 2025 and all PCB wastes subjected to environmentally sound management by 2028. Therefore, the methods for treating PCB-contaminated MIW are of paramount importance, as well as understanding the PCBs' transport mechanisms and sources within the mining context. In the West German collieries alone, some 16,784t of PCBs were used [5], highlighting the large amount of PCBs that may remain undetected at other mine sites around the world.

This review paper aims to focus on knowledge gaps regarding PCBs in MIW by addressing the aforementioned issues relevant to the mining industry. As most researchers and practitioners in the field of mine water studies are more familiar with inorganic compounds, this review also covers the health effects of PCBs on organisms, as well as their behaviour in aquatic environments and food webs. In addition, this review includes descriptions of sampling and potential analytical methods, with the aim of providing a comprehensive understanding of the subject for those concerned with PCBs in MIW.

Methods

For this review, peer reviewed articles were identified through literature searches in Clarivate's Web of Science and publisher's databases using the search term *("mine water" OR minewater OR "mine drainage" OR "mining influenced water" OR "mining impacted water" OR "mine impacted water" OR "mine wastewater" OR Grubenwasser) AND (PCB* AND polyc*)*. In addition, internet searches in English, French and German tried to identify grey Literature reports and mine sites, where PCBs were analysed in the water phase. References were screened using their abstracts, and full articles were obtained and read if the abstract appeared to provide relevant information. 296 articles, reports, theses, books and book chapters with the above-mentioned search terms were obtained and read. Additional references were identified from these article's Lists of references. To get further insights into PCB analysis in MIW, e-mails to 1142 colleagues from 61 countries were send out and 169 replies received. None of the answering colleagues could share results from mine water analysis on PCBs, but parts of this paper are based on these discussions with experts across Europe, Africa and North America about PCBs and the questions or misconceptions they had. Mine water literature was predominantly researched from the first author's mine water literature database (≈ 8900 references) and James Gusek's Mine Remediation and Reclamation Paper compilation (7590 entries as of January 2025 but only one relevant reference found therein).

Based on the results of the literature review and the discussions with colleagues, the main text of this review paper was divided into five subsections. This paper is intended for mine water researchers, consultants and regulators. It provides the most relevant information on PCBs for these audiences. As many of them may not have immediate access to specialised literature, relevant sections are covered by several references from different sources.

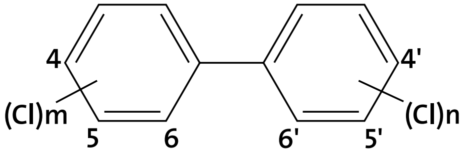

Fig. 1 General structure of the PCBs. m and n can range from 0 to 5 with a sum of m + n of at least 1 (source: modified after [109])

PCBs in the mine water context

Background on PCBs and their relevance to MIW

PCBs are xenobiotic, chlorinated organic aromatic compounds that have been derived from biphenyl with some or all the hydrogen atoms replaced by chlorine atoms (Fig. 1). They are often referred to as chlorinated biphenyls, chlorinated diphenyls, chlorobiphenyls or polychlorobiphenyls. Since their first description by Doebner [67] in 1876, and their first industrial manufacturing in 1929, PCBs have since been produced by prominent companies such as Monsanto, Kanegafuchi Chemical, and Bayer [59, 108, 139] with trade names, such as Aroclor, Clophen, Pyranol or Pyroclor [52, 108], to name just a few of them. In a comprehensive literature review, Breivik et al. [34] report a total international production of 1.3 Mt of PCBs between 1930 and 1993, with Monsanto and Bayer accounting for 60% of the total. Today, one of the main sources for newly, unintentionally formed PCBs (UP-PCBs) in the environment according to Annex C of the Stockholm Convention are combustion of wastes [109], de novo synthesis in thermal processes [117] and pigment production [10, 162]. Natural de novo formation of PCBs is negligible, although known from the Mt St. Helens, USA volcanic eruption, where three isomers of the PCB-homolog pentachlorobiphenyl were identified, possibly resulting from the pyrolysis of organic material in the presence of inorganic chlorides [61, 193].

A total of 209 PCB compounds (congeners) exists, and their number is based on their individual retention on a gas chromatography column depending on the position and number of the PCB's chlorine atoms. The current nomenclature mainly follows the Ballschmiter–Zell (BZ)-numbering system [3, 16]. Single congeners are pure, odourless, liquid or crystalline substances, characterised by a slightly yellowish colour or are sometimes colourless. However, commercial products which are a viscous blend of single PCB congeners have colours ranging from light to dark yellow (Fig. 2), become more viscous as more hydrogen atoms are replaced with chlorine [109] and might have a distinct smell [41]. These congeners were usually not used as individual substances but rather as technical mixtures [219], where the various PCB congeners in the mixture determined the characteristic of the mixture (e.g., Aroclor and Clophen) and the chlorine content was usually provided in percentages [109]. Known technical mixtures used in the mining context were Aroclor 1254 (≈ 52–54% chlorine content) and 1260 (≈ 60–62% chlorine content) in the USA [22] or Clophen A30 (≈ 40–42% chlorine content) and A40 (≈ 48% chlorine content) in closed systems in Germany [138]. Besides their chlorine content classification, they

Fig. 2 Commercial PCB mixtures from transformers (source: Sonia Álvarez, SertinLab Ecuador)

are often categorised into dioxin-like- (dl-PCBs) and non-dioxin-like PCBs, the former being the twelve PCBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, and 189 [109] that have a similarity in structure and toxicity mechanism (activating the aryl hydrocarbon receptor, AhR) with polychlorinated dibenzo-*p*-dioxins (PCDDs).

Due to their high flashpoints, PCBs are generally unreactive (inert) and extremely resistant to acids, alkalis, oxidants and fire. Other properties of PCBs include neutral charge, high permittivity, low vapour pressure and low solubility [139, 167]. Owing to their hydrophobicity, the solubility of chlorobiphenyls in water is extremely low, ranging from 0.0012 to 4830 µg L^{-1} [109]. For PCB-28 and PCB-52, which are PCBs commonly analysed in MIW samples, water solubilities of 134 and 34 µg L^{-1} can be calculated using data from Li et al. [145]. However, they are highly soluble in non-polar organic solvents, oils and biological lipids [109]. As impurities in PCB mixtures, other toxic organics, such as polychlorinated dibenzofurans (PCDFs), have been identified [253, 254] and might, therefore, occur in MIW as well.

PCBs have found major uses as dielectric fluids in transformers and capacitors, heat-transfer fluids, hydraulic fluids, lubricants and additives in plastics and dyes because of their outstanding dielectric properties in addition to chemical and thermal stability, high permittivity, and low vapour pressure. In addition, they have been widely used in plasticizers, coatings, inks, glues, fire retardants, insecticide extenders and paints [109, 139].

Though PCBs have been used since 1929, it was only in 1966 that their ubiquitous behaviour was identified [139]. This resulted predominantly from the invention and the application of electron-capture detectors in gas chromatography [152, 153]. While investigating DDT (dichlorodiphenyltrichloroethane), the Swedish scientists Sören Jensen and Gunnar Widmark found unknown chromatogram peaks that they could not attribute to known substances [11, 161]. In 1964, Jensen noticed that the "mysterious substance [he] discovered" is bioaccumulated in aquatic animals and birds feeding on them, but not in land mammals. His unknown substance was also in blood samples, Human breast milk and white-tailed eagle museum specimen Younger than 1942. In a crime-story-like approach, he was finally able to identify the unknown substances to be PCBs [115] and detected them also in many Swedish marine organisms [116].

Due to their low water solubility and inert nature, PCBs were among the original 12 substances and substance groups regulated under the Stockholm Convention and called "The Dirty Dozen". Today, 34 substances and substance groups are classified as persistent organic pollutants (POPs) under the Stockholm Convention in annexes A (elimination), B (restriction), and C (unintentional production) [230]. In general, POPs are highly toxic, persistent in the environment (due to high chemical and thermal stability), accumulate in lipids, and can be transported by water and by wind, which leads to their ubiquitous distribution. Though PCBs are not produced any more, they are still released into the anthroposphere and the environment. For this reason, university buildings have either been closed or dismantled (e.g., Ruhr University Bochum, Germany) and schools have been renovated [98]. Contaminated soils or sediments are releasing PCBs into the water phase or the air. During paint removal, large amounts of PCBs can accidently be released into the surrounding areas [113, 210]. In some areas, fish consumption is prohibited, because their tissue contains elevated PCB concentrations [151]. Recycling processes and waste management can be a highly relevant source of current PCB release [190].

The presence of PCBs and other POPs in the environment results from human activities and even can be found in geological deposits, where these pollutants serve as geochemical signatures [260]. Inside mines, these hazardous materials are generally limited to electrical equipment that contains PCBs [89]. This issue is of concern to the US EPA, which has the obligation to ensure that all PCB regulations are met, as the abandonment of PCB-containing equipment underground is likely to release PCBs into the environment and human exposure [159].

Humans together with other terrestrial and aquatic species have been exposed to PCBs because of improper disposal, accidental releases and during the use of compounds [161, 183]. The exposure has been exacerbated by industrialization which has ensured noticeable usage of devices that have PCB-containing material or liquids. Human exposure to high PCB concentrations has been linked with liver damage, dermal lesions, weight loss in infants, respiratory disorders, ocular signs, neurological disorders resulting in neurological symptoms, damage to the endocrine system, immunodeficiency, hypertension, and reproduction disorders. These toxic effects can be traced to the nature of PCBs, where they have been reported to circulate throughout the body in the blood and find storage in fatty tissue and organs, such as the liver, kidneys, lungs, adrenal glands, brain and skin [3, 24, 40, 199]. In fish, birds, and amphibians PCB exposure has been associated with birth defects and decline in fertility. As a result, extensive research has focused on PCBs due to their persistence in the environment, providing valuable insights into their behaviour [145]. In addition, studies have been driven by the widespread exposure of humans and other organisms to toxic PCB concentrations [228], with PCBs detected early on even in the Arctic [242, 248], including in coal mining communities on Svalbard [114].

The demand for safe drinking water has increased owing to the increase in world population and growth in industrialization. Since the invention of chemicals that are foreign to nature, water treatment has become more complex. At the same time, potential dangers posed by these chemicals to consumers have increased [42]. Therefore, regulations relating to PCBs in MIW and their release into the aquatic environment within the context of the United Nations Sustainable Development Goals (SDGs) have been established [80, 251]. Because of the PCB's toxicity, the limits are generally very low. In the USA, the maximum contaminant level (MCL) for PCB in drinking water is 0.5 µg L^{-1} [247]. The Ontario drinking water standard 2003 is 3 µg L^{-1} and suspended solids in German surface Waters must not exceed 20 µg kg^{-1} PCB for each of the six indicator PCBs [184]. However, the literature review showed that most countries do not define a specific limit for PCB in drinking or surface water.

Three natural processes are known for the elimination of persistent PCB compounds: combustion, photolysis and biodegradation. Not only is natural combustion uncommon but it also results in the formation of considerable higher toxic compounds from PCBs in particular PCDFs [107]. This negative effect is also common in photolysis. Microorganisms play major roles in the biodegradation of PCBs, where aerobic degradation and anaerobic degradation are the two most common forms [158]. It becomes apparent from the references in this section that nature has means to remove PCBs from the environment. However, these processes are only effective under special conditions. For example, anaerobic degradation relies on optimal concentrations, as degradation rates largely depend on initial PCB concentrations. Therefore, advanced techniques are necessary to ensure minimum concentrations of PCBs in the environment and, particularly, MIW.

Relevant PCBs in the mining industry and mine water

Application of commercial PCB mixtures in mines

In a 1936 advertisement by General Electric [87], the positive characteristics of a PCB mixture that was marketed under the trade name pyranol, especially for mines and tunnels, were highlighted: "It is possible to meet the safety requirements of the National Electrical Code for indoor installations more economically with G–E Pyranol transformers than with oil-filled units, because with Pyranol transformers many restrictions are eliminated. They are designed and built especially for use with Pyranol, the noninflammable and nonexplosive cooling and insulating liquid." and "PYRANOL – The Most Important Transformer Development Since Silicon Steel". This, other advertisements and published articles about PCBs, show that PCB was considered the silver bullet for many applications as it was considered safe and environmentally friendly. The carelessness with which mines operated historically, can also be seen by a 1987 groundwater quality report from West Virginia, USA [82]. According to the author, one of the contaminants found in the mining environment are "polychlorinated biphenyls (PCB's) from transformers which were typically left in the mines upon closure". Marcus [159] describes in 1997, that PCB-containing transformers and condensers can be commonly found at electrical storage sites of abandoned mine sites. Leakages of these older devices, draining them at site and using the PCB-containing oil for dust suppression was not unusual.

Germany, financed by the Commission of the European Communities, conducted research on "Flame retardant pressure fluids for hydraulic mining machines" at the end of the 1960 s, resulting from increased European legislative requirements to reduce fire potentials underground [203]. This research concluded that using "environmentally friendly HSD fluids on the basis of low-chlorinated biphenyls" is a future usage option for underground mines. At that time "a product for hydrostatic systems based on low-chlorinated biphenyls" was under development and one was "convinced that an environmentally friendly product will be available for the mining industry in the course of 1973". Until then, it was recommended to use BP-Olex SF-D 0204 in the mining environment, as it was approved by the 4th Luxemburg report on "Requirements and Tests applicable to Fire-Resistant Hydraulic Fluids used for Power Transmission and Control" [203]. PCBs in mines were used worldwide, but already in 1965 Monsanto indicated that Aroclors must be restricted to closed systems as "we had not seen data to show absence of toxic levels" in the mine air from the use in motors, which lost PCBs through volatilization [161]. In 1973, the member countries of the OECD (Organisation for Economic Co-operation and Development) restricted the use of PCBs to transformers (Fig. 3), capacitors, hydraulic fluids in mining equipment and heat-transfer fluids. Yet, at that time it was already known that these appliances, despite being called "closed" systems, may leak PCBs and underground, PCB-based hydraulic fluids can be considered substantial sources of contamination and most PCBs stay underground [59]. Since 1986, using appliances containing PCB is not allowed in European mining anymore, though existing appliances could still be used (Council Directive 76/769/EEC).

One of the PCB substitutes was the tetrachlorobenzyltoluene (TCBT) Ugilec 141, which is now considered to be similarly toxic to PCBs [180, 195] and is also found in fish tissue [84]. Based on their investigations, Murk et al. [180], therefore, concluded that "no apparent differences were observed in toxicity between Ugilec 141 and the

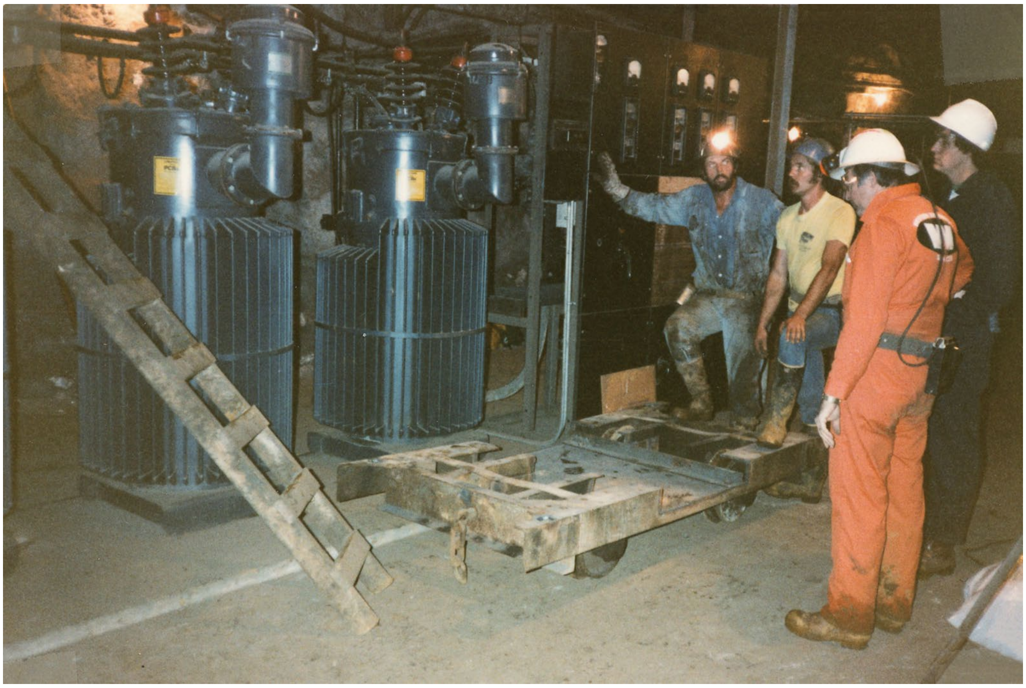

Fig. 3 Pyranol PCB Transformers at 20 level Eagle Mine at Gilman, Colorado, 1984 (source: U.S. Environmental Protection Agency, Dan W. Bench [24]; original text in presentation: "Two of three 76 gallon [288 L] Pyranol transformers underground at the 2010 substation. There were three drained 65 gallon [246 L] Pyranol transformers at the 1623 substation behind the fire seals that could not be removed. The mine was on fire at the time of the removal. About six gallons [23 L] of Pyranol remained in each of these 65 gallon transformers.")

PCBs, Aroclor 1254 and PCB-77. This turns Ugilec 141 and related TCBTs into very bad alternatives for PCBs". Their usage was stopped in the early 1990 s by EU Council Directive 91/339/EEC.

Schwarzbauer et al. [221] report that in the Year 1983 approximately 1,200 t of PCB-containing hydraulic fluids were used in the German Ruhr collieries, with only 10% recycled and 5% properly disposed of. The remaining ≈ 1000 t stayed somewhere underground. Though numbers vary in detail, ahu AG Wasser Boden Geomatik [5] compiled the available data and concluded that around 16,784 t of PCBs were used in West German collieries. This report also estimated for a German hard coal mining area a PCB loss of 34 to 51 g m^{-2} into the goaf, which might not be too different for other mining areas in the world. Meanwhile, the Luxemburg report has its 7th version, and the requirement for using PCBs in the mining industry is, obviously, omitted therein. Modern PCB-free solutions include emulsion-based and polymer-based options, as well as synthetic fluids [281]. Since the late 1970 s PCBs and PCB-containing products were banned in the USA, in 1992 their usage in the German mining industry completely stopped, and since 2001 their use and production were banned worldwide [5, 160, 230]. Within the European Union, they are regulated and explicitly banned under the Parliament and Council regulation 2019/1021 in accordance with Council Directive 96/59/EC. Nations that have ratified the Stockholm Convention are mandated to cease using PCBs in equipment by 2025 and to achieve environmentally sound waste management by 2028. This includes implementing environmentally sound waste management practices for PCB-containing Liquids and equipment contaminated with PCBs, specifically for materials with PCB concentrations exceeding 0.005% (50 mg kg^{-1}) [169, 230, 231]. North Korea was known to be producing PCBs until at least 2006 [181], intended to stop PCB production in 2012, but was still producing PCBs in 2016 [252] and 2020 [189], with no more recent production data published.

PCB analyses in mine water are not regularly reported, and results in the literature are, therefore, even more rarely available. One of the reasons might be that their concentration was often below the detection limit of the previously used methods. Arway [12] sampled seven locations in Pennsylvania, USA, concluding that "the analytical results from the pesticide and PCB testing did not indicate any unusual problems", without indicating what this statement could mean. Downstream of Marianna, he found PCB concentrations in fish ranging from 0.14 to 0.29 mg kg^{-1} and at Chartiers Morgan Township from 0.19 to 0.40 mg kg^{-1}. The general perspective can be illustrated by the U. S. Environmental Protection Agency [246], who wrote “for example, PCBs may be found at some historic mine sites, but are not a threat at most sites”. At around the same time, Cheam et al. [46] analysed PCBs in nine sediment samples around Canadian collieries and power plants and found “that the concentrations were very low, and only very few congeners were detected”. Very similar are the results of Dinger et al. [66], stating that “no significant concentrations of pesticides, nitrates, faecal coliform, orthophosphates, PCB’s, or volatile organics were detected” at the Sand Lick and Cow Branch sites in Eastern Kentucky, USA. As much as this is correct, the PCB problem nowadays resides less in the concentration and contamination of the water phase, but their accumulation in the food web. Therefore, even low PCB concentrations in MIW or the suspended solids might be a matter of concern at worldwide mine sites once released into the receiving environment, as Bench [24] clearly pointed out. Only recently, concentrations for over 50 PCB congeners in MIW were reported for different sites in Germany [270].

Sources of PCBs in the mining environment

Despite the widespread use in the mining industry, it is interesting that PCB analysis in mine water is not a standard procedure. Reasons for that might be the common assumption that PCBs are not soluble in water, that their concentration is below the detection limit or that they sorb to the solids within the mine. Results relating to PCB concentrations in the mining environment are, therefore, restricted and most of the available data are related to German hard coal mining. This might not imply that more PCB was used in the German hard coal mining, it is just an indication that the environmental relevance of PCBs has been recognised by the former mine operators and authorities.

It must also be pointed out that “below the detection limit” is not equal with “doesn’t exist”. Detection limits and analytical methods change over time and “below the detection limit” cannot be considered non-toxic in relation to POPs. One of the reasons is that the PCBs bioaccumulate, and a concentration that was “below the detection limit” might increase to substantial concentrations once bioconcentrated (uptake directly from the water or—though less commonly—from the air phase) or biomagnified (uptake from food) [55]. Risebrough et al. [206] made a point by writing: “Is there really an amount of polychlorinated biphenyl which is safe to breathe or to ingest?”

Because PCBs were often used in electrical equipment, they are found mainly in mine electrical equipment, such as transformers, capacitors, fluorescent light ballasts, in cables or as inflammable hydraulic oils [22, 25, 44]. These equipment in abandoned mines are likely to cause mine water contamination. Spillage or leaking of PCBs in underground mines will directly lead to water contamination as mines penetrate the water table. This is a problem, because there may be no easy solutions for retrieving the underground source after a mine is flooded and pollutes receiving water courses or the ground water [23, 24]. Once equipment used in mine workings is not maintained or repaired any more, it ultimately starts to leak. If not under the mine water table, these leakages might result in atmospheric transport and can also add to PCB contamination in the mining environment. In the 1980 s, NIOSH (US National Institute for Occupational Safety and Health) identified 900 out of 1800 mines still using PCB, which might be indicative for PCBs still residing in some of the older or abandoned mines [159].

In addition to PCBs used in mine machinery or electrical installations, another potential PCB source in MIW might be leakages from underground PCB waste storage sites [175]. These underground storages were specifically described in a “Technical guideline” and its amendments of the Basel Convention. Therein, it is explicitly described that “permanent storage in facilities located underground in geohydrologically isolated salt mines and hard rock formations is an option for separating hazardous wastes from the biosphere for geological periods of time”. However, caverns or tunnels used for storage “should be located in geological formations that are well below zones of available groundwater or in formations that are completely isolated by impermeable rock or clay layers from water-bearing zones” [53].

During mining, toxic chemicals used underground pose a potential risk in the event of flooding, as leaked compounds may still be present in the mine workings [197]. Contamination can occur both during active mining and after flooding, when dissolution and transport processes release pollutants into the environment as water levels rise. Some of these pollutants include mixtures of mineral oil hydrocarbons, which, due to their low solubility and high hydrophobicity, accumulate in organic-rich underground materials.

PCBs, which were previously mentioned as being resistant to fire were used in coal mines along with the tetrachlorobenzyltoluene (TCBT) Ugilec 141 in fire-retardant hydraulic fluids, between the 1950 s and 1980 s, depending on the country [124, 159, 244]. These fluids are suspected to have remained underground due to leaks and equipment failures. Although noticeable amounts of PCB-containing fluids may have leaked, detecting PCBs in mine water can be challenging, because they adsorb onto suspended solids or organic materials rather than remaining in dissolved form.

Since PCBs are semi-volatile compounds, they can adhere to or be absorbed by various materials, while more soluble semi-volatile pollutants may adsorb onto surfaces but are washed off by MIW. As a result, only low concentrations of dissolved PCBs may be found in mine water, making detection difficult. The mobilisation and transport of PCBs bound to suspended solids differ from that of true solutes, meaning that classical transport models based on solution and precipitation processes are insufficient. Instead, transport is governed by the properties of the carrier particles (suspended solids) and sorption–desorption equilibria.

Particles with sorbed PCBs may enter underground mine water, where they are eroded in turbulent flow and settle when flow rates decrease. The transport of fine particles in mine water is complex, as it depends on local hydrodynamic conditions. To better describe this transport and estimate the PCB concentration in mine water, Klinger et al. [124] developed a model incorporating sorption–desorption processes, flow velocity, and grain size distribution. However, the application of this model is complicated by limited information on particle size distribution in MIW. In abandoned mines, small particles remain mobile due to flow velocities in flooded workings, so the model was refined to consider three particle fractions [124]. This model was used to estimate solid content and PCB concentrations in discharged mine water from the Saar mines, where PCB concentrations of up to several hundred μg kg^{-1} were found in suspended solids at pump locations, though results varied substantially.

The study concluded that PCB transport via particles decreases as water levels rise, implying that full flooding of mine workings could immobilise PCBs. Consequently, maintaining high mine water levels may help reduce particle-bound pollutants in mining environments. In fully or partially flooded underground mines, allowing the water level to rise as high as possible in the final flooding stage can be beneficial. Lower flow velocities enable suspended particles to settle inside the mine before reaching discharge points.

However, suspended particles are not the only concern—contaminants like PCBs remain in mine water, presenting substantial environmental challenges. While proper water management helps control physical particles, chemical pollutants require different mitigation strategies. Managing persistent pollutants such as PCBs demands a deeper understanding of natural degradation processes, which are crucial for minimising the environmental impact of mine water discharge.

PCB concentrations in mining influenced water

Although published analyses of PCBs in MIW are scarce, available data suggest a decreasing trend in concentrations over time—from the earliest reports to the most recent findings. Just after the use of PCB was banned, concentrations reached the μg L^{-1} range, while 2–3 decades later, the concentrations decreased to the lower ng L^{-1} range (Table 1), which can be considered a positive development resulting from the PCB ban. In Germany, the environmental quality standard for PCBs sorbed to suspended solids is 20 μg kg^{-1} for each of the six indicator PCBs [184]. A report by Landesamt für Natur, Umwelt und Verbraucherschutz NRW et al. [135] concludes that locally, a mining connection of PCBs seems to be obvious as the congener distribution shows the characteristic congeners PCB-28 and 52, but many sampling sites show the signature of Clophen A60, which indicates other, possibly ubiquitous sources. For other countries, these detailed studies seem to be missing.

One of the earliest published results of PCB analyses related to MIW originates from the Pennsylvanian coalfields, where Arway [12] examined metal and PCB concentrations in fish. Though he did not indicate problematic concentrations of PCBs, two locations showed fish tissue PCB concentrations above the detection limit.

From about the same time are results from the Ibbenbüren colliery in Germany, where the surface and underground concentrations reached 10 to 314 ng L^{-1} between 1988 and 1991 [125]. In 1985, the use of PCBs at this colliery ceased; however, no analytical data are available from the period between 1985 and 1988 to assess the effects of this restriction on PCB concentrations in the water phase. The authors re-analysed the PCB concentrations in 2016, but unfortunately, no values are reported, just the three categories “no abnormalities”, “isolated abnormalities”, and “abnormalities” are given.

In 1990, Jäger et al. [111] investigated the potential of German underground collieries for the disposal of wastes. In the context of those studies, they analysed the PCB concentration in the Zeche Consolidation (shaft 4 level 11), which were below the detection Limit of 10 ng L^{-1}. Seventeen additional samples from pumped water within the Ruhr coal mining area (no precise locations given) ranged between 60 and 610 pg L^{-1}. No discussion of the results was conducted.

Regier [202] investigated the PCB concentrations in sediments and water of two German dams (Harkortsee, Echthausen dam) along the river Ruhr, which receives MIW of long abandoned collieries. The author identified one anomaly in the Harkortsee sediments from 1986, attributed to a potential accident but was not able to find any evidence for an accident in the Ruhr area at that time—the incidents in Walsum and Moers [221] are too far away to be considered responsible for this increase. Taking into consideration that a lot of PCB-containing appliances had to be handled in 1986, Due to

Table 1 List of published locations and PCB concentrations in various mining environments found by the authors after intense literature and internet reviews

Location	Sampling dates	PCB concentrations in Water Phase (ng L^{-1})	Total number of congeners analysed (specific congeners)	References
Phosphate mine connector wells, Florida, USA, 8 locations	1980	0.00 mg L^{-1} (US EPA); 0.00 µg L^{-1} (Kimrey et al.)	not specified: "PCB, Total"	U. S. Environmental Protection Agency [245], Kimrey et al. [123]
Lohberg colliery, Germany, Rheinpreußen shafts	1986	4000 (Lohberg), 9000 (Rheinpreußen)	not specified	Schwarzbauer et al. [221]
Ruhr Area (66 collieries), Germany	1986	< 10–5400	6 (PCBs 28, 52, 101, 153, 138, 180)	Poppe et al. [195]
Pennsylvania, USA, 7 locations	1988	"The analytical results from the pesticide and PCB testing did not indicate any unusual problems"; "The present FDA. action level of 2.0 ppm [in fish] was not approached"	not specified	Arway [12]
Ibbenbüren, Germany	1988–1991	10–314	not specified	Klinger et al. [125]
Ruhr Area, Germany, 17 locations	1990	< 10–610	6 (PCBs 28, 52, 101, 153, 138, 180)	Jäger et al. [111]
Ruhr Area, Germany, 12 locations	1991	< 10–120	not specified	mine operator, listed in Schwarzbauer et al. [221]
US EPA	2000	PCBs listed as contaminants of potential concern; until banned "the mining industry has traditionally used high levels of PCBs"; "PCBs […] have been identified in soils near mine waste sites"; "PCBs may be found at some historic mine sites, but are not a threat at most sites."	not specified	U. S. Environmental Protection Agency [246]
Příbram, mine № 19, Czech Republic	2004	18	6 (PCBs 28, 52, 101, 138, 153, 180)	Kalous et al. [119]
12th mine of Pingdingshan and Yanma colliery, China	2004	145 (Pingdingshan), 106 (Yanma bottom), 138 (Yanma roof)	7 (PCBs 28, 52, 101, 118, 138, 153, 180)	He [96]
Gold King Mine, USA	2015	110–240 per Aroclor mixture (reported values correspond to the method's estimated detection limits)	Aroclors 1016, 1221, 1232, 1242, 1248, 1254, 1260	MEC^{X} Aurora [168]
Ibbenbüren, Germany, 3 locations	2015	< 0.002–0.5	2 (PCBs 28, 52), the concentration in the water phase was calculated from the concentration in suspended solids	Landesamt für Natur, Umwelt und Verbraucherschutz NRW et al. [137]
Ruhr Area, 11 locations	2015	< 0.002–2.0	2 (PCBs 28, 52), the concentration in the water phase was calculated from the concentration in suspended solids	Landesamt für Natur, Umwelt und Verbraucherschutz NRW et al. [137]
Ibbenbüren, Germany, 1 location[a]	2015–2016	0.6	7 (PCBs 28, 52, 101, 118, 138, 153, 180)	Landesamt für Natur, Umwelt und Verbraucherschutz NRW et al. [136]
Ruhr Area, Germany, 4 locations[a]	2015–2017	0.1–6.4	7 (PCBs 28, 52, 101, 118, 138, 153, 180)	Landesamt für Natur, Umwelt und Verbraucherschutz NRW et al. [136]
Ruhr Area, Germany, 3 locations	2015–2018	0.1–9	7 (PCBs 28, 52, 101, 118, 138, 153, 180)	Mittelstädt et al. [175]

Table 1 (continued)

Location	Sampling dates	PCB concentrations in Water Phase (ng L^{-1})	Total number of congeners analysed (specific congeners)	References
Ibbenbüren, Germany, 1 location (different sampling times)[b]	2016	0.9 2.1–5.4	7 (PCBs 28, 52, 101, 118, 138, 153, 180) 9 (PCBs 4 + 10, 28, 52, 101, 118, 138, 153, 180)	Landesamt für Natur, Umwelt und Verbraucherschutz NRW et al. [136], Rahm et al. [200]
Ruhr Area, Germany, 3 locations	2016, 2017	0.3–29	6 (PCBs 28, 52, 101, 138, 153, 180)	Schwarzbauer et al. [221]
Ruhr Area, Germany, 4 locations[b]	2016	0.1–0.7 0.2–0.8	7 (PCBs 28, 52, 101, 118, 138, 153, 180) 9 (PCBs 4 + 10, 28, 52, 101, 118, 138, 153, 180)	Landesamt für Natur, Umwelt und Verbraucherschutz NRW et al. [136], Rahm et al. [200]
Minden, Fayette County, WV, USA, 7 locations (monitoring wells and mine outfalls)	2018	0.04–3700	209 (all congeners)	Weston Solutions Inc. [268]
Ruhr Area, Saarland, Germany, 5 locations	2020–2022	2.5–11 20–120	7 (PCBs 28, 52, 101, 118, 138, 153, 180) 58 (PCBs 1–21, 24, 26–28, 30–33, 38, 44, 49, 52, 53, 61, 62, 65, 77, 85, 99, 101, 105, 110, 116, 118, 128, 138, 146, 149, 153, 156, 167, 170, 180, 183, 187, 189, 194) + biphenyl (not included in provided concentrations)	Wiltschka et al. [270, 271]

Repetitive measurements in German mines are not listed individually. Detailed analytical procedures vary. Reported concentrations refer to concentrations in the water phase only. Concentrations are provided as sum of individual congeners detected. A differentiation of PCB speciation (freely dissolved, particle bound, and total PCBs) is not provided in the table. Details on PCB speciation, information on individual congeners that remained < LOD/LOQ, and further specific details can be found in the referenced literature (not specified in all sources)

[a] Reported are results from centrifuge sampling or 100-L sampling

[b] Reported are results from passive sampling

the restrictions imposed in 1985, the reason of this peak might be seen in elevated transport, dismantling, decontamination or incineration activities. The findings on the temporal distribution of PCBs in lake sediments align with global PCB production trends, peaking in the late 1970s at 11,000 ng g^{-1} in the Harkortsee and 2340 ng g^{-1} in the Echthausen dam. These spatio-temporal results are similar to results from a mining and sewage water influenced wetland in Lenasia, South of Johannesburg with 200–700 ng g^{-1} PCBs [186] and wetland sediments of the Lippe river, Germany with up to 2632 ng g^{-1} PCBs correlated with the Years 1980–1985 [97]. In none of the cases, the PCB concentrations in the water phase were recorded.

Another sediment study without analysing PCBs in the water phase was conducted by Ohlemacher et al. [185]. They investigated sediments in a wetland downstream of the abandoned German Haus Aden colliery, where Merkel et al. [173] reported 0.15 and 0.20 ng L^{-1} of the six indicator PCBs in the discharged MIW. Part of their investigations included the analysis of TOC, size fractions and concentrations of the six indicator PCBs in sediment and core samples. Based on their results, no correlation could be found between TOC and the size fraction < 0.63 mm and the sum of the six congeners ranged from 50 to 8610 µg kg^{-1} in the 11 sediment samples and from 10 to 40 µg kg^{-1} in the five core samples. Although they were unable to identify a source for the PCBs, they suggest that even 30 years after the PCB ban, they are still present in the environment at high concentrations.

During the investigation of mine water stratification in the Příbram, № 19 mine, Czech Republic, in 2004, one water sample just below the mine water table was also analysed for PCBs [119]. They analysed the indicator PCBs 28, 52, 101, 153, 138, and 180, with only PCB-28 and 52 being above the detection Limits. Their concentrations were 14 and 4.6 ng L^{-1}, respectively, summing up to 19 ng L^{-1}.

Landesamt für Natur, Umwelt und Verbraucherschutz NRW et al. [137] analysed and compared the results of three different laboratories from mine water in two different German hard coal mining areas (Ruhr and Ibbenbüren) with each other. Their analysis included also PCB-28, 52, 101, 118, 138, 153 and 180. Based on the PCB measurements of the suspended solids they deduced a PCB concentration in the water phase. Within these two mining areas samples from 14 locations were analysed in detail and in the suspended solids and ranged from below the detection Limits to 179 µg kg^{-1} dry weight. Calculated concentrations in the water phase were between the detection Limit and 2 ng L^{-1}, mostly around 0.005 ng L^{-1}. These low values, compared to other measurements in the water phase, might result from the calculation method, as they are roughly 100 to 1000 times lower than other data.

Merkel et al. [173] reported six PCB congeners in the water phase at the German Haus Aden colliery as part of a feasibility study on potential treatment methods for PCB-contaminated MIW. Their results, based on ahu (no source provided), ranged between 0.15 and 0.20 ng L^{-1}, and they assumed them to be representative for the Ibbenbüren and three other Ruhr collieries. As has been shown by the other investigations in the Ruhr area, this assumption can be considered valid.

In the Prosper Haniel colliery, Germany, suspended solids were sampled with a sediment sampler specifically developed for PCB analysis [212]. Reason was that the PCB concentrations in the water phase are very low, and as it was known that the PCBs are sorbed to the suspended solids, a specifically developed method became necessary. The concentrations ranged between 31 and 104 µg kg^{-1} on the suspended solids. In ten different water samples, PCB concentrations in the water phase averaged ≈ 0.4 ng L^{-1}. Between 2015 and 2018 PCB concentrations in the suspended solids phase were in the range 20–105 ng L^{-1} [136].

A range of PCBs related to the mixtures used in the German Saarland collieries was analysed during an intensive sampling programme of surface water and MIW [2]. They analysed individually PCB-28, 52, 101, 118, 138, 153, 180 sorbed to the suspended solids in two consecutive Years 2016 and 2017. Their results show that the concentrations of PCBs decrease with the increase in suspended solid concentrations (Fig. 4), suggesting an increased adsorption of PCBs with suspended solids increases. Because no size fractionation was done,

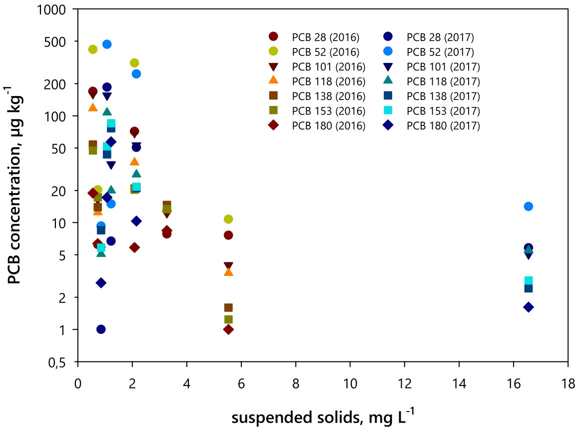

Fig. 4 PCB congener concentrations vs suspended solids in mine waters from the Saarland, Germany (source: authors compiled with data from [2])

reasons for that are not obvious from the published data. It is not clear if this could be related to a “dilution” of the PCBs resulting from the sorption. In summary, the PCBs sorbed to the suspended solids ranged between 30 and 1025 µg kg^{-1} suspended solids. Unpublished data shows similar sorption behaviour from one individual abandoned Saarland colliery. No PCB concentrations from the water phase were analysed.

Mine water from various mine water discharges in the German Ruhr and Ibbenbüren coal mining areas showed PCB concentrations of 0.2–2.1 ng L^{-1} [200]. Highest concentrations were measured in the Ibbenbüren colliery, were the PCB concentration in sediment samples increase from 850 µg kg^{-1} downstream the mine water discharge to 3200 µg kg^{-1} upstream. The mining prone congeners PCB-4, 10, 28, and 52 substantially increased in both, water and sediment samples.

In a report about the relationship of PCB concentrations and mine flooding, Klinger et al. [125] also compiled PCB concentrations in the mine water. Only historical data between 1988 and 1991 is reported and ranges from 10 to 314 ng L^{-1}. Current data are only classified, but no exact concentrations are provided.

Although these concentrations can be extrapolated to annual loads in the kg range due to the considerable MIW volumes [270], it is essential to contextualise these results. The atmospheric discharge is considerably greater and is in the kilogram to megagram range [27, 65, 190]. Nevertheless, MIW represents another persistent source of PCBs. Only recently, Wiltschka et al. [270] investigated MIW samples from five mine water effluents for a set of 58 PCB congeners and biphenyl by a specifically optimised SPME–GC–MS method: “As a result, 53 mono- to hepta-chlorinated congeners could be detected in concentrations of 0.01–25.9 ng L^{-1} per congener, of which mainly tri- but also di- and tetra-chlorinated PCBs were identified in higher concentrations”. The study results show that the previously investigated indicator PCBs (28, 52, 101, [118, as representative of dl-PCBs], 138, 153, 180), which are often assumed to occur in highest concentrations of all PCB congeners, occurred in the MIW in lower concentrations than other congeners that were not previously considered. The most abundant PCB congeners with the highest concentrations in all discharged MIWs were identified to be the four PCBs 18, 19, 31, and 52 (occurrence in all waters, part of the ten most abundant and highest concentrated PCBs) and additionally the PCBs 16, 17, 28, 32, 44, 49, and 53 (part of the 15 most abundant and highest concentrated PCBs). This grouping of PCB congeners is based on occurrence and concentration, whereas properties vary between these congeners. Only two of these eleven congeners (PCB-28 and 52) are part of the indicator PCBs. The congener patterns found in the MIW samples suggest that technical mixtures with lower chlorination degree such as Clophen A30 and A40 were used. The authors conclude that with total PCB concentrations of 0.02–0.12 mg m^{-3} (20–120 ng L^{-1}) and annual loads of 0.1–0.7 kg PCBs per mine, the relevance of MIW as an additional point source for PCB release to the environment is shown [270].

To facilitate a comparison of PCB concentrations in MIW and other compartments, the following section will discuss a selection of articles referring to surface water, the ocean, soil and air. Regarding PCB concentrations in these compartments, it was not possible to compile a single table with ranges, because the variability is extremely high. This can be demonstrated by the earlier results of the International Programme for Chemical Safety (IPCS) [110], who compiled these data on several tables.

Distribution in environmental media

PCBs in surface water

Like in mine water, the presence of PCBs in surface water results from the improper disposal of PCB-containing equipment, improper handling of PCBs or leakages. A major source for PCBs in surface water, especially in uncontaminated areas, is atmospheric dry and wet deposition [242], often related to the expansion in industrial output. Vlahos et al. [256] investigated the fluxes of chemicals across the water–atmosphere interface identifying the rates at which chemicals exchange through the air–water boundary through deposition, sorption and vitalization as the main processes. For PCBs they showed that site specific climate and hydrological parameters play a substantial role, and in most cases the flux was from the lakes into the atmosphere. Landesamt für Natur, Umwelt und Verbraucherschutz NRW et al. [136] showed a comparison of the six indicator PCBs and PCB-118 (water phase) in MIW (2016 data) and the German rivers Elbe, Saar, Rhein, Donau and Saale (2014 data) with 0.08–0.89 ng L^{-1} in MIW and 0.14–0.94 ng L^{-1} in the rivers, which is exactly in the same range.

A study on PCBs and organochlorinated pesticides in the Albanian part of the Drin and Buna river basins reported on the presence of PCBs in river samples [57]. Though the interaction of rivers, lakes, wetlands and groundwater in the ecosystem is a complex one, the authors identified mining as one of the major sources of PCB with minor contributions from municipal, industrial and agrochemical sources.

Surface water contamination by PCBs can be noted by making reference to PCB-contaminated sediments of the Hudson River [51]. This contamination has been linked to the prolonged discharge of PCBs from PCB manufacturing facilities. Analysis of the sediments revealed a change in PCB composition over the Years with highly chlorinated mixtures being transformed to Lightly chlorinated ones. This modification due to microbial degradation of the PCBs was confirmed by installing large enclosures in the Hudson River which were aerated to stimulate aerobic organisms. This led to a decrease in PCB concentrations within 10 weeks.

Zhuozhi et al. [288] report about a coal mine subsidence area in the Huainan municipality, China, that subsequently filled with surface water from the Nihe River. This river is fed by municipal and industrial wastewater and coal mine water from the Panyi coal mining area. Though part of their conclusions about potential PCB sources are not supported by data, their results ranging between 16 and 32 ng L^{-1} PCB in the water of the subsidence lake can be considered comprehensible.

PCBs in the ocean

As a result of the sorbing nature of PCBs on hydrophobic organic matter, PCBs in the ocean are sorbed onto suspended particulate matter in open ocean areas. However, since the concentration of suspended solids in the ocean is low, PCB concentration linked to suspended solids may be negligible [13]. Therefore, dissolved PCBs may account for the major content of PCBs in the ocean [72], where they bioaccumulate also in marine mammals [109] and are estimated to cause severe problems [63]. A recent study by Lohmann et al. provides information on the distribution of PCBs in oceans of the world [150] and global change is expected to have relevant effects on PCB concentrations and their distribution [257].

PCBs in soils

The presence of PCBs in soils can be attributed to improper disposal of PCB-containing material, spillage of liquids with traces of PCBs, floodings, as well as wet and dry atmospheric deposition. Various authors have, therefore, found PCBs in soils [6, 54, 128, 130], from where they can volatilise into the atmosphere. Due to continuous mixing as a result of churning and tillage, cultivated soils may act as a substantial repository for PCBs, from where these compounds are then mobilised. However, forest and grassland soils may also be fundamental because of bioturbation [54]. PCB concentrations in the soil vary with depth, where in general, PCB concentrations are higher in the upper 10 cm of the soil, whereas soils deeper than 10 cm may not be an important pool for PCBs. In soils, PCBs are usually sorbed to organic matter and only to a small degree on clay [232], which results in generally higher PCB concentrations in the upper layer of the soil.

PCBs may be buried deep into the soil layers, where they accumulate. Thus, cultivated soils serve as reservoir rather than sinks for PCBs [13, 73]. Rainwater can move PCBs into the soil through downward translocation. However, this process may not be substantial for noticeable build-up of PCBs in deeper soil layers because of the high partition coefficients to organic matter in the topsoil layers that make PCBs largely resistant to mass transfer through soils.

PCBs in ambient air

Because less chlorinated PCBs are more volatile, their presence in the atmosphere has been documented [13], with global concentrations in the 2010s ranging from 1 to 7,281 pg m^{-3} [28]. Bogdal et al. [28] reported the highest concentrations in India and the lowest in Chile. Current atmospheric concentrations are comparable to those recorded in the 1970s, indicating that PCB concentrations have remained relatively unchanged over time. Yet, the review results herein show that the temporal variation of PCB concentrations in outdoor air can show increasing trends in one region (e.g., Arctic or Bavaria, Germany) and decreasing ones in another region (Switzerland, Canada, and India), with PCB concentrations in rural areas usually lower than those in urban ones. A very recent compilation of global airborne PCB concentrations could not be found in the literature.

Sun et al. [234] measured PCB concentrations at six sites near the Great Lakes from 1990 to 2003. The authors investigated spatial trends in concentration data for several PCB congeners and total PCBs, and atmospheric PCB concentrations decrease slightly for tetra- and penta-chlorinated congeners. However, PCB concentration at sites near Lakes Michigan and Ontario decreased rapidly, which was attributed to efforts implemented to remediate the environment [234]. PCB concentrations in isolated areas may not decline at the same rate as compared to densely populated or contaminated areas, which has been shown by Gregor et al. [90], who could not detect a noticeable decline of PCB concentrations in the Canadian Agassiz Ice Cap over the three decades of their study.

A relevant source of atmospheric PCB concentrations are densely populated areas as demonstrated in studies for Switzerland, Canada, and India [27, 65, 190, 220]. PCB concentrations do not only decline in the atmosphere, but also in plant that have been reported to accumulate these pollutants. Based on the declining PCB concentrations in pine needles, Tremolada et al. [243] concluded that atmospheric PCB concentrations had decreased over time. The authors further elaborated that regional mean pine needle PCB concentrations were related to the population density, a result that could also be shown by Laxander et al. [141] for alpine areas in South Tyrol, Italy, and Weber et al. [263] from Bavaria, Germany. Weber et al. [263] also observed that plant PCB concentrations substantially declined in the past two to three decades but have reached a plateau since around 2009.

The role of sorption for environmental fate of PCBs

PCBs sorbed to suspended solids

Published and unpublished data shows a strong sorptive behaviour of PCBs on suspended solids, which depends on congener characteristics, such as hydrophobicity, chlorination degree or solubility [60]. It can, therefore, be inferred that the higher the suspended solids concentration in the aquatic environment the higher the total PCB concentration therein [221].

Karickhoff et al. [121] concluded that the degree of sorption can be estimated once the octanol/water distribution coefficients, the particle distribution and the organic carbon concentrations of the suspended solids or sediment are known. They showed that the smaller the particle size and the higher the organic carbon concentration, the higher the sorption on that suspended solid which can also be seen from recent data from abandoned collieries [2]. Similar results have been achieved by Strek et al. [232], who also showed that the higher the suspended solids concentration and organic carbon content, the less bioavailable Aroclor 1254 was to plants. This was attributed to the sorption of PCBs onto solid particles, with organic-rich materials showing greater sorption capacity than montmorillonite, which contains little organic carbon. In their plant studies, they found that increasing PCB concentrations (0–200 mg kg^{-1}) led to reduced growth of *Amaranthus retroflexus* L. (redroot pigweed).

In an extensive study of PCB sorption on suspended solids in MIW and mine water influenced surface water, no direct correlation between the suspended solids concentration and the congener sorption on these suspended solids could be shown [2]. Yet, there is an overall relationship between the indicator PCBs (PCB-28, 52, 101, (118), 138, 153, 180). sorbed to the suspended solids and the suspended solids concentration in the water: the lower the suspended solids concentration, the higher the PCB concentration sorbed on the solids. Because no size fraction or organic carbon determination was conducted, the reason for this sorption behaviour is unclear. In general, the adsorption of PCBs to dissolved organic matter (DOM) has to be considered in addition to adsorption to suspended solids [30, 74]. PCBs that are adsorbed to DOM can enhance PCB concentrations that are transported in the aqueous phase, similar to a water solubility enhancement of PCBs [47, 120].

PCBs sorption in biofilms

Biofilms are complex communities of microorganisms embedded in a self-produced matrix of extracellular polymeric substances that adhere to surfaces in aquatic environments [83]. These biofilms can be used as point of entry for several toxic contaminants into freshwater food webs, resulting in the build-up of toxins in freshwater and the food chain [91] and for the bioremediation or monitoring of POPs [75] in MIW. As biofilms are rich in carbon components, they provide sufficient binding sites for halogenated organic compounds such as PCBs, and the process through which toxics adsorb into the biofilm matrix varies with the presence and characteristics of the compound. Hobbs et al. [101] showed that stream and river biofilms adsorb and build-up halogenated organic compounds with PCBs reaching a thermodynamic equilibrium between water and biofilms at log K_{ow} between 5 and 7. The authors conducted multiple analysis in different stream and river biofilms in Washington State, USA, and found a linear relationship between the PCB concentrations in water and the biofilms (Fig. 5). Physical uptake of PCBs by biofilms as well as thermodynamic partitioning of the congeners control PCB uptake rather than internal uptake into internal fats. Where physical accumulation dominates, the highly lipophilic congeners bioaccumulate continuously and uptake is greatly influenced by hydrophobicity of the compound.

In a 6-month study conducted south of Trier, Germany, Schorer et al. [215] observed temporal variations in biofilm formation and the sorption of PCB-180. They conclude that biosorption and transport of pollutants in the aquatic environment is highly variable, especially in the view of biofilm build-up and breakdown, as this can sorb or desorb pollutants, such as PCBs. PCB concentrations in the water phase, therefore, are also a function of the temporal biofilm development and the available time for the PCBs to sorb on the biofilms.

PCBs sorbed to microplastics

Plastics are synthetic organic polymers derived from oil or gas and are widely used because of their durability, corrosion resistance and low cost [77]. They are divided into macroplastics and microplastics, the latter being defined as particles < 10 mm, although some sources use a cutoff of < 1 mm [36, 50]. In the mining industry, plastics perform a variety of functions, including pipe and tubing, cable insulation, ventilation systems, structural supports, safety equipment, components of mining machinery, seals, gaskets and ground support systems. Plastics have become a major concern in environmental pollution, with both macroplastics and microplastics being detected in even the most remote and deepest parts of the planet since the 1990 s [18]. Brožová et al. [38] identified plastic-coated paper, polyethylene terephthalate (PET), polyester (PES), tetrafluoroethylene–perfluoro-propylvinyl-ether (TFE/PPVE) and polypropylene (PP) in mine

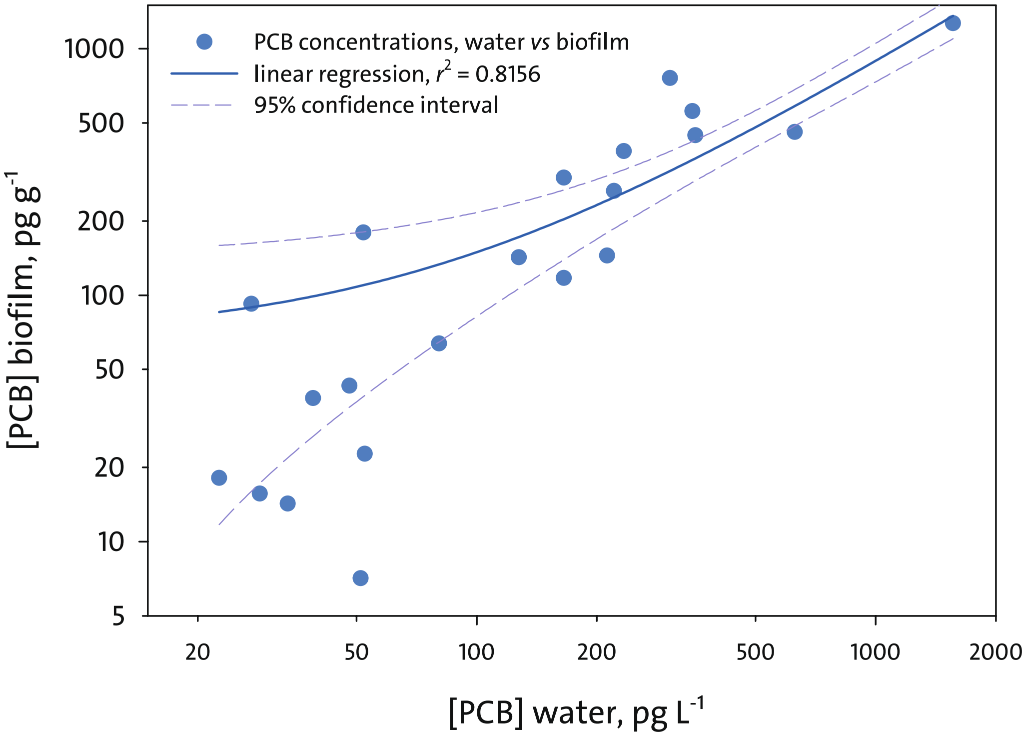

Fig. 5 Linear relationship between PCB concentration in water and biofilm, logarithmic scales (source: authors modified after [101])

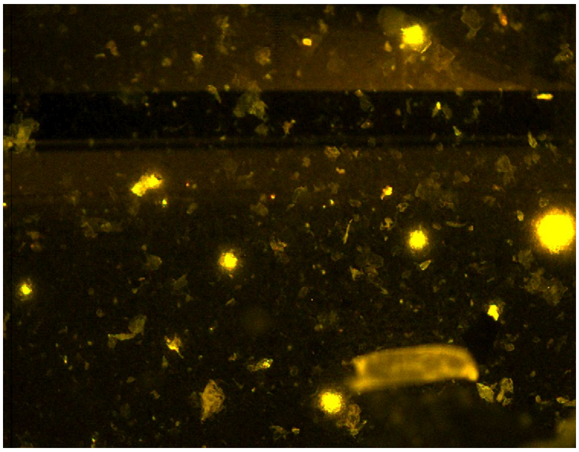

Fig. 6 Microplastics in filter residue of mining influenced water from the abandoned Straßberg/Germany fluorspar mine. Light, round dots are fluorescent microspheres (20 µm diameter), elongated objects are microplastics, granular objects unidentified, very likely Fe oxyhydrates. Width: ≈ 400 µm (source: authors; fluorescent microscopy image)

water samples, mainly as fibres and blue particles. Plastic microfibres were also observed among other microparticles during a mine water tracer test in Straßberg/Harz, Germany [sampling details described in [274] (Fig. 6).

Microplastics can originate from primary sources, such as cosmetic scrubbers, medical vectors or air blast media [62, 191], or from the fragmentation of macroplastics. Due to their small size, microplastics are bioavailable at all levels of the food web [50] and can act as vectors for persistent organic pollutants (POPs) such as PCBs. Their surfaces readily sorb contaminants, allowing PCBs to be transported through aquatic systems, including mine water discharges, affecting previously unpolluted ecosystems [284]. These POPs can later be released from microplastics through desorption, photodegradation by sunlight or other environmental processes, further contributing to their persistence and environmental distribution [9].

The hydrophobic nature of PCBs facilitates their sorption onto microplastics, resulting in high concentrations in the ng g^{-1} to µg g^{-1} range [18, 241]. Mato et al. [163] found PCBs on polypropylene resin pellets together with nonylphenols and DDE. Gas chromatography (GC) analysis of Japanese Waters detected PCB concentrations ranging from 39 to 1200 ng g^{-1} on plastic pellets [205], while Hirai et al. [100] reported even higher concentrations up to 10,000 ng g^{-1}. Research also shows that PCB sorption is influenced by the type of plastic, with polystyrene pellets accumulating higher PCB concentrations than the surrounding water [240]. These findings highlight the role of microplastics as secondary sources of

PCB contamination, allowing their long-range transport through aquatic environments or flooded mine workings.

Given their role in PCB transport, the removal of microplastics from wastewater and MIW is of critical importance. Lares et al. [140] investigated the removal efficiency of microplastics in wastewater treatment and found that membrane bioreactor (MBR) systems removed 99.4% of microplastics, outperforming conventional activated sludge processes (98.3%). Electrocoagulation has also been tested, with Perren et al. [194] achieving over 90% microplastic removal in synthetic wastewater, with a peak efficiency of 99.24% at pH 7.5. These results demonstrate that advanced treatment technologies can substantially reduce microplastic pollution and mitigate PCB transport through aquatic systems.

PCB accumulation and effects in biota

In aquatic environments, PCB congeners accumulate in sediments, where they sorb to organic matter, particularly those with high chlorine content [33, 109]. Over time, these compounds undergo partitioning, chemical transformation (e.g., dechlorination) and bioaccumulation [109]. Because PCBs are highly lipophilic, they bioaccumulate in aquatic organisms, with concentrations increasing at higher trophic levels. As a result, PCBs that initially enter MIW may ultimately affect human health through accumulation in the food web, reinforcing the need for better PCB monitoring and removal strategies.

In their study on global chemical pollution, Travis et al. [242] reported that elevated PCB concentrations in fish and aquatic mammals expose Arctic inhabitants to concentrations approaching toxicity. This exposure, driven by the bioaccumulation of PCBs in fish and their biomagnification in mammals, resulted in Inuit women having the highest concentrations of PCBs ever recorded in breast milk at the time. Aroclor 1260 concentrations ranged from 16 to 514 µg L^{-1} [64]. Furthermore, PCBs have been detected in the Antarctic, accumulating in krill, whales, seals, penguins, birds, and bird embryos [122, 129, 177, 222].

Laliberté et al. [131] investigated PCB concentrations in a Canadian lake affected by mining activities and found PCB concentrations in fish ranging from 1.0 to 740 µg kg^{-1}. Fish samples were collected from several lakes and PCB concentrations in fish flesh were analysed using a high-resolution mass spectrometer. Although all measured concentrations were below Health Canada's threshold of 2000 µg kg^{-1} for the commercial sale of fishery products, the authors noted that PCB concentrations in certain lakes exceeded the 160 µg kg^{-1} guideline established to protect fish-eating terrestrial wildlife. For example, lake trout (*Salvelinus namaycush*) had PCB concentrations above this wildlife safety threshold in some locations. One of the highest PCB concentrations (740 µg kg^{-1}) relating to MIW was determined in *S. namaycush* from Lac aux Dorés near the Copper Rand mine. However, high PCB concentrations (290 µg kg^{-1}) were also found in fish from Lac Chibougamau which is far away from the mines. Though the mines appear to be the major contributor to PCB pollution in the studied lakes, other sources also play a role leading to PCB detection in fish from lakes further from the mines.

Bollini [31] focused her research on PCBs and mercury in the aquatic biota of Torch Lake (Keweenaw area, USA), which has been affected by copper mining and milling between 1849 and 1970. This study reports Lipid normalised PCB concentrations between 5 and 58 µg g^{-1} (average 16 µg g^{-1} [16,000 µg kg^{-1}]) from the Years 2000 until 2022 in walleye (*Sander vitreus*). Consequently, fish consumption in the area is restricted since 1998.

In a study focusing on the analysis of organochlorine pesticides, PCBs and metals, Mazet et al. [166] reported on the presence of PCBs in fish from the Drôme river, with PCB concentrations increasing downstream. From the 16 congeners tested, PCB-153 and 138 were highest in concentration, representing 17.7% and 17.0% of the total congeners analysed, respectively. Though the source of PCBs was not identified, the authors believed that the increase in PCB concentration downstream was linked to urbanisation and associated negative effects of human activities. Another example of PCB uptake is the Korean crucian carp (*Carassius auratus*) which has been reported to have concentrations of up to 5.41 ng g^{-1} [176].

Because PCBs are distributed within the oceans, their occurrence and effects originate from various sources. Madgett et al. [156] found PCBs across four trophic levels in a Scottish marine food web, with biomagnification depending on diet. The extreme effects of PCB bioaccumulation are illustrated by an orca (*Orcinus orca*, killer whale) found stranded in Scotland in 2016, with toxicological analysis revealing PCB concentrations (25 congeners) of 957 mg kg^{-1} lipid weight [37]. Orcas are among the most heavily contaminated mammals worldwide. Based on a model framework and global PCB data, Desforges et al. [63] predicted that PCB-mediated effects on reproduction and immune function threaten the long-term viability of over 50% of all orca populations, with those near industrialised regions or feeding at high trophic levels being at greatest risk of collapse within the next 100 years.

PCB sampling and analysis

Introduction

In most instances, the determination of PCBs adopts sampling, extraction, and analysis as basic steps with the execution of these steps dependent on the type and nature of the sample. With respect to mine water samples, the very low concentrations of PCBs in matrix-rich water complicates sampling and analysis, where also adsorption of PCBs on the sampling vial has to be considered [139]. This also affects the investigation of their toxicity. In this review, attention was paid on sample extraction and analysis relevant for MIW. Additional methods for PCB analysis are discussed in several chapters of the book edited by Down et al. [68]. Landesamt für Natur, Umwelt und Verbraucherschutz NRW et al. [137] compared the results of three laboratories from the same mine water sampling locations with 10-L-bulk sampling and centrifuge sampling. They concluded that the results from different laboratories and methods cannot be compared directly, and the reasons for different detection limits could also not be determined.

Because analysing all 209 PCB congeners is time-consuming, methods were developed in the early 1980 s to focus on a smaller, representative subset [20, 35, 216–218] of three, six or seven congeners. These congeners were chosen as they represented one of the most abundant compounds within different homologue groups in the majority of the considered technical mixtures, could be analytically separated with ease at that time, and were available as individual standards for calibration [20, 39]. They were later included in national and international standards [109, 134]. Depending on the legislative context, the number of indicator PCBs may vary, but typically, the following six or seven congeners are considered: (PCB-28, 52, 101, (118), 138, 153, and 180) reported as indicator PCBs, $\sum PCB_6$ or $\sum PCB_7$ [109]. Because these congeners were also highly abundant across different environmental compartments at that time, they showed a correlation with total PCB concentrations in most environments and have been a practical choice for monitoring. Then, either the sum of the concentrations of the six-congener subset is reported, or the sum is multiplied by the empirical factor determined by LAGA ("Länderarbeitsgemeinschaft Abfall", Germany) in 1985, usually 5, to estimate the total PCB concentration in a sample. Nowadays, unintentionally produced (UP) PCBs, e.g., from thermal *de novo* formation or paint pigments, can play a relevant role with congener patterns deviating from patterns in the technical mixtures [10, 112, 207]. Consequently, the indicator PCBs cannot be used for the monitoring of such UP–PCBs. Because the PCB contamination in mines mainly results from the use of technical PCB mixtures, the indicator PCBs can in principle be used to assess release or contamination from mines. However, the indicator PCBs are neither specific to the MIW environment [270] nor should they be referred to as "Ballschmiter PCBs", as is sometimes mistakenly practiced in the mining context. Based on the results from a recent, detailed PCB analysis of MIW from different mines in Germany [270], certain limitations have to be considered when indicator PCBs are used to assess PCB discharge from mines: because mainly low-chlorinated technical mixtures were used in the investigated mines, only two of the indicator PCBs (28 and 52) can be found in higher concentrations, suggesting that other PCB congeners may be a better choice to assess PCB contamination of mines (in particular PCB 18), especially when PCBs occur in trace concentrations. Furthermore, the congener pattern in the MIW can deviate from the congener pattern in the technical mixtures due to congener specific dissolution, adsorption, or dechlorination of PCBs. Multiplication of summed indicator PCB concentrations by an empirical factor (to achieve presumed total PCB concentrations) is consequently inappropriate. Finally, UP–PCBs have to be considered as well in the mining context, as shown by PCBs 11 and 13 that were found in the MIW samples in higher concentrations than higher chlorinated indicator PCBs [270].

Terminology issues

In published and unpublished expert reports and publications, the terms "dissolved" and "total" PCB are used inconsistently. Some publications or reports define "dissolved" as the fraction of PCBs that passes through a 0.45 µm filter, in line with DIN/ISO terminology, which includes PCBs adsorbed to DOM, colloids, and very fine particles. Others, however, use "dissolved" strictly to refer to PCBs that are dissolved at the molecular level in water. This incoherent usage is a source for misunderstanding. It is, therefore, relevant to define which term means what in each article or report. IARC Working Group on the Evaluation of Carcinogenic Risks to Humans [109] pointed out that the PCB concentrations are strongly correlated with the concentrations of suspended solids, therefore, defines clearly:

- Unfiltered water includes dissolved components and those bound to colloids and suspended solids.
- Filtered water gives PCB concentration on suspended solids (residue on the filter) and dissolved or bound to colloids (filtrate).
- Passive sampling targets the dissolved fraction.

This definition is chemically and physically correct, because it distinguishes between the actually dissolved and colloidally bound load (which passes the filter) on one hand and the suspension load (which remains on the filter) on the other. Unfortunately, it does not agree with recent discussions claiming that everything that passes a filter is described as “dissolved” [this section partly translated and taken from [272, 273]].

Sampling

Sampling for PCB analysis should follow the relevant guidelines and standard procedures. In general, all plastic equipment, plastic containers and (thick) paper bags must be avoided, because the PCBs tend to sorb to plastic material or are released from the material into the sample [8]. Some regulatory bodies and mining companies in Germany are using 10-L-HDPE containers [5], which were also investigated by Andersson et al. [8]. Because these containers can negatively affect the analytical results, they need to be replaced by glass containers, except they are used for passive sampling [79]. Depending on the intend of the study, water may be filtered or unfiltered. Membrane filters to be used must consist of filter material that does not sorb PCBs, which should be verified in preliminary tests.

Alternatives, specifically for sampling freely dissolved PCBs, are passive samplers [32, 79, 165]. These samplers are deployed in the water for periods ranging from days to months, during which they integrate PCB concentrations over time, thereby reducing the influence of short-term variability [26, 79, 109, 150].

Sample extraction

Different methods exist for PCB extraction. Their selection and usage depend on the sample matrix and the PCB speciation of interest. For contaminated waters, it has to be generally differentiated between extraction and measurement of adsorbed and freely dissolved PCB concentrations or rather total concentrations as the sum of freely dissolved and bound molecules. Extraction may be conducted as continuous extraction with an organic solvent or adsorption utilising a carbon activated filter (Table 2). It is evident that these methods are time consuming and often laborious. In addition, the sensitivity of the methods is a function of the volume of sample used.

In a typical liquid–liquid extraction process for PCBs [57], a water sample, such as one litre (or, for very small concentrations of PCBs even 100 L), is first placed into a separatory funnel. A hydrophobic organic solvent, i.e., that does not mix with water, such as hexane or dichloromethane, is then added to the funnel. The mixture is shaken thoroughly, allowing the PCBs to partition into the organic phase, separating from the aqueous phase. After shaking, the two phases—organic and aqueous—are left to separate. The organic layer, which now contains the PCBs, is carefully collected. To remove any residual water, the organic layer is often chemically dried using sodium sulfate and then concentrated. The final extract is analysed for PCB content.

For the PCB extraction of particle-bound species, e.g., from suspended matter, the separation of particles from the liquid phase is commonly applied by centrifugation or filtering methods with subsequent solvent extraction of the solid phase. Relating to filters for PCB sampling, Wolkersdorfer [272] pointed out that cellulose nitrate(esther) filters for PCB analysis sorb up to 100% depending on the congener. It is, therefore, important to use adequate filter material when analysing PCBs in water.

Electric Power Research Institute (EPRI) [76] have shown that the sample matrix of water samples as well as potential background contamination in the laboratory can strongly influence the analytical results. In an interlaboratory study with eight selected laboratories as well as their own studies, they noticed that coal power plant wastewater from ash ponds posed an analytical challenge. Yet, they point out that additional studies with real-world environmental samples of higher complexity might be needed to gain an overall conclusion of laboratory background concentrations and analytical accuracy. During sampling and sample preparation also sorption of PCBs to plastic or borosilicate glass must be avoided as this might negatively influence the sample results [192].

Sample analysis

Gas chromatography–mass spectrometry in PCB analysis

Prior to the advent of electron-capture detectors (ECDs), PCBs remained undetected due to the limitations of analytical techniques and the prevailing assumption that they were not persistent [24]. In some cases, they were erroneously identified as DDT due to the constraints imposed by chromatographic techniques during that period [206]. Presently, GC has emerged as the preferred analytical method for PCBs, owing to its sensitivity, effective separation, and compatibility with mass spectrometry (MS) [139]. While ECDs initially dominated PCB analysis, MS has now become the most widely used detection method due to its higher specificity, as it provides molecular mass information and allows for differentiation from matrix background.

Gas chromatography–mass spectrometry (GC–MS) is commonly employed for PCB analysis, incorporating temperature-programmed injectors, capillary columns with varying dimensions, and a carrier gas operated at a constant flow rate. The employment of automatic injectors ensures precise delivery of samples, with analyte quantification typically performed in selected ion monitoring (SIM) mode. Although gas chromatography–electron-capture detection (GC–ECD) has been utilised for PCB detection in river and soil samples [166, 171], GC–MS offers enhanced specificity and lower detection limits. Furthermore, the utilisation of stable isotope-labelled

Table 2 Overview of techniques suitable to extract PCBs

Method name	Principle	Advantages	Disadvantages	Application examples	References
Liquid–liquid extraction (LLE)	Separation of compounds or metal complexes is based on relative solubilities in two different immiscible liquids	High capacity of the extractant and high selectivity of separation	Cannot be automated, uses higher volumes of solvents and samples, time consuming and laborious, formation of stable emulsions	Analysis of PCBs in river, lagoon, and runoff water samples	Dano et al. [57], Moret et al. [179], Sulej et al. [233]
Solid-phase extraction (SPE)	Dissolved or suspended compounds in a mixture are retained on a packed cartridge according to physical and chemical properties	Fast, presents low contamination risk and can be used online	Uses higher volumes of samples, uses solvents, time consuming and laborious, costly, complex matrix causes settling in cartridges, cannot be automated	Determination of PCBs in wastewater, lake water and water samples	Aydin et al. [14], Nellier et al. [182], Westbom et al. [267], Xu et al. [276]
Solid-phase microextraction (SPME)	Partitioning of analytes between the sample and a polymer-coated fibre	Rapid, simple, solvent free, extraction from the sample or the headspace above a sample, dissolved and total concentrations can be analysed	Costly infrastructure, fragile coating layer of fibre, laborious method development, longer analysis time per sample	Determination of PCBs in industrial harbour water, sediment pore water, water in bioconcentration studies, mine water	Böhm et al. [29], Hawthorne et al. [95], Lambropoulou et al. [133], Llompart et al. [149], Wiltschka et al. [270]
Stir bar sorptive extraction (SBSE)	SPME principle, polymer coating on a magnetic stirring rod	Allows usage of larger sample sizes and is more robust	The technique uses a desorption step which needs an additional cooling trap and is complex to automate	Analysis of PCBs in snow samples in the Aconcagua Mountains in the Andean Range and in environmental waters	Lei et al. [142], Quiroz et al. [198]
Passive sampling	Partitioning of analytes between the water phase and the passive sampling phase (here: a hydrophobic uptake material)	Analysis of trace concentrations, time weighted average concentrations	Laborious quantification	Analysis of PCB concentrations in water and sediments	Lohmann et al. [150], Mayer et al. [164], Smedes et al. [227]
Disperse liquid–liquid microextraction (DLLME)*	Fine droplets of extraction solvent are dispersed in an aqueous sample. High collective area of the solvents facilitates partitioning of analytes into the extraction phase	Short extraction time, uses small volumes of solvent and water, rapid and easy to use, cost-effective, no sample carryover, requires no instrument modification, high recovery of analytes	Difficult to automate, the use of dispersive solvents decreases the partition coefficient of analytes into the extraction solvent	Determination of PCBs in water and soil samples	Hu et al. [105], Rezaei et al. [204], Temerdashev et al. [239]
Ultrasound-assisted emulsification solvent extraction (USAEME)*	Ultrasonic radiation is applied to accelerate emulsification which favours the mass transfer of analytes from aqueous phase into organic phase thereby enhancing extraction efficiency	Viable, cost-effective, simple, rapid, less solvent and sample used	Excessive ultrasonic energy may degrade analytes and cause permanent damage to the properties of analytes	To enhance crystallisation processes in many industrial domains, such as chemical, pharmaceutical, and petrochemical industries, determination of PCBs in water samples	de Castro et al. [58], Ozcan et al. [188], Yurdakok-Dikmen et al. [282]
Membrane-assisted solvent extraction (MASE)*	Analytes are preconcentrated using a membrane that protect the acceptor phase or solvent, where the analytes from the donor phase or sample are concentrated	Allows extraction of analytes from extremely dirty matrices. Allows automation of solvent addition, extraction, and injection steps	Solvent may dissolve unwanted pyrolysis products, matrix material and other substances which may interfere with subsequent analysis	Extraction of PCBs from estuarine water, seawater, river water and beverages	Prieto et al. [196], Schellin et al. [213]

Table 2 (continued)

Method name	Principle	Advantages	Disadvantages	Application examples	References
Vortex-assisted liquid–liquid microextraction (VALLME)	Dispersion of the solvent phase into the aqueous solution provided using vortex and miniaturisation	Fast; short extraction time, repeatable, efficient, requires small volumes of solvent and sample, high recovery	Limited number of appropriate extractants	Extraction of PCBs from different water and wastewater samples	Ozcan [187], Yiantzi et al. [280]

[*] Method does not play a relevant role in PCB extraction at the time of writing this review

References are mainly case studies of where the method has been used for PCB analysis. They are not necessarily descriptions of the method

PCB congeners as internal standards facilitates their distinction from native molecules based on mass. Advancements in gas chromatography techniques, such as high-resolution mass spectrometry (GC–HRMS), have further enhanced the sensitivity and specificity of the analysis. Gas chromatography–ion trap mass spectrometry (GC–ITMS) facilitates additional fragmentation, thereby improving detection and separation, rendering it a valuable tool for the analysis of PCBs in complex matrices, such as milk [88]. The MS/MS capability of GC–ITMS increases selectivity while being more cost-effective than high-resolution MS and triple quadrupole MS [265].

Isotopic composition of PCBs and utilisation for PCB determination

This section underscores the prospective significance of distinguishing both PCB concentrations and the sources of water contamination, particularly within legal contexts that adhere to the polluter-pays principle [262]. While the necessity of isotope-specific analysis is not a customary component of routine environmental monitoring, compound-specific carbon isotope analysis (CSIA-δ^{13}C) utilising gas chromatography–isotope ratio mass spectrometry (GC–IRMS) emerges as a potent instrument for tracing the presence of anthropogenic organic pollutants. Despite the analytical challenges, advancements over the past two decades have enabled the detection of micropollutants and persistent organic pollutants (POPs) in the environment [1, 78]. Numerous studies have demonstrated the effectiveness of CSIA–δ^{13}C in identifying complex mixtures of organic pollutants, including PCBs [70, 78, 103, 214, 255].

Stable isotope analysis is a suitable method used for the determination of origins and fate of persistent organic compounds such as PCBs. This technique is based on the determination of stable carbon and hydrogen isotopes of POPs. Normally, element analyser–isotope ratio mass spectrometry (EA–IRMS) is used for the determination of bulk δ^{13}C and δ^{2}H values and has often been linked to gas chromatography enabling CSIA of δ^{13}C [255]. Isotope ratio mass spectroscopy (IRMS) is suitable to differentiate technical products from various manufacturers, metabolites from original POPs, and to address kinetic isotope effects (KIE) during transformation of POPs. Stable isotope analysis could help shed light in understanding if POPs residues in a sample are a result of long-range transport or not, if the POPs have biodegraded or not and to what extent, insight whether some of the compounds are metabolites of others and if there is one origin or multiple origins of the POP. The principle of stable isotope analyses of POPs is based on taking advantage of the ratio of the carbon isotopes (^{13}C, ^{12}C) and hydrogen (^{2}H, ^{1}H) isotopes in samples by means of IRMS. Despite its potential, the complexity of stable isotope measurements and the lack of reference standards have limited its widespread use in POP research. Gas chromatograms of POP extracts often show overlapping peaks, complicating analysis. Even at low concentrations, environmental degradation, linked to KIE, further challenges the process. Nonetheless, stable isotope data remains essential for understanding the behaviour of pollutants.

EA–IRMS, which is widely used for bulk δ^{13}C analysis, requires careful calibration to ensure accuracy, but analysing polyhalogenated compounds like PCBs is particularly challenging. Chlorine build-up during oxidation can affect the furnace performance. In contrast, GC–IRMS allows compound-specific analysis but requires converting analytes into measurable gases, making it technically demanding. Techniques like multidimensional gas chromatography (MDGC) are used to overcome co-elution issues, improving sensitivity and precision [102, 103].

Nuclear magnetic resonance (NMR) spectroscopy also contributes to isotope analysis by determining the distribution of deuterium isotopomers. Though it requires large sample amounts and is best suited for simple molecules, it provides valuable data on isotope distributions in POPs [183]. Despite the challenges, advances in stable isotope analysis using methods such as EA–IRMS, GC–IRMS and NMR continue to improve our understanding of the transformation and transport of POPs in the environment and MIW.

Source identification through PCB fractionation

CSIA, as described above, provides information on the isotopic composition of a single compound relative to a standard [214]. The original source of environmental contaminants can be traced using the isotopic signature. This approach is important especially on a local scale, where contaminants can be allocated to a specific source and allow for appropriate means of remediation. Isotopic signatures of chemicals show variations between producers depending on the method followed in synthesising the compound. This feature allows for tracing of the chemical or even trace the time the contaminant was released. Studies which have used this approach have shown the necessity to join fingerprinting techniques with compound-specific isotope analysis. This is because neither CSIA nor fingerprinting alone can provide conclusive results for source apportionment. For example, fingerprinting of *n*-alkane fractions in crude oil and refined products was combined with isotopic characterisation of carbon to allocate sources of sediment contamination [209].

One common challenge in assessment of biodegradation processes of specific contaminants is the difficulty to detect metabolites at trace concentrations. The difficulty in analysis is further brought about by the need for conclusive mass balances. Despite these challenges, CSIA has shown success when applied to investigate biodegradation. In most instances, substantial isotope fractionation has been noted during microbial biodegradation. These studies investigated the isotope ratio of the residual substrate, where fractionation takes place in the irreversible first enzyme reaction in the degradation pathway [178]. Fractionation was not influenced by uptake of the substrate or diffusion through the aqueous phase to the organism. The investigation of spatial distribution of biodegradation based on isotope data is only possible if only a single source of contamination exists. The source must have a defined source isolation composition of the contaminant. Depending on the transformation reaction type, isotope fractionation for a pollutant can vary a lot, which often complicates the explanation of data obtained from field studies. However, variations in isotope fractionation have been found handy in providing important information which has been used in understanding chemical and biochemical reactions. In addition to detection of compounds, isotope fractionation measurements in the field are also used for the quantification of *in situ* transformations at polluted sites [255].

PCB removal and elimination strategies

Introduction

Various physico-chemical techniques have been suggested for the reclamation of PCB-contaminated environments. For example, PCB-contaminated soils can be cleaned through processes, such as soil washing, incineration, and thermal desorption, while soil burial, though not a cleaning method *per se*, may be considered a remediation approach under certain conditions [236]. Aqueous phases can be treated using microbiological methods, sedimentation, or filtration, among others. Given the importance of removing PCBs from the environment, several methods relevant to MIW, mine wastes, and abandoned mine sites will be described in this section.

In this context, it is important to note that PCB destruction methods can lead to the formation of PCDFs, similar to what occurs during natural combustion processes [107, 261]. As these PCDFs are also toxic [253], it is essential to analyse for these compounds when considering high-temperature remediation methods—however, for the specific treatment of MIW, high-temperature methods may not be relevant, only for the destruction of PCB-contaminated suspended solids that may be generated by the treatment process.

When considering the decrease of PCB concentrations, both in natural environments and in artificial environments designed to eliminate PCBs, the transformation of PCBs into other compounds of concern must be considered in addition to their complete elimination. For example, the formation of hydroxylated PCBs (OH-PCBs) should be considered, as such transformation products have a higher water solubility but retain relevant toxicity [211, 238, 249]. The formation and occurrence of OH-PCBs in PCB-contaminated MIW can be expected, probably even at higher concentrations than PCBs. As no information is available on OH-PCBs in MIW, this is a relevant information gap.

Microbial breakdown

The microbial degradation of PCBs occurs through two main mechanisms: aerobic and anaerobic degradation. Both processes play a central role in the natural reduction of PCB contamination, with anaerobic processes being particularly relevant as they preferentially take place in highly contaminated, oxygen-poor environments such as sediments. Though PCBs are mostly resistant to chemical and biochemical transformation, biological transformation can take place under suitable environmental conditions as bacteria using biphenyl for gaining energy can be found widespread in nature [86]. Some restrictions in their biodegradation have been identified coming from various enzyme pathways in different microorganisms [56]. In general, the rate of PCB dissolution is a fundamental determination of the rate of natural attenuation of PCBs by biodegradation [51]. The potential for natural attenuation of PCBs is considered low for higher chlorinated PCBs and moderate for the lower chlorinated ones.

The use of activated carbon as an effective support material for the attachment of microorganisms has been reported [170]. This leads to the formation of multi-species biofilms some of which are capable of degrading PCBs. Though microorganisms may not readily mineralize PCBs, there are a few bacterial strains that are able to partly metabolise PCBs in the presence of oxygen [286]. Less chlorinated PCB congeners are degraded more under aerobic conditions. However, biotransformation of PCBs with chlorine atoms up to eight has been reported [286]. Natural degradation of PCBs under aerobic conditions is limited by low concentrations of bacteria. To counter this challenge, PCBs and PCB–degradation bacteria have been co-localised onto the surface of activated carbon, where the activated carbon acts as adsorbent for PCBs. Granular activated carbon has been preferred as a substrate material to powder activated carbon. Mercier et al. [172] have developed biofilms of indigenous bacteria from aquatic sediments onto granular activated carbon and found that the growth of biofilms was dependent on the properties of the activated carbon. They successfully selected a bacterial community from a PCB-polluted soil and utilised the bacterial colonies for the biodegradation of PCBs [171]. The authors found that microcosms inoculated with biofilm-coated granular activated carbon did not reduce the concentrations of extractable PCBs as efficient as a planktonic-cell suspension. They, furthermore, believed that the application of biofilm-coated granular activated carbon modifications should reduce the toxicity and concentration of extractable PCBs. Ahmed et al. [4] present another evidence of the degradation of PCBs by microorganisms. They successfully isolated two species of *Achromobacter* from sewage effluent, which degraded PCBs by fission of the benzene rings resulting in the production of meta-cleavage products. Based on the differences between spectral characteristics of degradation products, the authors concluded that divergent degradation pathways existed between the selected species.

When PCBs are degraded by PCB-degrading bacterial strains, biphenyl serves as carbon source and inducer of the active enzyme. Microorganisms degrade PCBs through reductive dechlorination [51], through a four step *meta*-cleavage degradation pathway, where a five-carbon compound is generated together with chlorobenzoic acid. Lambo et al. [132] isolated a biphenyl-utilising psychrotolerant bacterium from PCB-containing soils. The bacterium strains grew on biphenyl as the only source of carbon and energy. PCBs were metabolised at low temperatures, where up to 89% removal of monochlorobiphenyls was noted at 5 °C, whereas the removal of dichlorobiphenyls and trichlorobiphenyls ranged from 30 to 78% and 30 to 75%, respectively, over a period of 48 h. PCB removal showed dependence on the temperature. In agreement with other literature reports, the authors noted that congeners with two or more ortho chlorine were more resistant to degradation.

Furukawa et al. [85] studied microbial degradation of PCBs by bacterial strains isolated from a lake sediment using biphenyl as a carbon source. Various PCB components were metabolised by the bacterial strains of the genus *Alkaligenes*. However, degradation of less chlorinated rings was preferred, and the degradation followed two steps. In the first step, metabolic intermediates were produced. These metabolic intermediates were degraded to corresponding chlorobenzoic acids in the second step. It was noted that PCBs with all chlorines on one ring were degraded faster in comparison with those having a similar number of chlorines distributed between the two rings, and that the degradation rate decreased with increase in the number of chlorines.

Microbial degradation is one of the promising approaches for bioremediation of soils and sediments polluted with PCBs [158]. Anaerobic microbial communities residing in sediments are capable of dechlorinating PCBs to lesser chlorinated chlorobiphenyls. These can then be degraded by aerobic bacteria in a sequential anaerobic–aerobic process as has been shown by several studies in recent years [86], some of which can be applied by degrading PCBs in natural or constructed wetlands.

PCB elimination in natural and constructed wetlands

Wetlands, sometimes referred to as reed beds or treatment wetlands, have been presented as a promising technique for the remediation of PCB-contaminated water, where aquatic plants and soils have removed pollutants utilising processes, such as uptake, sorption and microbial degradation [43, 93, 226]. Wetlands include marshes, swamps, bogs and wet meadows [118]. Their unique properties are brought about by their inherent frequent wetness, changing chemical, physical and biological properties of soil, water and biota. As a result, constructed and natural wetlands have been applied in various ways to reduce contamination and help meet regulatory standards for water, soil, and biodiversity protection. They have been used to treat municipal wastewater, stormwater and MIW. The ability of wetlands to sorb PCBs has been reviewed by Haarstad et al. [93]. Wiltschka et al. [270] have shown that in a constructed wetland fed by mine water, the PCB concentration is reduced by an average of 32% over a flow distance of 500 m. Barber et al. [17] found that the Tres Rios Demonstration Constructed Wetlands removed 40–99% of pollutants that comprised of hydrophobic organic compounds (HOC), herbicides, pesticides and organic wastewater [17]. The wetlands utilise secondary-treated wastewater to maintain an aquatic ecosystem in an arid environment. From these studies, it is evident that wetlands can be used as an efficient passive ecological process for the remediation of PCB-polluted water. Li et al. [146] identified the bacteria *Hydrogenophaga taeniospiralis* associated with cattail roots known to live on biphenyl or cometabolise PCBs and, therefore, concluded that PCBs in the wetland water could be degraded.

Several studies have documented PCB and other POP accumulation in floodplain vegetation and soils, affecting livestock and human food production as well [15, 81, 99, 229, 264]. Livestock are at risk of taking up and accumulating PCBs both by grazing and harvested fodder. Contaminated soil is thereby of particular relevance when taken up by grazing animals or when adhering to harvested plants used as fodder. Before plants from wetlands, floodplains, or agricultural land irrigated with MIW are used as food or fodder, it is, therefore, essential to analyse both the plants and the soil for PCB and OH-PCB contamination.

Nanotechnology for PCB removal

Nanotechnology offers promising techniques for the removal of PCBs from contaminated water [33], addressing limitations of traditional water treatment methods. Nanomaterials such as nano-adsorbents, nanometals, nanometal oxides, and carbon nanomaterials possess exceptional properties such as high reactivity, large surface area, and strong sorption capacity that make them effective for the remediation of PCBs, potentially toxic metals, radionuclides, and other organic contaminants [19, 277, 278]. Though promising, no pilot-scale or real-world applications of nanomaterials for PCB removal have been reported in the literature to date, as also identified by [33].

Carbon-based nanomaterials, including carbon nanotubes (CNTs), have demonstrated high efficiency in adsorbing organic compounds like PCBs due to their large surface area and favourable interactions, such as hydrophobic effects, π–π bonds, and hydrogen bonding [279]. Carbon nanoparticles, particularly CNTs, interact with PCBs via multiple mechanisms, such as hydrophobic interactions, π–π bonding, and electrostatic forces. These interactions enhance the adsorption of PCBs onto the surface of carbon nanoparticles. For instance, single-walled and multi-walled carbon nanotubes (MWCNTs) have been successful in removing PCBs from contaminated water, thanks to their large mesoporous volume and chemical stability [224]. Shao et al. [225] demonstrated that MWCNTs grafted with methyl methacrylate achieved over 95% PCB removal within 24 h under ambient conditions, with pH being a statistically significant factor. Other studies showed similar results using functionalized MWCNTs, achieving high PCB removal efficiency, sometimes independent of pH. Graphene oxide, another carbonaceous nanomaterial, has emerged as a potent adsorbent due to its large surface area and high adsorption capacity [157]. It has shown PCB removal efficiencies over 99%, with temperature being a more relevant factor than pH in its effectiveness [21]. Unlike CNTs, graphene oxide's high removal capacity of PCBs is independent of pH, making it a versatile option for water treatment.

Photocatalytic processes using nanoparticles like titanium dioxide (TiO_2) have also proven effective for PCB degradation [49, 235]. TiO_2 nanoparticles, particularly carbon-modified versions, facilitate oxidative photocatalysis by generating reactive oxidants that break down PCBs into non-toxic compounds [94]. These particles are low-cost, stable, and offer high removal rates, with studies reporting up to 93% photodegradation of PCBs in 24 h under ambient conditions [223]. In addition to carbon-based materials, other nanocomposites such as magnetic carbon nanocomposites, gold nanoparticles, and nano-clays have been explored for PCB remediation [143, 237, 275]. Magnetic carbon nanocomposites are reusable and possess large surface areas, while gold and clay nanoparticles are highly selective due to strong interactions with organic pollutants. These materials, along with TiO_2 and graphene oxide, represent a diverse array of nanotechnology applications that enhance PCB removal from water, offering a potential solution to persistent contamination issues.

Iron oxide nanomaterials have been applied in the treatment of PCB-contaminated water due to their small size which provides a high surface area for sorption and selectivity. Improved efficiency was observed when an external magnetic field was applied [106]. To elevate the decontamination efficiency, some authors have used iron oxides in combination with other materials to enhance the removal of organic pollutants. As an example, Fe_3O_4 grafted on graphene oxide has shown 100% removal of PCB-28 when 50 mg of the synthesised nanoparticles was used to treat 200 mL of PCB-28 contaminated water in 0.5 h. The removal efficiency was found to be pH dependent [285]. Another modification to improve the performance of nanomaterials in the elimination of PCBs is the use of bimetallic nanoparticles combined with activated carbon scaffolds as done by Choi et al. [48]. In this system at pH above 6.5, monochlorobiphenyl was completely adsorbed to activated carbon within 2 days and subsequently dechlorinated by 90% by the Fe/Pd bimetallic nanoparticles.

Reductive treatment of organic and inorganic contaminants has been done using permeable reactive barriers (PRB), with Fe^0 and nano-Fe^0 (zero valent iron, ZVI, nZVI) which can be used instead of pump and treat systems. With respect to this technique, Fe^0-based PRB has gained favour in application owing to its low cost and effective treatment. This has seen several researchers investigating PCB removal using this technology. For instance, Du et al. [71] investigated the treatment of ground water polluted with PCBs using a PRB packed with iron powder, a combination of iron and zinc powder as well as a concoction of iron powder and activated carbon. From the three systems investigated, a mean PCB removal efficiency of 94% was achieved. The high treatment efficiency was attributed to the strong reducibility of Fe^0 and Zn^0, which provided electronic ability resulting in the reduction of chlorinated organic compounds to less harmful compounds. It was also acknowledged for the Fe^0–Zn^0 PRB that the formation of many small "batteries" lowered the activation energy of the reaction, which promoted the PCB reduction reaction efficiency. Finally, the iron oxide hydrate was noted to have a strong adsorption–flocculation performance, lowering the PCB concentration in the water. Wang et al. [258] used synthesised 1–100 nm nanoscale iron particles with a specific surface area (BET) of 33.5 $m^2\ g^{-1}$ for the rapid dechlorination of PCBs. Reddy et al. [201] summarises that

PCB removal by nZVI in combination with other methods might be a future option to improve the quality of PCB-contaminated water. Relating to mine water, where nZVI has been used for in-situ uranium removal, it is important to recognise, that underground nZVI reactors might produce oxygen and hydrogen which could result in explosions. Using nZVI for PCB removal in PCB-contaminated mine water is, therefore, only recommended in surface applications.

Palladium nanoparticles (Pd-NPs) have shown great promise in the degradation of POPs through catalytic hydrodechlorination [45, 154, 155, 269], a process where chlorine atoms in PCB molecules are replaced with hydrogen, resulting in less toxic or more easily degradable compounds. Pd-NPs facilitate the breakage of the C–Cl bonds in PCBs, making them highly effective for the breakdown of highly chlorinated congeners. This reaction typically uses molecular hydrogen or other reductants to supply the hydrogen atoms needed for the process. The effectiveness of Pd-NPs is further enhanced when combined with ZVI, forming a bimetallic system, where iron acts as the electron donor, and palladium accelerates the electron transfer to the PCB molecules [147, 259, 287]. This Pd/Fe combination substantially boosts the dechlorination process, enabling faster and more complete breakdown of PCBs, even in complex environmental settings, such as contaminated soil and groundwater. One of the key advantages of Pd-NPs is their rapid reactivity, often achieving substantial PCB reduction in short timeframes, compared to traditional methods. However, the application of Pd-NPs faces challenges, including the high cost of palladium, which limits large-scale use, and the potential for surface deactivation by sulfur compounds or trace metals, which can reduce their catalytic activity over time [127, 148, 208]. Research is ongoing to address these issues, with efforts focused on enhancing the reusability and cost-effectiveness of Pd-NPs, including combining them with other materials such as carbon-based or magnetic composites to improve performance and scalability. The protection of Pd catalysts by coatings is promising for the dechlorination of PCBs in MIW, as recently investigated by Wiltschka et al. (unpublished). Overall, Pd-NPs are a highly efficient and promising approach for PCB remediation, especially in environments, where traditional methods struggle, though further work is needed to optimise their application for larger scale environmental clean-ups.

Electrocoagulation

Coagulants such as alum and ferric chloride have been widely used for the production of clean drinking water from polluted fresh water sources with total dissolved solids less than 1000 mg L^{-1} [174]. Water treatment through coagulation follows three processes or steps, namely: coagulant formation, particle destabilisation and finally aggregation which results in floc formation. Coagulation processes as means to provide safe drinking water have been improved using electrolytic means to treat sewage water. This is not a new technology as Britain has had treatment facilities using iron electrodes since the late 1880 s [126].

In electrocoagulation, an electrical current is used to bind unwanted molecules of pollutants in solution to each other and to the materials in the reactor. Emulsions are also broken down when the negative end of polar anionic surfactants are bound to the positive charge of the iron complexes established in the electrical environment [104]. The pollutants are then removed by processes, such as flotation, settling, skimming or filtration. Efficiency of electrocoagulation reactors are influenced by the electrode metal, their spacing, orientation and accessibility.

The use of electrodes in water treatment increased in the early 1990 s as water treatment plants in the United States adopted the utilisation of steel electrodes in water treatment. To date, various countries are using electrocoagulation for wastewater reclamation. Mills [174] presented a continuous-flow electrocoagulation process that produces safe drinking water from a wide range of water sources. The system design allows for coagulant formation and particle destabilisation to occur in the turbulent flow through electrolytic cells, while in the flocculation stage, aggregates are formed.

Gutiérrez-Hernández et al. [92] used the photo electro-Fenton (PEF) process and tested the removal of PCB-28, 52, 101, 138, 153, 180 and 209 with 50 µg L^{-1} concentration each on a boron doped Diamond electrode. After a 6 h reaction time with a current density of 16 mA cm^{-2} and 365 nm UV Light to irradiate the mixture, they could remove up to 97% of their PCB. Another example of electrocoagulation for the treatment of PCB-contaminated water is the Duwamish Sediment Other Area and Southwest Bank Corrective Measure in Seattle, USA [7, 104]. In 2011, a former Boeing airplane manufacturing plant was demolished, requiring the removal of sediments polluted by PCBs, hydrocarbons and potentially toxic metals. Amec Foster Wheeler Environment and Infrastructure et al. [7] and Hsieh et al. [104] applied electrocoagulation as a primary treatment for the dredge material and treated over $150 \cdot 10^6$ L. Zanko et al. [283] also applied electrocoagulation to remove PCBs from harbour sediments. Uniquely, they treated the anaerobic, low-Eh sediments directly, achieving a 99% PCB reduction over a 55-month trial at New Bedford Harbour, Massachusetts, USA. Their method, called electrochemical geo-oxidation (ECGO) needed to operate for a longer period than initially anticipated. Although these studies point to the potential of electrocoagulation for the elimination of PCBs, the PCB concentrations in the aforementioned studies were often far above the respective maximum water solubilities of PCBs, or the remaining concentrations after electrocoagulation were still well above the maximum water solubility of PCBs, or still higher than the initial concentrations of PCBs in MIW. The applicability for trace concentrations or bound species was not demonstrated and a direct transferability of results to PCB elimination from MIW was not tested yet.

Camphausen, Germany, treatment plant

One of the world's first plants for the removal of PCBs from MIW has been built in Camphausen, Germany (Fig. 7). Commissioned in 2024, the plant treats MIW from the former Camphausen colliery, which ceased operations in 1990, and focuses on the removal of both H_2S and PCBs. The circumneutral MIW is pumped from Shaft II using a submersible pump at a rate of 1 to 2 million m^3 per year. To prevent the release of unpleasant smelling and toxic H_2S, the sulfide in the MIW is oxidised with H_2O_2, converting it to sulfate. During this process, the MIW temporarily passes through the stability field of elemental sulfur, resulting in the formation of nanosulfur precipitates that give the water a milky appearance. In theory, PCBs should sorb to these nanosulfur particles, allowing them to be removed by a thickener. As of early 2025, the plant is in trial operation and ongoing monitoring will determine how effective the process is. A key factor will be whether the elemental nanosulfur remains stable long enough to support PCB removal before eventually oxidising to sulfate.

Conclusion and research needs

Although banned for at least two decades in most countries of the world, contamination of environmental compartments with persistent, bioaccumulative, and toxic PCBs is still a pressing topic for environmental and human health. Mine water discharge to surface Waters can be a relevant point source of additional PCB input to and subsequent distribution in the environment. A key conclusion from this Literature research is that with the currently available data on PCB analysis in MIW, a worldwide overview of the PCB contamination in MIW is not possible. A global survey conducted in this study, reaching out to over 1100 experts, confirmed that no monitoring data on PCBs in MIW are available outside of Germany, highlighting a substantial gap in awareness and research on this issue. As most data are from Germany, more data are needed in the future both to get a better understanding of the spatial distribution of PCBs in MIW and to assess the potential risks arising from contaminated mining sites and MIW discharges to the environment. In this context, also transformation products such as OH-PCBs should be considered, because no information is available about their occurrence in MIW.

Though several methods for analysing PCBs in MIW exist, the results obtained can be highly variable and often the results cannot be fully compared with each other due to methodical differences. Even samples taken at the same location at the same time but analysed by various laboratories show different results. This can be

Fig. 7 Settling basin of the Camphausen MIW treatment plant for the removal of H_2S and PCB (source: Anse Sotiralis)

related, e.g., to PCB sorption on the sampling containers, the filter devices or on the filter material itself. The standard sampling methods currently used for PCBs in mine water appear to lack sufficient reproducibility, especially when trace concentrations are analysed in matrix-rich water. A more sensitive and reproducible approach, solid-phase microextraction (SPME) with internal standard correction, has recently been recommended. However, it is not part of the standard instrumentation in most routine laboratories. Clarification is also needed for the way in which PCB concentrations are specified. The informative value can be limited when relevant methodological information is missing, if it is unclear to which congeners the study refers (only one congener, all the congeners measured or if they are calculated results for the whole range of potential congeners in the sample), or rather if concentrations are based on the measurement of (freely) dissolved PCB species, bound species, or total concentrations. To overcome such uncertainties, a crucial requirement is to achieve an agreement on standardisation of sampling methods and sample preparation as well as the differentiation of various molecule specifications with subsequent laboratory comparisons in interlaboratory tests.

Because PCBs are largely sorbed to suspended solids, it is essential to reduce the discharge of suspended solids from mines. This can, for example, be done with installing sedimentation tanks or basins before the mine water is discharged, although limitations exist for high discharge volumes of MIW.

Though PCB concentrations in MIW are mostly below concentrations that are of acute toxicity, their danger results from a long-term, low-level exposure to all forms of life. This results in the bioaccumulation of the PCBs in aquatic life and their magnification in food webs that is also relevant for the uptake of PCBs by human. Using MIW for crop irrigation requires careful consideration due to the potential uptake of PCBs by plants. Therefore, removing low concentrations of PCBs from MIW, even when they only contribute to a small part to the total PCB concentrations in the receiving water courses, will help to improve the quality of our environment and the health of organisms and, in consequence, humans.

It is necessary to include a suitable method for extraction and detection of PCBs in regular mine water analysis and to ensure that their spread from abandoned or operating mines into the receiving environment is reduced to a minimum, which is also in accordance to international legislation. This may increase the cost of analysis and water treatment, but given the history of POPs, particularly in terms of their toxicity, persistence and previously accepted release to the environment, the consequences of past unawareness and shortcomings must be minimised for the future.

Abbreviations

BET	Brunauer–Emmett–Teller
CNT	Carbon nanotubes
CSIA-δ^{13}C	Compound-specific carbon isotope analysis
CSIA	Compound-specific isotope analysis
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DLLME	Disperse liquid–liquid microextraction
dl-PCBs	Dioxin-like PCBs
DOM	Dissolved organic matter
EA–IRMS	Element analyser–isotope ratio mass spectrometry
ECD	Electron-capture detector
ECGO	Electrochemical geo-oxidation
GC	Gas chromatography
GC–HRMS	Gas chromatography–high-resolution mass spectrometry
GC–IRMS	Gas chromatography–isotope ratio mass spectrometry
GC–ITMS	Gas chromatography–ion trap mass spectrometry
HOC	Hydrophobic organic compound
HRMS	High-resolution mass spectrometry
HSD	Hydraulikflüssigkeit (H), schwerentflammbar (S), wasserfrei (D) [Hydraulic fluid (H), flame retardant (S), anhydrous (D)]
IRMS	Isotope ratio mass spectroscopy
KIE	Kinetic isotope effects
LLE	Liquid–liquid extraction
MBR	Membrane bioreactor
MCL	Maximum contaminant level
MDGC	Multidimensional, heart-cut, or two-dimensional (2D) gas chromatography
MIW	Mining influenced water
MS	Mass spectrometry
MWCNT	Multi-walled carbon nanotubes
NMR	Nuclear magnetic resonance spectroscopy
nZVI	Nano-zerovalent iron (nano-Fe^0)
OH-PCB	Hydroxylated PCB
PCB	Polychlorinated biphenyl
PCDDs	Polychlorinated dibenzo-*p*-dioxins
PCDFs	Polychlorinated dibenzofurans
Pd-NPs	Palladium nanoparticles
PE	Polyethylene
PEF	Photoelectro-Fenton
PET	Polyethylene terephthalate
POPs	Persistent organic pollutants
PP	Polypropylene
PRB	Permeable reactive barriers
SBSE	Stir bar sorptive extraction
SDG	Sustainable Development Goal
SIM	Selected ion monitoring
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
TCBT	Tetrachlorobenzyltoluene
UP-PCB	Unintentionally produced PCB
USAEME	Ultrasound-assisted emulsification solvent extraction
VALLME	Vortex-assisted liquid–liquid microextraction
ZVI	Zerovalent iron (Fe^0)

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Author contributions
CW wrote the first concept of this paper and compiled and edited its final version. OTM conducted the literature review and wrote the first draft of this paper. KW and LB added further context and references. LB rearranged the sections into a more logical order and further modified and amended the text. CW and LB revised this paper following the peer-review process. All authors read and approved the final manuscript.

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Declarations

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Not applicable.

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Competing interests
The authors declare that they have no competing interests.

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