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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

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1 **A global 3-D ocean model for polychlorinated biphenyls (PCBs): Benchmark compounds**  
2 **for understanding the impacts of global change on neutral persistent organic pollutants**

3  
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23

24 **Key Points**

25

26 • Climate change will have the greatest impacts on the chemical lifetimes and distributions  
27 of volatile persistent organic pollutants.

28 • Marine sediment has sequestered 75% of cumulative releases of polychlorinated  
29 biphenyls since the onset of production in 1930.

30 • Arctic sea ice retreat is likely to enhance losses of volatile congeners but increase net  
31 deposition of higher molecular weight congeners.

32

33 **Abstract**

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

51

## 52 **1 Introduction**

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

66 PCBs are a class of 209 chlorinated aromatic compounds that were used extensively in  
67 industrial equipment and consumer products prior to a global phase out in the 1970s [Breivik *et al.*  
68 *et al.*, 2002; Breivik *et al.*, 2007]. PCB emissions peaked (ca. 1970) at approximately 3000 Mg a<sup>-1</sup>  
69 before they were phased out in most regions globally and they have subsequently declined to  
70 several hundred Mg a<sup>-1</sup> (ca. 2010) [Breivik *et al.*, 2002; Breivik *et al.*, 2007]. Atmospheric  
71 deposition is the main source of PCBs to the global oceans, and rivers are a minor contributor  
72 [Jurado *et al.*, 2004; Lammel and Stemmler, 2012; Wania and Daly, 2002]. High PCB  
73 concentrations in crustaceans from the deep Pacific Ocean illustrate their penetration to even the  
74 most remote regions of the ocean [Jamieson *et al.*, 2017]. Prior work has characterized PCB

75 behavior in the environment, quantified their physical-chemical properties, and developed global  
76 release inventories [*Breivik et al.*, 2007; *Corsolini and Sarà*, 2017; *Gioia et al.*, 2008b;  
77 *McLachlan et al.*, 2017; *Schwarzenbach et al.*, 2003]. This makes PCBs ideal as benchmark  
78 compounds for better understanding the behavior of persistent, bioaccumulative and toxic POPs  
79 in the ocean and interactions with different biogeochemical processes.

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

92         The main objective of this study is to better understand how the distribution of neutral  
93 hydrophobic POPs in seawater is affected by variability in ocean biogeochemistry. We develop a  
94 3-D global simulation for PCBs within an ocean general circulation model (MITgcm) forced by  
95 atmospheric inputs from the GEOS-Chem Chemical Transport Model (CTM) [*G. Forget et al.*,  
96 2015; *Friedman and Selin*, 2016]. We evaluate the model against observations and apply it to  
97 better understand the relative importance of different input and removal processes. We explore

98 variability across PCB congeners spanning a range of molecular weights and volatilities and use  
99 our simulation to estimate impacts of climate-driven changes in surface temperatures, sea ice  
100 cover and ocean circulation in the Arctic, where the largest changes are occurring.

## 101 **2 Model Description**

### 102 **2.1 General Model Description**

103 We added four PCBs (chlorinated biphenyl (CB)-28, CB-101, CB-153, CB-180) as  
104 tracers to the Massachusetts Institute of Technology general circulation model (MITgcm).  
105 Tracers were selected from the seven congeners frequently measured by the International  
106 Council for the Exploration of the Sea (ICES-7) and represent a range of physicochemical  
107 properties [Duinker *et al.*, 1988]. The MITgcm has a horizontal resolution of  $1^\circ \times 1^\circ$  globally,  
108 with higher resolution in the Arctic (40 km $\times$ 40 km) and near the equator ( $0.5^\circ \times 1^\circ$ ). It has 50  
109 vertical layers spanning 5 m intervals at the surface and 500 m near the ocean floor [G. Forget *et al.*, 2015]. Advection and diffusion of PCBs is based on ocean state estimates from the  
110 Estimating the Circulation & Climate of the Ocean (ECCO-v4) climatology. Surface boundary  
111 conditions (e.g., wind stress, seawater temperatures, and sea-ice cover) from the ERA-Interim re-  
112 analysis fields spanning 1992-2015 and ocean transport parameters are optimized in ECCO-v4 to  
113 produce a best fit to *in situ* and satellite observations of the physical ocean state and sea ice cover  
114 [Forget and Ponte, 2015; Gael Forget *et al.*, 2015; G. Forget *et al.*, 2015].

116 We forced the ocean model with monthly atmospheric concentrations and deposition of  
117 PCBs between 1930-2015 from the GEOS-Chem global atmospheric model [Friedman and  
118 Selin, 2016]. We assumed negligible concentrations of PCBs in the ocean prior to the onset of  
119 global production in 1930. The GEOS-Chem simulation estimates primary releases based on the  
120 high anthropogenic emissions scenario recommended in prior work and surface temperature



121 [Breivik *et al.*, 2007; Friedman and Selin, 2016]. Projected emissions to 2015 were based on  
122 continued product use trends suggested by the same authors [Breivik *et al.*, 2007]. We neglected  
123 inputs to the ocean other than atmospheric deposition because other work suggests they are small  
124 [Jurado *et al.*, 2004; Lammel and Stemmler, 2012].

## 125 **2.2 Model parameterization and sensitivity analysis**

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

134 PCBs rapidly reach equilibrium between the dissolved and solid phases in seawater  
135 [Sobek *et al.*, 2004]. Partitioning to suspended particles was therefore represented as a reversible  
136 equilibrium based on an empirically measured organic carbon partition coefficient ( $K_{OC}$ ) adjusted  
137 for temperature and salinity [Sobek *et al.*, 2004]. The physicochemical properties of the four  
138 congeners are detailed in the supporting information (Table S2) [Li *et al.*, 2003; Schenker *et al.*,  
139 2005; Schwarzenbach *et al.*, 2003; Wania and Daly, 2002]. Particle concentrations and vertical  
140 transport of PCBs associated with export fluxes were simulated using the ecological simulation  
141 (DARWIN-ECCO v4) embedded within the MITgcm. The ecological simulation has been  
142 described and evaluated elsewhere [Dutkiewicz *et al.*, 2012].

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

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

159           We ran the 1930-2015 simulation using the range of  $\log K_{OC}$  values reported in prior  
160 work (5.82 to 8.31) for CB-153, which is the most prevalent congener in many regions of the  
161 ocean [Hawker and Connell, 1988; Li *et al.*, 2003; Schenker *et al.*, 2005; Sobek and Gustafsson,  
162 2014; Sobek *et al.*, 2004]. The upper bound of  $K_{OC}$  values reported by Sobek *et al.* [2004] is  
163 higher than supported by recent data [Panagopoulos *et al.*, 2016; Stenzel *et al.*, 2013]. It can be  
164 used to explore model sensitivity to a potential underestimate in carbon export since both higher  
165  $K_{OC}$  values and higher particle concentrations will result in greater PCB partitioning to the solid

166 phase. We found the low and mid-range values of  $K_{OC}$  for CB-153 resulted in modeled dissolved  
167 concentration peaks (9-16  $\text{pg L}^{-1}$ ) at three tropical Atlantic Ocean stations that exceeded the  
168 ranges of measurements (0.06 to 3.5  $\text{pg L}^{-1}$ ) (Figure S1b). The best model performance was  
169 obtained using the upper 95<sup>th</sup> percentile confidence limit of the  $K_{OC}$ , reflecting combined  
170 influences of higher PCBs sorption to particles than predicted by the geometric mean  $K_{OC}$  and  
171 likely higher carbon export fluxes from the surface ocean. *Gustafsson et al.* [1997] reported PCB  
172 settling fluxes from the surface ocean mixed layer of the North Atlantic for CB-52, CB-128, and  
173 CB-194 that ranged from 0.02-12  $\text{pmol m}^{-2} \text{d}^{-1}$  based on  $^{234}\text{Th}$  and PCB concentrations in  
174 suspended particles. This compares well to our modeled results for different congeners (CB-28,  
175 CB-101, CB-153, and CB-180) of 0.0002-7  $\text{pmol m}^{-2} \text{d}^{-1}$ . Annually averaged settling fluxes in  
176 this study are lower than those reported by *Galbán-Malagón et al.* [2012] for the polar North  
177 Atlantic during peak biomass production. At this time, particle concentrations are approximately  
178 one order of magnitude higher than outside the spring-summer season [*Stramska and Stramski,*  
179 2005].

180 Polychlorinated POPs degrade through both photolytic and biological processes but rate  
181 data are not specifically available for PCBs [*Abramowicz, 1990; Friesen et al., 1990; Sinkkonen*  
182 *and Paasivirta, 2000*]. Assuming uniform degradation with depth, which has been used in other  
183 models [*Wania and Daly, 2002*], results in decreasing PCB concentrations with depth. Measured  
184 PCB concentrations increase with depth in the water column and peak between 400 m and 3000  
185 m (Figure S2) [*Booij et al., 2014; Gustafsson et al., 2005; Sun et al., 2016*]. Prior research  
186 suggests microbial degradation of PCBs is approximately one order of magnitude lower than  
187 photolytic degradation [*Sinkkonen and Paasivirta, 2000; Zhang et al., 2015*]. We thus used the  
188 following expression to represent degradation of PCBs in the water column:

189 
$$k_{deg} = (0.9 \frac{k_{base,T}}{RAD_{surf}} \times RAD_z + 0.1 k_{base,T} \times f_{remin,z}) \times 100 \quad (\text{Eq.1})$$

190 where  $k_{base,T}$  is the temperature adjusted degradation base rate,  $RAD_{surf}$  and  $RAD_z$  are the  
191 shortwave radiation intensity at the surface and at depth  $z$ , and  $f_{remin,z}$  is the remineralized  
192 fraction of organic carbon at depth  $z$ . Organic carbon remineralization rates are used as a proxy  
193 for bacterial activity in the water column [Dutkiewicz *et al.*, 2009; Zhang *et al.*, 2015]. Resulting  
194 modeled degradation half-lives in the upper ocean (top 1000 m) for CB-28 (3.8 years), CB-101  
195 (10.4 years), CB-153 (20.9 years), and CB-180 (27.2 years) agree well with those reported  
196 elsewhere [Galbán-Malagón *et al.*, 2013b; Sinkkonen and Paasivirta, 2000; Wania and Daly,  
197 2002].

### 198 **3 Results and Discussion**

#### 199 **3.1 Modeled global distribution of PCBs in seawater**

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

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

222 For other ocean regions, insufficient data are available to perform a quantitative model  
223 evaluation. In addition, ship-based sampling always faces the issue of shipboard contamination  
224 due to the potential presence of trace-level contaminants on the ship itself [*Lohmann et al.*,  
225 2004]. During active sampling, incomplete separation of the dissolved and solid phases in  
226 reported PCB measurements is known to occur [*Adams et al.*, 2007]. Such issues may explain the  
227 lack of clear latitudinal variability in ocean measurements compared to the distinct enrichment in  
228 the Northern Hemisphere in the model.

229 Model results indicate the global oceans contain approximately 6% of the  $\Sigma_4$ PCBs (sum  
230 of CB-28, CB-101, CB-153 and CB-180) released to the environment between 1930 and 2015. In  
231 2015, only 2% of the  $\Sigma_4$ PCBs (approximately 22 Mg) was present in the ocean above 1000 m  
232 depth (Figures 3 and 4). Burial of PCBs in benthic sediment in the deep ocean (9400 Mg) and in

233 coastal/shelf regions (3400 Mg) has sequestered 75% of cumulative releases between 1930 and  
234 2015 (Figure 3), emphasizing the importance of this pathway as a removal process [Jönsson *et*  
235 *al.*, 2003]. Our parameterization for PCB degradation in seawater suggests it has removed an  
236 additional 13% from environmental reservoirs (2200 Mg). This is substantially higher than in  
237 previous modeling studies and more than the present ocean reservoir [Wania and Daly, 2002].  
238 Thus, better observational constraints on PCB degradation rates in seawater have global  
239 significance for understanding their ultimate fate in the environment. As noted elsewhere,  
240 atmospheric oxidation is a less important loss pathway (3%) [Axelman and Gustafsson, 2002;  
241 Friedman and Selin, 2016]. The terrestrial environment contains the remainder of environmental  
242 releases included in our analysis since 1930. These results emphasize the effectiveness of natural  
243 sequestration mechanisms at reducing concentrations in the biosphere following a global phase  
244 out in chemical production.

### 245 **3.2 Temporal shifts in the global ocean reservoir**

246 The modeled global upper ocean reservoir (top 1000 m) of PCBs peaked during the  
247 highest atmospheric releases in the 1970s and 1980s and has declined by more than 90% since  
248 this time (Figure 4). In the deep ocean, the reservoir of CB-180 peaked in 1968, followed by CB-  
249 153 in 1979, CB-101 in 1990 and CB-28 in 1997 (Figure 4). This timing follows their molecular  
250 weight and associated volatilities, particle affinities and hydrophobicities [Schwarzenbach *et al.*,  
251 2003]. More rapid scavenging of high molecular weight PCBs increased the proportion of lighter  
252 congeners (CB-28 and CB-101) in the ocean from 20% of the  $\Sigma_4$ PCBs in 1970 to 58% in 2015  
253 and is consistent with enrichment of moderately chlorinated congeners in modern sediments  
254 [Gustafsson *et al.*, 2001]. Shifts in congener composition led to a 37% increase in modeled

255 global residence time of the sum of four PCBs in the upper ocean between 1970 and 2015  
256 (Figure S3).

257 The spatial distribution of PCBs in the ocean has shifted over time toward the Southern  
258 Hemisphere (Figure 5, Figure S4). In 1970, when primary emissions of PCBs were very high,  
259 64% of the global ocean reservoir in the ocean was contained in the North Atlantic and North  
260 Pacific Oceans. By 2015, this declined to 39%. Over the same time period, the Southern  
261 Hemisphere ocean reservoirs increased from 30% to 54% of the global total. These results  
262 illustrate the role of the Northern Hemisphere oceans as an ongoing exporter of historic pollution  
263 to the equatorial and southern ocean basins over multi-decadal timescales.

### 264 **3.3 Major biogeochemical processes driving global distribution**

265 Figure 6 shows the relative importance of different biogeochemical processes for PCB  
266 inputs and losses across the upper ocean (top 1000 m). Despite declines in PCB releases,  
267 atmospheric deposition to the surface ocean is still the most important input source to all ocean  
268 regions and accounted for 49-99% of total inputs across basins and congeners in 2015 (Figure 6a,  
269 Table S4). Almost 60% of modeled total deposition occurred in the North Pacific and North  
270 Atlantic basins even though they make up only 33% of surface area of the ocean [*Eakins and*  
271 *Sharman, 2010*]. This reflects their continued proximity to emissions sources from PCBs used in  
272 historic manufacturing in the global PCB inventory [*Breivik et al., 2007*]. More recent studies  
273 have suggested that global inventories of PCB releases should be updated to account for missing  
274 recent sources in the Southern Hemisphere [*Gioia et al., 2008b; Lohmann et al., 2012; Zhang*  
275 *and Lohmann, 2010*].

276 As discussed above, advection of PCBs from the Northern Hemisphere to the Southern  
277 Hemisphere ( $\Sigma_4\text{PCBs} = 2.5 \text{ Mg}$  in 2015) though lateral ocean circulation has become substantial

278 in recent years for some basins. Modeled fluxes of PCBs with lateral ocean circulation accounted  
279 for 48% of total inputs to the upper Equatorial and South Atlantic Ocean and 20% of inputs to  
280 the Indian Ocean in 2015. Other sources to the upper ocean such as upwelling from the deep  
281 ocean accounted for less than 10% of the modeled total inputs across basins.

282 Globally, we find modeled particle-associated scavenging of PCBs from the upper ocean  
283 accounted for 69% of total losses in 2015 (Figure 6b, Table S4). This is consistent with  
284 observational studies that have suggested the marine biological pump is a globally significant  
285 removal mechanism for PCBs from the upper ocean [*Dachs et al.*, 2002; *Galbán-Malagón et al.*,  
286 2012]. Across basins, particle-associated export of PCBs from the top 1000 m of the water  
287 column accounted for between 25% and 75% of losses in 2015 (Figure 6b, Table S4). The Arctic  
288 Ocean has a water column depth of less than 1000 m in many regions due to an expansive  
289 continental shelf. Thus, particle-associated removal is reflected by burial in benthic sediment in  
290 the Arctic basin (42% of the  $\Sigma_4$ PCBs losses), as has been noted elsewhere [*Sobek and*  
291 *Gustafsson*, 2014].

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



300 A single dominant removal process for PCBs from the upper ocean is less identifiable for  
301 the lower molecular weight congeners CB-28 and CB-101 with lower log  $K_{ow}$  values. For CB-  
302 28, modeled degradation is the dominant removal process in the Equatorial and South Atlantic  
303 (57%), Equatorial and South Pacific (54%), Indian Ocean (62%) and Mediterranean Sea (70%)  
304 but evasion is more important in the Arctic, North Pacific and Atlantic Ocean basins (21-41%)  
305 (Figure 6b, Table S4). This reflects higher winter wind speeds in Northern Hemisphere oceans  
306 that enhance PCB losses through evasion and greater shortwave radiation intensity near the  
307 tropics that enhance water column degradation. Removal processes for CB-101 in the upper  
308 ocean are diverse and depend on basin specific characteristics. The lack of a single dominant  
309 removal process for lower molecular weight PCB congeners demonstrates that the removal of  
310 some POPs can only be determined after characterizing basin-specific differences in  
311 biogeochemical properties.

312 Prior work suggests that accumulation of persistent organic contaminants in the  
313 subsurface ocean may provide an ongoing source to the surface ocean and atmosphere after  
314 elimination of primary emissions sources [*Hung et al.*, 2016; *Stemmler and Lammel*, 2013].  
315 These studies have proposed that the ocean could act as source rather than sink for some legacy  
316 POPs due to mixing, seasonal entrainment of the mixed layer, and diffusion of volatile chemicals  
317 back to the surface ocean, followed by evasion to the atmosphere [*Lohmann et al.*, 2012; *Nizzetto*  
318 *et al.*, 2010; *Stemmler and Lammel*, 2013]. Such processes have been proposed as one  
319 explanation for slowing declines in atmospheric concentrations of PCBs and even increases at  
320 some Arctic monitoring stations [*Gioia et al.*, 2008b; *Hung et al.*, 2016]. The simultaneous peak  
321 in environmental releases and the upper ocean reservoir of CB-153 and CB-180 suggest seasonal

322 entrainment does not exert a major influence on surface and atmospheric concentrations of these  
323 congeners (Figure 4).

324 For CB-28, we find an upper ocean response lag of ten years and a short half-life against  
325 evasion (2 months) in ocean surface mixed layer (Figure 3, 4 and 6). Vertical transport  
326 contributes similar amounts of CB-28 (9 Mg) and CB-153 (10 Mg) to the mixed layer (upper  
327 55m). However, the ratio of inputs to losses of CB-153 (1.0) in the mixed layer is less than half  
328 that of CB-28 (2.5), mainly due to rapid particle-associated removal and downward vertical  
329 transport (Figure 3). Thus, model results suggest in ocean basins with significant evasion, such  
330 as the Arctic, North Pacific and Atlantic Oceans, the subsurface PCB reservoir is a potential  
331 source of more volatile congeners to the atmosphere. Our findings show that differing  
332 meteorological conditions between basins drive removal of lighter molecular weight congeners  
333 indicating they will be affected more strongly by climate-driven changes to ocean  
334 biogeochemistry.

### 335 **3.4 Climate-driven changes in the Arctic Ocean**

336 In the Arctic, global temperature anomalies are two times higher than the global average  
337 [IPCC, 2014]. In 2017, September sea ice extent was 25% lower than the 1981-2010 average,  
338 reflecting changes in atmospheric circulation, weakened Atlantic Meridional Overturning  
339 Circulation and increased poleward heat transport [Delworth *et al.*, 2016; Ding *et al.*, 2017;  
340 IPCC, 2014; Rahmstorf *et al.*, 2015; Richter-Menge *et al.*, 2017; Stroeve *et al.*, 2007]. We  
341 examined the impacts of such rapid changes on PCB cycling in the Arctic Ocean by forcing the  
342 model with the ERA-Interim re-analysis fields that capture changes in temperature, sea-ice  
343 cover, and ocean circulation observed in the Arctic Ocean between 1992-2015 [G. Forget *et al.*,  
344 2015].

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

351 Differences in the directionality of changes in PCB concentrations between congeners  
352 reflect their contrasting sensitivity to physical/chemical processes. CB-28 is much more volatile  
353 and thus ice-free waters and longer seasonal ice-free periods resulted in greater losses through  
354 increased evasion (41% change) and degradation (28% change) using the 1992-2015  
355 climatology. The net increase in mean 2015 CB-153 concentrations with varying meteorological  
356 conditions relative to the constant climate scenario was small in our simulation (0.0004 pg L<sup>-1</sup> or  
357 1%). Larger increases of up to 100%, or 0.06 pg L<sup>-1</sup> were apparent in the areas with greatest sea-  
358 ice cover retreat such as the Canadian Basin, the East Greenland Rift Basin and on the Barents  
359 shelf (Figure 7B).

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

368 Arctic sea-ice cover is projected to retreat 60% in the coming decades and mean fall  
369 temperatures may increase by as much as 13°C by the end of the 21<sup>st</sup> century [IPCC, 2014].  
370 This is likely to further increase evasion of more volatile congeners. Extended seasonally ice-free  
371 waters and associated increases in light availability increased ocean productivity in the Barents  
372 Sea and the Eurasian Arctic between 2003-2017 [Richter-Menge *et al.*, 2017]. Melting of  
373 permafrost is expected to increase riverine inputs of labile DOC to the Arctic Ocean [Panneer  
374 Selvam *et al.*, 2017]. Satellite data suggest that net primary productivity increased by 20%  
375 between 1998-2009 and may reach 730 Tg C yr<sup>-1</sup> in an ice-free Arctic [Arrigo and van Dijken,  
376 2011]. Increases in particle-associated removal in a more productive ocean may attenuate any  
377 increases in atmospheric deposition of higher molecular weight congeners and ultimately reduce  
378 the residence times in ocean of high molecular weight compounds. Our findings suggest that  
379 changes in ocean biogeochemistry resulting from projected sea ice retreat, increasing surface  
380 temperatures, and changing ocean circulation will decrease concentrations of lighter molecular  
381 weight POPs and slow concentration declines of POPs with higher molecular weights. For PCBs,  
382 the large decline in emissions exerts the dominant influence on concentration trends. However,  
383 for neutral hydrophobic POPs with increasing production trends, such as organophosphate esters,  
384 changes in Arctic ecosystem properties may exert a much more pronounced pattern and result in  
385 differing trends among low and high molecular weight compounds [Li *et al.*, 2017; Sühring *et*  
386 *al.*, 2016].

#### 387 **4 Summary and Conclusions**

388 We developed a global ocean simulation for four PCB congeners between 1930 and  
389 2015. PCB concentrations in the upper ocean have declined by over 90% since 1970, mainly due  
390 to declines in primary emissions and particle-associated removal from the water column. We

391 estimate that burial in coastal and marine sediment accounts for cumulative removal of  
392 approximately 75% of the PCBs released to the atmosphere since 1930. In 2015, the global  
393 ocean reservoir of the four PCBs modeled in this study was equivalent to 6% of releases since  
394 1930, with only 2% in the upper ocean above 1000 m. The slowest decline in seawater PCB  
395 concentrations has occurred among the lightest molecular weight congeners, resulting in an  
396 increase in their proportion in the upper ocean reservoir in recent years. The enormous lack of  
397 data in the Southern, South Pacific, Indian, and South Atlantic Oceans highlights critical research  
398 needs for the future.

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

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

422

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668

669 **Figure Captions**

670 **Figure 1.** Modeled dissolved seawater concentrations of chlorinated biphenyl (CB)-28, CB-101,  
671 CB-153 and CB-180 at 5 m depth in 2008. Observations collected between 2000 and 2015 are  
672 shown as circles and the modeled year represents the mid-point of measurements. Data sources  
673 are as follows: Arctic Ocean: [Booij *et al.*, 2014; Galbán-Malagón *et al.*, 2012; Gioia *et al.*,  
674 2008a; Gustafsson *et al.*, 2005; Sobek and Gustafsson, 2014; Sobek *et al.*, 2004]  
675 North Atlantic Ocean: [Galbán-Malagón *et al.*, 2012; Gioia *et al.*, 2008b; Gioia *et al.*, 2008a;  
676 Lohmann *et al.*, 2012; Sun *et al.*, 2016]; South Atlantic Ocean: [Booij *et al.*, 2014; Gioia *et al.*,  
677 2008b; Lohmann *et al.*, 2012; Sun *et al.*, 2016]; Mediterranean Sea: [Berrojalbiz *et al.*, 2011;  
678 Lammel *et al.*, 2016], Pacific Ocean [Zhang and Lohmann, 2010]; Indian Ocean: [Booij *et al.*,  
679 2014]; Southern Ocean: [Galbán-Malagón *et al.*, 2013a].

680

681 **Figure 2.** Comparison of modeled and observed (2000-2015) dissolved concentrations of  
682 chlorinated biphenyl (CB)-28, CB-101, CB-153 and CB-180 in the upper 1000 m of the Arctic  
683 Ocean [Booij *et al.*, 2014; Galbán-Malagón *et al.*, 2012; Gioia *et al.*, 2008a; Gustafsson *et al.*,  
684 2005; Sobek and Gustafsson, 2014; Sobek *et al.*, 2004]. Modeled and observed concentrations  
685 were matched by year.

686

687 **Figure 3.** Modeled fate of PCBs released to the global environment between 1930 and 2015 to  
688 global reservoirs (sum of historical CB-28, CB-101, CB-153 and CB-180 releases) and major  
689 removal processes through degradation in the atmosphere and ocean. The 2015 atmospheric  
690 reservoir is estimated to be <0.01% of the cumulative releases since 1930 [Friedman and Selin,  
691 2016; Wania and Daly, 2002]. Bottom panels show 2015 global ocean budget of CB-28 and CB-

692 153. Atm. deposition includes wet and dry particulate, and wet gaseous deposition, vertical  
693 transport includes advective and diffusive transport. Upward diffusive transport at the air-sea  
694 boundary denotes gross evasion and downward diffusive transport denotes gross gaseous  
695 deposition.

696 \* The terrestrial reservoir is based on the difference between environmental releases and  
697 cycling/loss pathways included in our analysis and does not account for localized point sources  
698 not included in Breivik et al. [2007].

699

700 **Figure 4.** Modeled changes between 1930 and 2015 in the reservoir of PCBs in the upper ocean  
701 (top 1000 m) and deep ocean (below 1000 m to the seafloor).

702

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

706

707 **Figure 6.** Relative importance of different input (panel a) and loss (panel b) processes for PCBs  
708 across ocean basins and congeners. Modeled mass flows of PCBs for 2015 are normalized to the  
709 magnitude of the dominant process to illustrate their relative importance for each congener.  
710 Polygons with small, pointed areas indicate a single dominant removal process. Part. sinking  
711 denotes sinking sorbed to particles at 1000 m. Hor. transport denotes net horizontal advective  
712 and diffusive transport. Vert. transport denotes gross vertical advective and diffusive transport at  
713 1000 m.

714

715 **Figure 7.** Modeled differences in PCB concentrations in the Arctic Ocean simulated using 1992-  
716 2015 meteorology, ice cover, and ocean circulation relative to base results using constant 1992-  
717 1996 conditions. Upper panel shows results for CB-28 and lower panel shows CB-153.  
718