A consideration of polychlorinated biphenyls as a chemostratigraphic marker of the Anthropocene

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Abstract

Polychlorinated biphenyls (PCBs), organic pollutants of ~~purely~~ anthropogenic origin, were widely used in many industrial applications worldwide roughly from the 1930s to the 1970s. Both the use and disposal of PCBs contributed to their ubiquity in different environmental compartments and they show extremely high persistence ~~in the environment~~ because of their high physical and chemical stability. Concentrations of PCBs in environmental archives located in different parts of the world usually show an initial increase in the 1940s-1950s~~,~~ and maxima in the 1960s–1970s followed by a sharp decline following the ban in their use. Thus, the increase in PCB concentrations would appear to be suitable as a chronostratigraphic marker in Anthropocene strata. This manuscript discusses the PCBs record in different environmental archives in the context of temporal and spatial trends in production and application of these compounds as well as the advantages and disadvantages of the use of PCBs in the chemostratigraphy of the Anthropocene series.

Keywords

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Introduction

The beginning of the Anthropocene Epoch, which is being formally considered by the Anthropocene Working Group, is proposed to be the mid-twentieth century (Zalasiewicz et al., 2015; 2017). Thus, this geologic time unit differs from its precursors in Earth's history not only by its short duration, but also because it reflects human impact on a geological scale (Waters et al., 2016). This impact includes changes in both biotic and abiotic systems. Examples of markers of this impact that may support the eventual formalization of the Anthropocene as a geological time unit include changes in habitats and young fossil records (Kidwell, 2015; Williams et al., 2015), artificial radionuclides from nuclear bomb testing (Waters et al., 2015), technofossils and novel materials (Zalasiewicz et al., 2014; Gałuszka and Migaszewski, 2017), plastics (Zalasiewicz et al., 2016) and fly ash particles (Rose, 2015). Anthropogenic imprint on the environment is also clearly evidenced by pollutants accumulated over time in different environmental archives (Chiaia-Hernández et al., 2017; Gałuszka et al., 2017) and chemostratigraphic markers of the Anthropocene can be used to define the lower boundary of this chronostratigraphic unit and to indicate the Global Stratotype Section and Point (GSSP) required to define any new geological time period (Waters et al., 2018). Ideally, such markers should leave a global, synchronous, sharp and persistent signal at the start of the Anthropocene strata. One of the proposed chemical markers for the Anthropocene Epoch are persistent organic pollutants (Dachs and Méjanelle, 2010), including polychlorinated biphenyls (PCBs) (Gałuszka and Rose, 2019)~~.~~, ~~PCBs are~~ an important group of compounds included in the Stockholm Convention on Persistent Organic Pollutants because of their high persistence, their

long-range transport in the atmosphere and their bioaccumulation and toxicity in organisms (UNEP, 2001).

Recently, Waters et al. (2018) have discussed different environmental archives and their role in the potential recommendation of the GSSP for the Anthropocene. They suggest that due to the need for a highly resolved chronology, the choice of paleoarchive may be found in a wide range of different types of deposits including marine, estuarine and lacustrine sediments, glacial ice, or ombrotrophic peat bog (Fiałkiewicz-Kozieł et al., 2016) and coral reef sequences. Except for coral growth bands, the PCB record in all of these principal environments is well known from various locations worldwide (e.g. Vane et al., 2011; Bigus et al., 2014; Pavlova et al. 2014; Naffrechoux et al., 2015; Steinlin et al., 2015; Yang et al., 2016; Combi et al., 2017). This knowledge, as well as other features of PCBs, such as their ~~purely~~ synthetic origin, availability of data on historic production and emission trends and well recognized environmental fate make PCBs potentially one of the best chemostratigraphic markers of the Anthropocene.

The first synthesis of PCBs was in 1876, but the commercial production of these compounds started 53 years later, when the catalytic reaction of biphenyl with chlorine was developed (Schwarzbauer and Jovančićević, 2018). A total global production of PCBs in the period spanning 1930 to 1993 was estimated at 1,325,810 tonnes, of which 81.3% was manufactured in USA, West Germany, USSR (Russia) and France (Breivik et al., 2007).

Physical characteristics of PCBs, especially their excellent dielectric properties, resistivity to aggressive fluids such as acids or alkalis and extremely low flammability caused their wide

application in many industrial sectors. The most common use of PCBs was in capacitors and transformers as filling fluids, but they were also used as lubricants, hydraulic fluids in mining, and as additives to paints, plastics, rubber, copying paper, solvent extenders and sealants. PCBs were used in both open and closed applications. The open-system applications (e.g. in paints and plastics) were forbidden in many countries in the 1970s (Schwarzbauer and Jovančićević, 2018). Closed applications include completely closed systems (e.g. electrical equipment) and nominally closed systems (e.g. vacuum pumps, heat transfer equipment). The most common of these (two-thirds of PCBs produced) were the former, of which about 70% are probably still in service (Broeg and Theobald, 2017).The primary sources of PCBs in the environment are related to these intentional uses, but also to their inadvertent generation during synthesis of different compounds, the disposal and improper management of PCB-containing waste, and accidental releases (Breivik et al., 2002). Secondary sources include the release of PCBs from storage in melting glaciers (Bogdal et al., 2009), or re-emission of these pollutants from contaminated soils or sediments. As PCBs are semi-volatile compounds they easily undergo long-range transport in the atmosphere and this is important for their global distribution.

Here, we discuss the suitability of PCB records in environmental archives as a chemostratigraphic marker for the Anthropocene. Our focus is on the record of PCBs in different environmental archives but we also ~~consider the possibility of~~ signal the potential disadvantages of PCBs as a chronostratigraphic marker due to the lack of valid data on diagenetic changes of PCBs buried in sediments. Potential difficulties in selection of

appropriate PCB congeners that meet the criteria of an ideal Anthropocene marker (global distribution and maximum persistence in environmental archives) are also outlined. The significance of this review is in the potential application of PCBs in the on-going debate aimed at the selection and recommendation of a GSSP for the proposed Anthropocene Epoch (Waters et al., 2019).

Characteristics and environmental fate of PCBs

PCBs are synthetic chemicals having a general chemical formula $C_{12}H_{10-n}Cl_n$ and encompassing 209 congeners that depend on the number and position of chlorine atoms in their molecule (Fig. 1). Each congener may contain up to ten chlorine atoms ~~in the molecule~~. A characteristic feature of PCBs is that these compounds always occur in mixtures, both in technical products and in the environment, but usually, for practical reasons, only selected congeners are determined in environmental samples (Risso et al., 2016). The Stockholm Convention on Persistent Organic Pollutants, recommend that the six most abundant congeners (numbers 28, 52, 101, 138, 153 and 180) should be measured (IARC, 2016) while the International Council for the Exploration of the Sea, recommend reporting these six congeners plus the mono-*ortho* congener PCB-118.

In commercial mixtures PCBs occur as viscous yellow or dark liquids, however, as single congeners at room temperature they are light yellow or colorless crystals. PCBs are lipophilic (log K_{ow} 3.9-8.2) and have a low vapor pressure (from 6.3×10^{-6} Pa at 25°C for nonachlorobiphenyl to 1.1 Pa at 25°C for monochlorobiphenyl) (IARC, 2016). Commercial PCB

products differ in their congener composition depending on the manufacturer. They usually consisted of 100-140 congeners with a total chlorine content in the range of 21-68% (IARC, 2016).

Because PCB congeners differ in their physicochemical properties, including molecular weight, solubility in water and volatility, their fate in the environment differs. In general, congeners with a higher number of Cl atoms in their structure have lower water solubility and vapor pressure than lower-chlorinated congeners, but their persistence and lipophilicity are higher (Shiu and Mackay, 1986). Consequences of these differences for transport, accumulation and persistence in various environments will be discussed in the next two sections.

PCBs in environmental compartments

PCBs are ubiquitous in environmental compartments. They are poorly soluble in water and tend to accumulate in sediments, soils and living organisms. As a consequence, their lowest concentrations are found in air (10-1000 pg/m^3) and water (ng/L), whereas the highest concentrations are recorded in sediments and animal tissues (up to several thousand ng/g). Despite low levels of PCBs in the air as a consequence of relatively low vapor pressures, long-range atmospheric transport is the most important pathway for global dispersal. Currently, the major sources of PCBs in the atmosphere are: incineration processes, contaminated biomass burning, volatilization from contaminated water and soil, waste electrical and electronic equipment, as well as inadvertent formation during pigment production (Eckhardt et al., 2007; Khairy et al., 2015; Vorkamp, 2016; Breivik et al., 2016).

PCBs may occur in the air partly as vapors and partly as a fraction adsorbed onto particulates and the partitioning of PCBs between gaseous and particulate phases depends on temperature. Higher temperatures favor volatilization of PCBs, whereas at lower temperatures they tend to condense and be deposited (Wania and Mackay, 1993) and this process governs spatial and seasonal changes in PCB concentrations in the air. Moreover, a reversible deposition-volatilization exchange between the air and terrestrial/aquatic environments is observed (Eckhardt et al., 2007). Molecules with a higher number of Cl atoms occur mostly in the particulate-phase and are more easily deposited than lower-chlorinated compounds. This exchange allows the movement of PCBs, especially the more volatile congeners, to move from tropical and temperate regions to higher latitudes in a series of volatilization-transport-deposition 'hops' known as the 'grasshopper effect'. In this manner, more volatile PCBs may move preferentially to higher latitudes while less volatile congeners remain in warmer regions. This process has been termed 'global distillation' and may also occur as a result of lower temperatures due to increased altitude, rather than latitude. Hence, gradients in less volatile PCB concentrations maybe observed with altitude in the lakes, soils and organisms of mountain regions (Grimalt et al., 2004).

Although some studies have suggested that PCBs could be produced from natural sources (e.g. Berset et al. 2001; Zennegg et al 2007) any natural production may be considered negligible in comparison with anthropogenic sources. Global atmospheric emissions of PCBs reached their peak values of 3,000 tonnes/year in the 1970s and had declined to several hundred tonnes/year by the 2010s (Breivik et al., 2002; 2007) as a result of restrictions in production

following the ban in their use (Carlsson et al., 2018). In a study on air and fish of the North American Great Lakes, Hites and Holsen (2019) showed that the PCB degradation 'half-life' i.e. the time taken for concentrations to reduce by a factor of two, was 9-17 years, resulting in an exponential decline. By contrast, some PCB congener concentrations remain elevated. Concentrations of 3,3'-dichlorobiphenyl (PCB-11), which is inadvertently formed during production of yellow pigments, have not decreased since 2004 (Hites, 2018) while PCB emissions from e-waste management, recycling facilities, dumpsites and illegal burning are now important sources especially in Africa and Asia (Chakraborty et al., 2018; Hogarh et al., 2018; Liu et al., 2019).

PCBs may also be transformed in the atmosphere. For example, the reaction of PCBs in the gaseous phase with hydroxyl radicals leads to their degradation to chlorinated benzoic acids (Brubaker and Hites, 1998) and transformation by photodegradation results in the formation of hydroxylated and/or metoxylated PCBs (Sedlak and Andren, 1991; Tang et al., 2018). Deposition of PCBs from the atmosphere increases concentrations in surface waters and soils which, depending on environmental factors and volatility of specific congeners, may be a sink and/or a secondary source of PCBs. In water, PCBs that are either partitioned into dissolved or particulate-bound phases, can be transported with water flow, deposited with particulates or fecal pellets to bottom sediments, or taken up by aquatic organisms. Because of their very low water solubility, PCBs in aquatic environments occur mostly associated with suspended particles and sediments. They have been recorded in sediments of the remotest areas including the southern Mariana Trench at depths of 7000-11,000 m (Dasgupta et al., 2018).

Interestingly, these deepest ocean samples revealed much higher PCB concentrations than sediment samples collected from shallower marine locations (<500 m to 2500 m) (Dasgupta et al., 2018) and may be due to a lower rate of sedimentation in abyssal environments. A strong adsorption of PCBs to macro- and microplastics in the aquatic environment has been reported (Velzeboer et al., 2014) and these may also be a source to marine sediments.

PCBs accumulated in aquatic sediments may be transferred back to water through desorption, gas convection and bioturbation (Urbaniak, 2007). In sediments enriched in organic matter (OM), PCBs may be ~~released from sediments to water~~ following organic decomposition (deBruyn and Gobas, 2004). More direct inputs such as industrial effluents, landfills and urban run-off are also major sources of PCBs to surface waters.

Similarly to water, soils can be both a source of PCBs (re-mobilization of lower-chlorinated congeners) and a sink (higher-chlorinated congeners), but congener composition in soils may change through microbial activity. Aerobic microorganisms are responsible for dechlorination of lower-chlorinated PCBs, whereas anaerobic microorganisms participate in the degradation of highly-chlorinated to lower-chlorinated PCBs (Abramowicz, 1995). Forest soils are usually enriched in PCBs in comparison with soils in unforested areas as a result of scavenging of pollutants from the air by trees and transport with falling leaf litter to forest soils (forest filter effect) (Nizetto et al., 2006) or following rainfall, by washing accumulated PCBs from leaves to the forest floor (throughfall).

Plants take up PCBs from the air and transfer them into the food chain but root uptake and translocation from root to leaves is considered negligible (Tato et al., 2011). However, root

exudates are important in plant-microbial interactions in the rhizosphere and thus facilitate PCB biodegradation (Terzaghi et al., 2018; Pino et al., 2019). Concentrations of PCBs dramatically increase through many food chains (Corsolini and Sarà, 2017). Such biomagnification is caused by the bioaccumulation of these compounds in the fat tissue of animals during the consumption of lower trophic levels. There is an extensive literature on PCB transfer through terrestrial and aquatic food-chains, including human exposure, but this is beyond the scope of this review (e.g. Ross et al., 2004; Blankenship et al., 2005; Burreau et al., 2006).

Stability and transformations of PCBs in environmental archives

Persistence of PCBs in environmental archives is a key issue when discussing their suitability as a chemostratigraphic marker for the Anthropocene. Despite their very high stability in different environmental compartments, PCBs undergo biodegradation in soils and sediments. Biodegradation depends on the degree of chlorination in the congener, physico-chemical and environmental factors (i.e. redox potential, temperature, pH) and optimal conditions for bacterial growth (Borja et al., 2005). Reductive dechlorination of highly-chlorinated PCBs (≥5 Cl atoms) occurs under anaerobic conditions, whereas aerobic bacteria transform lower-chlorinated PCBs (<4 Cl atoms) into chlorobenzoic acids (Abramowicz, 1995). PCBs with two Cl atoms in the ortho-position of a single ring (2,6- or 2',6'-) and each ring (2-2' or 6,6') (Fig. 1) are the most resistant to biodegradation (Borja et al., 2005).

Fractionation of PCBs is a natural process resulting in changes to the congener profile in the

original commercial products following preferential partitioning of different congeners into environmental compartments and organisms, as well as volatilization and transformation. An example of such a fractionation process is the surface melting and refreezing of firn and ice which results in the accumulation of impurities on the surface of ice and decreased albedo (Pavlova et al., 2014). This also affects the partitioning of PCBs from the dissolved to the particulate phases as well as changes in congener profile as lower chlorinated PCBs are easily eluted with meltwater.

By contrast, studies on marine sediment cores collected from the Palos Verdes Shelf (California, USA), where municipal wastes had been deposited for about 45 years, showed no indication of PCB transformation by diagenetic processes (Eganhouse et al., 2000). Furthermore, in a study on weathering of marine sediments stored for 5 years in an outdoor environment after dredging, Couvidat et al. (2018) showed that concentrations of PCBs remained constant whereas the concentrations of other organic pollutants, such as polycyclic aromatic hydrocarbons and organotin compounds substantially decreased. Hence under favorable sedimentary conditions, environmental records of PCBs may remain stable for many decades and possibly centuries.

Historical production and use of polychlorinated biphenyls (PCBs) worldwide

Because PCBs were intentionally produced chemicals, reliable data on trends in their production are readily available (Table 1). Globally, the production of PCBs worldwide has been estimated at approximately 1.3 million tonnes (Zhao et al., 2017) and peaked in the

1960s-1970s.

Different PCB congener mixtures were produced by various companies under different trade names. Production of tri-, tetra- and penta-chorinated biphenyls amounted to more than 72% of PCB homologues (Fig. 2) while total content of mono-CB, nona-CB and deca-CB in produced mixtures was lower than 1%. Trade names of PCB products with details regarding their composition can be found elsewhere (e.g. IARC, 2016).

Global trends in consumption of PCBs show ~~that~~ clear latitudinal trends with almost 97% of these compounds ~~were~~ used in the Northern Hemisphere (Breivik et al., 2002). However, PCB-containing products were used worldwide, including in South and Central America and Africa, where PCBs were not manufactured.

Trends in PCBs pollution recorded in environmental archives

Temporal PCB concentration trends recorded in different environmental archives depend on many factors, including proximity to the source, congener profile, climate, geographic location and specific features of the archive. The highest concentrations of PCBs are found close to facilities that manufactured PCBs where these compounds were accidentally or intentionally released to rivers and lakes (IARC, 2016). For example, in northwest South Carolina, USA, where the Sangamo-Weston capacitor manufacturing plant discharged effluents contaminated with PCBs into a stream feeding Lake Hartwell, sediment cores from the lake were found to contain up to 138,000 ng/g Σ_{107}PCBs (Brenner et al., 2004). Similarly, extremely high concentrations of PCBs (up to $3 \cdot 10^6$ ng/g) were found in fluvial sediments collected from near

a former PCB production plant in Michalovce District, Slovakia (Kocan et al., 2001).

A range of environmental archives have been used to determine historical trends in PCBs in both remote and polluted areas. PCBs have been recorded in every location where they have been analyzed and may be considered to be globally ubiquitous.

Remote regions

Transport of PCBs in the atmosphere is considered the main transport pathway for PCBs to remote regions (Carlsson et al., 2018) and their semi-volatile nature and temperature-dependent transport in the atmosphere results in contamination of even the remotest sites located far from any direct source, such as ~~the~~ Arctic high mountain regions and the deepest oceans (Table 2).

Many studies of PCBs have been conducted in polar and mountainous regions and there are several reasons for this. A condensation effect causes increased deposition of atmospherically-transported PCBs at low temperatures while the grasshopper effect aids transport to higher latitudes and altitudes. PCBs are removed more slowly from remote regions than from historical source regions (Axelman and Broman, 2001) and therefore an increase in PCB concentrations in the Arctic is predicted from models (Carlsson et al., 2018). Lower-chlorinated congeners (tri- to penta-CBs) are more prone to long-range transport in the atmosphere. Thus, their concentrations in environmental samples collected in the Arctic are much higher than in samples collected in tropical areas, where these congeners are readily volatilized (Pavlova et al., 2014). In a recent study, which highlights a problem which may have been overlooked for decades, Bartlett et al. (2019) show how the synthesis of compounds during pigment

production and hazardous waste incineration have resulted in PCB deposition to snow on Svalvard, although distinguishing between long-range and local transport to the site remained problematic. Furthermore, the release of PCBs and other persistent organic compounds from secondary sources in cold regions, mainly from meltwaters following glacial retreat is of concern and has been reported by many authors (Bogdal et al., 2009; Sharma et al., 2015; Pavlova et al., 2016). Remobilization of legacy PCBs from melting Himalayan glaciers and their transport to the Ganges River was reported by Sharma et al., 2015 while Schmid et al. (2011) studied PCB profiles in lacustrine sediment cores collected from two Alpine lakes situated at a distance of about 8 km from each other. One of the lakes (Lake Stein) was proglacial and the other (Lake Engstlen) was non-glacial. Peak concentrations in sediment layers dated to the period of PCB use in Switzerland was recorded in both lakes, but higher PCB content in younger sediments (dated to 1990s) was only observed in the glacial lake as a consequence of intensive glacier melting. There is no consensus about the future trends in PCB level changes in the context of climate changes, but an increase in air temperature will most likely lead to a global decrease in PCB concentrations in the environment. The degradation of persistent organic pollutants is known to increase by a factor of 2 – 3 with a 10 °C temperature rise and so PCB degradation will be enhanced as global air temperatures increase (Nadal et al., 2015).

Polluted sites

Examples of PCB concentrations in environmental archives from polluted sites are shown in Table 3. Contamination from PCBs within heavily industrialized regions has been mostly caused

by leakage from systems containing these compounds (Zhao et al., 2017). Extreme pollution of soils and fluvial sediments close to the condenser plant in the city of Serpukhov ~~city~~ (Russia) ~~with~~ show Σ_7PCB ~~levels~~ concentrations up to 1169 mg/kg in soil and 119 mg/kg in sediment ~~were reported by~~ (Malina and Mazlova, ~~(~~2017).

Elimination of point sources of PCB pollution in developed countries has caused a clear decline in PCB concentration trends in environmental archives in the recent decades (Dachs and Méjanelle, 2010). The main sources of contemporary PCB pollution are the remaining PCB-containing products that are still in use (Davies and Delistraty, 2016) but especially electric/electronic waste (e-waste) recycling facilities (Breivik et al., 2016). Chakraborty et al. (2018) found up to 488 ng/g Σ_{26}PCBs in surface soils collected from informal e-waste recycling sites in India. However, e-waste is often transported from middle latitudes to subtropical and tropical regions, where PCBs are prone to volatilization and then, subsequently, to long-range atmospheric transport (Breivik et al., 2016) ~~and~~ thereby ~~likely to increase~~ increasing the likelihood of global PCB emissions ~~of PCBs~~ in the near future. In the longer term, PCB levels in the atmosphere will continue to decline and become negligible. Although results of simulations and modelling studies show that if no additional regulatory measures are taken, PCB emissions will continue until at least 2100 (Li and Wania, 2016).

Historical trends

There are many examples of studies on the reconstruction of historic deposition of PCBs in environmental archives and especially in dated sediment cores. Some examples of the trends

in different environmental archives are shown in Fig. 3. In the Northern Hemisphere, especially in Europe and North America, time trends in PCB concentrations in environmental archives usually show similar patterns with an onset during 1940s-1950s, a peak in 1960s-1980s and then a post-1980s decline. However, this trend of decreasing PCB concentrations has not been observed in remote areas of the Northern Hemisphere, and this may be explained by the lower volatilization of PCBs in cold regions (Axelman and Broman, 2001), secondary emissions of legacy PCBs from melting ice (Pouch et al., 2017), and an increase in global emissions of legacy PCBs caused by e-waste transport and recycling (Breivik et al., 2016).

The increase in PCBs in the 1930s and peak concentrations in the 1960s have been found in many locations. For example, in sediment cores from Lake Simcoe in south-eastern Canada (Helm et al., 2011) where PCB concentrations and trends correspond well with those recorded in sediment cores from the United States Great Lakes and with historical PCB emissions in the area.

Marine sediment cores show similar trends. Maximum PCB concentrations in sediment cores from the western Adriatic Sea between the 1960s and 1980s were recorded by Combi et al. (2016) and these decline significantly with concentrations reduced by up to 80% compared to peak values. Coastal Baltic Sea sediments also show the Northern Hemisphere pattern, with a trend of increasing PCB concentrations recorded by Sobek et al. (2015) in core sections dated to the 1940s-1960s and a peak in 1974. However, in offshore areas of the Baltic Sea, sediments showed elevated PCB concentrations in core sections from the 1960s-1980s with a peak in 1991 and ~~which~~ this may be explained by lower sediment deposition rates in the offshore

marine environment Only a slight decrease in PCB concentration is observed in both coastal and offshore sediments, suggesting that no significant reduction in PCBs may be expected in the near future (Sobek et al., 2015). Similarly, a 20 year lag in the appearance of PCBs in High Arctic lake sediments and their enrichment in more volatile congeners compared to lake sediments in lower latitudes as a result of global fractionation was observed by Muir et al. (1996).

Two periods of increase in PCB sediment profile from the continental shelf of the Korea Strait were found by Guerra et al. (2019). Peak values were recorded at the turn of the 1960s and also around 2000. The first increase in PCB concentrations correlates well with trends in PCB use from 1956 to 1983. The later peak may be due to emissions from regional secondary sources.

In the Southern Hemisphere, sediment cores collected from Admiralty Bay in Antarctica showed a slight increase in PCB concentrations starting from 1970. Peak concentrations occurred in the late-1980s but there has been no significant decrease in the recent decades (Combi et al., 2017). In urbanized areas of the Southern Hemisphere, elevated levels of PCBs can also be found (Connel et al., 1999). For example, in sediments collected in the Santos estuary (Brazil) the maximum PCB concentration was 190.7 ng/g in the 1980s (de Souza et al., 2018) declining in more recent decades and reflecting the slightly later peak in Brazilian emissions. However, while other sediment cores taken from this estuary showed similar trends, their peak PCB concentrations varied, occurring in the 1960s and c.1990. This suggests that dynamic environments such as the Santos Estuary may not be appropriate for defining an

Anthropocene chemostratigraphy.

In summary, despite differences in absolute PCB concentrations in environmental archives from different locations, historical concentration patterns reflect trends in the use and/or production of these compounds (Lorgeoux et al., 2016). In general, in the Northern Hemisphere, the increase in PCB concentrations, observed in environmental archives from the 1940s-1950s may be considered as the most appropriate chronological marker while in the Southern Hemisphere, there is about a 20-year delay in the PCB record in environmental archives.

Advantages and limitations of PCBs as a chemostratigraphic marker of the Anthropocene

In comparison with other pollutants, PCBs have several features which make them a very good candidate for a chemostratigraphic marker of the Anthropocene. They are synthetic compounds and ~~do not~~ have negligible natural ~~emission~~ sources. This makes interpretation of temporal trends in their concentrations much easier than in the case of other organic pollutants, such as polycyclic aromatic hydrocarbons or inorganic pollutants, such as trace metals. Another advantage is their relatively long-term production (since 1929) and use which together with their semi-volatility and long-range atmospheric transport, ~~which~~ have led to the contamination of many environments around the world. Both environmental and health concerns have made this class of pollutants one of the most ~~often~~ studied in environmental samples worldwide. This has contributed to well-established analytical protocols for PCB determination in a wide variety of samples (Konieczka et al., 2010) and to a greater

understanding of their global distribution ~~of PCBs~~ (Breivik et al., 2016). Availability of data on production, use and time trends in PCB concentrations recorded in environmental archives allow us to reconstruct the history of PCB pollution in many areas. Of great importance is also the high persistence of PCBs in the environment and their affinity with sediments which will provide a detectable signal over a long period of time.

The ability of microplastics to absorb and concentrate PCBs in sediments is also worth consideration in the context of chemostratigraphy (Velzeboer at al., 2014). This may be important for the Anthropocene as microplastics are another potential stratigraphic marker for this epoch (Zalasiewicz et al., 2016). PCB sorption onto microplastics in simulated seawater has been studied by Zhan et al. (2016). Chemical sorption was found to be the predominant mechanism while the sorption capacity of the plastic negatively correlates with particle size and temperature. Weathering and aging of microplastics increase their surface area and enhance their sorption capacities (Tourinho et al., 2019). Despite a lack of comprehensive knowledge on PCB sorption onto microplastics, it may be reasonable to use both microplastics and PCBs as combined markers for the Anthropocene.

However, while there are a number of characteristics that make PCBs good potential chemostratigraphic markers, there are some issues that may be problematic. These result mainly from physico-chemical features of specific congeners. Because of their higher volatility, lower-chlorinated PCBs predominate over higher-chlorinated PCBs in low temperature locations. Therefore, if a polar region were to be considered as a potential GSSP location, lower-chlorinated compounds would need to be determined in the archive. By contrast, in

subtropical and tropical regions, environmental archives will be depleted in lower-chlorinated PCBs and higher chlorinated compounds would need to be considered.

Other potential disadvantages are their potential mobility, post-depositional processes and biodegradation. Lower-chlorinated PCBs show post-depositional mobility in sediments which may cause their appearance in sediment layers prior to the time of their production (Bigus et al., 2014). Furthermore, although degradation of PCBs is very slow, post-depositional processes may change their congener profiles. Biodegradation of PCBs occurs in both aerobic and anaerobic conditions. However, little is known about biodegradation in deeply buried sediments and knowledge of this process has only been determined from laboratory experiments (Borja et al., 2005 and references cited therein). As with many other stratigraphic markers, further problems occur as a result of the nature of the archives themselves. Apart from the loss of ice records due to glacial retreat and ice-cap loss, the PCB record in different environmental archives may be disturbed by a number of natural factors. For example, some authors claim that because lower chlorinated PCB congeners are more water-soluble than higher chlorinated congeners, they are mobile in ombrotrophic peats, which may causes post-depositional migration and hence introduces errors to the reconstruction of temporal trends in PCB emission and deposition rates (Sanders et al., 1995; Berset et al., 2001; Thüns et al., 2014). Furthermore, results from studies of tree rings as environmental archives of PCBs are scarce and inconclusive. Meredith and Hites (1987) did not find any relationships between concentrations in tree rings and PCB emission history in a PCB contaminated landfill in

Bloomington, Indiana, whereas Odabasi et al. (2015) confirmed the usefulness of tree rings as environmental archives of PCB contamination.

Clearly, not all archives are appropriate for PCBs as chemostratigraphic markers although careful selection of archive, location and accumulating environment may overcome many of these disadvantages. Currently, it would appear that lacustrine and marine sediments offer the most promising sequences for a PCB chemostratigraphy.

Conclusions

Environmental records of PCBs may help find a suitable GSSP with which to formalize the Anthropocene as an epoch of geologic time. Of the different environmental archives that are under consideration for the Anthropocene GSSP, lake and marine sediments seem to be best due to their higher preservation potential for PCBs in comparison with ice, peat or corals. PCBs are ubiquitous and have been recorded in the remotest locations which means that they have met a key criterion of an ideal chemostratigraphic marker of the Anthropocene, which is a global range. If PCBs are to be considered as a chemostratigraphic marker, it is recommended that the initial increase in PCB concentrations in sediments dated from the mid-twentieth century be used as this is the most consistent on a global scale.

Another requirement for a chemostratigraphic marker is persistence. A lack of data on postdepositional changes in PCB concentrations in buried sediments does not allow us to give a straightforward answer to the question regarding the presence of PCBs in the strata of the far future. However, taking into account the results of laboratory experiments and the affinity

of PCBs to organic substrates including microplastics, these compounds will most likely be preserved in sediments for, at least, many decades.

Chemostratigraphic markers, such as PCBs, are just one of the possible markers for Anthropocene strata and it is unlikely that only one marker will be used in the search for the Anthropocene GSSP. Thus, PCBs together with microplastics, artificial radionuclides, fly-ash and other anthropogenic signals may be utilized together for this purpose.

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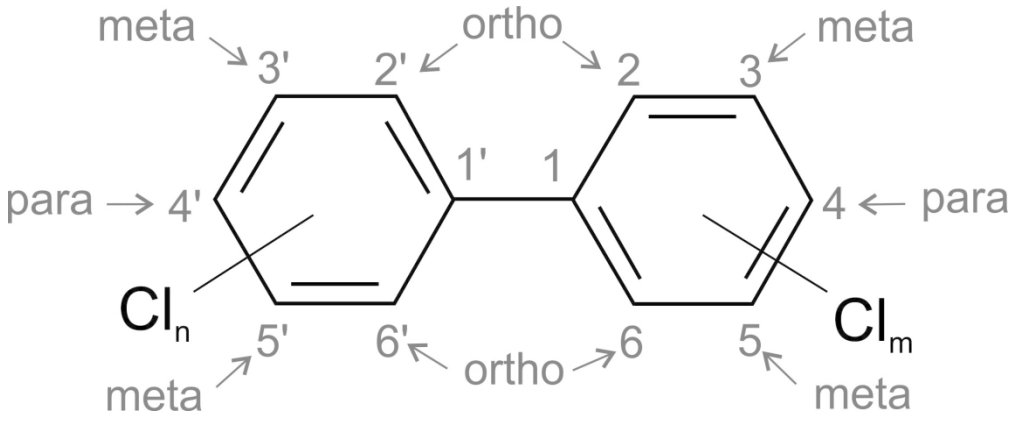
Figure captions

Fig. 1. A molecule of polychlorinated biphenyl. Different numbers of chlorine atoms (m+n) can be incorporated in 2,2',6,6' (ortho-), 3,3',5,5' (meta-) and 4,4' (para-) positions.

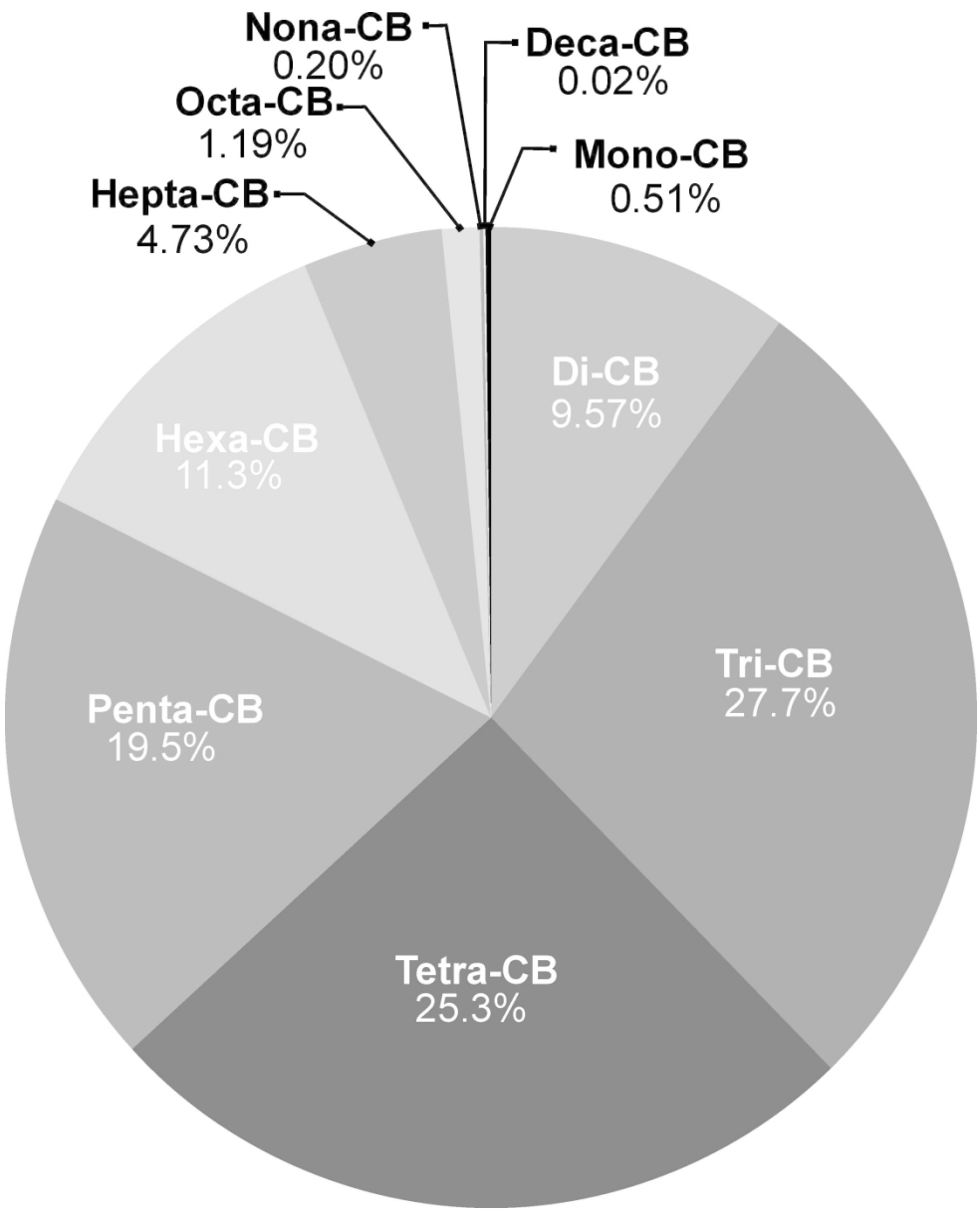
Fig. 2. Percentage of individual PCB homologues produced globally. Data compiled from Breivik et al., 2007.

Fig. 3. Examples of trends in PCB concentrations in dated environmental archives: A – Fiescherhorn glacier, Switzerland (Pavlova et al., 2014); B – Seine River basin, France (Lorgeoux et al., 2016); Great Lakes, North America and East China Marginal Seas (Wu et al., 2019).



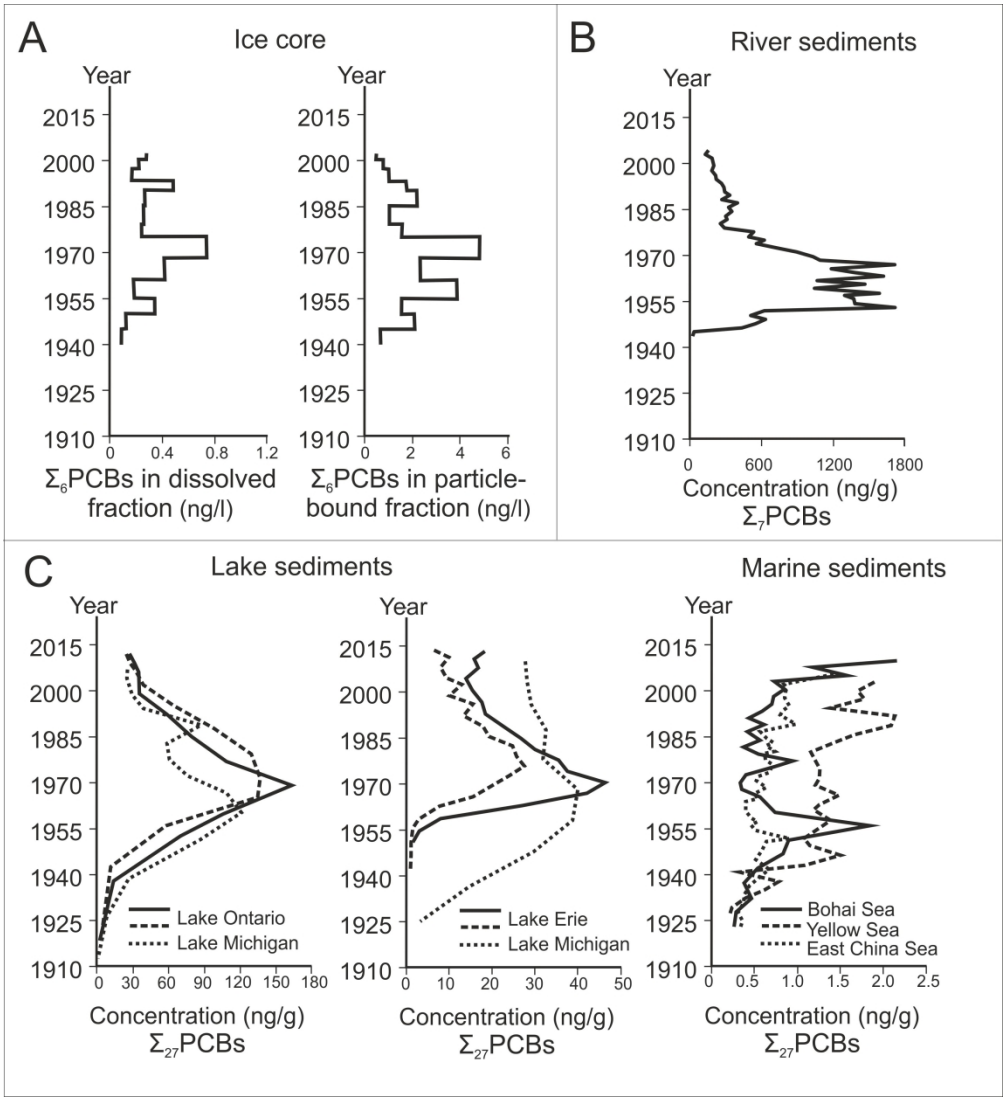
A molecule of polychlorinated biphenyl. Different numbers of chlorine atoms (m+n) can be incorporated in 2,2′,6,6′ (ortho-), 3,3′,5,5′ (meta-) and 4,4′ (para-) positions.

95x38mm (600 x 600 DPI)



Percentage of individual PCB homologues produced globally. Data compiled from Breivik et al., 2007.

121x148mm (600 x 600 DPI)



Examples of trends in PCB concentrations in dated environmental archives: A – Fiescherhorn glacier, Switzerland (Pavlova et al., 2014); B – Seine River basin, France (Lorgeoux et al., 2016); Great Lakes, North America and East China Marginal Seas (Wu et al., 2019).

149x163mm (600 x 600 DPI)

Table 1. Data on production of PCBs (compiled from de Voogt and Brinkman, 1989; IARC, 2016 and references cited therein).

Country	Start (year)	End (year)	Peak production (year)	Amount (tonnes)
USA	1930	1977	1970	641,700
Germany	1930	1983	1974	159,062
Russia	1939	1993	1980s	173,800
France	1930	1984	1978	134,654
United Kingdom	1954	1977	Late 1960s	66,542
Japan	1954	1972	1970	58,787
Italy	1958	1983	1973	31,092
Democratic Republic of Korea	1960	2012	Late 1980s	30,000
Spain	1955	1984	1975	29,012
Czechoslovakia	1959	1984	Unspecified	21,482
China	1965	1980	Mid-1970s	10,000
Poland	1966	1977	Unspecified	1679

Table 2. Examples of peak PCB concentrations found in different environmental archives in remote areas

Environmental archive	Location	Dating method	Peak concentration	Year(s) of peak concentrations	Number of congeners	Reference
Glacial ice	Lomonosovfonna glacier, Svalbard, Arctic	$\delta^{18}O$ annual layer counting	1.5 ng/L	1957–1966	209	Garmash et al., 2013
	Fiescherhorn glacier, Switzerland	annual layer counting, Saharan dust, ^{3}H, ^{137}Cs	5 ng/L	1970s	6	Pavlova et al., 2014
Snow/firn	Talos Dome (Antarctica)	^{3}H, volcanic sulfate	0.24 ng/L	1980s–1990s	7	Fuoco et al., 2012
	Western Anctarctic Penninsula	not applicable	1.1 ng/L	not applicable	29	Khairy et al., 2016
Lacustrine sediments	Silvretta Lake (proglacial lake), Swiss Alps	^{137}Cs, ^{239}Pu, ^{241}Am	0.80 ng/g	1960s	6	Pavlova et al., 2016
	High mountain lakes: Lake Redon, Spain (a); Długi Staw, Poland (b); Ladove, Slovakia (c)	^{210}Pb, ^{137}Cs, ^{241}Am	2.3 ng/g	1994	11	Grimalt et al., 2004
			15 ng/g	1990s		
			10 ng/g	1976–1997		
	Mt. Everest (samples from 8 lakes in Khumbu and Imja Valley)	not applicable	84.3 ng/g*	not applicable	14	Guzzella et al., 2016
Marine sediments	Admiralty Bay, King George Island, Antarctica	^{137}Cs	11.9 ng/g	1983–1986	7	Combi et al., 2017
	Western Spitsbergen fjords, Arctic	^{210}Pb	1.47 ng/g	2011–2013	7	Pouch et al., 2017
	Bering Sea	not applicable	0.088 ng/g	not applicable	46	Ma et al., 2015
	Bering Strait	not applicable	0.708 ng/g	not applicable	46	Ma et al., 2015
	Chukchi Sea	not applicable	1.0 ng/g	not applicable	46	Ma et al., 2015
	Iceland Station, Arctic	not applicable	203 ng/g	not applicable	46	Ma et al., 2015
	Mariana Trench	not applicable	4.2 ng/g	not applicable	36	Dasgupta et al., 2018

*values normalized to organic carbon content

Table 3. Examples of PCB concentrations found in different environmental archives in polluted areas

Environmental archive	Location	Dating method	Peak concentration (ng/g)	Year(s) of peak concentrations	Number of congeners	Reference
Estuarine sediments	Buenos Aires Province, Argentina	not applicable	17.6	not applicable	7	Tombesi et al., 2017
	Guajará Bay, Brazil	^{210}Pb and ^{137}Cs	4.58	early 1990s	51	Neves et al., 2018
	New York/New Jersey Harbor and Lower Hudson River	^{137}Cs	36,100*	1970s	132	Rodenburg and Ralston, 2017
	Clyde estuary, UK	$^{207/206}$Pb	5797	1965–1977	7	Vane et al., 2011
	Liaohe Estuary	not applicable	16.6	not applicable	not specified	Li et al., 2017
	Shuangtaizi Estuary	not applicable	36.68	not applicable	28	Yuan et al., 2015
Marine sediments	Coastal area of the Aegean Sea	not applicable	847	not applicable	18	Yılmaz et al., 2016
	Coastal area of Ionian Sea, S Italy	not applicable	1684	not applicable	not specified	Cardellicchio et al., 2007
	Bohai Sea, China	^{210}Pb	2.16	1975	27	Wu et al., 2019
	South Yellow Sea, China	^{210}Pb	2.20	2000	27	Wu et al., 2019
	East China Sea	^{210}Pb	1.21	2010	27	Wu et al., 2019
Fluvial sediments	Seine River basin, France	^{137}Cs	2300	1960	15	Lorgeoux et al., 2016
	Mondego River, Central Portugal	not applicable	5.3	not applicable	10	Dias-Ferreira et al., 2016
	Nara River, Central Russia	not applicable	119,000**	not applicable	7	Malina and Mazlova, 2017
Lacustrine sediments	Lake Bourget, France	not applicable	18	not applicable	7	Lécrivain et al., 2018
	Lake Greifensee, Switzerland	^{137}Cs	132	1957–1960	6	Zennegg et al., 2007
	Lake Manzala, Egypt	not applicable	31.27	not applicable	7	Barakat et al., 2012
	Lake Chaohu, China	not applicable	4	not applicable	34	He et al., 2016
	Lake Michigan	^{210}Pb	121	1960s–1970s	27	Wu et al., 2019
	Lake Ontario	^{210}Pb	165	1960s–1970s	27	Wu et al., 2019
	Lake Erie	^{210}Pb	46.4	1960s–1970s	27	Wu et al., 2019
Peat core	Cheshire, NW England	^{210}Pb, ^{137}Cs, ^{241}Am, pollen, magnetics	36.8	1964	25	Sanders et al., 1995
	SW Switzerland	^{210}Pb	19	1960–1976	7	Berset et al., 2001
Coral reefs	Egyptian Red Sea Coast	not applicable	48.3	not applicable	7	El Nemr et al., 2004
	French Frigate Shoals, Pacific Ocean	not applicable	267	not applicable	17	Miao et al., 2000

*A dominant source was capacitor plants near Hudson Falls, NY; **source of contamination was the Serpukhov condenser plant