

Global Biogeochemical Cycles

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Key Points:

- Climate change will have the greatest impacts on the chemical lifetimes and distributions of volatile persistent organic pollutants
- Marine sediment has sequestered 75% of cumulative releases of polychlorinated biphenyls since the onset of production in 1930
- Arctic sea ice retreat is likely to enhance losses of volatile congeners but increase net deposition of higher molecular weight congeners

Supporting Information:

- Supporting Information S1

Correspondence to:

C. C. Wagner,
cwagner@g.harvard.edu

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A Global 3-D Ocean Model for PCBs: Benchmark Compounds for Understanding the Impacts of Global Change on Neutral Persistent Organic Pollutants

Charlotte C. Wagner¹ , Helen M. Amos¹, Colin P. Thackray¹, Yanxu Zhang¹, Elizabeth W. Lundgren¹, Gael Forget³ , Carey L. Friedman^{4,5}, Noelle E. Selin⁵ , Rainer Lohmann⁶ , and Elsie M. Sunderland^{1,2} 

¹Harvard John A. Paulson School of Engineering and Applied Science, Harvard University, Cambridge, MA, USA,

²Department of Environmental Health, Harvard T.H. Chan School of Public Health, Boston, MA, USA, ³Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA, USA, ⁴Corning School of Ocean Studies, Maine Maritime Academy, Castine, ME, USA, ⁵Institute for Data, Systems, and Society, Massachusetts Institute of Technology, Cambridge, MA, USA, ⁶Graduate School of Oceanography, University of Rhode Island, Narragansett, RI, USA

Abstract Human activities have released large quantities of neutral persistent organic pollutants (POPs) that may be biomagnified in food webs and pose health risks to wildlife, particularly top predators. Here we develop a global 3-D ocean simulation for four polychlorinated biphenyls (PCBs) spanning a range of molecular weights and volatilities to better understand effects of climate-driven changes in ocean biogeochemistry on the lifetime and distribution of POPs. Observations are most abundant in the Arctic Ocean. There, model results reproduce spatial patterns and magnitudes of measured PCB concentrations. Sorption of PCBs to suspended particles and subsequent burial in benthic marine sediment is the dominant oceanic loss process globally. Results suggest benthic sediment burial has removed 75% of cumulative PCB releases since the onset of production in 1930. Wind speed, light penetration, and ocean circulation exert a stronger and more variable influence on volatile PCB congeners with lower particle affinity such as chlorinated biphenyl-28 and chlorinated biphenyl-101. In the Arctic Ocean between 1992 and 2015, modeled evasion (losses) of the more volatile PCB congeners from the surface ocean increased due to declines in sea ice and changes in ocean circulation. By contrast, net deposition increased slightly for higher molecular weight congeners with stronger partitioning to particles. Our results suggest future climate changes will have the greatest impacts on the chemical lifetimes and distributions of volatile POPs with lower molecular weights.

1. Introduction

Human activities release large numbers of persistent organic pollutants (POPs) to the environment, hundreds of which are known to be persistent, bioaccumulate in food webs, and may pose health risks to exposed wildlife and humans (Scheringer et al., 2012). The ocean is a terminal sink for many of these chemicals, some of which are regulated internationally under the Stockholm Convention (Lohmann et al., 2007; UNEP, 2001). Multimedia box models have been applied to better understand the global environmental fate of compounds with different molecular weights and volatilities (Axelman & Gustafsson, 2002; Mackay & Paterson, 1991; Scheringer et al., 2000; Wania & Daly, 2002). However, effects of climate-driven variability in ocean biogeochemistry on POPs are poorly characterized (Armitage & Wania, 2013). Such an analysis is enabled by satellite observations and ocean state estimates incorporated into Earth systems models. Here we develop a 3-D ocean simulation for polychlorinated biphenyls (PCBs) within such a model (the Massachusetts Institute of Technology general circulation model [MITgcm]) to better understand how variability in ocean biogeochemistry affects the transport, accumulation, and removal of hydrophobic neutral POPs.

PCBs are a class of 209 chlorinated aromatic compounds that were used extensively in industrial equipment and consumer products prior to a global phase out in the 1970s (Breivik et al., 2002, 2007). PCB emissions peaked (ca. 1970) at approximately 3,000 Mg/a before they were phased out in most

regions globally, and they have subsequently declined to several hundred Mg a^{-1} (ca. 2010; Breivik et al., 2002, 2007). Atmospheric deposition is the main source of PCBs to the global oceans, and rivers are a minor contributor (Jurado et al., 2004; Lammel & Stemmler, 2012; Wania & Daly, 2002). High PCB concentrations in crustaceans from the deep Pacific Ocean illustrate their penetration to even the most remote regions of the ocean (Jamieson et al., 2017). Prior work has characterized PCB behavior in the environment, quantified their physical-chemical properties, and developed global release inventories (Breivik et al., 2007; Corsolini & Sarà, 2017; Gioia, Lohmann, et al., 2008; McLachlan et al., 2017; Schwarzenbach et al., 2003). This makes PCBs ideal as benchmark compounds for better understanding the behavior of persistent, bioaccumulative, and toxic POPs in the ocean and interactions with different biogeochemical processes.

The global residence time and distribution of many organic contaminants is affected by biogeochemical characteristics of the ocean such as productivity, photochemistry, circulation, suspended particle dynamics, and sea-ice cover (Lohmann & Belkin, 2014; Schwarzenbach et al., 2003; Sobek & Gustafsson, 2014). Both evasion and particle scavenging can remove organic chemicals from the surface ocean (Galbán-Malagón et al., 2012). Chemicals evaded from the ocean to the atmosphere will be redeposited elsewhere and thus have an extended lifetime in the biosphere. Chemicals with a stronger propensity to sorb to particles will have a shorter lifetime in biologically relevant components of the environment due to faster burial and sequestration. Thus, the relative importance of evasion and sorption to particles is essential for understanding chemical fate and lifetime in the ocean. The balance between these processes depends on both the physical-chemical properties of pollutants and ecosystem conditions such as productivity, temperature, wind speed, and turbulence (L. Zhang & Lohmann, 2010).

The main objective of this study is to better understand how the distribution of neutral hydrophobic POPs in seawater is affected by variability in ocean biogeochemistry. We develop a 3-D global simulation for PCBs within an ocean general circulation model (MITgcm) forced by atmospheric inputs from the GEOS-Chem Chemical Transport Model (Forget, Campin, et al., 2015; Friedman & Selin, 2016). We evaluate the model against observations and apply it to better understand the relative importance of different input and removal processes. We explore variability across PCB congeners spanning a range of molecular weights and volatilities and use our simulation to estimate impacts of climate-driven changes in surface temperatures, sea ice cover, and ocean circulation in the Arctic, where the largest changes are occurring.

2. Model Description

2.1. General Model Description

We added four PCBs (chlorinated biphenyl [CB]-28, CB-101, CB-153, and CB-180) as tracers to the MITgcm. Tracers were selected from the seven congeners frequently measured by the International Council for the Exploration of the Sea and represent a range of physicochemical properties (Duinker et al., 1988). The MITgcm has a horizontal resolution of $1^\circ \times 1^\circ$ globally, with higher resolution in the Arctic ($40 \text{ km} \times 40 \text{ km}$) and near the equator ($0.5^\circ \times 1^\circ$). It has 50 vertical layers spanning 5-m intervals at the surface and 500 m near the ocean floor (Forget, Campin, et al., 2015). Advection and diffusion of PCBs is based on ocean state estimates from the Estimating the Circulation & Climate of the Ocean (ECCO-v4) climatology. Surface boundary conditions (e.g., wind stress, seawater temperatures, and sea-ice cover) from the ERA-Interim reanalysis fields spanning 1992–2015 and ocean transport parameters are optimized in ECCO-v4 to produce a best fit to in situ and satellite observations of the physical ocean state and sea-ice cover (Forget & Ponte, 2015; Forget, Campin, et al., 2015; Forget, Ferreira, et al., 2015).

We forced the ocean model with monthly atmospheric concentrations and deposition of PCBs between 1930 and 2015 from the GEOS-Chem global atmospheric model (Friedman & Selin, 2016). We assumed negligible concentrations of PCBs in the ocean prior to the onset of global production in 1930. The GEOS-Chem simulation estimates primary releases based on the high anthropogenic emissions scenario recommended in prior work and surface temperature (Breivik et al., 2007; Friedman & Selin, 2016). Projected emissions to 2015 were based on continued product use trends suggested by the same authors (Breivik et al., 2007). We neglected inputs to the ocean other than atmospheric deposition because other work suggests they are small (Jurado et al., 2004; Lammel & Stemmler, 2012).

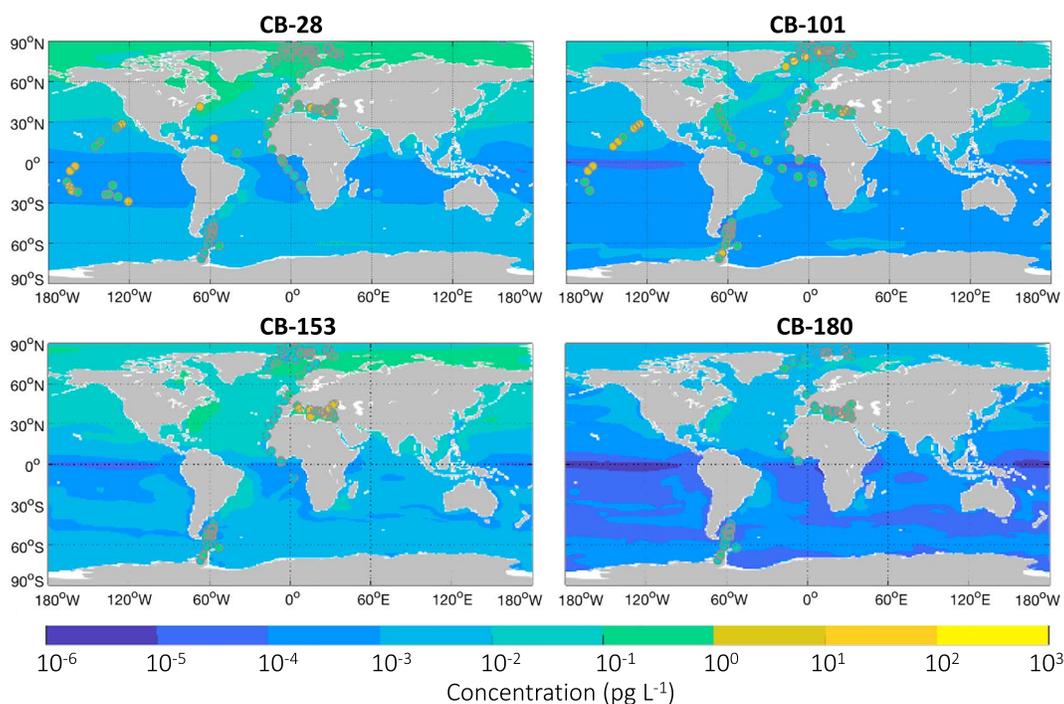


Figure 1. Modeled dissolved seawater concentrations of CB-28, CB-101, CB-153, and CB-180 at 5-m depth in 2008. Observations collected between 2000 and 2015 are shown as circles, and the modeled year represents the midpoint of measurements. Data sources are as follows: Arctic Ocean (Booij et al., 2014; Galbán-Malagón et al., 2012; Gioia, Nizzetto, et al., 2008; Gustafsson et al., 2005; Sobek et al., 2004; Sobek & Gustafsson, 2014); North Atlantic Ocean (Galbán-Malagón et al., 2012; Gioia, Lohmann, et al., 2008; Gioia, Nizzetto, et al., 2008; Lohmann et al., 2012; Sun et al., 2016); South Atlantic Ocean (Booij et al., 2014; Gioia, Lohmann, et al., 2008; Lohmann et al., 2012; Sun et al., 2016); Mediterranean Sea (Berrojalbiz et al., 2011; Lammel et al., 2016); Pacific Ocean (Zhang & Lohmann, 2010); Indian Ocean (Booij et al., 2014); and Southern Ocean (Galbán-Malagón, Del Vento, Berrojalbiz, et al., 2013). CB = chlorinated biphenyl.

2.2. Model Parameterization and Sensitivity Analysis

Air-sea exchange of PCBs was modeled using a standard two-layer thin film transfer model (Johnson, 2010). Chemical evasion in the polar oceans is thought to be enhanced by turbulence from sea-ice rafting (Loose et al., 2014). We thus doubled the piston velocity over regions partially covered with sea ice, following previous work (Y. Zhang et al., 2015). Model parameters for air-sea exchange of PCBs are provided in supporting information Table S1 (Duce et al., 1991; Friedman & Selin, 2016; Fuller et al., 1966; ITTC, 2006; Johnson, 2010; Laliberté, 2007; Liss & Slater, 1974; Nightingale et al., 2000; Sander, 1999; Smith, 1980; Tsilingiris, 2008; Tucker & Nelken, 1990; Wilke & Chang, 1955).

PCBs rapidly reach equilibrium between the dissolved and solid phases in seawater (Sobek et al., 2004). Partitioning to suspended particles was therefore represented as a reversible equilibrium based on an empirically measured organic carbon partition coefficient (K_{OC}) adjusted for temperature and salinity (Sobek et al., 2004). The physicochemical properties of the four congeners are detailed in Table S2 (N. Li et al., 2003; Schenker et al., 2005; Schwarzenbach et al., 2003; Wania & Daly, 2002). Particle concentrations and vertical transport of PCBs associated with export fluxes were simulated using the ecological simulation (Darwin project-ECCO v4) embedded within the MITgcm. The ecological simulation has been described and evaluated elsewhere (Dutkiewicz et al., 2012).

Some sorption to dissolved organic carbon (DOC) is also known to occur and is particularly important in the coastal environment (Burkhard, 2000). However, typical surface ocean DOC concentrations for pelagic marine regions (51–79 μM) and the mean partition coefficient for DOC ($\log K_{DOC} = 0.71 \log K_{OW} - 0.50$) suggest less than 5% of PCBs will be bound in this phase (Burkhard, 2000; Dutkiewicz et al., 2012; Hansell et al., 2009). Sorption coefficients for DOC may vary depending on organic carbon composition, but such data are not available to parameterize our model simulations, and we thus neglect sorption to DOC in our ocean simulation.

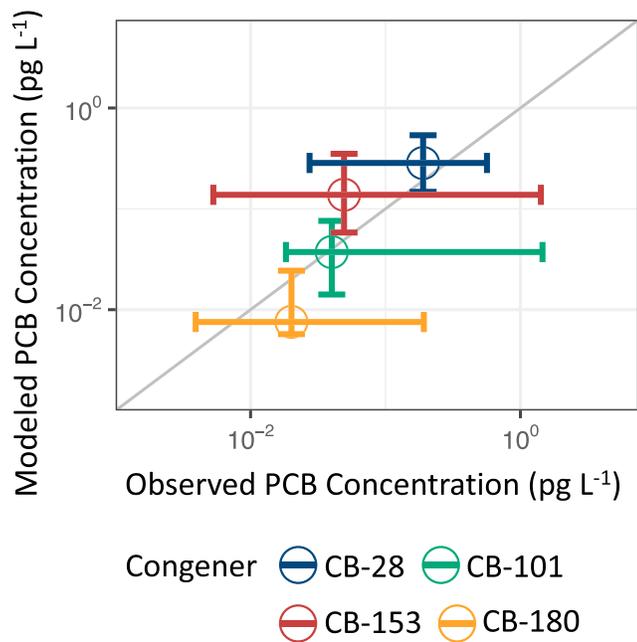


Figure 2. Comparison of modeled and observed (2000–2015) dissolved concentrations of CB-28, CB-101, CB-153, and CB-180 in the upper 1,000 m of the Arctic Ocean (Booij et al., 2014; Galbán-Malagón et al., 2012; Gioia, Nizzetto, et al., 2008; Gustafsson et al., 2005; Sobek et al., 2004; Sobek & Gustafsson, 2014). Modeled and observed concentrations were matched by year. CB = chlorinated biphenyl; PCB = polychlorinated biphenyl.

We conducted sensitivity simulations to explore the impacts of uncertainties in K_{OC} values, particle concentrations, carbon export fluxes, and degradation rates. Prior work has hypothesized that stronger relative sorption to organic carbon occurs in low productivity ecosystems such as the open ocean (Sobek et al., 2004). Marine primary productivity predicted by satellite measurements ranges from 44–57 Pg C a⁻¹ (Carr et al., 2006). Estimates of annual export of carbon from the euphotic zone vary widely (5 to >12 Pg C a⁻¹), and the simulation used here is on the lower end of this range (6 Pg C a⁻¹; Boyd & Trull, 2007; Henson et al., 2011). This results in a low bias in particle concentrations in the subsurface ocean.

We ran the 1930–2015 simulation using the range of log K_{OC} values reported in prior work (5.82 to 8.31) for CB-153, which is the most prevalent congener in many regions of the ocean (Hawker & Connell, 1988; N. Li et al., 2003; Schenker et al., 2005; Sobek et al., 2004; Sobek & Gustafsson, 2014). The upper bound of K_{OC} values reported by Sobek et al. (2004) is higher than supported by recent data (Panagopoulos et al., 2016; Stenzel et al., 2013). It can be used to explore model sensitivity to a potential underestimate in carbon export since both higher K_{OC} values and higher particle concentrations will result in greater PCB partitioning to the solid phase. We found the low and midrange values of K_{OC} for CB-153 resulted in modeled dissolved concentration peaks (9–16 pg L⁻¹) at three tropical Atlantic Ocean stations that exceeded the ranges of measurements (0.06 to 3.5 pg L⁻¹; Figure S1b). The best model performance was obtained using the upper 95th percentile confidence limit of the K_{OC} , reflecting combined influences of higher PCBs sorption to particles than predicted by the

geometric mean K_{OC} and likely higher carbon export fluxes from the surface ocean. Gustafsson et al. (1997) reported PCB setting fluxes from the surface ocean mixed layer of the North Atlantic for CB-52, CB-128, and CB-194 that ranged from 0.02–12 pmol·m⁻²·day⁻¹ based on ²³⁴Th and PCB concentrations in suspended particles. This compares well to our modeled results for different congeners (CB-28, CB-101, CB-153, and CB-180) of 0.0002–7 pmol·m⁻²·day⁻¹. Annually averaged settling fluxes in this study are lower than those reported by Galbán-Malagón et al. (2012) for the polar North Atlantic during peak biomass production. At this time, particle concentrations are approximately one order of magnitude higher than outside the spring-summer season (Stramska & Stramski, 2005).

Polychlorinated POPs degrade through both photolytic and biological processes, but rate data are not specifically available for PCBs (Abramowicz, 1990; Friesen et al., 1990; Sinkkonen & Paasivirta, 2000). Assuming uniform degradation with depth, which has been used in other models (Wania & Daly, 2002), results in decreasing PCB concentrations with depth. Measured PCB concentrations increase with depth in the water column and peak between 400 and 3,000 m (Figure S2; Booij et al., 2014; Gustafsson et al., 2005; Sun et al., 2016). Prior research suggests microbial degradation of PCBs is approximately one order of magnitude lower than photolytic degradation (Sinkkonen & Paasivirta, 2000; Y. Zhang et al., 2015). We thus used the following expression to represent degradation of PCBs in the water column:

$$k_{\text{deg}} = \left(0.9 \frac{k_{\text{base},T}}{RAD_{\text{surf}}} \times RAD_z + 0.1 k_{\text{base},T} \times f_{\text{remin},z} \right) \times 100, \quad (1)$$

where $k_{\text{base},T}$ is the temperature adjusted degradation base rate, RAD_{surf} and RAD_z are the shortwave radiation intensity at the surface and at depth z , and $f_{\text{remin},z}$ is the remineralized fraction of organic carbon at depth z . Organic carbon remineralization rates are used as a proxy for bacterial activity in the water column (Dutkiewicz et al., 2009; Y. Zhang et al., 2015). Resulting modeled degradation half-lives in the upper ocean (top 1,000 m) for CB-28 (3.8 years), CB-101 (10.4 years), CB-153 (20.9 years), and CB-180 (27.2 years) agree well with those reported elsewhere (Galbán-Malagón, Del Vento, Cabrerizo, et al., 2013; Sinkkonen & Paasivirta, 2000; Wania & Daly, 2002).

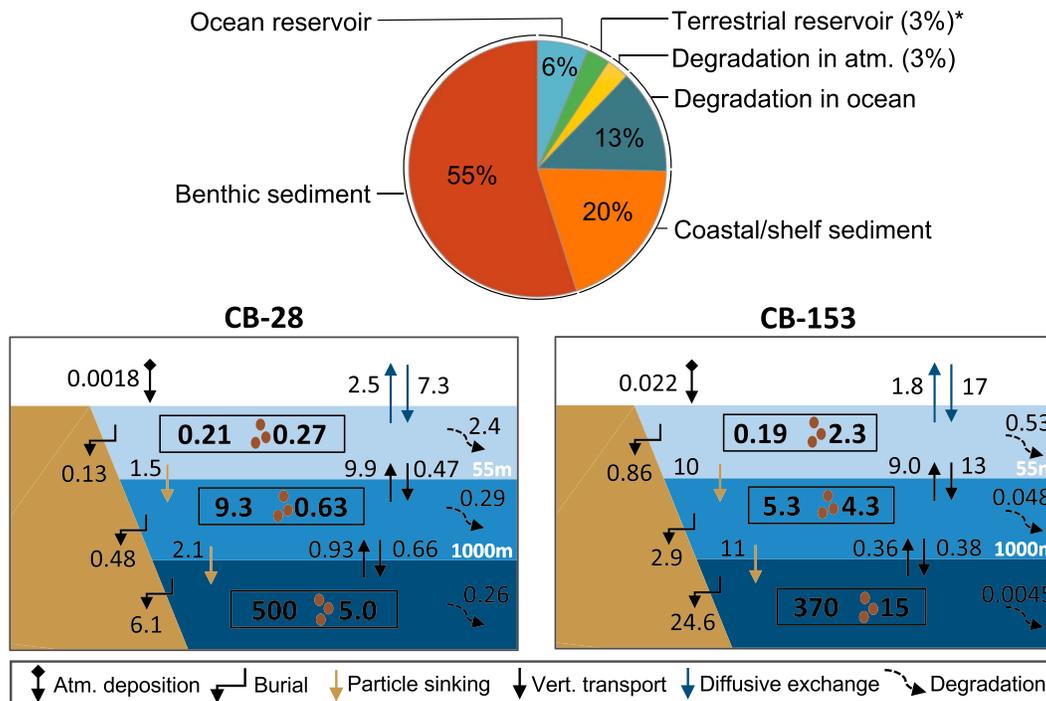


Figure 3. Modeled fate of polychlorinated biphenyls released to the global environment between 1930 and 2015 to global reservoirs (sum of historical CB-28, CB-101, CB-153, and CB-180 releases) and major removal processes through degradation in the atmosphere and ocean. The 2015 atmospheric reservoir is estimated to be <0.01% of the cumulative releases since 1930 (Friedman & Selin, 2016; Wania & Daly, 2002). Bottom panels show 2015 global ocean budget of CB-28 and CB-153. Atmosphere deposition includes wet and dry particulate, and wet gaseous deposition, vertical transport includes advective and diffusive transport. Upward diffusive transport at the air-sea boundary denotes gross evasion and downward diffusive transport denotes gross gaseous deposition. Superscripted asterisk (*) indicates the terrestrial reservoir is based on the difference between environmental releases and cycling/loss pathways included in our analysis and does not account for localized point sources not included in Breivik et al. (2007). CB = chlorinated biphenyl.

3. Results and Discussion

3.1. Modeled Global Distribution of PCBs in Seawater

Figure 1 shows the modeled global distribution of PCBs in the surface ocean (5-m depth, ca. 2008) compared to measurements collected between 2000 and 2015. Modeled seawater PCB concentrations were the highest in the Northern Hemisphere for all four congeners due to proximity to historic sources. Seawater measurements between 2000 and 2015 were clustered in the Mediterranean Sea and Arctic Ocean, and sparse data have been collected from other ocean regions (Figure 1 and Table S3). The atmospheric model used to force our ocean simulation has a relatively coarse resolution ($4^\circ \times 5^\circ$) and when combined with the narrow shape of the Mediterranean Sea produces anomalous deposition patterns due to multiple atmospheric grid cells that contain only a small fraction of water. We thus focus model evaluation on the Arctic Ocean.

Median modeled concentrations overlap with the measured ranges in surface seawater for all four PCB congeners and capture important spatial patterns (Figures 1 and 2). Both modeled and measured concentrations peak in the Norwegian and Greenland Seas and are the lowest in the high Arctic. Variability in observations is greater than for modeled concentrations, which reflects the coarser spatial resolution and associated spatial averaging that occurs in the model. Both the model and measurements indicate the most volatile congener (CB-28) is most abundant in the Arctic, and the highest molecular weight congener (CB-180) is approximately two orders of magnitude lower in concentration (Figures 1 and 2). This contrasts the modeled distribution at midlatitudes and in the tropics (Figure 1 and Table S3) where the higher molecular weight congener, CB-153, is most abundant due to higher deposition. Fractionation of more volatile congeners with increasing latitude is consistent with measurements in ocean water and sediment cores (Gustafsson et al., 2001; Sobek & Gustafsson, 2004).

For other ocean regions, insufficient data are available to perform a quantitative model evaluation. In addition, ship-based sampling always faces the issue of shipboard contamination due to the potential presence of

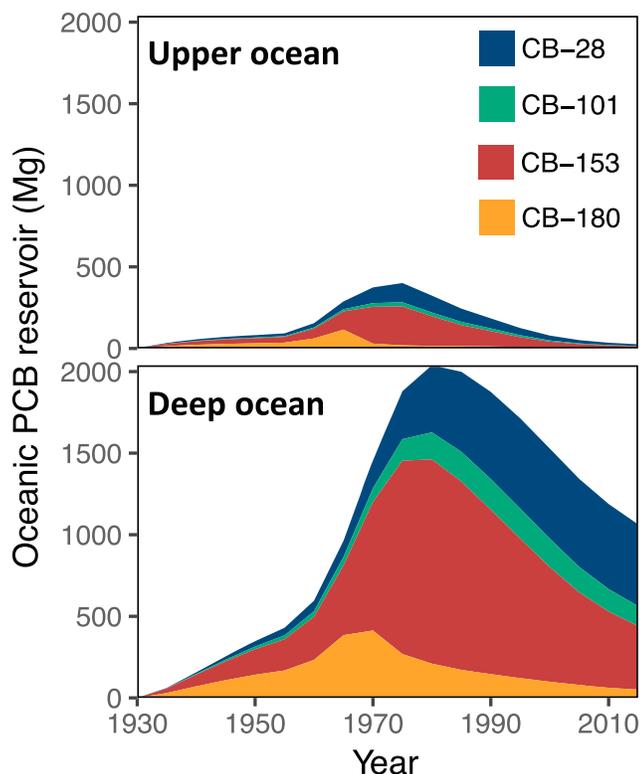


Figure 4. Modeled changes between 1930 and 2015 in the reservoir of PCBs in the upper ocean (top 1,000 m) and deep ocean (below 1,000 m to the seafloor). CB = chlorinated biphenyl; PCB = polychlorinated biphenyl.

trace-level contaminants on the ship itself (Lohmann et al., 2004). During active sampling, incomplete separation of the dissolved and solid phases in reported PCB measurements is known to occur (Adams et al., 2007). Such issues may explain the lack of clear latitudinal variability in ocean measurements compared to the distinct enrichment in the Northern Hemisphere in the model.

Model results indicate the global oceans contain approximately 6% of the Σ_4 PCBs (sum of CB-28, CB-101, CB-153, and CB-180) released to the environment between 1930 and 2015. In 2015, only 2% of the Σ_4 PCBs (approximately 22 Mg) was present in the ocean above 1,000-m depth (Figures 3 and 4). Burial of PCBs in benthic sediment in the deep ocean (9,400 Mg) and in coastal/shelf regions (3,400 Mg) has sequestered 75% of cumulative releases between 1930 and 2015 (Figure 3), emphasizing the importance of this pathway as a removal process (Jönsson et al., 2003). Our parameterization for PCB degradation in seawater suggests it has removed an additional 13% from environmental reservoirs (2,200 Mg). This is substantially higher than in previous modeling studies and more than the present ocean reservoir (Wania & Daly, 2002). Thus, better observational constraints on PCB degradation rates in seawater have global significance for understanding their ultimate fate in the environment. As noted elsewhere, atmospheric oxidation is a less important loss pathway (3%; Axelman & Gustafsson, 2002; Friedman & Selin, 2016). The terrestrial environment contains the remainder of environmental releases included in our analysis since 1930. These results emphasize the effectiveness of natural sequestration mechanisms at reducing concentrations in the biosphere following a global phase out in chemical production.

3.2. Temporal Shifts in the Global Ocean Reservoir

The modeled global upper ocean reservoir (top 1,000 m) of PCBs peaked during the highest atmospheric releases in the 1970s and 1980s and has declined by more than 90% since this time (Figure 4). In the deep ocean, the reservoir of CB-180 peaked in 1968, followed by CB-153 in 1979, CB-101 in 1990, and CB-28 in 1997 (Figure 4). This timing follows their molecular weight and associated volatilities, particle affinities, and hydrophobicities (Schwarzenbach et al., 2003). More rapid scavenging of high molecular weight PCBs increased the proportion of lighter congeners (CB-28 and CB-101) in the ocean from 20% of the Σ_4 PCBs in 1970 to 58% in 2015 and is consistent with enrichment of moderately chlorinated congeners in modern sediments (Gustafsson et al., 2001). Shifts in congener composition led to a 37% increase in modeled global residence time of the sum of four PCBs in the upper ocean between 1970 and 2015 (Figure S3).

The spatial distribution of PCBs in the ocean has shifted over time toward the Southern Hemisphere (Figures 5 and S4). In 1970, when primary emissions of PCBs were very high, 64% of the global ocean reservoir in the ocean was contained in the North Atlantic and North Pacific Oceans. By 2015, this declined to 39%. Over the same time period, the Southern Hemisphere ocean reservoirs increased from 30% to 54% of the global total. These results illustrate the role of the Northern Hemisphere oceans as an ongoing exporter of historic pollution to the equatorial and southern ocean basins over multidecadal time scales.

3.3. Major Biogeochemical Processes Driving Global Distribution

Figure 6 shows the relative importance of different biogeochemical processes for PCB inputs and losses across the upper ocean (top 1,000 m). Despite declines in PCB releases, atmospheric deposition to the surface ocean is still the most important input source to all ocean regions and accounted for 49–99% of total inputs across basins and congeners in 2015 (Figure 6a and Table S4). Almost 60% of modeled total deposition occurred in the North Pacific and North Atlantic basins even though they make up only 33% of surface area of the ocean (Eakins & Sharman, 2010). This reflects their continued proximity to emissions sources from PCBs used in historic manufacturing in the global PCB inventory (Breivik et al., 2007). More recent

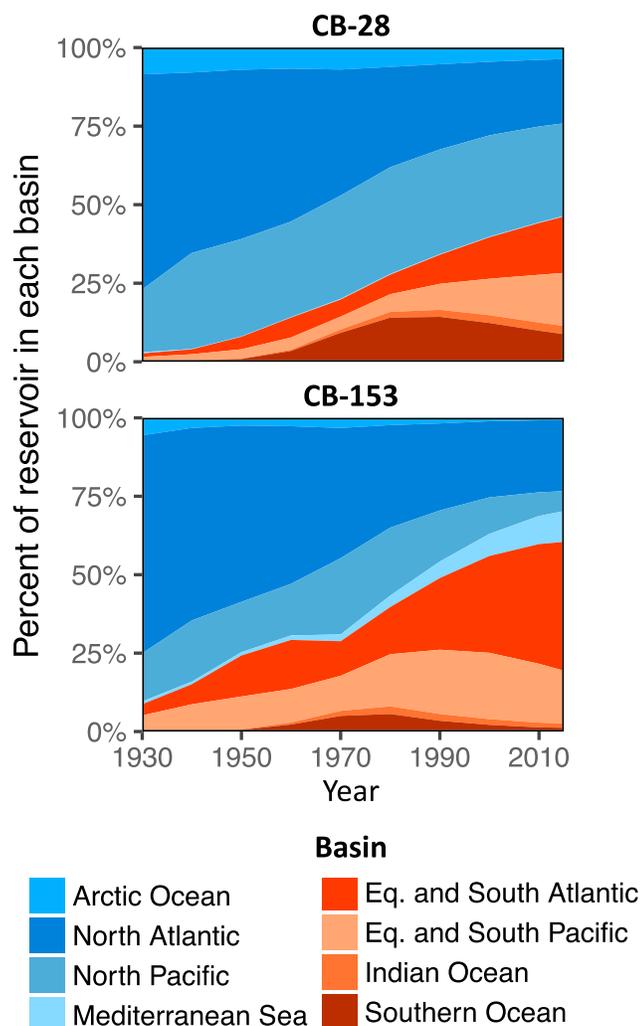


Figure 5. Changes in the mass distribution of CB-28 and CB-153 between ocean basins between 1930 and 2015. Northern hemisphere basins are shades of blue, and southern hemisphere basins are shades of red/orange. CB = chlorinated biphenyl.

studies have suggested that global inventories of PCB releases should be updated to account for missing recent sources in the Southern Hemisphere (Gioia, Lohmann, et al., 2008; Lohmann et al., 2012; L. Zhang & Lohmann, 2010).

As discussed above, advection of PCBs from the Northern Hemisphere to the Southern Hemisphere (Σ_4 PCBs = 2.5 Mg in 2015) though lateral ocean circulation has become substantial in recent years for some basins. Modeled fluxes of PCBs with lateral ocean circulation accounted for 48% of total inputs to the upper Equatorial and South Atlantic Ocean and 20% of inputs to the Indian Ocean in 2015. Other sources to the upper ocean such as upwelling from the deep ocean accounted for less than 10% of the modeled total inputs across basins.

Globally, we find modeled particle-associated scavenging of PCBs from the upper ocean accounted for 69% of total losses in 2015 (Figure 6b and Table S4). This is consistent with observational studies that have suggested the marine biological pump is a globally significant removal mechanism for PCBs from the upper ocean (Dachs et al., 2002; Galbán-Malagón et al., 2012). Across basins, particle-associated export of PCBs from the top 1,000 m of the water column accounted for between 25% and 75% of losses in 2015 (Figure 6b and Table S4). The Arctic Ocean has a water column depth of less than 1,000 m in many regions due to an expansive continental shelf. Thus, particle-associated removal is reflected by burial in benthic sediment in the Arctic basin (42% of the Σ_4 PCBs losses), as has been noted elsewhere (Sobek & Gustafsson, 2014).

The importance of other PCB removal processes from the upper ocean varies spatially and by congener. Globally, evasion accounts for 16% of total losses from the upper ocean, degradation for 11%, and deep water formation for 4% (Figure 6b and Table S4). For the higher molecular weight congeners (CB-153 and CB-180), scavenging by particles is the dominant removal process across all basins (59–97%; Figure 6b and Table S4). These two compounds have log octanol water partition coefficients (K_{OW}) of greater than 7.31, which is linearly related to their K_{OC} (upper bound greater than 8.31) and a good proxy for partitioning to lipids (Chiou, 1985; Sobek et al., 2004).

A single dominant removal process for PCBs from the upper ocean is less identifiable for the lower molecular weight congeners CB-28 and CB-101 with lower log K_{OW} values. For CB-28, modeled degradation is the dominant removal process in the Equatorial and South Atlantic (57%), Equatorial and South Pacific (54%), Indian Ocean (62%), and Mediterranean Sea (70%), but evasion is more important in the Arctic, North Pacific, and Atlantic Ocean basins (21–41%; Figure 6b and Table S4). This reflects higher winter wind speeds in Northern Hemisphere oceans that enhance PCB losses through evasion and greater shortwave radiation intensity near the tropics that enhance water column degradation. Removal processes for CB-101 in the upper ocean are diverse and depend on basin specific characteristics. The lack of a single dominant removal process for lower molecular weight PCB congeners demonstrates that the removal of some POPs can only be determined after characterizing basin-specific differences in biogeochemical properties.

Prior work suggests that accumulation of persistent organic contaminants in the subsurface ocean may provide an ongoing source to the surface ocean and atmosphere after elimination of primary emissions sources (Hung et al., 2016; Stemmler & Lammel, 2013). These studies have proposed that the ocean could act as source rather than sink for some legacy POPs due to mixing, seasonal entrainment of the mixed layer, and diffusion of volatile chemicals back to the surface ocean, followed by evasion to the atmosphere (Lohmann et al., 2012; Nizzetto et al., 2010; Stemmler & Lammel, 2013). Such processes have been proposed as one explanation for slowing declines in atmospheric concentrations of PCBs and even increases at some

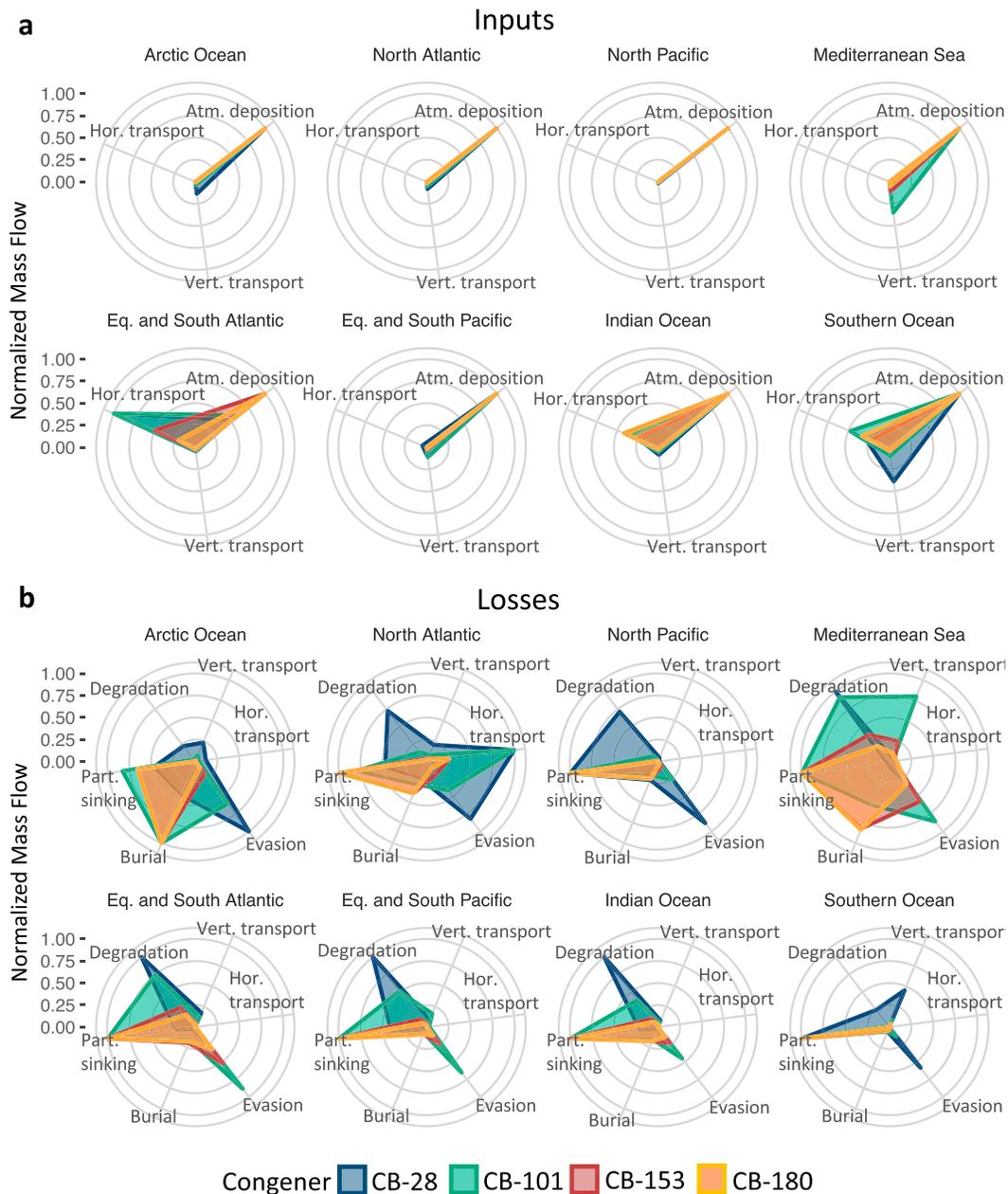


Figure 6. Relative importance of different input (a) and loss (b) processes for polychlorinated biphenyls across ocean basins and congeners. Modeled mass flows of PCBs for 2015 are normalized to the magnitude of the dominant process to illustrate their relative importance for each congener. Polygons with small, pointed areas indicate a single dominant removal process. Part. sinking denotes sinking sorbed to particles at 1,000 m. Hor. transport denotes net horizontal advective and diffusive transport. Vert. transport denotes gross vertical advective and diffusive transport at 1,000 m. CB = chlorinated biphenyl.

Arctic monitoring stations (Gioia, Lohmann, et al., 2008; Hung et al., 2016). The simultaneous peak in environmental releases and the upper ocean reservoir of CB-153 and CB-180 suggest seasonal entrainment does not exert a major influence on surface and atmospheric concentrations of these congeners (Figure 4).

For CB-28, we find an upper ocean response lag of 10 years and a short half-life against evasion (2 months) in ocean surface mixed layer (Figures 3, 4, and 6). Vertical transport contributes similar amounts of CB-28 (9 Mg) and CB-153 (10 Mg) to the mixed layer (upper 55 m). However, the ratio of inputs to losses of CB-153 (1.0) in the mixed layer is less than half that of CB-28 (2.5), mainly due to rapid particle-associated removal and downward vertical transport (Figure 3). Thus, model results suggest in ocean basins with

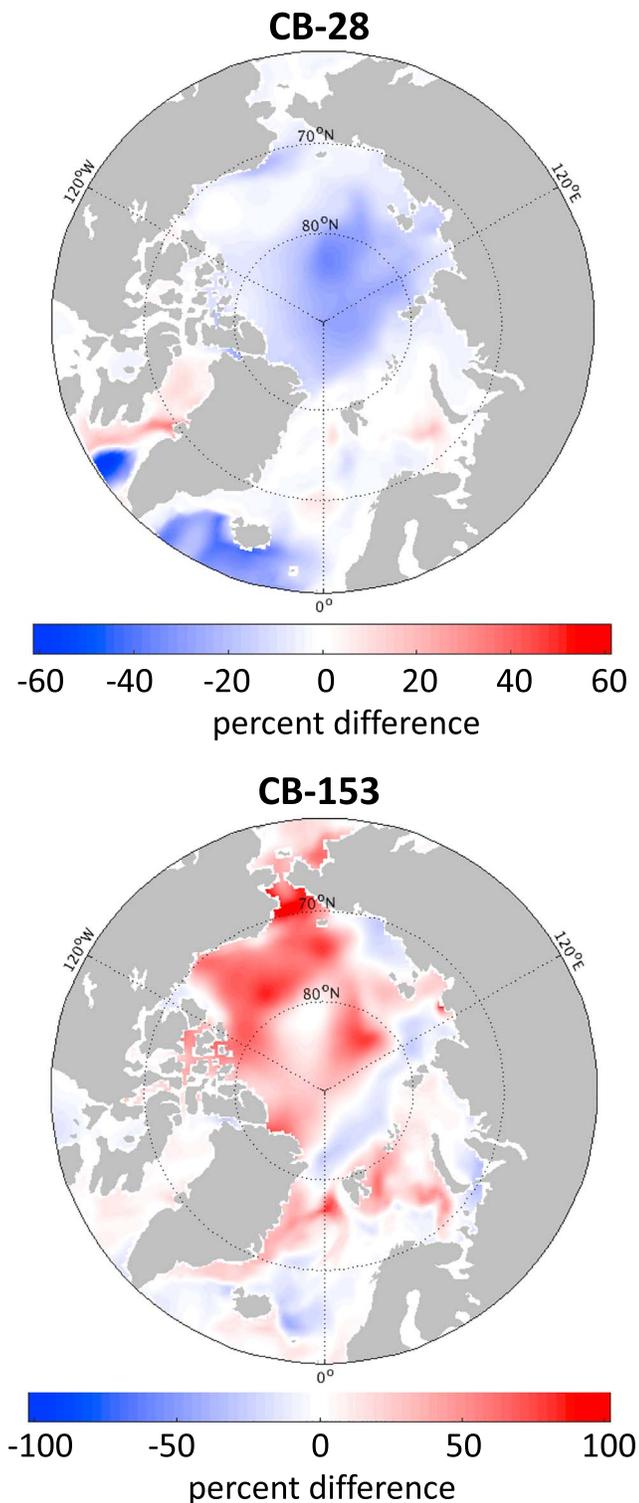


Figure 7. Modeled differences in polychlorinated biphenyl concentrations in the Arctic Ocean simulated using 1992–2015 meteorology, ice cover, and ocean circulation relative to base results using constant 1992–1996 conditions. Upper panel shows results for CB-28 and lower panel shows CB-153. CB = chlorinated biphenyl.

significant evasion, such as the Arctic, North Pacific, and Atlantic Oceans, the subsurface PCB reservoir is a potential source of more volatile congeners to the atmosphere. Our findings show that differing meteorological conditions between basins drive removal of lighter molecular weight congeners indicating they will be affected more strongly by climate-driven changes to ocean biogeochemistry.

3.4. Climate-Driven Changes in the Arctic Ocean

In the Arctic, global temperature anomalies are two times higher than the global average (Bekryaev et al., 2010; IPCC, 2014). In 2017, September sea-ice extent was 25% lower than the 1981–2010 average, reflecting changes in atmospheric circulation, weakened Atlantic Meridional Overturning Circulation, and increased poleward heat transport (Delworth et al., 2016; Ding et al., 2017; IPCC, 2014; Rahmstorf et al., 2015; Richter-Menge et al., 2017; Stroeve et al., 2007). We examined the impacts of such rapid changes on PCB cycling in the Arctic Ocean by forcing the model with the ERA-Interim reanalysis fields that capture changes in temperature, sea-ice cover, and ocean circulation observed in the Arctic Ocean between 1992 and 2015 (Forget, Campin, et al., 2015).

Figure 7 shows modeled differences in 2015 seawater PCB concentrations due to variability in ocean circulation and sea-ice cover between 1992 and 2015 compared to a baseline simulation with constant ocean state conditions (1992–1996). Results show changes in ocean conditions resulted in a decline in CB-28 seawater concentrations by an additional 54% compared to the constant meteorology scenario. In contrast, model results show an increase in concentrations of CB-153 in Arctic surface seawater relative to the constant climate scenario.

Differences in the directionality of changes in PCB concentrations between congeners reflect their contrasting sensitivity to physical/chemical processes. CB-28 is much more volatile, and thus ice-free waters and longer-seasonal ice-free periods resulted in greater losses through increased evasion (41% change) and degradation (28% change) using the 1992–2015 climatology. The net increase in mean 2015 CB-153 concentrations with varying meteorological conditions relative to the constant climate scenario was small in our simulation (0.0004 pg/L or 1%). Larger increases of up to 100%, or 0.06 pg/L, were apparent in the areas with the greatest sea-ice cover retreat such as the Canadian Basin, the East Greenland Rift Basin, and on the Barents shelf (Figure 7b).

CB-153 has a greater propensity for binding to particles leading to greater stability and retention in the surface ocean. Thus, declining sea-ice cover in the Arctic Ocean resulted in a net increase in atmospheric deposition and overall increase in seawater concentrations in some regions. Such patterns are consistent with observed increases and stabilization in biotic concentrations in the Arctic. For example, data from 358 time series covering Arctic mussels, marine fish, seals, and polar bears suggest that the annual rate of decline in CB-153 concentrations in biota was reduced from 3.7% in the 1980s and 1990s to 2.5% after 2000 (AMAP, 2016b).

Arctic sea-ice cover is projected to retreat 60–100%, and mean temperatures may increase by >10°C by the end of the 21st century (IPCC, 2014). This is likely to further increase evasion of more volatile congeners. Extended seasonally ice-free waters and associated increases in light

availability increased ocean productivity in the Barents Sea and the Eurasian Arctic between 2003 and 2017 (Richter-Menge et al., 2017). Melting of permafrost is expected to increase riverine inputs of labile DOC to the Arctic Ocean (Panneer Selvam et al., 2017). Satellite data suggest that net primary productivity increased by 20% between 1998 and 2009 and may reach 730 Tg C year⁻¹ in an ice-free Arctic (Arrigo & van Dijken, 2011). Increases in particle-associated removal in a more productive ocean may attenuate any increases in atmospheric deposition of higher molecular weight congeners and ultimately reduce the residence times in ocean of high molecular weight compounds. Our findings suggest that changes in ocean biogeochemistry resulting from projected sea ice retreat, increasing surface temperatures, and changing ocean circulation will decrease concentrations of lighter molecular weight POPs and slow concentration declines of POPs with higher molecular weights. For PCBs, the large decline in emissions exerts the dominant influence on concentration trends. However, for neutral hydrophobic POPs with increasing production trends, such as organophosphate esters, changes in Arctic ecosystem properties may exert a much more pronounced pattern and result in differing trends among low and high molecular weight compounds (J. Li et al., 2017; Sühring et al., 2016).

4. Summary and Conclusions

We developed a global ocean simulation for four PCB congeners between 1930 and 2015. PCB concentrations in the upper ocean have declined by over 90% since 1970, mainly due to declines in primary emissions and particle-associated removal from the water column. We estimate that burial in coastal and marine sediment accounts for cumulative removal of approximately 75% of the PCBs released to the atmosphere since 1930. In 2015, the global ocean reservoir of the four PCBs modeled in this study was equivalent to 6% of releases since 1930, with only 2% in the upper ocean above 1,000 m. The slowest decline in seawater PCB concentrations has occurred among the lightest molecular weight congeners, resulting in an increase in their proportion in the upper ocean reservoir in recent years. The enormous lack of data in the Southern, South Pacific, Indian, and South Atlantic Oceans highlights critical research needs for the future.

Biogeochemical processes driving PCB inputs and losses vary among basins and by congener. Atmospheric deposition is the most important input source for the surface ocean. Model results suggest 56% of global deposition was located in the North Atlantic and North Pacific basins in 2015. Lateral transport of legacy PCB pollution from the Northern Hemisphere to the Southern Hemisphere oceans through thermohaline circulation has become increasingly important in recent years, particularly for the Equatorial and South Atlantic Ocean. For the higher molecular weight PCB congeners, particle-associated removal dominates losses across all basins but a combination of evasion, degradation, particle settling, and lateral transport is important for the lighter molecular weight congener removal. For the lighter molecular weight congeners, basin-specific biogeochemical conditions such as high winds in the North Atlantic determine the major loss processes, suggesting the importance of future climate-driven changes in the global oceans for the fate of many anthropogenic pollutants. Differences among high and low molecular weight PCB congeners observed in this study may be more pronounced for neutral hydrophobic POPs with stable or increasing emissions.

Increases in seawater temperature, changes in circulation, and reductions in sea-ice cover between 1992 and 2015 in the Arctic Ocean increased evasion of the lowest molecular weight PCB (CB-28). A small increase in net deposition to the surface ocean occurred for CB-153 due to sorption to particles and thus greater stability in seawater. Continued declines in sea-ice cover and increases in seawater temperature are projected for the next several decades (IPCC, 2014). Thus, increases in Arctic seawater concentrations of some persistent pollutants (e.g., CB-153) and neutral POPs with high K_{OW} (>7.3 in this study), but decreases for more volatile compounds (e.g., CB-28), may be expected. Potential climate-driven mobilization of legacy POP reservoirs in permafrost, glaciers, and sea ice should also be considered (AMAP, 2016a).

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