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Concentrations, Trends, and Air–Water Exchange of PCBs and Organochlorine Pesticides Derived from Passive Samplers in Lake Superior in 2011

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1 **Concentrations, trends, and air-water exchange of PCBs and organochlorine**
2 **pesticides derived from passive samplers in Lake Superior in 2011**

3 by Zoe Ruge¹, Derek Muir², Paul Helm³, Rainer Lohmann^{1*}

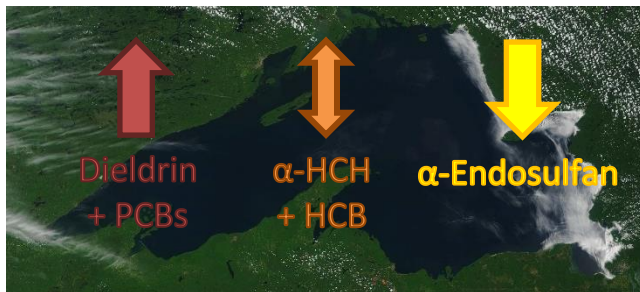
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12
13 **Graphical TOC**



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16 (TOC map from

17 [http://coastwatch.glerl.noaa.gov/modis/modis.php?region=s&page=4&template=sub&image=t1.](http://coastwatch.glerl.noaa.gov/modis/modis.php?region=s&page=4&template=sub&image=t1.15206.1638.LakeSuperior.143.250m.jpg)

18 [15206.1638.LakeSuperior.143.250m.jpg](http://coastwatch.glerl.noaa.gov/modis/modis.php?region=s&page=4&template=sub&image=t1.15206.1638.LakeSuperior.143.250m.jpg))

19
20

21 **Abstract**

22 The largest fresh water body in North America, Lake Superior, has the potential to both accumulate
23 and serve as a secondary source of persistent bioaccumulative toxins, such as polychlorinated
24 biphenyls (PCBs) and organochlorine pesticides (OCPs). Polyethylene passive samplers (PEs)
25 were thus simultaneously deployed at 19 sites in surface water and near surface atmosphere across
26 Lake Superior to determine air and water concentrations and air-water gradients of 18 PCBs and
27 24 OCPs. PCBs in the air and water were characterized by penta- and hexachlorobiphenyls with
28 distribution along the coast correlated with proximity to developed areas. Surface water and
29 atmospheric concentrations were dominated by α -HCH (average 250 pg L^{-1} and 4.2 pg m^{-3} ,
30 respectively), followed by HCB (average 17 pg L^{-1} and 89 pg m^{-3} , respectively). Decreases in open
31 lake concentrations of PCBs in water and air from spring to summer were consistent with on-going
32 volatilization from the surface layer as the main cause. Conversely, α -endosulfan was consistently
33 deposited into the surface water of Lake Superior. Results implied that PCBs were depleted in the
34 surface mixed layer, implying a physical limit on evasive fluxes. This was corroborated with
35 measurements from a vertical profile, displaying greater PCB concentrations at depth.

36

37 **Introduction**

38 The Lake Superior watershed is the least industrialized and least populated of the Great
39 Lakes¹, and its air quality is considered to be representative of regional background atmospheric
40 concentrations. The largest agricultural regions in North America have historically been located to
41 the west and south/southeast of the Great Lakes. Organochlorine pesticides (OCPs) are transported
42 to Lake Superior by long-range atmospheric transport and deposited from the air into the surface
43 water by wet and dry deposition, as well as by diffusive chemical exchange.^{1,2,3} Passive transfer
44 of molecules across the air-water interface is driven by the concentration gradient of the analyte,
45 such that the additions of OCPs to surface water can reverse the gradient and result in
46 volatilization.³ Wind-speed was identified as the other key driver of air-water exchange fluxes.⁴
47 Lastly, volatilization is also strongly temperature-dependent, creating seasonal flux cycles with
48 greatest release to the atmosphere at the warmest time of year.^{5,6}

49 Lake Superior's large surface area, long retention time, and colder water temperatures have
50 allowed accumulation of these persistent pollutants over the past several decades.^{7,8} OCP
51 concentrations in Great Lakes atmosphere and biota have been decreasing since regulatory controls
52 were put into effect.^{9,10,8} Reduced emissions from primary sources to the atmosphere have resulted
53 in steady state and even net volatilization of "legacy" OCPs from the surface water to the overlying
54 air.¹ Continued losses of legacy pesticides from both the air and water may lead to the virtual
55 elimination of most OCPs from the Lake Superior environment by the mid-21st century.⁵ This trend
56 will be accelerated by the observed warming of Lake Superior water.¹¹ Pesticides in current- or
57 recent-use, such as α -endosulfan and its metabolites, may take longer to purge from Lake Superior.

58 Polychlorinated biphenyls (PCBs) share a similar timeline as OCPs. PCBs were used
59 extensively in industry and urban applications from the 1930s through the 1970s.¹² They were one

60 of the original persistent organic pollutants (POPs) added to the Stockholm Convention¹³ and are
61 known to bioaccumulate and cause adverse effects in fish, birds, and mammals in the Great Lakes
62 region.¹⁴ Prenatal exposure to PCBs in the Great Lakes region has resulted in lower IQ and
63 provided evidence that PCBs are neurobehavioral toxicants.^{15,16}

64 There is very little information available on air and water trends of OCPs and PCBs in Lake
65 Superior. Most of the available atmospheric data stems from the IADN network, which operates
66 one master station in Lake Superior, at Eagle Harbor. Results from this invaluable long-term
67 monitoring network have shown the temporal trends of various organic pollutants in the
68 atmosphere. Yet, on the scale of the largest of the Great Lakes, there is little knowledge on spatial
69 trends across Lake Superior.^{17,18} A reversal of the air-water exchange of POPs leading to net
70 volatilization has been predicted², but empirical evidence remains rare.^{18,19}

71 Passive samplers provide an effective means of achieving good spatial coverage of Lake
72 Superior, as they can be deployed by various agencies as part of seasonal monitoring and servicing
73 of weather and/or navigational buoys, and can also be deployed by volunteers for simultaneous
74 deployments across multiple sites. Passive samplers, such as polyethylene (PE) samplers, rely on
75 diffusion to measure time-integrated gas- and freely dissolved-phase analytes²⁰, excluding
76 confounding influences from particulates, precipitation, and colloids.²¹ The freely dissolved
77 fraction is important to the cycling of POPs because it is available for bio-uptake²² and free to
78 diffuse across the air-water boundary.²⁰ PEs are an inexpensive alternative to active high-volume
79 air sampling and can expand spatial and temporal monitoring of Lake Superior. Additionally, PEs
80 can be deployed simultaneously in air and water to determine the magnitude of OCP exchanges
81 across the air-water interface at each deployment site.

82 This study utilized PEs to measure gaseous and dissolved concentrations of various OCPs
83 and PCBs to (1) determine their overall concentrations and distribution patterns across Lake
84 Superior; (2) establish the direction of OCP and PCB gas exchange across the air-water interface
85 between mid- and late-summer 2011; and (3) derive time-trends of OCPs/PCBs in Lake Superior
86 relative to prior data.

87

88 **Materials and Methods**

89 Detailed materials and methods pertaining to the passive sampling and analytical methods
90 employed in this study were described in Ruge et al. (2015).²³ Information specific to the PCB and
91 OCP analytes are specified below and in the Supporting Information.

92

93 *Sampling Methodology*

94 Low density polyethylene (2 mil) from commercial sheeting (Berry Plastics Corporation,
95 Evansville, IN) was cut into appx. 10x40 cm strips of appx. 2 g each. PEs were cleaned and spiked
96 with performance reference compounds (PRCs) as described previously.²³ Air PEs were deployed
97 in inverted bowl stations at 11 coastal and 3 open-lake sites (see Table SI 1 and Figure SI 1).
98 Surface water PEs were deployed in tandem with the coastal air samplers, as well as at three open-
99 lake sites and two additional coastal sites. Samples were deployed for ~ 2 months each during
100 April-June, June-August, and August-October 2011. Duplicate air samples and triplicate water
101 samplers were deployed at two sites during each deployment. Field blanks were taken from 2-3
102 sites per deployment period. After retrieval, samplers were wrapped in foil, shipped to the lab and
103 stored at 4°C until analysis.

104

105 *Analytical Methodology*

106 PEs were wiped clean with Kimwipes and extracted for 24 hours in ethyl acetate. Extracts
107 were spiked with 40 ng of $^{13}\text{C}_6$ HCB and $^{13}\text{C}_{12}$ p,p'-DDT surrogates (from Cambridge Isotopes,
108 Andover, MA, USA) and 50 ng of labeled PCBs ($^{13}\text{C}_{12}$ -CB8, $^{13}\text{C}_{12}$ -CB28, $^{13}\text{C}_{12}$ -CB52, $^{13}\text{C}_{12}$ -
109 CB118, $^{13}\text{C}_{12}$ -CB138, $^{13}\text{C}_{12}$ -CB180, $^{13}\text{C}_{12}$ -CB209 from Cambridge Isotopes, Andover, MA, USA)
110 to determine analyte recovery during sample processing. Target compounds were analyzed on
111 an Waters Quattro micro GS Micromass MS-MS (mass spectrometer) using 30m x 0.250mm
112 i.d. (film thickness 0.25 μm) DB-5MS column, as described elsewhere.^{24,25} OCP samples were held
113 at 100 °C for 1 minute, ramped up to 220 °C at 5 °C/min and held for 10 minutes, then ramped up
114 to 280 °C at 4 °C/min and held for 5 minutes. PCB samples were held at 100 °C for 1 minute,
115 ramped up to 180 °C at 11 °C/min, ramped up to 260 °C at 3 °C/min, then ramped up to 300 °C at
116 20 °C/min and held for 6 minutes.

117

118 *Quality Assurance/Quality Control*

119 Method blanks were prepared with each batch of samples to monitor for laboratory
120 contamination (see Tables SI 6 and SI 18). Samples were blank-corrected by subtracting the
121 average of the method and field blank concentrations. Only sample amounts greater than three
122 times the standard deviation of the average blank values are reported. Standard checks were
123 analyzed every ten samples to monitor instrument performance.

124 Matrix spikes were prepared in each batch of approximately 20 samples. Spiked matrix
125 recoveries were typically ca. 80-120% for PCBs and 27-100% for OCPs (see Tables SI 7 and SI
126 19).

127

128 *Calculations/Data Analysis*

129 At each site, 24 OCPs and 18 PCBs were determined (for details, see Tables SI 3 and SI
130 15). Truly dissolved concentrations of POPs in water, C_W (ng L^{-1}), and gas-phase atmospheric
131 concentrations, C_A (ng m^{-3}), were calculated according to Adams et al. (2007).²⁶ K_{PEW} and K_{PEA}
132 values were obtained from Lohmann (2012)²⁷, temperature-corrected, and used to determine air-
133 water exchange ratios as described in Ruge et al. (2015)²³ (see SI pages 6-8).

134

135 **Results and Discussion**

136 **Water Distributions**

137 *PCB Water Distributions*

138 PCBs were detected at every site from June-August (Figure 1A). The highest and most
139 varied concentrations along the coast were at Sault Ste. Marie (40 pg L^{-1}), followed by other urban
140 areas: Duluth (7.4 pg L^{-1}), and Ashland (6.9 pg L^{-1}). Coastal rural sites exhibited the lowest
141 dissolved concentrations ($<1 \text{ pg L}^{-1}$), while open lake sites were similar to developed coastal areas
142 ($2.6\text{-}7.0 \text{ pg L}^{-1}$) (Table 1). Hexa- and pentachlorinated congeners dominated in the water at
143 approximately half of the sampling sites while tri- and tetrachlorinated congeners dominated
144 dissolved concentrations at Duluth, Ashland, and the open lake sites.

145 In August-October distributions and relative congener contributions were nearly the same
146 as in June-August, with the exceptions of Duluth and the open lake sites (Table 1). At these
147 locations, dissolved concentrations decreased dramatically due to losses of tri- and
148 tetrachlorobiphenyl (Figure 1B).

149 Venier et al. (2014)¹⁷ used XAD-2 resin adsorption to sample three nearshore sites ($<20 \text{ m}$
150 depth) and three offshore stations ($>50 \text{ m}$ depth) in spring 2011, reporting an average total PCB
151 (sum of 84 congeners) concentration of $120\pm 18 \text{ pg L}^{-1}$. The comparison is complicated by the fact
152 that grab samples are compared to an integrated sampler over weeks, different laboratories

153 performed the analysis, and that active sampling co-extracts analytes bound to colloids. Not
154 surprisingly, better agreement was found for compounds with lower affinity for colloids (HCHs,
155 HCB, see below).

156

157 *OCP Water Distributions*

158 *Overview*

159 Eight OCPs were measured above the detection limit at all sites from June-October: α -
160 HCH, HCB, heptachlor epoxide, trans- and cis-chlordane, trans-nonachlor, p,p'-DDE, and
161 combined p,p'-DDD+o,p'-DDT (Table 2). Marquette and Sturgeon Bay were not measured from
162 August-October, so are excluded from spatial averages. α -Endosulfan was not consistently
163 detected in the water. Dissolved OCP concentrations in Lake Superior surface water were
164 dominated by α -HCH (average 250 pg L⁻¹), followed by HCB (average 17 pg L⁻¹) (Table 2).
165 Heptachlor epoxide was present at fairly uniform concentrations across the lake (1.1-5.5 pg L⁻¹).
166 Dieldrin was also present at most coastal sites (average 24 pg L⁻¹). Deposition from the atmosphere
167 by precipitation and gas exchange has historically been the input of OCPs to Lake Superior²⁸ rather
168 than from inflow of contaminants in tributaries. For many of these compounds, the dissolved
169 concentrations decreased at most sites from June-August to August-October, with the exceptions
170 of α -HCH, heptachlor epoxide, and dieldrin. Ontonagon exhibited increased concentrations of
171 most of these compounds over the same time period (see Table SI 20).

172

173 *Hexachlorocyclohexane (HCH)*

174 Technical HCH is a mixture of five HCH isomers used as a broad-spectrum insecticide in
175 the United States and Canada from the 1940s to 1970s; while lindane (γ -HCH) was used until the

176 mid 2000s.¹² α -HCH was the dominant dissolved OCP (ca. 40-90% of total OCPs measured)
177 (Figure 2A), >10 times HCB concentrations, opposite to atmospheric ratios (see below). Excluding
178 Ontonagon, where α -HCH was only 12 pg L⁻¹, the average concentration in surface lake water was
179 270 pg L⁻¹ (range 120 pg L⁻¹ at Eagle Harbor to 450 pg L⁻¹ in eastern open lake water).
180 Concentrations of α -HCH decreased at open lake sites up to three times between June-August and
181 August-October, when temperature changes in both the atmosphere and surface water were
182 greatest. Venier et al. (2014) also found α -HCH to be the dominant pesticide in Lake Superior
183 (average 300±80 pg L⁻¹).¹⁷

184

185 *Hexachlorobenzene (HCB)*

186 HCB is a former pesticide, impurity in other OCPs, and a byproduct of chlorine-based
187 bleaching.^{5,29} HCB was also present at all monitored sites, and exhibited similar distribution
188 patterns as α -HCH. Coastal concentrations were fairly uniform, mostly ranging from 5.4 to 18 pg
189 L⁻¹. Again, the open lake sites exhibited concentrations (average 23 pg L⁻¹) greater than the coastal
190 sites. HCB concentrations at Ashland were unusually elevated at 37 pg L⁻¹. In addition to its
191 application to agricultural seeds as an antifungal agent, HCB was also emitted in the waste streams
192 of wood-preserving plants and the incineration of municipal waste.³⁰ Lumber treatment and other
193 heavy industry in Ashland could be the source of this HCB signal in the nearby water. Venier et
194 al. (2014) reported an average concentration of 12±2.6 pg L⁻¹.¹⁷

195

196 *Heptachlor Epoxide*

197 Heptachlor epoxide is the product of heptachlor degradation. Like heptachlor, it is
198 persistent, bioaccumulative, and toxic.³¹ Heptachlor epoxide represented ca. 1-2% total OCP

199 concentrations at most coastal sites. Heptachlor epoxide concentrations were fairly uniform across
200 the lake, ranging from 1.1 to 5.5 pg L⁻¹. Its parent compound, heptachlor, was only measured
201 sporadically and at very low concentrations, implying no new input to the Lake. Venier et al.
202 (2014) reported an average concentration of 39±17 pg L⁻¹.¹⁷

203

204 *Chlordane*

205 Technical chlordane (trans-chlordane (TC), cis-chlordane (CC), and trans-nonachlor) was
206 used as an insecticide, herbicide, and termiticide between 1947 and 1988 at which time it was
207 deregistered for all uses in the United States, and 1990 when it was banned for all uses in
208 Canada.^{3,29,30} The sum of trans- and cis-chlordane was elevated at urban and industrial sites
209 (average ca. 1.2 pg L⁻¹) compared to rural sites (Eagle Harbor 0.39 pg L⁻¹).

210 Urban sources near the Great Lakes, namely Chicago and Toronto, have continued
211 emissions of racemic chlordane (TC/CC = 1.17).¹⁰ However, rural Great Lakes sites have low
212 TC/CC ratios (annual average 0.72)¹⁰, suggesting atmospheric chlordane concentrations in the
213 region are aged and volatilized from microbially-processed soils.²⁹ In our study, TC/CC ratios
214 averaged 0.84, but were as low as 0.54 at Eagle Harbor. This was in contrast to atmospheric
215 chlordane signatures in this study, which were racemic (see below), implying tributaries and
216 sediments as likely sources of aged chlordanes to the water column. Venier et al. (2014) reported
217 an average cis-chlordane concentration of 32±30 pg L⁻¹, and an average trans-chlordane
218 concentration of 19±18 pg L⁻¹, resulting in a lake-wide average TC/CC of 0.59.¹⁷

219

220 *Dichlorodiphenyltrichloroethane (DDT)*

221 Technical DDT (65-80% p,p'-DDT, 15-21% o,p'-DDT, <4% p,p'-DDD) was used
222 extensively in the 1940s and 1950s in urban aerial sprays to control mosquitoes⁹ and widely used
223 on a variety of agricultural crops in the 1960s.²⁹ DDTs are less volatile than most OCPs;
224 concentrations tend to be greater near urban sources and contaminated soils^{29,9}; though there is
225 evidence of long-range transport from its recent use further south.³² p,p'-DDT was not measured
226 above the detection limit at every site; where detected, it was <0.7 pg L⁻¹. The presence of DDT
227 metabolites and overall low concentrations indicate no new inputs of technical DDT in the Lake
228 Superior region (see Table SI 20). These results agree with previous sediment measurements where
229 surficial sediment concentrations of DDE (0.43 ng g⁻¹) were also greater than those of DDT (0.11
230 ng g⁻¹).⁸ Venier et al. (2014) reported average concentrations of 28±24 pg L⁻¹, 4.0±2.0 pg L⁻¹,
231 27±22 pg L⁻¹ for p,p'-DDT, o,p'-DDT, and p,p'-DDD, respectively.¹⁷ Lower concentrations
232 derived from passive sampling could indicate the importance of colloidal or particle-associated
233 DDT or chlordane captured by the active sampling.

234

235 *Dieldrin*

236 Dieldrin was used extensively from 1950 to 1974 as an insecticide on cotton, corn, citrus
237 fruits, as well as for termite control.^{13,29} It was banned for most uses in the United States in 1987.³⁴
238 In addition to direct emissions, dieldrin is also metabolized from aldrin, another insecticide also
239 listed on the Stockholm Convention of POPs¹³, and both are highly toxic to humans.³⁵ Dieldrin
240 was regularly present in the water at many sites, in stark contrast to the air, where it was not
241 consistently detected. Where present, dieldrin represented 10-20% of total dissolved OCPs
242 measured in Lake Superior water. Excluding Ontonagon, Duluth, and the open lake sites where
243 the analyte was not present above the detection limit, average dieldrin concentration was 45 pg L⁻¹

244 ¹. Dieldrin was twice as high at Pointe Aux Pins, the only site that exhibited consistent dieldrin
245 concentrations in the air (average 5.0 pg m⁻³). Venier et al. (2014) reported an average
246 concentration of 57±15 pg L⁻¹.¹⁷

247

248 *Endosulfan*

249 α -Endosulfan is a broad spectrum insecticide used on fruits, vegetables, cotton, tobacco,
250 and trees, as well in the preservation of wood.^{7,29} Use began in the 1950s and continued until
251 recently in the US and Canada.³⁵ α -Endosulfan was not consistently detected in Lake Superior
252 water, only averaging 0.63 pg L⁻¹. Venier et al. (2014) reported an average concentration of 32±21
253 pg L⁻¹.¹⁷ Endosulfan sulfate, an endosulfan metabolite, was only detected at a few sites from June-
254 October (averaging 44-360 pg L⁻¹). The presence of this metabolite may possibly indicate a
255 tendency for endosulfan to degrade in Lake Superior water, however measurements were very
256 inconsistent and do not illustrate any definitive trends.

257

258 **Air Distributions**

259 *PCB Air Distributions*

260 PCBs were detected in the atmosphere at nearly every site during the sampling season,
261 however distributions were not spatially and temporally uniform. Sault Ste. Marie and Marquette
262 had the highest Σ_{18} PCB concentrations from June-August (49 and 59 pg m⁻³, respectively), >20x
263 higher than the other sites (Table 1). These two sites also had the greatest number of different PCB
264 congeners present above detection (Figure 1C), suggesting that Sault Ste. Marie and Marquette are
265 current sources of PCBs, probably due to historical use of these compounds at both locations. In
266 general, PCB concentrations were higher and more diverse near populated or industrialized areas,

267 as expected for anthropogenic products with no known natural emissions.^{3,36,37} Despite
268 associations with larger populations, PCB concentrations were relatively low at the Duluth and
269 Thunder Bay/Welcome Isle stations over the same time period (3.4 and 4.3 pg m⁻³, respectively).
270 As mentioned elsewhere²³, the Duluth site was located northeast of the downtown while the
271 Welcome Isle site was 7 km southeast of the nearest ship and rail facilities in Thunder Bay. Thus
272 neither site may have received direct emissions from the city. Likewise, historical consumption of
273 PCBs was lower in Canada than in the United States (3% of global use versus 46%), possibly
274 contributing to lower observed concentrations at Thunder Bay.^{3,38} Significant quantities of PCBs
275 are still in use as dielectric fluids in transformers and capacitors in the industrialized regions to the
276 south of Lake Superior¹⁴, likely contributing to atmospheric PCB levels along the southern shore.
277 Current atmospheric PCB levels indicate a decrease in gaseous PCBs in Lake Superior air over the
278 past decade, even accounting for different number of congeners being included. Previous IADN
279 studies reported ΣPCB at Eagle Harbor ca. 63-95 pg m⁻³ from 1990-2003.^{6,36,38}

280 Hexachlorinated congeners dominated in the atmosphere across the lake from June-August
281 (see Table SI 12), representing 40-100% of gaseous concentrations. Σ₁₈PCB concentrations at
282 Sault Ste. Marie and Marquette also had significant contributions from tetra- (33% and 54%,
283 respectively) and pentachlorobiphenyls (30% and 39%, respectively).

284 Although general distribution patterns of Σ₁₈PCB were similar, atmospheric concentrations
285 decreased at a number of sites from the June-August deployment to the August-October
286 deployment (Figure 1D), in particular at the open Lake sites.

287

288 ***OCP Air Distributions***

289 *Overview*

290 Nine analytes were consistently found in the gas-phase across the lake: α -HCH, HCB, α -
291 endosulfan, heptachlor epoxide, trans-chlordane, cis-chlordane, trans-nonachlor, p,p'-DDE, and
292 combined p,p'-DDD+o,p'-DDT (Table 2). Concentrations were averaged for each site over the
293 second and third deployments (June-October 2011). Gaseous OCP concentrations in the
294 atmosphere were dominated by HCB at all sites across Lake Superior (Figure 2B), within a narrow
295 range (42-130 pg m^{-3}). α -HCH was also routinely detected, at an average of 4.3 pg m^{-3} . Of the
296 other 24 OCP analytes measured, only α -endosulfan was present above 1 pg m^{-3} (average 1.7 pg
297 m^{-3}). The greatest concentration of α -HCH was measured at Thunder Bay/Welcome Isle (9.6 pg
298 m^{-3}), followed closely by ODAS45004 (9.1 pg m^{-3}) and the two other open lake sites. The greatest
299 concentrations of α -endosulfan and chlordanes were detected in populated areas. In general, lowest
300 concentrations of heptachlor epoxide, α -endosulfan, chlordanes, and DDTs were found in the open
301 lake atmosphere at stations ODAS45001 and ODAS45006. Conversely, the eastern open lake site,
302 ODAS45004, exhibited slightly elevated concentrations, similar to Thunder Bay and other
303 populated areas (see Table SI 21).

304

305 *Hexachlorocyclohexane (HCH)*

306 Relatively uniform distribution across Canada and the United States is expected for a
307 persistent compound with no current use.³⁹ Our results are consistent with these patterns, showing
308 fairly uniform distributions of α -HCH across Lake Superior, where it is present at almost every
309 site (range 1.0 to 9.6 pg m^{-3} ; below detection at Michipicoten Bay). Previous studies of OCPs in
310 the atmosphere over Lake Superior⁴⁰ reported an α -HCH range of 6-170 pg m^{-3} with decreasing
311 trends over the past 20 years.^{5,12,39} Since production was discontinued, atmospheric concentrations
312 of α -HCH are no longer determined by primary sources, but are now primarily a result of

313 evaporation from terrestrial and aquatic surfaces.³⁹ Our data suggests that α -HCH is revolatilizing
314 from Lake Superior (see OCP air-water exchange below), causing atmospheric concentrations over
315 open lake waters to be slightly elevated relative to coastal lake regions.

316 The remainder of technical HCH historically produced was composed of 1-13% β -HCH
317 and 10-15% γ -HCH, or lindane. These two isomers were not detected regularly across Lake
318 Superior in this study (see Table SI 21).

319

320 *Hexachlorobenzene (HCB)*

321 HCB dominated in Lake Superior air, representing >80% of the OCPs measured at every
322 site. Like α -HCH, it is thought that the current source of HCB to the atmosphere is volatilization
323 from contaminated soils and possibly from large bodies of water as atmospheric concentrations
324 decrease and permit an equilibrium shift across the air-water interface.^{10,29,24} HCB was relatively
325 elevated everywhere across Lake Superior, measured at all sites with a range of 42 pg m^{-3} at
326 Ontonagon to 130 pg m^{-3} at Foster Island. Average Eagle Harbor gaseous concentration was 65 pg
327 m^{-3} , similar to the value reported from 2000-2001 (80 pg m^{-3}).²⁹

328

329 *Endosulfan*

330 Previous studies conducted from 2000-2001 reported α -endosulfan to be the dominant OCP
331 in the North American atmosphere (range 3.1-690 pg m^{-3}), with Lake Superior concentrations
332 among the lowest across the continent (27 pg m^{-3}).²⁹ Results from our study indicated similar
333 concentrations, ranging from 0.33 to 2.7 pg m^{-3} . Open lake sites at Stations ODAS45001 and
334 ODAS45006 had the lowest concentrations (0.44 and 0.33 pg m^{-3} , respectively), possibly as a
335 result of their distance from terrestrial sources where this compound is still being emitted.

336 However, the eastern open lake site, ODAS45004, displayed a concentration similar to coastal
337 sites (2.5 pg m⁻³). β-endosulfan was not significantly present at any of the Lake Superior sites
338 included in this study (see Table SI 21). Endosulfan sulfate, a degradation product of endosulfan,
339 was only detected in the atmosphere at a few sites and at very low concentrations. Concentrations
340 may be lower than 2000-2001 values due to the recent (2012-2016) discontinuation of use in the
341 US and Canada between sampling periods, or due to sampling differences between polyethylene
342 and XAD passive sampling.

343

344 *Heptachlor epoxide*

345 Heptachlor epoxide was detected in the atmosphere at all sites across Lake Superior at an
346 average of 0.67 pg m⁻³ (range 0.30-1.1 pg m⁻³) from June-October. Concentrations were low and
347 fairly uniform across the lake, in-line with its volatilization from soils. Concentrations greater than
348 1 pg m⁻³ were measured at Thunder Bay/Welcome Isle and Sault Ste. Marie, two populated areas
349 where heptachlor may have been used by the shipping industry. The eastern open lake site also
350 displayed concentrations of 1.1 pg m⁻³. Secondary sources are also suggested by inconsistent
351 detection of heptachlor, which is more volatile than heptachlor epoxide and is expected to dissipate
352 more quickly by evaporation.³¹ Heptachlor, a parent compound of its epoxide, impurity in
353 chlordane, was present at fewer than half of the sites, mainly elevated near populated and industrial
354 areas, highest at Thunder Bay/Welcome Isle (1.2 pg m⁻³).

355

356 *Chlordane*

357 Total chlordane (sum of trans-chlordane and cis-chlordane) averages from June to October
358 ranged from 0.19 to 1.6 pg m⁻³, generally greater near urban areas (average 1.0 pg m⁻³) and lower

359 at rural (average 0.58 pg m^{-3}). Previous gas-phase measurements at Eagle Harbor from 1996-1998
360 were $8.6 \pm 1.3 \text{ pg m}^{-3}$, ten times higher than values measured in this study.⁶

361

362 *Dichlorodiphenyltrichloroethane (DDT)*

363 Technical DDT compounds measured in this study were present across Lake Superior at
364 very low concentrations ($<0.77 \text{ pg m}^{-3}$). *p,p'*-DDT was often below detection and *p,p'*-DDD+*o,p'*-
365 DDT was detected at low concentrations at every site ($0.018\text{-}0.44 \text{ pg m}^{-3}$). Average *p,p'*-DDE
366 concentrations ranged from 0.075 to 1.4 pg m^{-3} during the sampling period, highest at Marquette
367 (1.4 pg m^{-3}) and Sault Saint Marie (1.1 pg m^{-3}).

368

369 *Dieldrin*

370 Dieldrin was not consistently detected in Lake Superior air (mean 0.70 pg m^{-3}).
371 Atmospheric concentration at Eagle Harbor was $8.8 \pm 1.4 \text{ pg m}^{-3}$ in 1996-1998⁶ and 7.5 pg m^{-3} in
372 2000-2001²⁹, however, it was below detection in atmospheric samples for this study. Dieldrin was
373 only present at one site, Pointe Aux Pins, both during the June-August sampling period and the
374 August-October sampling period (average 5.0 pg m^{-3}). Aldrin and endrin were generally below
375 detection in the atmosphere over Lake Superior.

376

377 **PCB Air-Water Exchange**

378 Net volatilization fluxes of Σ PCB congeners from June-August 2011 were exhibited at
379 locations with the highest dissolved-phase concentrations: Sault Ste. Marie, Pointe Aux Pins,
380 Duluth, Ashland, and the eastern open lake. Sault Ste. Marie, Pointe Aux Pins, and Ashland
381 exhibited net volatilization of hexachlorobiphenyls, while the eastern open lake site exhibited net

382 volatilization of tetrachlorobiphenyls, and all open lake site air-water ratios indicated volatilization
383 of trichlorobiphenyls. Marquette exhibited net deposition of tetra- and pentachlorobiphenyls. Most
384 other sites had fluxes either below detection or not significantly different from equilibrium.

385 From August-October, hexachlorobiphenyls were significantly volatilizing at more sites
386 across Lake Superior than June-August, the predominant PCBs volatilizing at Sault Ste. Marie,
387 Point Aux Pins, Ashland, Ontonagon, Sturgeon Bay, and the open lake sites. The open lake sites
388 also exhibited volatilization of pentachlorobiphenyls.

389

390 *PCB trends in water due to evaporation*

391 The observed evaporative flux of PCB 52 was sufficient to effectively remove it from a
392 well-mixed surface mixed layer (ML) of ca. 20 m. This was in-line with our observation that
393 dissolved concentrations during the August-October deployment were below the detection limit.
394 In turn, this would suggest that the open Lake Superior could repeatedly lose the amount of PCBs
395 contained in the ML. In other words, the evaporative loss is limited physically by the proportion
396 of POPs residing in the surface ML depth (~20 m) to the average lake depth (150 m).⁴¹ This should
397 lead to a concentration gradient across the thermocline, with greater concentrations in deeper, non-
398 ventilated water layers. To test this, passive samplers were deployed at 48.860 N, 91.930 W from
399 May-November 2015 at 1 m and 40 m depth. Indeed, PCB concentrations in deeper water were
400 either similar or greater than at surface, in-line with our expectations (see Figure 3, Table SI 9). In
401 the case of higher MW congener, such as PCB 209, their relative depletion in the surface is
402 probably the result of settling with particles (biological pump).⁴²

403

404 *PCB temporal trends in water concentration*

405 PCB concentrations in the Lake Superior water column have been declining for the past
406 few decades^{12,28}, removed primarily by volatilization rather than sedimentation.⁴³ Overall half-
407 lives for PCBs in both the air and water were estimated to be 5-9 years.¹

408 We also compared our derived average dissolved congener concentrations to those
409 measured in Lake Superior in 1993 and 1997 by Environment Canada. For the few congeners that
410 were regularly detected in all three years (see Table SI 10), there was a general steep decrease in
411 concentration observed, with $t_{1/2}$ on the order of 5-15 years (we note that these half-lives are not
412 statistically significant with $n=3$, but indicate a strong trend). This is very similar in magnitude to
413 the latest time-trends reported by IADN for atmospheric PCBs.⁴⁴

414

415 **OCP Air-Water Exchange**

416 From June-August, many OCP analytes were either below detection or exhibited air-water
417 ratios not significantly different from equilibrium (ratio of the PE-concentrations at equilibrium
418 >3.9 or <0.14), as expected for compounds with no current emission sources. Two notable
419 exceptions were the observed deposition of α -endosulfan at most sites, and the volatilization of α -
420 HCH at Duluth, Michipicoten Bay, and Sturgeon Bay.

421 From August-October, α -endosulfan continued to deposit into the lake. Additionally,
422 where present, dieldrin and oxychlordanes volatilized from most sites. Spatially, Ashland and
423 Ontonagon displayed net deposition of many analytes present, notably HCH congeners. The
424 central and western open lake sites generally exhibited net volatilization of the analytes present, in
425 contrast to the eastern open lake site, where most detected analytes were being deposited into Lake
426 Superior. HCB exchange ratios were indicative of equilibration at most sites, and α -HCH was only
427 significantly volatilizing at Point Aux Pins and Michipicoten.

428 Our results imply trends of α -HCH and HCB air-water exchange consistent with
429 diminishing sources to Lake Superior. In 2002-2003, HCB was reported undergoing net
430 deposition, while α -HCH was approximately in equilibrium⁴⁰ with subsequent observations of
431 volatilization from Lake Superior surface water.^{10,39} Similarly, Lake Superior seems to be serving
432 as an important secondary source of dieldrin to the atmosphere at some sites.

433

434 **Implications**

435 PCB concentrations measured in the air and water across Lake Superior exhibited a clear
436 association with urban and industrial areas, consistent with past findings in the Great Lakes
437 region.⁴⁵ Decreases in open lake concentrations of PCBs in water and air from spring to summer
438 were consistent with on-going volatilization from the surface layer as the main cause. This was
439 corroborated with measurements from a vertical profile, displaying greater PCB concentrations at
440 depth. Comparison to previously reported dissolved PCB concentrations imply an on-going
441 recovery of Lake Superior from PCBs, with half-lives ranging from 5-15 years.

442 OCP concentrations were dominated by gaseous HCB in the air and dissolved α -HCH in
443 the water. Their detection at nearly every site and relatively even distributions are consistent with
444 trends of persistent pesticides with a history of extensive use and well-established regulation. Air-
445 water exchange gradients for HCB and α -HCH tended to be either near equilibrium or volatilizing
446 from the surface of Lake Superior to the atmosphere. Most other legacy compounds were present
447 at very low concentrations and appear to be cycling between the air and water, indicating near-
448 steady state fluxes and overall trends toward virtual elimination from the Lake Superior
449 environment. OCPs with recent emissions, such as α -endosulfan, were still undergoing

450 atmospheric transportation to the lake, resulting in strong net deposition across the entire lake
451 surface.

452 Continued monitoring is required to determine the long-term effects of regulation and fate
453 of these compounds in the Lake Superior region. Polyethylene passive samplers make it possible
454 to easily and affordably monitor continuing POP trends at a high resolution, distinguishing
455 between background concentrations likely transported over long distances and local influences
456 from populated areas. PEs could be deployed year-round over the next several years to fully
457 establish seasonal and annual cycles in addition to long-term trends. In addition, passive samplers
458 can be biomimetic of lower trophic levels, as the uptake of POPs by PE or lipids is similar in
459 nature. Passive samplers can thus also serve as useful proxies for understanding and predicting the
460 bioaccumulation of persistent organic chemicals by lower trophic levels.⁴⁶

461

462 **Supporting Information Available**

463 Additional information on sampling locations, physicochemical constants, sampling rates,
464 QA/QC, analysis, calculations and concentrations of PCBs and OCPs and their air-water exchange
465 available free of charge via the Internet at <http://pubs.acs.org/>.

466

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480

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597
598

Tables and Figures

Table 1: Σ_{18} PCB concentrations in gas-phase (pg m^{-3}) and dissolved-phase (pg L^{-1}) across Lake Superior by deployment period in 2011

| Site | Air (pg m^{-3}) | | | Water (pg L^{-1}) | | |
|--------------------------|----------------------------|-------------|----------------|------------------------------|-------------|----------------|
| | April-June | June-August | August-October | April-June | June-August | August-October |
| Sault Ste. Marie | 33 | 49 | 32 | 40 | 32 | 34 |
| Pointe Aux Pins | | 2.1 | 1.1 | | 3.2 | 2.0 |
| Ashland | 1.5 | 0.24 | 14 | 8.1 | 6.9 | 8.8 |
| Thunder Bay/Welcome Isle | | 4.3 | 4.3 | | 2.3 | 2.0 |
| Station 139 | | | | | 2.4 | 4.1 |
| Marquette | 12 | 59 | 23 | 22 | 5.1 | N/A |
| Ontonagon | | 0.6 | 24 | | 0.61 | 1.4 |
| Duluth | 3.2 | 3.4 | 2.2 | | 7.4 | 2.3 |
| Michipicoten Bay | | 0.80 | 0.62 | | 0.48 | 0.075 |
| Sturgeon Bay | | 0.28 | 0.056 | | 0.20 | 0.87 |
| Foster Island | | 0.69 | bd | | 0.090 | 0.19 |
| Eagle Harbor | bd | 0.063 | bd | | 0.015 | 0.20 |
| Eastern Open Lake | | .83 | 0.030 | | 7.0 | 2.2 |
| Central Open Lake | | 0.90 | bd | | 2.6 | 1.1 |
| Western Open Lake | | 0.44 | bd | | 3.7 | 0.97 |

Σ_{18} PCB = sum of CB-8, 18, 28, 44, 52, 66, 101, 105, 118, 128, 138, 153, 170, 180, 187, 195, 206, and 209

bd = below detection limit of GC/MS

N/A = not available due to lost polyethylene samplers

Table 2: June-October 2011 OCP concentrations in gas-phase (pg m⁻³) and dissolved-phase (pg L⁻¹) averaged across deployment sites

| OCP Analyte ^b | Air (pg m ⁻³) | | | | | | Water (pg L ⁻¹) ^a | | | | | |
|--------------------------|---------------------------|-----------|-------------|--------------|-----------------|----------------------|--|-----------|-------------|--------------|-----------------|----------------------|
| | Mean | Minimum | Maximum | Median | >LOD (of 28) | No. Sites (of 14) | Mean | Minimum | Maximum | Median | >LOD (of 26) | No. Sites (of 13) |
| α-HCH | 4.3 | bd | 9.6 | 3.2 | 17 | 13 | 250 | 12 | 450 | 230 | 21 | 13 |
| HCB | 88 | 42 | 130 | 91 | 27 | 14 | 17 | 5.4 | 37 | 17 | 26 | 13 |
| Heptachlor epoxide | 0.67 | 0.30 | 1.1 | 0.61 | 27 | 14 | 3.8 | 1.1 | 5.5 | 3.5 | 26 | 13 |
| Trans chlordane | 0.32 | 0.10 | 0.80 | 0.33 | 25 | 14 | 0.44 | 0.13 | 1.2 | 0.36 | 25 | 13 |
| α-Endosulfan | 1.7 | 0.33 | 2.7 | 2.0 | 26 | 14 | <i>0.63</i> | <i>bd</i> | <i>2.1</i> | <i>0.33</i> | 7 | 7 |
| Cis chlordane | 0.40 | 0.085 | 0.84 | 0.40 | 25 | 14 | 0.52 | 0.14 | 1.5 | 0.50 | 25 | 13 |
| Trans nonachlor | 0.64 | 0.21 | 2.0 | 0.54 | 25 | 14 | 0.86 | 0.26 | 2.9 | 0.73 | 26 | 13 |
| p,p'-DDE | 0.50 | 0.075 | 1.4 | 0.53 | 26 | 14 | 1.1 | 0.095 | 2.4 | 0.71 | 25 | 13 |
| Dieldrin | <i>0.70</i> | <i>bd</i> | <i>5.0</i> | <i>bd</i> | 5 | 4 | 24 | bd | 73 | 30 | 12 | 7 |
| p,p'-DDD +o,p'-DDT | 0.14 | 0.018 | 0.44 | 0.11 | 23 | 14 | 0.84 | 0.095 | 8.2 | 0.21 | 21 | 13 |
| p,p'-DDT | <i>0.054</i> | <i>bd</i> | <i>0.33</i> | <i>0.012</i> | 9 | 8 | <i>0.15</i> | <i>bd</i> | <i>0.68</i> | <i>0.090</i> | 14 | 10 |

Calculations are based upon site averages from the second (June-August) and third (August-October) deployments

bd = below detection limit of GC/MS

^aExcludes Marquette and Sturgeon Bay because not present during both June-August and August-October 2011

^bAnalytes with medians below detection were excluded, except dieldrin

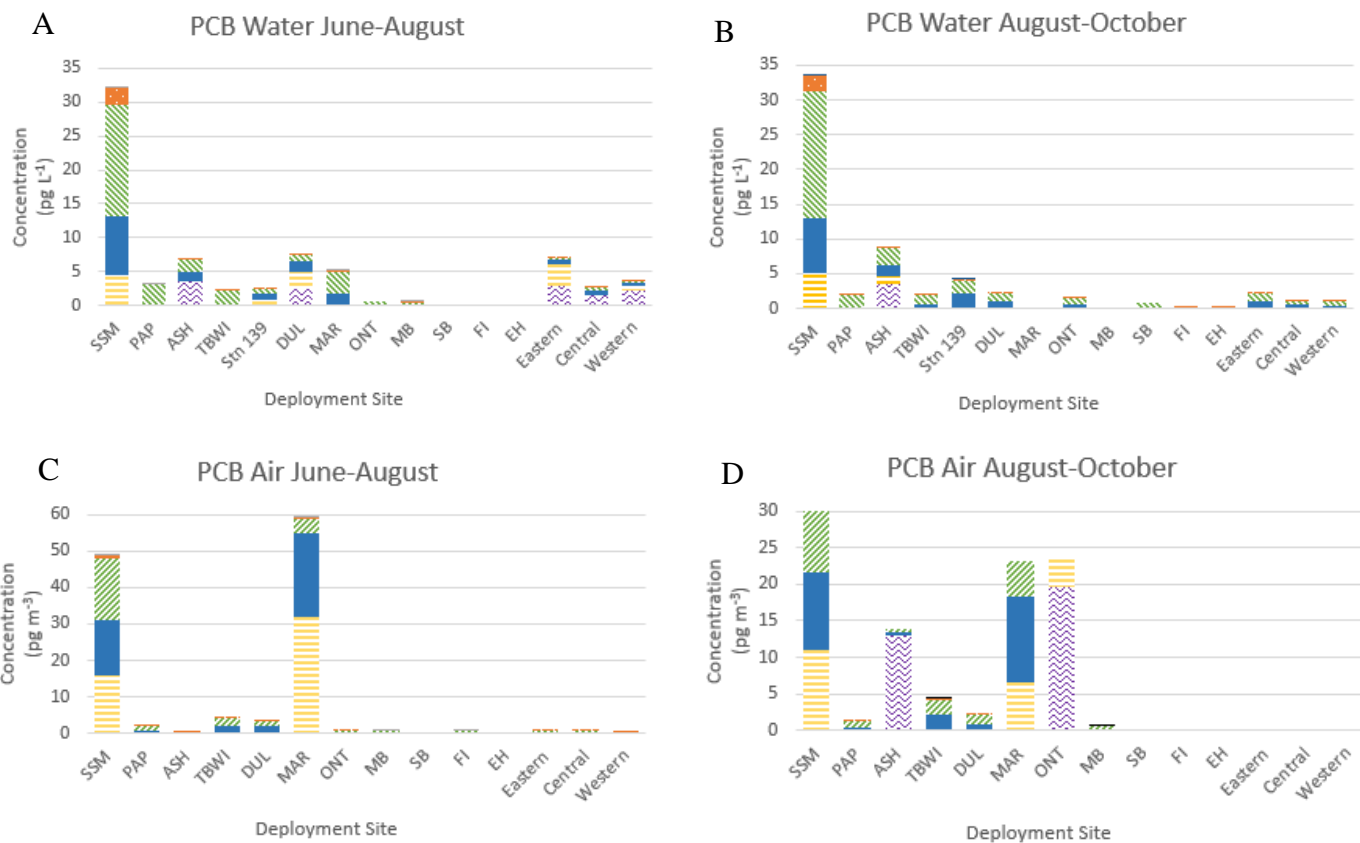


Figure 1: Gaseous (pg m^{-3}) and dissolved (pg L^{-1}) PCB concentrations at Lake Superior sampling sites grouped by degree of urban development. (A) Dissolved PCB concentrations averaged for June-August 2011. (B) Dissolved PCB concentrations averaged for August-October 2011. (C) Atmospheric PCB concentrations averaged for June-August 2011. (D) Atmospheric PCB concentrations averaged for August-October 2011. Legend: Pink = dichlorobiphenyl (CB8), Purple zigzag = trichlorobiphenyls (CB18, 28), Yellow horizontal stripes = tetrachlorobiphenyls (CB44, 52, 66), Blue solid = pentachlorobiphenyls (CB101, 105, 118); Green diagonal stripes = hexachlorobiphenyls (CB128, 138, 153); Orange dotted = heptachlorobiphenyls (CB170, 180, 187); Grey = octachlorobiphenyl (CB195); Red = nonachlorobiphenyl (CB206); and Black = decachlorobiphenyl (CB209).

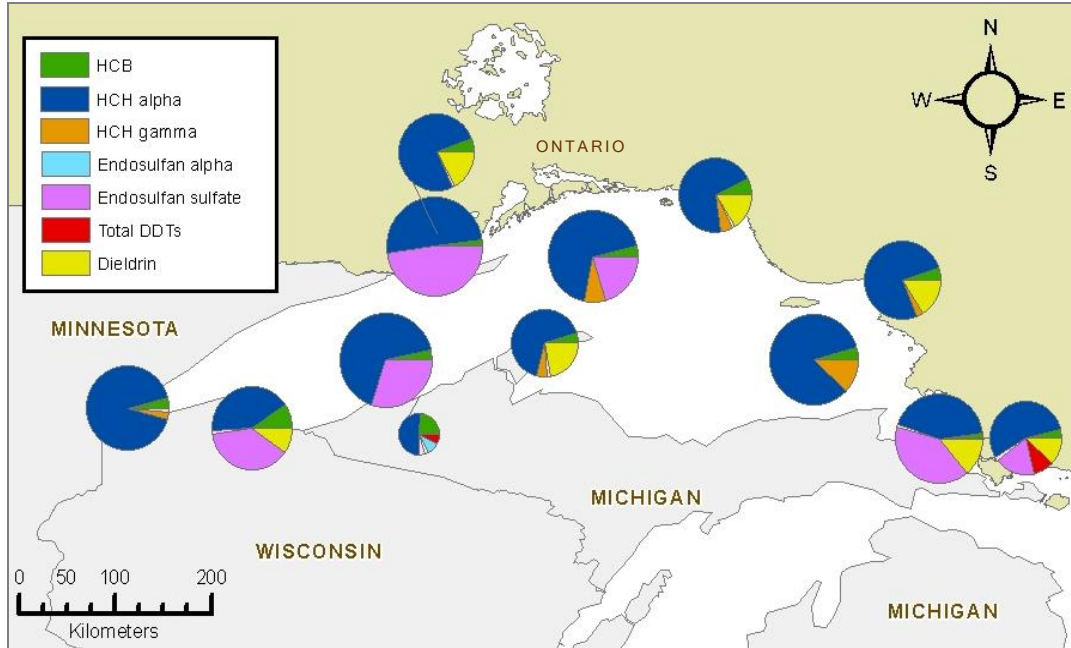
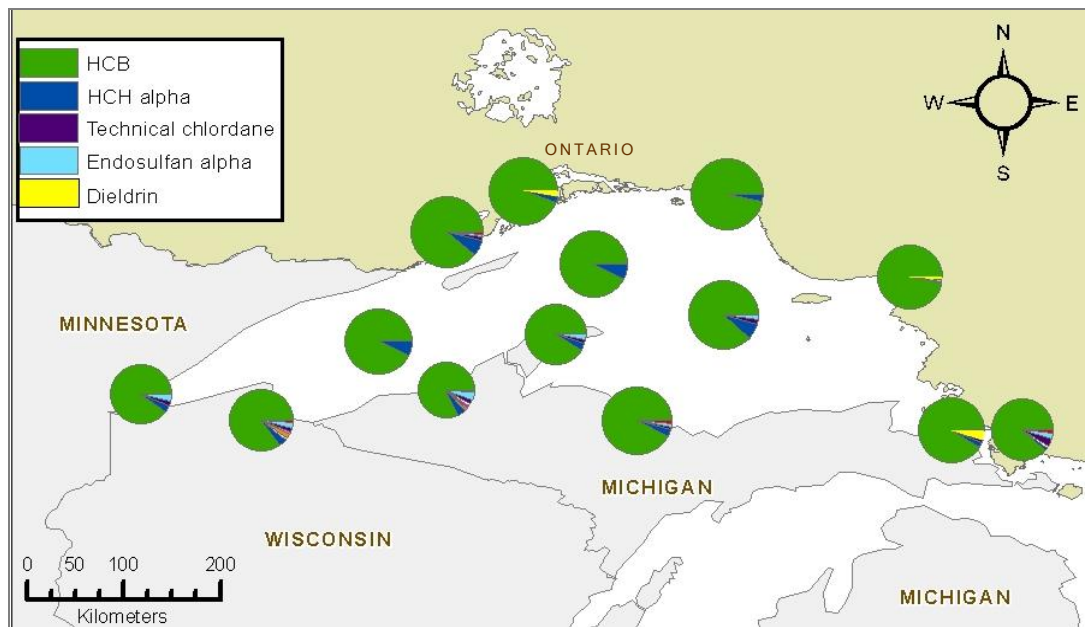
A**B**

Figure 2: Relative average Σ_{24} OCP concentrations at each station for June-October 2011 indicated by circle size. (A) Surface water concentrations; average Σ_{24} OCP ranged from 23 (pg L^{-1}) at Ontonagon to 770 (pg L^{-1}) at Station 139, offshore from Thunder Bay/Welcome Isle. Marquette and Sturgeon Bay are not included because samplers were only recovered for June-August 2011. (B) Air Concentrations; average Σ_{24} OCP ranged from 51 (pg m^{-3}) at Ontonagon to 140 (pg m^{-3}) at Thunder Bay/Welcome Isle and Foster Island.

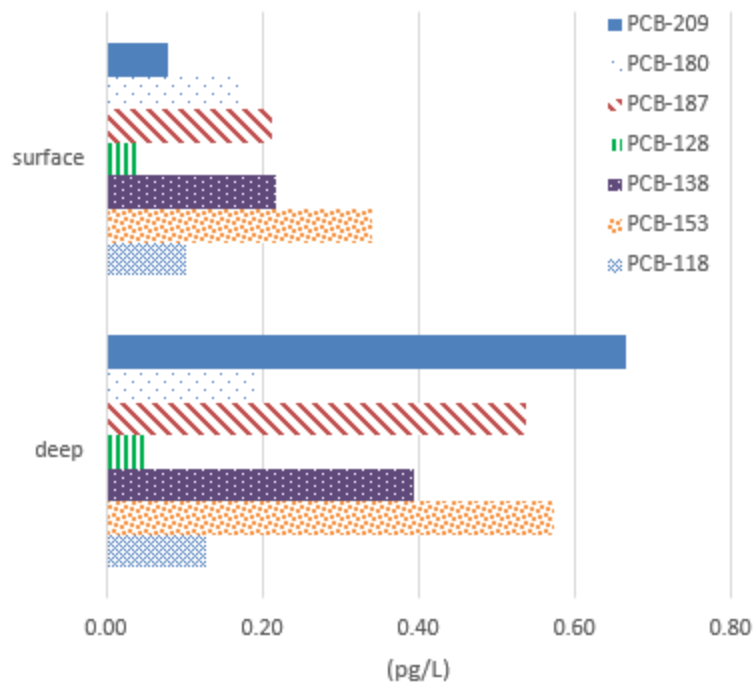


Figure 3: Dissolved water concentrations (pg/L) of seven PCB congeners collected using polyethylene passive samplers deployed at two depths (1m and 40m) in Lake Superior (48.860 N, 91.930 W) from May 15 – November 6, 2015.