A Comparison of Dreissenid Mussels and Passive Samplers as Monitors of Contaminants of Emerging Concern and Polycyclic Aromatic Hydrocarbons in the Great Lakes

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A Comparison of Dreissenid Mussels and Passive Samplers as Monitors of Contaminants of Emerging Concern and Polycyclic Aromatic Hydrocarbons in the Great Lakes

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Gina M. Raimondo Secretary	Richard W. Spinrad Under Secretary	Nicole LeBoeuf Assistant Administrator

EXECUTIVE SUMMARY

Advancements in the use of passive sampling devices (PSDs) for environmental monitoring of contaminants has led to suggestions that PSDs could be used to replace traditional biomonitoring approaches such as sentinel organisms (*e.g.*, mussels). PSDs offer a number of advantages over the use of organisms for aquatic biomonitoring, including the ability to measure contaminants in impaired environments that would be stressful to aquatic biota, and the known relationship between hydrophobic contaminant levels in PSDs and aquatic organisms. Though relationships between hydrophobic legacy contaminants measured using PSDs and mussels have been well studied, there is a lack of information comparing levels of hydrophilic contaminants of emerging concern (CECs) in PSDs and sentinel organisms. Consequently, the present study aimed to utilize data from several place-based assessments in the Great Lakes where PSDs (Polar Organic Chemical Integrative Samplers [POCIS] and Semi Permeable Membrane Devices [SPMDs]) and dreissenid mussels were co-deployed to compare the occurrence and concentrations of a suite of CECs and polycyclic aromatic hydrocarbons (PAHs) in PSDs and mussels. For the pharmaceutical and personal care products (PPCPs), POCIS was more effective at accumulating a broad suite of hydrophilic compounds compared to mussels alone, though mussels accumulated a small number of PPCPs that were never detected using PSDs. Overall, poor correlation between concentrations of a suite of five PPCPs in POCIS and mussels was observed, with significant relationships observed for only two of five compounds (diphenhydramine and sertraline). Similar findings were observed for pesticides, with POCIS more effective at accumulating hydrophilic current use compounds compared to mussels, and more hydrophobic legacy contaminants detected in mussels. The current use herbicide atrazine, a known priority contaminant in the Great Lakes basin, had a weak, non-significant relationship between concentrations measured using POCIS and mussels. In terms of PAHs measured using SPMDs, good agreement was observed between compounds detected in SPMDs and mussels, as well as strong, highly significant relationships between concentrations of total parent and total alkylated PAHs in mussels and SPMDs. However, the composition of PAHs accumulated between the two matrices showed several significant differences, leading to variation in PAH diagnostic ratios calculated using either PSDs or mussels. Finally, legacy pesticide detections and concentrations measured using SPMDs and mussels generally showed good agreement. Implications for designing environmental monitoring studies and potential limitations of different sampling approaches are discussed further within. This study will support the design and implementation of effective environmental monitoring within the Great Lakes.

KEY FINDINGS

- POCIS was found to accumulate more pharmaceutical and personal care products (64 compounds) compared to mussels alone (47 compounds).
- Several PPCP compounds including gemfibrozil, valsartan, and carbamazepine were commonly detected in POCIS (detection frequencies of 96, 100, and 56%, respectively) but never detected in mussels.
- Of five compounds with adequate data coverage for comparison of concentrations in POCIS and mussels, significant relationships were only found for two (sertraline and diphenhydramine).
- POCIS was found to accumulate a greater number of hydrophilic current use pesticides compared to mussels which preferentially accumulated legacy hydrophobic compounds.
- A weak, non-significant relationship between atrazine concentrations measured in POCIS and mussels was found, though a highly significant relationship was observed for its primary transformation product, desethylatrazine.
- Findings suggest that POCIS is more effective at accumulating hydrophilic, largely non-bioaccumulative CECs compared to mussels, though mussels may be needed to contextualize PSD data.
- For PAHs, total parent and alkylated PAH concentrations measured using SPMDs were strongly correlated with concentrations in mussels, suggesting SPMDs can be used to adequately predict total PAH residues in mussels.
- Differences in PAH compositions between SPMDs and mussels were observed, with higher relative concentrations of pyrene and phenanthrene in SPMDs relative to mussels.
- Results suggest SPMDs and mussels are not equivalent in terms of determining source apportionment of PAHs, likely due to contribution of particulate-bound PAHs to mussel PAH residues which are not reflected by SPMDs.
- Legacy pesticides measured in SPMDs and mussels showed good agreement in terms of detections and total concentrations.
- Recommendations for environmental monitoring programs are presented within.

Table of Contents

COMMONLY USED ACRONYMS

AOC Area of Concern

CEC Contaminants of Emerging Concern

GLRI Great Lakes Restoration Initiative

MWP Mussel Watch Program

PAH Polycyclic Aromatic Hydrocarbons

POCIS Polar Organic Chemical Integrative Samplers

PPCP Pharmaceutical and Personal Care Product

PRC Performance Reference Compound

PSDs Passive Sampling Devices

SPMD Semi Permeable Membrane Device

Introduction

Chemical pollutants, including contaminants of emerging concern (CECs) and legacy pollutants, have been identified as one of the major stressors facing the Laurentian Great Lakes and its aquatic biota (Smith et al., 2019, USEPA, 2020). The Great Lakes Restoration Initiative (GLRI) was subsequently introduced in 2010 to accelerate restoration and monitoring efforts within the basin, including a focus area on contaminant monitoring (GLRI, 2019). Consequently, a range of long-term contaminant monitoring initiatives including the Great Lakes Fish Monitoring and Surveillance Program and the NOAA Mussel Watch Program (MWP) have been established, focusing on contaminant levels in top predator fish and invasive dreissenid mussels, respectively (Burlakova et al., 2018; Kimbrough et al., 2018). These monitoring programs have been operated over large spatial and temporal scales and have been used in part to assess the efficacy of management and remediation activities aimed at reducing levels of contaminants (Zhou et al., 2018). In general, the use of aquatic organisms for chemical biomonitoring is advantageous since accumulation within tissue directly reflects the bioavailability and potential for trophic transfer and/or ecological health impacts (Joyce et al., 2016). Among the aquatic organisms routinely used for monitoring, bivalve molluscs such as mussels possess a suite of characteristics that make them effective indicators of environmental contaminants including a limited capacity to metabolize xenobiotics, sessile nature, and widespread abundance. Consequently, mussels have been used in global biomonitoring programs for a suite of contaminants including heavy metals (Kraak et al., 1991), pesticides (Scarpato et al., 2010), and polychlorinated biphenyls (PCBs; Richman et al., 2011).

Concomitantly, over the past decade significant advances have been achieved in the monitoring of bioavailable contaminants in the aquatic environment using passive sampling devices (PSDs). Passive sampling involves deployment of a sorption phase in a given medium (typically water or sediment), where the targeted compounds are sampled at a rate proportional to the difference in chemical activity between sampler and medium, and where the uptake kinetics are controlled by passive processes including diffusion and ambient convection (Booij et al., 2016). PSDs assess the freely dissolved and bioavailable concentration of a given contaminant, compared with traditional techniques such as grab sampling that provide the total concentration (*i.e.*, freely dissolved and colloidally bound). In addition, PSDs can be used to target CECs that are not present at sufficient concentrations to be measured using traditional grab sampling, or more hydrophilic compounds (*i.e.*, Log K_{ow} < 3) that are not as bioaccumulative in aquatic biota (Alvarez et al., 2014). Consequently, agencies conducting chemical monitoring within the Great Lakes have adopted the use of passive samplers for basin-wide monitoring of CECs and legacy contaminants (Alvarez et al., 2021; Loken et al., 2022).

Passive sampling is thought to have several advantages over biomonitoring in terms of its potential use in monitoring programs (Burgess et al., 2022). For example, passive samplers can be deployed in habitats and environments that are highly stressful to aquatic organisms, such as hypoxic or high temperature areas (Burgess et al., 2022), or where sufficient biomass of the target biomonitoring species is unavailable. Furthermore, studies have indicated that freely dissolved bioavailable concentrations of contaminants measured using passive samplers are highly correlated with tissue residues in aquatic organisms (Harwood et al., 2013; Joyce et al., 2016; Schmidt and Burgess, 2020). In recent years, emphasis has been placed on minimizing the use of living organisms for scientific research (National Research Council, 2007), conferring another advantage for passive sampling (Burgess et al., 2022). Consequently, a number of studies have focused on comparing accumulation of contaminants in co-deployed passive samplers and bivalve molluscs under field conditions (Alvarez et al., 2014; Harman et al., 2011; Burgess et al., 2015). The majority of these studies focus on legacy contaminants such as PCBs (Burgess et al., 2015, 2022) and polycyclic aromatic hydrocarbons (PAHs; Boehm et al., 2005; Bourgeault and Gourlay-France, 2013), with comparatively fewer studies considering emerging contaminant groups such as pharmaceuticals and personal care products (PPCPs; Grabicová et al., 2022; Pintado-Hererra et al., 2020). For more hydrophobic compounds (*i.e.* log K_{ow} > 4), previous studies have found significant positive correlations between freely dissolved concentrations measured using passive samplers and levels in mussel tissue (Alvarez et al., 2014; Peven et al., 1996; Smedes et al., 2007).

Introduction

These findings are not ubiquitous however, with a number of studies finding that concentrations of PAHs measured using SPMDs were not robust predictors of levels in mussel tissue (Bourgeault and Gourlay-Francé, 2013; Harman et al., 2011). For pharmaceuticals, Grabicová et al., (2022) demonstrated a relationship between presence and concentrations in zebra mussels compared to POCIS passive samplers, whereas Pintado-Herrera et al., (2020) found accumulation of different personal care compounds between silicone rubber samplers and clams. Bioaccumulation in bivalves is influenced by a suite of abiotic and biotic factors including ambient temperature, conductivity, reproductive status (Gonzalez-Fernandez et al., 2016), and exposure level of a given xenobiotic (Gilroy et al., 2014). Comparatively, accumulation of contaminants on SPMD and POCIS devices can be influenced by biofouling (Harman et al., 2009), levels of dissolved organic matter (Li et al., 2016), and effects of temperature, pH and flow on sampling rates (Li et al., 2011, 2016). Further studies comparing the differences between CEC accumulation in passive samplers and biomonitors under different environmental conditions are required to elucidate the factors driving potential differences and assess the performance of passive samplers in lieu of sentinel organisms.

Taking these knowledge gaps into account, the present study aimed to compare accumulation of a large suite of CECs in passive samplers (POCIS and SPMDs) and caged dreissenid mussels from several place-based assessments conducted in the Great Lakes from 2015 - 2018. These studies included deployment in known areas of concern (AOCs) such as the Milwaukee Estuary and Maumee River, as well as areas of lower contamination (Table 1). AOCs are defined as 'geographic areas designated by the Parties where significant impairment of beneficial uses has occurred as a result of human activities at the local level' (GLWQA, 2012). The present study focuses on the differences between CEC accumulation in passive samplers and mussels; thus, detailed descriptions of place-based assessments are available elsewhere (Kimbrough et al., 2018). Specifically, this paper aims to; 1) assess the efficacy of using passive samplers where biomass of source dreissenids is limited; 2) assess differences between accumulation in passive samplers and mussels; 3) detail this multimatrix approach. Elucidating the differences between passive samplers and active biomonitoring using dreissenid mussels is fundamental to designing and implementing appropriate monitoring techniques for effective environmental management.

Table 1. Locations, dates and durations of passive sampler deployments in the Great Lakes. P = POCIS deployment, S = SPMD deployment.

Study Location	Year	POCIS/SPMD	Deployment Dates	Deployment Duration (days)
Maumee River	2015	P	5/11/2015 - 6/9/2015	29
Ottawa River	2015	P	5/11/2015 - 6/9/2015	29
Maumee River	2016	P	5/24/2016 – 6/20/2016	27
Rouge River	2016	P	5/25/2016 - 6/22/2016	28
Milwaukee Bay	2017	P, S	6/7/2017 - 8/1/2017	55
Milwaukee Bay	2018	P, S	6/7/2018 - 7/10/2018	33
Muskegon Pierhead	2018	P, S	5/2/2018 - 5/29/2018	27
Muskegon Pierhead	2018	P, S	5/29/2018 - 6/26/2018	28
Muskegon Pierhead	2018	P, S	6/26/2018 - 9/18/2018	84
Muskegon Pierhead	2018	P, S	9/18/2018 - 11/27/2018	39

Methods

2.1 Deployment Locations, Durations and Study Design

Passive samplers (POCIS and SPMDs) were co-deployed with dreissenid mussels as part of several area-focused studies within the Great Lakes from 2015 - 2018, including the Maumee and Ottawa Rivers, Milwaukee Bay, and the mouth of Muskegon Lake. SPMDs were only deployed in the Milwaukee Bay and Muskegon Studies in 2017 and 2018, whereas POCIS were recorded at all the aforementioned sites in 2015 - 2018. Colocated samples were deployed and retrieved at the same time at each site, providing a consistent comparison throughout the dataset. Caged mussels were used at all sites and deployments excluding the Muskegon study (Table 1, Table A1). Durations and dates for all deployments are shown in Table 1. Specific locations for individual sites are shown in Table A1 and Figure A3.

The Maumee and Ottawa Rivers, sampled in 2015 and 2016 and 2015 respectively (Table A1, Figures A1 and A3), were part of a targeted study focusing on CEC and legacy contaminant presence within the Maumee area of concern (Kimbrough et al., 2018). The Maumee AOC comprises > 2000 km^2 and represents one of the largest AOCs within the United States, with a total of 8 current beneficial use impairments (USEPA, 2022). The area comprises cultivated cropland as well as highly developed areas in the Toledo area (Kimbrough et al., 2018). Passive sampler and mussel deployment within this area included a site downstream of the Toledo Wastewater Treatment Plant (WWTP), a site at the confluence of the Maumee River and Lake Michigan, and three sites in the Ottawa River (Table A1). In addition, three sites on the Rouge River were included in 2016, all of which were located in the highly developed Detroit area (Table A1). The Rouge river sites included a site downstream of the Detroit WWTP, a site located near to a combined sewage outflow, and a site near a highly industrialized islet (Table SX). Passive sampler deployments in 2017 and 2018 focused on the Milwaukee Estuary, another AOC which incorporates highly industrialized and developed areas within the city of Milwaukee (USEPA, 2022). Previous studies have demonstrated high levels of PAHs within the estuary, as well as emerging contaminants such as pharmaceuticals (Li et al., 2017). The sites included within this study span several tributaries to the estuary (Milwaukee, Kinnickinnic, and Menomonee Rivers) as well as nearshore and offshore sites (Table A1, Figure A3). Finally, a temporal study was conducted in 2018 involving repeated collection of dreissenid mussels in conjunction with passive sampler deployment at a site located at the mouth of Muskegon Lake (Table A1). This area is known to be of lower contamination relative to other areas within the Great Lakes basin (Kimbrough et al., 2014).

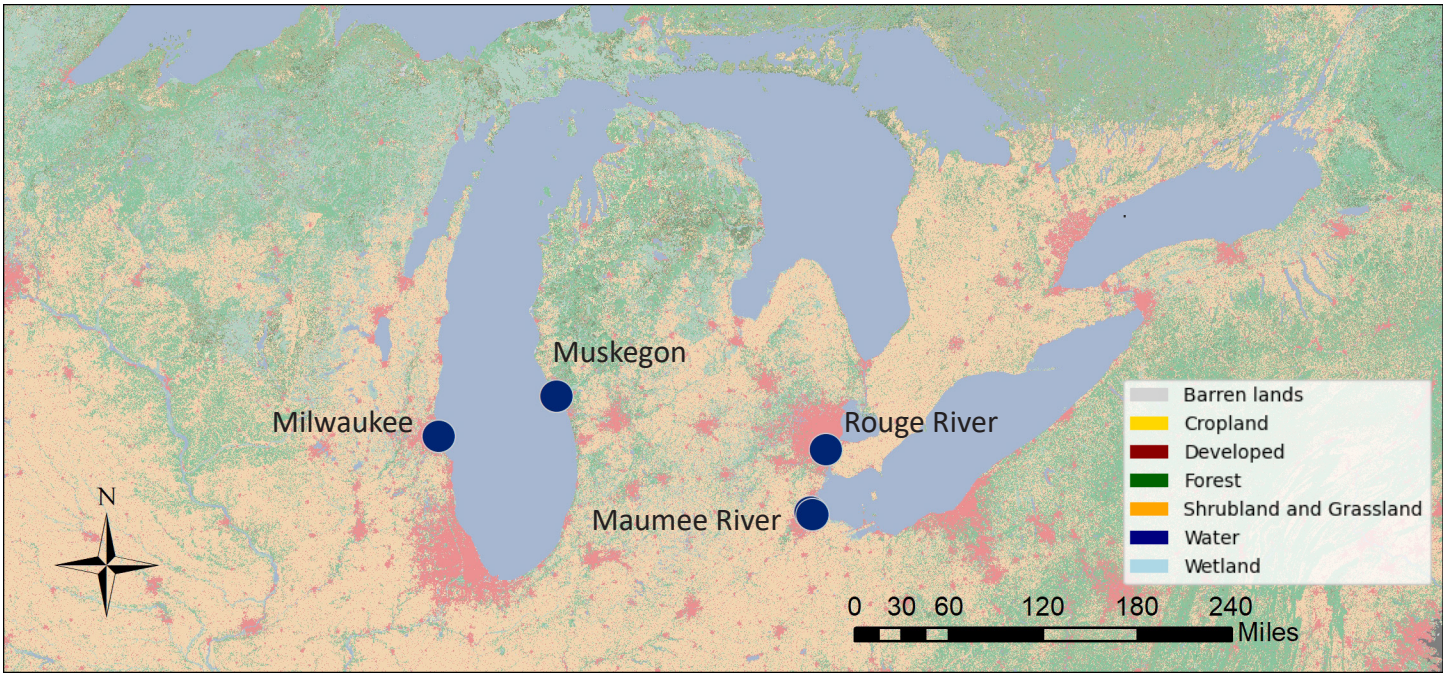

Figure 1. Geographical location of SPMD and POCIS deployments with associated land use. Further details on specific sites are available in Table 1 and Table A1 of the appendix.

Methods

For the caged mussel deployments, mussels were collected from a source site and immediately transferred to an aerated 26 L cooler prior to deployment. All mussels were collected by SCUBA divers and removed from substrate using a metal paint scraper and transferred to cages at targeted sampling sites within 48 h. A subsample of the source mussels were taken to assess background contamination. Cages were torpedo-shaped metal minnow traps secured approximately 0.5 m above the riverbed, with each cage containing approximately 300 – 500 mussels per cage. Upon retrieval, approximately 200 - 400 mussels were taken for analysis of chemical contaminants. Analysis of CECs and PAHs were conducted by SGS AXYS (Sidney, BC, Canada) and TDI-Brooks International (College Station, TX, USA), respectively. All mussels samples were shipped on ice to the corresponding labs within two days of collection.

2.2 POCIS Deployments

The polar organic chemical integrative sampler (POCIS) is composed of two sheets of microporous (0.1µm pore size) polyethersulfone membrane encasing a solid phase sorbent. Two types of sorbent are commercially available in POCIS dependent on the targeted compounds, either a triphasic admixture of 80:20 (w/w) Isolute ENVþ: Ambersorb 1500 dispersed on S-X3 Bio Beads (pesticide-POCIS) or Oasis Hydrophilic-Lipophilic Balance (HLB) sorbent (pharmaceutical-POCIS). Pharmaceutical POCIS offers several advantages over the pesticide configuration, including a broader suite of extractable compounds and availability of standardized extraction methods. POCIS is thought to target more hydrophilic organic contaminants with log K_{ow} values ≤ 3 (Alvarez et al., 2007). All studies were conducted using pharmaceutical-POCIS purchased from EST-lab (St Joseph, Missouri). For each deployment excluding the Muskegon 2018 study, POCIS were deployed on cage moorings along with dreissenid mussels for varying durations dependent on the study design (Table 1, Figure 1). Two types of blanks were used, a field blank, which accounts for potential contamination during transport and deployment, as well as the influence of storage and field processing. A lab blank, used to determine potential processing contamination during laboratory procedures, was also used for POCIS analysis. After retrieving cages, all POCIS samples were shipped to SGS AXYS (Sidney, British Columbia, Canada) on ice for analysis. Concentrations were converted from ng/POCIS to time weighted average (TWA) aqueous concentration using the below equation 1

$$C_w = \frac{N_s}{R_s t} \quad (1)$$

Where R_s was the average sampling rate from published literature (in L/d), t is the deployment time (in days) and N_s is the amount of a given compound in ng/sampler (Alvarez et al., 2007).

2.3 SPMD Deployments

The semipermeable membrane device (SPMD) is composed of lay flat, low density polyethylene tubing containing a thin film of a pure, high-molecular weight lipid (triolein). SPMDs are designed to sample hydrophobic contaminants with log K_{ow} values ≥ 3.0 (Alvarez et al., 2007). For SPMD deployments, performance reference compounds (PRCs) were used. PRCs were developed to account for the various exogenous factors that can influence the adsorption of contaminants onto samplers, including water flow, temperature, and presence of biofilms (Alvarez et al., 2010).

PRCs are loaded onto the samplers prior to deployment, and the amount of PRC loss during deployment can be used to adjust calculations of time weighted concentrations based on actual site-specific sampling rates. For this study, three PRCs were used: anthracene d-10, fluoranthene d-10, and dibenzo[a,h]anthracene d-14. The former two PRCs were used to calculate sample specific sampling rates for the PAH compounds, whereas the latter (dibenzo[a,h]anthracene d-14) was used as a photolysis marker to track potential photodegradation of compounds over the deployment period (Alvarez et al., 2021). Sample-specific sampling rates were determined at each individual time point using the following equations:

Methods

$$k_e = -\ln\left[\left(\frac{N}{N_0}\right)\right]/t \qquad (1)$$

$$\log K_{sw} = a_0 + 2.321 \log K_{ow} - 0.1618(\log K_{ow})^2 \qquad (2)$$

Where k_e is the PRC's release rate constant, N_0 is the initial amount of PRC added to the SPMD, N is the amount of PRC remaining on the SPMD, and t is the deployment time. The SPMD-water partitioning coefficient (log K_{ow} is determined from a regression model of the PRCs log K_{ow} value, where a_0 is the intercept, which is determined to be -2.61 for PCBs, PAHs and non-polar pesticides. Next, individual chemicals sample-specific sampling rates were determined using the third order polynomial equation shown below (equation 5) where ai/PRC is the compound-specific effect on the sampling rate and the relationship between the R_s,PRC and R_s,i (shown in equation 5). Finally, the ambient chemical concentration (C_w) was calculated as shown in equation 6 (Alvarez et al., 2009, 2021).

$$\log a_{\left(\frac{i}{PRC}\right)} = 0.0130(\log K_{ow})^3 - 0.3173(\log K_{ow})^2 + 2.244 \log K_{ow} \qquad (4)$$

$$R_{s,i} = R_{s,PRC}\left(\frac{a}{a_{PRC}}\right) \qquad (5)$$

$$C_w = N/V_s K_{sw}\left[1 - \exp\left(-\frac{R_s t}{V_s K_w}\right)\right] \qquad (6)$$

For the compounds that did not have PRCs, C_w values were calculated according to the methods described in Huckins et al., (2006). All C_w values were blank corrected using both the field blank (exposed to air for the duration of the deployment period) and the fabrication blank (fabricated concurrently with the field samplers and not exposed to air/water).

Figure 2. Example of the SPMD passive sampler (left), POCIS passive sampler (middle), and caged mussels (right). SPMD and mussels are shown pre-deployment, with the POCIS shown post-deployment.

2.4 Chemical Analysis

2.4.1 Dreissenid Mussels

Dreissenid mussels were analyzed for a suite of 64 PAHs at TDI-Brooks. Mussels were shucked, homogenized and an aliquot analyzed before the remaining sample of the homogenate was shipped to SGS AXYS for CEC analysis. The following groups of CECs were analyzed in mussels: pesticides (76 compounds), pharmaceutical and personal care products (PPCPs, 141 compounds), and alkylphenols (4 compounds). Alkylphenol data is not presented given these compounds were not analyzed in any passive samplers. A full list of the contaminants analyzed is available in table A2. The method for analysis of PPCPs was based on EPA method 1694 (U.S.EPA 2007a, b) and samples were analyzed using isotope dilution/surrogate standard quantitation with liquid chromatographic–electrospray ionization tandem mass-spectrometry (LC/ESI-MS/MS). The pesticide method was based on EPA method 1699 and samples were analyzed by high resolution gas chromatography with high resolution mass spectrometric detection (HRGC/HRMS).

2.4.2 Passive Samplers

POCIS were analyzed at SGS AXYS according to the established method MLA-075 REV 07 VER 06, which is based on the EPA method 1694 (USEPA, 2007). This method analyzes PPCPs and hormones in solid, aqueous, tissue, and POCIS samples by liquid chromatography-mass spectrometry (LC-MS/MS). Further details on the method are available in Deere et al., (2020) and from SGS AXYS. For SPMDs, samples were analyzed according to SGS-AXYS Method MLA-021, which is based on USEPA Methods 1625B and 8270C/D. A total of 78 PAH compounds were analyzed in SPMDs, including a suite of 28 alkylated PAHs and three PRCs.

2.5 Statistical Analysis

Regression analysis was used to quantify the relationship between tissue concentration and passive sampler concentration for select compounds. To provide a robust assessment, regression analysis was limited to compounds with more than 5 degrees of freedom. Only data above the method detection limit (MDL) in both matrices were used for regression due to the potential of substituted values below the MDL to influence results (Helsel et al., 2006). Log-log relationships were used for regression following Joyce et al., (2016). All analyses and visualization were conducted in R statistical software (R Core Team, 2022).

Random Forest, a multivariate ensemble learning method based on decision trees, was used to identify patterns in PPCP, pesticides, and PAH relative concentration data (Afanadora et al., 2016; Raschka and Mirjalili, 2019). The unsupervised Random Forest method that utilizes proximity as a calculation of distance followed multidimensonal scaling (MDS) for dimension reduction. Cluster analysis, using the R Mclust package (Fraley and Raftery, 2006), was employed to determine the appropriate number of clusters.

Results

3.1 PPCP Detections in POCIS

A heatmap displaying presence/absence of all PPCPs analyzed in POCIS is displayed in Figure 3. Overall, out of a total of 141 PPCPs analyzed in POCIS, 64 compounds were detected at least once across all deployments. Three compounds including the insect repellent DEET, the lipid regulating medication gemfibrozil, and the anticonvulsant carbamazepine were detected in every sample analyzed (100% detection frequency, Figure 3). Conversely, several compounds including paroxetine, clotrimazole, benztropine, and cimetidine were detected in only a single sample (Figure 3). Several of the more hydrophobic PPCP compounds were detected in POCIS, including verapamil, sertraline, and atorvastatin (Log K_{ow} values of 4.8, 5.29, and 6.10, respectively).

3.2 PPCP Detections in POCIS & Mussels

A heatmap showing the detections of PPCPs in POCIS only, mussels only, or detected in both POCIS and mussels at the same site is shown in Figure 4. Overall, a total of 82 PPCPs were detected at least once in either POCIS or mussels. Of these 82 compounds, 34 (41.5%) were detected only in POCIS, 19 (23.2%), were detected only in mussels, and a total of 28 (34.1%) compounds were detected in POCIS and mussels in colocated samples at any given site (Figure 4). A single compound, sulfadimethoxine, was detected in both POCIS and mussels but never at the same site. Comparing the total number of compounds that were detected using POCIS and mussels, a total of 64 compounds were detected in POCIS at least once, compared to 47 in mussels (Figures 3 and 4). Several compounds including gemfibrozil, carbamazepine, and valsartan were commonly detected in POCIS (detection frequencies of 96, 100, and 64%) but were not detected in mussel tissue at any site (Figure 4). The antidepressant, amitriptyline, was the compound most commonly detected in both POCIS and mussels when deployed at the same site, with 58% of amitriptyline detections occurring in both POCIS and mussels at the same site. Linear regression was used to analyze the relationship between POCIS time-weighted average aqueous concentrations and tissue residues for compounds that were detected in at least eight colocated mussel and POCIS samples (Figure 5). Of the five PPCP compounds with adequate coverage, significant positive relationships between POCIS and tissue concentrations were found for only two; the antidepressant sertraline (Linear regression, $r^2 = 0.371$, $p < 0.05$) and the antihistamine, diphenyhydramine (Linear regression, $r^2 = 0.357$, $p < 0.05$).

To further emphasize the compositional differences between POCIS and mussels, random forest was conducted utilizing relative concentration data of PPCPs (Figure 6). Two distinct clusters were observed, consisting of the mussel and POCIS datasets, suggesting that compositions were distinct between each matrix. Given that the both POCIS and mussels were deployed on the same mooring, for the same period of time, and exposed to the same environmental contamination this is clear evidence of the different sampling mechanisms detailed earlier.

Results

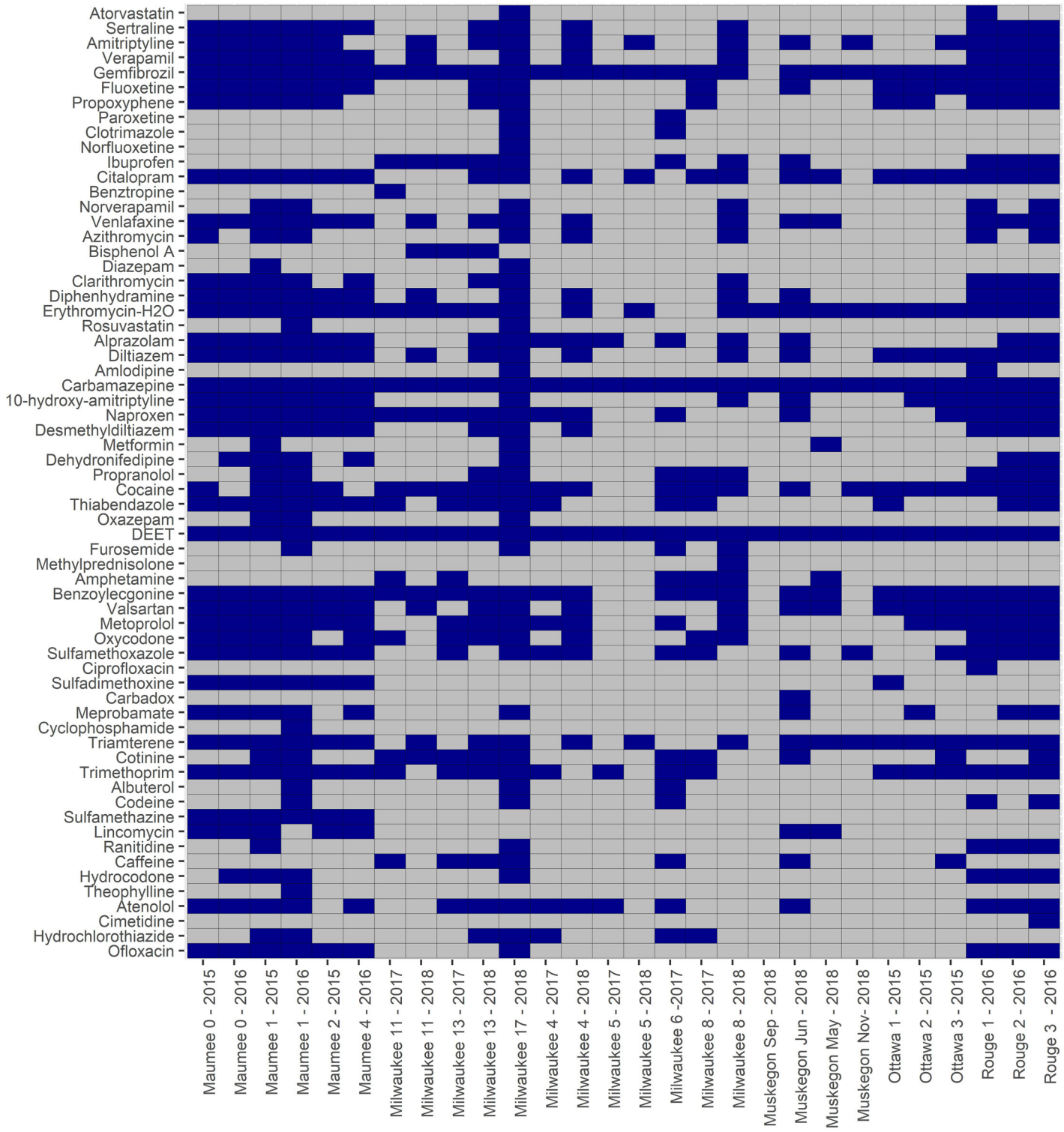

Figure 3. Heatmap of all PPCPs detected in POCIS across all deployments. Compounds are organized by Log K_{ow} value, with the K_{ow} values increasing from bottom to top. Dark blue cells (■) indicate presence of a given compound in POCIS, whereas grey cells (■) indicate absence of a compound.

Results

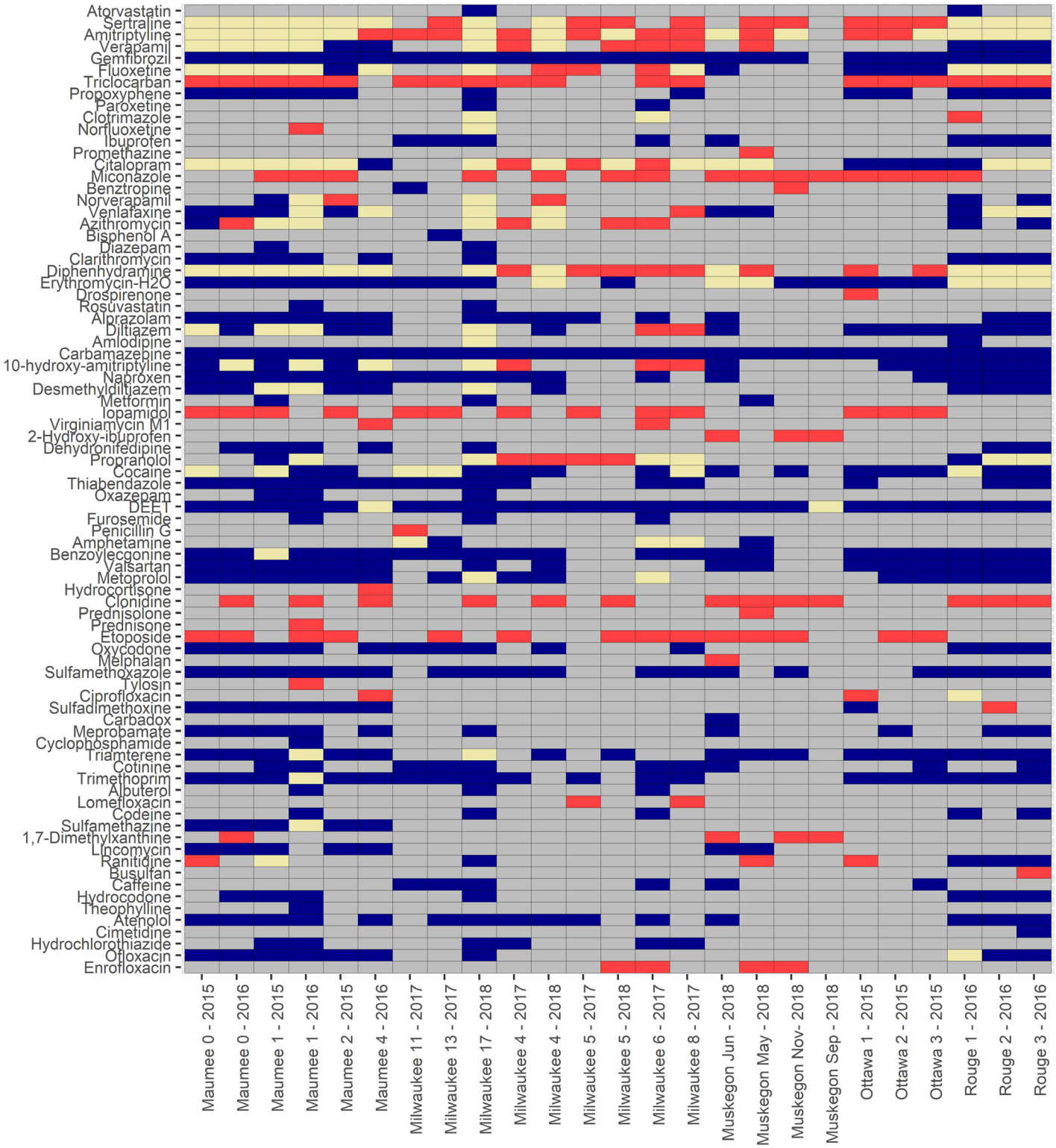

Figure 4. Heatmap of all PPCPs detected in POCIS only ( ), mussels only ( ), and both POCIS and mussels ( ). Compounds not detected were coloured grey ( ). Compounds are organized by Log K_{ow} with K_{ow} values increasing from bottom to top.

Results

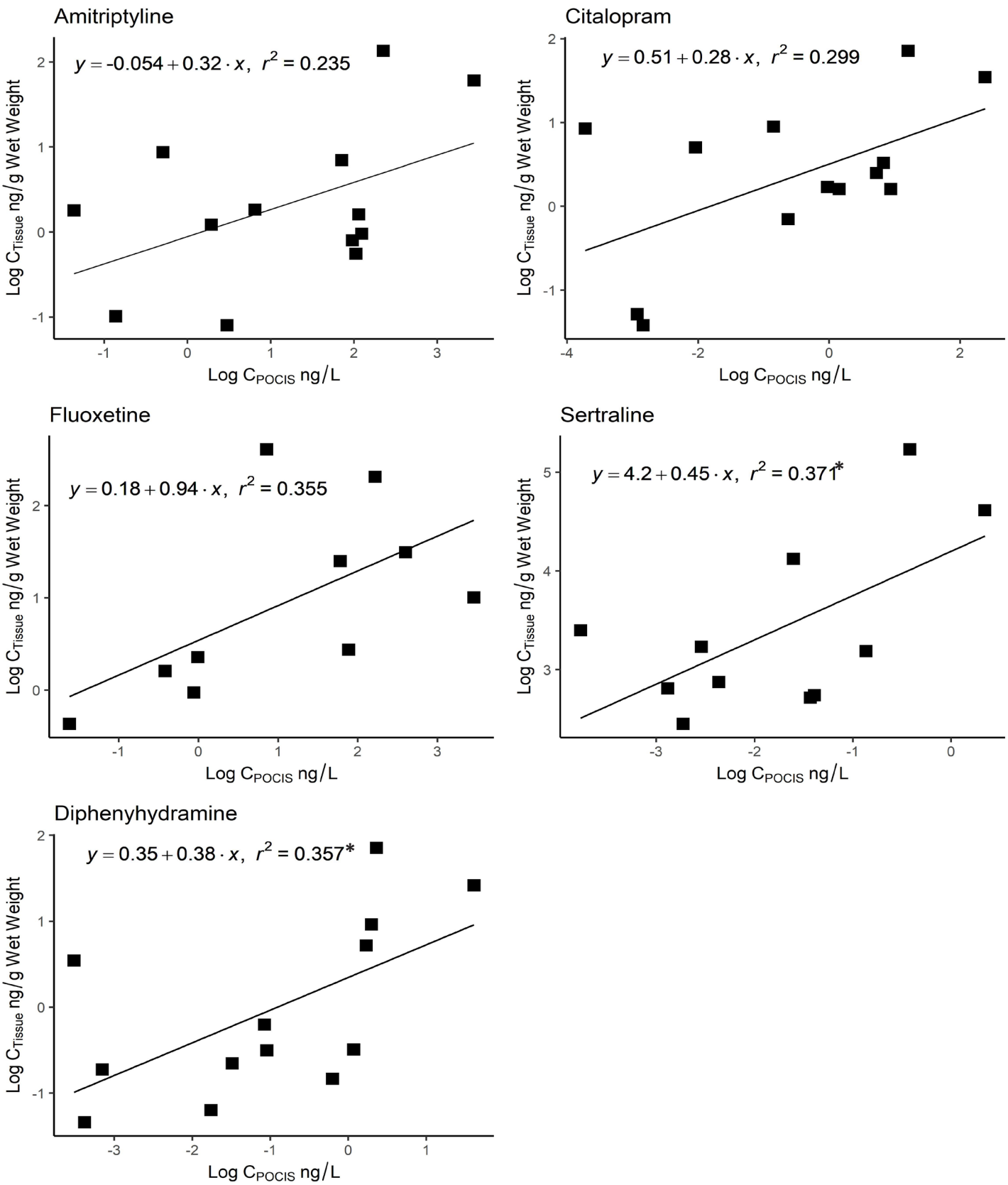

Figure 5. Relationship between aqueous concentrations of PPCPs measured using POCIS and tissue concentrations in dreissenid mussels. Compounds were selected based on the presence in at least eight colocated POCIS and mussel samples. Significant relationships (*, Linear regression, $p < 0.05$) were observed for sertraline and diphenyhydramine only.

Results

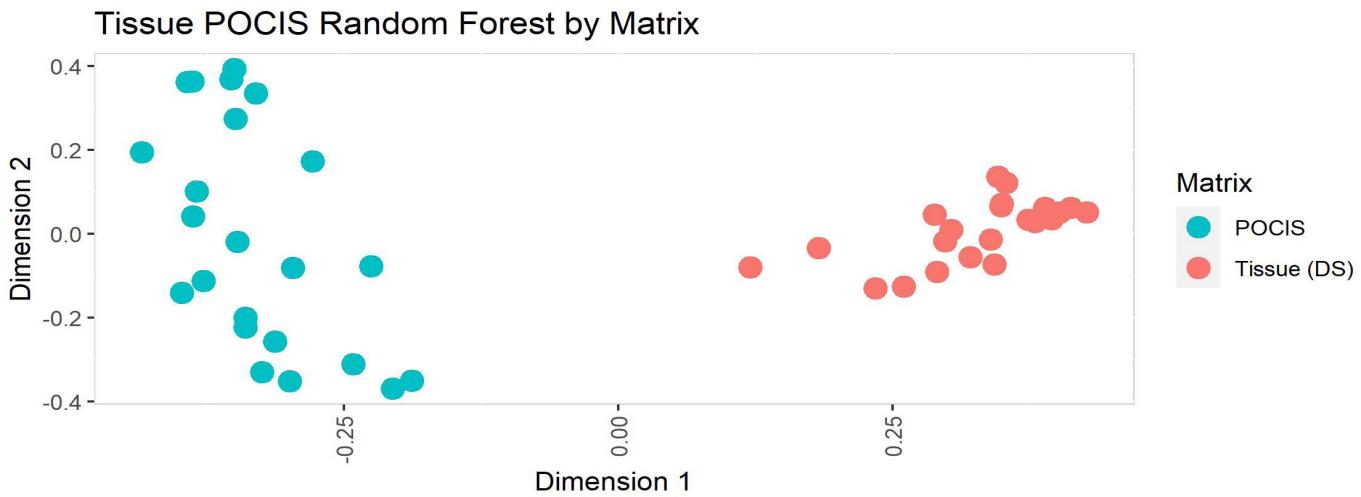

Figure 6. Random Forest analysis of PPCP relative concentrations in POCIS (light blue points) and tissue (DS; Dreissenids, red points). Distance between the POCIS and mussel clusters is evidence that the two matrices have distinct compositions of PPCPs. Overlap was not found for colocated sites.

3.3. Pesticide Detections in POCIS

Overall, a total of 45 pesticides were detected in POCIS out of a total of 104 analyzed (Figure 7, Table A2). Several current use pesticides (CUPs) including atrazine, simazine, dimethenamid, metolachlor, and the atrazine degradate, desethylatrazine, were detected in every sample analyzed (Figure 7). Generally, fewer detections of the more hydrophobic legacy pesticides with Log Kow values > 6.0 were observed, as anticipated based on the characteristics of POCIS.

3.4 Pesticide Detections in POCIS & Mussels

Comparing detections in POCIS and dreissenid mussels, a total of 14 compounds were detected only in POCIS, with 7 detected only in mussels and the remaining 24 detected in both POCIS and mussels at any given site (Figure 8). Several hydrophilic current use pesticides including dimethenamid (Log Kow = 2.17) simazine (Log Kow = 1.97), and chlorpyrifos-oxon (Log Kow = 2.14) were detected only in POCIS, whereas the more hydrophobic DDT degradates such as 4,4'-DDD, 4,4'-DDT, and 2,4'-DDT (Log Kow > 6.0) were found only in mussels. Dieldrin and heptachlor epoxide were the most commonly detected in both POCIS and mussels, in 100 and 96% of samples respectively. Two CUPs had adequate data coverage for comparison, atrazine and desethylatrazine, with desethylatrazine concentrations in POCIS and tissue residues having a significant positive relationship (Linear regression, $r^2 = 0.733$, $p < 0.05$, Figure 9), whereas no significant relationship between aqueous atrazine concentrations and tissue resides was observed (Linear regression, $r^2 = 0.145$, Figure 9). For the legacy pesticides detected in POCIS and mussels, a significant positive relationship was observed for dieldrin only (Linear regression $r^2 = 0.29$, $p < 0.05$), with no significant relationship between POCIS and tissue concentrations of 4,4'-DDE and aldrin (Figure 9, Linear regression, $p > 0.05$).

The Random Forest analysis and subsequent cluster analysis of pesticides identified two clusters associated with mussel and POCIS matrices, again suggesting that compositions were distinct between each matrix (Figure 10). Using distance as a measure of difference, some POCIS measurements were more similar to mussel relative concentrations than other POCIS measurements. The similarities of some samples could be associated with the large percentage of legacy compounds such as chlordane and dieldrin that were found in both matrices.

Results

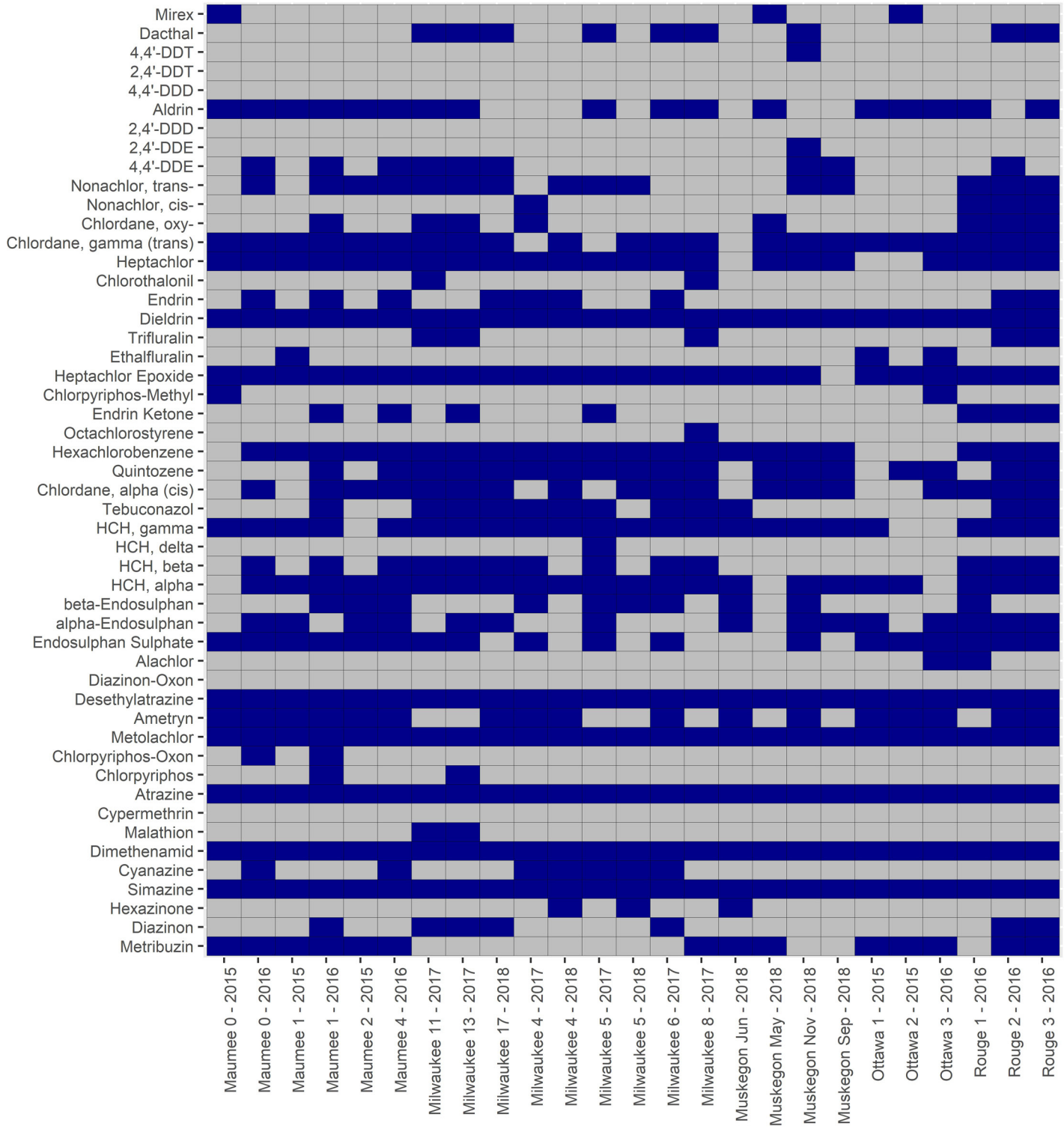

Figure 7. Heatmap of all pesticides detected in POCIS across all deployments. Compounds are organized by LogKow value, with values increasing from bottom to top. Dark blue cells (■) indicate presence of a given compound in POCIS, whereas grey cells (■)indicate absence of a compound.

Results

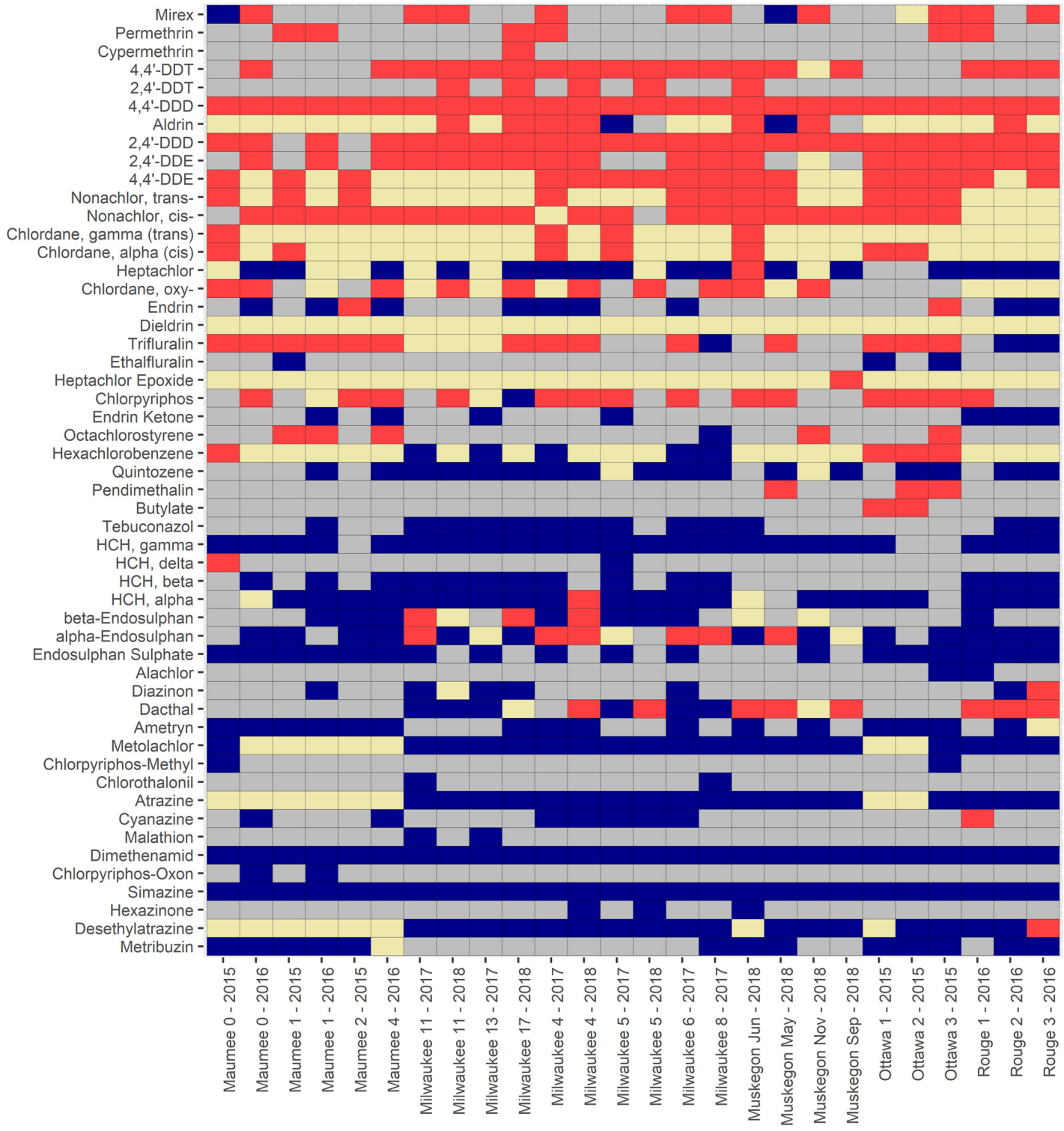

Figure 8. Heatmap of all pesticides detected in POCIS only (■), mussels only (■), and both POCIS and mussels (■). Compounds not detected were coloured grey (■). Compounds are organized by LogKow with LogKow values increasing from bottom to top.

Results

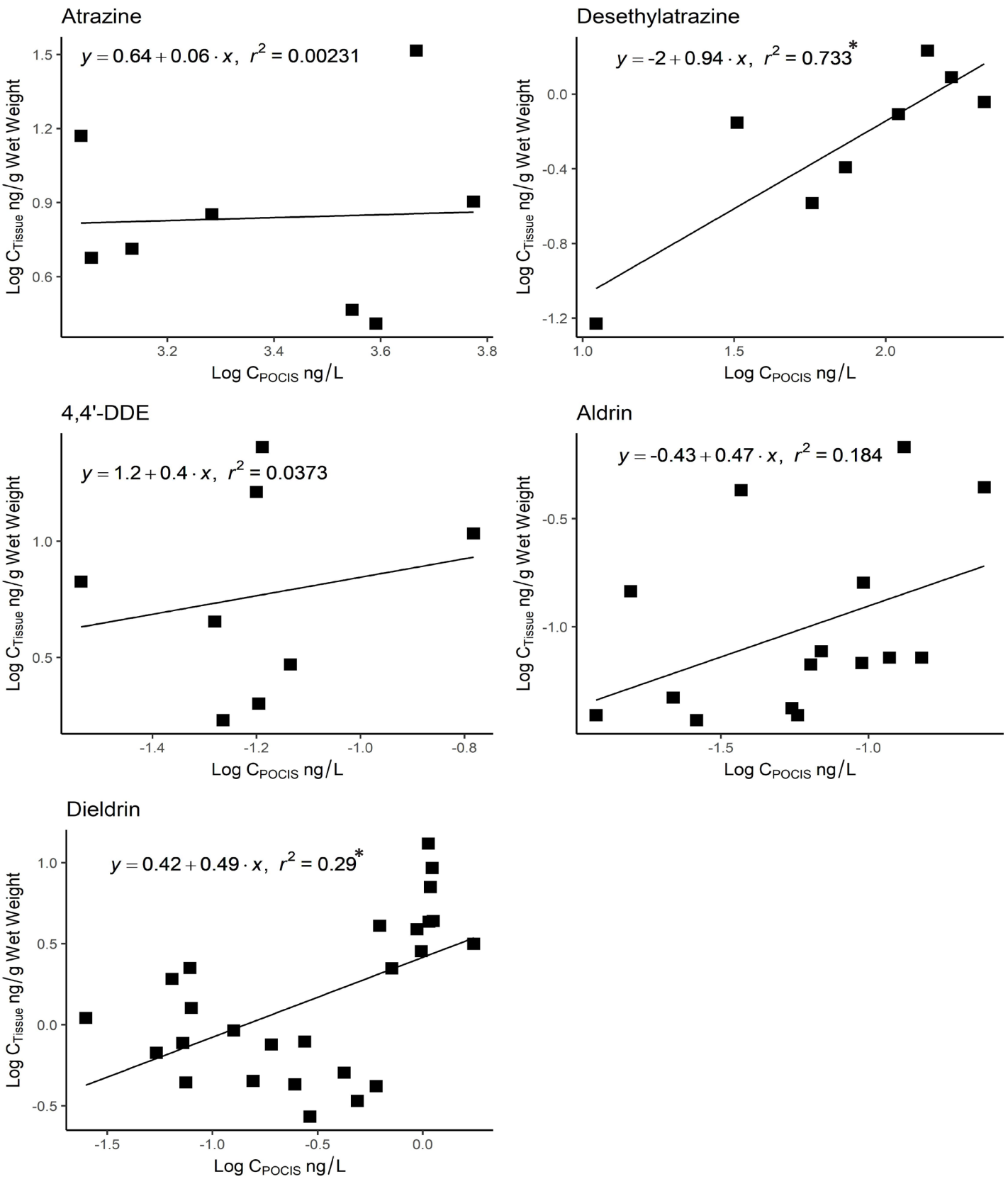

Figure 9. Relationship between aqueous concentrations of CUPs (atrazine and its transformation product, desethylatrazine) and legacy compounds (DDE, aldrin, dieldrin). Significant relationships (*) were observed for desethylatrazine and dieldrin only.

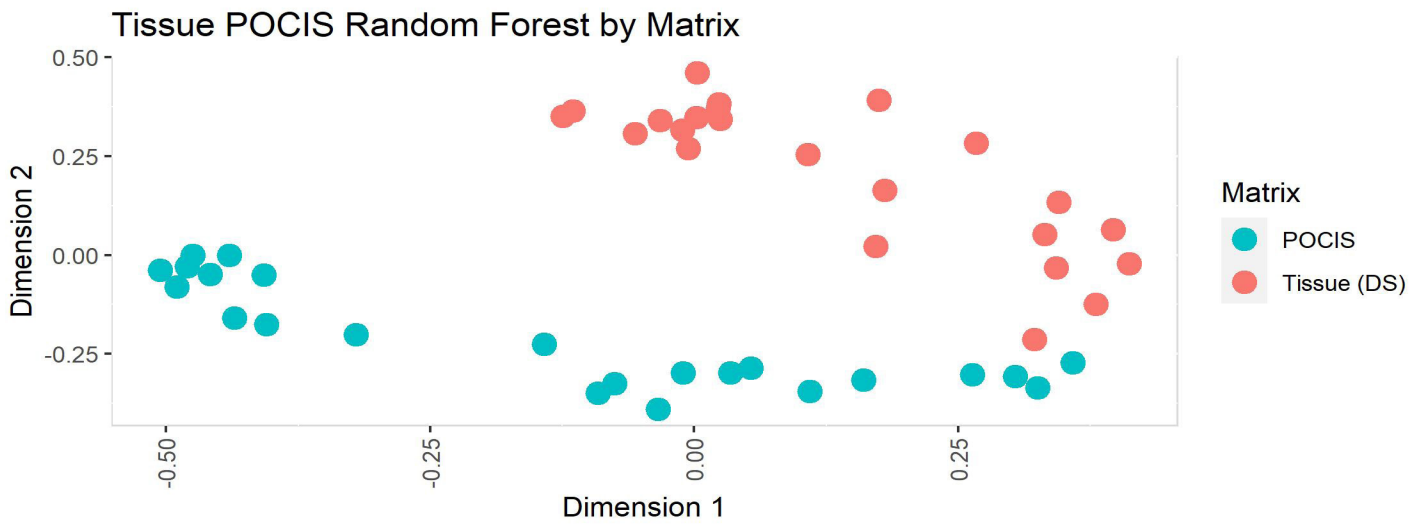

Figure 10. Random Forest analysis of pesticides relative concentrations in POCIS (light blue points) and tissue (DS; Dreissenids, red points).

3.5 PAH Detections in SPMDs

Across all SPMD deployments, 74/74 (100%) of the PAH compounds monitored were detected at least once (Figure 11). The majority of the compounds were detected in every SPMD sample, with the lowest detection frequencies observed for the alkylated PAHs; C4-Benzo[a]anthracenes/Chrysenes, C4-Dibenzothiophenes, and C4-Fluoranthenes/Pyrenes which were detected in 47%, 67%, and 67% of samples, respectively. Naphthalene was commonly detected in both laboratory and field blank SPMD samples, leading to lower detection frequencies following blank correction.

3.6 Comparing PAH Detections in SPMDs and Mussels

The majority of compounds were detected in both SPMDs and tissue, with select alkylated PAHs including C2-Naphthalenes, C3-Chrysenes, and C4-Naphthalenes detected more frequently in SPMDs compared to mussels (Figure 12). The relationship between total concentrations of parent and alkylated PAHs in SPMDs and dreissenid mussel tissue are shown in Figure 14. A significant positive relationship was observed for both parent PAHs (Linear regression, $r^2 = 0.882$, $p < 0.05$) and alkylated PAHs (Linear regression, $r^2 = 0.922$, $p < 0.05$). The composition of PAHs detected in SPMDs and dreissenid mussels are shown in Figure 15. For several parent PAHs, the composition was different between SPMDs and mussels, with chrysene being the most dominant PAH recorded in mussel tissue (accounting for 17 - 24% of total PAH concentrations), whereas this compound was less dominant in SPMDs (7 - 14% of total PAH concentrations. Comparatively, fluoranthene was the most dominant PAH detected in SPMDs, accounting for 29 - 35% of total PAH concentrations, whereas fluoranthene represented 8 - 21% of total PAH concentrations in tissue. Finally, both pyrene and phenanthrene represented a greater relative proportion of total PAHs in SPMDs (ranges: 13 - 28% and 6 - 31% for pyrene and phenanthrene, respectively) compared to mussel tissue (ranges: 4 - 14% and 2 - 8%, respectively).

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Results

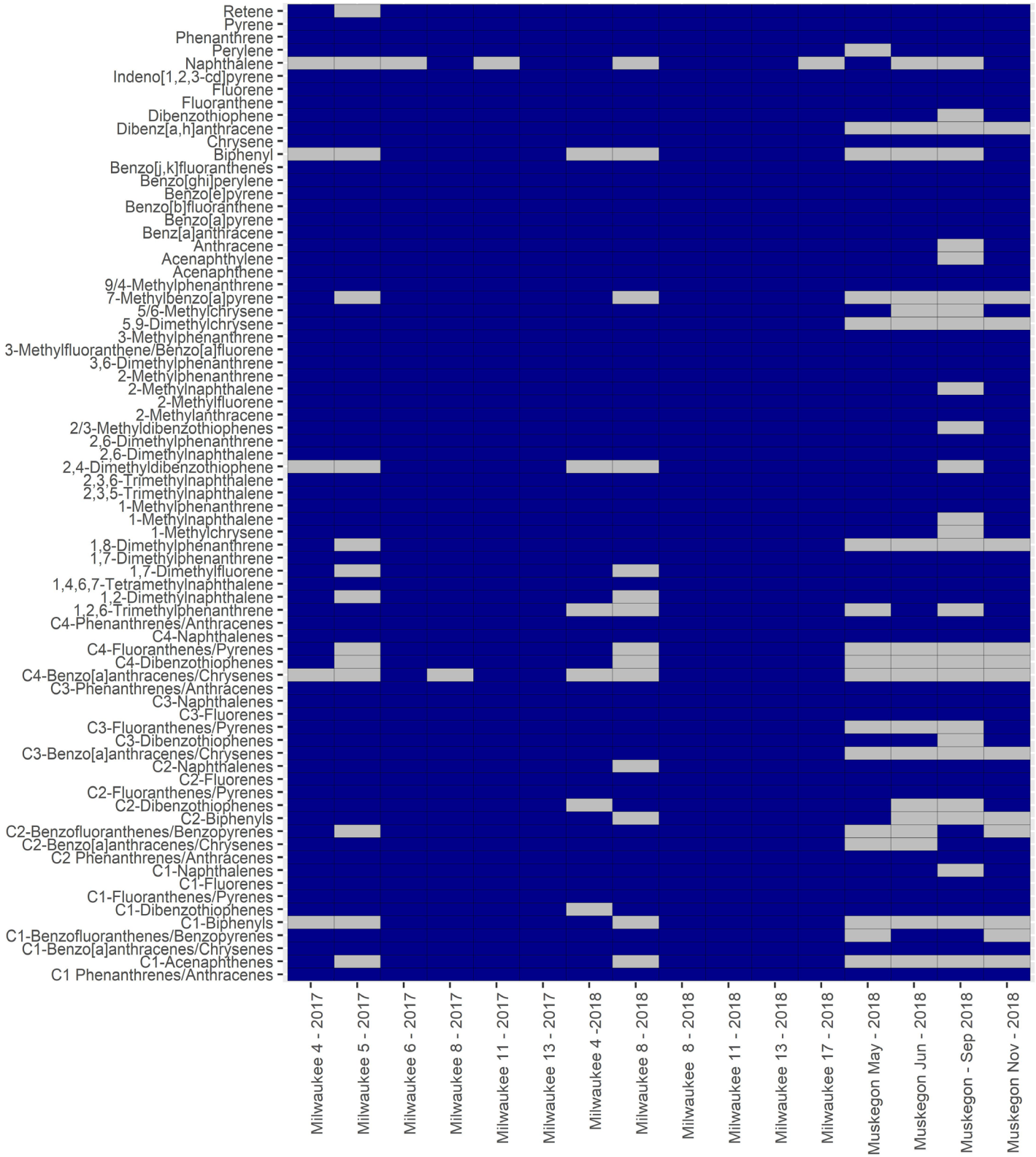

Figure 11. Heatmap of all PAHs detected in SPMDs across all deployments. Dark blue cells (■) represent presence of a given compound, whereas grey (■) represents absence.

Results

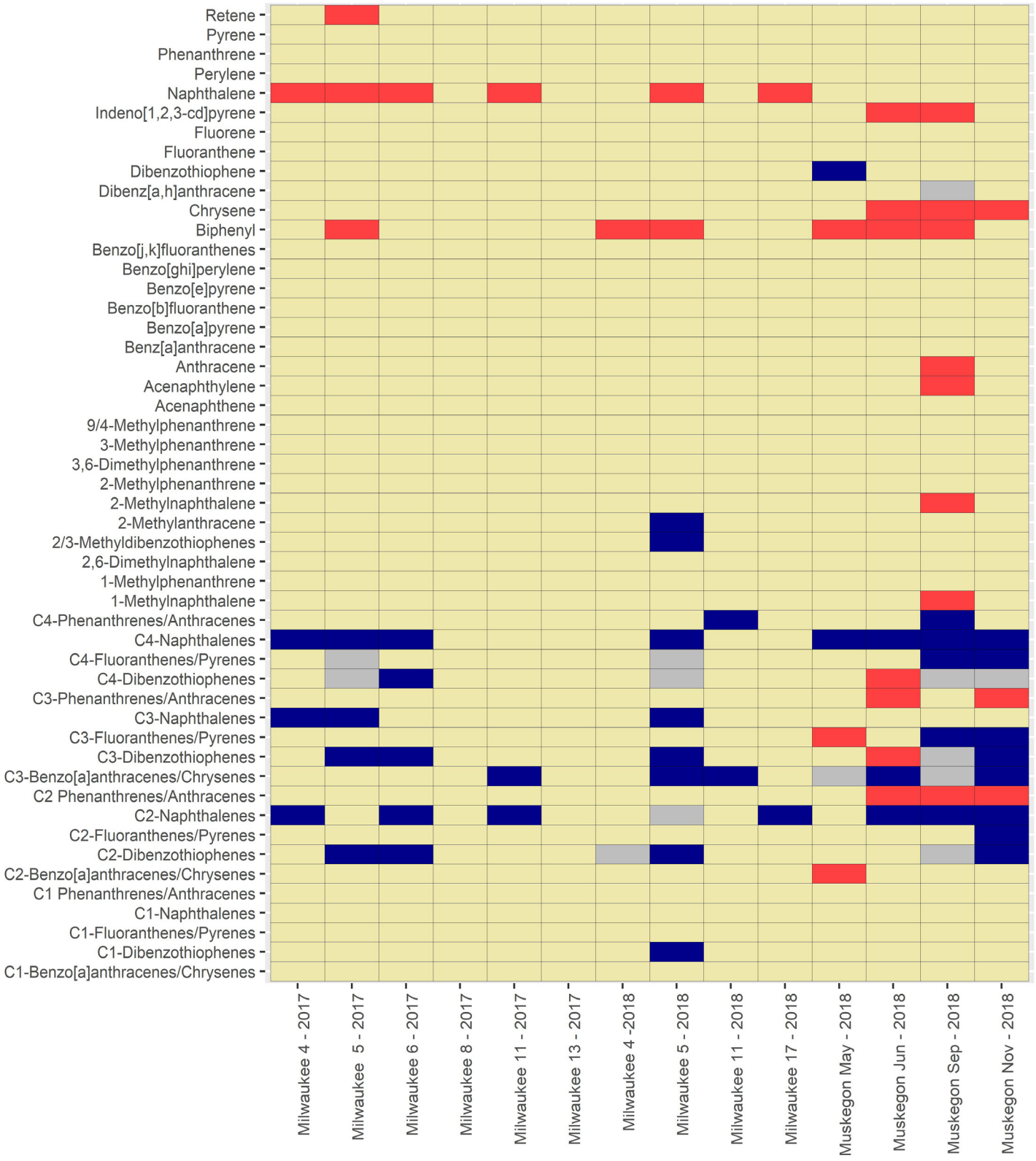

Figure 12. Heatmap of all PAHs detected in SPMDs only ( ), mussels only ( ) and both SPMDs and mussels ( ).Grey cells ( ) indicate absence of a given compound in any matrix.

Results

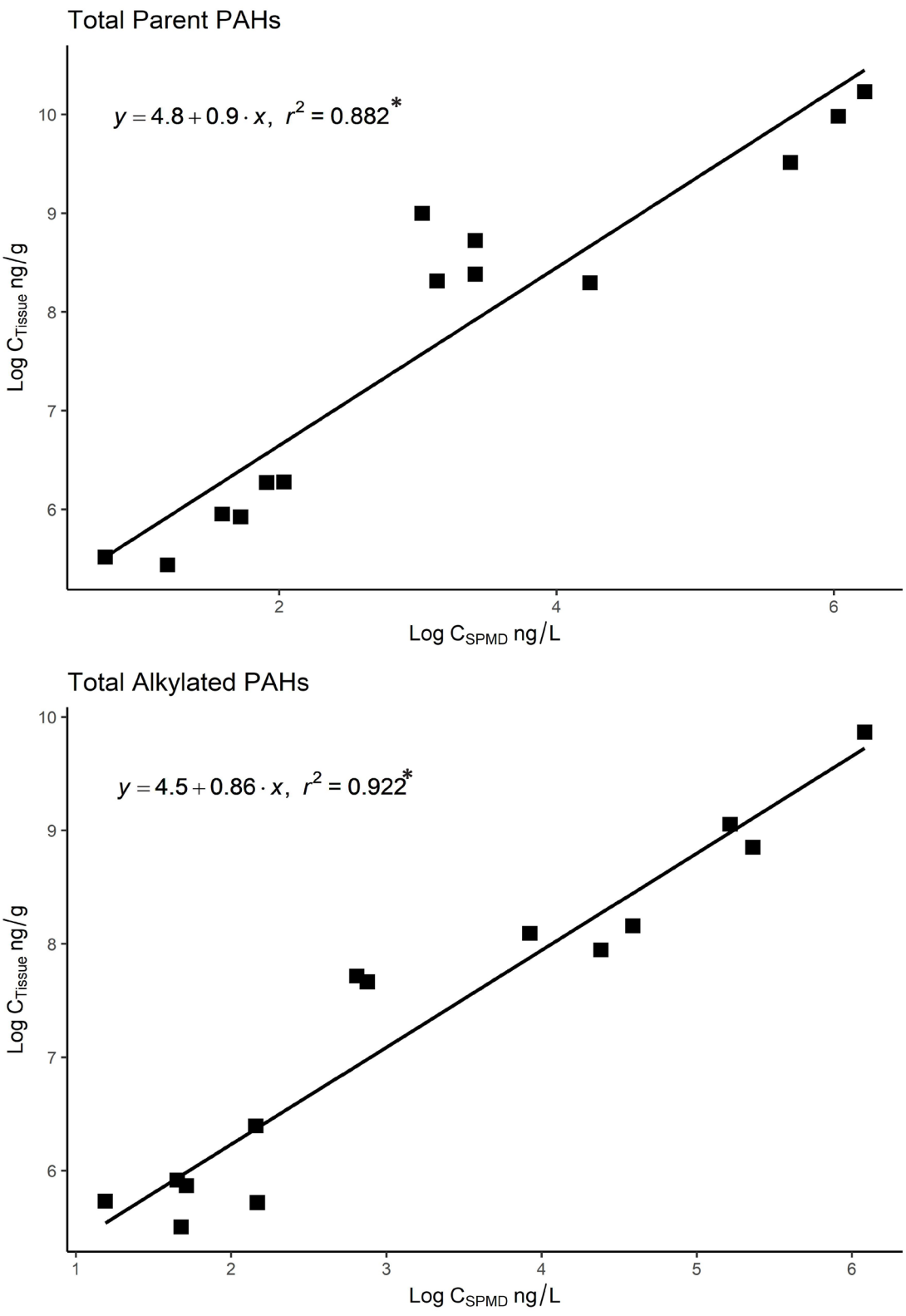

Figure 14. Relationship between total parent PAHs (top) and total alkylated PAHs (bottom) in SPMDs and dreissenid mussels. Both relationships were statistically significant (*, Linear regression, $p < 0.05$).

Results

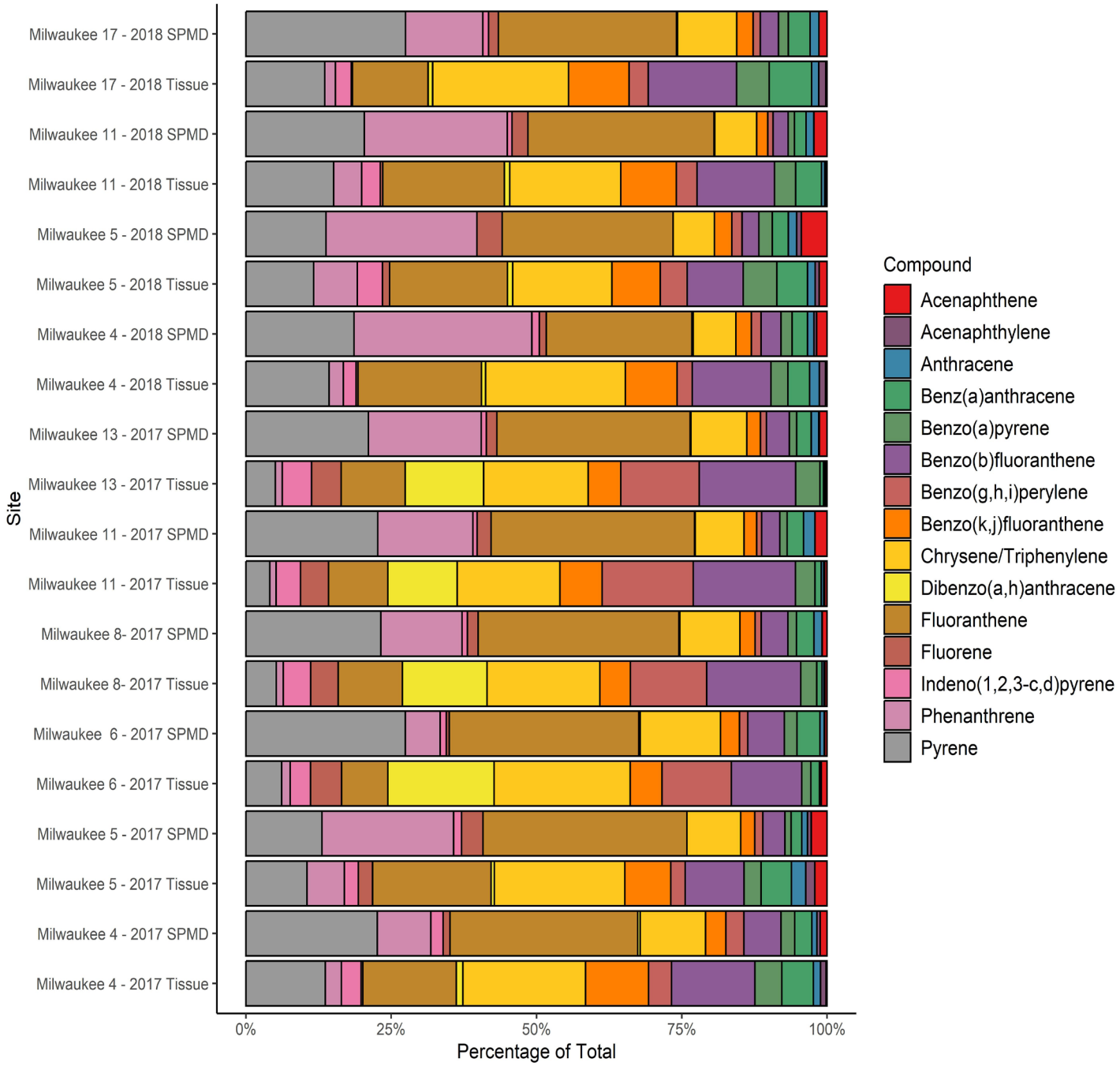

Figure 15. Comparison of the composition of priority parent PAHs in tissue and SPMD at each individual deployment site. Compounds are represented as the percentage of total concentrations for both SPMDs and tissue.

Results

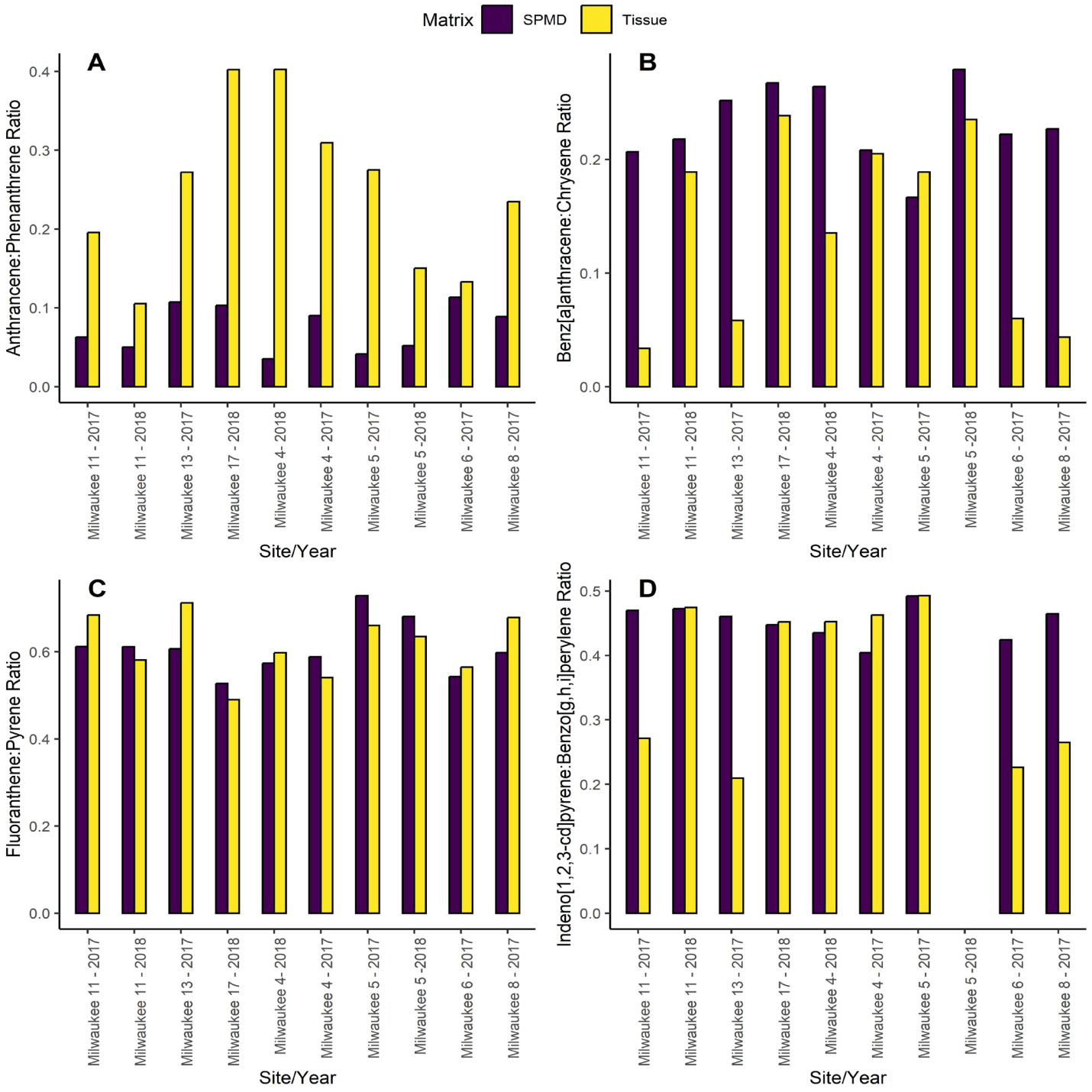

Figure 16. PAH Diagnostic ratios including A) anthracene:phenanthrene, B) benzo[a]anthracene:chrysene, C) fluoranthene:pyrene and D) Indeno[1,2,3-cd]pyrene:benzo[g,h,i]perylene calculated using SPMD data (blue bars) and tissue data (yellow bars). Note that benzo[g,h,i]perylene was not detected in Milwaukee 5 - 2018, thus the bar is empty.

To further investigate potential differences in PAH composition between matrices, several PAH diagnostic ratios commonly used to distinguish between petrogenic and pyrogenic sources were calculated including anthracene:phenanthrene, benz[a]anthracene:chrysene, fluoranthene:pyrene,and indeno[1,2,3,-cd]pyrene: benzo[g,h,i]perylene for both SPMDs and mussel data (Figure 16). The anthracene:phenanthrene ratio was consistently different between SPMDs and mussels, with a fourfold lower ratio observed in SPMDs compared

to mussels across all deployment sites (Figure 16A). For the benz[a]anthracene:chrysene ratio, site-specific differences were observed with several sites having comparable values (Figure 16B), and SPMDs having higher values at others (Figure 16B). Of the four ratios, fluoranthene:pyrene was the most similar between matrices (Figure 16C), with site-specific differences observed for the indeno[1,2,3-cd]pyrene:benzo[g,h,i]perylene ratio.

Similar to the other compound groups mentioned previously, random forest of SPMD and tissue data for PAHs further emphasized the different compositions observed between the two matrices (Figure 17).

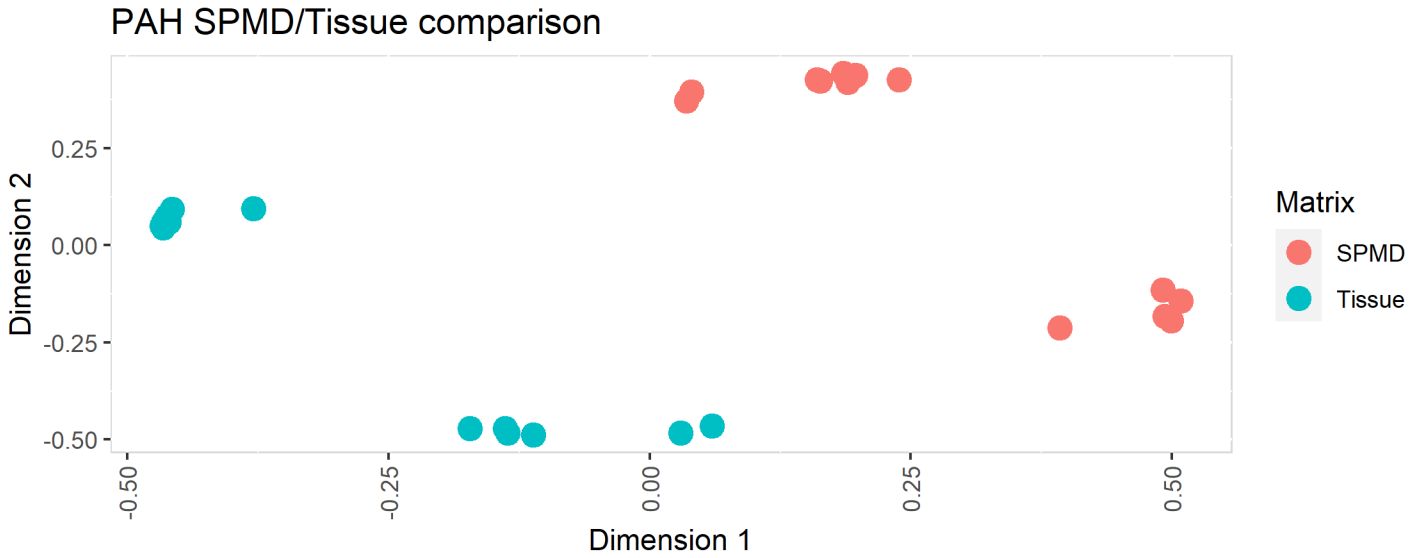

Figure 17. Random Forest analysis of PAHs relative concentrations in SPMDs (light blue points) and tissue (Dreissenid mussels, red points). Distance between the POCIS and mussel clusters is evidence that the two matrices have distinct compositions of PAHs.

3.7 Legacy Pesticides

A total of 23 legacy pesticides were detected in SPMDs across all deployments, out of a total of 28 analyzed (Figure 18, 82.1%). Several compounds including alpha- and gamma-chlordane, two DDT degradates (4,4'-DDE and 4,4'-DDD), hexachlorobenzene and heptachlor epoxide were recorded in 100% of SPMD samples. Comparing detections in SPMDs and mussels, a total of 24 compounds were detected in either matrix at least once. Of these compounds, 79.2% were detected in both mussels and SPMDs, with a single compound, mirex, (4.10%) detected in mussels but never recorded in SPMDs (Figure 19). Finally, 16.7% of compounds including endrin, endosulfan sulphate, methoxychlor, and gamma hexachlorocyclohexane (gamma-HCH) were detected in SPMDs but never recorded in mussel tissue. As with the PAH SPMD/mussel comparison, the two matrices sample similar suite of compounds, however, Random Forest analysis points to differences in relative concentration (Figure 20). The relationship between concentrations of total legacy pesticides in SPMDs and tissue is shown in a single plot in Figure 21 due to the large number of compounds detected in both matrices. A significant positive relationship between legacy pesticide concentrations measured using SPMDs and mussels was recorded (Linear regression, $r^2 = 0.45$, $p < 0.05$).

Results

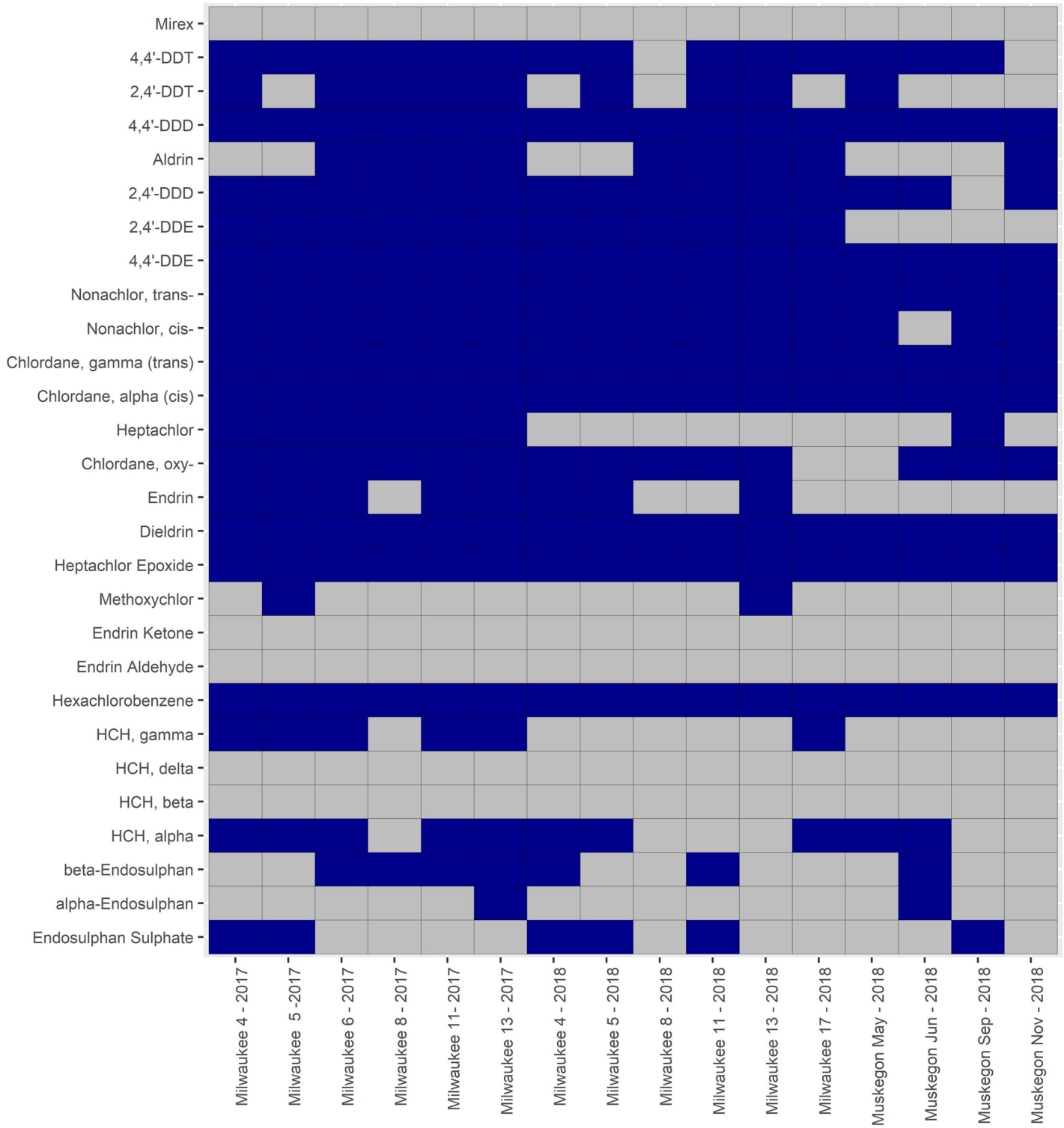

Figure 18. Heatmap of all legacy pesticides detected in SPMDs across all deployments. Dark blue cells (■) represent presence of a given compound, whereas grey (■) represents absence.

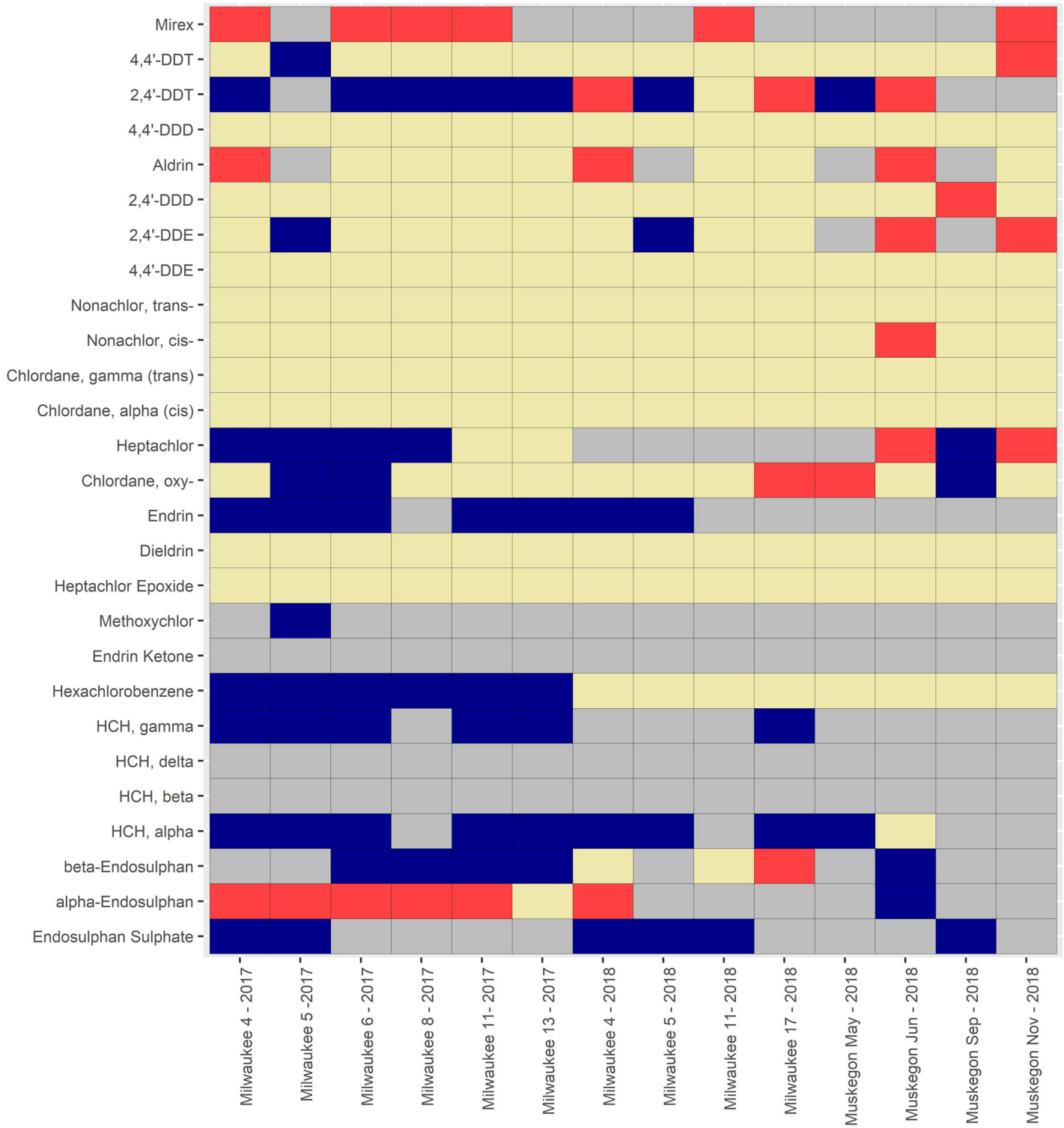

Figure 19. Heatmap of all legacy pesticides detected in SPMDs only (■), mussels only (■), and both SPMDs and mussels (■) across all deployments. Grey cells (■) represent absence in any matrix.

Results

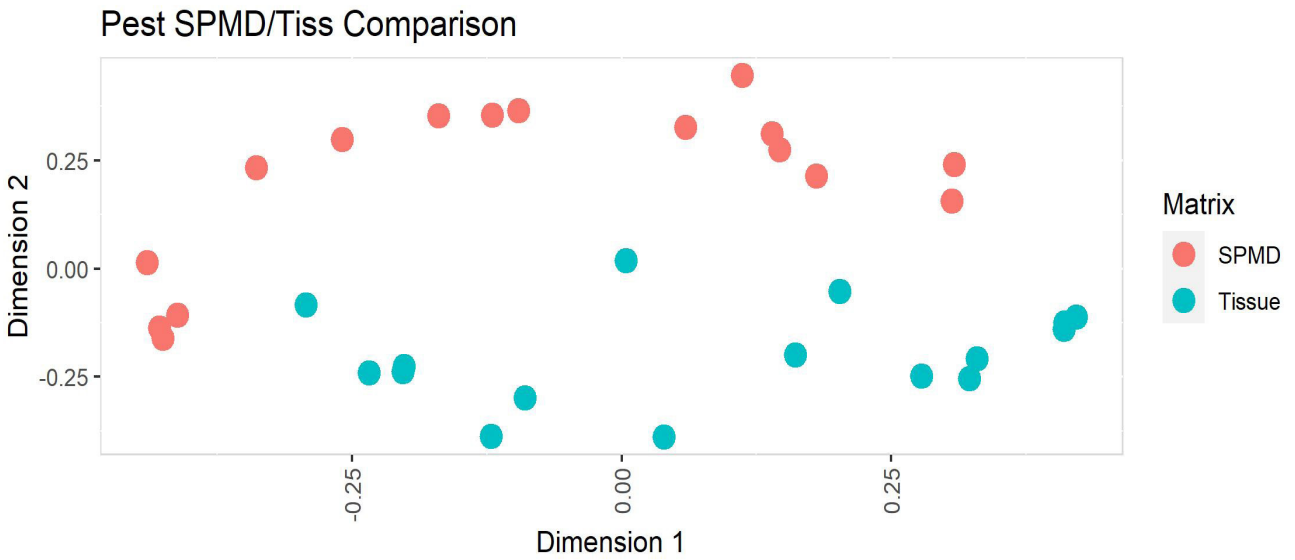

Figure 20. Random Forest analysis of legacy pesticides relative concentrations in SPMDs (light blue points) and tissue (Dreissenid mussel; red points). Distance between the POCIS and mussel clusters is evidence that the two matrices have distinct compositions of legacy pesticides.

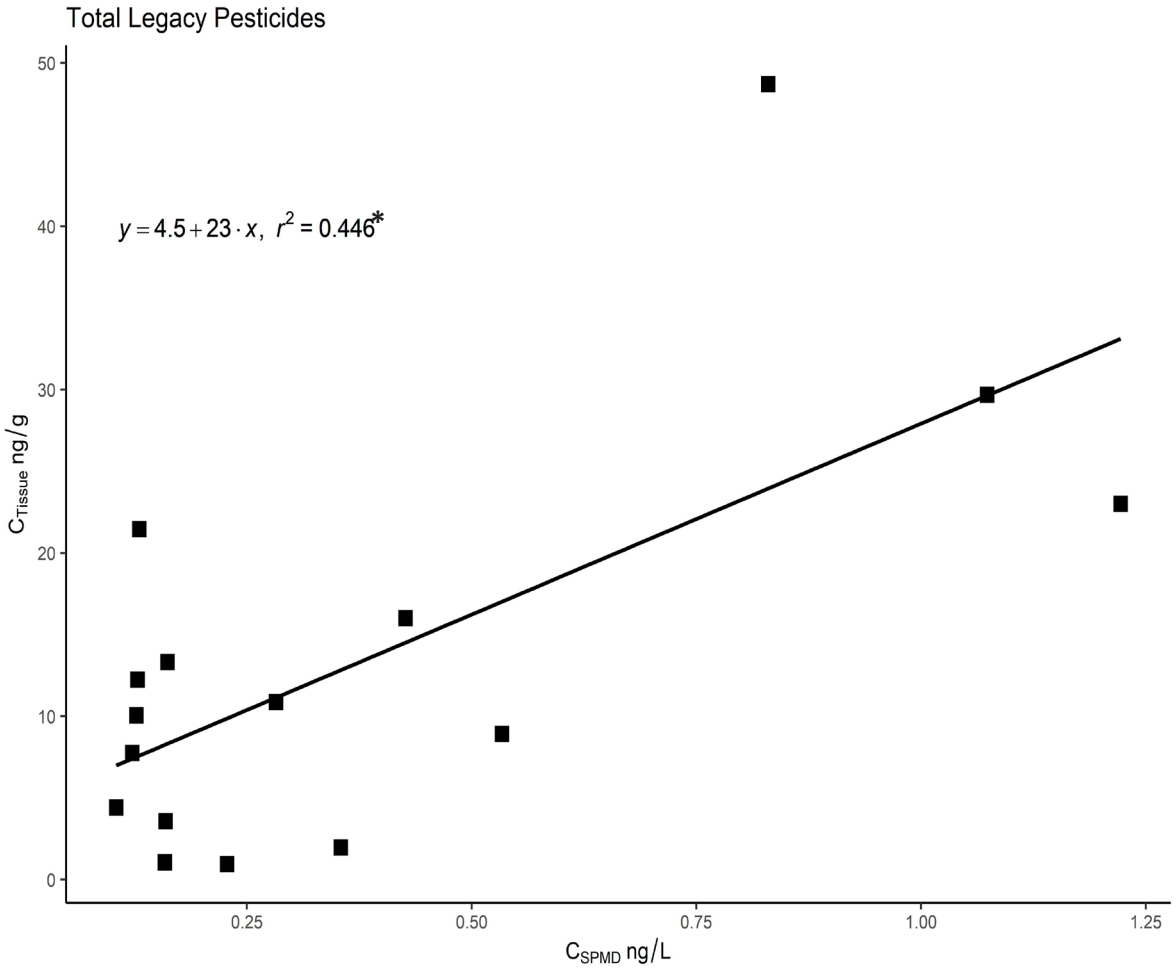

Figure 21. Relationship between total concentrations of legacy pesticides measured in SPMDs and dreissenid mussel tissue. A statistically significant relationship was observed (*,$p < 0.05$).

Discussion

The present study aimed to compare the use of passive samplers (POCIS and SPMDs) and dreissenid mussels as monitors of CECs and PAHs using data from several place-based assessments within the Great Lakes. Elucidating the differences between the sampling approaches is fundamental to designing and implementing appropriate monitoring techniques for effective environmental management.

4.1 PPCPs in POCIS

For the POCIS dataset, a greater number of contaminants were detected using POCIS (34/82, 41.5%) compared to mussels alone (19/82, 23.2%), with a total of 28 compounds (28/82, 34.1%) detected in both matrices at the same site at least once. Though this suggests that POCIS is more effective at accumulating primarily hydrophilic PPCPs than mussels, a number of compounds were detected in mussels only including several highly hydrophilic pharmaceuticals such as enrofloxacin (Log K_{ow} = 1.36) and 1,7-Dimethylxanthine (Log K_{ow} = 2.45). These findings are different to a previous study comparing a smaller suite of CECs in POCIS and caged mussels (*Mytilus* spp.) on the California coast (Alvarez et al., 2014), which found only a single compound, diphenhydramine, was present in both mussels and POCIS out of a total of 40 analyzed. Comparatively, a similar study using co-deployed zebra mussels, *Dreissena polymorpha*, and POCIS in the Czech Republic found greater overlap in the contaminants detected between matrices; 27 out of 55 compounds were present in both matrices (49.0%), with 25 (45.5%) present in POCIS only, and the remaining 3 present in mussels only (5.5%, Grabicová et al., 2022). Finally, Pintado-Hererra et al., (2020) studied accumulation of a suite of priority contaminants including synthetic fragrances, UV filters, and antimicrobials in silicone rubber passive samplers and clams, *Ruditapes philippinarum*, over a years deployment period in SW Spain. The authors found fewer compounds detected in clams compared to passive samplers as well as greater sensitivity of passive samplers to detect spatiotemporal changes in contaminant levels (Pintado-Hererra et al., 2020). Though differences in the analytical method, specific compounds, and study design used between studies precludes a direct comparison, taken together these findings emphasize the efficacy of passive samplers in detecting a broader suite of PPCPs relative to bivalves under field conditions.

To further investigate the relationship between PPCP accumulation in POCIS and co-deployed mussels, linear regression of contaminant levels in both matrices was conducted where adequate data was available. Of the five compounds used for comparison (amitriptyline, fluoxetine, sertraline, diphenhydramine, and citalopram), positive relationships between aqueous concentrations measured using POCIS and tissue residues were observed for all five compounds, though only two were statistically significant (diphenhydramine and sertraline, section 3.2). Furthermore, model fit for all five compounds was relatively poor (i.e., $r^2 < 0.40$) compared to a previous critical review focusing on the relationship between accumulation of hydrophobic organic contaminants in passive samplers and aquatic organisms (Joyce et al., 2016). Across 21 studies analyzed in Joyce et al., (2016), r^2 values of contaminant levels in passive samplers and aquatic organisms ranged from 0.31 - 0.98, with all but one study having higher r^2 values than the present study. This finding indicates poorer model fit for the PPCP data in the present work compared to more hydrophobic contaminants such as PAHs and PCBs which were the focus of Joyce et al., (2016). Bioconcentration potential in bivalves is typically thought to be positively related to Log K_{ow} values (Joyce et al., 2016); thus, this finding is expected based on the hydrophilicity and low bioconcentration potential of many PPCP compounds. However, the compounds measured in both POCIS and mussels used for regression analyses were the more hydrophobic PPCPs, with Log K_{ow} values ranging from 3.04 - 5.29. Therefore, the poor correlation between concentrations in POCIS and mussels for these compounds cannot be explained by lower relative accumulation in mussels alone since accumulation of these compounds would be anticipated based on established relationships between Log K_{ow} values and bioconcentration factors (Geyer et al., 2000).

A number of factors may influence the preferential accumulation of contaminants in either passive sampling devices or biota. Accumulation of contaminants on passive samplers can be influenced by biofouling (Khulu et al.,

2022), as well as the *in-situ* sampling rate which in turn can be impacted by levels of dissolved organic matter and a range of abiotic factors including temperature and pH (Li et al., 2016). Comparatively, accumulation in mussels can be influenced by a suite of factors including reproductive stage, age, sex, and condition index (Pintado-Hererra et al., 2020). In addition, extraction and quantification of contaminants from passive samplers often facilitates greater analytical sensitivity compared to similar analyses from biological tissue, due to the cleaner matrix associated with passive samplers (Pintado-Hererra et al., 2020). Finally, it is important to consider that PRCs and *in situ* field sampling rates were not used for the POCIS component of this study, with literature values used to convert POCIS concentrations to TWA aqueous concentrations (Table A3). Given that data was pooled from multiple years and sampling areas within the Great Lakes, variation in hydrological conditions between areas and the subsequent effects on *in situ* sampling rates may have introduced additional variability within the POCIS dataset.

4.2 Pesticides in POCIS

For the pesticides analyzed in POCIS, a total of 45 compounds were detected at least once, with several current use compounds including atrazine, simazine, and desethylatrazine detected in 100% of samples. Comparing with detections in tissue, 14/45 compounds (31.1%) were recorded in POCIS only, 7/45 were detected in mussels only (15.6%) and the remaining 24 (53.3%) were found in both matrices in at least one site. As anticipated based on the design of POCIS, many of the compounds found only in passive samplers were the more hydrophilic current use compounds (Section 3.4, Figure 8). For example, simazine and dimethanimid (Log K_{ow} values of 1.97 and 2.17, respectively) were both recorded only in POCIS, and several similar compounds were recorded more commonly in POCIS than mussels, such as metribuzin (Log K_{ow} = 1.70) which was recorded in 50% of POCIS samples but only a single mussel sample (Figure 8). Comparatively, many of the more hydrophobic and bioaccumulative legacy pesticides including the DDT degradates 4,4'-DDD, 4,4'-DDT, and 2,4'-DDE were detected only in mussels (Figure 8). Few studies have compared pesticide residues in both POCIS and mussels in the natural environment, with Scully-Engelmeyer et al., (2021) finding no overlap between a suite of current use pesticide occurrence in bivalves collected *in situ* and POCIS deployed in Oregon coastal watersheds.

The herbicide atrazine and its major degradation product, desethylatrazine, were the only two current use compounds with adequate data coverage for comparison of residues measured using POCIS and in mussel tissue. Though positive relationships were observed for both compounds, a strong, positive significant relationship was observed for desethylatrazine (r^2 = 0.781), whereas a weak, non-significant relationship was recorded for atrazine (r^2 = 0.145). In general, both atrazine and desethylatrazine are thought to have low bioaccumulation potential in bivalves (Jacomini et al., 2006; Nuchan et al., 2022); thus, the significant positive relationship between residues in POCIS and mussels for desethylatrazine was unexpected. Compared with atrazine which has been well studied in terms of its environmental fate and transport, further research is required to determine the bioconcentration potential of desethylatrazine both in the laboratory and in the natural environment.

4.3 SPMDs - PAH

For PAHs, all of the compounds analyzed in SPMDs were detected at least once across all deployments, with good agreement between the compounds detected in both SPMDs and mussels (Section 3.6, Figure 12). Furthermore, strong, significant positive relationships were recorded between parent and alkylated PAH concentrations in SPMDs and mussels (r^2 = 0.882 and 0.922 for parent and alkylated, respectively). These relationships are consistent with the critical review of Joyce et al., (2016), who found significant positive relationships between PAH levels in a range of different passive sampling devices and aquatic organisms. However, the composition of PAHs recorded in SPMDs exhibited several differences to those in mussels (Section 3.6, Figure 15), with passive samplers from all sites having greater relative proportions of fluoranthene, pyrene,

and phenanthrene relative to mussels at the same site. Furthermore, values for the two PAH diagnostic ratios anthracene:phenanthrene and benz[a]anthracene:chrysene showed large differences when calculated using either SPMD or mussel data. For example, at 70% of the sites where SPMDs were co-deployed with mussels, anthracene:phenanthrene ratios for mussels indicated pyrogenic sources of PAHs (> 0.1, Tobiszewski and Namieśnik, 2009), whereas the same ratio calculated for SPMDs indicated petrogenic sources (< 0.1, Tobiszewski and Namieśnik, 2009).

Different compositions of PAHs in SPMDs compared to co-deployed mussels have been observed previously by Boehm et al., (2006), who co-deployed SPMDs and the Pacific blue mussel, *Mytilus trossulus*, at oil spill sites in Alaska. The authors found that SPMDs were depleted in the 3-4 ring higher molecular weight PAHs such as fluoranthene and pyrene relative to mussels, whereas SPMDs contained a higher proportion of lower molecular weight PAHs such as naphthalene and fluorene (Harman et al., 2011). Similar findings were observed by Peven et al., (1996), who found a reduction in higher molecular weight compounds in SPMDs compared to blue mussels (*Mytilus edulis*) deployed in Dorchester and Duxbury bays (MA, USA). Conversely, other studies have found similar PAH profiles between SPMDs and mussels (Axelman et al., 1999; Baussant et al., 2001). Several factors may have contributed to the differences in PAH profiles between SPMDs and mussels observed in the present study. In general, reduced sampling rates for higher molecular weight PAHs and chlorinated hydrocarbons have been observed, whereas the smaller more water-soluble PAH compounds are sequestered in the triolein of the SPMDs and sampled at higher rates (Huckins et al., 1990; Peven et al., 1996). However, given that the compositional differences between SPMDs and mussels recorded in the present study did not appear directly related to molecular weight (Section 3.6, Figure 15), the differences between the two matrices are likely due to the differences in uptake of PAHs between SPMDs and mussels. Mussels accumulate PAHs from the dissolved, colloidal, and particulate phases and ingest particulate-bound contaminants on sediment and food particles (Boehm et al., 2006), whereas SPMDs accumulate contaminants only in the dissolved and colloidal forms by direct adsorption within the polyethylene membrane (Luellen and Shea, 2003).

4.4 SPMDs - Legacy Pesticides

For the legacy pesticides, good agreement between the compounds detected in SPMDs and mussels was observed, with 79% of the compounds detected in both matrices which is anticipated based on the hydrophobic nature of the legacy pesticides and expected performance of SPMDs (i.e., targeting compounds with Log K_{ow} values > 4.0). Given the large number of legacy pesticides measured and the lower interest in banned compounds from a management perspective, these compounds were analyzed as summed totals. A significant positive relationship between total legacy pesticide residues in both SPMDs and mussels was observed (Section 3.7, Figure 20). These findings are supported by previous studies suggesting that SPMDs and associated hydrophobic passive samplers can be used to predict the availability of legacy compounds such as the DDT group for mussels (Tomaszewski et al., 2008; Joyce et al., 2016).

4.5 Limitations

One potential limitation of this study is the differences in deployment durations used across studies, with durations ranging from 27 - 84 days (Table 1). For both POCIS and SPMDs, deployment durations are typically 30 days or less in environmental monitoring studies (Alvarez et al., 2010; Harman et al., 2012). Though few studies have considered the influence of longer deployment durations (*i.e.*, > 30 days) on time-weighted average concentrations, it is possible that equilibrium and/or sorbent capacity may have been reached during the longer deployment durations, which could in turn influence sampling rates of compounds (Harman et al., 2012). Furthermore, a greater degree of biofouling would be expected in longer deployments, which can further influence sampling rates (Harman et al., 2012; Wang et al., 2022). Though many of these factors are likely to have been mitigated by the

use of performance reference compounds (PRCs, Harman et al., 2012), these were used for SPMDs only in the present study. Thus, the variation in deployment dates may have influenced the sampling rates of compounds and subsequent estimations of time weighted average concentrations in POCIS deployments.

4.6 Recommendations for Environmental Monitoring Programs

The present study aimed to compare the relationship between contaminants of emerging concern and PAHs in colocated passive samplers and mussels during several place-based assessments within the Great Lakes. For the CECs, a large suite of PPCPs were analyzed in both POCIS and mussels, with POCIS found to accumulate a much broader range of compounds compared to mussels alone. Therefore, for the purpose of detecting contaminants in the aquatic environment and determining potential exposure, POCIS should be used preferentially over caged mussels for monitoring. However, a total of 18 compounds were detected in mussels only and never POCIS, which was not clearly related to the octanol-water partitioning coefficient and expected performance of the passive sampler. Furthermore, poor agreement between concentrations of several pharmaceuticals in POCIS and mussels was observed for several compounds, suggesting that analysis of mussels may be required to contextualize the findings from passive sampling devices for more hydrophilic compounds that do not readily bioaccumulate. Overall, similar findings were observed for analysis of pesticides in POCIS, with a broader suite of compounds found using POCIS than mussels, emphasizing the ability of POCIS to accumulate hydrophilic current use compounds more effectively than mussels. For example, the herbicide atrazine was detected in only 30.7% of mussel samples, despite being present in 100% of POCIS samples. Given that atrazine has been identified as being present in concentrations sufficient to cause deleterious effects in several basin-wide Great Lakes studies (Alvarez et al., 2021; Corsi et al., 2019; Loken et al., 2022), effective biomonitoring of this compound is of particular importance within the basin. Taking this into account and the poor relationship between atrazine concentrations measured in POCIS and mussel tissue, POCIS is recommended for comprehensive biomonitoring of current use pesticide compounds.

In terms of the SPMD dataset, aqueous total concentrations of parent and alkylated SPMDs were found to be highly correlated with tissue residues in mussels, suggesting that SPMDs can be used interchangeably with mussels in terms of predicting total PAH exposure. However, the composition of PAHs accumulated in SPMDs and mussels appeared different, leading to differences in several commonly used diagnostic ratios used for PAH source apportionment. Therefore, based on the findings of this study, SPMDs can be used in place of mussels for estimating total PAH exposure, but should not be used for tracing sources of PAHs to biota. Finally, good agreement was recorded between the occurrence and concentration of a suite of legacy pesticides in SPMDs and mussels, suggesting that passive samplers can adequately capture exposure to legacy contaminants. Taken together, these findings will support the design and implementation of effective environmental monitoring within the Great Lakes. Whilst this study focused on POCIS and SPMDs, many other passive sampling devices are commonly used including silicone rubber configurations, solid-phase microextraction (SPME) fibers, and polyethylene sheets (Vrana et al., 2005). Furthermore, recent advancements in the use of *in situ* active samplers such as the continuous low-level aquatic monitoring (CLAM) system (Coes et al., 2014) warrant further study to compare a broader suite of monitoring techiques with sentinel organisms such as mussels.

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Appendix

Table A1. Site details, coordinates, and year(s) sampled for all locations where passive samplers and mussels were colocated. Further details are available in Table 1.

Site Code	Site Description	Year(s) Sampled	Area	Latitude	Longitude
Milwaukee 4	Northern Outer Harbor	2017, 2018	Milwaukee Estuary	43.04319	-87.8878
Milwaukee 5	Lake Michigan Offshore	2017, 2018	Milwaukee Estuary	43.05943	-87.8647
Milwaukee 6	North Jones Island	2017	Milwaukee Estuary	43.0247	-87.8976
Milwaukee 8	Upper Milwaukee River	2017, 2018	Milwaukee Estuary	43.05679	-87.8983
Milwaukee 11	Upper Menominee River	2017, 2018	Milwaukee Estuary	43.03296	-87.9396
Milwaukee 13	Upper Kinnikinic River	2017	Milwaukee Estuary	43.0046	-87.9067
Milwaukee 17	Jones Island Outfall	2018	Milwaukee Estuary	43.01408	-87.5366
Muskegon	Muskegon Pierhead	2018 (May, June, September, November)	Muskegon Lake	43.2266	-86.3414
Maumee 0	Grassy Island	2015, 2016	Maumee River	41.70061	-83.4597
Maumee 1	Toledo WWTP	2015, 2016	Maumee River	41.68919	-83.4769
Maumee 2	Downtown Toledo	2015	Maumee River	41.655367	-83.5251
Maumee 4	Swan Creek Upstream	2016	Maumee River	41.63617	-83.5311
Ottawa 1	Confluence	2015	Ottawa River	41.7329	-83.4682
Ottawa 2	Summit Street Bridge	2015	Ottawa River	41.72475	-83.4798
Ottawa 3	Suder Ave Bridge	2015	Ottawa River	41.7106	-83.4994
Rouge 1	Detroit WWTP	2016	Rouge River	42.28009	-83.1226
Rouge 2	O'Brien Drain	2016	Rouge River	42.2859	-83.1394
Rouge 3	Fordson Island	2016	Rouge River	42.29521	-83.1492

Appendix

Table A2. List of compounds analyzed in tissue and passive samplers, organized by chemical class.

Compound Class	Compound
Tissue	
Polycyclic Aromatic Hydrocarbons (PAHs)	1,6,7-Trimethylnaphthalene, 18a-Oleanane 1-Methyldibenzothiophene, 1-Methylfluorene, 1-Methylnaphthalene, 1-Methylphenanthrene, 2,6-Dimethylnaphthalene, 2/3-Methyldibenzothiophene, 2-Methylanthracene, 2-Methylfluoranthene, 2-Methylnaphthalene, 2-Methylphenanthrene, 3,6-Dimethylphenanthrene, 3-Methylphenanthrene, 4/9-Methylphenanthrene, 4-Methyldibenzothiophene, Acenaphthene, Acenaphthylene, Anthracene, Benz(a)anthracene, Benzo(a)fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(b)fluorene, Benzo(e)pyrene, Benzo(g,h,i)perylene, Benzo(k,j)fluoranthene, Benzothiophene, Biphenyl, C1-Benzothiophenes, C1-Chrysenes, C1-Decalins, C1-Dibenzo(a,h)anthracenes, C1-Dibenzothiophenes, C1-Fluoranthenes/Pyrenes, C1-Fluorenes, C1-Naphthalenes, C1-Naphthobenzothiophenes, C1-Phenanthrenes/Anthracenes, C20-TAS, C21-TAS, C26(20R)/C27(20S), TAS C26(20S), TAS C27(20R), TAS C28(20R), TAS C28(20S), TAS C29, Hopane, C2-Benzothiophenes, C2-Chrysenes, C2-Decalins, C2-Dibenzo(a,h)anthracenes, C2-Dibenzothiophenes, C2-Fluoranthenes/Pyrenes, C2-Fluorenes, C2-Naphthalenes, C2-Naphthobenzothiophenes, C2-Phenanthrenes/Anthracenes, C30-Hopane, C3-Benzothiophenes, C3-Chrysenes, C3-Decalins, C3-Dibenzo(a,h)anthracenes, C3-Dibenzothiophenes, C3-Fluoranthenes/Pyrenes, C3-Fluorenes, C3-Naphthalenes, C3-Naphthobenzothiophenes, C3-Phenanthrenes/Anthracenes, C4-Benzothiophenes, C4-Chrysenes, C4-Decalins, C4-Dibenzothiophenes, C4-Fluoranthenes/Pyrenes, C4-Naphthalenes, C4-Naphthobenzothiophenes, C4-Phenanthrenes/Anthracenes, Carbazole, Chrysene/Triphenylene, cis/trans Decalin, Dibenzo(a,h)anthracene, Dibenzofuran, Dibenzothiophene, Fluoranthene, Fluorene, Indeno(1,2,3-c,d)pyrene, Naphthalene, Naphthobenzothiophene, Perylene, Phenanthrene, Pyrene, Retene
Pesticides	Tecnazene, Hexachlorobenzene, Quintozene, Heptachlor, HCH-alpha, HCH-gamma, HCH-beta, HCH- delta, Chlorothalonil, Aldrin, Dacthal, Octachlorostyrene, Chlordane-oxy,-Heptachlor Epoxide, Chlordane-gamma (trans), Chlordane-alpha (cis), Nonachlor, trans, Nonachlor, cis, alpha-Endosulphan, beta-Endosulphan, Dieldrin, 2,4'-DDD, 4,4'-DDD, 2,4'-DDE, 4,4'-DDE, 2,4'-DDT, 4,4'-DDT, Captan, Perthane, Endrin, Endosulphan Sulphate, Mirex, Methoxychlor, Endrin Ketone, Desethylatrazine, Simazine, Atrazine, Ametryn, Metribuzin, Cyanazine, Hexazinone, Phorate, Terbufos, Diazinon-Oxon, Diazinon, Disulfoton, Fonofos, Dimethoate, Chlorpyriphos-Methyl, Parathion-Methyl, Pirimiphos-Methyl, Chlorpyriphos, Fenitrothion, Malathion, Parathion-Ethyl, Chlorpyriphos-Oxon, Disulfoton Sulfone, Ethion, Phosmet, Azinphos-Methyl, Permethrin, Cypermethrin, Butylate, Ethalfluralin, Trifluralin, Triallate, Dimethenamid, Alachlor, Butralin, Flufenacet, Metolachlor, Linuron, Pendimethalin, Flutriafol, Tebuconazole

Appendix

Table A2 (Continued). List of compounds analyzed in tissue and passive samplers, organized by chemical class.

Pharmaceutical & Personal Care Products	Albuterol, Amphetamine, Atenolol, Atorvastatin, Cimetidine, Clonidine, Codeine, Cotinine, Enalapril, Hydrocodone, Metformin, Oxycodone, Ranitidine, Triamterene, Bisphenol A, Furosemide, Gemfibrozil, Glipizide, Glyburide, Hydrochlorothiazide, 2-Hydroxy-ibuprofen, Ibuprofen, Naproxen, Triclocarban, Triclosan, Warfarin, Acetaminophen, Azithromycin, Caffeine, Carbadox, Carbamazepine, Cefotaxime, Ciprofloxacin, Clarithromycin, Clinafloxacin, Cloxacillin, Dehydronifedipine, Diphenhydramine, Diltiazem, Digoxin, Digoxigenin, Enrofloxacin, Erythromycin-H2O, Flumequine, Fluoxetine, Lincomycin, Lomefloxacin, Miconazole, Norfloxacin, Norgestimate, Ofloxacin, Ormetoprim, Oxacillin, Oxolinic Acid, Penicillin G, Penicillin V, Roxithromycin, Sarafloxacin, Sulfachloropyridazine, Sulfadiazine, Sulfadimethoxine, Sulfamerazine, Sulfamethazine, Sulfamethizole, Sulfamethoxazole, Sulfanilamide, Sulfathiazole, Thiabendazole, Trimethoprim, Tylosin, Virginiamycin M1, 1,7-Dimethylxanthine, Alprazolam, Amitriptyline, Amlodipine, Benzoylecgonine, Benztropine, Betamethasone, Cocaine, Desmethyldiltiazem, Diazepam, Fluocinonide, Fluticasone, Propionate, Hydrocortisone, 10-hydroxy-amitriptyline, Meprobamate, Methylprednisolone, Metoprolol, Norfluoxetine, Norverapamil, Paroxetine, Prednisolone, Prednisone, Promethazine, Propoxyphene, Propranolol, Sertraline, Simvastatin, Theophylline, Trenbolone, Trenbolone acetate, Valsartan, Verapamil, Diatrizoic acid, Iopamidol, Citalopram, Tamoxifen, Cyclophosphamide, Venlafaxine, Amsacrine, Azathioprine, Busulfan, Clotrimazole, Colchicine, Daunorubicin, Doxorubicin, Drospirenone, Etoposide, Medroxyprogesterone Acetate, Metronidazole, Moxifloxacin, Oxazepam, Rosuvastatin, Teniposide, Zidovudine, Melphalan, Anhydrochlortetracycline [ACTC], Anhydrotetracycline [ATC], Chlortetracycline [CTC], Demeclocycline, Doxycycline, 4-Epianhydrochlortetracycline [EACTC], 4-Epianhydrotetracycline [EATC], 4-Epichlortetracycline [ECTC], 4-Epioxytetracycline [EOTC], 4-Epitetracycline [ETC], Isochlortetracycline [ICTC], Minocycline, Oxytetracycline [OTC], Tetracycline [TC], DEET
POCIS	
Pesticides	Alpha endosulfan, Mirex, Beta endosulfa, Endrin, Aldrin, Dichlorprop, MCPA, Dacthal, Methoxychlor, Endrin Ketone, Dinoseb, Ametryn, 2,4,5-TP [Silvex], Perthane, Cyanazine, Endosulfan sulfate, HCH-alpha, HCH- beta, Hexazinon,e 2,4,5-T, 2,4-D, Nonachlor, cis, 2,4’-DDD, 4,4’-DDD, 2,4’-DDE, 4,4’-DDE, 2,4’-DDT, 4,4’-DDT, Triallate, Alachlor, Butralin, Flufenacet, Linuron, Pendimethalin, Flutriafol, Tebuconazole, Tecnazene, HCH-delta, Chlorothalonil, Octachlorostyrene, Nonachlor, trans, Ethalfluralin, Trifluralin, Diazinon, Azinphos-Methyl, Butylate, Diazinon-Oxon, Fonofos, Dimethoate, Ethion, Parathion-Methyl, Pirimiphos-Methyl, Chlorpyrifos, Fenitrothion, Malathion, Chlorpyriphos-Oxon, Parathion-Ethyl, Chlorpyrifos-Methyl, Phorate, Disulfoton, Disulfoton Sulfone, Heptachlor Epoxide, Chlordane-gamma (trans), Methomyl, Aldicarb Sulfone, Pirimicarb, Piperonyl butoxide, Imidacloprid ,Chlorpyrifos, Diazinon, Hexachlorobenzene, Heptachlor, Dieldrin, HCH- gamma, Chlordane-alpha (cis), Chlordane- oxy, MCPP, Quintozene, Dimethenamid, Simazine, Triclopyr, Metribuzin, 2,4-D, Desethylatrazine, Metolachlor, Atrazine

Table A2 (Continued). List of compounds analyzed in tissue and passive samplers, organized by chemical class.

Pharmaceuticals and Personal Care Products	Oxycodone, Cotinine, Clonidine, Melphalan, Zidovudine, Codeine, Ranitidine, Hydrocodone, Enalapril, Verapamil, Furosemide, Albuterol, Medroxyprogesterone, Acetate, Atenolol, Atorvastatin, Glipizide, Naproxen, Triclocarban, Azathioprine, Colchicine, Daunorubicin, Doxorubicin, Ormetoprim, Etoposide, 17 beta-Estradiol, 17 alpha-Estradiol, Allyl, Trenbolone, Androsterone, Theophylline, Trenbolone, Trenbolone acetate, Bisphenol A, Teniposide, Glyburide, Hydrochlorothiazide, 2-Hydroxy-ibuprofen, Ibuprofen, Amsacrine, Busulfan, Clotrimazole, Cocaine, Desmethyldiltiazem, Diazepam, Fluocinonide, Fluticasone,, propionate, Metronidazole Moxifloxacin, Oxazepam, 17 alpha-Ethinyl-Estradiol, Cyclophosphamide, Amsacrine, Azathioprine, Busulfan, Clotrimazole, Metronidazole, Moxifloxacin, Cefotaxime, Ciprofloxacin, Clarithromycin, Clinafloxacin, Dehydronifedipine, Diphenhydramine, Diltiazem, Triclosan, Warfarin, Flumequine, Fluoxetine, Melphalan, Lomefloxacin, Miconazole, Norfloxacin, Norgestimate, 17 alpha-Dihydroequilin, Equilenin, Equilin, Diatrizoic acid, Rosuvastatin, Teniposide, Zidovudine, Rosuvastatin, Prednisolone, Prednisone, Promethazine, Norethindrone, Benztropine, Tamoxifen, Cyclophosphamide, Amitriptyline, Amlodipine, Carbadox, Sulfadiazine, Betamethasone, Sulfamerazine, Sulfamethazine, Propoxyphene, Propranolol, Ofloxacin, Simvastatin, 10-Hydroxy-amitriptyline, Iopamidol, Enrofloxacin, Sulfadimethoxine, Sertraline, Acetaminophen, Trimethoprim, Azithromycin, Caffeine, Methylprednisolone, Metoprolol, Norfluoxetine, Norverapamil, Paroxetine, Diatrizoic acid, Sulfamethizole, Sulfanilamide, Virginiamycin M1, Iopamidol, Digoxin, Digoxigenin, Sulfachloropyridazine, 1,7-Dimethylxanthine, Roxithromycin, Sarafloxacin, Meprobamate, Sulfathiazole, Sulfamethoxazole, Norgestrel, Alprazolam, Penicillin V, Oxolinic Acid, Mestranol, Tylosin, Estriol, Thiabendazole, Testosterone , Progesterone, Cimetidine, Cloxacillin, Oxacillin, Penicillin G, Benzoylecgonine, Triamterene, Citalopram, Amphetamine, Erythromycin-H2O, Metformin, Venlafaxine, Gemfibrozil, Valsartan, Lincomycin, Carbamazepine, Estrone, Androstenedione, DEET
SPMDs	
Legacy Pesticides	Hexachlorobenzene, HCH-alpha, HCH-beta, HCH-gamma, Heptachlor, Aldrin, Chlordane-oxy, Chlordane-gamma (trans), Chlordane- alpha (cis), Nonachlor- trans, Nonachlor-cis, 2,4’-DDD ,4,4’-DDD, 2,4’-DDE, 4,4’-DDE, 2,4’-DDT, 4,4’-DDT, Mirex, HCH-delta , Heptachlor Epoxide, alpha-Endosulphan, Dieldrin, Endrin, beta-Endosulphan, Endosulphan Sulphate, Endrin Aldehyde, Endrin Ketone, Methoxychlor, Toxaphene
Polycyclic Aromatic Hydrocarbons (PAHs)	Naphthalene, Acenaphthylene, Acenaphthene, 2-Methylfluorene, C2 Phenanthrenes/Anthracenes, Fluorene, Phenanthrene, Anthracene, C1 Phenanthrenes/Anthracenes, Fluoranthene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[j,k]fluoranthenes, Benzo[e]pyrene, Benzo[a]pyrene, Perylene, Dibenz[a,h]anthracene, Indeno[1,2,3-cd]pyrene, Benzo[ghi]perylene, 2-Methylnaphthalene, 1-Methylnaphthalene, C1-Naphthalenes, Biphenyl, C1-Biphenyls, C2-Biphenyls, C2-Naphthalenes, 1,2-Dimethylnaphthalene, 2,6-Dimethylnaphthalene, C3-Naphthalenes, 2,3,6-Trimethylnaphthalene, 2,3,5-Trimethylnaphthalene, C4-Naphthalenes, C1-Acenaphthenes, C1-Fluorenes, 1,7-Dimethylfluorene, C2-Fluorenes, C3-Fluorenes, Dibenzothiophene, C1-Dibenzothiophenes, 2/3-Methyldibenzothiophenes, C2-Dibenzothiophenes, 2,4-Dimethyldibenzothiophene, C3-Dibenzothiophenes, C4-Dibenzothiophenes, 3-Methylphenanthrene, 2-Methylphenanthrene, 2-Methylanthracene, 9/4-Methylphenanthrene, 1-Methylphenanthrene, 3,6-Dimethylphenanthrene, 2,6-Dimethylphenanthrene, 1,7-Dimethylphenanthrene, 1,8-Dimethylphenanthrene, C3-Phenanthrenes/Anthracenes

Appendix

Table A3. Sampling rates (in liters per day) and references for select compounds detected in POCIS

Compound	R_s (L/d)	Reference
PPCPs		
Amitryptiline	0.625	Alvarez et al., (Unpublished data)
Citalopram	0.445	Li et al., (2010)
Diphenyhydramine	0.849	Bartelt-Hunt et al., (2011)
Fluoxetine	0.196	Alvarez et al., (2004)
Sertaline	0.729	Li et al., (2011)
Pesticides		
4,4'-DDE	0.032	Alvarez et al., (2007)
Aldrin	0.032	Alvarez et al., (2007)
Atrazine	0.227	Alvarez et al., (2007)
Desethylatrazine	0.260	Alvarez et al., (2007)
Dieldrin	0.086	Alvarez et al., (2007)

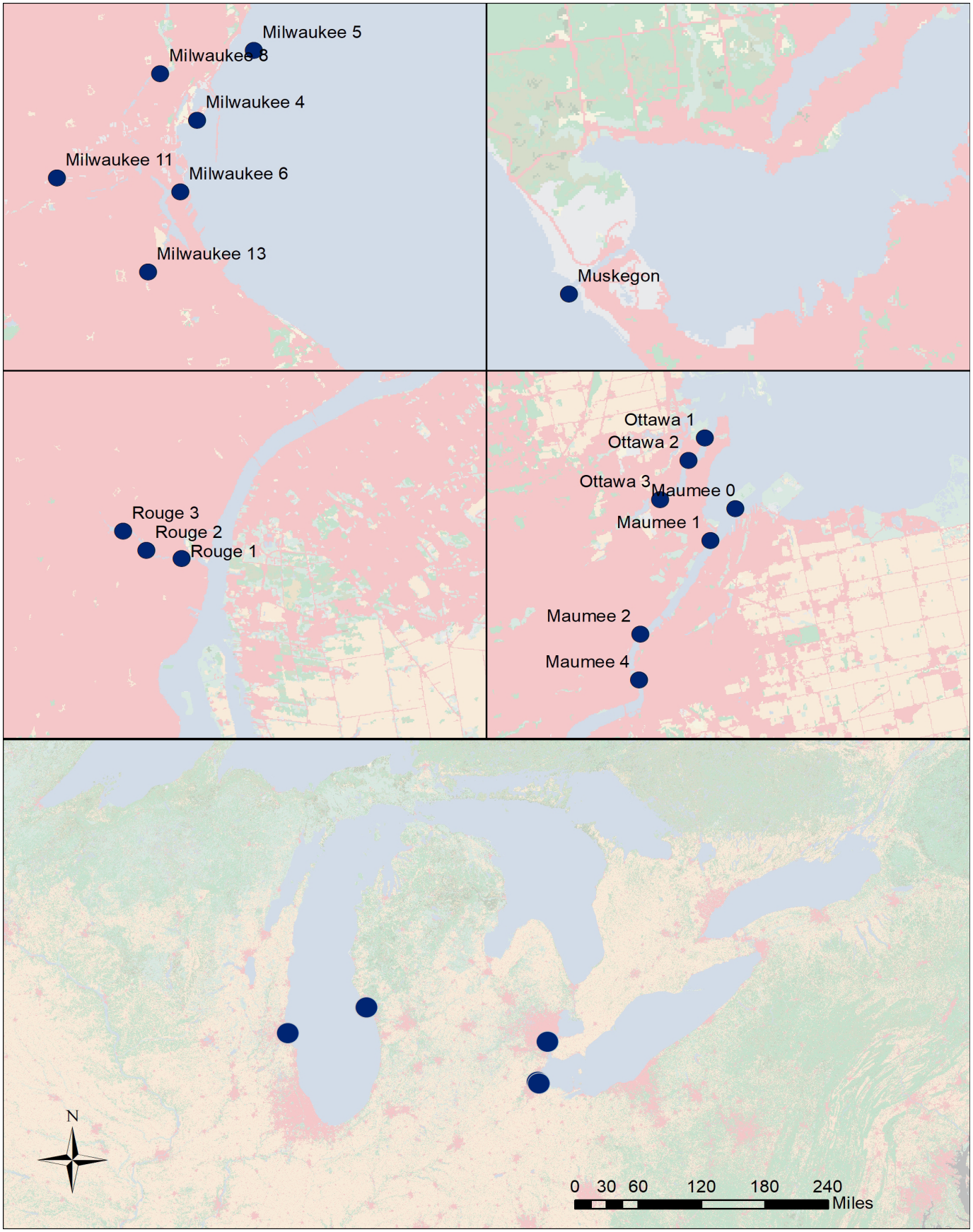

Figure A3. Specific locations of the sites of POCIS and SPMD deployments in the present study. Latitudes and longitudes are available in Table A1.

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