Passive-sampler derived PCB and OCPs in the waters of the world – first results from the AQUA-GAPS/MONET network

Rainer Lohmann[1,*], Branislav Vrana[2], Derek Muir[3], Foppe Smedes[2], Jaromir Sobotka[2], Eddy Zeng[4], Lian-Jun Bao[4], Ian J Allan[5], Peleg Astrahan[6], Ricardo O. Barra[7], Terry Bidleman[8], Evgen Dykyi[9], Nicolas Estoppey[10,11], Gilberto Fillmann[12], Naomi Greenwood[13], Paul A. Helm[14], Liisa Jantunen[15], Sarit Kaserzon[16], J. Vinicio Macías[17], Keith A. Maruya[18], Francisco Molina[19], Brent Newman [20,21], Raimon M. Prats[22], Manolis Tsapakis[23], Mats Tysklind[8], Barend L. van Drooge[22], Cameron J Veal[24,25], Charles S. Wong[18]

[1] Graduate School of Oceanography, University of Rhode Island, Narragansett, Rhode Island 02882-1197, United States; Email: rlohmann@uri.edu

[2] RECETOX, Faculty of Science, Masaryk University, Kotlarska 2, 61137 Brno, Czech Republic

[3] Environment and Climate Change Canada, Aquatic Contaminants Research Division, 867 Lakeshore Road, Burlington, Ontario, Canada L7S 1A1

[4] Guangdong Key Laboratory of Environmental Pollution and Health, School of Environment, Jinan University, Guangzhou 511443, China

[5] Norwegian Institute for Water Research (NIVA), Økernveien 94, 0579 Oslo, Norway

[6] Israel Oceanographic and Limnological Research, Kinneret lake laboratory, 3109701 Israel.

[7] Faculty of Environmental Sciences and EULA Chile Centre, University of Concepción, Concepción 4070386, Chile.

[8] Department of Chemistry, Umeå University, Linnaeus väg 6, SE-901 87 Umeå, Sweden.

[9] National Antarctic Scientific Center, Taras Shevchenko Boulevard 16, 01601 Kyiv, Ukraine

[10] School of Criminal Justice, University of Lausanne, Batochime building, 1015 Lausanne, Switzerland

[11] Norwegian Geotechnical Institute (NGI), P.O. Box. 3930 Ullevål Stadion, N-0806 Oslo, Norway

[12] Instituto de Oceanografia, Universidade Federal do Rio Grande (IO-FURG), Av. Itália s/n, Campus Carreiros, 96203-900 Rio Grande, RS, Brazil

[13] Centre of Environment, Fisheries and Aquaculture Science, Pakefield Road, Lowestoft, UK, NR33 0HT, UK

[14] Ontario Ministry of the Environment, Conservation and Parks, Toronto, Ontario, Canada M9P 3V6

[15] Air Quality Processes Research Section, Environment and Climate Change Canada, 6248 Eighth Line, Egbert, ON, L0L1N0, Canada

[16] Queensland Alliance for Environmental Health Sciences, (QAEHS), The University of Queensland, 20 Cornwall Street, Woolloongabba, Queensland 4102, Australia

[17] Instituto de Investigaciones Oceanológicas, Universidad Autónoma de Baja California, Fracc. Playitas, Ensenada 22860, Mexico

[18] Southern California Coastal Water Research Project Authority, 3535 Harbor Blvd., Suite 110, Costa Mesa, California 92626, USA

[19] Escuela Ambiental, Universidad de Antioquia, UdeA, Calle 70 No 52-21, Medellín, Colombia

[20] Coastal Systems Research Group, CSIR, P.O. Box 59081, Umbilo, 4075, Durban, South Africa

[21] Nelson Mandela University, P.O. Box 77000, Port Elizabeth 6031, South Africa

[22] Institute of Environmental Assessment and Water Research (IDAEA-CSIC), Jordi Girona 18, 08034 Barcelona, Spain

[23] Institute of Oceanography, Hellenic Centre for Marine Research, PO Box 2214, GR-71003, Heraklion, Crete, Greece

[24] Seqwater, 117 Brisbane Road, Ipswich, Queensland, Australia, 4305

[25] School of Civil Engineering, The University of Queensland, St Lucia, Queensland, Australia, 4067

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Abstract

Persistent organic pollutants (POPs) are recognized as pollutants of global concern, but so far, information on trends of legacy POPs in the waters of the world has been missing due to logistical, analytical, and financial reasons. Passive samplers have emerged as an attractive alternative to active water sampling methods as they accumulate POPs, represent time-weighted average concentrations, and can easily be shipped and deployed. As part of the AQUA-GAPS/MONET network, passive samplers were deployed at 40 globally distributed sites between 2016-2020, for a total of 21 freshwater and 40 marine deployments. Results from silicone passive samplers showed α-hexachlorocyclohexane (HCH) and γ-HCH displaying the greatest concentrations in the northern latitudes/ Arctic Ocean, in stark contrast to the more persistent penta (PeCB)- and hexachlorobenzene (HCB), which approached equilibrium across sampling sites. Geospatial patterns of polychlorinated biphenyl (PCBs) aqueous concentrations closely matched original estimates of production and use, implying limited global transport. Positive correlations between log-transformed concentrations of Σ_7PCB, ΣDDTs, Σendosulfan and Σchlordane, but not ΣHCH, and the log of population density ($p<0.05$) within 5 and 10 km of the sampling sites also supported limited transport from use sites. These results help understand the extent of global distribution, and eventually time-trends, of organic pollutants in aquatic systems, such as across freshwaters and oceans. Future deployments will aim to establish time-trends at selected sites, while adding to the geographical coverage.

Keywords

Passive sampler, polychlorinated biphenyls, hexachlorobenzene, hexachlorocyclohexanes, organochlorine pesticides, cyclodiene pesticides, global fractionation, silicone rubber, long-range transport.

Synopsis

First results from a passive-sampler-based global POPs monitoring campaign demonstrate the global dispersion of legacy organochlorine compounds in water bodies.

Introduction

The Stockholm Convention on Persistent Organic Pollutants (POPs) came into force in May 2004 with the aim of protecting the global environment from the adverse impacts of POPs[1]. The original list of POPs, the so-called "dirty dozen”, were all chlorinated hydrophobic compounds that were largely previously banned [2]. Over time, additional compounds were added, including polybrominated diphenyl ethers (PBDEs) and polar compounds such as perfluorooctane sulfonic acid (PFOS) [3] and perfluorooctanoic acid (PFOA) [4]. Current monitoring in support of the Stockholm Convention is restricted to breast milk and air through the Global Atmospheric Passive Sampling (GAPS) program, and direct water analysis only for PFOS, PFOA, and perfluorohexane sulfonic acid (PFHxS)[5] . Global atmospheric monitoring has been useful in documenting changes in direct emissions and the slower change in secondary (re-)emissions of POPs [6]. Yet there is not necessarily a direct link between atmospheric observations and trends affecting POPs in water bodies and related aquatic foodwebs, which was the impetus for the establishment of AQUA-GAPS/MONET.

Water, as a global solvent, is a key matrix for the exposure, transport, and fate of many POPs, and a key exposure route to (aquatic) foodwebs. The recognition of increasing concentrations of hexachlorocyclohexanes (HCHs) in the colder Arctic water masses led to the formation of the cold condensation theory [7]. The biomagnification of POPs in aquatic environments is ultimately supported by the partitioning of POPs from water into lower food web organisms [8, 9] . Yet despite the general interest in measuring organic contaminants in global waters, there is a general lack of data, in particular simultaneous results covering large geographical scales or temporal trends. As of now, most available data were reported from single cruises covering one region [10], or limited regional passive sampling deployments [11]. This typically also means that the available concentrations were reported from different laboratories, sampling strategies and analytical methodologies, making comparisons or time-trend analysis challenging.

As an example, the existing large-scale studies on the distribution of polychlorinated biphenyls (PCBs) have established the presence, distribution and trends of targeted PCBs in the atmosphere [12], global soil [13], global shelf sediment [14], and even biotic matrices (butter) [15], but nothing comparable exists for water. In modelling global PCBs in the oceans, Wagner et al. [9] noted, that current data (2000-2015) for PCBs in the open oceans and coastal marine waters were sparse except for the Arctic Ocean. Regional seas such as the Baltic and the Mediterranean, as well as the Great Lakes, have better coverage using active [16-18] and passive sampling approaches,[19, 20] but involved multiple research groups and analytical techniques.

Inspired by the success of the Global Atmospheric Passive Sampling (GAPS) program, a group of scientists with support from Jinan University (Guangzhou, China) and Centre RECETOX from Masaryk University (Brno, Czech Republic) met in 2016 to discuss how to set up a global sampling initiative relying on passive samplers in the waters of the world, named AQUA-GAPS [21, 22]. Within the initiative, RECETOX research infrastructure took the role of a central laboratory by providing the chemical analysis, data reporting and storage by its MONET monitoring network. A number of freshwater and coastal sites were identified that could regularly deploy passive samplers while available open ocean sites were not included, given the difficulty in access, turnaround times, and concerns over detection limits. Prior to exposure, samplers were dosed with performance reference compounds (PRCs) to help in assessing the sampler-water exchange progress towards equilibrium, necessary to convert analyte uptake to free dissolved concentrations. Relying on the same type of passive samplers, and their analysis in one central laboratory to reduce the data variability [23], is arguably the only way of achieving comparable aqueous samples data on a global scale.

During these initial AQUA-GAPS/MONET deployments, the two most widely used passive sampling materials, i.e. low density polyethylene (LDPE) and silicone rubber (SSP, polydimethyl siloxane) were co-deployed at all sites. The data obtained from these deployments were used for a detailed comparison of the performance of the two passive sampling phases. [24] In brief, for almost all target compounds, the detection frequencies was slightly higher in the SSP than in LDPE: 87% versus 78% for Σ_7 PCBs,90% vs 80% for ΣDDTs; 41% vs 16% for ΣHCHs and 62% vs 40% for other OCs. [20] Detection frequencies in SSP ranged from

100% for PCB 52, HCB, o,p'-DDD, p,p'-DDD and trans-chlordane, to 2% for δ-HCH, with a median frequency of 79% for 36 target compounds. In LDPE, the median detection frequency was 60% ranging from 100% for HCB to zero for δ-HCH and several other OCPs. Otherwise, there was no discrepancy between both sampler types, but given the greater frequency of detection in SSP (aided by a 4-times greater SSP mass deployed), we will focus exclusively on the results obtained from the SSP samplers for this manuscript.

The aim of the AQUA-GAPS/ MONET [21] is to derive baseline concentrations, and time-trends, of various dissolved hydrophobic organic contaminants (HOCs) globally relying on the same sampling tool and a centralized sample analysis that allows for direct comparison of data while minimizing measurement uncertainty. Herein the focus is on PCBs and organochlorine pesticides (OCPs). A forthcoming paper will report on data of polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), other novel and brominated flame retardants and organophosphate esters.

The main objectives of the current study were to (i) deploy passive samplers for hydrophobic organic compounds at a wide range of lake, estuarine, coastal and oceanic sites across the world; (ii) determine background concentrations of PCBs and OCPs across the waters of the world; (iii) assess the relation of dissolved HOC concentrations with latitude, temperature and population density, and (iv) use the information gained from the first set of deployments to optimize sampler and site distribution for long-term monitoring effort for a wider range of organic contaminants of concern.

Materials and Methods

Study design

A glossary of terms used in the text is provided in Table S1. A list of institutions and teams involved in sampler deployment and retrieval is given in Table S2 and sampling locations in Table S3. Briefly, these criteria were used for site selection: (i) sites away from known point sources; (ii) global geographic coverage (all continents, both hemispheres); (iii) a range of environments including representative lake, estuarine, coastal and oceanic sites; (iv) sites were preferred with a future vision of regular deployment of passive samplers for temporal trend identification; and (v) more than 40 sites were envisaged, while the real number of reported samples reflects some losses during sampling and sample rejection because of failing QA/QC criteria (e.g. Antarctic samples).

Investigated compounds

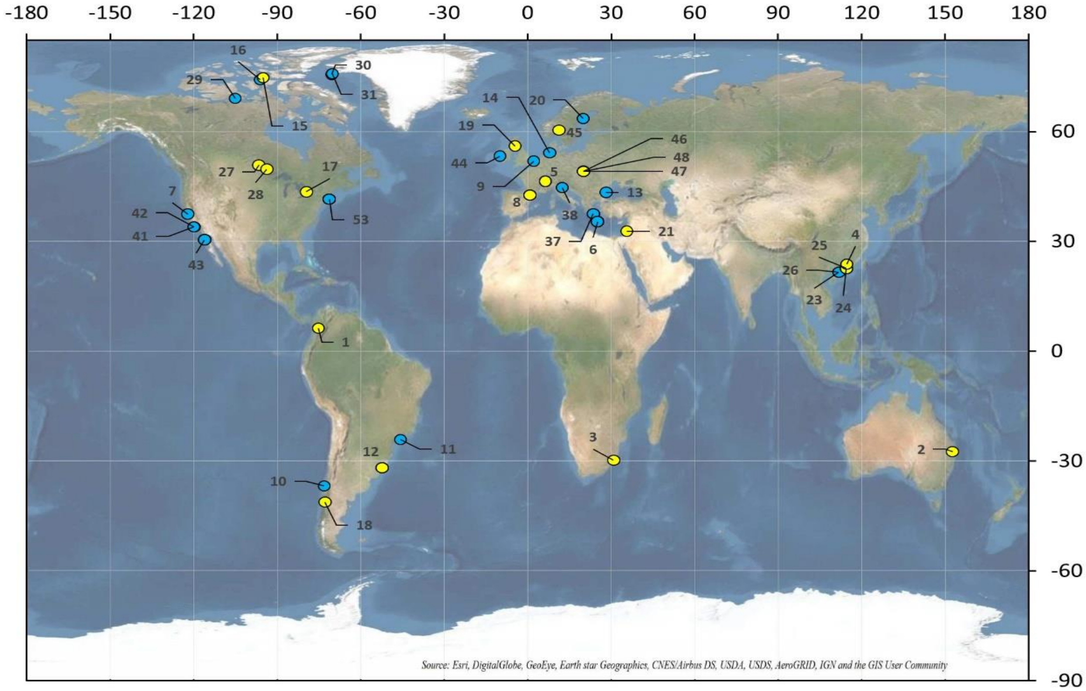
Investigated compounds included the seven International Council for *the Exploration of the Sea* (ICES) indicator PCBs (CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180, see Table S4-1), 11 OCPs including pentachlorobenzene (PeCB), hexachlorobenzene (HCB), hexachlorocyclohexane (HCH) isomers, 1,1,1-trichloro-2,2-(bis)(4-chlorophenyl)ethane (DDT) and its metabolites, and 17 cyclodiene pesticides and their transformation products (Table S4-2). Selected HOCs are included in the Stockholm Convention on POPs and regulated as priority substances in the aquatic environments in Europe, USA or other countries.

Passive sampler preparation

Translucent silicone polymer sheets with 0.25 mm thickness (Shielding Solution, UK; density ($\rho = 1.14$ g cm^{-3}) were cut into 5.5×9.5 cm sheets (~1.5 g), punctured to make holes (5 mm diameter) for mounting onto the deployment device, and Soxhlet extracted in ethyl acetate at 77 °C for 100 h. SSP sheets were homogenously dosed with 14 performance reference compounds (PRCs; D_{10}-biphenyl and 13 PCB congeners not occurring in technical mixtures, see Table S4) according to a procedure described in Smedes and Booij.[25] One sampler consisted of 16 sheets of SSP (12 sheets used for deployment in water and four sheets as a field blank). The total SSP sheet surface area exposed (both sides) to water was 1,250 cm^2/sampler. Samplers were packed in separate amber jars and stored in a freezer at −18 °C until shipment and exposure. Further details are provided in Sobotka et al.[24].

Sampling locations and deployments

Sampling was performed in the period between July 2016 and October 2020; the worldwide sampling locations aimed to represent sites away from known point sources (Figure 1). In total, 40 sites (21 marine and 19 freshwater) were sampled, yielding a total of 61 exposed samplers (40 marine and 21 freshwater). A complete list of sampling sites (denoted L1 to L48) with sampling periods is available in Supplementary information (Table S3).



Source: Esri, DigitalGlobe, GeoEye, Earth star Geographics, CNES/Airbus DS, USDA, USDS, AeroGRID, IGN and the GIS User Community

Figure 1: Overview of freshwater (yellow) and marine (blue) location sites with numbers.

Deployment and retrieval

Volunteer network partners worldwide (Table S2-1) deployed and retrieved the samplers according to agreed standard operating procedures. In the marine environment, the samplers were mounted in durable stainless steel cages[25] or custom-made holders equipped with sampler sheet mounting positions (For details, see Figure S2-1 in Sobotka et al., [24]) attached to the available structures (stationary buoys, moorings). In the freshwater environment, the samplers were mounted (i) on ~4 cm steel wire mesh ("BBQ ") frames using cable ties, (ii) on the 'tube shroud' holder or (iii) on a custom-made frame with mounting plates designed for the cage (for details, see [24]). The samplers were mounted on these holders just before exposure. The freshwater and seawater deployments were approximately two meters below the water surface, and sampler exposures lasted between 36 and 400 days. The sampler deployment duration differed for reasons of site accessibility, and longer exposures were performed at sites with expected low contaminant concentrations. Immediately after each sampler's recovery, the sheet's surfaces were cleaned from fouling by wiping them using a pre-cleaned (in methanol and dried) nylon scouring pad while immersed in water collected at the sampling site. Cleaned samplers were placed back to the corresponding amber jars, transported to the central processing laboratory by fast courier services in containers cooled to 4 °C and stored in a freezer (−18 °C) until further processing. During the sampler mounting and retrieval operations, four SSP sheets not exposed to water were exposed to air to estimate contamination related to the handling, transport and storage of the samplers, stored, and transported to the laboratory in separate jars and further processed as quality control field blank samples. Additional sets of six clean SSP sheets from each production batch were stored in the laboratory and further processed as quality control fabrication blank samples and provided reference, or initial PRC concentrations.

Sampler analysis

Processing of silicone sheets

Samplers were processed in three extraction batches according to Table S3 (see "analysis batch" column), slightly differing in their processing, as described in detail in SI section S1. Compounds were analyzed by GC-MS/MS; further details are given in Sobotka et al.[24].

Calculation of dissolved concentrations

Aqueous concentrations of POPs, C_w, were calculated using the first-order uptake model to equilibrium according to Smedes and Booij [25], taking into account the POPs amounts measured in exposed samplers, the SSP/water partition coefficients (Table S5-1) as well as in procedural, fabrication, and field blanks as described below and in Vrana et al. [26]. The analyte amounts in exposed samplers were converted to C_w using the sampled volume of each compound in each sampling, as estimated from the release of PRCs [25] (Table S5-2), and as detailed by Sobotka et al.[24]. A measure for C_w's limit of detection (LOD) was set based on three times the standard deviation of the compound amounts in fabrication blanks. Reported C_w data were not adjusted for the effect of temperature or salinity on analyte partitioning from water to silicone, except to assess the effect of temperature on calculated dissolved concentrations of PeCB and HCB, given that the two compounds were suspected to approach equilibrium distribution[27] . The temperature-corrected C_w calculation involved use of the compound's and PRC's temperature adjusted SSP/water partition coefficients, according to Jonker et al. [23], in the calculation model[21] (Table S6).

Quality Assurance and Quality Control (QA/QC)

Recovery internal standards (RIS) were added to all samples before sample preparation (Table S7-1, section S5 and Tables S8-1 to S8-4).

LODs expressed as amounts in SSP samplers and as water concentrations are given in Tables S9-1 to S9-4. Values below the LOD were replaced with ½ the LOD since the majority of the 36 PCB/OCP analytes were detected in all samples (median detection frequency 80% in

SSP). Although other methods are available, substitution with ½ LOD has been shown to provide reliable estimates of true probabilities for datasets with low degrees of censoring [28, 29].

Several OCPs are reported here for which QA/QC was not ideal; given the uniqueness of the data collected here, we report them with caveats. We consider the cyclodiene and pentachlorobenzene results as semi-quantitative; recoveries of several cyclodienes from procedural blanks in batch 1 and batch 2 were low for endrin ketone and isodrin (<40% recovery in 2 tests), dieldrin and *cis*-heptachlor epoxide had recoveries of natives <40% in one of 2 tests. RIS including ^{13}C-labeled pentachlorobenzene, aldrin, dieldrin, endrin aldehyde, endrin ketone, α-endosulfan, β-endosulfan, and mirex had average recoveries from the 3rd batch of samples less than 40%. While included in this manuscript, the data referred to above is deemed less reliable.

Statistical analysis

Population density within a 5, 10, 50 and 100 km radius of each sampling site was determined using the SEDAC Population Estimation Service by inputting decimal coordinates (https://sedac.ciesin.columbia.edu/mapping/popest/pes-v3/). Density (population/km^2) was calculated by dividing the total population by the area within each radius (Table S10).

Concentration and population density data were log-transformed to meet the assumptions of normality. Normality was tested using the Shapiro-Wilk test (passed = p>0.05). Relationships between water concentrations and population density were tested through regression analysis using SigmaStat V4 and graphed using Systat V13 (https://systatsoftware.com/products/).

Principal component analysis (PCA) to compare contamination pattern differences in water of PCB congeners (7 compounds), DDT and its metabolites (6 compounds) and the entire PCB/OCP spectrum (36 compounds) was performed using OriginPro 2021b (Origin Lab Corporation). For PCA, data was standardized by calculating the percentage of each compound in the investigated mixture in water, focusing on relative patterns.

Results and Discussion

Detection of compounds in SSP passive samplers

Results for SSP samples were available for 40 sampling sites, with 10 locations having from two to four sampler deployments between late 2016 and late-2020. Not regularly detected (< 50% of samples) were β-HCH, δ-HCH, heptachlor, trans-heptachlor, methoxychlor, aldrin, isodrin, endrin aldehyde, endrin ketone and β-endosulfan. Maps showing the global distribution of individual POPs are provided in Figure S1-1 to S1-36 as a separate file. All individual concentrations can be found in https://data.genasis.cz/#/outdoor/spatial-distribution#project@212.

Comparing HOC concentrations from multiple deployments

During the pilot sampling campaign more than one sampling was performed at 3 freshwater sites (L12 in Brazil, L8 in Spain, and L5 in Switzerland; listed in Table S3) and 8 marine sites (L4 and L23 in China, L6 and L37 in Greece, L38 in Italy, L43 in Mexico, L20 in Sweden, and L53 in USA). Among these sites, sampling was repeated at a minimum frequency once per year over three consecutive years (L8 Spain, L5 Switzerland, L12 Brazil, and L6 in Greece). Some of those sites are intended for future long-term observation with the aim to identify temporal trends of POPs in surface water at sites with background pollution. Although the available dataset covers only short time periods with a small number of samples, which are not sufficient to unambiguously identify temporal trends, it provides valuable information on observed variability of aqueous concentrations. Both changes in environmental POP concentrations and the precision of passive sampling method contribute to the observed variability.

We expressed the observed variability of concentrations as a relative percentage difference (RPD in %; n=2) or coefficient of variation (CV in %; n≥3) of repeated measurements. At all 11 sites, the RPD or CV did not exceed 200% for any compound. The median CV of all measurements was 37%, which indicates a low variability of most POPs concentrations. The median 29% RPD of two consecutive measurements performed within the same year at 4 sites was even lower, indicating a good method repeatability, when assuming a low seasonal variability.

Distribution of PCBs and OCPs

i) Polychlorinated biphenyls (PCBs)

PCBs were, not surprisingly, detected at every location, though not all targeted congeners. The detection frequency of the seven targeted PCBs generally decreased with increasing degree of chlorination: 98% for PCB 28, 100% for PCB 52, 95% for PCB 101, 89% for PCB 118, 84% for PCB 138, 92% for PCB 153 and 67% for PCB 180.

Average concentrations of different PCB congeners ranged from 1.3 pg L^{-1} for PCB 180 to 4.1 pg L^{-1} for PCB 153, while median concentrations varied by about a factor of 2 (0.24 pg L^{-1} for

PCB 180 and 0.53 pg L^{-1} for PCB 153) (Figure S1-1 to S1-7). The greatest concentrations (170 pg L^{-1}) were recorded at Prudence Island (Narragansett Bay, USA), while the smallest concentrations were obtained from Lake Wivenhoe (L2) in Australia (0.18 pg L^{-1}). Dissolved concentrations of PCB congeners depend on proximity of local sources and the influence of long-range transport and deposition; changes in relative profiles are discussed below.

In terms of geographical distribution, concentrations of Σ_7PCBs peaked in two latitudinal bands, where individual concentrations exceeded 10 pg L^{-1}. Most elevated concentrations were observed in the northern hemisphere (NH), close to industrial source regions (roughly 35°–45° N), but also in the southern hemisphere (SH) at around 35° S (Figure S2).

A comparison of the sum concentrations of dissolved PCBs with estimated historical usage from Breivik et al. [30] showed remarkable agreement. Greatest dissolved concentrations occurred in the region of 40°-60 °N, similar to historical usage (Figure 2). Other elevated concentrations (>5 pg L^{-1}) were observed > 60 °N, in line with some global fractionation and condensation in the Arctic region. A similar trend was seen in a compilation of PCB concentrations in global soils [13]. Conversely, the observation of elevated concentrations at 38 °S (L10; Chile) seems mostly an indication of a local source of PCBs. This is confirmed by the much lower levels observed in the nearby Llanquihue Lake, Los Lagos (L18) (Figure S1-1 to S1-7 and Figure 2).

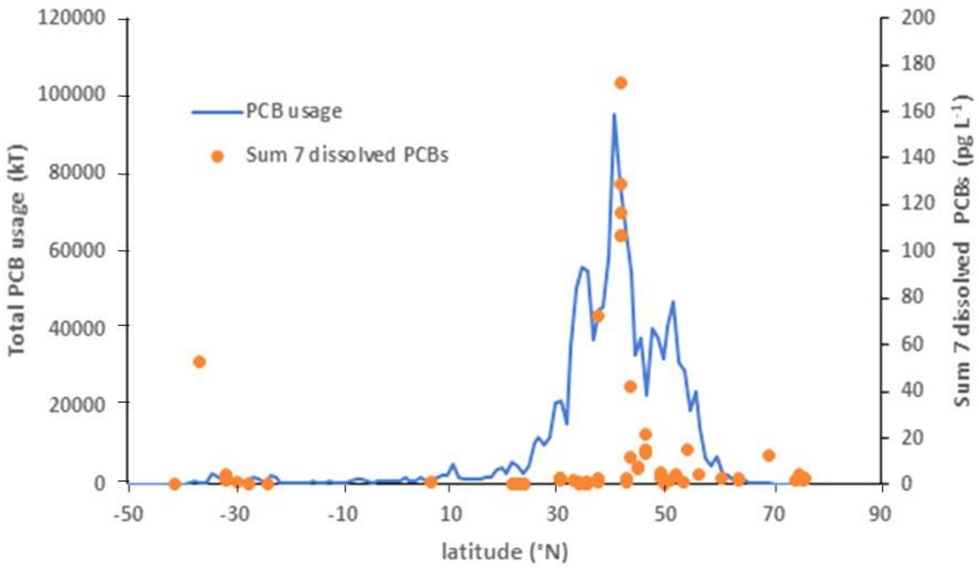


Figure 2: Comparison of the Sum of 7 dissolved PCBs (pg L^{-1}) with estimated historical PCB usage (kT) [30].

We investigated the change in relative abundance of PCBs via PCA. Two factors were extracted, that explained 55% (PC1) and 18% (PC2) of the variance. The PCA plot separated PCB 28 and PCB 52 from the remaining PCBs on the PC1, while PCBs 138, 153 and 180 clustered together (Figure S3-2). As suggested above, a relative enrichment of PCB 52 was associated with the Arctic samples, indicating some evidence of fractionation with latitude.

We, therefore, investigated trends in PCB profiles as a function of temperature or latitude (Figure S4). There were no significant correlations of the relative abundance of PCB congeners changing with the inverse temperature. Contribution of PCB 52 to Σ_7PCBs exceeded 50% in the Arctic samples, indicative of cold condensation. For the fraction of PCB 28 to Σ_7PCBs, there was a significant negative slope with latitude, while there was a positive slope for the fraction of PCB 101 with latitude; all other slopes were not significantly different from zero.

Lastly, all 36 compounds were included in a “total PCB/OCP” PCA analysis (Figure S3-3). The first 2 components explained only 38% of the variance. The graph shows a distinct pattern on PC2 (correlated with DDTs) for sites in China: L23, L24, L25, L26 (sites are listed in Table S3), while PC1 was correlated with PCBs and high positive score is for Narragansett Bay (L53), Concepcion Bay (L10; Chile), Dubarton Bridge (L7; California) and North Adriatic Sea (L38; Mediterranean Sea). The high scores on PC1 were driven by dieldrin, heptachlor, cis- and trans-chlordane and PCBs 28, 52 and 101 (Figure S3-3). The increased presence of DDTs in the compound mixture composition at sites in coastal waters in southern China, is related to the presence of local DDT contamination source(s). Similarly, the increased percentage of PCBs in the contaminant mixture can be explained by the vicinity of sites to local PCB emission sources."

For the other 2 PCA plots (Fig. S3-1 and Fig. S3-2) I think the PCB and DDT patterns have been sufficiently discussed in the existing text.

ii) Pentachlorobenzene (PeCB) and hexachlorobenzene (HCB)

PeCB and HCB were detected at nearly every sampling location and sampling event (98% detection frequency for PeCB and 100% for HCB). Concentrations ranged from < LOD -14 pg L^{-1} (average 2.5 pg /L^{-1}, median 2.0 pg L^{-1}) for PeCB, and from 0.36 – 27 pg L^{-1} (average 7.9 pg L^{-1}, median 5.2 pg L^{-1}) for HCB (Figure S1-8 and S1-9). The greatest concentrations were obtained in the glacial lake Veľké Hincovo pleso in High Tatras mountains (L48; Slovakia) for PeCB and HCB, with the lowest concentrations observed for Lake Winnipeg (L27; Canada).

Aqueous concentrations of PeCB and HCB (Figure S5) approached global equilibrium driven by temperature[31]: Plotting the (temperature -corrected) natural log of either dissolved HCB or PeCB concentrations versus 1/T yielded significant correlations ($P<0.01$; Figure 3), the slope of which represents the enthalpy of phase change (Table S6). For HCB and PeCB, these enthalpies were 56±6.6 kJ/mol and 37±7.3 kJ/mol, respectively. Given that the passive samplers were deployed in surface waters, we interpret these enthalpies as representing air-water exchange. Shen and Wania [32] published internally consistent values of internal phase transfer energies of 50 and 44 kJ/mol for HCB and PeCB, respectively. These values matched closely our field derived values and were within the 95% uncertainty intervals. The globally homogeneous concentrations and their correlation with phase change enthalpies imply that these compounds are at or near equilibrium and are continuously cycling between the atmosphere and surface waters worldwide.

Similar results were observed using temperature un-adjusted dissolved concentrations (enthalpies were 67±6.6 kJ/mol for HCB, and 48±7.3 kJ/mol for PeCB) (see also Figure S6, and Table S6). These results suggest that temperature correction of passive sampling data does not seem to be essential and was thus not applied to the other studied compounds.

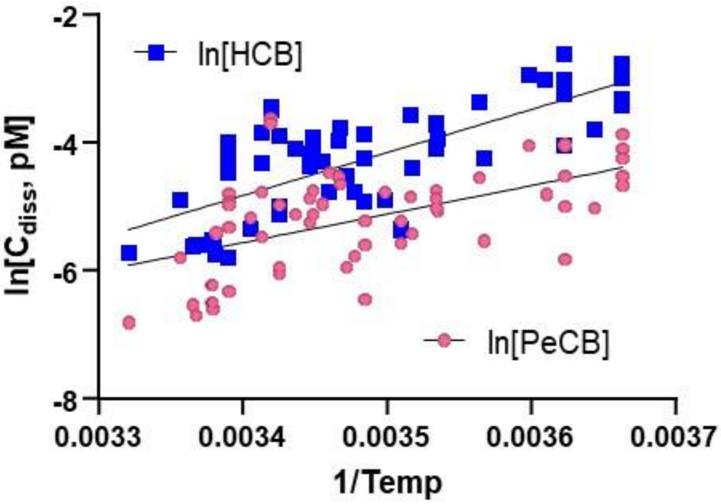


Figure 3: Natural logarithm of dissolved concentrations of PeCB and HCB (pM) versus inverse temperature (°K^{-1}) [Results from Lake Winnipeg were excluded as outliers; ln[HCB]=6687 x ln[C_{diss}]-27.6 (r^2=0.55; n=61, p<0.001); ln[PeCB]=4460 x ln[C_{diss}]-20.7 (r^2=0.31; n=60, p<0.001)**]**.

iii) α-, β-, γ- and δ-hexachlorocyclohexanes (HCHs)

The detection frequencies varied strongly among the different HCH isomers: 77% and 74% for α-HCH and γ-HCH, but only 10% and 2% for β-HCH and δ-HCH, respectively. Accordingly, we will only focus on α-HCH and γ-HCH henceforth. Average (median) concentrations found were in tens of pg/L for both isomers: 83 (29) pg L^{-1} for α-HCH, and 57 (24) pg L^{-1} for γ-HCH (Figure S1-10 to S1-12). None of the isomers were detected at Daya Bay Marina (L24 and L25; China), Lake Wivenhoe (L2; Australia), Concepcion Bay (L10; Chile), and the North Adriatic Bay (L38; Mediterranean Sea); while the greatest concentrations were observed in Lake Geneva (L5; Switzerland) for γ-HCH and in Cambridge Bay (L29; Canadian Arctic) for α-HCH.

Overall, though, α-HCH and γ-HCH displayed the greatest concentrations in the northern latitudes/ Arctic Ocean (Figure 4), in stark contrast to the more persistent HCB and PeCB (Figure S5). Correlations of individual HCHs with latitude in the northern hemisphere were significant

($p<0.01$), but only explained 26% (α-HCH) to 29% (γ-HCH) of the observed variance (data not shown). There were no significant correlations between any HCH isomer and inverse temperature. Concentrations of α-HCH and γ-HCH in the southern hemisphere did not exceed 50 pg/L, but reached > 1,000 pg L^{-1} in the NH (Figure 4). There was some indication of enhanced usage of γ-HCH in the SH, at freshwater sites impacted by likely agricultural and urban uses.

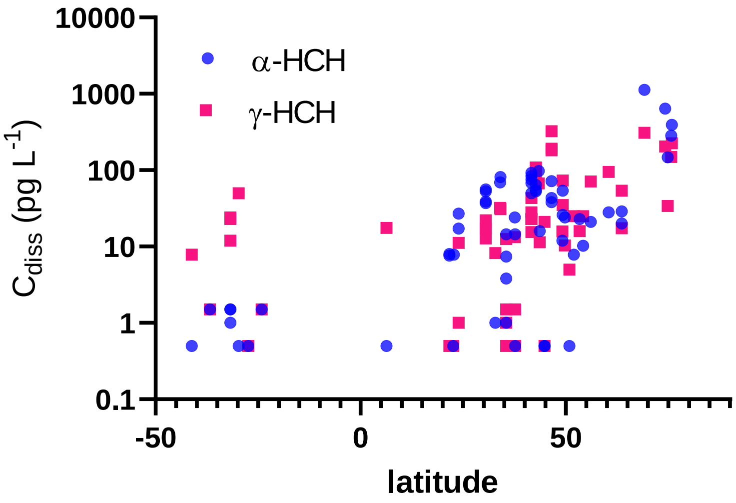


Figure 4: Dissolved concentrations of α-HCH and γ-HCH (pg L^{-1}) as a function of latitude. Note the logarithmic scale on the y-axis.

iv) Dichlorodiphenyltrichloroethane (DDT) isomers

The ΣDDTs is the sum of *p,p'*-DDT, *o,p'*-DDT and its main metabolites *o,p'*-DDD, *o,p'*-DDE *p,p'*-DDD, and *p,p'*-DDE (Figure S1-14 to S1-19). Detection frequencies of the DDTs were > 90% for all isomers, except for *o,p'*-DDT (at 79%). Average (median) concentrations were greatest for *p,p'*-DDD at 15 (3.2) pg L^{-1}, followed by 7.4 (2.6) pg L^{-1} for *p,p'*-DDE and 4.5 (0.6) pg L^{-1} for *p,p'*-DDT, and were smallest for *o,p'*-DDE at 0.4 (0.1) pg L^{-1}.

The DDTs displayed very different trends compared to the HCB/PeCB or HCHs. For DDTs, greatest concentrations occurred in mid-temperate regions of 20°-40° N (Figure 5), with the highest concentrations in Hailing Bay (L23 and L26) in coastal southern China., impacted by (legacy) local source (s). [33]

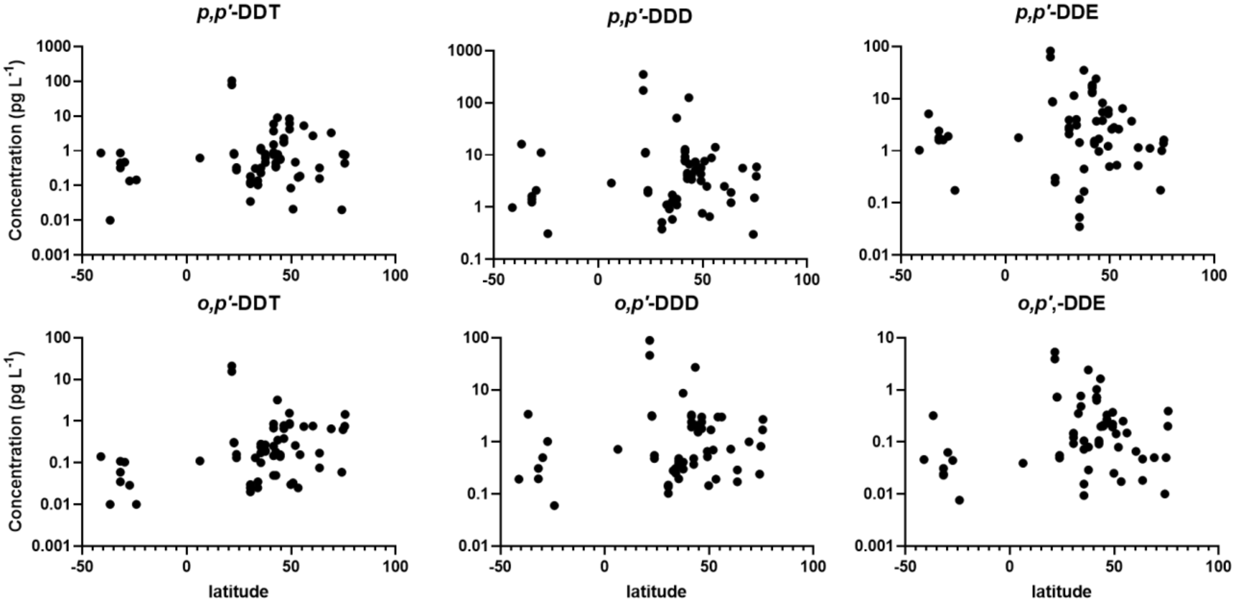


Figure 5: Dissolved concentrations of DDT, DDD and DDE isomers (pg L^{-1}) as a function of latitude. Note logarithmic vertical axes, and varying scales.

We plotted the ratio of *p,p'*-DDT versus *p,p'*-DDE, its aerobic breakdown product, as an indication of fresher versus aged DDT contamination in the water (Figure S7). In the air, the ratio of *p,p'*-DDT /*p,p'*-DDE = 2.8 was found to be in equilibrium with the WHO composition of technical DDT [34], which we adopted for water. Surprisingly, there was a "fresher" signature (ratio ≥3) apparent at several sites in the northern hemisphere, including a glacial lake site in the High Tatras mountains in Slovakia (L46-L48), sites off Crete in the Eastern Mediterranean (L6), and the site at Cambridge Bay (L29; Victoria Island) in the Canadian Arctic. In the case of

Cambridge Bay, elevated DDT concentrations were found in four-horned sculpin (a bottom feeding fish) and in stream water flowing into the bay, compared to remote background sites was reported in a study conducted in the 1990s [35]. The authors speculated that this was due to use at a nearby military radar site. At the high-altitude lake site, the apparent presence of "fresh DDT" might indicate the release of DDT stored from the past in "frozen" compartments, ice and snow. The site off Crete might have been affected by dicofol use in Eastern Mediterranean countries [36].

We extracted again 2 principal components from PCA analysis of the DDT profiles, that explained 47% (PC1) and 26% (PC2) of the variance. The PCA plot separated the DDE isomers on the PC1, while PC 2 separated the DDTs from the DDDs. Geographically, samples enriched in DDEs were mostly from the US and Mexico, while samples enriched in DDTs were from Slovakia, Greece and Canada.

v) Endosulfan

The breakdown product endosulfan sulfate was the most dominant of the three targeted compounds (α- and β-endosulfan and endosulfan sulfate) both in terms of its detection frequency and concentrations (Figure S1-29 to S1-31). The average (median) concentration for endosulfan sulfate was 93 (12) pg L^{-1} (detection frequency 80%), compared to 0.83 (0.5) pg L^{-1} for α-endosulfan (67%) and 2.1 (1.0) pg L^{-1} for β-endosulfan (41%). Greatest concentrations, up to 1,400 pg L^{-1}, were observed in samples from the Xinfeng reservoir (L4) and Hailing Bay (L23 and L26; all in China). Overall, the highest concentrations of endosulfan sulfate (> 50 pg L^{-1}) were exclusively found in the northern hemisphere, but as opposed to the HCHs, not in the northernmost samples (Figure S8).

The prevalence of endosulfan sulfate could be an indication of past, not current applications. At the same time, endosulfan sulfate is more persistent than the present compounds, so it can also be explained as a build-up based on atmospheric delivery of α- and β-endosulfan, and their subsequent degradation in seawater. A greater concentration of endosulfan sulfate than its parent compounds in Arctic seawater was already reported prior to its ban. [37, 38]

vi) Cyclodiene pesticides

Of the various "drins" (dieldrin/aldrin/isodrin/endrin, endrinaldehyde and -ketone), only dieldrin (79%), endrin (57%), endrin ketone (52%) and isodrin (52%) were detected in over half of all samples (Figure S1-24 to S1-28). Dieldrin dominated with average concentrations of 48 pg L^{-1} (median 17 pg L^{-1}; see Figure S9), followed by endrin with average concentrations of 2.1 pg L^{-1} (median 0.47 pg L^{-1}) and aldrin (average 0.39 pg L^{-1}, median 0.10 pg L^{-1}). Given that aldrin degrades to dieldrin, these results are expected [39]. All drins displayed the greatest concentrations in samples from the northern hemisphere, at 40 ° N and Arctic samples.

The ΣChlordanes is the sum of trans- and cis-chlordane, oxychlordane, heptachlor and heptachlor epoxide. Of the chlordanes, cis- and trans-chlordane and its degradation product oxychlordane were among the most prevalent compounds, with widespread detection (>98%) (Figure S1-32 to S1-34). In terms of concentrations, *cis*-chlordane displayed average (median) concentration of 1.7 (0.61 pg L^{-1}), followed by *trans*-chlordane 1.4 (0.33 pg L^{-1}) and oxychlordane with 0.41 (0.09 pg L^{-1}). There was an increase in chlordanes concentrations around 40 °N (Figure 6a), likely driven by historical usage and a secondary peak at Arctic latitudes. Overall, though, chlordane concentrations generally increased with increasing latitude (Figure 6a), comparable to HCHs (Figure 4).

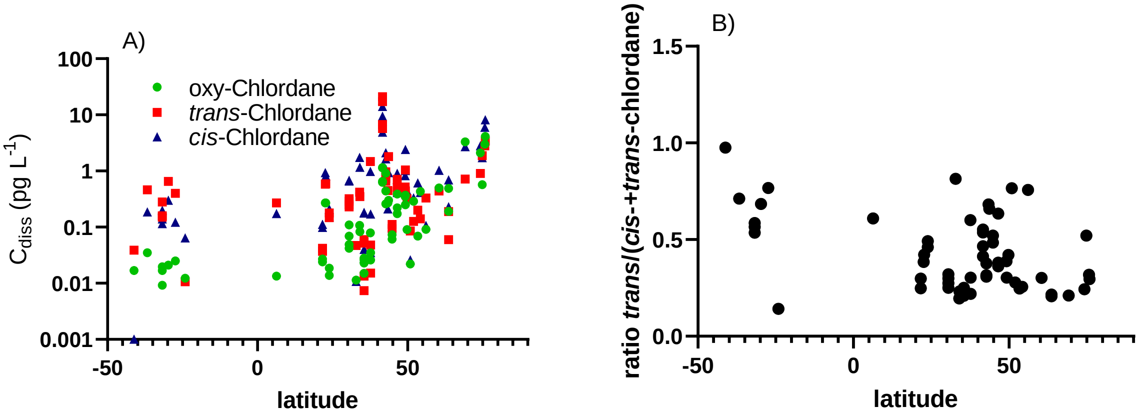


Figure 6: (a) Concentration of chlordanes (pg L^{-1}) and (b) trans/(*cis*+*trans*) chlordane (CD) ratio as a function of latitude. Note the vertical logarithmic axis for concentrations in (a).

The ratio of trans- to *cis*- + *trans*-chlordane has been used to assess fresh from aged chlordanes [40], where ratios > 0.5 imply fresh chlordane. Surprisingly, the ratio was >0.5 at 20 of 61 samples (Figure 6b), mostly at mid-latitude sites in both hemispheres. This could reflect the release of legacy chlordane (with the original cis- to trans- ratio > 0.5) from storage reservoirs, to which it was (atmospherically) deposited and re-released during summer warming. There is evidence for this from air monitoring, i.e., that is, in a warm season increase, although it is also associated with long range transport [40]. Alternatively, it might simply indicate that this ratio approach, which has been used for air samples, does not apply in water, reflecting different solubilities, transport and fate processes for both isomers in water.

Of the three targeted heptachlors (heptachlor, and *cis*- and *trans*-heptachlor epoxides), *cis*-heptachlor epoxide dominated with detection in just over half of samples (57%), and average (median) concentrations of 2.5 (0.67) pg L^{-1}. Heptachlor was only detected in 43% of all samples; trans-heptachlor epoxide in 46%. The dominance of the epoxide indicates old, aged heptachlor sources in the environment. *Cis*- and *trans*-heptachlor epoxides displayed the greatest concentrations in the Arctic, with concentrations decreasing towards the southern-most samples, similar to HCHs (Figure S10).

vii) Other OCPs

Methoxychlor was rarely detected (20% detection frequency) (Figure S1-35); mirex was regularly detected (62%) but, except for two samples from Daya Bay (L24) at 1-2 pg L^{-1}, its concentrations were < 0.1 pg L^{-1} (Figure S1-36).

Comparison of PCB/OCP concentrations with other data

We searched the recent literature for measurements by passive or active sampling near or at the deployment locations. Published data from 2011 to 2020 for PCBs, DDT, HCHs, HCB, and endosulfan were available for several sites (Table S10), so the comparison focused on those analytes.

Concentrations of ΣHCH in the SSP passive samplers deployed in Barrow Strait (Resolute Bay; 848 pg/L) were within 30% of those reported by Ma et al. [41] (592 pg/L) using LDPE samplers and agreed well with results of Pućko et al. [42] based on active sampling (776 pg/L) (Table S10). ΣHCH in Cambridge Bay (L29) were higher than those at other sites (1411 pg L^{-1})

but within the range observed by Pućko et al. [43] in an earlier study of surface seawater in the southeastern Beaufort Sea in 2007 (average 1180 pg L^{-1}). HCB concentrations in SSP passives at Barrow Strait (L16) and Baffin Bay (L30 and L31; 9.4-10.3 pg L^{-1}) were similar to concentrations reported by Ma et al. [41], while results for Σendosulfan were about 2 to 7 fold higher than those reported by Pućko et al. [42] and Jantunen et al. [37] for active samples collected in 2011 and 2013, respectively. The range of Σ_7PCB concentrations in SSP passives (1.5-12.7 pg L^{-1}) in Canadian archipelago waters were within the range (1.2-26.5 pg L^{-1}) reported for the sum of the same 7 congeners in other studies. The higher Σ_7PCB in Cambridge Bay seawater may reflect local legacy contamination from the military radar site, as discussed above.

Comparison of the SSP passives results for the Lake Ontario deployment was also possible with previous passive and active studies [16, 44] (Table S10). Concentrations of ΣDDT, HCB and ΣEndosulfan from LDPE passives were within 2-fold of the SSP results, while ΣHCH levels were much higher (Khairy et al [44] reported non-detect values possibly reflecting use of LDPE samplers with higher detection limits). Major differences were apparent between the SSP passive and the active sample results reported by Venier et al. [16] for ΣPCBs, ΣHCH, ΣDDT, HCB and ΣEndosulfan (Table S10). Although difficult to fully explain, the XAD method used for the active sampling in the Great Lakes does extract POPs associated with dissolved organic carbon, so values greater than dissolved concentrations measured by the passives can be expected [45]. However, average SSP results for the two sampling periods in Northern Baltic (L20) were comparable to average concentrations from active sampling with XAD-2 resin in 2011-2012 [46] (Table S10).

Comparisons were also possible with recent passive sampling in Wivenhoe Lake (L2,)[47], Lake Geneva (L5)[48, 49], Lake Redon (L8)[50], and in the Piedras river (in the same region as the Peñol-Guatapé Reservoir; L1) [51] . Σ_7PCB concentrations were very similar, e.g. Lake Geneva, Lake Redon. However, there were major differences in concentrations of some OCPs between this study and the other reports, e.g. ΣHCH, HCB, and ΣEndosulfan in Wivenhoe Lake, as well as ΣDDT and HCB in the Piedras river. These differences may reflect seasonal trends in water flow, e.g .dry vs rainy seasons, which could influence mobilization of legacy OCPs.

Influence of population density on PCBs/OCPs

Population density within 100 km of the deployment sites ranged from zero at Station BA06 in Baffin Bay (L30) to over 1,200 persons/km^2 at two sites in Daya Bay (L24 and L25) near the megacity of Shenzhen in South China (Table S11-1). Regression analyses showed that log-transformed concentrations of ΣPCB, ΣDDT, Σendosulfan, Σchlordane and PeCB, were positively related to log of /population density ($P<0.05$) within 5 km and 10 km of the sampling sites (Table S11-2; Figure S11A – D). ΣHCH negatively related to density within 50 km (Table S11-2; Figure S11F) and 100 km (data not shown) but showed no significant correlation with population density at 5 km and 10 km. This negative relationship was unique and implies that the higher concentrations ΣHCH, in northern latitudes/ Arctic Ocean (Figure 4) may be driven by cold condensation [7]. ΣDrins, Σchlordane, and HCB also had negative relationships to density within 50 km (Figure S11G, H, J) but the trends were not statistically significant (Table S11-2).

Among the PCB congeners, PCB 28, PCB 52, and PCB 153 had the strongest relationships of seven measured congeners with population density at 5 km and 10 km (Table S11-2). Similarly, p,p'-DDE and p,p'-DDT had the strongest relationships of six DDT related compounds. In general, PCB congeners and DDT compounds were not significantly related to density at 50 km (Table S11-2). This was consistent with our hypothesis that density close to the sampling site would influence measured concentrations. A positive relationship of dissolved brominated diphenyl ether has previously been shown in passive water sampling in the lower Great Lakes waters [45]. α-endosulfan and β-endosulfan were also positively related to population density at 5 and 10 km, with good statistical power at α=0.05 probability (0.95-0.98), while endosulfan sulfate, of the three targeted endosulfans, was not significantly related (Table S11-2).

The major chlordane isomers (cis-, trans-chlordane) and ΣChlordane were significantly related to density at 5 km and 10 km while oxychlordane showed no relationship (Table S11-2). Heptachlor related compounds, which we included in Σchlordane due to their presence in technical mixtures, showed no relationships to population density (data not shown).

Implications and future AQUA-GAPS/MONET activities

Results from the first deployments provided a previously unmatched synchronous spatial coverage of the concentrations of legacy POPs across freshwater and marine sites, all reported from the same laboratory. Among the more surprising results was the observation that dissolved PCBs have not migrated far from their points of use. These results mirror earlier studies on the distribution of PCBs in soils [13] or sediments [14], likely due to PCBs being sorbed to organic carbon, limiting their transport. In contrast, results for HCHs and cis-heptachlor epoxide showed a strong increase in concentration with latitude in the northern hemisphere, as expected from global fractionation theory. Dieldrin and endosulfan sulfate emerged as the OCP with greatest concentrations, indicating greater persistence and mobility. Lastly, concentrations of HCB and PeCB were closest to equilibrium partitioning across the tested water bodies.

Future AQUA-GAPS/MONET deployments will rely on the SSP passive samplers to minimize the work of deployment and recovery, with all analyses being conducted at the central laboratory at RECETOX, Masaryk University in Czech Republic. The first results from the global deployments of passive samplers in the waters of the world highlighted some of the challenges of operating a global network of passive samplers, in terms of securing samplers and sites covering the globe. Currently, the operating sites are still skewed towards North America and Europe, while Africa, South America and large parts of Asia remain under-sampled. Future deployments will aim to establish time-trends at selected sites, while adding to the geographical coverage. While direct ocean observatories would be ideal, the logistics have proven most difficult. Some sites have been impacted by local sources, and will ideally be replaced by those representing background conditions (i.e., indicated by low population density) as far as possible.

Supplementary Information

The SI contains additional method, QA/QC details and figures. The final dissolved concentration data is available in the GENASIS information system, at https://www.genasis.cz/

(https://data.genasis.cz/#/outdoor/spatial-distribution#project@212), and can also be obtained on request.

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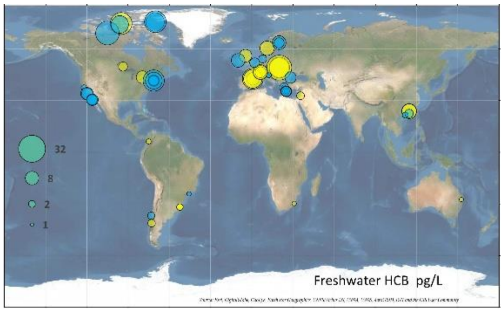
We are grateful to the deployment teams for their efforts, which are listed in the SI.

Graphical TOC



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