



HHS Public Access

Author manuscript

Sci Total Environ. Author manuscript; available in PMC 2024 September 20.

Published in final edited form as:

Sci Total Environ. 2023 September 20; 892: 164566. doi:10.1016/j.scitotenv.2023.164566.

Diffusive Fluxes of Persistent Organic Pollutants Between Arctic Atmosphere, Surface Waters and Sediments

Ian L Moran^a, Lane Tidwell^a, Michael Barton^a, Molly Kile^b, Pamela Miller^c, Diana Rohlman^{a,b}, Samarys Seguinot-Medina^c, Bobby Ungwiluk^c, Vi Waghiyi^c, Kim Anderson^a

^aDepartment of Environmental and Molecular Toxicology, Oregon State University, Corvallis, OR, USA

^bCollege of Public Health and Human Sciences, Oregon State University, Corvallis, OR, USA

^cAlaska Community Action on Toxics, Anchorage, AK, USA

Abstract

Arctic communities are disproportionately exposed to pollutants from sources including global atmospheric transport and formerly used defense sites (FUDS). The effects of climate change and increasing development in the Arctic have the potential to exacerbate this problem. Yupik People of Sivuqaq, or St Lawrence Island, Alaska are one such community with documented exposures to pollutants from FUDS, and their traditional lipid-rich foods such as blubber and rendered oils of marine mammals. Troutman Lake, adjacent to the Yupik community of Gambell, Alaska, was used as a disposal site during the decommission of the adjacent FUDS, leading to community concern about exposure to military pollution and intrusion from historic local dump sites. In collaboration with a local community group, this study utilized passive sampling devices deployed in Troutman Lake. Air, water and sediment deployed samplers were analyzed for unsubstituted and alkylated polycyclic aromatic hydrocarbons (PAHs), brominated and organophosphate flame retardants and polychlorinated biphenyls (PCBs). PAH concentrations were low and comparable to other remote/rural locations. PAHs were generally in deposition from the overlying atmosphere into Troutman Lake. Of the flame retardants, brominated diphenyl ether-47 was detected in all surface water samplers while triphenyl phosphate was detected in all environmental compartments.

Corresponding Author: Kim Anderson, kim.anderson@oregonstate.edu, Mailing Address: Oregon State University - EMT Dept., 1007 Ag & Life Sciences Building, Corvallis, Oregon 97331 .

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

CRedit author contributions statement

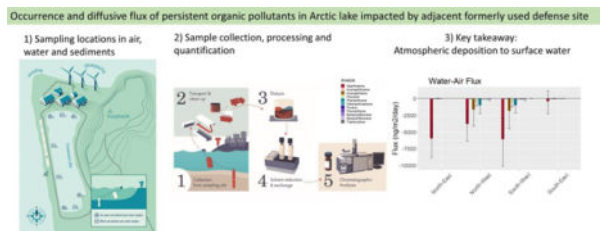
Ian L Moran: Conceptualization, Formal Analysis, Investigation, Writing – Original Draft, Visualization, **Lane Tidwell:** Conceptualization, Methodology, Resources, Investigation, Writing – Review and Editing, **Michael Barton:** Software, Data Curation, **Molly Kile:** Conceptualization, Funding Acquisition, **Pamela Miller:** Conceptualization, Project Administration, **Diana Rohlman:** Visualization, Writing – Review & Editing, **Samarys Seguinot-Medina:** Conceptualization, Writing – Review & Editing **Bobby Ungwiluk:** Conceptualization, Writing – Review & Editing, Investigation, **Vi Waghiyi:** Conceptualization, Writing – Review & Editing, **Kim Anderson:** Conceptualization, Methodology, Resources, Writing – Review & Editing, Supervision, Project Administration, Funding Acquisition

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Both were at concentrations equivalent or lower than other remote locations. Of particular interest, we measured higher atmospheric concentrations of tris(2-chloroethyl) phosphate (TCEP) (0.75–2.8 ng/m³) than previously reported in the literature for remote Arctic sites (<0.017–0.56 ng/m³). TCEP was found to be in deposition to Troutman Lake at magnitudes from 290 to 1300 ng/m²/day. No PCBs were detected in this study. Our findings demonstrate the relevance of both modern and legacy chemicals from local and global sources. These results help us to understand the fate of anthropogenic contaminants in dynamic Arctic systems providing valuable data for communities, policy makers and scientists.

Graphical abstract



Keywords

Arctic chemical movement; passive sampling; polycyclic aromatic hydrocarbons; organophosphate esters; community engaged research

1 Introduction

Persistent organic pollutants (POPs) pose a unique hazard to Indigenous peoples living in the Arctic. Indigenous peoples in the far north are disproportionately exposed to contaminants as a result of global atmospheric transport, the abundance of current and former military facilities, and traditional subsistence diets rich in marine mammals which are known to contain high levels of many POPs due to biomagnification¹. Global climate change has the potential to exacerbate these issues. The effects of climate change are magnified at extreme latitudes and altitudes making the Arctic an important locus for understanding these impacts. Changes in precipitation, temperature driven changes in chemical partitioning, and melting sea ice, glaciers and permafrost all pose challenges to assessing the movement of chemicals in the Arctic². Other impacts of climate change such as altered species distribution and trophic transfer are poorly understood, yet have caused important changes in food web mediated exposure to POPs^{3,4}. A growing body of literature has demonstrated the release of POPs from melting sea ice, glaciers, and permafrost yet many knowledge gaps remain about the effect of global climate change on contaminant movement in the cryosphere^{5–7}.

Sivuqaq lies south-west of Nome in the northern Bering Sea approximately 60km from the Siberian Chukchi Peninsula. The island is home to Sivuqaq Yupik People who practice a traditional subsistence lifestyle, harvesting edible plants, berries, birds, fish and marine mammals⁸. During the Cold War, two military installations were developed on Sivuqaq due to its proximity to Russia. One installation was at the Native Village of Gambell and upon closure in the 1950's debris and chemical waste were buried by the military

in disposal sites around the village and in the adjacent Troutman Lake. Despite the use of the lake by the military as a disposal site for hazardous waste, there has been little investigation into chemical contaminants in the lake conducted by the Army Corps of Engineers⁹. A recent study conducted by Zheng et al. revealed the occurrence of polychlorinated biphenyls, brominated and organophosphate flame retardants in addition to per/polyfluorinated compounds in the tissues of resident fish in Troutman Lake¹⁰. However, the source of these chemicals and their abundance in the abiotic compartments of the lake is not well understood. In addition, several studies have demonstrated that some flame retardants may be subject to long range transport demonstrating the importance of research to better understand the interplay between point source and global transport of these POPs in Troutman Lake and across the Arctic^{11–14}.

One effective tool to address these knowledge gaps is passive sampling. Passive sampling devices (PSDs) have been previously established as a sampling technique well suited to measuring trace levels of organic pollutants in a variety of environmental matrices. PSDs are particularly well suited to sampling in remote environments where logistical constraints prevent the application of other sampling techniques^{15–17}. PSDs accumulate chemicals from the freely dissolved or vapor phase and as a result can provide a highly sensitive measure that reflects the time weighted average concentration, capturing episodic temporal variations. Lowdensity polyethylene (LDPE) is a lipophilic polymer capable of sampling semi-volatile organic compounds with a wide range of physico-chemical properties facilitating simultaneous investigation of several compound classes¹⁸. Using passive sampler derived concentrations in models of diffusive flux allow us to determine the direction and magnitude of chemical movement between environmental compartments, improving our understanding of pollution sources and chemical transport^{19–21}. We demonstrate the utility of pairing passive sampling and diffusive flux models to determine the movement of chemicals in a remote Arctic environment. To our knowledge this represents the first use of passive samplers to describe diffusive flux of persistent organic pollutants between sediments, surface water and atmosphere in the Arctic.

Responsive to community concerns, this study describes the occurrence and movement of flame retardants, PCBs and PAHs between air, water and sediments none of which had previously been measured in Troutman Lake and are rarely monitored in remote Arctic communities. These compound classes were selected due to documented releases of fuels and PCB containing materials and community interest in flame retardant exposures. We use flame retardant and PAH fugacity to better understand the dynamic contributions of point sources and global transport in remote Arctic regions where climate change driven processes affect chemical movement and Indigenous Peoples of the North.

2 Materials and Methods

2.1 Study Area

Troutman Lake lies directly south of the village of Gambell on the north-west corner of Sivuqaq. Approximately three-square kilometers, the lake is bordered by an airstrip and rocky beach to the west, ephemeral wetlands to the south and Naayghaq Mountain to the east. During remediation 38 sites of concern were identified by the Army Corps

of Engineers including military landfills, discarded chemical storage drums, munitions and electrical transformers⁹. In particular, the north side of Troutman Lake was used as a disposal site by the US military. Investigations into reports of munitions in the lake revealed metal debris and 55-gallon drums, the contents of which are unknown⁹. In response to community concerns, in 2017 an Agency for Toxic Substances and Disease Registry (ATSDR) health consultation was released which determined the safety of recreation in Troutman Lake was uncertain due to insufficient characterization of chemical contamination. The extent of characterization of chemical contaminants in Troutman Lake is a single surface water sample collected by the US Army Corps of Engineers in 1985 and analyzed for water quality parameters described in the ATSDR health consultation for Gambell FUDS²².

2.2 Sampler Deployment

PSDs were prepared as described in detail elsewhere²³. PSDs were deployed in and around Troutman Lake in the air, water and sediment pore water (referred to hereafter as sediment) in July, 2019. Air samplers were deployed within 5m of the shoreline at 4 locations (North-East, North-West, South-West and South-East corners of the lake) and water and sediment samplers were deployed at 8 locations along the north, west and south sides of the lake (Figure 1). Air samplers consisted of 5 low density polyethylene (LDPE) strips housed in a sheet metal box with open ends. Surface water samplers utilized 5 LDPE strips deployed in a perforated steel cage while samplers consisted of a single strip of LDPE housed in a perforated steel probe driven into the sediment²⁴. Triplicate samplers were deployed in air and water at the north-west corner of the lake. Each water sampler was deployed approximately 1m deep, suspended on a cable between a weight and a floating buoy. Sediment probes containing PSDs were collocated with each water sampler and placed in the sediment with the top of the probe flush with the sediment-water interface and the middle of the sampler approximately 16–17cm deep. Samplers were deployed for 7 days, collected and returned to Oregon State University for extraction and analysis. Upon return to the laboratory, samples were stored at –20C prior to cleaning and extraction²⁵.

2.3 LDPE Cleaning and Extraction

PSDs were cleaned to remove biofouling and extracted as described elsewhere^{23,26}. Prior to extraction, samplers were spiked with surrogate standards to assess recovery across the extraction process. PSDs were extracted by two rounds of hexane dialysis. Solvent extracts were reduced to 1mL using a TurboVap closed cell evaporator. Sample aliquots were spiked with internal standards for the respective analytical methods as applicable. All solvents used were Optima grade or better.

2.4 Instrumental Analysis

Samples were analyzed for 41 unsubstituted and 22 alkylated polycyclic aromatic hydrocarbon (PAH) targets by gas chromatography-triple quadrupole mass spectroscopy (GCTQMS). The analysis was conducted using an Agilent 7890A GC and an Agilent 7000C tandem mass spectrometer using the method described in Anderson et al. 2015²⁷. Analysis for 52 polychlorinated biphenyls (PCBs) utilized an Agilent 6890M GC with electron capture detector. An Agilent 7890A GC and an Agilent 5975C mass spectrometer were

used to measure 44 organophosphate and brominated diphenyl ether flame retardants (OP and BDE, respectively). Instrument parameters and details on internal standards, surrogates, targets and detection limits for each analysis can be found in supplemental information (SI) section 3. PAH surrogate recoveries ranged from 38% to 78% with an average recovery of 57%. Surrogate recoveries for PCB analysis ranged from 58% to 77% with an average recovery of 67%. PAH concentrations were surrogate corrected to account for loss during the extraction process.

2.5 Quality Control

A variety of quality control (QC) samples were used to ensure sample integrity during PSD construction, deployment, retrieval, transportation and laboratory processing. No targets were detected in any instrument blanks and check standards confirmed instrument calibration in all cases. No PCBs or flame retardants were detected in any QC samples. Low levels of some PAHs were detected in QC samples. The average of laboratory QC sample concentrations were used for background subtraction. Targets detected in QC samples and background subtracted concentrations can be found in Table S7. Samplers deployed in triplicate had an average RSD of 37% and 27% for PAHs and flame retardants, respectively, for compounds above the limit of quantitation. Duplicate aliquots were analyzed for PAHs and flame retardants. The average relative percent difference between duplicate aliquots was 13% for PAHs. No flame retardant targets were detected in either of the duplicate aliquots. Matrix spike samples were analyzed for PAHs and flame retardants and the average recovery was 63% and 88%, respectively.

2.6 Calculations

Time weighted average concentrations in air, water and sediment were calculated using the empirical uptake model²⁶. Depuration of performance reference compounds (PRCs) were used to calculate in-situ sampling rates. Detailed equations are provided in SI section 2.

Diffusive flux was calculated using models described in detail elsewhere^{24,28,29}. Briefly these models use derivations of Fick's first law in which the concentration gradient between two compartments is multiplied by a mass transfer coefficient to derive the diffusive flux of targets across the air-water and sediment-water interfaces (See SI section 2.2 and 2.3 for equations). Uncertainties in calculated flux were described using two complementary approaches, a Monte Carlo simulation approach and the propagation of error approach described in detail elsewhere^{24,30}. Briefly both approaches use observed variability in replicate samplers and assumed uncertainty in mass transfer coefficients and Henry's Law constants to describe the uncertainty in estimates of diffusive flux (Additional details available in SI section 2.4). Standard deviation equivalents were derived from the relevant quantiles of the Monte Carlo simulated distribution of flux values.

2.7 Data sharing

With our partners, the leadership of Sivuqaq and Alaska Community Action on Toxics (ACAT), we implemented a policy around data sharing. The policy stipulates that data must be reviewed by the Sivuqaq Working Group, and the Native Village of Gambell Tribal Council prior to dissemination. Additionally, community partners are integrally involved

in presentations and publications. A six-page summary report was developed, highlighting the results of air, water and sediment sampling across three chemical categories: polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and flame retardants. The report was developed following guidelines from the Clear Communication Index³¹ and written at an 8th grade reading level or lower. A cover letter described the background and rationale of the study, including background on the work done by ACAT. Community questions were listed in parallel to the results of the data to provide a high-level overview of how the data were interpreted. A graphical map identified the general locations of the samplers. Subsequent pages described the levels of chemicals in and around Troutman Lake, and comparisons to other areas of the US were provided as context. Information on the passive samplers was provided in an infographic. The report was internally developed and reviewed, and then reviewed by ACAT, the Sivuqaq Working Group, and the Native Village of Gambell Tribal Council. Following final changes and approval, ACAT provided the report to the Tribe and other stakeholders. (See SI for report back materials)

3 Results and Discussion

3.1 PAHs

3.1.1 - Air, water and sediment concentrations—Unsubstituted PAHs, referred to hereafter as PAHs, were detected in all air samplers with sum PAH concentrations ranging from 18 to 40 ng/m³. Higher concentrations were observed on the west side of the lake compared to the east side of the lake (Figure 2). The distribution of individual PAHs was similar between sites. Vapor phase PAHs were predominantly two and three ring compounds (92% and 8%, respectively). Four ring PAHs represented less than 1% of the total in all cases. No PAHs were detected in the air with greater than four rings. In the surface water the PAH composition and concentrations were relatively homogenous with sum PAH concentrations ranging from 1.4 to 3.2 ng/L. Similar to vapor phase results, naphthalene was the most abundant compound in the surface water composing 92% and 87% of the measured PAH concentrations in the air and water, respectively. Sediment concentrations were generally lower than surface water concentrations with sum PAH concentrations ranging from all targets below detection limits to 0.93 ng/L. Greater heterogeneity was observed in the sediment samplers relative to surface water samplers with markedly higher concentrations at North-West sampling location (0.93ng/L compared to 0.10ng/L at the next highest site). Sediment samplers had fewer detections and lower concentrations than surface water samplers. In contrast to surface water and air measures, sediment contained predominantly three ring PAHs, especially phenanthrene and sulfur containing heterocycle dibenzothiophene. Pyrene was the only four ring PAH detected in sediment samplers, constituting less than 5% of the total. Naphthalene was not detected in any sediment samples.

Alkylated PAHs displayed similar patterns, with alkylated naphthalenes composing the majority of measured alkyls in air and water (Figure 3). Sum of alkyl PAHs ranged from 2 to 15ng/m³ in the air and 0.15 to 0.42ng/L in surface water. In the sediment only alkylated naphthalenes and phenanthrene were detected. At three of the eight sites all targets were below detection limits. The highest concentrations were measured in the sediment at Center-

North where the sum of alkyls was 0.42ng/L. Unsubstituted and alkylated PAHs were correlated with each other in the air and water, with the highest concentrations of both unsubstituted and alkylated PAHs measured at the South-West corner of the lake.

The concentrations observed in this study are similar to results from other rural locations and are in concordance with modern anthropogenic inputs (Figure 4)^{24,28,32–36}. Combustion is the largest emission source of vapor phase naphthalene³⁷. Potential local sources include diesel combustion in the community power plant, burning stove oil for heating residential homes, gasoline powered vehicles and cigarette smoke. The range of vapor phase sum unsubstituted and alkylated PAH concentrations measured here are slightly lower than the range of values reported for rural communities around the Pacific Northwest during the summer in 2019–2022 (37 – 293 ng/m³)³². Similarly, surface water concentrations reported in this study are comparable to the concentrations measured in the Willamette River, Oregon, upriver of major industrial sources in Corvallis and Newberg in 2003 (3.22 ng/L +/- 1.22 (SE, n=2) and 1.72 ng/L +/- 0.54, respectively)³⁵. The sediment concentrations measured here are lower than the values reported in Minick et al. 2019 which measured sediment pore water concentrations at tribal clamming beaches in Washington State (1.2 – 15 ng/L)³⁴ and lower than measures in the Willamette River²⁴.

3.1.2 - Diffusive flux—Across the air-water interface PAHs were found to be predominantly in deposition throughout the lake. The greatest magnitude of depositional flux was on the west side of the lake, corresponding to the higher measured vapor phase concentrations at the North-West and South-West sample sites. The sum of depositional fluxes ranged from 16,000 ng/m²/day at the South-West sample site to 200 ng/m²/day at the South-East location (Figures 5,6). The number of compounds in deposition, when accounting for uncertainty, ranged from 1 to 15 with the most compounds in deposition at the South-West sample site. The compounds with the largest depositional magnitude were naphthalene and alkylated derivatives of naphthalene. The only instance of volatilization was 1,2-dimethyl naphthalene at South-West which had a magnitude of 93 ng/m²/day. The magnitude of atmospheric inputs of naphthalene and its alkylated derivatives suggest that the water concentrations we observed are a result of and share a common source with the measured vapor phase compounds rather than migration from the sediments.

The majority of diffusive flux across the sediment-water interface was naphthalene in deposition from the overlying surface water (Figure 4.B). The next largest contributor to deposition was phenanthrene. Diffusive release from sediment into surface water was of lower magnitude and included dibenzothiophene and various alkylated naphthalenes. The low magnitudes of diffusive flux across the sediment-water interface reflect the small differences in concentration between the compartments. This is likely a result of mixing between water and sediment pore water due to the high permeability of the gravel lakebed³⁸.

3.2 Flame retardants

3.2.1 - Air, water, sediment concentrations—Two flame retardants were detected in all air samplers, tris(2-chloroethyl) phosphate (TCEP) and triphenyl phosphate (TPP), with a range of concentrations of 0.75–2.8 ng/m³ and 0.001–0.004 ng/m³, respectively. Higher

concentrations were observed at the north end of the lake compared to the south (Figure 7). Two flame retardants were found in all water samplers, TPP and BDE-47. TPP was the more abundant of the two compounds with concentrations from 0.017 to 0.07 ng/L. BDE-47 was present in all water samplers between 0.002 and 0.016 ng/L. Only TPP was detected in the sediment and only at two locations, North-East and Airstrip-South at 0.038 and 0.065 ng/L, respectively.

These results are in concordance with a previous study investigating flame retardant concentrations in fish in Troutman Lake. The two flame retardants detected in the surface water in this study, triphenyl phosphate and BDE-47, were detected in fish tissue in Troutman Lake by Zheng et al. 2020¹⁰. While other flame retardants were detected by Zheng et al., BDE-47 was found to be the most abundant BDE congener present in fish tissue. The previous detection of additional compounds in fish not detected in surface waters in the current study is likely a result of their bioconcentration into fish and the limited sampling duration of seven days. Compared to other studies in the literature, the surface water concentrations of BDE-47 and TPP measured in this study are comparable to those reported by McDonough et al. 2018 in marine Arctic surface waters (Below detection limit (BDL)-0.015ng/L and (0.001–0.04ng/L) for BDE-47 and TPP, respectively³⁹.

One challenge to contextualizing atmospheric concentrations of flame retardants is methodological differences between studies. Several previous studies have reported data on particulate phase measurements as many OPFRs are expected to be primarily associated with atmospheric particulates^{12,40–42}. However, OPFRs have a wide range of physico-chemical properties and many are predominately in the vapor phase, including TCEP^{43,44}. Relative to other studies measuring vapor phase concentrations of TPP in the Arctic (0.01–0.25ng/m³), the concentrations measured here are more than an order of magnitude lower (Figure 8)⁴⁵. Concentrations of TCEP are higher than vapor phase concentrations measured outdoors in urban environments (0.032 – 0.60 ng/m³)^{46,47}. Studies reporting particulate phase or combined vapor and particulate phase concentrations have reported mean values as high as 10.5 and 14.6 ng/m³ in Shanghai, China and Shimizu, Japan, respectively^{42,48}. However, the concentrations measured in this study are higher than any values reported in the literature for similar remote Arctic sites (BDL-0.56 ng/m³)⁴⁵. During the summer of 2014 passive samplers were deployed near the Native Village of Savoonga, located 63 Km from Troutman Lake, as part of the Global Atmospheric Passive Sampling Network. That study reported TCEP below detection limit (<0.017 ng/m³), one to two orders of magnitude lower than the concentrations reported in the current study⁴⁵. While long range transport of chlorinated organophosphates is described in the literature, the magnitude of the values measured in this study compared to other comparable Arctic sites suggest local point sources may contribute to vapor phase TCEP concentrations around Troutman Lake^{12,39,45,49}. While commercially developed in the mid 1960's the majority of use of organophosphate flame retardants like TCEP has been in the last twenty years as a replacement for brominated flame retardants, which were phased out in the early 2000s⁵⁰. The occurrence of these organophosphate flame retardants is unlikely to be associated with the FUDS as the defense site precedes the use of these chemicals. TCEP is widely used as a flame retardant in polyurethane foam, upholstery and building materials and has been found in high concentrations in the air around landfills in other studies^{51,52}. Local waste disposal

practices and a nearby open-air landfill may represent an important source of atmospheric TCEP concentrations in this area. While the landfill is 900 and 1400m from the North-West and North-East sampling locations, respectively, the concentrations reported in this study are very similar to concentrations reported by Kerric et al. 2021 which described a mean combined vapor and particulate phase concentration of 2.4 ± 0.4 (SE) ng/m³ around a municipal landfill near Montreal, Canada⁵¹. Waste management practices in the Arctic are the product of unique logistic and socioeconomic constraints⁵³. In some cases, landfill conditions have resulted in hazardous emissions to residents of other Arctic communities, however there are few data on emissions from waste management practices in the Arctic⁵⁴.

3.2.2 - Diffusive flux—The largest contributor to diffusive flux was the deposition of TCEP from the atmosphere into the surface water (Figure 7E). Deposition of TCEP was higher at the north end of the lake than the south end of the lake, corresponding to the higher air concentrations measured on the north side of the lake (Figure 7A). The most deposition occurred at the North-West site with a magnitude of 1300 ng/m²/day (Figure 7E). The least diffusive flux of TCEP across the air-water interface occurred at the South-East sample site at a rate of 290 ng/m²/day. BDE-47 and TPP showed little movement between air and water with all locations showing less than 2 ng/m²/day (Figure 7F).

The direction of diffusive flux at the water-sediment interface was primarily deposition from the surface water (Figure 7G). TPP had a larger magnitude in all cases and ranged from 17 ng/m²/day to 5.2 ng/m²/day for deposition into sediment. TPP was in release from the sediment at only one site, Airstrip-South with a magnitude of 22 ng/m²/day. At most sites BDE-47 was in deposition into the sediment with magnitudes ranging from 0 to 7.3 ng/m²/day. Overall, the magnitude of diffusive flux across the sediment-water interface was very low as a result of the low concentrations and small gradient measured in the surface water and sediment (Figure 7C and D).

3.3 – PCBs

No PCBs were detected in any samples. See table S4 for a full list of target analytes and detection limits. PCBs were previously detected in fish in Troutman Lake by Zheng et al. which found hexachlorinated biphenyls to be the most abundant congeners. As previously mentioned, compounds detected in fish by Zheng et al, not detected in the present study are likely the result of bioconcentration in fish, and therefore not captured in the relatively short, seven day passive sampling duration.

4 Conclusions

To our knowledge this study represents the first use of passive sampling devices combined with diffusive flux models to describe the movement of chemicals between air, surface water and sediment in remote arctic environments. While we did not observe evidence of chemicals in release from military landfills with melting permafrost or re-volatilization of historic sinks, this work demonstrates the utility of passive samplers to address the challenges to assessing chemical fate in the era of climate change. Air-water partitioning of semi-volatile organic chemicals is highly temperature sensitive and as temperatures increases, the direction and magnitude of diffusive flux across the air-water interface may

shift dramatically. Studies like this one can provide site specific information about the movement of chemicals to improve our understanding of chemical fate in the Arctic as climate change continues to affect these systems. The implication of local, modern sources is in line with a growing body of literature recognizing the importance of evaluating both long range transport and local emissions to understand anthropogenic pollution in the Arctic^{55–57}. The data in this study can inform the Yupik People of Sivuqaq and other local, regional and global stakeholders in their efforts to protect human and ecosystem health in the Arctic.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

We appreciate the contribution of members of the Sivuqaq working group, Chris Kookooka and Erika Apatiki for reviewing report back materials, assistance with local place names and logistical support, respectively.

Funding

Research reported in this publication was supported by the National Institute of Environmental Health Sciences of the National Institutes of Health under award numbers P42ES016465, P30ES030287, T32ES007060. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health.

Bibliography

- (1). Arctic Monitoring and Assessment Programme. AMAP Assessment 2009: Human Health in the Arctic; Arctic Monitoring and Assessment Programme: Oslo, Norway, 2012.
- (2). Macdonald RW; Mackay D; Li Y-F; Hickie B How Will Global Climate Change Affect Risks from Long-Range Transport of Persistent Organic Pollutants? Hum. Ecol. Risk Assess. Int. J 2003, 9 (3), 643–660. 10.1080/713609959.
- (3). Borgå K; A. McKinney, M; Routti, J. Fernie K; Giebichenstein J; Hallanger I; G. Muir D. The Influence of Global Climate Change on Accumulation and Toxicity of Persistent Organic Pollutants and Chemicals of Emerging Concern in Arctic Food Webs. Environ. Sci. Process. Impacts 2022. 10.1039/D1EM00469G.
- (4). Moe SJ; De Schamphelaere K; Clements WH; Sorensen MT; Van den Brink PJ; Liess M Combined and Interactive Effects of Global Climate Change and Toxicants on Populations and Communities. Environ. Toxicol. Chem 2013, 32 (1), 49–61. 10.1002/etc.2045. [PubMed: 23147390]
- (5). Hung H; Halsall C; Ball H; Bidleman T; Dachs J; Silva AD; Hermanson M; Kallenborn R; Muir D; Sühling R; Wang X; Wilson S Climate Change Influence on the Levels and Trends of Persistent Organic Pollutants (POPs) and Chemicals of Emerging Arctic Concern (CEACs) in the Arctic Physical Environment – a Review. Environ. Sci. Process. Impacts 2022. 10.1039/D1EM00485A.
- (6). Ma J; Hung H; Tian C; Kallenborn R Revolatilization of Persistent Organic Pollutants in the Arctic Induced by Climate Change. Nat. Clim. Change 2011, 1 (5), 255–260. 10.1038/nclimate1167.
- (7). Ren J; Wang X; Gong P; Wang C Characterization of Tibetan Soil As a Source or Sink of Atmospheric Persistent Organic Pollutants: Seasonal Shift and Impact of Global Warming. Environ. Sci. Technol 2019, 53 (7), 3589–3598. 10.1021/acs.est.9b00698. [PubMed: 30821446]
- (8). Miller PK; Waghiyi V; Welfinger-Smith G; Byrne SC; Kava J; Gologergen J; Eckstein L; Scudato R; Chiarenzelli J; Carpenter DO; Seguinot-Medina S Community-Based Participatory Research Projects and Policy Engagement to Protect Environmental Health on St Lawrence Island, Alaska. Int. J. Circumpolar Health 2013, 72 (1), 21656. 10.3402/ijch.v72i0.21656.

- (9). USACE. Decision Document, Gambell Formerly Used Defense Site, Site F10AK0696, St Lawrence Island, Alaska, 2005.
- (10). Zheng G; Miller P; von Hippel FA; Buck CL; Carpenter DO; Salamova A Legacy and Emerging Semi-Volatile Organic Compounds in Sentinel Fish from an Arctic Formerly Used Defense Site in Alaska. *Environ. Pollut* 2020, 259, 113872. 10.1016/j.envpol.2019.113872. [PubMed: 32069693]
- (11). Breivik K; Wania F; Muir DCG; Alaee M; Backus S; Pacepavicius G Empirical and Modeling Evidence of the Long-Range Atmospheric Transport of Decabromodiphenyl Ether. *Environ. Sci. Technol* 2006, 40 (15), 4612–4618. 10.1021/es060730s. [PubMed: 16913114]
- (12). Möller A; Sturm R; Xie Z; Cai M; He J; Ebinghaus R Organophosphorus Flame Retardants and Plasticizers in Airborne Particles over the Northern Pacific and Indian Ocean toward the Polar Regions: Evidence for Global Occurrence. *Environ. Sci. Technol* 2012, 46 (6), 3127–3134. 10.1021/es204272v. [PubMed: 22332897]
- (13). Prats RM; van Drooge BL; Fernández P; Grimalt JO Occurrence and Temperature Dependence of Atmospheric Gas-Phase Organophosphate Esters in High-Mountain Areas (Pyrenees). *Chemosphere* 2022, 292, 133467. 10.1016/j.chemosphere.2021.133467. [PubMed: 34974042]
- (14). Sun Y; De Silva AO; St Pierre KA; Muir DCG; Spencer C; Lehnerr I; MacInnis JJ Glacial Melt Inputs of Organophosphate Ester Flame Retardants to the Largest High Arctic Lake. *Environ. Sci. Technol* 2020, 54 (5), 2734–2743. 10.1021/acs.est.9b06333. [PubMed: 32013404]
- (15). Yao Y; Meng X-Z; Wu C-C; Bao L-J; Wang F; Wu F-C; Zeng EY Tracking Human Footprints in Antarctica through Passive Sampling of Polycyclic Aromatic Hydrocarbons in Inland Lakes. *Environ. Pollut* 2016, 213, 412–419. 10.1016/j.envpol.2016.02.035. [PubMed: 26946176]
- (16). Lohmann R; Muir D Global Aquatic Passive Sampling (AQUA-GAPS): Using Passive Samplers to Monitor POPs in the Waters of the World. *Environ. Sci. Technol* 2010, 44 (3), 860–864. 10.1021/es902379g. [PubMed: 20104908]
- (17). Prats RM; van Drooge BL; Fernández P; Grimalt JO Field Comparison of Passive Polyurethane Foam and Active Air Sampling Techniques for Analysis of Gas-Phase Semi-Volatile Organic Compounds at a Remote High-Mountain Site. *Sci. Total Environ* 2022, 803, 149738. 10.1016/j.scitotenv.2021.149738. [PubMed: 34481164]
- (18). Vrana B; Allan IJ; Greenwood R; Mills GA; Dominiak E; Svensson K; Knutsson J; Morrison G Passive Sampling Techniques for Monitoring Pollutants in Water. *TrAC Trends Anal. Chem* 2005, 24 (10), 845–868. 10.1016/j.trac.2005.06.006.
- (19). Ruge Z; Muir D; Helm P; Lohmann R Concentrations, Trends, and Air–Water Exchange of PAHs and PBDEs Derived from Passive Samplers in Lake Superior in 2011. *Environ. Sci. Technol* 2015, 49 (23), 13777–13786. 10.1021/acs.est.5b02611. [PubMed: 26436513]
- (20). Prats RM; van Drooge BL; Fernández P; Grimalt JO Passive Water Sampling and Air–Water Diffusive Exchange of Long-Range Transported Semi-Volatile Organic Pollutants in High-Mountain Lakes. *Sci. Total Environ* 2023, 860, 160509. 10.1016/j.scitotenv.2022.160509. [PubMed: 36436648]
- (21). Khairy MA; Lohmann R Using Polyethylene Passive Samplers To Study the Partitioning and Fluxes of Polybrominated Diphenyl Ethers in an Urban River. *Environ. Sci. Technol* 2017, 51 (16), 9062–9071. 10.1021/acs.est.7b02418. [PubMed: 28701037]
- (22). Gambell_FUDS_HC_092020–508.Pdf. https://www.atsdr.cdc.gov/hac/pha/Gambell/Gambell_FUDS_HC_092020-508.pdf (accessed 2022-11-22).
- (23). Anderson KA; Sethajintanin D; Sower G; Quarles L Field Trial and Modeling of Uptake Rates of In Situ Lipid-Free Polyethylene Membrane Passive Sampler. *Environ. Sci. Technol* 2008, 42 (12), 4486–4493. 10.1021/es702657n. [PubMed: 18605575]
- (24). Minick DJ; Anderson KA Diffusive Flux of PAHs across Sediment–Water and Water–Air Interfaces at Urban Superfund Sites. *Environ. Toxicol. Chem* 2017, 36 (9), 2281–2289. 10.1002/etc.3785. [PubMed: 28262984]
- (25). Donald CE; Elie MR; Smith BW; Hoffman PD; Anderson KA Transport Stability of Pesticides and PAHs Sequestered in Polyethylene Passive Sampling Devices. *Environ. Sci. Pollut. Res* 2016, 23 (12), 12392–12399. 10.1007/s11356-016-6453-3.

- (26). Huckins JN; Booi K; Petty JD Introduction to Passive Sampling. In *Monitors of Organic Chemicals in the Environment*; Springer US: Boston, MA, 2006; pp 1–28. 10.1007/0-387-35414-X_1.
- (27). Anderson KA; Szelewski MJ; Wilson G; Quimby BD; Hoffman PD Modified Ion Source Triple Quadrupole Mass Spectrometer Gas Chromatograph for Polycyclic Aromatic Hydrocarbon Analyses. *J. Chromatogr. A* 2015, 1419, 89–98. 10.1016/j.chroma.2015.09.054. [PubMed: 26454790]
- (28). Tidwell LG; Allan SE; O’Connell SG; Hobbie KA; Smith BW; Anderson KA PAH and OPAH Flux during the Deepwater Horizon Incident. *Environ. Sci. Technol* 2016, 50 (14), 7489–7497. 10.1021/acs.est.6b02784. [PubMed: 27391856]
- (29). Bamford HA; Offenberger JH; Larsen RK; Ko F-C; Baker JE Diffusive Exchange of Polycyclic Aromatic Hydrocarbons across the Air–Water Interface of the Patapsco River, an Urbanized Subestuary of the Chesapeake Bay. *Environ. Sci. Technol* 1999, 33 (13), 2138–2144. 10.1021/es981324e.
- (30). Liu Y; Wang S; McDonough CA; Khairy M; Muir D; Lohmann R Estimation of Uncertainty in Air–Water Exchange Flux and Gross Volatilization Loss of PCBs: A Case Study Based on Passive Sampling in the Lower Great Lakes. *Environ. Sci. Technol* 2016, 50 (20), 10894–10902. 10.1021/acs.est.6b02891. [PubMed: 27623269]
- (31). The CDC Clear Communication Index Is a New Evidence-Based Tool to Prepare and Review Health Information. 10.1177/1524839914538969.
- (32). Ghetu CC; Rohlman D; Smith BW; Scott RP; Adams KA; Hoffman PD; Anderson KA Wildfire Impact on Indoor and Outdoor PAH Air Quality. *Environ. Sci. Technol* 2022, 56 (14), 10042–10052. 10.1021/acs.est.2c00619. [PubMed: 35803593]
- (33). Paulik LB; Smith BW; Bergmann AJ; Sower GJ; Forsberg ND; Teeguarden JG; Anderson KA Passive Samplers Accurately Predict PAH Levels in Resident Crayfish. *Sci. Total Environ* 2016, 544, 782–791. 10.1016/j.scitotenv.2015.11.142. [PubMed: 26674706]
- (34). Minick DJ; Paulik LB; Smith BW; Scott RP; Kile ML; Rohlman D; Anderson KA A Passive Sampling Model to Predict PAHs in Butter Clams (*Saxidomus Giganteus*), a Traditional Food Source for Native American Tribes of the Salish Sea Region. *Mar. Pollut. Bull* 2019, 145, 28–35. 10.1016/j.marpolbul.2019.05.020. [PubMed: 31590789]
- (35). Villeneuve DL; Curtis LR; Jenkins JJ; Warner KE; Tilton F; Kent ML; Watral VG; Cunningham ME; Markle DF; Sethajintanin D; Krissanakriangkrai O; Johnson ER; Grove R; Anderson KA Environmental Stresses and Skeletal Deformities in Fish from the Willamette River, Oregon. *Environ. Sci. Technol* 2005, 39 (10), 3495–3506. 10.1021/es048570c. [PubMed: 15954223]
- (36). Allan SE; Smith BW; Anderson KA Impact of the Deepwater Horizon Oil Spill on Bioavailable Polycyclic Aromatic Hydrocarbons in Gulf of Mexico Coastal Waters. *Environ. Sci. Technol* 2012, 46 (4), 2033–2039. 10.1021/es202942q. [PubMed: 22321043]
- (37). Jia C; Batterman S A Critical Review of Naphthalene Sources and Exposures Relevant to Indoor and Outdoor Air. *Int. J. Environ. Res. Public. Health* 2010, 7 (7), 2903. 10.3390/ijerph7072903. [PubMed: 20717549]
- (38). Vervier P; Gibert J; Marmonier P; Dole-Olivier M-J A Perspective on the Permeability of the Surface Freshwater–Groundwater Ecotone. *J. North Am. Benthol. Soc* 1992, 11 (1), 93–102. 10.2307/1467886.
- (39). McDonough CA; De Silva AO; Sun C; Cabrerizo A; Adelman D; Soltwedel T; Bauerfeind E; Muir DCG; Lohmann R Dissolved Organophosphate Esters and Polybrominated Diphenyl Ethers in Remote Marine Environments: Arctic Surface Water Distributions and Net Transport through Fram Strait. *Environ. Sci. Technol* 2018, 52 (11), 6208–6216. 10.1021/acs.est.8b01127. [PubMed: 29787253]
- (40). Sühring R; Diamond ML; Scheringer M; Wong F; Pu ko M; Stern G; Burt A; Hung H; Fellin P; Li H; Jantunen LM Organophosphate Esters in Canadian Arctic Air: Occurrence, Levels and Trends. *Environ. Sci. Technol* 2016, 50 (14), 7409–7415. 10.1021/acs.est.6b00365. [PubMed: 27309668]
- (41). Salamova A; Hermanson MH; Hites RA Organophosphate and Halogenated Flame Retardants in Atmospheric Particles from a European Arctic Site. *Environ. Sci. Technol* 2014, 48 (11), 6133–6140. 10.1021/es500911d. [PubMed: 24848787]

- (42). Ren G; Chen Z; Feng J; Ji W; Zhang J; Zheng K; Yu Z; Zeng X Organophosphate Esters in Total Suspended Particulates of an Urban City in East China. *Chemosphere* 2016, 164, 75–83. 10.1016/j.chemosphere.2016.08.090. [PubMed: 27580260]
- (43). Sühring R; Wolschke H; Diamond ML; Jantunen LM; Scheringer M Distribution of Organophosphate Esters between the Gas and Particle Phase–Model Predictions vs Measured Data. *Environ. Sci. Technol* 2016, 50 (13), 6644–6651. 10.1021/acs.est.6b00199. [PubMed: 27144674]
- (44). Wang Y; Bao M; Tan F; Qu Z; Zhang Y; Chen J Distribution of Organophosphate Esters between the Gas Phase and PM2.5 in Urban Dalian, China. *Environ. Pollut* 2020, 259, 113882. 10.1016/j.envpol.2019.113882. [PubMed: 31926391]
- (45). Rauert C; Schuster JK; Eng A; Harner T Global Atmospheric Concentrations of Brominated and Chlorinated Flame Retardants and Organophosphate Esters. *Environ. Sci. Technol* 2018, 52 (5), 2777–2789. 10.1021/acs.est.7b06239. [PubMed: 29406704]
- (46). Pevery AA; Ma Y; Venier M; Rodenburg Z; Spak SN; Hornbuckle KC; Hites RA Variations of Flame Retardant, Polycyclic Aromatic Hydrocarbon, and Pesticide Concentrations in Chicago’s Atmosphere Measured Using Passive Sampling. *Environ. Sci. Technol* 2015, 49 (9), 5371–5379. 10.1021/acs.est.5b00216. [PubMed: 25874663]
- (47). Saini A; Clarke J; Jariyasopit N; Rauert C; Schuster JK; Halappanavar S; Evans GJ; Su Y; Harner T Flame Retardants in Urban Air: A Case Study in Toronto Targeting Distinct Source Sectors. *Environ. Pollut* 2019, 247, 89–97. 10.1016/j.envpol.2019.01.027. [PubMed: 30665191]
- (48). Ohura T; Amagai T; Senga Y; Fusaya M Organic Air Pollutants inside and Outside Residences in Shimizu, Japan: Levels, Sources and Risks. *Sci. Total Environ* 2006, 366 (2), 485–499. 10.1016/j.scitotenv.2005.10.005. [PubMed: 16298419]
- (49). Li J; Xie Z; Mi W; Lai S; Tian C; Emeis K-C; Ebinghaus R Organophosphate Esters in Air, Snow, and Seawater in the North Atlantic and the Arctic. *Environ. Sci. Technol* 2017, 51 (12), 6887–6896. 10.1021/acs.est.7b01289. [PubMed: 28537717]
- (50). Chupeau Z; Bonvallet N; Mercier F; Le Bot B; Chevrier C; Gloennec P Organophosphorus Flame Retardants: A Global Review of Indoor Contamination and Human Exposure in Europe and Epidemiological Evidence. *Int. J. Environ. Res. Public Health* 2020, 17 (18), 6713. 10.3390/ijerph17186713. [PubMed: 32942622]
- (51). Kerric A; Okeme J; Jantunen L; Giroux J-F; Diamond ML; Verreault J Spatial and Temporal Variations of Halogenated Flame Retardants and Organophosphate Esters in Landfill Air: Potential Linkages with Gull Exposure. *Environ. Pollut* 2021, 271, 116396. 10.1016/j.envpol.2020.116396. [PubMed: 33535362]
- (52). Final Scope of the Risk Evaluation for Tris(2-Chloroethyl) Phosphate (TCEP) CASRN 115–96-8. 107.
- (53). Burns C; Orttung RW; Shaiman M; Silinsky L; Zhang E Solid Waste Management in the Arctic. *Waste Manag.* 2021, 126, 340–350. 10.1016/j.wasman.2021.03.021. [PubMed: 33798822]
- (54). The impact of a landfill fire on ambient air quality in the north_ A case study in Iqaluit, Canada | Elsevier Enhanced Reader. 10.1016/j.envres.2015.06.018.
- (55). Schmale J; Arnold SR; Law KS; Thorp T; Anenberg S; Simpson WR; Mao J; Pratt KA Local Arctic Air Pollution: A Neglected but Serious Problem. *Earths Future* 2018, 6 (10), 1385–1412. 10.1029/2018EF000952.
- (56). Choi S-D; Baek S-Y; Chang Y-S; Wania F; Ikonomou MG; Yoon Y-J; Park B-K; Hong S Passive Air Sampling of Polychlorinated Biphenyls and Organochlorine Pesticides at the Korean Arctic and Antarctic Research Stations: Implications for Long-Range Transport and Local Pollution. *Environ. Sci. Technol* 2008, 42 (19), 7125–7131. 10.1021/es801004p. [PubMed: 18939536]
- (57). Law KS; Roiger A; Thomas JL; Marelle L; Raut J-C; Dalsøren S; Fuglested J; Tuccella P; Weinzierl B; Schlager H Local Arctic Air Pollution: Sources and Impacts. *Ambio* 2017, 46 (S3), 453–463. 10.1007/s13280-017-0962-2. [PubMed: 29076019]

Highlights for diffusive flux manuscript

- Atmospheric deposition was the primary route of chemical movement in Troutman Lake
- PAH and PCB concentrations were low and comparable to other remote/rural locations
- Tris(2-chloroethyl)phosphate was higher than previously reported for Arctic atmosphere
- Demonstrates relevance of modern and legacy sources emitted both globally and locally

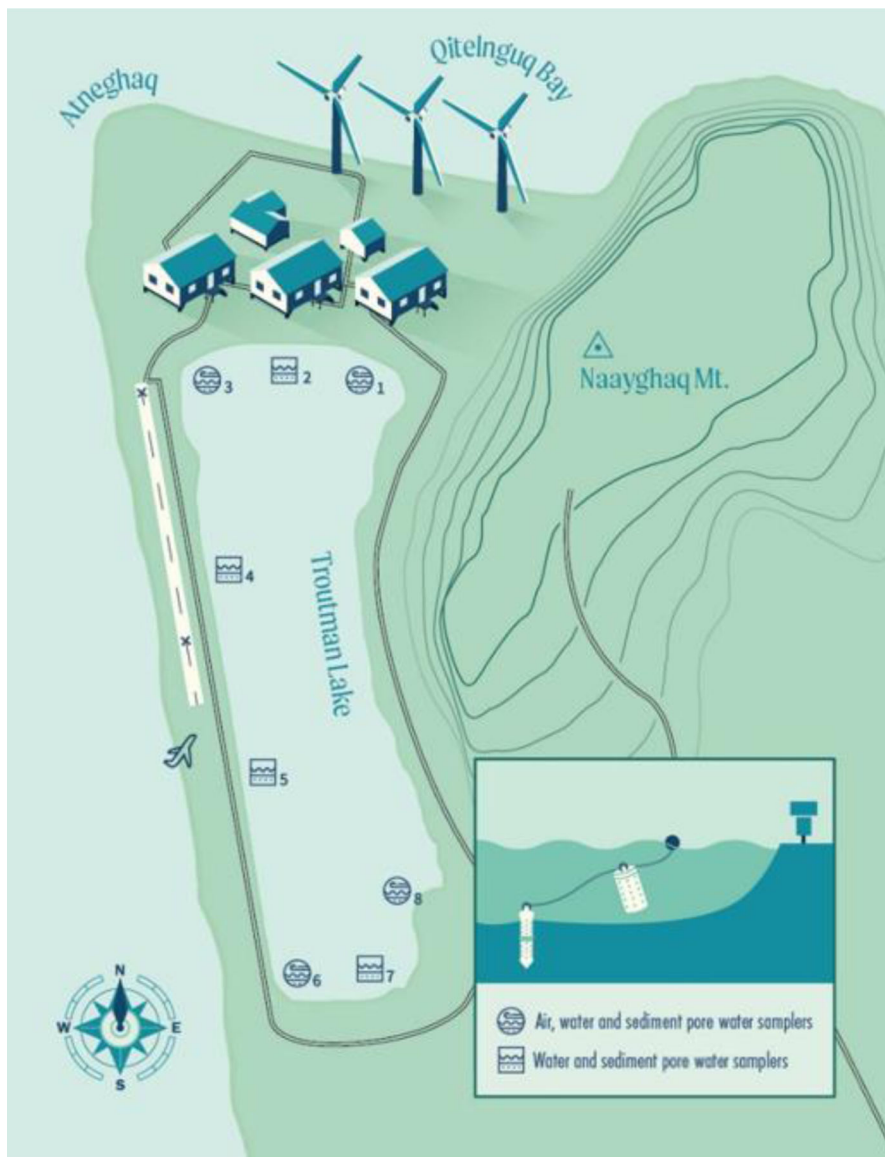


Figure 1. Location of passive sampling devices deployed in Troutman Lake. Site names used in manuscript provided along with local place names. 1) North-East (Maqneghlugaq), 2) Center-North (Tapeghaq), 3) North-West (near Pitegseghaghviget), 4) Airstrip-North (South of Tekeghaghpak), 5) Airstrip-South (Naayvam Ketlighnegha), 6) South-West (near Qamughtut), 7) Center-South (Naayvam Kenlenga), 8) South-East (near Siighmiik). See SI Table S1 for sampling location GPS coordinates.

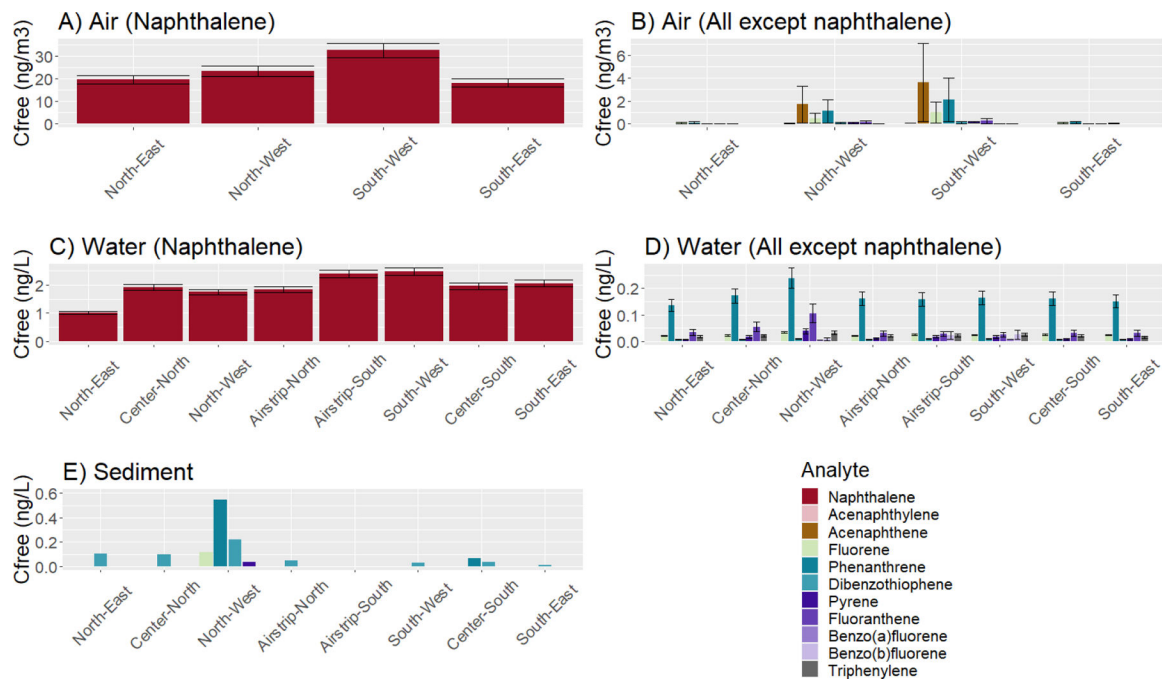


Figure 2. Concentrations of unsubstituted PAHs in air (A & B), water (C & D), and sediment (E). Concentrations were generally low with naphthalene constituting the majority of measured compounds in air and water while sediment detections were primarily three ringed PAHs. Error bars represent standard deviation of triplicate field deployed samplers.

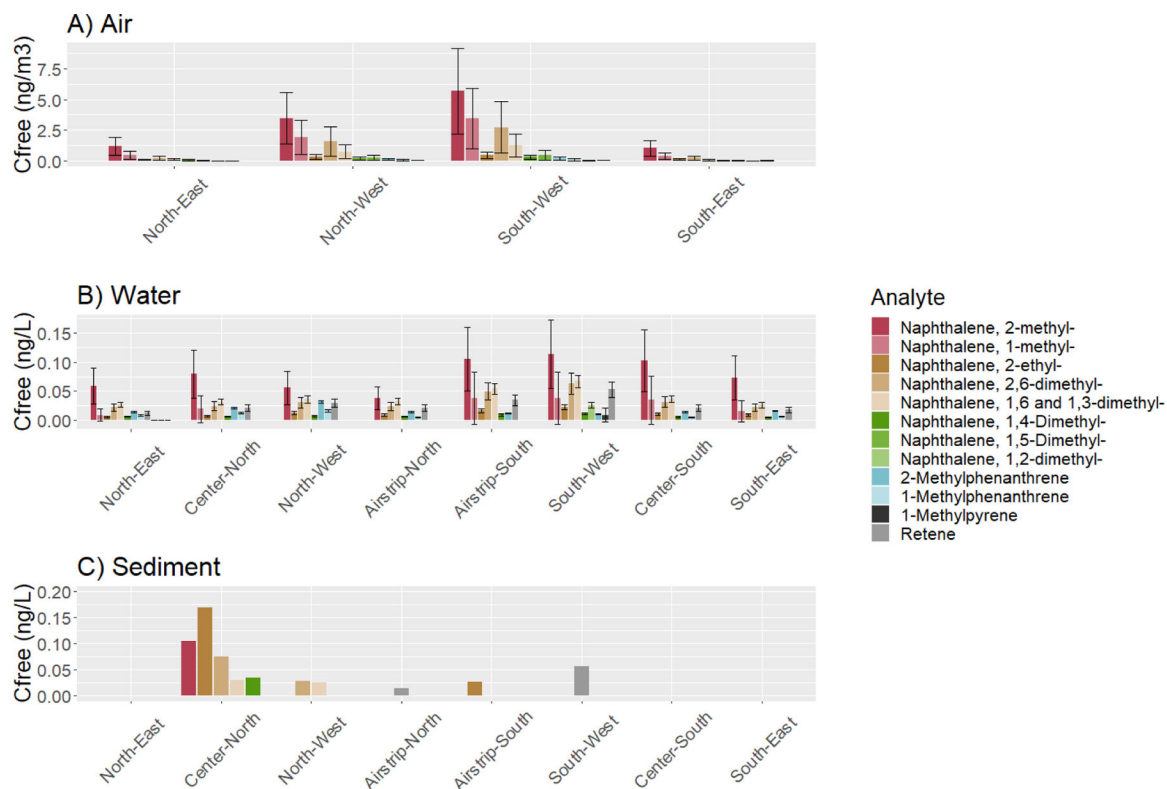


Figure 3. Concentrations of alkylated PAHs in air (A), water (B), and sediment (C). Concentrations were generally low with alkylated naphthalenes constituting the majority of measured compounds. Error bars represent standard deviation of triplicate field deployed samplers.

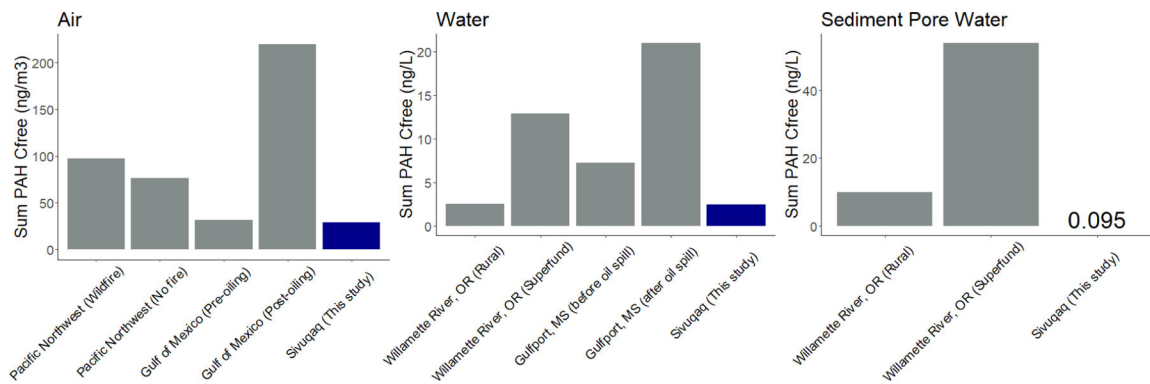


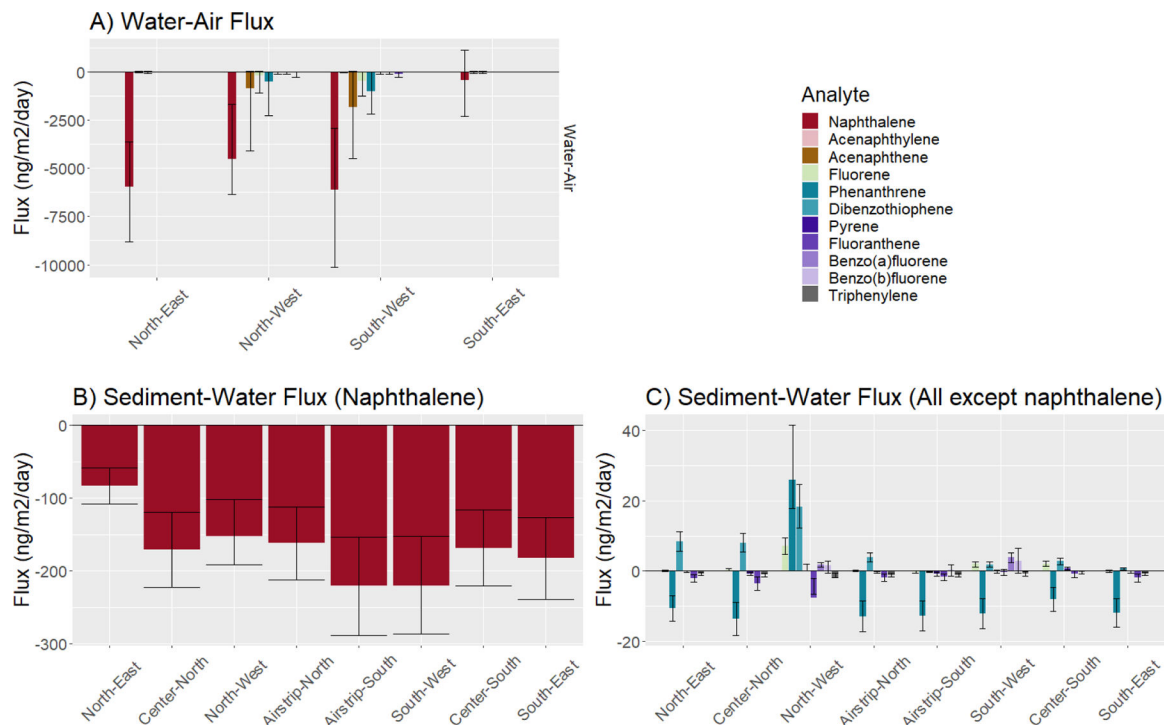
Figure 4. Sum PAH concentrations measured in this study were equivalent or lower than values measured elsewhere at rural or unimpacted sites in North America.^{18,22,26-30}

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript

**Figure 5.**

Fluxes of unsubstituted PAHs across the air-water (A) and sediment-water (B & C) interfaces were predominantly in deposition with naphthalene comprising the majority of chemical movement. Error bars represent prediction intervals from Monte Carlo simulations corresponding to plus or minus one standard deviation (68%) accounting for replicate variability and uncertainty in model parameters as described in supplemental information.

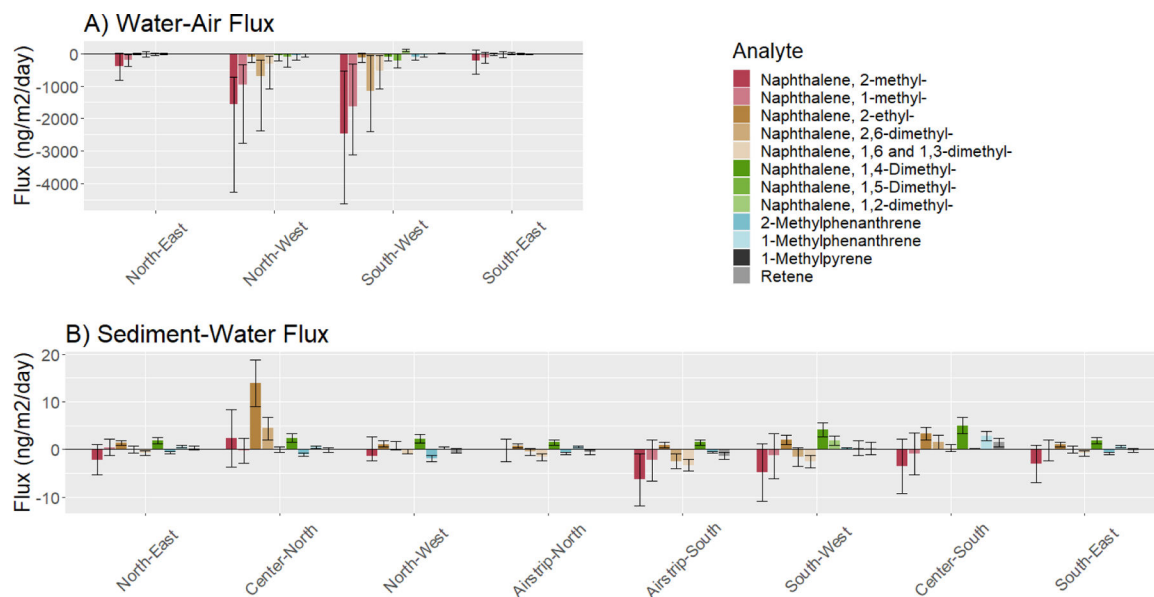


Figure 6. Fluxes of alkylated PAHs across the air-water interface (A) were predominantly in deposition with alkylated naphthalenes comprising the majority of chemical movement. Across the sediment-water interface (B) there was a mix of deposition and release, primarily of alkylated naphthalenes. Error bars represent prediction intervals from Monte Carlo simulations corresponding to plus or minus one standard deviation (68%) accounting for replicate variability and uncertainty in model parameters as described in supplemental information.

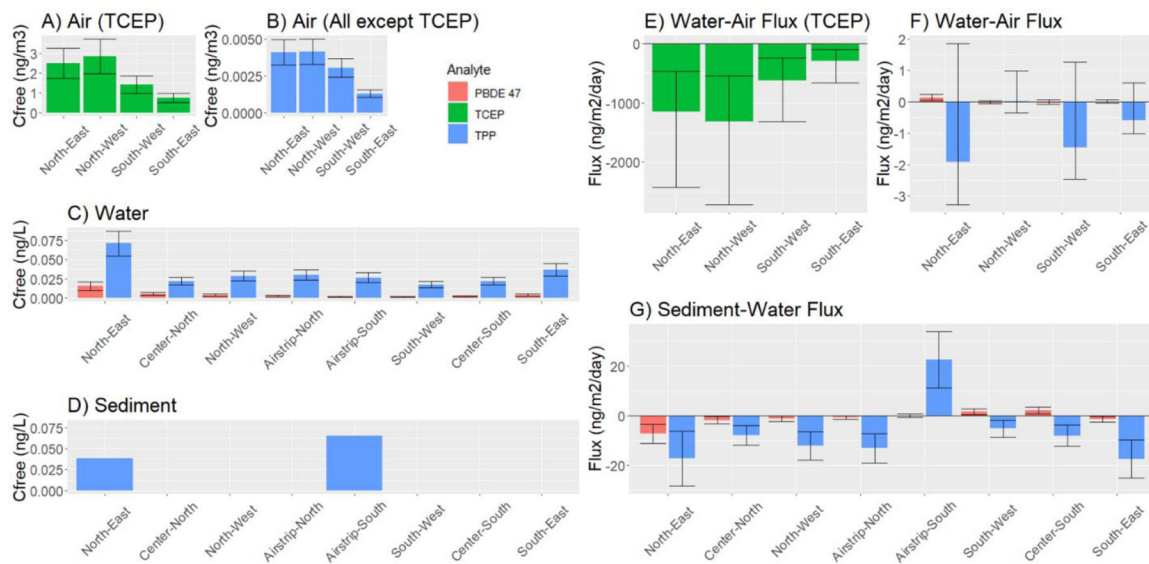


Figure 7. A through D depict freely dissolved concentrations of brominated and organophosphate flame retardants in the air (A and B), water (C) and sediment (D). Error bars represent standard deviation of triplicate field deployed samplers. The remaining panels represent diffusive fluxes of brominated and organophosphate flame retardants across the air-water (E and F) and sediment-water (G) interfaces. Error bars represent prediction intervals from Monte Carlo simulations corresponding to plus or minus one standard deviation (68%) accounting for replicate variability and uncertainty in model parameters as described in supplemental information.

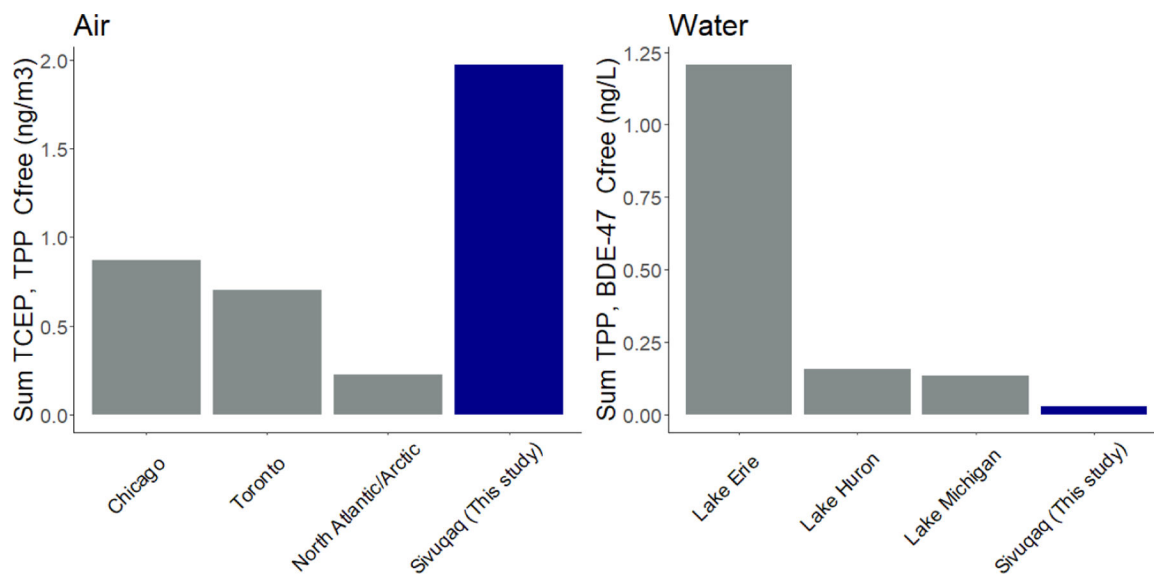


Figure 8. Median sum concentrations of flame retardant detected in this study were higher than published vapor phase values in the atmosphere but lower than published surface water concentrations. Data presented here are limited to vapor phase measures, see Wong et al. 2018 and Li et al. 2017 for comparisons with particulate only and combined vapor and particulate concentrations^{41,47}. No comparison values available in the literature for sediment pore water.