



Polycyclic aromatic compounds in a northern freshwater ecosystem: Patterns, sources, and the influences of environmental factors[☆]

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ABSTRACT

Polycyclic aromatic compounds (PACs) - a large group of organic chemicals naturally present in petroleum deposits (i.e., petrogenic) or released into the environment by incomplete combustion of organic materials (i.e., pyrogenic) - represent a potential risk to the health of aquatic ecosystems. In high latitude freshwater ecosystems, concentrations of PACs may be increasing, yet there are limited studies in such systems to assess change and to understand threats. Using 10 years of contemporary data from passive samplers deployed across five regions (n = 43 sites) in the Mackenzie River Basin, we (i) describe baseline levels of PACs, (ii) assess spatiotemporal patterns, and (iii) evaluate the extent to which environmental factors (fire, snowmelt, and proximity to oil infrastructure) influence concentrations in this system. Measured concentrations were low, relative to those in more southern systems, with mixtures primarily being dominated by non-alkylated, low molecular weight compounds. Concentrations were spatially consistent, except for two sites near Norman Wells (an area of active oil extraction) with increased levels. Similarly, observed annual variation was minimal, with 2014 having generally higher levels of PACs. We did not detect effects of fire, snowmelt, or oil infrastructure on concentrations. Taken together, our findings suggest that PACs in the Mackenzie River are currently at low levels and are primarily petrogenic in origin. They further indicate that ongoing monitoring and testing of environmental drivers (especially at finer spatial scales) are needed to better predict how ecosystem change will influence PAC levels in the basin and in other northern systems.

1. Introduction

Polycyclic aromatic compounds (PACs) – a group of >100 lipophilic organic chemicals – are formed under low temperature and high-pressure conditions over geological time scales (i.e., petrogenic) or released from the rapid and incomplete combustion of organic matter at high temperatures (i.e., pyrogenic) and can persist in the environment by binding to sedimentary organic carbon (Abdel-Shafy and Mansour, 2016; Wallace et al., 2020; Hsieh et al., 2021). In high-latitude marine and freshwater ecosystems, PACs have been documented at all trophic levels, with apparent recent increases in lower trophic level biota (De

Laender et al., 2011; Provencher et al., 2020). As some PACs are known carcinogens and some are cardiotoxic, genotoxic, and immunotoxic for vertebrates and invertebrates (Bolden et al., 2017; Idowu et al., 2019; Wallace et al., 2020; Gyasi et al., 2022), understanding the extent to which PACs represent potential threats to northern freshwater ecosystems and implementing effective monitoring requires quantifying baseline levels of PACs across a broad geographic scale (Elmes et al., 2016). Yet there are scant data describing PACs in freshwater ecosystems of Arctic and subarctic North America (Balmer et al., 2019; Marvin et al., 2021; but see Yunker et al., 2002; Mundy et al., 2019; Lévesque et al., 2023). Further, proximate factors and the transport pathways that

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influence observed spatial and annual patterns in PACs, especially in northern systems, remain poorly understood, limiting our ability to predict how ongoing environmental change may affect occurrence and distribution of these pollutants.

Northern Canada's largest watershed, the Mackenzie River Basin covers a surface area of approximately 1.8×10^6 km², which is currently being impacted by climate change, while also being increasingly developed for mining and oil and gas extraction (Woo, 2008; Rood et al., 2017; Culp et al., 2023). Hydrocarbon reserves with natural seepage and extraction sites are located throughout the basin, including near the community of Norman Wells, Northwest Territories, where oil extraction operations have been present for over a century (Bone and Mahnic, 1984; Lockhart et al., 1987; Headley et al., 2002; Lumb et al., 2006). These reserves and associated operations, as well as erosion of geological formations, influence Mackenzie River Basin PAC levels, and while most early research in this system indicates a predominance of petrogenic PACs (i.e., with alkyl substituents, typically ≤ 3 aromatic rings, lower molecular weight) that are released by hydrological processes, such studies primarily measured PACs in sediments and suspended particulates, rather than surface water (Carey et al., 1990; Yunker and Macdonald, 1995; Headley et al., 2002; Yunker et al., 2011). This early work suggests that source attribution of PACs in the Mackenzie River is distinct from other high-latitude riverine systems, where pyrogenic source (wood combustion) PACs (i.e., mainly 'parent' PACs – without alkyl groups – and predominantly with higher molecular weights) often dominate mixtures (Yunker et al., 2002; Elmquist et al., 2008). However, there are limited contemporary data to evaluate whether source inputs have changed concurrent with ongoing global change during recent decades (Muir and Galarnau, 2021).

For example, wildfires have typically increased (in terms of burned area) at high latitudes, especially in western North America, and could be becoming a more important source of PACs in the Mackenzie Basin. Wildfire-derived PACs could enter the system either from transport of contaminated soil and ash via runoff, or through atmospheric transport and subsequent deposition of volatilized compounds (Jones et al., 2022; Kieta et al., 2023), with elevated atmospheric PACs related to forest-fire events being observed at great distances from the fires (Yu et al., 2019). Although atmospheric contributions of PACs, especially those from human and industrial activities, are considered minimal in the Mackenzie Basin, the relative contribution of this transport pathway may have changed in recent decades (Tevlin et al., 2021; Li et al., 2022). In particular, PACs that are transported in the atmosphere during the winter period can be deposited on and accumulate in snowpacks in cold regions (Ahad et al., 2021; Vecchiato et al., 2024). Evidence of PACs from snowpack being found in riverine surface water samples is equivocal, however, and may be dependent on surrounding landscape (Birks et al., 2017; Nguyen et al., 2018).

To characterize a suite of 42 PACs in surface water throughout the Mackenzie River Basin and to better understand which processes could be influencing variation in PACs in this northern freshwater ecosystem, we analyzed ten years (2012–2021) of surface water data collected across the basin by the Northwest Territories' Community Based Monitoring (CBM) (NWT-wide Community-based Water Quality Monitoring Program, 2022). Our specific objectives were to i) describe baseline levels of PACs at a basin-wide scale; ii) characterize spatial and annual patterns of PACs (relative abundance and concentrations) in surface water; and iii) to evaluate how variability in extent of wildfire, amount of snowmelt, and presence of oil infrastructure might influence these patterns. Based on historic data, we expected that levels of PACs in surface water would be low, relative to more anthropogenically affected systems, and that petrogenic PACs would dominate mixtures (Yunker and Macdonald, 1995; Yunker et al., 2011). We also expected that burning of soil and vegetation during wildfires would lead to elevated levels of soil-bound (i.e., high molecular weight) pyrogenic PACs in the watershed and that subsequent runoff would influence the PACs detected in surface water (Kieta et al., 2023). Specifically, we anticipated that

increasing fire extent in the year preceding our measurements would result in elevated concentrations of higher molecular weight PACs in our samples. Although transfer of atmospherically-derived PACs (deposited onto the snowpack) and snowmelt-induced pulses in PACs have been observed in some systems (alpine and urban streams), we did not expect this pathway would be significant in the Mackenzie River Basin, where atmospheric contributions of most PACs are minimal (Yunker et al., 1993). Rather, we predicted that increasing snowmelt would dilute PAC concentrations in surface water, resulting in a negative relationship between measured levels and snowpack in the preceding year. Finally, because we assumed that presence of oil infrastructure (i.e., petroleum wells) on the landscape would reflect the presence of natural deposits of hydrocarbons, we expected to observe a positive relationship between the relative abundance of petrogenic PACs and the number of wells in the surrounding area.

2. Materials and methods

2.1. Data collection and preparation

2.1.1. Polycyclic aromatic compounds

To conduct our analyses, we compiled data from 2012 to 2021, collected by the CBM (NWT-wide Community-based Water Quality Monitoring Program, 2022). To augment the sampling sites for this dataset, we also included concentrations from samples we collected in 2021. In both cases, lipid-free polyethylene membrane devices (PMDs) were deployed to passively sample PACs that are most bioavailable to aquatic species (i.e., lighter and more water-soluble; Wallace et al., 2020) over a 15–30 day period between June and September. We acknowledge that PMDs consistently under sample PACs that bind to sediment (i.e., high molecular weights) and may not provide a comprehensive assessment of all PACs (Gustafson and Dickhut, 1997; Mzoughi and Chouba, 2011; Rabodonirina et al., 2015), but as indicated by others, maintain that these types of samplers are a valuable tool for beginning to understand ecological risk (Lohmann, 2012; Alvarez et al., 2014).

Performance reference compounds (PRCs) were spiked inside each PMD during fabrication. PRCs were used to calculate PAC concentrations, while accounting for variable temperature, water flow, and build up on the membrane during deployment (McGrath and Di Toro, 2009). We placed PMDs at various sites (ranging from 60 to 68.6° N; n = 43 sites) across the Arctic drainage area and the Great Slave Lake drainage area of the Mackenzie River Basin (Fig. 1), with the final dataset comprising 480 samples (1–31 samples per site) and 42 measured PACs (Table A1). All PMDs were analyzed at the Biogeochemical Analytical Service Laboratory at the University of Alberta, with detailed analytical methods available elsewhere (Anderson et al., 2008; Alvarez, 2010). All measured PACs had method detection levels less than 3.3 ng/L. Fabrication blanks, certified reference material, and duplicate samples were used as quality control measures. The relative percent difference between duplicates was <7%, well below the recommendation of <20% for reliable results (Kelly et al., 2009).

To prepare data for analyses, we replaced all measurements less than the detection limit with half the detection limit (Fromme et al., 2004; Wan et al., 2007; Ratelle et al., 2020, see Tables A2 and A3). To reduce statistical issues related to collinearity and the impact of non-detects, we then summed measured PACs into six sub-class groupings representing PACs of interest, due to relationships with source attribution and toxicity (Ahad et al., 2021; Provencher et al., 2022; Thomas et al., 2022). Sub-class included parent lower molecular weight compounds (PLMW), parent higher molecular weight compounds (PHMW), parent heterocyclic aromatic compounds (PHET), alkylated lower molecular weight compounds (ALMW), alkylated higher molecular weight compounds (AHMW), and alkylated heterocyclic aromatic compounds (AHET) (Table A1).

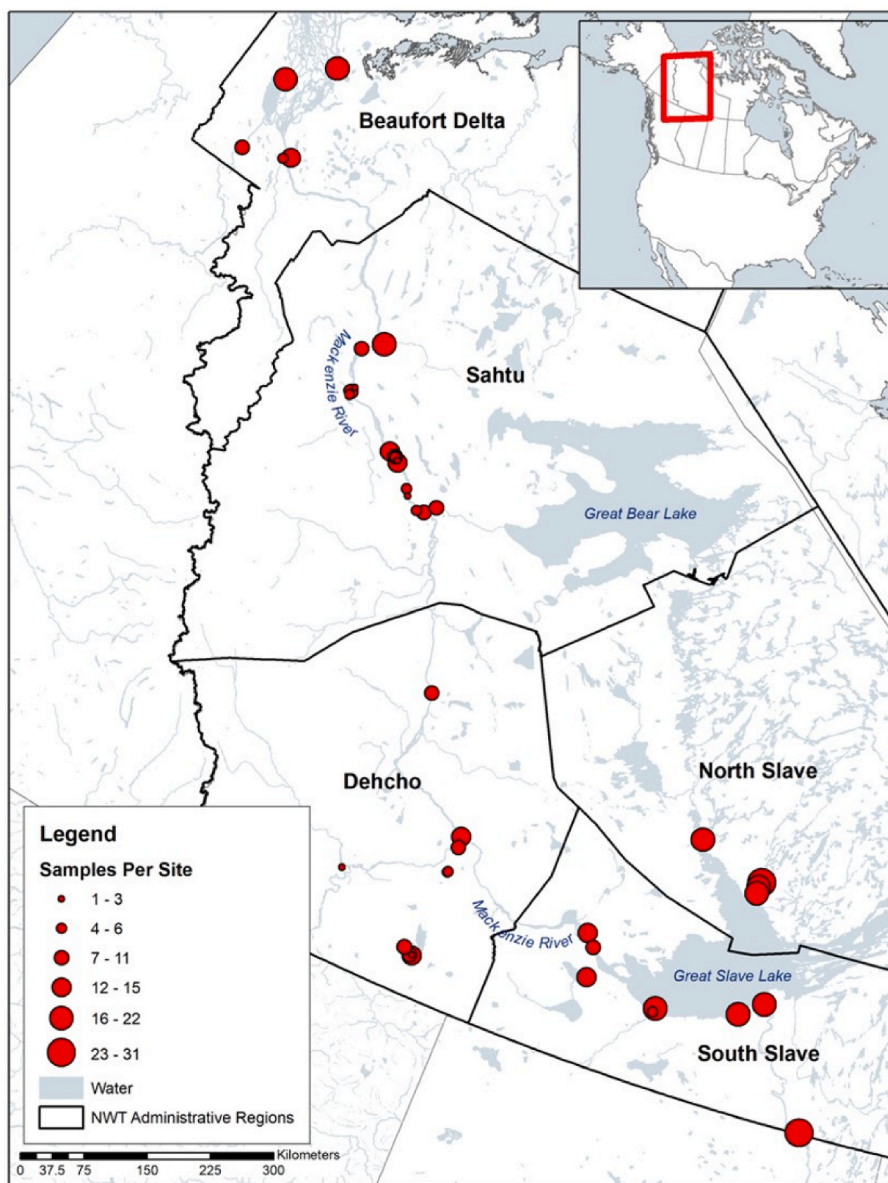


Fig. 1. An overview of the sampling locations and frequencies over the sample period (2012–2021) in the Mackenzie River basin with Northwest Territories, Canada administrative regions outlined.

2.1.2. Environmental covariates

We extracted landscape-level data including snowmelt, wildfire burn areas, and both federally and non-federally regulated oil wells. To select the most appropriate spatial resolution for data extraction, we used a Principal Components Analysis (PCA) of the six PAC sums to assess the variance attributed to the differing levels of spatial aggregation in PACs (major basins, sub basins, and sub-sub basins) in the watershed boundaries (National Hydro Network, 2020). We visually determined that very little variation existed at any level (see Figure A1). Therefore, we extracted snowmelt and burn area data at the major basin level. We removed parts of the watershed that were not located on the mainland (i. e., Canadian Arctic Archipelago) to more accurately determine the influence of environmental covariates on water in the Mackenzie River basin.

To estimate annual snowmelt, we obtained snow water equivalent (mm) measurements within the watersheds in April of the year of PAC measurements using the ERA5-Land dataset (Muñoz Sabater, 2019; Mortimer et al., 2020), which is the optimal time to measure peak snowfall for the winter. Snow water equivalent is measured as the depth

of the water if the snow melted and spread evenly over the grid box (9 km grid spacing across the watershed). We extracted the area of wildfire burn for each major basin that included sampling locations in the year prior to PAC measurements from a dataset compiled by Robinne (2020). The Office of the Regulator of Oil & Gas Operations and the Canada Energy Regulator provided oil well locations, from which we determined the number of oil wells within 10 km of each site using QGIS version 3.28.3- Firenze (QGIS Development Team, 2022), assuming that wells within this radius were a suitable proxy for natural hydrocarbon deposits in the area.

2.2. Statistical analysis

All statistical analyses and plotting were conducted in R version 4.2.2 (R Core Team, 2022). Figures were produced using the packages ggplot2 (Wickham, 2016), ggpubr (Kassambara, 2023), and gridExtra (Auguie, 2017). Prior to analysis, all PAC sums (total PACs, PLMW, PHMW, PHET, ALMW, AHMW, AHET) were log-transformed to achieve normal distributions.

We used linear mixed models (LMM) to determine the impact of environmental covariates on PAC concentrations using the package *lmerTest* (Kuznetsova et al., 2017). LMMs allow us to account for covariance among clustered measurements at the site, year, and month levels while focusing on the effects of environmental covariates on PACs (Littell et al., 2006). The random effects structure was selected by comparing structures using the model with the most parameters (Zuur et al., 2009). As we were more interested in the environmental factors affecting PAC concentrations compared to the spatial and temporal variation, we included site and year within the random structure. We also used month within year in the random structure as the PMDs were not deployed every month in every year. First, we investigated the sum of all PACs as our response variable. Next, we focused on four PAC groups: PLMW, ALMW, PHMW, and AHMW. We chose PLMW and ALMW because they are indicative of a petrogenic source (Neff et al., 2005; Stogiannidis and Laane, 2015), and preliminary data summaries indicated that PLMW and ALMW PACs were the most abundant in the Mackenzie River basin. To incorporate more pyrogenic PACs, we chose PHMWs and AHMWs because they were more variable between years and sites compared to PHET and AHET during preliminary analyses.

We constructed a candidate model set for each response variable (see Table A4). We compared the relative strength of support for the inclusion of each environmental factor using Akaike's Information Criterion and Akaike weights (w_i) to rank models (Burnham and Anderson, 2002; Carreira et al., 2023). Our predictor variables included the number of oil wells within 10 km of the PMD deployment site, burn percentage in the previous year, and snow water equivalent (referred to as snowmelt from this point forward). All predictor variables were standardized (converted to z-scores) to avoid scaling issues. Burn percentage and snowmelt were correlated and not used in the same models ($r = -0.7$). We also included quadratic terms for our three predictor variables to test for potential non-linear relationships. Conclusions regarding fixed effects was based on precision (85% confidence intervals, CI) of the regression coefficient (β) (Arnold, 2010).

Afterwards, we completed a post-hoc analysis to determine if there were any differences between sites or administrative regions (see Fig. 1) that may indicate that more fine-scale environmental factors not sampled in this study could be influencing PAC levels and composition at a scale smaller than a water basin. These post-hoc mixed effects models included year and month within year in the random structure. We used packages *multcomp* (Hothorn et al., 2008) and *emmeans* (Lenth, 2023) to determine differences between sites or regions within

the model.

3. Results

3.1. Baseline levels and observed patterns

Across all sampled locations of the Mackenzie River Basin, surface water concentrations of PACs (all compounds combined) were typically low, ranging from just over 3 ng/L in some years to a high of approximately 300 ng/L in 2014, with parent compounds consistently being the dominant class (Table 1). Across the PAC sub-classes, low molecular weight compounds were typically more prevalent than either high molecular weight or heterocyclic compounds, with the latter consistently being the lowest in relative abundance (and therefore not investigated further in this study). In most years, PLMWs were the predominant PAC sub-class. ALMWs were usually the second greatest contributor to the summed PAC concentrations, apart from 2012 to 2013, when their relative contribution was greater than that of PLMWs (Table 1). Concentrations of total PACs were generally similar across sites, although concentrations of lower molecular compounds (both PLMW and ALMW) in 2014 were higher to the north and west of Great Slave Lake, with smaller increases in PHMWs and AHMWs (Fig. 2). In 2017, there was a noticeable increase in levels of all sub-classes west of Great Bear Lake.

The composition of PAC mixtures across regions tended to follow the same general patterns as at the basin level, where in most cases, the parent compounds were more abundant than alkylated compounds (Fig. 3). The temporal trend of increased relative abundance of ALMWs compared to PLMWs in 2012 and 2013 was observed in all five regions, while in most other years and regions, PLMWs were more dominant than ALMWs (Fig. 3). These trends were also similar for higher molecular weight compounds. In 2012 and 2013, relative abundance of AHMWs was consistently greater or equal to that of PHMWs across regions, except for the North Slave region. In most other cases, the relative abundance of PHMWs was greater than that of AHMWs, especially in 2015 (all regions), when the ratio of AHMWs to PHMWs decreased substantially (Fig. 2). Overall, the temporal trends were similar between regions.

Regarding differences in concentrations of specific PACs, some PACs were above the detection level in over 50% of samples in all regions (Phenanthrene, Benz[a]anthracene, Benzo[b]fluoranthene, Chrysene, Fluoranthene, Pyrene, C1–C3 Fluorene, C3–C4 Naphthalene, C1–C3 Phenanthrenes/anthracenes, C1–C2 Chrysenes, and C1 Fluoranthenes/

Table 1

Summary of the mean, standard deviation (SD), and range of PAC concentrations by year and sub-class (ng/L). PAC sub-classes include parent lower molecular weight (PLMW), parent higher molecular weight (PHMW), parent heterocyclic (PHET), alkylated lower molecular weight (ALMW), alkylated higher molecular weight (AHMW), and alkylated heterocyclic (AHET).

Year		PACs	Parent PACs	PLMW	PHMW	PHET	Alkylated PACs	ALMW	AHMW	AHET
2012	Mean (SD)	7.16 (3.56)	1.78 (0.84)	1.43 (0.78)	0.32 (0.16)	0.03 (0.04)	5.38 (3.17)	4.51 (2.90)	0.49 (0.41)	0.39 (0.24)
	Range	1.85–19.57	0.79–4.53	0.59–4.14	0.07–0.67	0.01–0.14	0.85–17.14	0.81–15.84	0.01–1.65	0.01–0.99
2013	Mean (SD)	11.43 (14.15)	4.85 (7.69)	3.65 (6.58)	1.14 (2.81)	0.07 (0.11)	6.57 (8.57)	4.72 (5.66)	1.14 (1.63)	0.71 (1.58)
	Range	3.12–96.73	1.82–57.71	1.68–56.57	0.11–22.28	0.02–0.58	1.16–61.21	0.86–39.30	0.12–11.01	0.01–10.90
2014	Mean (SD)	37.91 (47.41)	21.62 (30.77)	17.72 (28.75)	3.78 (6.50)	0.11 (0.09)	16.29 (21.43)	14.04 (18.51)	1.51 (2.64)	0.74 (1.83)
	Range	3.30–303.92	2.49–248.99	1.32–246.16	0.02–31.77	0.08–0.53	0.58–94.86	0.52–89.79	0.02–18.42	0.05–12.45
2015	Mean (SD)	11.80 (14.45)	6.61 (8.06)	5.07 (5.00)	1.43 (3.85)	0.11 (0.18)	5.20 (7.19)	4.76 (6.42)	0.19 (0.38)	0.24 (0.57)
	Range	3.21–92.41	2.57–62.77	2.33–37.51	0.04–24.08	0.08–1.33	0.58–40.54	0.52–36.73	0.02–2.20	0.04–4.20
2016	Mean (SD)	15.05 (21.09)	11.04 (18.84)	10.10 (18.75)	0.86 (2.20)	0.08 (0.02)	4.01 (4.50)	3.55 (3.99)	0.30 (0.44)	0.16 (0.28)
	Range	3.15–153.52	2.57–133.96	2.39–133.39	0.02–13.28	0.08–0.26	0.58–25.15	0.52–21.96	0.02–2.46	0.05–1.95
2017	Mean (SD)	14.29 (8.69)	9.42 (5.33)	8.45 (4.80)	0.88 (1.64)	0.08 (0.03)	4.88 (4.86)	4.38 (4.30)	0.31 (0.37)	0.19 (0.36)
	Range	3.01–50.99	2.43–22.18	2.33–20.97	0.03–10.31	0.08–0.30	0.58–28.81	0.52–24.45	0.02–2.05	0.05–2.30
2018	Mean (SD)	14.76 (12.50)	9.51 (8.51)	8.92 (8.48)	0.50 (0.44)	0.09 (0.03)	5.25 (5.92)	4.63 (5.53)	0.31 (0.26)	0.32 (0.39)
	Range	3.15–39.97	2.56–25.76	2.40–25.44	0.05–1.80	0.08–0.17	0.58–18.71	0.52–16.53	0.02–1.01	0.05–1.60
2019	Mean (SD)	9.02 (5.38)	5.86 (3.30)	5.30 (2.82)	0.47 (0.54)	0.09 (0.03)	3.16 (2.35)	2.60 (1.70)	0.35 (0.58)	0.22 (0.19)
	Range	3.38–21.99	2.70–13.05	2.47–11.00	0.06–1.87	0.08–0.18	0.68–8.94	0.60–6.31	0.03–1.97	0.05–0.66
2020	Mean (SD)	6.97 (2.57)	5.17 (1.93)	4.75 (1.80)	0.34 (0.29)	0.08 (0)	1.80 (1.09)	1.56 (0.89)	0.15 (0.19)	0.09 (0.07)
	Range	3.39–12.27	2.72–9.32	2.43–8.49	0.03–0.99	0.08–0.08	0.58–3.84	0.52–3.58	0.02–0.64	0.05–0.30
2021	Mean (SD)	8.05 (4.43)	5.83 (4.04)	5.42 (4.01)	0.33 (0.25)	0.08 (0)	2.22 (1.28)	1.85 (0.92)	0.24 (0.32)	0.12 (0.11)
	Range	3.36–20.55	2.45–17.74	2.33–17.23	0.05–1.01	0.08–0.08	0.91–5.95	0.77–4.23	0.05–1.30	0.05–0.43

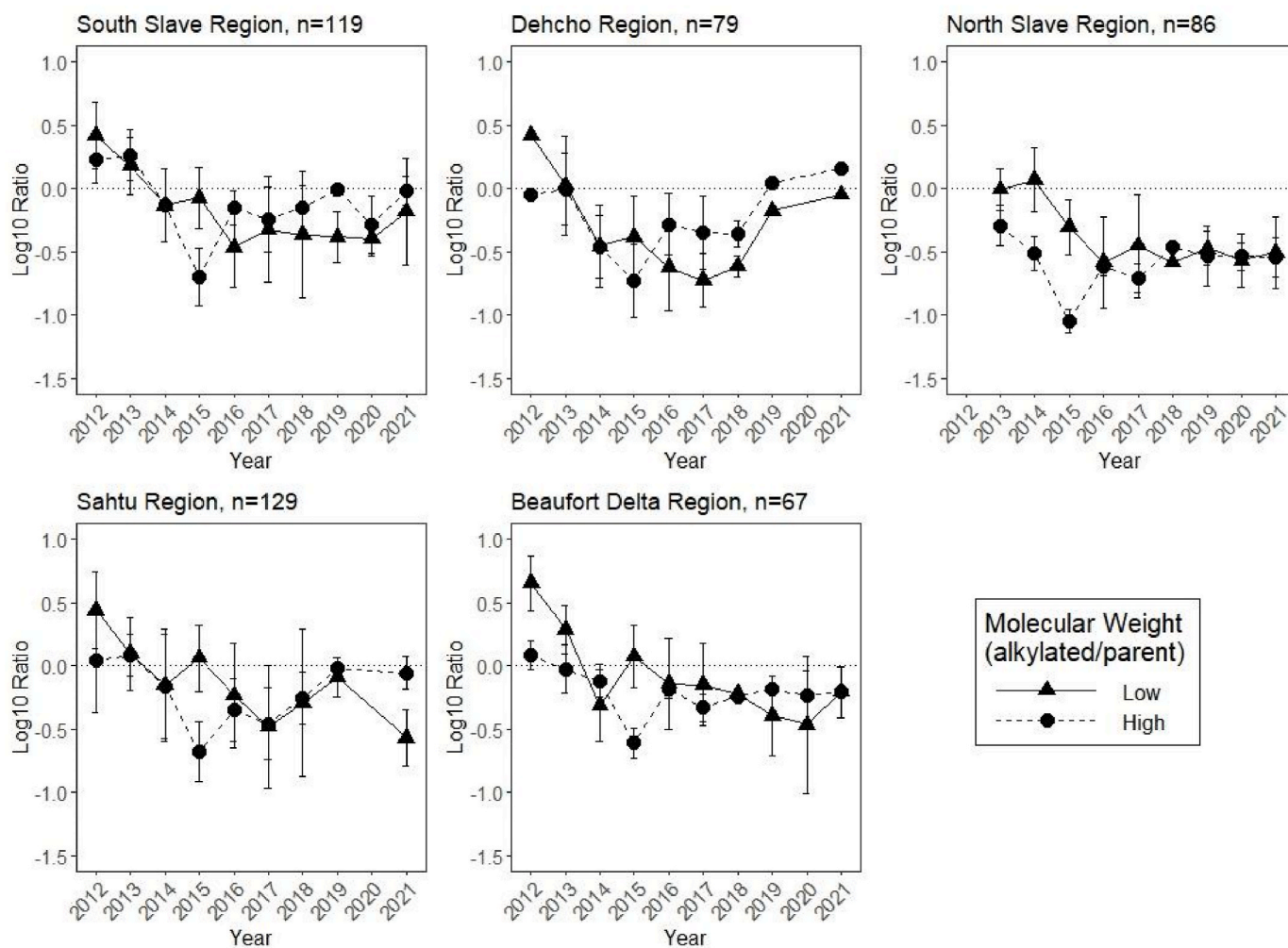


Fig. 2. Scatterplots of \log_{10} transformed polycyclic aromatic compound ratios for each administrative region of the Northwest Territories, Canada within the study period. These ratios include alkylated lower molecular weights/parent lower molecular weights and alkylated higher molecular weights/parent higher molecular weights. The error bars are standard deviation. The sample size for each region is at the top of each plot. The point where the abundance of both alkylated and parent PACs are equal is marked with a dotted line.

pyrenes; see Table A2). Other PACs were above the detection level less than 50% of the time for all regions (Biphenyl, Fluorene, Dibenzo[a,h]anthracene, Ideno[1,2,3-c,d]pyrene, Dibenzothiophene, and C3–C4 Chrysenes). The region with the most PACs that were above the detection level for 50% or more of the samples was the Beaufort Delta Region (29/42 PACs; see Table A2). The regions with the least PACs above the detection level for over 50% of samples were the Dehcho and North Slave regions (23/42 PACs). Some PACs that were detected in the Beaufort Delta Region, but not the other regions were Acenaphthene and C1 Dibenzothiophenes.

Regarding specific PAC differences between years, 2012, 2014, and 2018 had the most PACs that were detected in at least 50% of the samples (30, 29, and 29 respectively; Table A3). The year with the least samples detected at least 50% of the time was 2020 (18/42). The PACs that were above the detection level in over 50% of samples for all years were Benz[a]anthracene, Chrysene, Fluoranthene, Pyrene, C2 Fluorene, C3 Naphthalene, C1–C3 Phenanthrenes/anthracenes, C1 Chrysenes, and C1 Fluoranthenes/pyrenes (Table A3). The PACs that were above the detection level less than 50% of the time for all years were Ideno[1,2,3-c,d]pyrene, Dibenzothiophene, C3–C4 Chrysenes, and C4 Fluoranthenes/pyrenes. PACs that were only above the detection level in over 50% of samples for the years 2012, 2014, or 2018 were Biphenyl, Fluorene, and Dibenzo[a,h]anthracene.

3.2. Processes influencing variation in PAC concentrations

For all five response variables, the most-supported model was the random effects and intercept only model (Table 2). Accounting for variation, the estimated average values for all the sub-classes were: PLMWs 4.48 ± 1.12 ng/L (Standard Deviation, SD), ALMWs 2.68 ± 1.15 ng/L (SD), PHMWs 0.37 ± 1.19 ng/L (SD), and AHMWs 0.19 ± 1.21 ng/L (SD). The estimated value for total PACs was 9.20 ± 1.11 ng/L (SD).

There were two response variables that had a second-ranked model with an Akaike weight equal to or above 0.10, providing only scant evidence of any other effects of the environmental variables we measured. Based on these weakly supported models, snowmelt and PLMW levels may be negatively correlated ($w_i = 0.10$; $\beta = -0.04$, 85% CI = -0.07 to -0.01). In addition, AHMW levels might be negatively correlated with fire ($w_i = 0.17$; $\beta = -0.09$, 85% CI = -0.15 to -0.02). No quadratic terms were in any of the higher ranked models.

Post-hoc tests for location (controlled by year and month) indicate that the sum of all PACs differed between regions ($F_{4,464} = 3.23$, $p = 0.012$) and sites ($F_{42,420} = 5.77$, $p < 0.001$, Fig. 4). While there were many differences between various sites across the study area, there was no clear spatial pattern. However, two Norman Wells sites (out of six) in the Sahtu region had significantly ($p < 0.05$) higher levels of PACs than 28 of the other 41 sites.

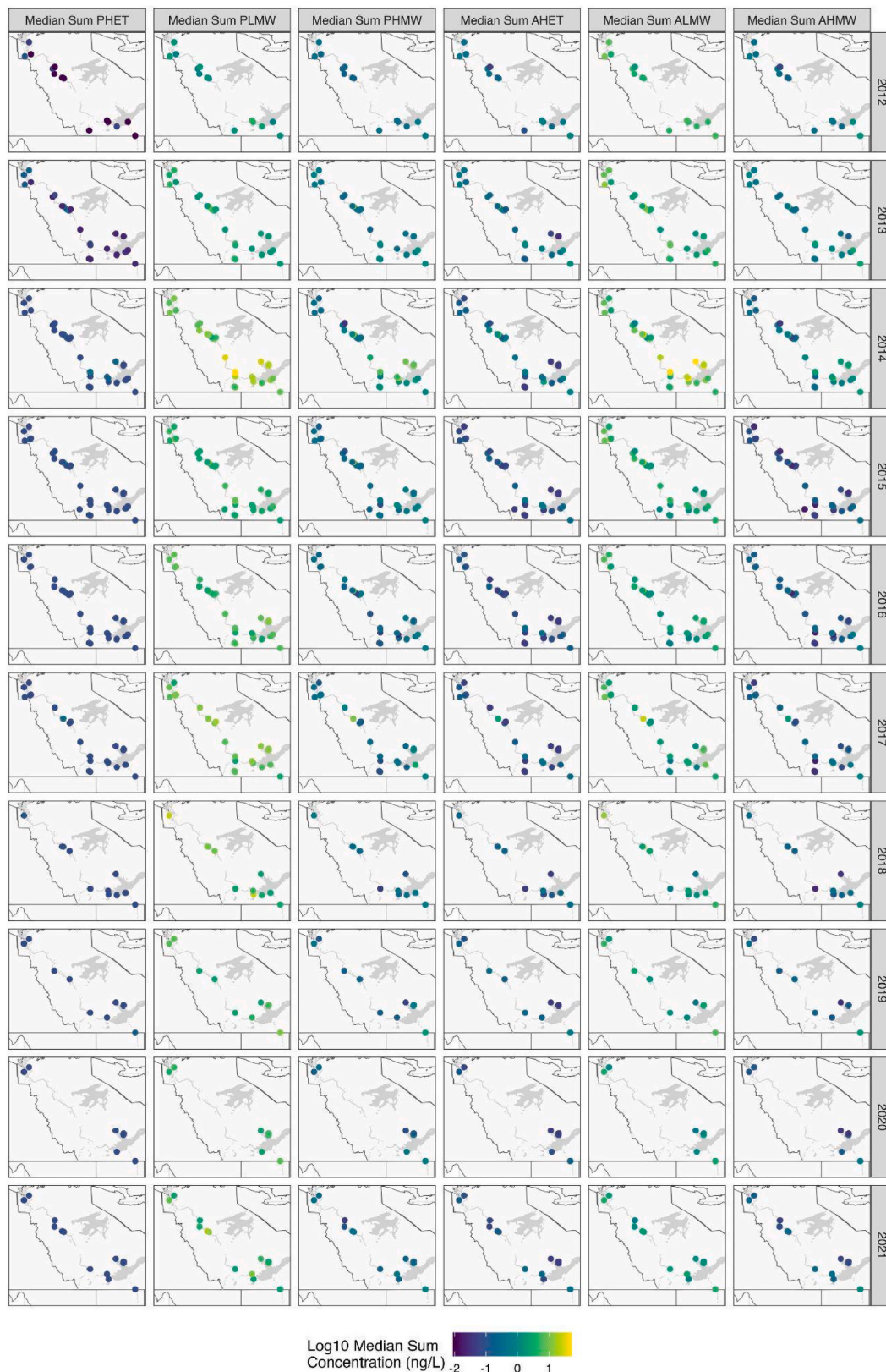


Fig. 3. Spatial and temporal patterns of polycyclic aromatic compound (PACs) sub-classes. Each site has a median value for that year. The maps of the study areas are separated by years and PAC sub-classes: parent heterocyclic aromatic compounds (PHET), parent lower molecular weight (PLMW), parent higher molecular weight (PHMW), alkylated heterocyclic aromatic compounds (AHET), alkylated lower molecular weights (ALMW), and alkylated higher molecular weights (AHMW). Lighter colours indicate increasing concentration.

Table 2

The top models for each response variable. Response variables (sums of PACs) are in the left column. Random effects (site, year within site, month within year) and fixed effects are included, with the ✓ indicating which predictor variables were retained in top-ranked models. Month is the month when the recording period began, snow is the snow water equivalent for April of the year of sampling, fire is the percentage of land burned in the basin in the previous year, and number of oil wells is the number of oil wells within 10 km of the sampling location. If the quadratic term was included in the model, a² was included with the ✓. Models are ranked by differences in Akaike's Information Criterion, corrected for sample size (ΔAICc). Models with an Akaike weight (w_i) of at least 0.01 were included in this table.

	Random		Predictor Variables				Model Selection Criteria		
	Site	Year (Site)	Month (Year)	Snow	Fire	Number of Oil Wells	Deviance	ΔAIC _c	w _i
PLMW	✓	✓	✓				252.5	0.00	0.83
	✓	✓	✓	✓			254.7	4.25	0.10
	✓	✓	✓	✓ 2			255.5	7.11	0.02
	✓	✓	✓		✓		257.6	7.15	0.02
	✓	✓	✓			✓	258.4	7.95	0.02
ALMW	✓	✓	✓				261.8	0.00	0.85
	✓	✓	✓			✓	265.3	5.55	0.05
	✓	✓	✓		✓		265.6	5.85	0.05
	✓	✓	✓	✓			266.8	7.05	0.03
	✓	✓	✓			✓ ²	267.5	9.81	0.01
	✓	✓	✓	✓ ²			267.5	9.81	0.01
	✓	✓	✓		✓ ²		267.6	9.91	0.01
PHMW	✓	✓	✓				536.4	0.00	0.82
	✓	✓	✓			✓	539.4	5.05	0.07
	✓	✓	✓	✓			540.4	6.05	0.04
	✓	✓	✓		✓		540.6	6.25	0.04
	✓	✓	✓	✓ ²			540.1	7.81	0.02
AHMW	✓	✓	✓			✓ ²	541.2	8.91	0.01
	✓	✓	✓				419.3	0.00	0.66
	✓	✓	✓		✓		419.9	2.65	0.17
	✓	✓	✓			✓	422.1	4.85	0.06
	✓	✓	✓	✓			423.1	5.85	0.04
	✓	✓	✓	✓ ²			421.8	6.61	0.02
	✓	✓	✓		✓ ²		422.8	7.61	0.01
	✓	✓	✓		✓		422.9	7.71	0.01
	✓	✓	✓			✓ ²	423.4	8.21	0.01
	✓	✓	✓			✓	186.4	0.00	0.90
All PACs	✓	✓	✓				190.9	6.55	0.03
	✓	✓	✓		✓		191.3	6.95	0.03
	✓	✓	✓	✓			191.9	7.55	0.02
	✓	✓	✓		✓ ²		192.2	9.91	0.01
	✓	✓	✓	✓ ²			192.6	10.31	0.01

4. Discussion

4.1. Baseline levels and observed patterns

Concentrations of all PACs were below the water quality guidelines for the protection of aquatic life (Canadian Council of Ministers of the Environment, 1999) and were typically lower than levels measured in systems in more developed southern areas. For example, Kelly et al. (2009) reported PAC concentrations downstream of oil sands development in the Athabasca River and its tributaries (Alberta, Canada) that ranged from 63 ng/L to 202 ng/L on average using PMDs in the summer. All years in our study had mean total PAC concentrations below these levels (see Table 1). Further, a study in Toronto, Canada measured only nine PACs (compared to our 42) within the Highland Creek watershed and reported levels ranging from 18 ng/L to 4500 ng/L depending on flow conditions during snowmelt (Meyer et al., 2011). Though Meyer et al. (2011) used one-time water samples instead of PMDs, making our studies less comparable, the PAC concentrations measured in Toronto suggest that the Mackenzie River system possibly has lower concentrations of PACs overall. However, while our levels were low, we note that water quality guidelines were last updated in 1999 and are available for nine of the 42 PAC compounds that we assessed (Canadian Council of Ministers of the Environment, 1999). A critical review and official update of guidelines regarding PACs is needed (Marvin et al., 2020).

In most years, PAC mixtures were predominated by PLMWs, with ALMWs being secondary, potentially highlighting the importance of petrogenic sources for PACs in the Mackenzie Basin due to the presence of low molecular weight PACs (Kieta et al., 2023), which is similar to other sites in northern Canada, although alkylated petrogenic PACs were

usually more abundant at other sites (Mundy et al., 2019; Provencher et al., 2020). While petrogenic sources are likely important in the basin, we note that concentrations of ALMWs were usually lower than those of PLMWs, possibly indicating that another PAC source (besides oil seeps or leaks, which tend to produce alkylated PACs) is important in this system (Wang et al., 2004; Stogiannidis and Laane, 2015). Alternatively, Mundy et al. (2019) placed semipermeable membrane devices in shallow lentic waterbodies, while our PMDs were in a variety of waterbody types, primarily lotic. Perhaps different flow rates and depths can affect the uptake of different sub-classes of PACs, affecting our PLMW to ALMW ratio. Flow rate should be accounted for by the performance reference compounds present in the PMDs, but a change in flow rates could also change other factors that could affect PAC uptake such as temperature or total dissolved solids. Future research should focus on how waterbody type affects PMD effectiveness as the effect of flow rate on various membrane device effectiveness is contested (Wang et al., 2009; Chang et al., 2015).

Concentrations of low molecular weight PACs (both PLMW and ALMW) were elevated around Great Slave Lake in 2014. According to the Government of Northwest Territories (2023), there were multiple petroleum spills greater than 1000 L in the North Slave and South Slave administrative regions in 2014 (including a 300,000 L spill on the landscape). PLMWs and ALMWs are usually present in the environment due to petrogenic sources, so these petroleum spills might be responsible for these higher levels. Measuring PAC levels in the water immediately after spills and continued monitoring over time will provide improved insights regarding the effects of different volumes of spills and time on PAC concentrations. In addition, there was an increase in concentration of all PACs west of Great Bear Lake (around Norman Wells) in 2017. The

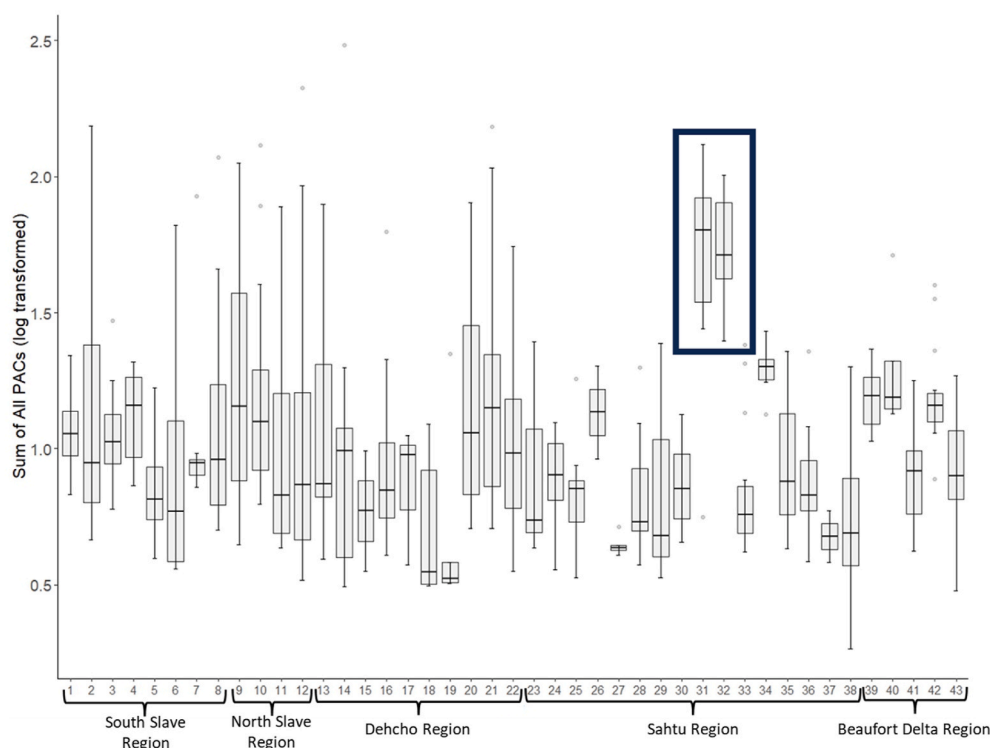


Fig. 4. The \log_{10} transformed sum of all polycyclic aromatic compounds (PACs) across all 43 sites from 2012 to 2021. This boxplot indicates the interquartile range and median. The five administrative regions are indicated by brackets. The black box highlights two Norman Wells sites that are significantly different ($p < 0.05$) from 28 of the other sites.

refinery in Norman Wells ceased production in 2016 due to issues with pipelines but resumed operations in 2018 (Imperial Oil, 2018) – increased PAC levels in the area could have been related to increased industrial activity during repairs. This could have been due to increased vehicle (or other equipment) exhaust or smaller spills during the repair. Despite being elevated, the PAC concentrations in the river continued to be low compared to guidelines in 2017.

Apart from 2012 to 2013, parent PACs were more abundant than alkylated PACs in our samples. In addition, 2012, 2014, and 2018 had more PACs above the detection level than any other year. Although levels are still low overall for all PACs, these contaminants that are detected in more than 50% of samples may be the main components of change between years, although we do not know what causes this variation. While a discrepancy in detection levels could be the driver for differences between years, detection levels were not consistently lower or higher than other years across all PACs and within PAC sub-classes, suggesting environmental factors affected PAC concentrations in these years. Specifically, this pattern indicates a shift in the relative contribution of different PAC sources, with petrogenic sources being more important in these two earlier years than pyrogenic sources. However, this pattern could also possibly be due to the implementation of more rigorous sampling protocols in 2014 by the CBM to further limit the exposure of potential contaminants to the sensitive PMDs or perhaps to natural variability, but more work is needed to determine the cause. Regarding pyrogenic PACs, the relative abundance of PHMWs compared to AHMWs increased markedly in 2015, which may have been related to increased wildfire activity in 2014, although more research is needed to determine the effects of fire in this system. In other years, our estimates of the percentage of basin burned ranged from 0.01% (2020) – 1.06% (2015) but averaged 1.70% in 2014. This increased fire activity may have been the driver of increased PAC levels in the surface water in 2014 as well, possibly due to atmospheric deposition as opposed to runoff during the next year's snowmelt.

We reported higher levels of low molecular weight PACs compared

to high molecular weight PACs. However, there is a limitation regarding the use of PMDs that may have exacerbated this difference. PMDs measure contaminants in the water that can cross a semipermeable membrane (dissolved contaminants such as PLMWs and ALMWs) (Huckins et al., 2006; Alvarez, 2010). As PHMWs and AHMWs are more hydrophobic than the low molecular weight PACs and tend to bind to particulates, PMDs consistently measure them at a lower concentration (Gustafson and Dickhut, 1997; Mzoughi and Chouba, 2011; Rabodonirina et al., 2015). The patterns of variability regarding PHMWs and AHMWs would be accurately measured by the PMDs, but the direct comparisons between low molecular weight and high molecular weight concentrations should be considered with caution. Water grab and sediment sampling paired with PMDs would give future studies a clearer understanding of the overall PAC concentrations in this system.

4.2. Processes influencing variation in PAC concentrations

As the top-ranked model for all response variables included the random structure and intercept only, this indicates that we do not have the correct fixed effects in our model to explain the variation. As PAC concentrations were different between sites or regions (especially at two sites near Norman Wells, an area of active oil extraction), there may be a different variable at the site or region level influencing the abundance and composition of PACs in the Mackenzie River Basin. In addition, the Beaufort Delta Region had more PACs above the detection level than any other region, although the South Slave only had one less PAC, highlighting the difference in PAC mixtures between regions. Future research should focus on site-level assessments that evaluate these other factors (i.e., boat activity, flow rate, temperature, total suspended or dissolved solids). Interestingly, oil wells did not affect any PAC concentrations in the models, which was unexpected with the high levels of PLMWs and ALMWs in the environment. The number of oil wells in this environment may not be a good proxy for the number of natural oil seeps present and this should be investigated in the future.

As PHMWs are more prevalent in the output from pyrogenic sources (e.g., fire) than AHMWs (Boehm, 1964; Andersson and Achten, 2015), an increase in fire should result in more PHMWs than AHMWs that are incorporated into the surface water during runoff after snowmelt the next year. However, while AHMWs had possible evidence of a fire effect, PHMWs did not, contrary to our predictions and the potential effect of fire in 2014 discussed previously and in Fig. 2. Therefore, it seems like an increase in area burned in the previous year possibly results in less AHMWs but does not affect PHMWs. Conversely, the average decrease in concentration of AHMWs with increasing fire was less than 0.5 ng/L, which could be within the normal variation of concentrations, indicating that fire may not affect AHMWs at this scale. More research on fire at varying landscape scales and time periods before measurement and how it is related to both PHMWs and AHMWs is necessary to determine if this pattern is not an artifact of natural variation or due to some other unknown source.

There was also weak evidence of an effect of snowmelt on the abundance of PLMWs (10% of the weight of evidence). As snowmelt increased, PLMWs decreased, potentially due to dilution of the PLMW concentrations as we predicted. As PLMWs had the highest concentration of all PACs, this pattern may have been more prevalent in this subclass than the other sub-classes, perhaps because many of the PACs had adsorbed to particulates by melt. More research is required to determine if this weak evidence is a result of snowmelt or due to natural variation.

5. Conclusion

Our study confirms the importance of petrogenic PAC sources in the Mackenzie River Basin and offers valuable baseline data for future studies. PAC concentrations were relatively uniform spatially with the exception of two sites near the oil operations in Norman Wells. In addition, while there was interannual variation of PAC concentrations, we do not know the mechanism driving this variation, although fire ash runoff into the Mackenzie River system may be partly responsible. Future research should focus on more fine-scaled environmental factors at the site or region level. These factors could include industrial sources besides oil wells, natural oil seeps, smaller and more localized fires with varying lag times, snowmelt at a smaller scale, human activity (e.g., boats, cooking, snowmobiles, etc.), the flow rate of the waterbody, water depth, timing of melt, and sediment deposition rate. In addition, measuring the concentration of PACs immediately following a fire, an oil spill, or snowmelt may uncover patterns hidden from our study due to volatilization or binding to sediment of PACs. Furthermore, our study has introduced a baseline regarding PAC levels in surface water for the Mackenzie River. Future studies can use our results as a starting point to select the PAC parameters that may be more useful in determining the more fine-scaled patterns that could be present in this system (i.e., specific PACs).

Although PAC levels are low overall compared to existing guidelines, it is difficult to determine if there is risk to humans along the Mackenzie River without updated guidelines. Ratelle et al. (2020) reported higher PAC levels in people living within this region compared to the Canadian average. Therefore, it is important for future studies to determine all PAC sources and pathways of exposure in the Mackenzie River Basin (e.g., water, soil, cooking) as well as the effects they may have on the environment and humans.

CRedit authorship contribution statement

Jordyn A. Stalwick: Writing – review & editing, Writing – original draft, Visualization, Methodology, Formal analysis, Data curation. **Gila Somers:** Project administration, Methodology, Investigation, Data curation, Conceptualization. **Kristin M. Eccles:** Writing – review & editing, Visualization, Formal analysis. **Philippe J. Thomas:** Writing – review & editing, Conceptualization. **Christopher Cunada:** Investigation, Data Curation, Writing – review & editing. **Kirsty E.B. Gurney:**

Methodology, Funding acquisition, Conceptualization, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

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

Data availability

This data is available on the Mackenzie Datastream Website.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2024.123962>.

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