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SPATIAL AND TEMPORAL COMPARISON OF PERSISTENT ORGANIC POLLUTANTS IN THE BOARDMAN RIVER

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SPATIAL AND TEMPORAL COMPARISON OF PERSISTENT ORGANIC
POLLUTANTS IN THE BOARDMAN RIVER

By

Collin J. Diedrich

A THESIS

Submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In Biological Sciences

MICHIGAN TECHNOLOGICAL UNIVERSITY

2021

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This thesis has been approved in partial fulfillment of the requirements for the Degree of
MASTER OF SCIENCE in Biological Sciences.

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Abstract

Dam removal is a critical part of river and stream remediation projects around the world. Frequently dams are associated with impoundment ponds containing sediments that can act as a sink of various persistent organic pollutants (POPs) that can pose risks for human and aquatic wildlife. In this study, we deployed semi-permeable membrane devices (SPMDs) at multiple locations along a 25-mile stretch of the Boardman River in Traverse City Michigan to passively sample POP concentrations in this area that has recently undergone dam and impoundment pond sediment removal. Concentrations of polychlorinated biphenyl (PCB), di-chloro-diphenyl-trichloroethane (DDT) and cyclodiene compounds were in the low ng/L range and below regulatory guidelines considered to pose chronic risks to aquatic health. Spatial patterns in POP profiles were present among the different deployment sites and were considered to generally reflect differences in land-use patterns along the rural to urban gradient of the monitored area of the river.

1 Introduction

Across the world, the natural flow of most major rivers has been anthropogenically altered for human uses such as water diversion and storage, hydroelectricity generation, flood protection, and navigation (Dynesius and Nilsson 1994, Nilsson et al. 2005). These alterations frequently change the natural course of the river thereby fragmenting these ecosystems such that longitudinal connectivity is lost within the river system (Belletti et al. 2020). Among these anthropogenic alterations, the construction of dams for power generation and water storage along a river has further implications for a river's state. The impoundment of waters behind dams can also lead to the accumulation of significant sediment materials (Rosinska et al. 2011). The longer a dam remains in place, the more sediment is able to accumulate. These sediments often have the capacity to act as a reservoir of persistent organic pollutants present in the environment. When dams are removed to restore natural river course and habitat, the persistent organic pollutants that have built up over time can be released. Consequently, the effective management and removal of retained sediments is an important remediation goal for nearly half of the dam removal projects planned across the United States (Bellmore et al. 2017).

As attention has been brought to the negative impacts dams can have on a river system, interest in river restoration has driven a substantial increase in dam removal initiatives. For example, in the US alone there are likely more than one million dams which are over 50 years old and more than 1200 of these have been removed in the past 20 years (Bellmore et al. 2017). Additionally, aging infrastructure occasionally is costlier to maintain than to remove due to evolving safety and environmental standards (Foley et

al. 2017). Given this as well as shifting societal values, it is likely that the growing trend of dam removal and river system restoration in the US will continue to grow in the near future. As these efforts increase across the US, it is important to understand how river systems will respond to dam removal and to assess both the benefits and hazards to help quantify potential risks.

As an example of the scale of river restoration projects currently underway across the United States, the largest dam removal project is the Klamath River restoration effort in southern Oregon and northern California (Klamath River Renewal Corporation 2016). This restoration effort is aimed at removing four large hydroelectric dams in order to restore natural flow regimes across over 400 miles of river and associated tributary habitat within the Klamath River watershed. Within the state of Michigan, the Boardman River system near Traverse City Michigan is a prime example of a site that has been physically altered by historical dam construction and is now undergoing the removal of such legacy dams to reduce fragmentation and restore connectivity along this waterway (Fig. 1). The Boardman River effort is the largest river restoration and dam removal project in Michigan with over 20 miles of river length included in the project area. The Michigan Department of Natural Resources, Fisheries Division designated the headwaters of the Boardman River upstream of the restoration area as a top-quality trout stream (Kalish et al. 2018). The restoration of ecosystem connectivity in the Boardman River primarily aims to re-establish the lower reaches of the Boardman River into an additional 20 mile stretch of high-quality habitat for native species including Brook Trout (*Salvelinus fontinalis*; U.S. Army Corps Engineers 2005).

The history of Boardman River fragmentation extends back to 1847 when Horace Boardman purchased the land at the mouth of the Boardman River on Lake Michigan's Grand Traverse Bay and built a sawmill. In 1851, the sawmill was sold to Hannah, Lay, & Co. and expanded. The expansion of the sawmill attracted more settlers to the area and the community expanded into the current Traverse City area. The Boardman River was chosen as a location of several new dams for hydroelectric power generation in the late 1800's by Queen City Light and Power and the first dam created was the Union St. Dam in 1867 (Table 1; The Boardman River Dams Project 2020). This dam was constructed one and a half miles upstream from the river mouth in order to supply power to an existing flour mill. The next dam built along the course of the river was the Boardman Dam built initially in 1894 at river mile 6.1. The third dam to be constructed was the Sabin Dam and was initially installed in 1902 but later rebuilt (along with the Boardman Dam) in 1930. Although it was the third dam to be constructed, the Sabin Dam was built downstream from the Boardman Dam and located approximately 5.3 miles upstream of the river mouth. Both the Boardman and Sabin Dams were installed specifically for hydroelectric power generation. The last dam built on the Boardman River was the Brown Bridge Dam in 1921, 18.5 miles upstream. The construction of each of these dams significantly altered the flow of the Boardman River and created several large ponds, the Boardman Pond (Keystone Pond), the Sabin Pond, and the Brown Bridge Pond. As these dams fell into disrepair and no longer performed their original functions, removal initiatives have started dam removal and channel restoration efforts in order to restore natural river connectivity.

Efforts to remove dams and restore connectivity along the Boardman River were initiated in 2012 with the Brown Bridge dam being the first to be removed in 2013. The removal of the Boardman Dam was completed in 2017, with Sabin Dam deconstruction and river channel restoration in this reach of the Boardman River being completed in 2018. The capstone of these river restoration efforts is the FishPass Project which will result in the construction of a fish ladder that is designed to facilitate bi-directional selective passage of target species at the Union St. Dam location (Muir et al., 2019). The FishPass project will be constructed in place of the removal of the Union St. Dam in part due to the importance of the Union St. Dam in maintaining the water level of Boardman Lake, a natural waterbody located approximately 0.25 miles upstream of the Union St. Dam (United States Army Corps of Engineers 2014).

In addition to dam removal along the Boardman River, between 65,000 – 272,000 cubic yards of sediment materials that had accumulated in the impoundment ponds behind each of the dams were also removed. A specific concern associated with accumulated sediments in impoundment ponds is the potential for the contamination of these materials with legacy pollutants such as mercury and persistent organic pollutants (POPs) including polychlorinated biphenyls (PCBs) and organochlorine pesticides such as dichloro-diphenyl-trichloroethylene (DDT). Impounded sediments are able to act as a sink for such persistent organic pollutants primarily as a function of their organic carbon content. Specifically, the sorption of hydrophobic persistent organic pollutants to organic particles is a dominant process affecting the abiotic fate of these pollutants in aquatic ecosystems (Luthy 2004; Werner et al. 2010). Sorption kinetics are driven by the proportion or fraction of organic carbon in sediment materials (f_{oc}) and the organic

carbon-water partitioning coefficient (K_{oc}) which itself is a function of pollutant hydrophobicity as represented by the octanol-water partition coefficient ($\text{Log } K_{ow}$; Karickhoff 1981; Werner et al. 2010). Particle size distribution and surface area are also important factors contributing to the capacity of persistent organic pollutants to accumulate in sediment materials (Luthy et al. 1997). For waterways such as the Boardman River where impoundments have existed for over a century, the potential for thermodynamic equilibrium between dissolved water concentrations and the fraction of pollutants sorbed to organic carbon can occur (Karickhoff 1981). Such equilibrium is likely a function of the time frame since impoundment construction, water volume retention time, and the organic carbon fractions dissolved in the water and present in sediments (Karickhoff 1981). As dams are removed during restoration and impoundment volumes drained, sediments can subsequently act as a source of pollutants. This is due to the establishment of a concentration gradient that can result in pollutant partitioning from contaminated sediments and into the clean restored river flow (Karickhoff 1981; Werner et al. 2010). Subsequently, efforts to remove impoundment sediments during restoration projects are also necessary to minimize such possible release of sediment sorbed pollutants during and following river restoration efforts.

Monitoring dissolved concentrations of organic environmental pollutants in aquatic ecosystems following sediment removal and restoration efforts is an effective method for evaluating the success of the remediation programs. For hydrophobic pollutants such as PCBs and DDT, it is critical to sample a large volume of water to generate sufficient pollutant mass for analytical detection, allowing for accurate quantification of very low dissolved concentrations (Alvarez 2008). Consequently, such

large sample volumes can be affected by sporadic pulse events, such as rainstorms, and remain limited for integrating longer term pollutant presence. In contrast, passive sampling techniques can help to quantify temporal and spatial patterns in environmental pollutants without the need for large volume collection and extraction techniques.

Passive sampling devices are manufactured devices that sample and extract chemical residues from environmental media in a purely passive manner that is mediated by diffusion kinetics (Huckins et al. 2006). A prominent technology used for monitoring pollutant concentrations in aquatic environments are semi-permeable membrane devices (SPMDs; Fig. 2). SPMDs are commonly flat, low density polyethylene tubing that contain a small volume of a non-polar (hydrophobic) matrix that provides the partitioning capacity for the passive diffusion of dissolved target analytes from the water into the deployed SPMD. Most commonly, the synthetic lipid triolein (approx. 1 mL) is added as the non-polar liquid phase to the inner volume of the SPMD tubing. This non-polar phase is frequently spiked with a suite of performance reference compounds (PRCs) at known concentrations prior to field deployment. The selection of PRCs typically depends on the range of chemical properties for the target analytes at the deployment location while avoiding potential interference or coelution during analysis and quantitation (Huckins et al. 2002). During deployment, the changes in PRC concentrations that occur permit the calculation of an exposure adjustment factor. This factor can subsequently be used to compensate for changes in SPMD sampling rates that occur during deployment due to considerations such as variations in temperature, biofouling of the SPMD membrane, and flow turbulence at the device surface (Huckins et al. 2002). The polyethylene tubing dimensions range between 60 – 91 x 2.5 (l x w) centimeters in size and have a wall

thickness of 70 – 95 μm . The tubing material also contains 10 angstrom transport corridors that allow for the selective diffusion of the compounds of interest. Sampling periods are typically a number of weeks as it takes time for the SPMD to reach steady state concentrations with the dissolved concentrations of the target pollutants at the deployment location. This period for an SPMD having the above dimensions and characteristics is approximately 30 days (Alvarez 2008).

The persistent organic pollutants of particular interest to this study include polychlorinated biphenyls (PCBs), dichloro-diphenyl-trichloroethylene (DDT), and other chlorinated pesticides. The presence of these organic pollutants is largely due to the agricultural and industrial practices of the 20th century, especially the early and middle 20th century (Murphy et al. 2012). PCBs are a class of chlorinated hydrocarbons consisting of 209 different congeners which were first commercially introduced in 1930 as nonflammable oils used in connection with electrical transformers, condensers, and paint (Cairns & Siegmund 1981). Generally, PCB were marketed in mixtures of various congeners worldwide with approximately 1.5 million metric tons of PCBs having been produced around the world (Safe 1992). DDT was a synthetic insecticide, developed in the 1940s, which was used to combat malaria, typhus, and other insect-borne diseases. It was also found to be effective for insect control for agricultural purposes. Similarly, cyclodienes, such as chlordane, are also chlorinated compounds used as pesticides for their neurotoxic activity.

These compounds are all considered recalcitrant and thus are still present in the environment despite no longer being produced. This is largely due to the hydrophobicity

of the POPs of interest. These POPs have octanol-water partition coefficients ($\text{Log}K_{\text{ow}}$) between 3.7 and 8.2 (Hawker and Connell 1988). Speaking generally this indicates that this group of compounds is relatively hydrophobic, thus partitioning into accumulated sediments and persisting in the area for decades. We would expect to see higher proportions of the less hydrophobic (lower $\text{Log}K_{\text{ow}}$ values) compounds in our samples as they would more readily be released from disturbed sediments.

In 1972 the EPA issued a cancellation order on DDTs due to concerns of adverse environmental effects and human health risks due to neurotoxic activity (U.S. EPA 2021). By 1984, the United States EPA no longer permitted the production and use of PCBs due to concerns with food contamination (U.S. EPA 2021). Similarly, other chlorinated pesticides such as endrin and dieldrin were used as general insecticides but were phased out through the 1970s and 1980s due to similar neurotoxic activity. With the addition of mercury, PCBs, dioxins, chlordane, DDT and its metabolites contribute to ninety-six percent of fish consumption advisories in the US (Orris et al. 2004). Thus, despite being banned for nearly 50 years, it is evident that these POPs are still a health concern and thereby warrant continued environmental monitoring.

1.1 Thesis goals and objectives

The Boardman River restoration represents an excellent opportunity for a comparison of the concentrations of different persistent organic pollutants throughout a river system both before and after the initiation of dam removal projects. The Boardman River dams were all constructed just after the industrial revolution, thus the pollutants of

interest were manufactured and in-use prior to the establishment of the United States Environmental Protection Agency and regulations that restricted their accidental or intentional release into the environment. Therefore, this project will provide insight into the restored connectivity within the ecosystem as well as the efficacy of the restoration efforts at the various dam sites along the Boardman River.

The primary goals of this research are to deploy passive sampling devices to monitor the concentrations of persistent organic pollutants (POPs) including multiple PCB congeners, DDT and its primary metabolites, and a range of additional organochlorine pesticides in the Boardman River as well as conducting passive sampling of POP concentrations in the Boardman River over two consecutive field seasons. The first objective of this research is to characterize and quantify the presence and concentrations of the target POPs along the 20-mile spatial gradient of the Boardman River that has been subject to dam removal and restoration efforts, including those locations previously affected by dam impoundments and sediment accumulation. Our second objective is to quantify potential temporal patterns in POP concentrations that may occur between successive years following dam removal and river channel restoration. I predict that concentrations of POPs will reflect the fragmentation of the river, with higher dissolved PCB and organochlorine pesticide concentrations for the deployment locations that are representative of former impoundment ponds at the dam removal sites. Further, I predict that the concentrations of pollutants will decline between the sampling years. Testing these hypotheses will allow for improved knowledge of the river system and contribute to our understanding of the progress of the restoration efforts.

2 Methods

2.1 SPMD preparation, deployment and retrieval

Semi-permeable membrane devices for deployment in this study were purchased pre-prepared from Environmental Sampling Technologies, St. Joseph, MO (www.est-lab.com). Each SPMD consisted of lay-flat polyethylene tubing (91.4 x 2.5 cm) having welded loops at each end to connect to the SPMD carrier and housed in the deployment cage (Fig. 2). Each SPMD had 1 mL of ultra-high purity triolein pipetted into the inner SPMD space. Prior to adding to the SPMDs, the triolein was spiked with 35 ng each of PCBs 7, 23, 61, 109 and 173 as performance reference compounds for field deployment. Following triolein addition, SPMDs were transferred onto the carriers using a gloved hand and then placed in a stainless-steel container that was purged with Argon and sealed for shipping. All SPMDs remained within the sealed containers and stored at -20 °C until ready for transport and deployment at the specific field location.

Six locations for SPMD deployment were chosen within the 25-mile reach of the Lower Boardman River subject to dam removal and restoration (Fig. 3). The deployment sites were chosen in association with current and former dam impoundment locations in addition to monitoring from the river mouth in Traverse City, Michigan extending to the upper reach of the restored length of the river (Brown Bridge Dam). At each location, SPMDs were deployed in triplicate with an additional set of triplicate SPMDs deployed in Grand Traverse Bay, Michigan as an atmospheric control site. For deployment, SPMD cages were cabled to a standard 16" concrete cinder block and submerged in approximately 2' of water. The cinder blocks were also anchored to the river bottom and the nearby shore to avoid removal and or vandalism. Water temperatures were recorded

daily at each site with an automated temperature logger (Onset Hobo Tidbit; www.onsetcomp.com) attached to each SPMD cage to capture changes in water temperature during the sampling period. Deployment periods extended over a total of 34 and 27 days during the 2019 and 2020 field seasons, respectively. Deployment period occurred over July 16th – August 19th 2019 and from July 2nd – 28th in 2020. These approximately 30-day deployments are determined to be sufficient for SPMDs to achieve steady-state with dissolved concentrations of pollutants in the water column but also minimize the possible extent of algal growth and biofouling that can impede SPMD sampling rates (Alvarez 2010). All SPMDs remained sealed until the time of deployment to minimize air-sampling by the SPMDs prior to being submersed at the target location. In order to account for any air sampling by the SPMDs that occurred between their removal from the sealed container and subsequent immersion at the deployment location, a field blank was exposed to ambient air for the same amount of time (~ 1 minute) that other SPMDs were exposed prior to deployment. At the time of retrieval, SPMDs were transferred from the submerged cages and into pre-labelled, solvent rinsed stainless steel containers and sealed for transport back to the laboratory and frozen at -20 °C until ready for extraction and analysis. Transfer from the submerged cage to the storage container was completed as quickly as possible to minimize exposure to the air and/or potential contamination.

2.2 SPMD extraction

To initiate the extraction procedure, each SPMD was individually removed from the carrier and immediately cleaned to remove surficial particulate matter and biofilm. Cleaning was performed by scrubbing the SPMD surface with a gloved hand, rinsing

with deionized water, and followed by a quick surface rinse with acetone and hexane. The cleaned SPMD was then placed in a 200 mL glass beaker with sufficient volume (approx. 100 mL) of hexane to completely immerse the SPMD in the extraction solvent. The beakers were then allowed to stand for 24 hours in a fume hood while covered with solvent (acetone-hexane) rinsed-foil. After the first extraction period, the hexane was transferred into a 250 mL round bottom flask and a second similar volume (~100 mL) of hexane was added to the beaker. This second extraction period was performed for an additional 24 hours. After that, the hexane volumes from both extraction steps were combined and the SPMD was discarded. The samples were then passed through with pre-combusted sodium sulfate to remove residual water content from the extraction volume. The samples were then evaporated to an approximately 2 mL volume and stored overnight at 4 °C until ready for Florisil™ clean-up chromatography.

2.3 Clean-up chromatography

Florisil™ (60 - 200 mesh; Fisher Scientific) clean-up was conducted using 35 x 1 cm glass chromatography columns equipped with a 250 mL reservoir. Each column contained a small plug of glass wool and was pre-filled with ~150 mL of an initial hexane rinse. Six grams of Florisil™ was then wet-packed into the column and capped with approximately 2 g sodium sulfate. The hexane rinse volume was drained through the column and the sample extract then added as the rinse approached the surface of the sodium sulfate cap. The round bottom flask containing the sample extract was rinsed twice with ~ 1 mL from a subsequent 50 mL hexane rinse for PCB clean-up. Each 1 mL sample rinse was added to the chromatography column and a clean 125 mL round bottom flask was placed under the column to collect the eluent. Once the sample rinses had been

added to the column, the remaining volume of the 50 mL hexane was added to the column and the flow rate adjusted to 1-2 mL·min⁻¹. As the 50 mL hexane rinse approached the sodium sulfate cap, a 50 mL rinse of a 15% dichloromethane and 85% hexane mixture was added to the column. This volume was for organochlorine pesticides clean-up and was collected in a separate 125 mL round bottom flask. Following Florisil™ clean-up, all sample fractions were reduced under vacuum to a 1 mL final volume in iso-octane, transferred to 2 mL gas chromatography vials and stored at 4 °C until ready for analysis via micro-electron capture detection gas chromatography.

2.4 Gas chromatography analysis

All sample peak identification and quantitation were completed using an Agilent 6890 Series Plus Gas Chromatograph (GC) equipped with a ⁶³Ni-micro Electron Capture Detector (μECD). The GC oven was equipped with 60 x 0.25 mm I.D. x 0.10 μm DB-5 film thickness. 1 μL of sample is injected using a splitless injection mode at 250°C and the detection temperature was 300°C. The carrier gas was ultra-high purity He at a flow rate of 22 cm·sec⁻¹ at 90°C (column head pressure 22.88 psi). The oven temperature program began at 90 °C and was maintained for one minute. The temperature was then increased at a rate of 20 °C·min⁻¹ up to 200 °C, held for two minutes. Then the temperature was further increased at a rate of 3 °C·min⁻¹ to 280°C, held from five minutes. The equilibration time was three minutes. The makeup gas used at the ECD consisted of Ar/CH₄ (95%/5%) at a flow rate of 50 mL·min⁻¹.

The detector used in tandem with the gas chromatograph was an electron capture detector. This particular detector functions by having an electron emission source and a makeup gas, typically an inert gas, with both being accelerated towards an anode

together. Makeup gas molecules collide with the emitted electrons, generating more free electrons due to the relatively low excitation energy exhibited by the makeup gas. These free electrons continue to accelerate towards the anode, thus generating a background current. This signal is then able to be modified by the presence of an analyte. In our case the halogenated POPs are very electronegative and capture some of the free electrons, reducing the background signal. This reduction is then proportional to analyte concentration.

The resulting chromatograms were exported to OpenChrom[®] (ver. 1.0.0), an open source chromatogram processing software developed by Lablicate and various members of the scientific community associated with the Eclipse Science Working Group (Kupfer 2014). Sample peak identification and quantitation were completed against the Quebec Ministry of the Environment PCB congener mixture standard for PCBs and against an organochlorine (OC) pesticide standard containing 17 priority compounds (Table 2; Table 3). Sample chromatograms were individually processed with sample peak identities characterized by retention times relative to those for the respective PCB, OC pesticide or PRC standard (± 0.1 min; Figures A1, A2, A3). Peak areas were blank corrected and then converted to POP masses (ng) based on the known concentration of compounds present in the PCB and OC pesticide reference standards. Lastly, individual POP masses were converted to water concentrations at each site using PRC-derived sampling rates and an empirical uptake model developed by Huckins et al. (2006) and provided in Alvarez (2010 a, b).

2.5 Data analysis

Analysis of variance (ANOVA) was used to compare POP concentrations across the SPMD deployment locations. In addition to individual congener and OC pesticide concentration comparisons, pairwise comparison of Σ PCB, Σ Cyclodienes (oxychlordane + *t*-chlordane + *c*-chlordane + *t*-nonachlor + *c*-nonachlor) and Σ DDT (*p,p'*-DDE + *p,p'*-DDD + *p,p'*-DDT) concentrations were also completed. Prior to any statistical evaluation, data were tested for normality using q-q plots as well as Shapiro-Wilk tests. Data that did not meet the assumptions of normality following either $\log_{10}$, square root or z-score normalization efforts were subsequently evaluated using non-parametric statistical methods (Kruskal-Wallis test).

Principal component analysis (PCA) was used to evaluate if there were any spatial or temporal patterns in the POP biomonitoring data. Briefly, PCA is a multivariate data summarization technique that can help to reduce redundancy in the number of variables required to describe a dataset if they are correlated (Stevens & Neilson 1989). PCA eliminates this redundancy in correlations among multiple variables by calculating principal component (PC) axes along which the major variables in a dataset are correlated. Individually, each of these PC axes summarize a proportion of the total variance associated with the entire dataset with individual variables from the reduced dataset and loading ('correlating') either positively or negatively along each PC axis. Subsequently, PCA generates a score for each sample on each PC axis that can be used to plot samples in a graphical representation based on the suite of variables included in the original analysis.

For the PCAs completed here, only those PCB congeners and OC pesticides detected in at least half of the samples collected each year were included in the analysis.

Subsequently, only PCBs 49, 44, 74, 70, 95, 101, 99, 149, 138, 180 and the OC pesticides TCB-1, HCB, b-BHC, *t*-chlordane, and *p,p'*-DDD were included in the 2019 analysis.

For the PCA completed using the 2020 monitoring results, this included PCBs 99, 177, 191 and OC pesticides TCB-1, TCB-2, HCB, b-BHC, *t*-chlordane, and *p,p'*-DDD. For any remaining non-detects, each value was replaced with a random number between zero and the compound method detection limit generated using Excel's random number function (Paterson et al. 2020). Individual PCB congeners and OC pesticide compounds were then reported as a proportion of Σ PCBs or Σ OC pesticides, respectively with the resulting proportional values for each POP being logit transformed prior to completing the PCA (Warton and Hui 2011). All statistical evaluations were completed using the R statistical package (R Core Team 2021), SYSTAT for Windows version 11 (SYSTAT 2004), and the Microsoft Excel data analysis add-in package.

3 Results

Figure 4 provides a summary of Σ PCB, DDT, and cyclodiene concentrations during the 2019 and 2020 sampling seasons. Sum PCB concentrations measured during the 2019 field deployments were highest for the SPMDs deployed at the site of the former Sabin dam (65.0 ± 3.4 pg/L; Fig. 4A). This contrasts the average Σ PCB concentration determined from the SPMDs deployed at the Grand Traverse Bay control location (13.6 ± 0.3 pg/L). Sum PCB concentrations were significantly different across the SPMD deployment sites (Table 5; $p < 0.001$). Pairwise comparison indicated that Σ PCBs estimated from deployments at the Union St. Dam and the Lower Boardman sites were not statistically different from the Grand Traverse Bay control values. Across the six Boardman River sites, the highest Σ DDT concentrations were observed at the Lower Boardman site (202.5 ± 2.3 pg/L) compared to the control site (84.3 ± 3.0 pg/L). Analysis of variance demonstrated Σ DDT concentrations at the Brown Bridge and Sabin Dam locations to be significantly lower than the control location ($p \leq 0.0033$). No other statistical differences in Σ DDT concentrations were evident across the remaining deployment sites. For Σ Cyclodienes in 2019, there was greater variability among all the sites with the Union St. Dam location having a noticeably lower average concentration (3.7 ± 0.2 pg/L) than the control site (129.6 ± 3.0 pg/L). Further, the highest average Σ Cyclodiene concentration was determined for the Lower Boardman site (220.7 ± 5.7 pg/L) which was determined to be significantly higher relative to the control ($p = 0.015$).

Sum PCB concentrations estimated from the 2020 deployments ranged from 14.7 ± 0.5 pg/L to 32.9 ± 0.8 pg/L with the Grand Traverse Bay control and Sabin Dam sites representing the extremes of this range, respectively (Fig. 4B). During this field season,

Σ PCB concentrations averaged 27.8 ± 4.3 pg/L across the six Boardman River SPMD deployment sites with Σ PCBs for all Boardman River deployment locations being higher relative to the Grand Traverse Bay control location ($p < 0.001$). Sum PCB concentrations estimated from the 2020 Boardman Lake deployments were not significantly different from those estimated for the Lower Boardman River and Union St. Dam sites ($p \geq 0.306$). Concentration estimates for all classes of organochlorine pesticides were substantially lower for all 2020 deployments. For example, the highest average Σ DDT concentration was determined from the Wadsworth Street deployment at 0.8 ± 0.04 pg/L with average Σ Cyclodiene concentrations ranging from 0.6 ± 0.03 pg/L from SPMDs deployed at the Brown Bridge site to 2.4 ± 0.2 pg/L for the Wadsworth St. deployment. For both Σ DDTs and Σ Cyclodienes, significant differences were evident among the sampling locations (Table 5; $p < 0.001$).

A comparison of PCB congener profiles (% of Σ PCB) is provided in Figure 5. From the 2019 deployments, tetrachlorobiphenyl congeners (PCBs 44, 49, 52, 70, 74) were the most predominant homolog group among all sites and averaged 67.8 ± 31.6 % of Σ PCBs (Fig. 5A). Pentachlorobiphenyls (PCBs 87, 95, 99, 105/132, 110, 118) were the second most abundant homolog group averaging 8.1 ± 10.2 % of Σ PCBs with all other homolog groups averaging ≤ 7.1 % of Σ PCBs across all sites. The most highly chlorinated congeners including octa- (PCBs 194, 195/208, 199, 205) nona- (PCB206) and decachlorobiphenyls (PCB209) were only detected in extract from the SPMDs deployed at the Grand Traverse Bay control location. This contrasts the 2020 field season results for which pentachlorobiphenyl (54.5 ± 3.4 %) and heptachlorobiphenyl (PCBs 170, 177, 180, 183, 187, 191; 44.1 ± 3.4 %) congeners were indicated to be the

predominant homologs in SPMD extracts with PCB177 being the predominant individual congener identified from this homolog group. Trichlorobiphenyls (PCBs18/17, 31/28, 33) averaged 0.4 ± 0.3 % of Σ PCBs in 2020 relative to an average of 2.8 ± 3.8 % of Σ PCBs for this homolog group in the 2019 deployments. Octa-, nona- and decachlorobiphenyl congeners combined to < 1 % of Σ PCBs across all sites in 2020 with PCB209 not being detected in any of this field seasons' SPMD extracts.

Figure 6 depicts the contributions of PCBs and all organochlorine pesticides as proportions of the total load (ng/SPMD) of persistent organic pollutants sampled by the SPMDs at each sampling site. In 2019, PCBs contributed between 1.8 – 32.3 % of the total pollutant loads quantified at each sampling location with the Wadsworth St. and Sabin Dam locations representing this range, respectively (Fig. 6A). For the Grand Traverse Bay control location, PCBs represented 2.8 ± 0.01 % of the total SPMD load in 2019. Organochlorine pesticides generally dominated the 2019 SPMD profiles with contributions that ranged from 67.7 – 98.2 % of the total SPMD load. For 2020, PCBs were identified to be the predominant compounds detected in SPMD extracts (Fig. 6B). For example, PCB contributed between 49.1 – 92.3 % in the Boardman River sampling sites and an average of 84.0 ± 1.9 % of the total pollutant loads determined from the extracts for the Grand Traverse Bay control site. In contrast to 2019, OC pesticides represented lower proportions of the total SPMD loads ranging from 7.7 ± 0.4 % of the total load for the Boardman Lake deployment to 50.9 ± 0.8 % for the Union St. Dam location.

Principal component analysis (PCA) demonstrated spatial patterns in POP profiles among the Boardman River and Grand Traverse Bay locations in 2019 (Table 6; Fig. 7)

described by PCB191, TCB-1, *p,p'*-DDD and *t*-chlordane with b-BHC, TCB-2 and PCB99 loading negatively on this axis. For the third principal component in this analysis, only TCB-2, *p,p'*-DDD and HCB had loadings exceeding $\geq \pm 0.3$ and this axis accounted for 14.2 % of the total variance. A plot of the sample scores using PC1 and PC2 is provided in Fig. 8A. Profiles for the SPMDs deployed at Brown Bridge, Sabin Dam, Boardman Lake and the Lower Boardman River site all scored positively on PC1 with remaining locations ordinating negatively on this axis. The Grand Traverse Bay control site scored slightly positively along PC2 and close to the origin of PC1. SPMDs deployed at the Wadsworth St. site were the only other samples to plot in the positive direction along PC2. A plot of the sample ordinations using PC1 and PC3 is provided in Fig. 8B. Here, the Grand Traverse Bay control SPMDs generally plotted near the graph origin and only slightly positive on PC3 with the exception of one sample that plotted negatively on PC3. SPMDs deployed at the Lower Boardman River and Sabin Dam also plotted in the positive direction of PC3. All other locations had POP profiles that resulted in negative scores along PC3.

4 Discussion

This study demonstrated both spatial and temporal patterns in PCB and OC pesticide concentrations in the Boardman River using SPMDs as monitors of these pollutants during the 2019 and 2020 field seasons. These results support the first hypothesis of this research in that spatial patterns of POP loadings among the sites were predicted to differ. For the second hypothesis focusing on temporal differences between sampling years, the ability to reject this hypothesis is less clear. It must be noted that these POP concentrations determined for the Boardman River in both field seasons were approaching methodological limits of detection. For example, the United States Environmental Protection Agency's (USEPA) recommended criteria for Σ PCBs for aquatic wildlife is 14 ng/L and 1 ng/L for *p,p'*-DDT and between 36 – 56 ng/L for some of the cyclodiene compounds included in the current study (USEPA 1985). These results suggest that significant anthropogenic or point-source inputs of POPs of the Boardman River are likely limited or absent and that the potential release of sediment-sorbed pollutants following remediation and restoration in the Boardman River is also negligible. However, the presence of spatial patterns in POP profiles among the sampling sites may represent subtle effects potentially as associated with land-use patterns and other anthropogenic contributions along the stretch of Boardman River monitored here.

The concentrations of compounds including Σ PCBs, Σ DDTs and Σ Cyclodienes measured in this study are similar to those recently reported for other locations within the Great Lakes basin. For example, Buell et al. (2021) reported Σ PCB concentrations ranging from 5 – 75 pg/L and from 1 – 29 pg/L for Σ DDTs across and four locations in Lake Huron's Georgian Bay. These compare to a range of 8 – 65 ng/L Σ PCBs and from

19.4 – 202.5 pg/L for Σ DDTs. Similarly, Buell et al. (2021) reported a range of concentrations from 5 – 49 pg/L for cyclodiene compounds in Georgian Bay. In the Boardman River Σ cyclodiene concentrations, although still low and below water quality criteria, were higher relative to the results reported by Buell et al. (2021) for Georgian Bay waters ranged from 0.6 – 220.7 pg/L. Cyclodiene concentrations also demonstrated a general pattern of increasing concentrations along the length of the Boardman River, from the Brown Bridge site to the Wadsworth St. and Lower Boardman River sites downstream. This trend may reflect the changes in land-use patterns that occur over the 20 mile stretch of the Boardman River sampled in this study. For example, the Brown Bridge site is located in a region of the watershed where over 70% of land-use is predominated by forest cover and open grasslands (Cummings et al. 1990). This contrasts the lower river sampling sites from Union St. Dam to the Lower Boardman River site that were located within the residential stretch of the river that is predominated by residential and commercial development (Cummings et al. 1990). Chlordane was a predominant cyclodiene pesticide used in the state of Michigan for the domestic control of termites and carpenter ants until restrictions were placed on its use in the early 1980s (Engler & Harding 2000). Chlordane has a half-life in soils of up to 3500 days which suggests a timeframe of over 40 years for complete dissipation from this type of environmental media (National Pesticide Information Center 2000). Thus, the downstream trend in cyclodiene concentrations may represent remaining trace evidence of such residential chlordane application and use for domestic pest control in this stretch of the Boardman River. This contrast in land use patterns and also the history associated with the

remediation and restoration of the river may also contribute to some of the patterns observed in POP concentrations along the monitored stretch.

From the principal components analysis of the SPMD loads, there was a separation of sites that corresponded to their general locations along the Boardman River. As an example, the ordination of the Brown Bridge and Sabin Dam sites were similar in this multivariate analysis. In addition to being locations of former dam impoundments, these locations were also the furthest from the river mouth and generally located in more rural areas of the watershed. The ordination of these 2019 samples also reflected a greater contribution of PCBs and increasingly hydrophobic compounds to the total load of pollutants quantified on SPMDs deployed at these sites. In this analysis, the positive direction of the first principal component was primarily associated with increased proportions of PCBs with OC pesticides describing the negative direction along this axis. Both the Brown Bridge and Sabin Dam SPMD deployment sites were in areas where dam impoundments were formerly located. Sediment sorption is the primary fate of POPs in aquatic ecosystems (Luthy 2004; Werner et al. 2010). Given that increasingly hydrophobic higher $\text{Log}K_{\text{ow}}$ compounds tend to sorb more tightly to organic materials relative to less hydrophobic compounds (Karickhoff 1981; Werner et al. 2010), the similar ordination of these two locations may reflect legacy effects of the former sediment impoundments. For example, over 65,000 and 260,000 yd^3 of sediment were removed from these locations during restoration (US Army Corps of Engineers 2014). The OC pesticides included in this study had an average $\text{Log}K_{\text{ow}}$ of 5.3 which compares to a value of 6.7 for the PCBs quantified here. Thus, the similar ordination of the SPMD profiles for these two sites may reflect residual effects of the former impoundments on

the overall profile. It must be noted though that although the POP profiles at these locations possibly reflect such former sediment impoundments, they do not appear to represent significant sources of POP release into the river. Specifically, the magnitudes of the POP concentrations remain below guideline levels. Also, the Brown Bridge and Sabin Dam sites are more rural relative to the other downstream locations which are within the urban and residential area of Traverse City region (Cumming et al. 1990). This compares to the Sabin Dam and Brown Bridge locations that are generally surrounded by land-use practices that include primarily grassland and forested habitats, respectively, (Cummings et al. 1990) that may have experienced reduced degrees of OC pesticides use relative to urban and residential areas.

The spatial patterns in the 2020 PCA analysis were similar to the 2019 analysis with a separation of the Brown Bridge and Sabin Dam sites being closely ordinated on the first and second principal component axis, establishing a similar rural fingerprint to what was observed in the 2019 PCA analysis. The spatial association among the more urban sampling sites was less clear for the 2020 sampling as these locations were less closely ordinated but also distinct from the more rural Brown Bridge and Sabin Dam locations. An additional spatial pattern demonstrated from the PCA analyses was that the Union St. Dam site tended to have a more unique profile that didn't associated with a general rural or urban designation. For example, in 2019 this site ordinated very close to the origin of the first plot (PC1 vs PC2) suggesting that POP profiles were dominated by neither PCBs or OC pesticides. This compares to the 2020 PCA in which this site plotted in the negative directions of the first and second principal components suggesting an influence of OC pesticides in the SPMD loads. The Union St site is unique in the

Boardman River as it is the only site that still has a dam present and used to help regulate water levels in upstream Boardman Lake. This lake has a surface area of 340 acres and a maximum depth of 64 feet (Brown, 1939) and thus represents a substantial dilution volume just upstream of the Union St Dam site. Further, the Traverse City Regional Wastewater Treatment Plant discharge is located at the outflow of Boardman Lake and < 0.5 miles upstream of the Union St. Dam site. Wastewater treatment plants are well established as sources of legacy and emerging pollutants (Köck-Schulmeyer et al., 2013) and the presence of this facility immediately upstream from Union St. Dam has the potential to influence the suite of POPs accumulated by SPMDs deployed here. It is worth noting that despite these potential influences and a differing POP signature, the magnitudes of POP concentrations quantified from the Union St Dam SPMDs compared to the other sampled sites or the control also did not exceed any regulatory criteria.

In addition to the spatial comparison of POP patterns and concentrations among the different Boardman River deployment locations, a second aim of this study was to compare for any changes in POP concentrations between the two deployment years. While Σ PCB concentrations demonstrated limited overall change in magnitude, there was a general shift in congener profiles from the less hydrophobic tri- and tetrachlorobiphenyls that were predominant in the 2019 samples, to a predominance of penta- and heptachlorobiphenyl congeners for the 2020 SPMDs. Also, OC pesticide concentrations estimated from the 2020 deployments were significantly lower relative to those determined from the 2019 deployments. It is most likely that this result is associated with analytical rather than environmental variability. Specifically, the clean-up chromatography method used here to separate among PCBs and OC pesticides used

Florisol, a form of magnesium silicate that is activated through drying at temperatures ranging from 110 – 130 °C for POP analysis (Carroll 1961; Lazar et al. 1992). During the course of SPMD extraction and analysis of the 2020 samples, an analytical equipment failure is likely to have reduced the level of activation of the Florisol used here. Subsequently, increased moisture absorption by Florisol during storage likely hindered the extent of clean-up for the less hydrophobic lower Log K_{ow} compounds including some of OC pesticide compounds and the less chlorinated PCB congeners (Carroll 1961). Multivariate analysis of the 2020 results did demonstrate a spatial pattern among the various sampling locations in addition to a similar degree of precision among the individual SPMDs deployed at each of the sites. These spatial patterns in the results suggest that the environmental variability was captured but that the lower concentrations, especially for OC pesticides, indicate a lower degree of recovery of some of the compounds from the 2020 samples relative to the 2019 data. This corroboration provides a level of confidence in that the patterns observed are not simply the result of solely an analytical artifact and that the underlying spatial pattern in POP profiles were captured during the 2020 sampling. Also, despite a similarity in Σ PCB concentrations between the two sampling years, the differences in the suite of PCB congeners that predominated the 2019 vs. 2020 collections, precludes the capacity to properly compare Σ PCB concentrations between the sampling years. Given that POP concentrations appear to be near or close to limits of detection within the Boardman River, it is likely that a much longer time frame than encompassed during the current study would be required to quantify any temporal changes in POP concentrations.

The overall results of this study demonstrate that POP concentrations in the Boardman River approach limits of analytical detection, are consistent with other recent Great Lakes sampling results, and below regulatory criteria for these compounds for the protection of aquatic wildlife from long-term chronic effects associated with exposure (Buell et al. 2021; USEPA 1985). The POP concentrations quantified among the Boardman River sites were also very similar to that of our Grand Traverse Bay control. However, the POP profiles determined from the SPMD loads for some sites did differ from those for the control suggesting that there may be minor contributions of some of these pollutants due to such considerations such as land-use practices, urban run-off and potentially wastewater treatment plant effluent (Cumming et al. 1990; Köck-Schulmeyer et al., 2013). Broadly, these results suggest that the remediation and restoration efforts completed along the lower 25-mile stretch of the Boardman River did not result in a high degree of POP loading into the system. Lastly, it is considered that these efforts have likely been successful in mitigating any residual anthropogenic contamination of the Boardman River as associated with dam and associated impoundment removal.

5 General Conclusions

Passive sampling using semi-permeable membrane devices (SPMDs) is a valuable technique for monitoring concentrations of multiple anthropogenic pollutants including polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides, and polynuclear aromatic hydrocarbons (PAHs; Bennett et al. 1996; O'Toole et al. 2006; Buell et al. 2021). Additionally, the use of SPMDs is not limited to freshwater applications such as in the current research as they have also been used in marine environments (Degger et al., 2006), to quantify airborne levels and also quantify concentrations in soils (Bonetta et al., 2009). A further complement to such passive sampling methods is the addition of performance reference compounds (PRCs) during deployment. This approach provides the capacity to not only estimate time-weighted average concentrations (Buell et al. 2021) but also that the concentration estimates derived therein represent an integration of sporadic events such as high pulse storm run-off events, low flow conditions, and biofouling (Alvarez 2010). Passive sampling devices such as SPMDs also permit the sampling of much larger volumes of environmental media that are challenging to capture with traditional techniques such grab sampling methods (Huckins et al. 2006). From these perspectives, the use of SPMDs for monitoring POP concentrations following remediation and restoration efforts such as dam removal can be highly valuable for evaluating the success of such efforts at mitigating potential POP contamination associated with the legacy of dam construction along river ecosystems.

The primary aim of this research was to use SPMDs to investigate spatial and temporal patterns in POP contamination of the Boardman River as generally associated

with the removal of dams and impoundment pounds along the lower 25-mile stretch of this waterway. Overall, this study demonstrated very low levels of POP contamination in this region of the Boardman River that suggest negligible legacy contamination of this ecosystem. For example, previous analysis of sediments collected from Boardman Lake demonstrated low levels of PCB contamination in this region of the river (U.S. Army Corps of Engineers 2014). Given that lake sediments tend to represent a long-term sink of POPs, this suggests that historical contamination or point source loadings into headwaters of the Boardman River above the lake were likely negligible. However, this study did demonstrate subtle differences in the overall profiles of PCBs and OC pesticides among the different sites. For example, the differences in POP contamination profiles at the Brown Bridge and Sabin Dam locations were suggested to reflect the potential legacy effects of the impoundments that previously existed at these locations. Although the concentrations of the specific pollutants that characterized these locations were not above guideline levels, these differences potentially emphasize the capacity of SPMDs, and other passive sampling deployment techniques, to sample large volumes of water and capture spatial trends that otherwise may not be detected using single time point samples such as grab sampling (Huckins et al., 1993).

Given the trace levels of POP contamination quantified in the Boardman River in this study, it is difficult to conclude regarding the effectiveness of the short-term nature of the temporal comparison conducted here and regardless of any analytical considerations. It would be valuable, however, to revisit this study design following a longer time period to determine if any changes in POP concentrations were evident. Most importantly, such a study would be more likely to assess increases in POP contamination

given the generally clean assessment that could be concluded for the Boardman River from this study. Additional seasonal sampling such as following snow-melt in the spring could also be valuable to assess the extent to which such events contribute a possible pulse loading of POPs into the river. The seasonal migration of Great Lakes salmonid predators into inland tributaries such as the Boardman River could also represent an additional opportunity to conduct seasonal SPMD deployment to assess the magnitude to which such behavior could contribute to POP loading into this ecosystem (O'Toole et al. 2006; Gerig et al. 2020)

The contamination of Great Lakes surface waters with pollutants such as PCBs, OC pesticides and PAHs continues to pose concern in regions such as those designated as Great Lakes Areas of Concern (Helfrich and Armstrong 1989; Buell et al. 2021). More recently additional classes of pollutants such as pharmaceuticals, illicit compounds and poly- and perfluoroalkylated substances (PFAS) have become pollutants of emerging concern within the Great Lakes basin (Klecka et al. 2010). Recent improvements in passive sampling techniques to capture dissolved concentrations of these potentially more water-soluble compounds have increased the scope for monitoring trace levels of these emerging pollutants. For example, wastewater treatment plant (WWTP) effluents are known sources of such classes of pollutants into receiving waters (Köck-Schulmeyer et al. 2013). Given that the Traverse City Regional WWTP discharges its treated effluent into the Boardman River, passive monitoring techniques could be used to assess the extent to which such pollutants are potentially released from the WWTP following the sewage treatment process. Such a design could help establish the extent to which WWTPs contribute to the spatial patterns within an aquatic ecosystem such as observed

in this study. This may be especially true for PFAS which have been observed in varying levels throughout the Great Lakes area over the past decade (Gewurtz et al 2019) and typically exhibit carcinogenic characteristics (Temkin et al. 2020). Such a study could prove worthwhile to expand the application of passive sampling techniques to complement the current information available regarding PFAS concentrations present in Michigan surface waters.

6 References

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7 Thesis tables

Table 1: Summary information for dams located on the Boardman River, Grand Traverse and Kalkaska Counties, Michigan.

Dam	Location (river mi) ^a	Impoundment area (acres) ^a	Year constructed ^a	Year removed ^b	Sediment volume removed (yd ³) ^{c,d}
Union St. Dam	1.5	339	1867	N/A	N/A
Sabin Dam	5.3	40	1902	2018	65,750
Boardman Dam	6.1	103	1894	2017	272,000
Brown Bridge Dam	18.5	191	1921	2013	260,000

^a United States Army Corps of Engineers (2005).

^b Information retrieved from the Boardman River restoration website (<http://theboardman.org/boardman-river/history.html>).

^c Information retrieved from the Boardman River restoration website (<http://theboardman.org/userfiles/filemanager/526/> - Phase I: The Brown Bridge Dam removal).

^d Inter-fleuve and URS (2014).

Table 2: Semi-permeable membrane device (SPMD) deployment site information including river mile from the mouth of the Boardman River, average water temperature recorded during deployments at each site, and the approximate latitude and longitude of each deployment location.

Deployment location	River mile distance (Mi)	Average water temperature ^a (°F)		Approximate latitude and longitude (°N/°W)
		2019	2020	
Lower Boardman	0.4	69.4	71.3	44.76469 -85.61985
Wadsworth	0.8	69.5	71.6	44.76355 -85.62818
Union St. Dam	1.1	69.5	71.4	44.76206 -85.62369
Boardman Lake	1.9	71.3	73.3	44.75660 -85.61009
Sabin Dam	5.4	65.9	67.4 ^b	44.70775 -85.62318
Brown Bridge	18.3	60.9	63.1	44.64340 -85.50939
Grand Traverse Control	N/A	71.9	74.5	44.92821 -85.49096

^a Temperature profiles recorded during each SPMD deployment are provided in Appendix figures A4 – A10.

^b Temperature for Sabin Dam location estimated using data recorded at upstream and downstream locations in 2019 and 2020.

Table 3: PCB congeners of interest to this study and their associated octanol-water partition coefficients (Log K_{ow}). Congener Log K_{ow} values are from Hawker and Connell (1988).

PCB Congener	Log K_{ow}
PCB 18	5.24
PCB 17	5.25
PCB 31	5.67
PCB 28	5.67
PCB 33	5.60
PCB 52	5.84
PCB 49	5.85
PCB 44	5.75
PCB 74	6.20
PCB 70	6.20
PCB 95	6.13
PCB 101	6.38
PCB 99	6.39
PCB 87	6.29
PCB 110	6.48
PCB 151	6.64
PCB 82	6.20
PCB 149	6.67
PCB 118	6.74
PCB 153	6.92
PCB 105	6.65
PCB 132	6.58
PCB 138	6.83
PCB 158	7.02
PCB 187	7.17
PCB 183	7.20
PCB 128	6.74
PCB 177	7.08
PCB 156	7.18
PCB 171	7.11
PCB 180	7.36
PCB 191	7.55
PCB 169	7.42
PCB 170	7.27
PCB 199	7.20
PCB 195	7.56
PCB 208	7.71
PCB 194	7.80
PCB 205	8.00
PCB 206	8.09
PCB 209	8.18

Table 4: Octanol-water partition coefficients (Log K_{ow}) for the select organochlorine pesticide compounds analyzed for in extracts from semi-permeable membrane devices (SPMD) deployed in the Boardman River, Traverse City, Michigan in 2019 and 2020. Abbreviations for each compound as used within the thesis text are also provided. Log K_{ow} values for each compound reflect those reported by Alvarez (2010 a,b).

Organochlorine compound	Abbreviation	Log K_{ow}
1,2,4,5-TCB	TCB-1	4.60
1,2,3,4-TCB	TCB-2	4.64
Pentachlorobenzene	QCB	5.18
α - hexachlorocyclohexane	a-BHC	3.86
Hexachlorobenzene	HCB	5.71
β - hexachlorocyclohexane	b-BHC	3.86
γ - hexachlorocyclohexane	Lindane	3.71
Octachlorostyrene	OCS	6.29
Oxychlordan	-	5.48
Trans-chlordan	<i>t</i> -chlordan	5.38
Cis-chlordan	<i>c</i> -chlordan	5.38
Trans-nonachlor	<i>t</i> -nonachlor	6.35
<i>p,p'</i> -DDE	-	6.14
<i>p,p'</i> -DDD	-	5.75
Cis-nonachlor	<i>c</i> -nonachlor	6.20
<i>p,p'</i> -DDT	-	5.47
Mirex	-	6.89

Table 5: Summary analysis of variance (ANOVA) statistics comparing Σ PCB, Σ Cyclodienes and Σ DDT concentrations (pg/L) and total persistent organic pollutant loads (POP load – ng/SPMD) across Boardman River semi-permeable membrane device deployment locations in 2019 and 2020 field seasons.

Pollutant group	2019		2020	
	<i>F</i> -statistic	<i>p</i> -value	<i>F</i> -statistic	<i>p</i> -value
Σ PCBs	$F_{6,14} = 3964.6$	< 0.001	$F_{6,14} = 155.3$	< 0.001
Σ Cyclodienes	$F_{6,14} = 5889.3$	< 0.001	$F_{6,14} = 28.26$	< 0.001
Σ DDTs	$F_{6,14} = 4188.9$	< 0.001	$F_{6,14} = 8.885$	< 0.001
POP load	$F_{6,14} = 4753.6$	< 0.001	$F_{6,14} = 227.6$	< 0.001

Table 6: Principal component loadings for select PCB congeners and organochlorine pesticides quantified in semi-permeable membrane device extracts following deployment in the Boardman River, Traverse City MI in 2019. Total percent variance explained by each principal component is also provided. Compound names associated with organochlorine abbreviations are provided in Table 4.

Persistent organic pollutant	Principal component 1	Principal component 2	Principal component 3
PCB44	-0.128	0.857	-0.096
PCB49	0.178	0.882	0.191
PCB74	0.854	-0.145	-0.243
PCB70	0.653	-0.001	0.650
PCB95	0.060	0.934	0.016
PCB101	-0.420	0.639	0.219
PCB99	0.927	0.022	-0.017
PCB149	0.667	0.354	0.433
PCB138	0.877	-0.293	-0.268
PCB180	0.726	0.526	-0.041
TCB-1	-0.010	-0.786	0.537
HCB	-0.496	0.146	0.786
<i>t</i> -chlordane	0.020	0.099	0.948
<i>p,p'</i> -DDD	-0.159	-0.201	0.892
Total variance (%)	30.4	28.5	24.5

Table 7: Principal component loadings for select PCB congeners and organochlorine pesticides quantified in semi-permeable membrane device extracts following deployment in the Boardman River, Traverse City MI in 2020. Total percent variance explained by each principal component is also provided. Compound names associated with organochlorine abbreviations are provided in Table 4.

Persistent organic pollutant	Principal Component 1	Principal Component 2	Principal Component 3
PCB99	0.930	-0.116	0.065
PCB177	0.873	0.353	0.098
PCB191	-0.686	0.584	-0.099
TCB-1	0.480	0.811	<0.001
TCB-2	-0.623	-0.208	-0.439
HCB	0.038	0.111	0.970
b-BHC	-0.911	-0.380	0.104
<i>t</i> -chlordane	-0.009	0.947	0.057
<i>p,p'</i> -DDD	0.162	0.855	0.330
Total variance (%)	39.7	33.0	14.2

8 Thesis figures

Figure 1: Boardman River watershed location in Grand Traverse and Kalkaska Counties, Michigan. Inset indicates location of the Boardman River within the Great Lakes basin.

Figure 2: Examples of (A) a semi-permeable membrane device (SPMD) mounted on a carrier for field deployment and (B) the protective cage into which the carrier is placed during SPMD field deployment. Image courtesy of Environmental Sampling Technologies (<https://www.est-lab.com/spmd.php>).

Figure 3: Location of SPMD deployment locations in the Boardman River in 2019 and 2020. A control set of SPMDs was deployed in Grand Traverse Bay, Lake Michigan. A set of control SPMDs were deployed in Grand Traverse Bay, MI (not shown).

Figure 4: Average Σ PCB, Σ DDT and Σ Cyclodiene water concentrations (pg/L) estimated from SPMDs deployed in the Boardman River in (A) 2019 and (B) 2020. Bars indicate average $\pm$ 1 standard deviation. In panel (B), Σ DDT and Σ Cyclodiene concentrations are plotted against secondary y-axis. Note differences in y-axis scales between panels.

Figure 5: Composition of polychlorinated biphenyl congener chlorination groups quantified in Boardman River SPMDs during deployment in (A) 2019 and (B) 2020. Chlorination groups are expressed as a proportion of sum PCBs (Σ PCB). Bars represent average $\pm$ 1 standard deviation.

Figure 6: PCB (1° y-axis) and OC pesticides (2° y-axis) as a proportion of total SPMD load (ng/SPMD) quantified in (A) 2019 and (B) 2020. Bars indicate average $\pm$ 1 standard deviation. Note differences in y-axis scales between panels.

Figure 7: Principal component (PC) ordination of persistent organic pollutant loads quantified during SPMD deployment in the Boardman River, 2019. Panel (A) provides the plot of PC1 vs PC2 with panel (B) providing the plot of PC1 vs PC3. Percent total variance included in each component is included with axis labels. Principal component analysis results are presented in Table 6.

Figure 8: Principal component (PC) ordination of persistent organic pollutant loads quantified during SPMD deployment in the Boardman River, 2020. Panel (A) provides the plot of PC1 vs PC2 with panel (B) providing the plot of PC1 vs PC3. Percent total variance included in each component is included with axis labels. Principal component analysis results are presented in Table 7.

A Appendices

Table A1: Method limits of detection (LOD) for PCBs quantified in this study and provided by the Great Lakes Institute for Environmental Research's Organic Analytical Laboratory Standard Operating Procedure: Organic Analytical Methods.

PCB Congener	Method LOD (ug/kg)
PCB 18	0.076
PCB 17	0.076
PCB 31	0.076
PCB 28	0.076
PCB 33	0.076
PCB 52	0.038
PCB 49	0.027
PCB 44	0.060
PCB 74	0.024
PCB 70	0.024
PCB 95	0.032
PCB 101	0.090
PCB 99	0.044
PCB 87	0.022
PCB 110	0.076
PCB 151	0.023
PCB 82	0.023
PCB 149	0.054
PCB 118	0.064
PCB 153	0.071
PCB 105	0.074
PCB 132	0.074
PCB 138	0.023
PCB 158	0.071
PCB 187	0.063
PCB 183	0.050
PCB 128	0.044
PCB 177	0.065
PCB 156	0.124
PCB 171	0.124
PCB 180	0.048
PCB 191	0.076
PCB 169	0.124
PCB 170	0.076
PCB 199	0.039
PCB 195	0.074
PCB 208	0.074
PCB 194	0.039
PCB 205	0.023
PCB 206	0.061
PCB 209	0.040

Table A2: Method limits of detection (LOD) for the select organochlorine pesticide compounds analyzed for in extracts from semi-permeable membrane devices (SPMD) deployed in the Boardman River, Traverse City, Michigan in 2019 and 2020. Abbreviations for each compound as used within the thesis text are also provided. Compound detection limits are provided from University of Windsor's Great Lakes Institute for Environmental Research's Organic Analytical Laboratory Standard Operating Procedure: Organic Analytical Methods and specific for the gas chromatographic methods used in this study.

Organochlorine compound	Abbreviation	Method LOD (ug/kg)
1,2,4,5-TCB	TCB-1	0.079
1,2,3,4-TCB	TCB-2	0.039
Pentachlorobenzene	QCB	0.030
α -benzene-hexachloride	a-BHC	0.032
Hexachlorobenzene	HCb	0.055
β -benzene-hexachloride	b-BHC	0.068
Lindane	-	0.048
Octachlorostyrene	OCS	0.025
Oxychlordan	-	0.076
Trans-chlordan	<i>t</i> -chlordan	0.051
Cis-chlordan	<i>c</i> -chlordan	0.040
Trans-nonachlor	<i>t</i> -nonachlor	0.025
<i>p,p'</i> -DDE	-	0.073
<i>p,p'</i> -DDD	-	0.011
Cis-nonachlor	<i>c</i> -nonachlor	0.049
<i>p,p'</i> -DDT	-	0.032
Mirex	-	0.018

Figure A1: Sample chromatogram of organochlorine pesticide standard used to identify and quantify organochlorine pesticide compound residues in SPMD extracts. Compound abbreviations are provided in Table 4.

Figure A2: Sample chromatogram of the Environment PCB congener standard used to identify and quantify PCB congener residues in SPMD extracts. Numbers associated with each peak represent individual or coeluting congeners (Table 3).

Figure A3. Sample chromatogram of five performance reference PCB congeners used for spiking SPMDs prior to deployment and for calculation of dissolved water concentrations of target analytes in Tables 3 and 4.

Figure A4: Temperature profiles for SPMDs deployed at Brown Bridge site in (A) 2019 and (B) 2020. Data points represent mean $\pm$ 1 standard deviation.

Figure A5: Temperature profiles for SPMDs deployed at Sabin Dam site in (A) 2019 and (B) 2020. Due to remote logger malfunction, temperatures for 2020 were estimated using 2019 data and difference to upstream site (Brown Bridge). Data points represent mean $\pm$ 1 standard deviation.

Figure A6: Temperature profiles for SPMDs deployed at Boardman Lake site in (A) 2019 and (B) 2020. Data points represent mean $\pm$ 1 standard deviation.

Figure A7: Temperature profiles for SPMDs deployed at Union St. Dam site in (A) 2019 and (B) 2020. Data points represent mean $\pm$ 1 standard deviation.

Figure A8: Temperature profiles for SPMDs deployed at Wadsworth St. site in (A) 2019 and (B) 2020. Data points represent mean $\pm$ 1 standard deviation.

Figure A9: Temperature profiles for SPMDs deployed at Lower Boardman River site in (A) 2019 and (B) 2020. Data points represent mean $\pm$ 1 standard deviation.

Figure A10: Temperature profiles for SPMDs deployed at Grand Traverse Bay Control site in (A) 2019 and (B) 2020. Data points represent mean $\pm$ 1 standard deviation.