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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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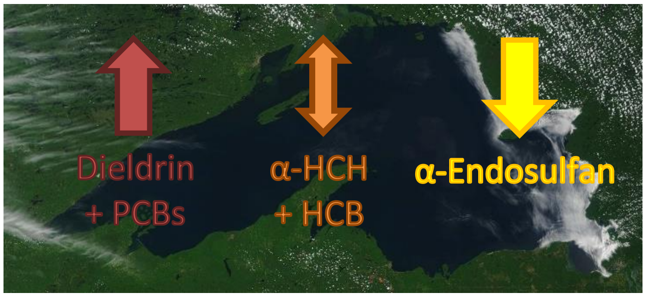
Graphical TOC



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

Abstract

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

Introduction

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

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

Polychlorinated biphenyls (PCBs) share a similar timeline as OCPs. PCBs were used extensively in industry and urban applications from the 1930s through the 1970s.[12] They were one of the original persistent organic pollutants (POPs) added to the Stockholm Convention[13] and are known to bioaccumulate and cause adverse effects in fish, birds, and mammals in the Great Lakes region.[14] Prenatal exposure to PCBs in the Great Lakes region has resulted in lower IQ and provided evidence that PCBs are neurobehavioral toxicants.[15,16]

There is very little information available on air and water trends of OCPs and PCBs in Lake Superior. Most of the available atmospheric data stems from the IADN network, which operates one master station in Lake Superior, at Eagle Harbor. Results from this invaluable long-term monitoring network have shown the temporal trends of various organic pollutants in the atmosphere. Yet, on the scale of the largest of the Great Lakes, there is little knowledge on spatial trends across Lake Superior.[17,18] A reversal of the air-water exchange of POPs leading to net volatilization has been predicted[2], but empirical evidence remains rare.[18,19]

Passive samplers provide an effective means of achieving good spatial coverage of Lake Superior, as they can be deployed by various agencies as part of seasonal monitoring and servicing of weather and/or navigational buoys, and can also be deployed by volunteers for simultaneous deployments across multiple sites. Passive samplers, such as polyethylene (PE) samplers, rely on diffusion to measure time-integrated gas- and freely dissolved-phase analytes[20], excluding confounding influences from particulates, precipitation, and colloids.[21] The freely dissolved fraction is important to the cycling of POPs because it is available for bio-uptake[22] and free to diffuse across the air-water boundary.[20] PEs are an inexpensive alternative to active high-volume air sampling and can expand spatial and temporal monitoring of Lake Superior. Additionally, PEs can be deployed simultaneously in air and water to determine the magnitude of OCP exchanges across the air-water interface at each deployment site.

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

Materials and Methods

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

Sampling Methodology

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

Analytical Methodology

PEs were wiped clean with Kimwipes and extracted for 24 hours in ethyl acetate. Extracts were spiked with 40 ng of $^{13}C_6$ HCB and $^{13}C_{12}$ p,p'-DDT surrogates (from Cambridge Isotopes, Andover, MA, USA) and 50 ng of labeled PCBs ($^{13}C_{12}$-CB8, $^{13}C_{12}$-CB28, $^{13}C_{12}$-CB52, $^{13}C_{12}$-CB118, $^{13}C_{12}$-CB138, $^{13}C_{12}$-CB180, $^{13}C_{12}$-CB209 from Cambridge Isotopes, Andover, MA, USA) to determine analyte recovery during sample processing. Target compounds were analyzed on an Waters Quattro micro GS Micromass MS-MS (mass spectrometer) using 30m x 0.250mm i.d. (film thickness 0.25µm) DB-5MS column, as described elsewhere.[24,25] OCP samples were held at 100 ^{o}C for 1 minute, ramped up to 220 ^{o}C at 5 ^{o}C/min and held for 10 minutes, then ramped up to 280 ^{o}C at 4 ^{o}C/min and held for 5 minutes. PCB samples were held at 100 ^{o}C for 1 minute, ramped up to 180 ^{o}C at 11 ^{o}C/min, ramped up to 260 ^{o}C at 3 ^{o}C/min, then ramped up to 300 ^{o}C at 20 ^{o}C/min and held for 6 minutes.

Quality Assurance/Quality Control

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

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

Calculations/Data Analysis

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

Results and Discussion

Water Distributions

PCB Water Distributions

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

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

Venier et al. (2014)[17] used XAD-2 resin adsorption to sample three nearshore sites (<20 m depth) and three offshore stations (>50 m depth) in spring 2011, reporting an average total PCB (sum of 84 congeners) concentration of 120±18 pg L^{-1}. The comparison is complicated by the fact that grab samples are compared to an integrated sampler over weeks, different laboratories performed the analysis, and that active sampling co-extracts analytes bound to colloids. Not surprisingly, better agreement was found for compounds with lower affinity for colloids (HCHs, HCB, see below).

OCP Water Distributions

Overview

Eight OCPs were measured above the detection limit at all sites from June-October: α-HCH, HCB, heptachlor epoxide, trans- and cis-chlordane, trans-nonachlor, p,p'-DDE, and combined p,p'-DDD+o,p'-DDT (Table 2). Marquette and Sturgeon Bay were not measured from August-October, so are excluded from spatial averages. α-Endosulfan was not consistently detected in the water. Dissolved OCP concentrations in Lake Superior surface water were dominated by α-HCH (average 250 pg L^{-1}), followed by HCB (average 17 pg L^{-1}) (Table 2). Heptachlor epoxide was present at fairly uniform concentrations across the lake (1.1-5.5 pg L^{-1}). Dieldrin was also present at most coastal sites (average 24 pg L^{-1}). Deposition from the atmosphere by precipitation and gas exchange has historically been the input of OCPs to Lake Superior[28] rather than from inflow of contaminants in tributaries. For many of these compounds, the dissolved concentrations decreased at most sites from June-August to August-October, with the exceptions of α-HCH, heptachlor epoxide, and dieldrin. Ontonagon exhibited increased concentrations of most of these compounds over the same time period (see Table SI 20).

Hexachlorocyclohexane (HCH)

Technical HCH is a mixture of five HCH isomers used as a broad-spectrum insecticide in the United States and Canada from the 1940s to 1970s; while lindane (γ-HCH) was used until the mid 2000s.[12] α-HCH was the dominant dissolved OCP (ca. 40-90% of total OCPs measured) (Figure 2A), >10 times HCB concentrations, opposite to atmospheric ratios (see below). Excluding Ontonagon, where α-HCH was only 12 pg L^{-1}, the average concentration in surface lake water was 270 pg L^{-1} (range 120 pg L^{-1} at Eagle Harbor to 450 pg L^{-1} in eastern open lake water). Concentrations of α -HCH decreased at open lake sites up to three times between June-August and August-October, when temperature changes in both the atmosphere and surface water were greatest. Venier et al. (2014) also found α-HCH to be the dominant pesticide in Lake Superior (average 300±80 pg L^{-1}).[17]

Hexachlorobenzene (HCB)

HCB is a former pesticide, impurity in other OCPs, and a byproduct of chlorine-based bleaching.[5,29] HCB was also present at all monitored sites, and exhibited similar distribution patterns as α-HCH. Coastal concentrations were fairly uniform, mostly ranging from 5.4 to 18 pg L^{-1}. Again, the open lake sites exhibited concentrations (average 23 pg L^{-1}) greater than the coastal sites. HCB concentrations at Ashland were unusually elevated at 37 pg L^{-1}. In addition to its application to agricultural seeds as an antifungal agent, HCB was also emitted in the waste streams of wood-preserving plants and the incineration of municipal waste.[30] Lumber treatment and other heavy industry in Ashland could be the source of this HCB signal in the nearby water. Venier et al. (2014) reported an average concentration of 12±2.6 pg L^{-1}.[17]

Heptachlor Epoxide

Heptachlor epoxide is the product of heptachlor degradation. Like heptachlor, it is persistent, bioaccumulative, and toxic.[31] Heptachlor epoxide represented ca. 1-2% total OCP concentrations at most coastal sites. Heptachlor epoxide concentrations were fairly uniform across the lake, ranging from 1.1 to 5.5 pg L^{-1}. Its parent compound, heptachlor, was only measured sporadically and at very low concentrations, implying no new input to the Lake. Venier et al. (2014) reported an average concentration of 39±17 pg L^{-1}.[17]

Chlordane

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

Urban sources near the Great Lakes, namely Chicago and Toronto, have continued emissions of racemic chlordane (TC/CC = 1.17).[10] However, rural Great Lakes sites have low TC/CC ratios (annual average 0.72)[10], suggesting atmospheric chlordane concentrations in the region are aged and volatilized from microbially-processed soils.[29] In our study, TC/CC ratios averaged 0.84, but were as low as 0.54 at Eagle Harbor. This was in contrast to atmospheric chlordane signatures in this study, which were racemic (see below), implying tributaries and sediments as likely sources of aged chlordanes to the water column. Venier et al. (2014) reported an average cis-chlordane concentration of 32±30 pg L^{-1}, and an average trans-chlordane concentration of 19±18 pg L^{-1}, resulting in a lake-wide average TC/CC of 0.59.[17]

Dichlorodiphenyltrichloroethane (DDT)

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

Dieldrin

Dieldrin was used extensively from 1950 to 1974 as an insecticide on cotton, corn, citrus fruits, as well as for termite control.[13,29] It was banned for most uses in the United States in 1987.[34] In addition to direct emissions, dieldrin is also metabolized from aldrin, another insecticide also listed on the Stockholm Convention of POPs[13], and both are highly toxic to humans.[35] Dieldrin was regularly present in the water at many sites, in stark contrast to the air, where it was not consistently detected. Where present, dieldrin represented 10-20% of total dissolved OCPs measured in Lake Superior water. Excluding Ontonagon, Duluth, and the open lake sites where the analyte was not present above the detection limit, average dieldrin concentration was 45 pg L^{-}

[1]. Dieldrin was twice as high at Pointe Aux Pins, the only site that exhibited consistent dieldrin concentrations in the air (average 5.0 pg m^{-3}). Venier et al. (2014) reported an average concentration of 57±15 pg L^{-1}.[17]

Endosulfan

α-Endosulfan is a broad spectrum insecticide used on fruits, vegetables, cotton, tobacco, and trees, as well in the preservation of wood.[7,29] Use began in the 1950s and continued until recently in the US and Canada.[35] α-Endosulfan was not consistently detected in Lake Superior water, only averaging 0.63 pg L^{-1}. Venier et al. (2014) reported an average concentration of 32±21 pg L^{-1}.[17] Endosulfan sulfate, an endosulfan metabolite, was only detected at a few sites from June-October (averaging 44-360 pg L^{-1}). The presence of this metabolite may possibly indicate a tendency for endosulfan to degrade in Lake Superior water, however measurements were very inconsistent and do not illustrate any definitive trends.

Air Distributions

PCB Air Distributions

PCBs were detected in the atmosphere at nearly every site during the sampling season, however distributions were not spatially and temporally uniform. Sault Ste. Marie and Marquette had the highest Σ_{18}PCB concentrations from June-August (49 and 59 pg m^{-3}, respectively), >20x higher than the other sites (Table 1). These two sites also had the greatest number of different PCB congeners present above detection (Figure 1C), suggesting that Sault Ste. Marie and Marquette are current sources of PCBs, probably due to historical use of these compounds at both locations. In general, PCB concentrations were higher and more diverse near populated or industrialized areas, as expected for anthropogenic products with no known natural emissions.[3,36,37] Despite associations with larger populations, PCB concentrations were relatively low at the Duluth and Thunder Bay/Welcome Isle stations over the same time period (3.4 and 4.3 pg m^{-3}, respectively). As mentioned elsewhere[23], the Duluth site was located northeast of the downtown while the Welcome Isle site was 7 km southeast of the nearest ship and rail facilities in Thunder Bay. Thus neither site may have received direct emissions from the city. Likewise, historical consumption of PCBs was lower in Canada than in the United States (3% of global use versus 46%), possibly contributing to lower observed concentrations at Thunder Bay.[3,38] Significant quantities of PCBs are still in use as dielectric fluids in transformers and capacitors in the industrialized regions to the south of Lake Superior[14], likely contributing to atmospheric PCB levels along the southern shore. Current atmospheric PCB levels indicate a decrease in gaseous PCBs in Lake Superior air over the past decade, even accounting for different number of congeners being included. Previous IADN studies reported ΣPCB at Eagle Harbor ca. 63-95 pg m^{-3} from 1990-2003.[6,36,38]

Hexachlorinated congeners dominated in the atmosphere across the lake from June-August (see Table SI 12), representing 40-100% of gaseous concentrations. Σ_{18}PCB concentrations at Sault Ste. Marie and Marquette also had significant contributions from tetra- (33% and 54%, respectively) and pentachlorobiphenyls (30% and 39%, respectively).

Although general distribution patterns of Σ_{18}PCB were similar, atmospheric concentrations decreased at a number of sites from the June-August deployment to the August-October deployment (Figure 1D), in particular at the open Lake sites.

OCP Air Distributions

Overview

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

Hexachlorocyclohexane (HCH)

Relatively uniform distribution across Canada and the United States is expected for a persistent compound with no current use.[39] Our results are consistent with these patterns, showing fairly uniform distributions of α-HCH across Lake Superior, where it is present at almost every site (range 1.0 to 9.6 pg m^{-3}; below detection at Michipicoten Bay). Previous studies of OCPs in the atmosphere over Lake Superior[40] reported an α-HCH range of 6-170 pg m^{-3} with decreasing trends over the past 20 years.[5,12,39] Since production was discontinued, atmospheric concentrations of α-HCH are no longer determined by primary sources, but are now primarily a result of evaporation from terrestrial and aquatic surfaces.[39] Our data suggests that α-HCH is revolatilizing from Lake Superior (see OCP air-water exchange below), causing atmospheric concentrations over open lake waters to be slightly elevated relative to coastal lake regions.

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

Hexachlorobenzene (HCB)

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

Endosulfan

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

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

Heptachlor epoxide

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

Chlordane

Total chlordane (sum of trans-chlordane and cis-chlordane) averages from June to October ranged from 0.19 to 1.6 pg m^{-3}, generally greater near urban areas (average 1.0 pg m^{-3}) and lower at rural (average 0.58 pg m^{-3}). Previous gas-phase measurements at Eagle Harbor from 1996-1998 were 8.6±1.3 pg m^{-3}, ten times higher than values measured in this study.[6]

Dichlorodiphenyltrichloroethane (DDT)

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

Dieldrin

Dieldrin was not consistently detected in Lake Superior air (mean 0.70 pg m^{-3}). Atmospheric concentration at Eagle Harbor was 8.8±1.4 pg m^{-3} in 1996-1998[6] and 7.5 pg m^{-3} in 2000-2001[29], however, it was below detection in atmospheric samples for this study. Dieldrin was only present at one site, Pointe Aux Pins, both during the June-August sampling period and the August-October sampling period (average 5.0 pg m^{-3}). Aldrin and endrin were generally below detection in the atmosphere over Lake Superior.

PCB Air-Water Exchange

Net volatilization fluxes of ΣPCB congeners from June-August 2011 were exhibited at locations with the highest dissolved-phase concentrations: Sault Ste. Marie, Pointe Aux Pins, Duluth, Ashland, and the eastern open lake. Sault Ste. Marie, Pointe Aux Pins, and Ashland exhibited net volatilization of hexachlorobiphenyls, while the eastern open lake site exhibited net volatilization of tetrachlorobiphenyls, and all open lake site air-water ratios indicated volatilization of trichlorobiphenyls. Marquette exhibited net deposition of tetra- and pentachlorobiphenyls. Most other sites had fluxes either below detection or not significantly different from equilibrium.

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

PCB trends in water due to evaporation

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

PCB temporal trends in water concentration

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

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

OCP Air-Water Exchange

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

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

Our results imply trends of α-HCH and HCB air-water exchange consistent with diminishing sources to Lake Superior. In 2002-2003, HCB was reported undergoing net deposition, while α-HCH was approximately in equilibrium[40] with subsequent observations of volatilization from Lake Superior surface water.[10,39] Similarly, Lake Superior seems to be serving as an important secondary source of dieldrin to the atmosphere at some sites.

Implications

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

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

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

Supporting Information Available

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

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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

	Air (pg m^{-3})			Water (pg L^{-1})		
Site	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

	Air (pg m^{-3})						Water (pg L^{-1})[a]					
OCP Analyte[b]	Mean	Minimum	Maximum	Median	>LOD (of 28)	No. Sites (of 14)	Mean	Minimum	Maximum	Median	>LOD (of 26)	No. Site (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	*0.63*	*bd*	*2.1*	*0.33*	*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	*0.70*	*bd*	*5.0*	*bd*	*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	*0.054*	*bd*	*0.33*	*0.012*	*9*	*8*	*0.15*	*bd*	*0.68*	*0.090*	*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

[a] Excludes Marquette and Sturgeon Bay because not present during both June-August and August-October 2011

[b] Analytes with medians below detection were excluded, except dieldrin

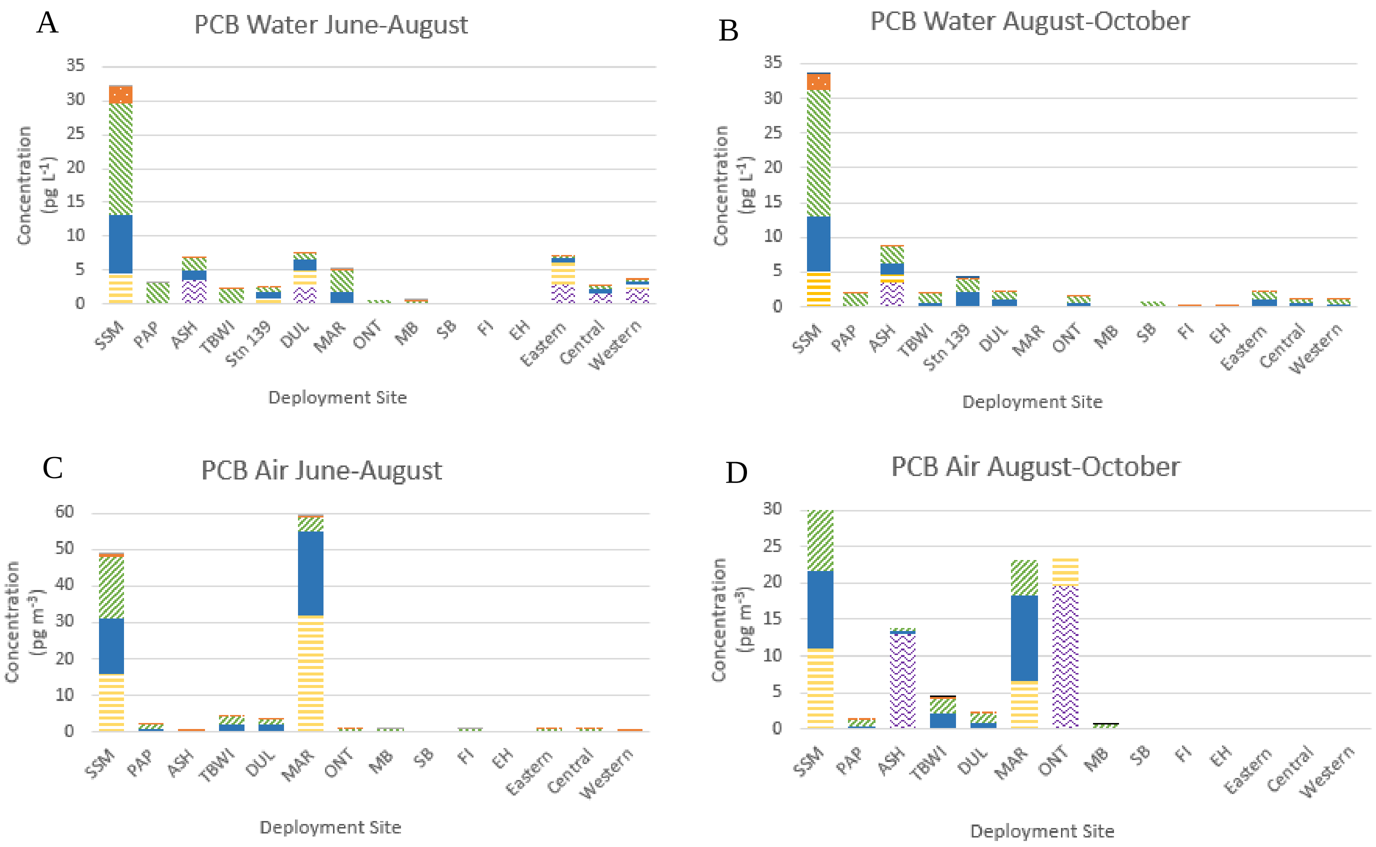

Figure 1: Gaseous (pg m^{-3}) and dissolved (pg L^{-1}) PCB concentrations at Lake Superior sampling sites grouped by degree of urban development. (A) Dissolved PCB concentrations averaged for June-August 2011. (B) Dissolved PCB concentrations averaged for August-October 2011. (C) Atmospheric PCB concentrations 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).

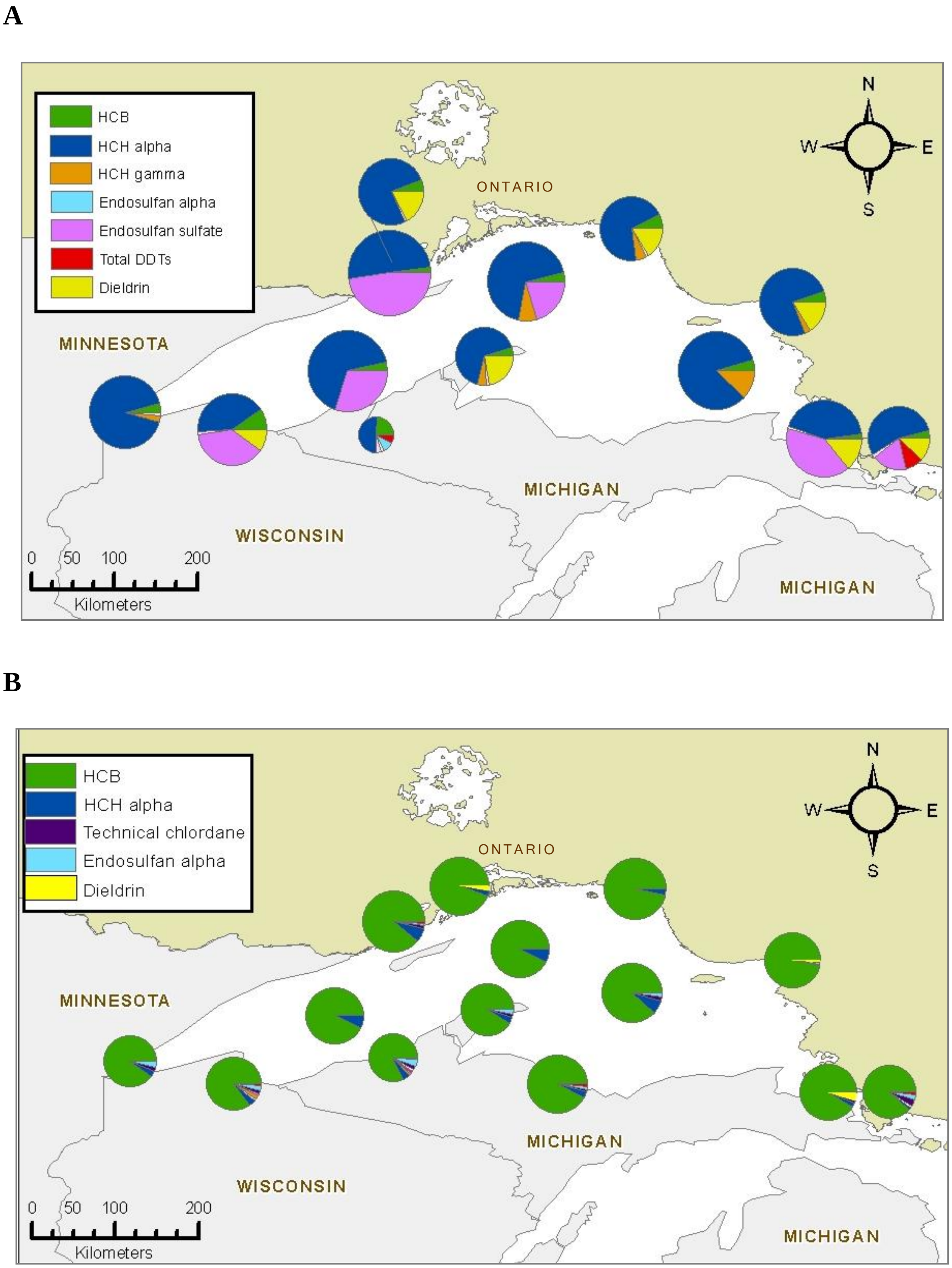

Figure 2: Relative average Σ_{24}OCP concentrations at each station for June-October 2011 indicated by circle size. (**A**) Surface water concentrations; averageΣ_{24}OCP ranged from 23 (pg L^{-1}) at Ontonagon to 770 (pg L^{-1}) at Station 139, offshore from Thunder Bay/Welcome Isle. Marquette and Sturgeon 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.

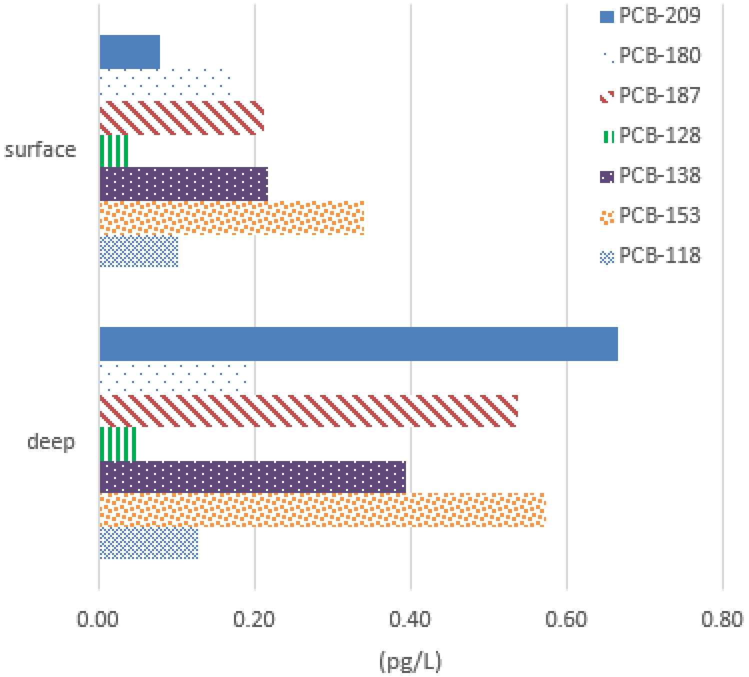

Figure 3: Dissolved water concentrations (pg/L) of seven PCB congeners collected using polyethylene passive samplers deployed at two depths (1m and 40m) in Lake Superior (48.860 N, 91.930 W) from May 15 – November 6, 2015.