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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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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.

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

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 and Gustafsson*, 2002; *Mackay and Paterson*, 1991; *Scheringer et al.*, 2000; *Wania and Daly*, 2002]. However, effects of climate-driven variability in ocean biogeochemistry on POPs are poorly characterized [*Armitage and 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 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; *Breivik et al.*, 2007]. PCB emissions peaked (ca. 1970) at approximately 3000 Mg a^{-1} 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; *Breivik et al.*, 2007]. Atmospheric deposition is the main source of PCBs to the global oceans, and rivers are a minor contributor [*Jurado et al.*, 2004; *Lammel and Stemmler*, 2012; *Wania and 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

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.

2 Model Description

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 $1°\times1°$ globally,

108   with higher resolution in the Arctic (40 km$\times$40 km) and near the equator ($0.5°\times1°$). It has 50

109   vertical layers spanning 5 m intervals at the surface and 500 m near the ocean floor [*G. Forget et*

110   *al.*, 2015]. Advection and diffusion of PCBs is based on ocean state estimates from the

111   Estimating the Circulation & Climate of the Ocean (ECCO-v4) climatology. Surface boundary

112   conditions (e.g., wind stress, seawater temperatures, and sea-ice cover) from the ERA-Interim re-

113   analysis fields spanning 1992-2015 and ocean transport parameters are optimized in ECCO-v4 to

114   produce a best fit to *in situ* and satellite observations of the physical ocean state and sea ice cover

115   [*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 (51-79µM) 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^{-1} *[Carr et al., 2006]*. Estimates of annual

156   export of carbon from the euphotic zone vary widely (5 to >12 Pg C a^{-1}) and the simulation used

157   here is on the lower end of this range (6 Pg C a^{-1}) *[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 pg L^{-1}) at three tropical Atlantic Ocean stations that exceeded the

168   ranges of measurements (0.06 to 3.5 pg L^{-1}) (Figure S1b). The best model performance was

169   obtained using the upper 95th 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   setting 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 pmol m^{-2} d^{-1} based on ^{234}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 pmol m^{-2} 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:

9

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

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].

3   Results and Discussion

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°×5°) 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 Σ_4PCBs (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 Σ_4PCBs (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 Σ_4PCBs 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 (Σ_4PCBs = 2.5 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 Σ_4PCBs 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^{-1} or

357   1%). Larger increases of up to 100%, or 0.06 pg L^{-1} 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 21st 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^{-1} 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].

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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Figure Captions

Figure 1. Modeled dissolved seawater concentrations of chlorinated biphenyl (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 mid-point of measurements. Data sources are as follows: Arctic Ocean: [*Booij et al.*, 2014; *Galbán-Malagón et al.*, 2012; *Gioia et al.*, 2008a; *Gustafsson et al.*, 2005; *Sobek and Gustafsson*, 2014; *Sobek et al.*, 2004] North Atlantic Ocean: [*Galbán-Malagón et al.*, 2012; *Gioia et al.*, 2008b; *Gioia et al.*, 2008a; *Lohmann et al.*, 2012; *Sun et al.*, 2016]; South Atlantic Ocean: [*Booij et al.*, 2014; *Gioia et al.*, 2008b; *Lohmann et al.*, 2012; *Sun et al.*, 2016]; Mediterranean Sea: [*Berrojalbiz et al.*, 2011; *Lammel et al.*, 2016], Pacific Ocean [*Zhang and Lohmann*, 2010]; Indian Ocean: [*Booij et al.*, 2014]; Southern Ocean: [*Galbán-Malagón et al.*, 2013a].

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

Figure 3. Modeled fate of PCBs 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 and Selin*, 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.

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