

Long title: A framework for integrated monitoring of status and trends in water balance, water chemistry and contamination of shallow lakes across a remote dynamic freshwater delta

Short title: A monitoring framework for shallow lakes in remote landscapes

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Submitted to: PLOS Water

October 30, 2023

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Keywords:

aquatic ecosystem monitoring; hydrology; water quality; contaminants; Ramsar Wetland; floodplain lake; Peace-Athabasca Delta; Wood Buffalo National Park Action Plan

Abstract

Systematic and sustainable monitoring approaches capable of tracking the status and trends of keystone characteristics are critical for detecting aquatic ecosystem degradation, identifying the influence of multiple potential stressors, informing environmental protection policy and anticipating future change. At remote lake-rich landscapes, ability to implement and maintain long-term monitoring is often challenged by logistical and financial constraints. At the Peace-Athabasca Delta (PAD; northeastern Alberta, Canada), an internationally recognized remote freshwater landscape threatened by climate change and upstream industrial development (hydroelectric regulation of river flow, oil sands mining and processing), the need for an integrated aquatic ecosystem monitoring program has long been recognized to track changes to the flood regime, water balance, water quality, and contaminant deposition in the abundant shallow lakes. The remoteness and hydrological complexity of the landscape, among other factors, have hindered the implementation of such a program. In recent years, concern over aquatic ecosystem degradation has led to renewed and urgent calls by international and national governance agencies for implementation of a long-term monitoring program. Here, we report on intensive, multi-faceted research performed during 2015-2021 at 60 lakes spanning the delta's broad hydroecological gradients to develop, evaluate, and apply a framework for integrated assessment of status and trends in water balance, water chemistry and contaminant enrichment. We present the design and approaches used, synthesize the knowledge gained from data collected during the 7-year-long research phase, and provide a foundation for a long-term aquatic ecosystem monitoring program that addresses several recommendations stemming from assessments by UNESCO and key priorities within the Wood Buffalo National Park Action Plan. We suggest the monitoring framework is readily transferable to other remote shallow lake- and pond-rich landscapes threatened by multiple potential stressors.

1. Introduction

Effective freshwater ecosystem monitoring programs are needed to define status, detect trends, and understand the timing, magnitude and causes of environmental change – information that is imperative for evidence-based decision-making, climate-change adaptation and mitigation planning, and development and assessment of policy and management interventions [1-4]. Key principles of effective monitoring programs include 1) scientifically defined objectives that are aligned with priorities of stakeholders, 2) sound study design, and 3) measurement of responsive, informative variables at appropriate spatial and temporal scales [5-9]. Central to adhering to these principles is a strong knowledge base of the fundamental processes that influence ecosystem structure and function [10, 11]. Knowledge generated from substantive prior research and long-term primary data acquisition, thus, constitutes an important initial and foundational step towards implementation of successful long-term freshwater ecosystem monitoring programs [8, 12-15].

There are many effective long-term freshwater ecosystem monitoring programs in temperate and subtropical regions that adhere to the above key principles. Examples include Sweden's National Surface Water Monitoring Program (since circa 1972) [16], the Water Quality Monitoring Program for the Laurentian Great Lakes (circa 1972) [17, 18], the National Hydrological Monitoring Program and the Upland Waters Monitoring Network in the UK (circa 1988) [19-21], and Korea's National Aquatic Ecological Monitoring Program (circa 2003) [22]. The long-term monitoring programs in Sweden and the UK operate under the European Union's Water Framework Directive (WFD), a multi-national legislation for integrated management of inland, transitional and coastal surface waters and groundwater that monitors >146,500 surface water and 15,000 groundwater bodies across 180 river basins in the European Union and UK [23, 24]. These and other successful long-term freshwater ecosystem monitoring programs typically are situated in regions where population density and infrastructure are substantial (including road access to sampling sites), and where there is adequate availability of well-trained personnel and long-term commitment of funding [25]. Substantial challenges exist, however, for aquatic ecosystem monitoring within remote lake-rich landscapes, such as in northern Canada, Alaska, and Russia, where concern has been mounting over ecosystem

degradation by climate change and expansion of industrial activities [26-30]. The challenges include, but are not limited to, logistical and financial barriers associated with access to remote sampling sites, local capacity to maintain monitoring activities, insufficient availability of data to inform selection of approaches, and contrasting priorities of a diverse set of stakeholders and rightsholders. These constraints place high emphasis on designing programs that are logistically feasible and measure the most responsive and cost-effective variables at appropriate spatial and temporal scales to ensure the programs are both informative and sustainable [5, 31].

The need for implementing an effective long-term aquatic ecosystem monitoring program has long been recognized at the Peace-Athabasca Delta (PAD), a hydrologically dynamic landscape with abundant shallow lakes situated in a remote region of northeastern Alberta, Canada [32-34]. Approximately 80% of the delta, which is recognized as a Ramsar Wetland of International Importance (since 1982), is contained within Wood Buffalo National Park (WBNP) and it contributes to the park's designation as a UNESCO World Heritage Site (since 1983). The remainder is within the reserve of the Athabasca Chipewyan First Nation (ACFN; Indian Reserve No. 201), traditional lands of the Mikisew Cree First Nation (MCFN) and Fort Chipewyan Métis Nation (FCMN), and Crown Land. More than 50 years ago, the PAD Project Group, a multi-jurisdictional environmental impact assessment of Peace River flow regulation by the W.A.C. Bennett Dam, recommended that a long-term monitoring program is required to obtain "a full understanding of the complex interrelationships of the hydrologic and biological processes and to provide some predictive capability for planning and decision making" [32]. Since then, periodic government-led reassessments of environmental conditions at the PAD have reiterated this need but a long-term delta-wide aquatic ecosystem monitoring program has remained elusive, even as concern has grown over environmental degradation of the delta's aquatic ecosystems. This primarily includes observed and recorded drawdown of lake and river water levels, variably attributed to hydroelectric regulation of Peace River flow and climate [32, 35-45], and the potential for pollution of lakes via transport of substances of concern from upstream oil sands development along the Lower Athabasca River [46-48]. In 2014, the MCFN petitioned that WBNP be inscribed on UNESCO's List of World Heritage in Danger, in large part because of the threats of industrial activities to the delta's aquatic ecosystems [49]. The petition

initiated national and international investigations by the Government of Canada, UNESCO's World Heritage Convention (WHC) and the International Union for Conservation of Nature (IUCN) [50-52; full list of documents/reports available at <https://whc.unesco.org/en/list/256/documents/>]. Collectively, these investigations prompted and informed a collaborative WBNP Action Plan that outlines priorities and actions to ensure improved protection and stewardship of the park's numerous 'Outstanding Universal Values', and greater involvement of Indigenous rightsholders in the decision-making process [53]. One goal of the Action Plan includes implementing an "integrated PAD Research and Monitoring program ... to detect cumulative effects on the PAD and generate information that informs land-use management and regulatory decision making" [53; p. 57], reiterating the unfulfilled priority first identified by the PAD Project Group in the early 1970s.

The large size (~6000 km²), abundance of shallow lakes, remote northern location, and hydrological complexity of the PAD have presented formidable impediments to establishing an informative and sustained aquatic ecosystem monitoring program. The delta consists of two main sectors, the northern Peace sector and the southern Athabasca sector. The latter is a low-lying, active delta at the terminus region of the Athabasca River, whereas the former is a relict delta where bedrock inliers provide greater topographic relief [54]. Water flows northward through the delta, from the Athabasca River and its distributaries (including the Embarras River, Mamawi Creek and Fletcher Channel) to Lake Athabasca, and to the Peace River via the Rivière des Rochers, Chenal des Quatre Fourches and Revillon Coupé (Figure 1). The Peace River flows along the northern margin of the delta and exerts control over the hydrology of the PAD mainly by regulating the rate of outflow. The Peace River, however, episodically contributes inflow to the delta during high discharge events when major ice-jams form, which raise water levels sufficiently to reverse flow direction and inundate broad areas [35, 54, 55]. Shallow lakes (typically 0.5 to 3 m maximum depth) are abundant across both sectors and span a broad gradient of hydrological connectivity from classically termed open-drainage (e.g., Lake Claire, Mamawi Lake, Richardson Lake) to restricted- and closed-drainage [32, 56]. The latter two are collectively referred to as perched lakes, with a main distinction that restricted-drainage lakes are more flood-prone during the open-water season whereas closed-drainage lakes typically

receive input of floodwaters only during less frequent spring ice-jam events. The perched lakes are therefore most vulnerable to evaporative drawdown during periods when the frequency and magnitude of flooding is reduced, whereas open-drainage and restricted-drainage lakes are most vulnerable to fluvial supply of contaminants [57-60]. These features challenge traditional monitoring approaches designed for less hydrologically complex landscapes.

Locations of monitoring sites

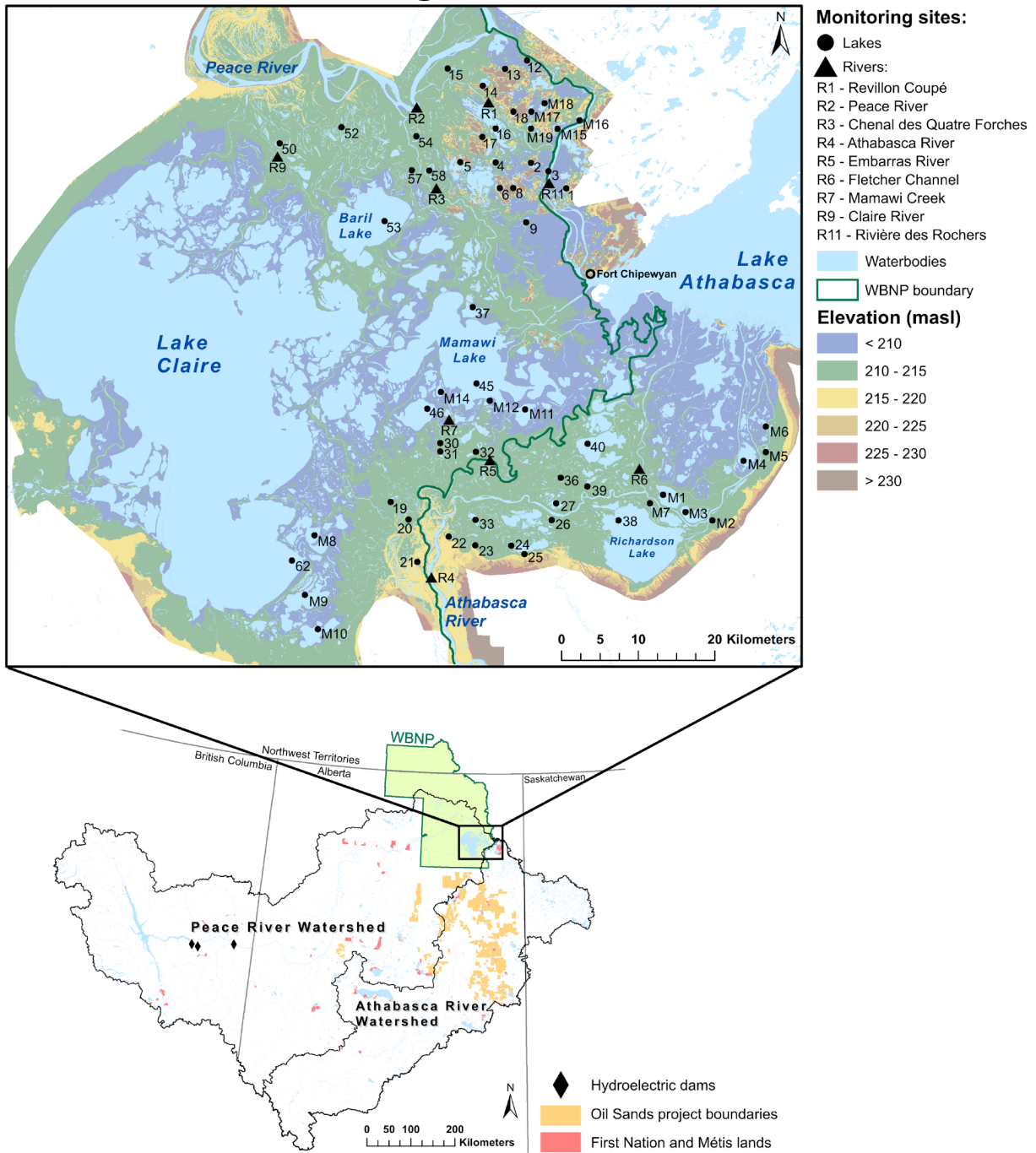


Fig 1. Maps showing the locations of 60 lake (circles) and 9 river (triangles) monitoring sites in the Peace-Athabasca Delta (PAD), Alberta and the location of the PAD within Wood Buffalo National Park and the western Canadian provinces. A high-resolution digital elevation model released in 2022

(<https://catalogue.ec.gc.ca/geonetwork/srv/api/records/ca0f663f-acfc-4915-9210-3729a86b2e94>) is included to highlight the topographic relief of the study region (210-230 masl). The delta

occupies an area between the Peace and Athabasca rivers (<https://natural-resources.canada.ca/science-and-data/science-and-research/earth-sciences/geography/topographic-information/geobase-surface-water-program-geeau/watershed-boundaries/20973>) at the western end of Lake Athabasca. The boundary of Wood Buffalo National Park (WBNP) is outlined in dark green (<https://open.canada.ca/data/en/dataset/9e1507cd-f25c-4c64-995b-6563bf9d65bd>), surface water bodies (DMTI Spatial Inc., 2023) are light blue and First Nation and Métis legislative boundaries (<https://open.canada.ca/data/en/dataset/522b07b9-78e2-4819-b736-ad9208eb1067>) are light red. Three hydroelectric dams along the Peace River are identified as black diamonds and oil sands mining project boundaries from 1985-2015 (<http://osip.alberta.ca/library/Dataset/Details/671>) are light orange. Figure was created using ArcGIS Desktop version 10.8.2 and assembled by Laura Neary.

Two Indigenous-led community-based monitoring (CBM) programs have operated in the PAD since 2008 (MCFN) and 2010 (ACFN), which focus on protection of traditional lands, food sources and navigation routes of Indigenous rightsholders, as per Section 35 (Aboriginal and Treaty Rights) of the Constitution Act 1982, at locations selected by Elders and land-users who hold local and Traditional Knowledge [61]. The CBM programs, thus, have focused more on the open-drainage lakes and river channels than the perched lakes. Historically, there have been several short-lived localized research and monitoring efforts on various aspects of lake hydrology and ecology (e.g., [36, 57, 62-67]). However, a delta-wide long-term sustainable aquatic ecosystem monitoring program that addresses water quantity and water and sediment quality concerns at lakes spanning the full hydrological gradient of the PAD has yet to be established. We recognize that other factors have also hindered the establishment and implementation of such a program, including socio-political challenges associated with inter-jurisdictional and transboundary water governance and ongoing constitutional conflict between governing bodies and Indigenous rightsholders [68-72].

More than 20 years ago, our research program initiated paleolimnological investigations to address controversy about the relative roles of Peace River flow regulation and climate on the observed drawdown of the delta's perched lakes during the 1980s and 1990s. The aquatic ecosystem monitoring framework we report here is an outcome of key observations and developments achieved during this period at the PAD, and informed by our research at other water-rich landscapes in northern Canada. During our first field visit in October 2000, we

conducted a spatial survey of 60 lakes spanning the hydroecological gradients of the PAD and the major rivers for measurements of water isotope composition, water chemistry and aquatic biota to facilitate interpretation of the paleoenvironmental data obtained from analyses of lake sediment cores [73]. The results revealed profound variability over space in the influence of hydrological processes on lake water balances and water chemistry. Following that first delta-wide lake and river water isotope survey, [73] provided a spatial representation of lake water evaporation-to-inflow (E/I) ratios (which we refer to as 'isoscapes'; see [58]) that displays variation in lake water balances across the Peace and Athabasca sectors of the delta in map form. This visual snapshot of hydrological conditions across the vast landscape was viewed as a distinct strength of the approach, because it communicated effectively to a variety of audiences where 'hotspots' of lake drawdown by evaporation occurred and where lakes were replenished by floodwaters (see also [74]). Another early isoscape was used to hypothesize that a recent geomorphic change in the flow path of the Athabasca River had a major influence on the water balance of lakes across the Athabasca sector [75]. Subsequent systematic application of water isotope tracers to characterize hydrological conditions of lakes across other remote northern landscapes, including the Slave River Delta (Northwest Territories), Hudson Bay Lowlands (northern Manitoba) and Old Crow Flats (Yukon Territory), was used to establish quantitative relations with drivers including meteorological conditions, river discharge and catchment characteristics, often communicated as isoscapes [76-81]. These collective efforts and experiences ultimately led to motivation and confidence that similar systematic application of water isotope tracers across lakes of the PAD could provide novel opportunity to capture the influence of evaporation and river floodwaters on lake water balances, the two most important and scrutinized hydrological processes, over space and time.

Early during our paleolimnological research in the PAD, we observed layers of black sediment in cores retrieved from flood-prone oxbow lakes [82]. Analyses revealed they contained old carbon that we hypothesized was potentially sourced from upstream exposures of bitumen and coal deposits that had been eroded, transported, and deposited by episodic flood events for centuries. Since this stratigraphic discovery, concern has been increasingly expressed about aquatic ecosystem degradation at the PAD by releases of substances of

concern from rapidly expanding oil sands development, which led us to identify a new research opportunity – to use analyses of sediment cores from lakes in the PAD to generate ‘pre-development’ concentration baselines as a valuable reference point for quantifying the enrichment of substances of concern attributable to industrial activities. Indeed, highly critical reviews of regional monitoring programs had identified the absence of knowledge of the range of natural concentrations of these substances of concern before onset of large-scale bitumen mining and processing as a key limitation undermining an ability to evaluate the extent of contamination attributable to oil sands development within the Lower Athabasca River and the PAD [47, 83, 84]. This recognition led to a recommendation by the Federal Oil Sands Advisory Panel that sediment cores from floodplain lakes be used to establish the “natural, pre-development state” of the river and delta [85; p. 31-32]. In response to this recommendation and to address this critical knowledge gap, our foundational contaminant studies in the PAD have demonstrated the unique value of using sediment core records from upland lakes and floodplain lakes in the PAD to establish pre-development baseline concentrations for substances of concern, and to quantify the degree of enrichment since oil sands development via atmospheric and fluvial pathways, respectively [86-93]. These studies analysed concentrations of polycyclic aromatic compounds (PACs), trace elements, and total mercury, and established pre-development baselines from sediment deposited before 1920 to characterize the range of variation before industrial development in the Lower Athabasca River watershed. Their measurement in aquatic sediment and periphytic biofilm is useful because most have low solubility in water and, thus, are mainly adhered onto sediment particles and organic matter [94].

Based on knowledge gained from several spatial surveys of water isotope composition and paleolimnological research conducted between 2000 and 2014, which included recommendations for an aquatic ecosystem monitoring program for the PAD detailed in a synthesis of paleolimnological results [37], we developed a proposal in February 2014 for research to inform the design of an integrated aquatic ecosystem monitoring framework. Early concepts were communicated beforehand at multi-stakeholder meetings in Fort Chipewyan and Edmonton (Alberta), organized by WBNP under the former PAD Ecological Monitoring Program

(PADEMP). The meetings were pivotal because they facilitated exchange of ideas and stimulated new collaborative opportunities and partnerships that allowed us to launch the project in 2015. The research received financial support from the Natural Sciences and Engineering Research Council of Canada Collaborative Research and Development partnership program, with financial and logistical support from stakeholders in government (Alberta Environmental Monitoring, Evaluation and Reporting Agency (now Alberta Environment and Protected Areas)), industry (BC Hydro, Canadian Natural Resources Ltd., Suncor Energy Inc.), and Parks Canada Agency. This support was subsequently used to leverage other grants, including the Global Water Futures / Northern Water Futures program, which extended the duration of research from 2 to 5 years. Multi-agency support for the program provided clear indication of the importance and need for this research. WBNP employees and members of the local CBMs continued critical aspects of the sampling program during the Covid pandemic (2020-2021), funded in part by the WBNP Action Plan, which extended some of the data sets to 7-year duration.

Here, we synthesize results from the 7-year-long research phase and detail the development, evaluation and application of a monitoring framework capable of tracking changes to water balance, water chemistry and concentrations of substances of concern at lakes spanning the broad hydroecological gradients of the PAD. These key components form three ‘pillars’ of the monitoring framework, which we refer to hereafter as Hydrological Monitoring, Water Chemistry Monitoring and Contaminants Monitoring. They directly address key concerns for lake drying, water-quality deterioration and pollution of lakes [51]. We describe the selection and development of methods for sampling and analysis, which were informed by existing knowledge of environmental processes operating in the landscape, and we demonstrate their successful application in the PAD. We also present the approaches we developed for effective analysis and display of the data to inform about status and trends in key metrics, and for integration of information among the three components. We present original research along with a synthetic overview of the advances generated since key pillar contributions by [58-60, 92, 93]. For the Hydrological Monitoring component, water isotope tracers and water depth loggers are used to track spatial and temporal patterns of hydrological processes and their influence on lake water balances and water-level variation, including ice-jam and open-water flooding, snowmelt, rainfall, and evaporation. A suite of physical and

chemical variables were measured for the Water Chemistry Monitoring component. For the Contaminants Monitoring component, concentrations of a suite of metal(loid)s were measured in lake surface sediment and periphytic biofilms that accrued on artificial substrate samplers, and they are compared to pre-development baseline concentrations established from paleolimnological analysis of sediment deposited before onset of oil sands development. Based on the extensive research conducted, we provide recommendations for a long-term aquatic ecosystem monitoring program at the PAD that addresses the key principles of effective monitoring programs stated above, and which may have transferability to other remote regions with an abundance of shallow lakes and ponds in hydrologically complex terrain subject to the effects of multiple stressors.

2. Materials and methods

2.1 Selection, location and description of lake monitoring sites

Selection of lake monitoring sites was finalized at an annual PADEMP Forum in February 2015, where the researchers, WBNP employees and local stakeholders and knowledge holders convened. Sixty lakes were selected to span much of the geographic extent of the PAD and capture the broad range of hydrological conditions, which includes lakes with open-, restricted- and closed-drainage. They include 41 lakes from the initial October 2000 survey reported in [73] and 19 lakes where local community-based monitoring programs were already tracking changes in muskrat populations, water depth and ice thickness (the latter are denoted with the prefix “M” in the site IDs in Fig 1 and S1 Table). The lakes are roughly divided between the two sectors, with 26 lakes in the Peace sector and 34 lakes in the Athabasca sector. Nine river sites were also selected, eight of which were used to characterize the water isotope composition and water chemistry of flowing rivers (one river was non-flowing) to identify the influence of floodwaters at the monitoring lakes.

2.2 Fieldwork

In total, 21 field sampling campaigns were carried out during 2015-2021. Fig 2 provides a timeline for key developments of the lake monitoring framework, and an overview of when sampling occurred for each of the three monitoring components. Due to absence of roads and

an abundance of dense terrestrial vegetation and waterlogged terrain in the PAD, travel by river and land was inefficient for accessing the lakes. Almost all the sample collection and deployment of equipment, thus, was conducted from a helicopter with fixed floats. Water samples for measurement of isotope composition and chemistry, limnological measurements with a YSI multimeter, photographs and field observations were systematically obtained three times per year (typically end of May, mid-July and mid-September) to characterize the spatial and temporal variation in water balance, hydrological processes and water chemistry during the open-water season at each of the lake and river sites. This holds true for every year except spring of 2016 when extensive forest fires in the region caused the fieldwork to be delayed until late June. Since 2018, water-depth loggers have been deployed at a central location in each lake from May to September. Samples for the Contaminants Monitoring component were collected less frequently than for the other two components. This included deployment of artificial-substrate samplers in all lakes from May to September of 2017 and 2018, and collection of lake surface sediment at all lakes in 2017 and at 20 spring-flooded lakes in 2018.

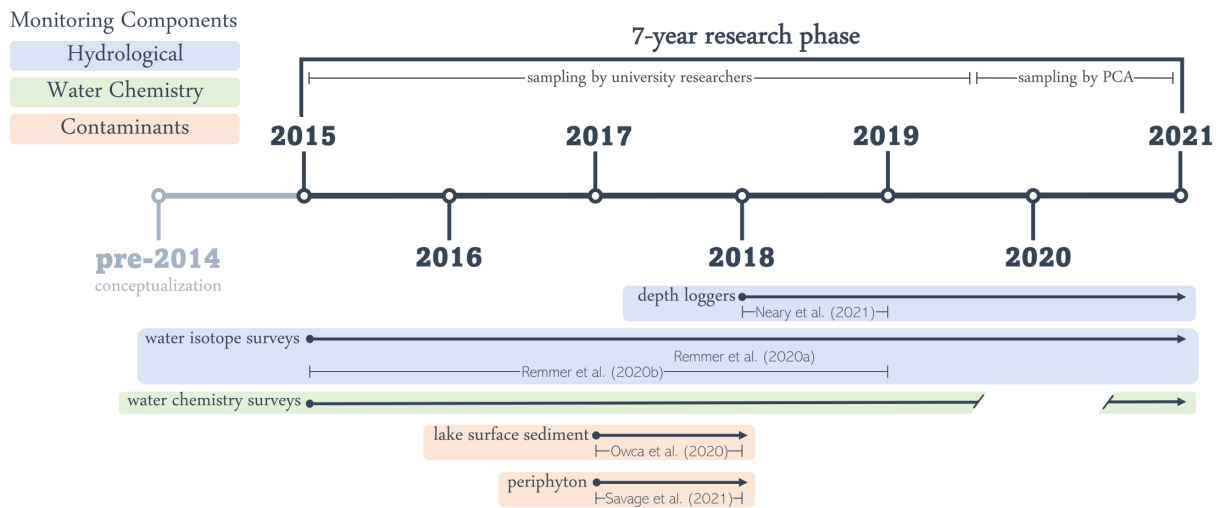


Fig 2. Conceptual diagram illustrating when key developments of the aquatic ecosystem monitoring framework occurred (2014-2021), PCA = Parks Canada Agency. Coloured boxes indicate sampling performed under each Monitoring Component, as identified in the key, and include primary research articles associated with each.

Below, we detail the field, laboratory and analytical methods associated with each monitoring component.

2.3 Hydrological Monitoring component

2.3.1 Measurement of water isotope composition

During each sampling campaign, a water sample was collected from ~10 cm below the water's surface and stored in a 30 mL HDPE bottle for measurement of water isotope composition. Sample collection in May is intended to capture influence of input from snowmelt and ice-jam induced floodwaters on lake water balance, whereas the July samples inform about the influence of rainfall, open-water flooding and evaporation at the time of peak biological productivity and the September samples capture open-water season hydrological conditions before ice cover forms. After each sampling episode, these samples were analyzed at the University of Waterloo – Environmental Isotope Laboratory (UW-EIL) using a Los Gatos Research (LGR) Liquid Water Isotope Analyser (LWIA) model T-LWIA-45-EP instrument with precisions (2σ) of $\delta^2\text{H} = \pm 0.8 \text{ ‰}$ and $\delta^{18}\text{O} = \pm 0.2 \text{ ‰}$. A suite of water standards (Vienna Standard Mean Ocean Water, Vienna Standard Light Antarctic Precipitation) from the International Atomic Energy Agency (IAEA) were used as reference materials and duplicate samples were run at a minimum of every tenth sample. Isotope compositions are expressed as δ -values, representing deviations in per mil (‰) from Vienna Standard Mean Ocean Water (VSMOW). Results of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analyses are normalized to -55.5‰ and -428‰ , respectively, for Standard Light Antarctic Precipitation [95].

Lake water isotope compositions were used to estimate the evaporation-to-inflow (E/I) ratio, an informative metric of lake water balance [96-99]. Positive water balance ($E/I < 1.0$) identifies when input exceeds evaporative water loss, whereas negative water balance ($E/I > 1.0$) identifies when evaporation exceeds input. E/I ratios were estimated using a coupled isotope tracer approach [100] (S2 Table). For more detail on isotope mass-balance equations that were used to estimate E/I ratios, see S1 Text. For samples collected during 2015-2019, we utilize the same isotope framework from [58]. For samples collected during 2020-2021, when average ice-free season flux-weighted relative humidity rose by 4.6%, we utilize a modified

framework [101]. The parameters that comprise each of these frameworks are recorded in S3 Table. Ordinary kriging was used to generate 'isoscapes' for each sampling episode, which provide representations of the spatial distribution of lake E/I ratios across the landscape. The isoscapes were generated using ArcMap V.10.8.2, and interpolation by ordinary kriging was justified based on statistically significant Moran's I values (at $\alpha = 0.05$) for each isoscape (S4 Table). These methods are consistent with [58], with the additional improvement of a masking grid layer (i.e., a shapefile) that provides a more accurate delineation of the PAD by excluding Lake Claire, Lake Athabasca and a bedrock region to its north, and an elevated area of sand dunes beyond the southern margin of the delta.

2.3.2 Continuous water depth measurements from data loggers

From 2018 to 2021, water depth loggers (onset HOB0 Water Level Data Logger (0-4 m); SKU: U20-001-04) were deployed at a central location in each lake between May and September [60]. Before deployment, the loggers were set to record at hourly intervals and attached to a rock-sock anchor with sufficient rope to allow a wooden float to remain at the lake water surface. A variable number of loggers were successfully retrieved from the lakes each year (48 in 2018, 53 in 2019, 45 in 2020 and 31 in 2021). The hourly logger data obtained from each lake were converted from absolute pressure (psi) to lake depth (m) using the Barometric Compensation Assistant in the HOB0ware Pro software program and ambient air temperature and pressure data recorded by a logger deployed outside the field house in Fort Chipewyan at the same hourly intervals. This is true for all the years except in 2021 when air temperature and pressure recorded at a local meteorological station in Fort Chipewyan (Alberta) were used to convert lake-deployed logger pressure readings to water depth. The lake depth data were compiled using Microsoft Excel (S5 Table) and a 24-hour moving average was computed in RStudio V2023.06.0 to reduce minor high-frequency variability in the datasets. The amount of drawdown that occurred at each pond was determined as the minimum depth minus initial depth and expressed in centimeters. Lake-depth variations were then sorted into the four lake-level categories (stable, drawdown, gradual rise and sharp rise) identified by [60] to inform about the main hydrological processes influencing lake depth variations (S6 Table).

2.4 Water Chemistry Monitoring component

During each field sampling campaign in 2015-2019 and 2021 (samples were not collected in 2020), ~5 litres of water were collected from each lake and river site at ~10 cm below the surface using a 4-L carboy and a 1-L Nalgene bottle. This quantity exceeded the requirement for subsequent water chemistry measurements (~750 mL) but was collected to ensure ample volume in case of processing errors. Also, *in situ* measurements of pH, temperature, turbidity and specific conductivity were obtained at ~10 cm below the water surface using a YSI ProDSS multiparameter water quality meter.

The water samples were stored in a refrigerator at the field base (Fort Chipewyan) until further processed. The processing involved filling a 500 mL bottle for measurement of ‘total’ constituents (i.e., turbidity, pH, and concentrations of total phosphorus (TP), total nitrogen (TN), and major ions), and 250 ml of lake water after passing it through a 0.45- μm pore-size cellulose acetate filter (using a vacuum pump) for measurement of ‘dissolved’ constituents (i.e., dissolved inorganic carbon (DIC), and dissolved organic carbon (DOC)). The processed water chemistry samples were promptly shipped (refrigerated) to the Biogeochemical Analytical Service Laboratory (BASL) at University of Alberta (Edmonton, Canada) for analysis. Samples were analyzed for the following: pH, turbidity, and concentrations of TN, TP, conductivity, dissolved silica (DSi), DIC, DOC, bicarbonate (HCO_3^-), major anions (Cl^- , SO_4^{2-}) and major cations (Ca^{2+} , K^+ , Mg^{2+} , Na^{2+} ; S7 Table). Concentrations of TN, TP, and DSi were determined by Flow Injection Analysis (TN Method: 353.2; TP Method: 4500-P-G; DSi Method: 370.1) using a Lachat QuickChem QC8500 FIA Automated Ion Analyzer. Concentrations of DIC and DOC were determined using a Shimadzu TOC-5000A Total Organic Carbon Analyzer (Method 415.1). Conductivity and pH in water samples were determined using the PC-titrate instrumentation (pH Electrometric Method 4500-H+B). Turbidity was determined using a Hach 2100N Turbidimeter (Method 180.1). Ionic concentrations were determined using a Thermo ICAP-6300 Inductively Coupled Argon Plasma – Optical Emission Spectrometer (Method 200.7). Some variables were measured both *in situ*, using the handheld YSI, and at BASL. We used *in situ* pH and turbidity measurements because of potential effects resulting from sample storage. For

instances when the handheld YSI reported nonsensical turbidity values due to interference by macrophyte, we used measurements determined at BASL.

Principal component analysis (PCA), a form of multivariate ordination, was used to explore patterns of variation in water chemistry at 59 of the lakes (PAD 18 was removed because it serves as an index lake for the water isotope framework) and 8 river sites (site R9 was removed because it was non-flowing) in the spring, summer and fall of 2015-2019 and 2021. Prior to analysis by PCA, all variables were tested for normality, log-transformed if non-normal, and centred and standardized using `mvn` and `factoextra` packages in RStudio V2023.06.0 [102, 103]. Variables that were log transformed include TN, TP, Cl^- , SO_4^{2-} , Na^{2+} , K^+ , DSi and turbidity. The PCA was generated using the `prcomp` function in base R [104]. The water chemistry data from 2021 were included passively in a PCA of the 2015-2019 data to reduce the influence of a year with unusually widespread flooding [105] on the sample scores and environmental vectors. To visualize relations between gradients of water chemistry variables (defined by PCA axes 1 and 2) and hydrology, lakes were colour-coded in the ordination biplot according to three hydrologically distinctive categories: open-drainage lakes, flooded perched lakes and non-flooded perched lakes. Open-drainage lakes include Lake Claire (PAD 62), Mamawi Lake (PAD 45) and Richardson Lake (PAD 38).

Flooded and non-flooded perched lakes were distinguished using water isotope composition, specific conductivity and field observations for 2015-2019 (see data recorded in Table 1 of [58]). Similar methods were applied to the 2020 and 2021 water chemistry data; however, specific conductivity was not used in 2021 because it was not measured consistently that year (see S8 Table). We are, therefore, less confident in the designations of flood status in 2021. Our determination of whether a perched lake flooded during the weeks to months before sample collection is potentially influenced by the varying 'memory' of the isotope composition and specific conductivity of lake water, which reflects an unknown period of time before sampling took place. For example, perched lakes designated as flooded in spring received river floodwater between late winter and the time of spring sampling. In summer and fall, flooded perched lakes may have either flooded between the spring sampling episode and the summer or fall episodes, or retained the signal of spring flooding beyond the summer or fall sampling

episodes. As demonstrated below, separation of sample scores according to the three hydrological categories was apparent along PCA axis 2, thus we explored the spatial distribution of PCA axis 2 sample scores for each sampling episode. We refer to these geostatistical products (maps) as 'limnoscapes'. As for the isoscapes, we used ordinary kriging in ArcMap V.10.8.2 because Moran's I values were statistically significant at $\alpha = 0.05$ for all limnoscapes except Fall 2015.

2.5 Contaminants Monitoring component

For the Contaminants Monitoring component, we synthesize results from samples of periphytic biofilm obtained from 49 lakes in 2017 and 42 lakes in 2018, and from systematic surface sediment sample collection at 58 lakes in 2017 and from opportunistic sampling of a subset of 20 lakes (8 in the Peace sector, 12 in the Athabasca sector) in 2018 after they received influx of ice-jam induced floodwaters [92, 93, 106]. Surface sediment was not collected at PAD 9 and PAD 20 because they contained little to no water in 2017. The surface sediment samples (uppermost ~1 cm) were collected at the centre of each lake in mid-September 2017 and July 2018 using 3-4 deployments of a mini-Glew corer [107], and stored at 4 °C in a Whirl-Pak bag. In both years, artificial substrate samplers (52.5 x 18 cm HDPE sheets), attached via nylon rope between a 45-cm-long wooden float and rock-sock anchor, were deployed in May at the centre of each lake. During collection in September, the samplers and accrued periphytic biofilm were retrieved, placed into large Ziploc bags, and stored frozen. Shortly after collection, the surface sediment and artificial substrate samplers were shipped in coolers with ice packs to the University of Waterloo for analysis.

Biofilms were scraped off the artificial substrate samplers using a plastic spatula, placed into containers and frozen until further processing. Lake surface sediment samples and biofilm-sediment mixtures were frozen, freeze-dried, homogenized using a mortar and pestle and a sufficient mass was subsampled for analysis of elemental concentrations. Lake surface sediment samples were analyzed at ALS Canada Ltd. (Waterloo, Canada) following the method EPA 200.2/6020A and the biofilm-sediment mixtures were analyzed at ALS Canada Ltd. (Vancouver, Canada) following EPA Method 200.3/6020A for a suite of 34 elements.

Here we focus on analyses performed on concentrations of nickel (Ni) and vanadium (V) because they serve as key indicator metals from oil sands development due to their elevated concentrations in the mined bitumen ore relative to other geological sources, and in mining wastes [83, 94], and because their analysis is cost-effective relative to other compounds (e.g., polycyclic aromatic compounds). We quantify the enrichment of Ni and V by comparing concentrations in the surface sediment and periphytic biofilm samples to sector-specific (Peace, Athabasca) pre-development baselines that have been generated from analyses of river-supplied sediment deposited before 1920 (see [89, 91-93]). Our program has continued to improve the pre-development baselines by increasing the number of sites and samples, thus, here, we present the most updated pre-development baselines, established using radiometrically dated-sediment cores from 7 lakes in the Athabasca sector (PAD 26, PAD 30, PAD 31, PAD 32, PAD 71, M2, M7), 3 lakes in the Peace sector (PAD 52, PAD 65, PAD 67) and sediment from riverbank exposures from both rivers (S9 Table). For all samples, concentrations of Ni and V are normalized to aluminum (Al) concentration to account for confounding influence of natural variability in mineralogy and changes in sediment grain size caused by shifting flow energy, as occurs in floodplains [108, 109]. Concentrations of Ni and V in the surface sediment samples are expressed as Enrichment Factor (EF) to quantify the degree of enrichment, using the sector-specific baselines (S10 Table). EFs were computed with the same equation used by [89, 91, 92], which express the Al-normalized concentrations relative to the pre-development baseline, such that an EF of 1.0 indicates no enrichment relative to the baseline whereas an EF of 2.0 indicates the concentration has doubled relative to the baseline:

$$\text{Enrichment Factor (EF)} = \frac{(M/Al)_{\text{sample}}}{(M/Al)_{\text{pre-development}}} \quad \text{EQ (1)}$$

This equation expresses the observed concentrations relative to expected concentrations, where $Al_{\text{pre-development}} = Al_{\text{sample}}$ and the $M_{\text{pre-development}}$ values are predicted using the pre-development linear regression equations (provided in Fig 7). M_{sample} is the measured concentration of Ni and V in surface sediment collected in 2017 and 2018. We evaluate the EFs using thresholds defined in a comprehensive review by [110], based on analyses of >10,000 samples, where an EF value ≤ 1.5 indicates no change relative to the pre-development baselines,

an EF value >1.5 indicates 'minimal enrichment', and an EF >3.0 indicates 'moderate enrichment'.

2.6 Hydrometric and meteorological data

Hydrometric and meteorological data were extracted from publicly available sources to evaluate their influence on the status and trends in metrics derived from the monitoring components. The hydrometric data include measurements of daily discharge for the Peace River at Peace Point (station 07KC001; 59°07'05" N, 112°26'13" W) and the Athabasca River at Embarras Airport (station 07DD001; 58°18'45" N, 111°30'54" W), and daily measurements of open-drainage network water levels at Lake Athabasca (station 07MD001; 58°42'47" N, 111°07'20" W) and Mamawi Lake (station 07KF003; 58°37'54" N, 111°20'03" W). Hydrometric data were obtained from <https://wateroffice.ec.gc.ca/> and <https://rivers.alberta.ca/>. Meteorological data (air temperature, precipitation, snow depth) were obtained from the Fort Chipewyan airport (station 3072658; 58°46'12" N, 111°07'12" W). These data were obtained from https://climate.weather.gc.ca/historical_data/search_historic_data_e.html. The meteorological station at Fort Smith (station 2202202; 60°01'34" N, 111°55'46" W), NWT, ~140 km north of Fort Chipewyan, was used to fill gaps in the Fort Chipewyan meteorological record for daily precipitation in 2016 and snow on the ground in 2018 and 2019. To contextualize hydrometric and meteorological data during 2015-2021, we compare the data with variable-specific long-term averages and interquartile ranges (IQR). We based these on a 30-year interval spanning 1981-2010, when possible. For the variables with substantial missing data during 1981-2010, we derived the long-term averages and IQRs using data that were available. This included 1971-1984 for Athabasca River discharge measurements and 1968-1984 for snow depth measurements.

3. Results and Discussion

Below we summarize the variation in hydrometric and local meteorological conditions and present results obtained during the research phase conducted at 60 lakes and 9 river sites over 7 years (2015-2021) to inform the design of an integrated aquatic ecosystem monitoring program for the PAD. Our focus is to present results for key metrics within each of the three

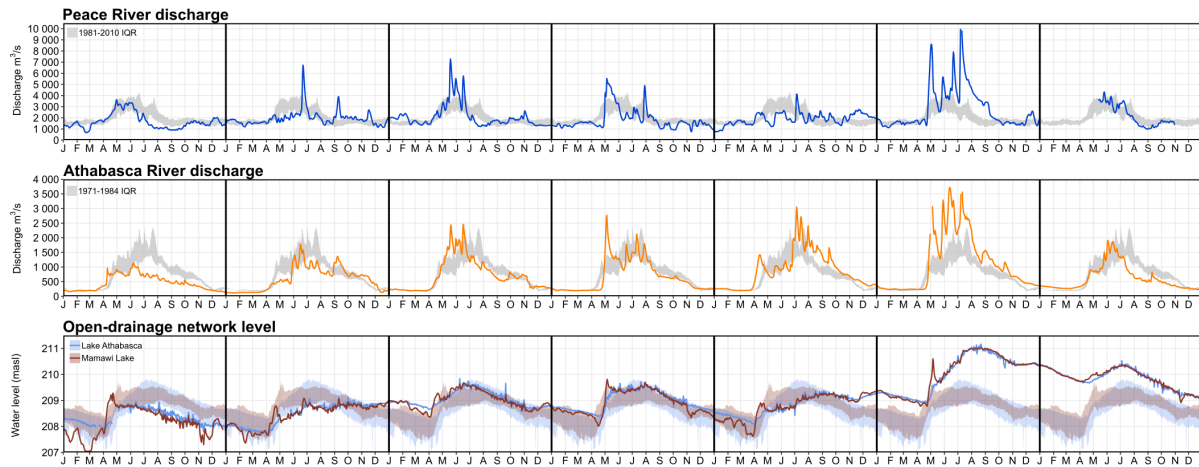
monitoring components and provide examples of data analyses, forms of data visualization, and integration of the key metrics that inform about status and trends and identify the influential factors affecting the shallow lakes in the PAD.

3.1 Hydrometric and local meteorological conditions in 2015-2021

The 7-year research phase spanned marked seasonal and interannual variation in hydrometric and local meteorological conditions (Fig 3). Hydrographs of the Peace and Athabasca rivers at the PAD exhibit a nival flow regime typical of their temperate-boreal location and headwaters in alpine areas of the Rocky Mountains [111], characterized by low discharge during winter (typically November – late April), rapid rise of discharge during the spring freshet (late April to early May), high discharge during summer (mid-May – August) supported by meltwater from the alpine areas and rainfall across their watersheds, and decline of discharge during late summer and autumn (September – October; Fig 3a). Flow regulation, however, increases discharge in the Peace River during winter months and reduces discharge during summer months, with little change during the spring freshet when ice-jams form episodically [45, 112, 113]. Discharge is considerably higher in the Peace River (typically 1500 to 5000 m³/s) than in the Athabasca River (200-2000 m³/s), but the Athabasca River flows directly into the PAD and Lake Athabasca and, therefore, strongly influences variation of open-drainage network water levels. For example, the first two years (2015, 2016) are characterized by below-average discharge during the summer in both rivers and below average water levels in the open-drainage network (Lake Athabasca and Mamawi Lake). At the other extreme, sharp rise of Peace and Athabasca river discharge in late April and early May of 2018 and 2020 to above average values, a result of ice-jams [59, 105, 106, 114], coincided with a steep rise in the open-drainage network water level. During the open water season of 2020, Peace and Athabasca river discharge reached the highest values of the 7-year period (~9,500 m³/s and ~3,500 m³/s, respectively), which coincided with the highest water level in Lake Athabasca since 1935 (~211 masl) and caused extensive flooding in the PAD [105, 114]. During the intervening years of 2017 and 2019, river discharge and open-drainage network water levels were near-average, except for July through December of 2019 when Athabasca River discharge and open-drainage network water levels rose to above average prior to the ice-jam floods of 2020.

During 2021, river discharge returned to near-average values but water levels in the open-drainage network remained well above average and sufficiently high to inundate extensive areas of the delta (e.g., [60, 114]). Overall, water levels in the open-drainage network increased during the 7-year research phase from below-average values in 2015 and 2016 to above-average values in 2020 and 2021 (Fig 3a).

a) Hydrometric data



b) Local meteorological data

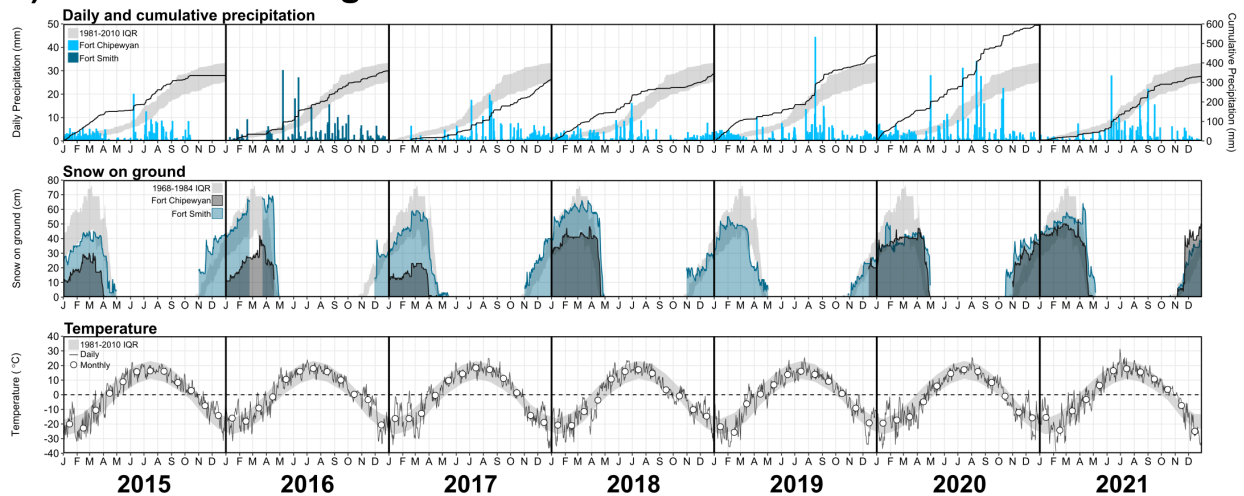


Fig 3. a) Hydrometric data from 2015-2021: Mean daily discharge (m^3/s) for the Peace River at Peace Point (07KC001) and Athabasca River at Embarras Airport (07DD001) are indicated as blue and orange lines, respectively. Daily mean water level (masl) of the open-drainage network from 2015-2021 includes Lake Athabasca (07MD001) and Mamawi Lake (07KF003) and are identified by blue and red lines, respectively. **b)** Local meteorological data recorded at Fort Chipewyan, AB (3072659) and Fort Smith, NT (2202202) from 2015-2021. Climate variables include daily mean air temperature ($^{\circ}\text{C}$), daily snow on ground (cm) and daily and cumulative precipitation (mm). The grey ribbons in all the graphs, and the red and blue ribbons on the open-drainage network

panel, represent the interquartile range of long-term values (typically the 1981-2010 climate normal, but with some exceptions as described in the Methods).

Local meteorological conditions varied considerably during the study period (Fig 3b), but the variation did not always align with changes in hydrometric variables because the latter are also influenced by regional meteorological conditions operating across the vast watersheds of the Peace and Athabasca rivers (302,500 km² and 159,000 km², respectively). For example, local snowpack depth was below normal in 2015 and 2016 when water levels in the open-drainage network were below average. During the summer months, however, local precipitation was above average and average in 2015 and 2016, respectively, and water levels in the open-drainage network closely tracked variation in Athabasca River discharge (Fig 3). Due to missing data at the Fort Chipewyan station, however, our inferences about daily and cumulative precipitation in 2016 were drawn from the Fort Smith station located ~150 km to the north. Snowpack depth is typically greater at Fort Smith than at Fort Chipewyan, which may have resulted in the overestimation of annual precipitation in 2016 at the PAD. Also, water levels in the open-drainage network were near the long-term average during most months in 2017 and 2018 when river discharge was also close to average, but snowpack depth and cumulative precipitation was below average in 2017 and above average in 2018. The atypical rise of water levels in the open-drainage network during late summer and fall of 2019 coincided with above-average Athabasca River discharge and local precipitation. High water levels persisted throughout 2020 in the open-drainage network, coincident with above-average precipitation and above-average discharge in the Athabasca and Peace rivers. In 2021, above-average water levels in the open-drainage network appear to have been supported by unusually thick local snowpack and possibly also hysteretic effects of high water in 2020 (e.g., [114]), because cumulative precipitation and river discharge had returned to average values. Air temperature followed a regular pattern of seasonal variation. Winters of 2015, 2018, 2019, and 2021 were relatively cold and the summer of 2021 was relatively warm, with the daily average exceeding 30°C in late July (Fig 3b). The above hydrometric and local meteorological data are critical for determining the factors regulating hydrological conditions, water chemistry and contaminant deposition across the PAD, because hydrometric variables are likely to promote changes most strongly at the open-drainage lakes with high hydrological connectivity whereas local

meteorological conditions are likely to exert greatest influence at the disconnected perched lakes.

3.2 Hydrological Monitoring component: lake water balances and water levels

Hydrological monitoring of lake water balance forms the critical foundation of the integrated aquatic ecosystem monitoring framework. As compiled in [60] (see their Table 2), several hydrological processes potentially regulate variation of lake water balances in the PAD, as conveyed in Equation (2):

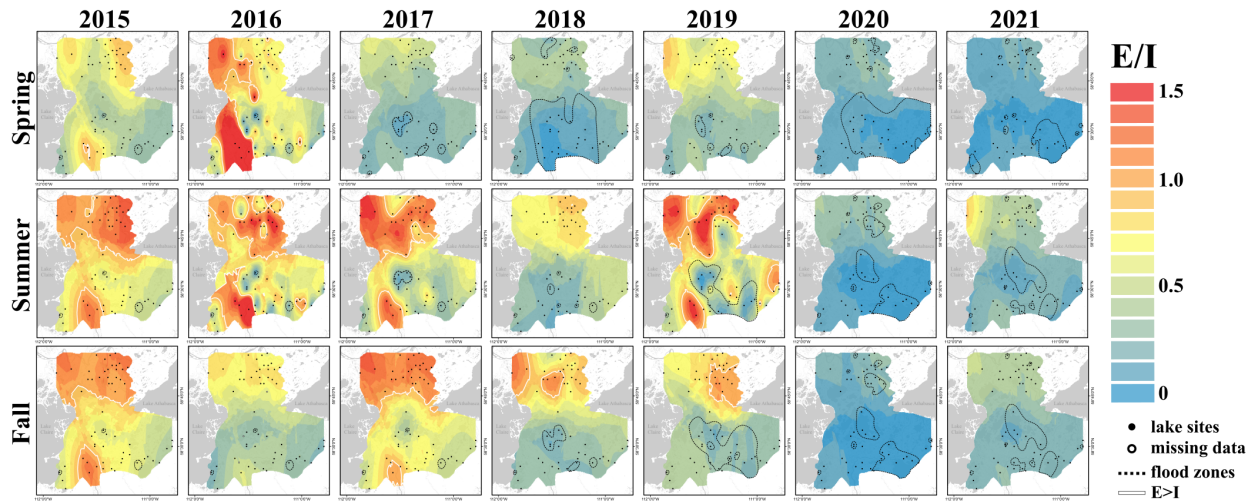
$$\text{lake water balance} = \mathbf{IJF} + \mathbf{OWF} + \mathbf{ODN} + Sm + Rf - E - O \quad \mathbf{EQ (2)}$$

In EQ (2), input sources derived from river-driven processes are distinguished by bold font, and their variability over space and time strongly influences lake water balances and water levels. Episodic ice-jam flooding (**IJF**) from the Athabasca and Peace rivers enter lakes in spring when hydroclimatic conditions (e.g., snowmelt and rainfall runoff, air temperature, ice thickness/strength during the freshet) promote dynamic breakup of river ice [35, 44, 115]. Open-water flooding (**OWF**) occurs when Athabasca River discharge is sufficiently high to overtop levees and enter lakes in the Athabasca sector during the ice-free season, which occurs more frequently than IJF [36, 55, 60, 116]. Flow reversals of the Rivière des Rochers occur when the Peace River is elevated above Lake Athabasca, and they enhance IJF or generate localized OWF in the Peace sector [54, 114]. Lateral hydrological connectivity in the centrally located open-drainage network (**ODN**), driven mainly by episodes of elevated discharge on the Athabasca River and its tributaries, raises the water level in the large open-drainage lakes (Lake Claire, Mamawi Lake, Richardson Lake) to elevations that overtop their shoreline and inundate adjacent restricted-drainage lakes by back-flooding via distributary channels [36, 57, 60, 114]. Hydrological processes influenced strongly by meteorological conditions include input from snowmelt (Sm) and rainfall (Rf), which interact with lake catchment characteristics and other potential input sources (i.e., IJF, OWF or ODN). Loss of water potentially occurs via outflow (O) and evaporation (E). Outflow is limited to lakes that possess an outlet channel or during short-lived episodes when floodwaters recede after rising above the sill elevation. In the absence of IJFs and sufficient runoff contributions from the catchment, water levels of perched

lakes tend to draw down by evaporation, but the rate is highly variable across the landscape [54, 60]. Groundwater is considered a negligible component of lake water balances due to the low hydraulic conductivity of fine-grained glaciolacustrine and deltaic sediments that underlie the PAD and, therefore, is not included in EQ (2) [57, 117, 118]. Approaches capable of tracking the occurrence and relative influence of hydrological processes in EQ (2) over space and time are essential for monitoring the status and trends in lake water balance and water levels and informing water resource stewardship decisions.

Data and metrics obtained from systematic, repeated measurements of lake water isotope composition (2015-2021) and continuous hourly water depth measurements (2018-2021) capture marked variation over space and time in lake water balances and lake levels associated with specific hydrological processes (EQ (2); Fig 4). Expression of the water isotope composition data as a time-series of isoscapes effectively illustrates the broad gradients of lake water balance that exist across the PAD, and the substantial variation at seasonal, interannual and multiannual time scales (Fig 4a). For example, 'hotspots' of net evaporative water loss from perched lakes, identified as orange and red hues bordered by a white dashed line (where E/I ratios exceed 1.0), often occur in some areas of the PAD at the same time when perched lakes in other areas have strongly positive water balance (identified as blue hues where E/I ratios are at or below 0.5). This situation occurred in spring of 2016, summer of 2016, 2017 and 2019, and fall of 2015 and 2017-2019, and thus, is not uncommon in the PAD. Particularly marked spatial variation is evident in the isoscapes for spring and summer of 2016 and 2019. In 2016, relatively thin winter snowpack and unusually hot and arid conditions (Fig 3b) generated strongly negative water balance (E/I ratios >1) in perched lakes across the Peace sector and the southwest portion of the Athabasca sector during spring and summer, while perched lakes adjacent to some distributary channels and open-drainage lakes had strongly positive water balance (E/I <0.5) because of substantial input of river floodwater (as IJF and/or OWF) that offset influence of evaporation (Fig 4a). In summer and fall of 2019, above average Athabasca River discharge (Fig 3b) raised water levels in the open-drainage network and flooded perched lakes across an extensive area of the Athabasca sector while strong net evaporation influenced lake water balance across the non-flooded areas of the delta (Fig 4a).

a) Lake water balances:



b) Lake level patterns:



Fig 4. a) Isoscapes of lake water balances (interpolated evaporation-to-inflow ratios) at 60 lakes in spring, summer and fall of 2015-2021. The isoscapes for 2015-2019 are improved from versions reported in [58] via use of a shapefile to delineate the delta. Warm colours indicate high E/I ratios, while cool colours indicate low E/I ratios, as described in the legend. Solid white contour lines identify regions where E/I ratios exceeded 1.0 and black-dashed lines identify lakes and regions that received river floodwaters. **b)** Pie charts show the proportion of lakes in the four prominent lake level categories within each sector (Peace and Athabasca) based on hourly water depth measurements in the open-water seasons of 2018-2021 and following methodology developed in [60]. The lakes in each category are presented in S6 Table.

At interannual timescales, the isoscapes reveal substantial variation in the spatial distribution of flooding in spring by ice-jam events (identified as areas with blue hues bordered by black dashed lines in Fig 4a). Ice-jam flooding of perched lakes was limited to small areas of the Athabasca sector in 2015-2017 and 2019, whereas larger ice-jam floods in 2018 and 2020 inundated perched lakes across expansive portions of the Athabasca sector and smaller areas in the Peace sector. The extent of flooding depicted in the spring 2020 isoscape compares well with evidence obtained from analysis of remote sensing imagery [105], which builds confidence in our methodology based on water isotope composition. Also, when ice-jam flooding occurs, isotope-based mixing models can be used to quantify the relative contributions of input waters, including river water and runoff from snowmelt and rainfall (see [59]).

At multiannual timescales, the isoscapes reveal that perched lakes are prone to net evaporative water loss across the Peace sector and a southwestern region of the Athabasca sector, which are areas where lakes have been observed to desiccate [58, 73]. Apparent in the 7-year time-series of isoscapes is a trend to more positive water balance of the delta's perched lakes, associated with increased discharge in the Athabasca and Peace rivers and rising water levels in the open-drainage network since fall of 2019, above average cumulative precipitation in 2020 and substantial snowpacks in late-winters of 2020 and 2021 (Fig 3, 4a). Higher relative humidity in 2020 and 2021 also influenced lake water balance by reducing rates of evaporation [101]. Seasonal variability of lake water balance is greater in lakes of the Peace sector than the Athabasca sector and is characterized as a shift from typically positive water balances in spring to strongly negative water balances in summer and fall. Exceptions to this include 2020 and 2021 when relatively extensive flooding and wet meteorological conditions supported positive water balances across most of the delta.

Open-water season flooding has remained an under-recognized mechanism of perched lake recharge in the Athabasca sector [60, 114]. The isoscapes reveal, however, that extensive open-water season flooding occurred in this part of the delta during 4 of the 7 study years (2018-2021; Fig 4a). Integration of this information with continuous hourly water depth measurements from the data loggers provides valuable additional knowledge on the timing and mechanism of floodwater input to perched lakes during the open-water season. As demonstrated in [60] (see their Fig 5), comparison of the time and rate at which lake depth increased (suddenly vs gradually) with the timing of water level rise in the Athabasca and Peace rivers and in the open-drainage network enabled an ability to discern whether each lake received river floodwater directly from overbank flooding (= lakes in the rapid rise category) or from back-flooding via rise of water levels in the open-drainage lakes (= lakes in the gradual rise category). Here we present pie charts as an effective means to summarize differences among years in the frequency distribution of the lake-level patterns (drawdown, stable, sharp rise, gradual rise) in the Peace and Athabasca sectors of the PAD. They reveal that a higher portion of lakes experienced sharp and gradual rise of water levels in 2019 and 2020 than in 2018 in response to above average river discharge and marked rise of open-drainage network water

levels. In 2020, when discharge peaked in both rivers and the open-drainage water level exceeded 210 masl for the first time in the data series, a substantial proportion of the lakes in the Peace sector experienced rapid rise of water level and no lakes fell in the drawdown category, which did not occur in 2018 and 2019 (Fig 3, 4). The positive lake water balances based on water isotope composition and illustrated in the isoscapes for 2020 (i.e., E/I ratios were below 0.5 at all lakes) are consistent with an absence of lake-level drawdown based on the continuous water depth measurements. Also, the isoscapes reveal that lakes which received open-water flooding in the Peace sector in 2020 (i.e., those within the black dashed lines in Fig 4a) are located adjacent to distributary channels (Rivière des Rochers, Revillon Coupé, Chenal des Quatre Fourches) and few are near to open-drainage lakes, which is consistent with the higher proportion of lakes in the rapid rise category than the gradual rise category. Similarly, most of the lakes identified as flooded during the 2020 open-water season in the Athabasca sector are located adjacent to the rivers and major distributaries, which is consistent with the high proportion of lakes that exhibited a sharp rise of water level (Fig 4). Unfortunately, the retrieval rate for the data loggers was low in 2021 when water levels remained unusually high across the delta, likely because substantial lake-level rise lifted the logger units off the lake bottom and caused the loggers to drift to the shore where they could not readily be located among the shoreline vegetation. If so, without measurements of water isotope composition and display as isoscapes, this would have resulted in underestimation of the number of lakes that received open-water flooding.

Integration of the information provided by the isoscapes and water depth loggers with hydrometric and meteorological records improves understanding of the hydrological processes influencing water balance and levels of perched lakes across the PAD. For example, as captured by the isoscapes, 2019 was a year of marked spatial and seasonal variation in lake water balance in the PAD (Fig 4a). Snowpack depth, river discharge, and the water plane of the open-drainage were near the long-term average prior to the 2019 open water season, but Athabasca River discharge rose rapidly just prior to sampling for water isotope composition in July (Fig 3). These conditions, combined with relatively low precipitation during May through August, resulted in substantial open-water season flooding of lakes in the Athabasca sector during the summer and

strong influence of evaporation on perched lake water balance outside the zone of floodwaters (Fig 3, 4a). Athabasca River discharge and open-drainage network water levels remained above average during the late summer and fall, and substantial rainfall occurred in August and September, which resulted in extensive open-water season flooding in the Athabasca sector and offset the influence of evaporation on water balance of non-flooded perched lakes during the fall (Fig 3, 4). The pie charts reveal a substantial proportion of perched lakes received open-water season flooding in the Athabasca sector but not in the Peace sector, and lake-level drawdown was common in both sectors in response to the hydrometric conditions of 2019. This contrasts with 2018 when hydrometric conditions were close to the long-term average and a lower proportion of lakes received open-water season flooding (i.e., those in the rapid and gradual rise categories), and with 2020 when hydrometric conditions were well above the long-term average and resulted in a higher proportion of lakes in the sharp and gradual rise categories and an absence of lakes in the drawdown category. Ability to detect such variation in lake hydrology across both space and time and relate them to shifts in hydrometric conditions is a major strength of the dual hydrological monitoring approach.

3.3 Water Chemistry Monitoring component

As demonstrated by [119], systematic measurement of lake water chemistry variables across the PAD and analysis of the data by multivariate ordination provide an approach to track limnological changes mediated by hydrological processes. Based on their repeated measurements at 9 lakes across the PAD over three years (2003-2005), analysis of the data by principal component analysis (PCA) revealed that input of river floodwaters raises concentrations of suspended sediment, TP, DSi and SO_4^{2-} in perched lakes and reduces concentrations of TN, DOC and most ions. For the Water Chemistry Monitoring component, we employed a similar approach to identify patterns of variation in lake water chemistry and determine associations with hydrological variables in our dataset, which includes a larger number of lakes and years than the study by [119].

The PCA ordination of the water chemistry data spanning 2015-2019 explains 51.9% of total variation along axes 1 (35.9%) and 2 (16.0%) (Fig 5). Axis 1 is most strongly associated with variation in conductivity and concentrations of DIC and major ions (Ca^{2+} , Cl^- , Na^+ , HCO_3^- , Mg^{2+} ,

K⁺), whereas turbidity, pH and concentrations of DOC, DSi and SO₄²⁻, are most strongly correlated with axis 2 (Fig 5a; S11 Table). Concentrations of TP, TN and K⁺ are equally correlated with both axes 1 and 2. Sample scores of the non-flooded perched lakes are broadly distributed across axis 1, which likely reflect differences in influence of evaporative concentration of ions in the absence of flooding, basin morphometry and catchment characteristics. The vast majority of non-flooded perched lakes are situated within largely impermeable fluvial-deltaic sediments and lack groundwater influence [117]. These lakes span a gradient of solute concentration from near-equivalent to rivers to several-fold higher, which accounts for their broad distribution along axis 1. Sand dunes, which form the southern and eastern border of the Athabasca sector, likely exist as a large shallow open aquifer. Input of solute-poor water from this aquifer affects a few lakes (M2, M5) adjacent to these sand dunes, which are positioned to the far right along axis 1 because ionic content is more dilute than river water.

Sample scores of the open-drainage lakes and flooded perched lakes are positioned high on axis 2, associated with relatively high turbidity and high concentrations of DSi and SO₄²⁻, and relatively low pH and low DOC concentration (Fig 5b). In contrast, the sample scores of the non-flooded perched lakes are positioned relatively low along axis 2. The 90% ellipsoid about the sample scores of the flowing rivers is located high along axis 2 and overlaps extensively with the ellipsoids for open-drainage lakes and flooded perched lakes. In contrast, the overlap between ellipsoids of the flowing rivers and non-flooded perched lakes is small. Thus, axis 2 separates water chemistry of the lakes along a gradient of high to low hydrological connectivity, and the variables that are most strongly associated with axis 2 are consistent with those identified by [119] more than 15 years earlier. Persistence of these relations through the 17 sampling episodes conducted during 2015-2021 identifies use of PCA axis 2 sample scores for monitoring status and trends in lake water chemistry in the PAD across a hydrological connectivity gradient (S12 Table), and they can be geospatially interpolated to create maps we call 'limnoscapes', which are complementary to the isoscapes. The lower variability along axis 2 compared to axis 1 is likely due to the well-known homogenizing effect of floodwaters on lake water chemistry [120].

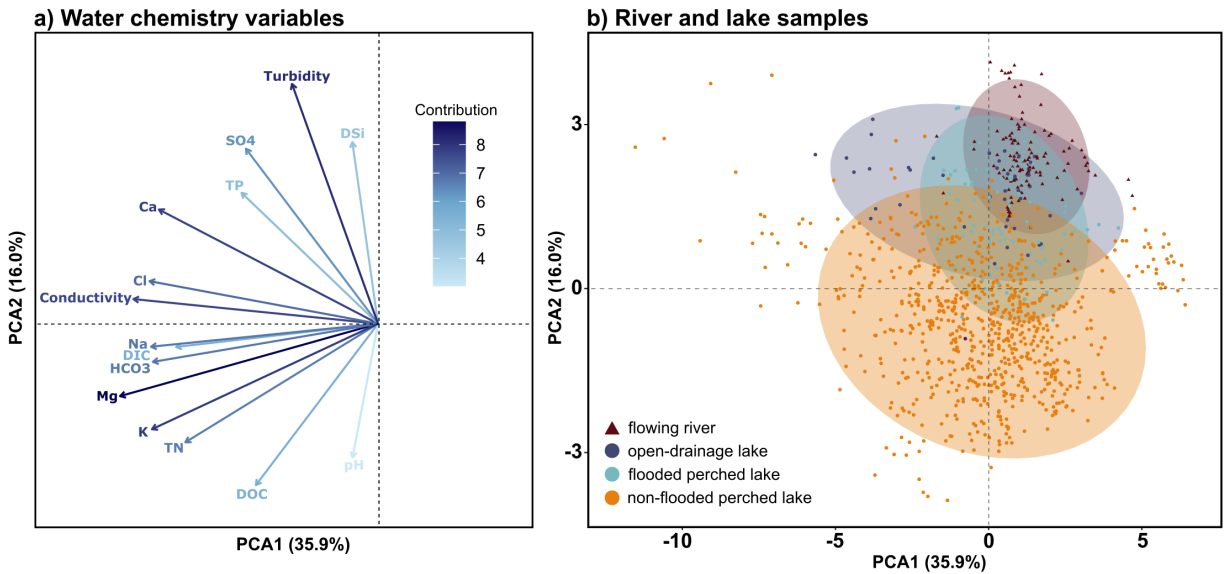


Fig 5. Principal components analysis (PCA) ordination plot showing **a)** associations between 15 water chemistry variables and their contribution (%) to variation along axes 1 and 2, and **b)** the distribution of sample scores for the flowing rivers (red triangles), open-drainage lakes (dark blue circles), flooded perched lakes (light blue circles) and non-flooded perched lakes (orange circles) sampled in spring, summer and fall of 2015-2019 across the Peace-Athabasca Delta. Confidence ellipsoids (90%) are included for each category. Samples from 2021 were included passively due to large-scale flooding that occurred in 2020 [105]. The distribution of values for each water chemistry variable in each of the lake and river categories is shown in S1 Fig.

The limnoscaples effectively illustrate that variation in PCA axis 2 sample scores over space and time at the PAD (Fig 6) corresponds closely with the variation in lake water balance, as revealed in the isoscaples (Fig 4a). Areas of the isoscaples with red and orange hues, where lake water balance is negative (i.e., $E/I > 1$), typically correspond with areas with green hues in the limnoscaples, where low PCA axis 2 scores identify the lake water is relatively high in pH and DOC concentration and relatively low in turbidity and concentrations of DSi and SO_4^{2-} . This includes persistent green hues in most of the limnoscaples across much of the Peace sector and the small southwestern area of the Athabasca sector where E/I ratios are highest. At the other end of the gradients, areas of the isoscaples with blue hues, where lake water balance is strongly positive (i.e., $E/I < 0.5$), correspond well with the areas with blue hues in the limnoscaples, where PCA axis 2 scores are high due to relatively high turbidity and high concentrations of DSi and SO_4^{2-} . Consistent with this, lakes identified as recently flooded in the isoscaples have the darkest blue hues in the limnoscaples.

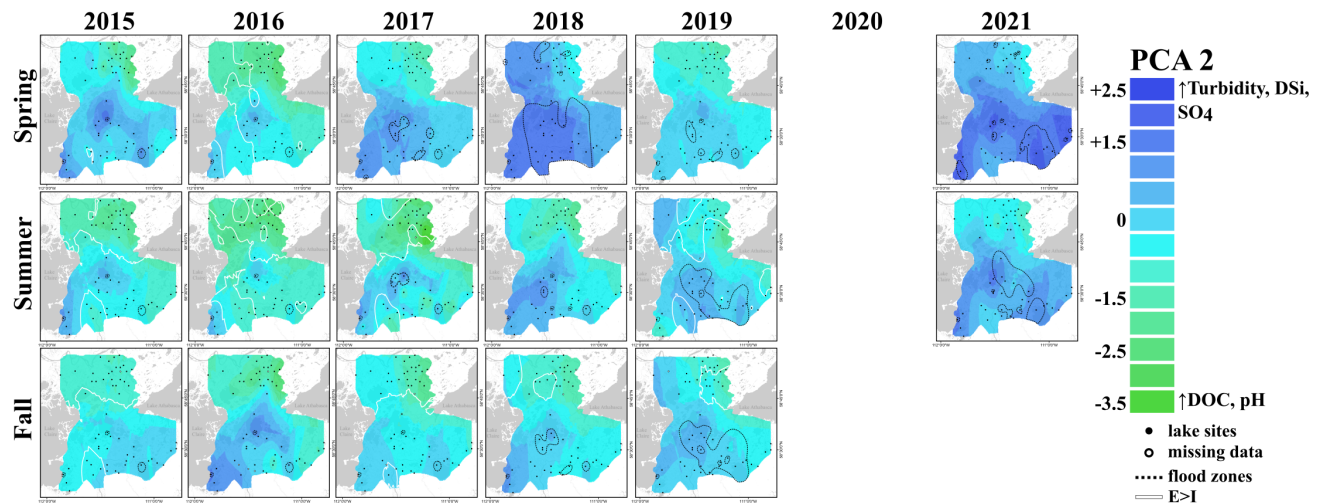


Fig 6. ‘Limnoscapes’ showing geospatial interpolation of PCA axis 2 scores (from Fig 5). Blue hues indicate higher sample scores along PCA axis 2 (associated with higher turbidity and concentrations of DSi and SO_4^{2-}) which occur in flowing rivers, open-drainage lakes and flood perched lakes. Green hues, in contrast, indicate lower sample scores along PCA Axis 2 (associated with higher concentrations of DOC and pH) typical of non-flooded perched lakes. Lake sampling sites are indicated as black dots. Solid white contour lines indicate areas of the delta where E/I ratios exceed 1.0 and dashed-black contour lines indicate areas where lakes received floodwaters (according to Fig 4a). Note that water samples were not collected in 2020 and samples were missing from too many lakes in fall of 2021 to display the results as a limnoscape.

3.4 Contaminants Monitoring component: metals in lake surface sediment and periphytic biofilm

Contaminants monitoring is needed to address long-standing and rising concern for aquatic ecosystem degradation by releases of substances of concern from upstream industrial activities [49-53, 121]. Recent leaks of oil sands process water from tailings ponds and anticipated governmental legislation that will allow the release of treated wastewater from oil sands leases into the Athabasca River have been identified as serious new and emerging threats to aquatic ecosystems at the PAD, which require ongoing surveillance [51, 122, 123]. Here we synthesize results from the assessment of enrichment of oil sands indicator metals Ni and V in surface sediment and periphytic biofilm relative to pre-development baseline concentrations in lakes spanning the broad hydrological gradients of the PAD [92, 93].

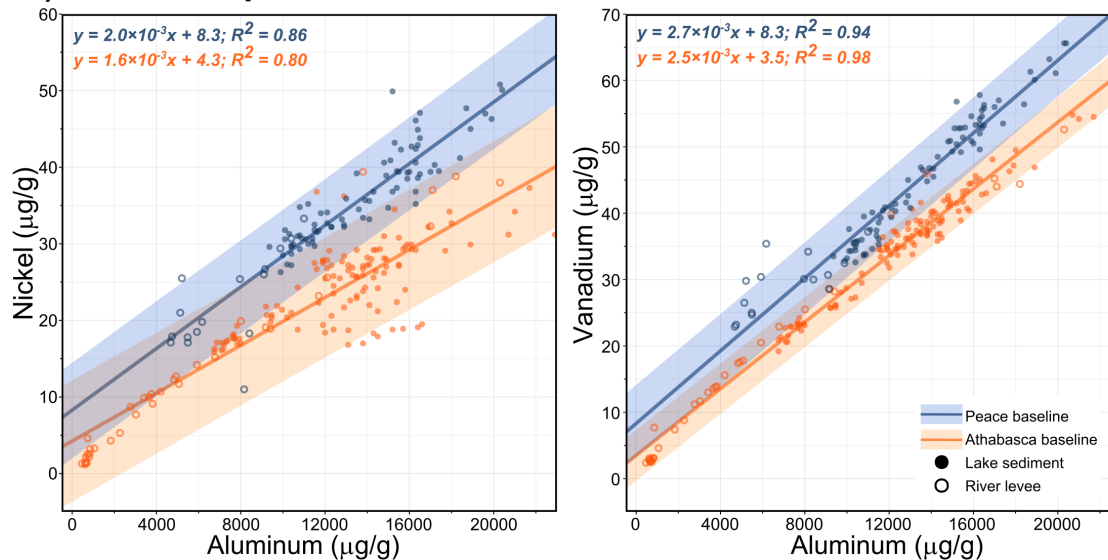
Results reveal that concentrations of Ni and V, and the geochemical normalizer Al, in the lake surface sediment and periphytic biofilm samples span the same range of values as the

sediment-derived pre-development baselines (Fig 7). The slope of the relations between the indicator metals (Ni, V) and the geochemical normalizer (Al) for the pre-development baselines is significantly steeper for sites in the Peace sector than in the Athabasca sector, because concentrations of Ni and V are naturally higher in sediment transported by the Peace River [92]. High coefficients of determination for the relations between Ni and V with Al ($R^2 = 0.80 - 0.98$) in the pre-development sediment samples demonstrate the effectiveness of Al as a geochemical normalizer (Fig 7a). Al-normalized Ni and V concentrations in the 2017 and 2018 surface sediment and periphytic biofilm samples fall close to the pre-development baselines and mostly within the 95% prediction intervals, indicative of little to no enrichment (Fig 7b). For Ni, only one surface sediment sample and four periphyton samples fall above the upper 95% prediction interval. For V, all periphyton biofilm samples and all but three surface sediment samples fall within the variation of the pre-development baseline captured by the 95% prediction intervals. As developed below, the deviations of the surface sediment samples from the pre-development baseline regressions can be expressed as enrichment factors. Periphytic biofilm samples have lower concentrations of Ni (0-25 $\mu\text{g/g}$) and V (0-21 $\mu\text{g/g}$) than lake surface sediment (Ni: 19-44 $\mu\text{g/g}$; V: 22-60 $\mu\text{g/g}$), presumably because they are diluted by higher organic matter content of the biofilms.

As revealed in Fig 8c, EFs computed for Ni and V in the lake surface sediment samples collected in 2017 and 2018 are close to 1.0 and below the 1.5 threshold for 'minimal enrichment' [110]. While these results indicate no enrichment of Ni and V relative to natural concentrations that existed before 1920, this approach can be applied in the future to samples collected at regular intervals (e.g., every 3 to 5 years), and opportunistically after widespread flooding of lakes (as was done in 2018), to assess if EFs begin to rise in response to further expansion of oil sands development, accidental releases of wastewater from tailings ponds (as occurred in 2022 and 2023; [122, 123]) and anticipated release of treated oil sands process water (OSPW) into the Athabasca River to mitigate an overabundance of mine wastewater and enable mine reclamation and closure, once new legislation is enacted [124]. Indeed, ongoing studies are taking advantage of recent widespread flooding to examine metal(loid) concentrations in surface sediments collected in 2023, to evaluate for recent evidence of

enrichment and to further establish baseline reference conditions in advance of release of treated OSPW [125].

a) Pre-development sediment baselines



b) Lake surface sediment and periphyton

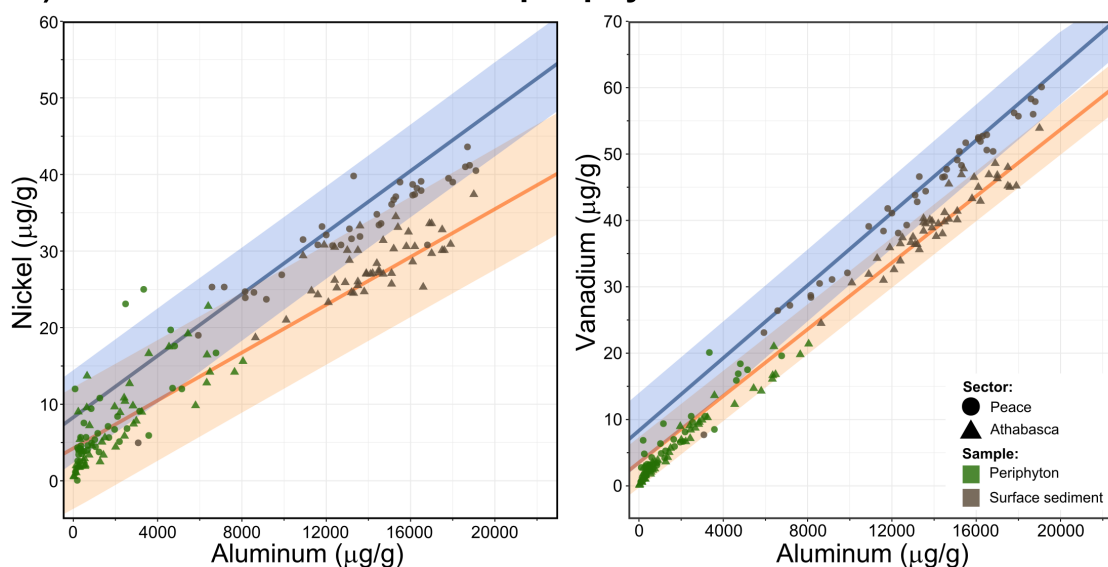


Fig 7. Cross-plots showing linear relations between concentrations for oil sands indicator metals (nickel and vanadium) and the geochemical normalizing agent aluminum in **a)** pre-development, and **b)** lake surface sediment (brown) and periphyton (green) from the Peace (circles) and Athabasca (triangles) sectors collected in 2017 and 2018. The Peace sector and Athabasca sector regression lines (blue and orange lines, respectively) and their 95% prediction intervals (blue and orange shaded area) are based on concentrations in lake sediment (closed circles) and river levee samples (open circles) deposited before 1920. Periphytic biofilm metals data are from [93] and surface sediment metals data are from [92].

3.5 Integration of monitoring components for assessment of status and trends, and improved understanding of the influence of hydroclimatic variation

Integration of key metrics measured within each of the three monitoring components provides opportunity to assess the status and trends in water balance, water chemistry and contamination at lakes in the PAD, and to discern the causes of change. Also, comparison of temporal trends with hydrometric and meteorological records and climate indices inform about the vulnerability of the lake ecosystems to hydroclimatic shifts. To this end, we have selected a set of informative indices based on knowledge gained during the research phase, which we present in three formats in Fig 8-10. These include E/I ratios as a Water Balance Index, PCA axis 2 sample scores as a Water Chemistry Index and EFs for Ni and V based on lake surface sediment as a Contamination Index.

The status of index values at each lake are displayed as boxplots and dot plots in Fig 8, which illustrate the distribution of values obtained during 2015-2019. These years capture the interval before unusually high water inundated substantial areas of the PAD. In all three panels of Fig 8, the lakes are distinguished according to sector (orange = Athabasca sector, blue = Peace sector), and they are presented in ascending order based on their mean E/I ratio. This form of display illustrates the broad range of lake water balances that exists across the delta (Fig 8a). The E/I ratios of the 60 monitoring lakes span from near zero (where inflow \gg evaporation) to >1.0 (where evaporation $>$ inflow). E/I ratios tend to be higher and more variable in Peace sector lakes than Athabasca sector lakes, although there are a few lakes in the Athabasca that also exhibit high and variable E/I ratios (e.g., PAD 19, PAD 20, PAD 21, PAD 22, PAD 37 [Jemis Lake]). Average E/I ratios exceeded 1.0 at one lake in the Athabasca sector (PAD 19) and 10 lakes in the Peace sector (PAD 3, PAD 5, PAD 12, PAD 17, PAD 50, PAD 52, PAD 57, PAD 58, M15, M19). These lakes may serve as key long-term monitoring sites for early detection of perched lake drawdown. During field sampling, we witnessed the two lakes with the largest range of E/I ratios, PAD 20 in the Athabasca sector and PAD 9 in the Peace sector, progressively desiccate during 2015-2017. Ten lakes have consistently low E/I ratios, which include the three large open-drainage lakes (PAD 62 [Lake Claire], PAD 45 [Mamawi Lake], PAD 38 [Richardson Lake],

and the flood-prone perched lakes M2 [Marta's lake], M5 [Big Egg Lake], PAD 46 [Otter Lake], PAD 30 [Mamawi Pond], PAD 31 [Johnny Cabin Pond], PAD 25 [Blanche Lake] and PAD 54 [Horseshoe Slough]. Apart from the river-proximal oxbow lake PAD 54, the flood-prone perched lakes are located in the Athabasca sector. Most of these open-drainage and flood-prone perched lakes possess Water Chemistry Index values that overlap with or approach the range of values for the flowing rivers (Fig 8b). The Water Quality Index scores are less variable than the Water Balance Index scores. Lakes that possess lower Water Balance Index scores, however, typically have high Water Chemistry Index scores associated with high turbidity and high concentrations of DSi and SO_4^{2-} whereas lakes with high Water Balance Index scores typically have low Water Chemistry Index scores indicative of higher DOC concentration and pH. Despite the marked range of lake water balance, from low E/I ratios due to constant and near-constant river inflow to high E/I ratios in the absence of floodwater input, and substantial variation in water chemistry captured at the 60 lakes over 15 sampling episodes, the Ni and V enrichment factors, based on surface sediment obtained in 2017 and 2018, spanned a narrow range (1.0-1.4) with mean Ni EFs of 1.05 and 0.99 and mean V EFs of 1.01 and 0.98 for lakes in the Athabasca and Peace sectors, respectively (Fig 8c). Notably, there are no systematic differences in EF values between the two sectors or among lakes with markedly different water balance and water chemistry arising from differences in river water input. This provides compelling evidence for no contamination by upstream industrial activities because power analysis reported in [92] has revealed strong ability (>99% power) to detect minor enrichment (10% enrichment, or a rise in EF by 0.10 units) in lake surface sediment relative to pre-development baselines. The status and range of environmental conditions, as defined here for each lake during 2015-2019, can serve as benchmark references for comparison to future monitoring data to quantify the extent of aquatic ecosystem degradation caused by hydrological change and contamination, and associated shifts in water chemistry. The knowledge gained may also be used to select a subset of lakes with specific characteristics that enable quantification of trends in contaminant deposition via atmospheric versus fluvial pathways to lakes of the PAD (e.g., [90, 91]).

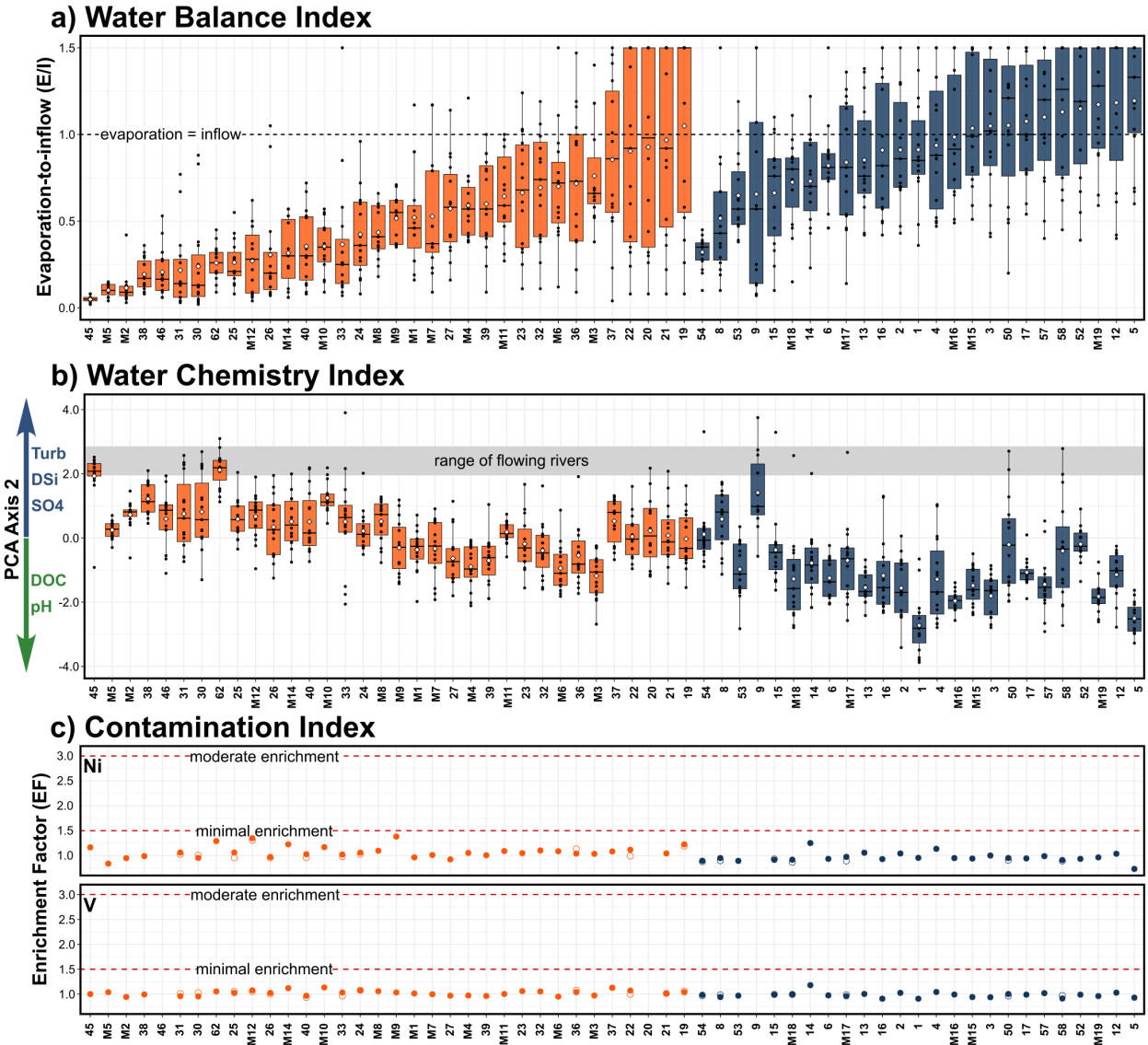


Fig 8. Indices for **a)** Water Balance, **b)** Water Chemistry and **c)** Contamination presented for each monitoring lake. The ‘Water Balance Index’ and ‘Water Quality Index’ are derived from mean evaporation-to-inflow ratios and PCA Axis 2 scores at each monitoring lake over 15 sampling episodes (spring, summer and fall of 2015-2019). The ‘Contamination Index’ is represented by nickel and vanadium enrichment factors (EFs) from lake surface sediment collected at all monitoring lakes in 2017 (closed circles) and 20 lakes in 2018 (open circles) that flooded prior to sample collection.

Display of the results in the form of maps may benefit monitoring programs by improving communication of the important knowledge gained to stakeholders and decision-makers. This is the motivation for our use of geospatial interpolation to present the distribution of mean values of the three indices across the delta as the maps shown in Fig 9,

along with illustration of variability of measurements. The variability of water balance at each lake is communicated by the size of the symbols, which demonstrate highest variability at the lakes in the southwestern portion of the Athabasca sector, followed by the lakes in the eastern, western and central Peace sector (Fig 9a). The variability at most of these lakes is attributable to strong influence of evaporation during 2015-2017 and summer of 2019, punctuated by influence of ice-jam flooding in spring of 2018 and rainfall in fall of 2018 and 2019 (Fig 3, 4, 9a). The lakes with most variable water balance possess relatively high variability of the Water Chemistry Index, as illustrated in Fig 9b. Presentation of the spatial distribution of the Contamination Index scores as a map communicates perhaps more effectively the conclusions drawn from our other forms of display of the Ni and V EFs that industrial activities have not increased concentrations of these substances of concern among lakes, and that values are similar among lakes despite marked variation in water balance and water chemistry (Fig 9c).

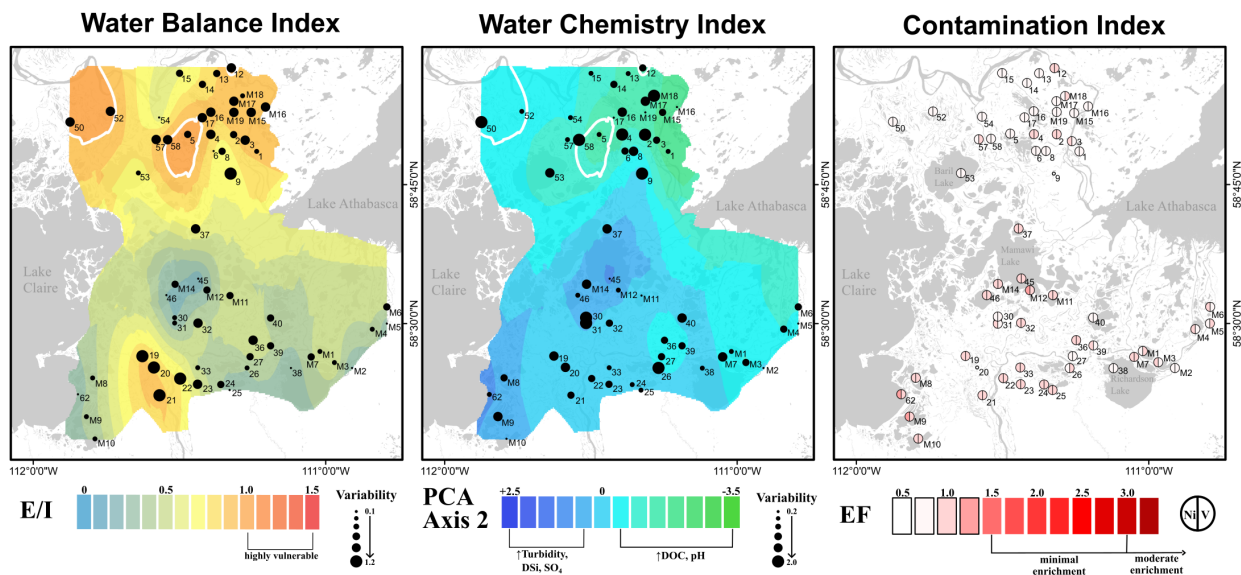


Fig 9. Maps of the Water Balance Index (isoscapes) and Water Chemistry Index (limnoscapes) depict mean E/I ratios and mean PCA axis 2 scores at the monitored lakes over 15 sampling episodes (spring, summer and fall of 2015-2019). Ordinary kriging was used to generate the two interpolated maps (Moran's I: 0.57, 0.54; z-score: 7.64, 7.31). The relative size of each sampling site (black-filled circles) identifies the variability in E/I ratios and PCA axis 2 scores according to the upper and lower whiskers in Fig 8. The white contour identifies regions where mean lake E/I ratios are greater than 1.0. The Contamination Index is represented by mean nickel and vanadium enrichment factors (EFs) from lake surface sediment collected in 2017 and 2018.

Knowledge gained from the results displayed in summary maps can be used to identify lakes that are most vulnerable to aquatic ecosystem degradation caused by changes in hydrological processes and contaminant deposition. This information may be used when operationalizing a monitoring program to select sites that will provide the greatest information content about lake status and to detect changes and trends, or to guide modifications to the sampling regime if the monitoring program encounters financial and logistical constraints. The Water Balance Index map, for example, enables an ability to readily identify regions of the delta where lakes are most prone to evaporative drawdown, which include much of the Peace sector and a southwestern portion of the Athabasca sector (the areas with orange hues in Fig 9a). These lakes are where episodic input of floodwaters provides most benefit. They are also the key perched lakes that should be monitored in the PAD to assess if strategic releases from the W.A.C. Bennett Dam in spring are successful in generating widespread flooding of perched lakes, as is currently contemplated within the WBNP Action Plan [53] and recommended in UNESCO's Reactive Monitoring Mission report [51] to mitigate potential effects of Peace River flow regulation. Thus, they should be high priority lakes for inclusion in an operationalized long-term aquatic ecosystem monitoring program. At the other extreme are the large open-drainage lakes (Mamawi Lake (PAD 45), Lake Claire (PAD 62), Richardson Lake (PAD 38)) where Water Balance Index and Water Chemistry Index values have remained constant throughout the 7-year research phase despite considerable hydroclimatic variation. Monitoring of these lakes is not likely to capture marked changes in hydrological processes, but due to (near)constant throughflow of water from the Athabasca River they may be very insightful for early detection of contamination by releases of substances of concern from oil sands operations.

As reported in a recent strategic environmental assessment for WBNP, Indigenous rightsholders of the region often use the phrase 'water is boss' to communicate their profound understanding of the ways that water and hydrological processes create vibrant ecosystems in the PAD [52]. The hydrological processes operating in the delta are known to be strongly influenced by climatic conditions across the vast watersheds of the Peace and Athabasca rivers, the Fond du Lac River at the eastern end of Lake Athabasca and the Birch River at the western end of Lake Claire [54, 114, 126, 127]. The strong influence of regional climatic conditions on

water balance and water chemistry of lakes in the PAD is evident when time series of Climate Indices (PDO Index, ONI) are compared to time series of the Water Balance Index and Water Chemistry Index developed during the 7-year research phase (Fig 10). These indices are based on large-scale sea surface temperature anomalies that characterize modes of low-frequency ocean-atmosphere circulation and are well known to affect variation of hydroclimatic conditions over broad areas of North America, including western Canada [128, 129]. Common patterns of change are evident in all the indices. This includes strongly positive values of both Climate Indices during the first two years (2015-2016), associated with strong expression of the El Niño phase of the El Niño Southern Oscillation that produces warmer winters and greater summer moisture deficits in western Canada [130, 131]. The devastating Fort McMurray wildfire occurred in 2016, which was then the globally hottest year on record [132, 133]. Peak Water Balance Index values occurred in both sectors of the delta during 2015-2016, and the GAM-estimated mean values for the E/I ratios exceeded 1.0 for lakes in the Peace sector signifying widespread negative water balances. The most strongly negative Water Chemistry Index values also occurred in 2015-2016, indicating lake water was relatively high in pH and DOC concentration in response to the minimal flooding and strong influence of evaporation during these years (note that the vertical axis scale of the Water Chemistry Index is flipped in Fig 10c so that the direction of the correlations among all the indices is consistent). Average values of the Climate Indices occurred between 2017 and 2019, and they correspond to average values for the GAM-estimated trendlines for the Water Balance and Water Chemistry Indices. The marked shift to strongly negative values of the Climate Indices occurred after 2019 coincides with onset of a 3-year La Niña phase between 2020 and 2022, which resulted in cooler winters, thicker snowpacks and greater summer precipitation [134-137]. Coincident with this change, the GAM-estimated trend lines for the Water Balance Index declined to the lowest values of the 7-year record. The average E/I ratio fell to below 0.25 for lakes in both sectors of the delta indicating a marked shift to positive lake water balances during open water seasons of 2020 and 2021 due to widespread flooding of lakes and wet meteorological conditions (Fig 10b). Water chemistry data were not obtained in 2020, but a response of lake water chemistry to the shift to positive lake water balance is evident as higher Water Chemistry Index scores during the open-water season of 2021 (appears as relatively low on the flipped vertical axis in Fig 10c),

which signifies a shift to higher turbidity and higher concentrations of DSi and SO_4^{2-} , and lower pH and DOC concentration caused mainly by widespread flooding of lakes. Throughout the study period, the GAM trendlines for the Water Balance Index show coincident changes for lakes in the Peace and Athabasca sector, despite that Peace River flow is regulated whereas Athabasca river flow is not. Variability of the trendlines is greater for the Peace sector, including greater decline of values in spring of 2018 when extensive ice-jam flooding occurred in the Athabasca sector, a feature which demonstrates the strong influence of climatic forcing on perched lake water balance in the Peace sector. Also, the Water Balance Index trendlines are consistently higher for the lakes in the Peace sector than the Athabasca sector, which captures well the greater influence of evaporation on lakes in the Peace sector due to its slightly higher elevation and greater topographic relief, and the greater influence of floodwaters on lakes in the Athabasca sector due to its lower elevation and flatter terrain. Importantly, correspondence between shifts in the Water Balance and Water Chemistry Indices with shifts in the Climate Indices suggests that monitoring records for these indices may be used to predict lake responses in the PAD to future hydroclimatic conditions once the monitoring records span a sufficiently long period of time, as has been done for the Canadian Prairies [138] and the North Saskatchewan River Basin [139].

4. Summary and Recommendations

Here, we have presented the most informative results and products achieved during a 7-year research phase to guide a long-term aquatic ecosystem monitoring program for the internationally recognized, hydrologically complex Peace-Athabasca Delta that addresses pressing concern for degradation by upstream industrial development. The research phase coincided with a period of marked hydroclimatic variation. This provided excellent opportunity to evaluate the effectiveness of the methodologies and identify informative metrics, and their response to changes in river discharge, open-drainage network water levels, snowpack depth, rainfall and evaporation between the early 'drier' years (2015-2016) and the later 'wetter' years of the study (fall 2019 through 2021). Indices were developed for lake water balance, water chemistry and contaminant enrichment, which are amenable for display in several formats to

inform about status and trends over both space and time, enable integration of the information provided by each index, assist with identifying causes of change, and should resonate with decision makers. Geospatial interpolation of the indices as maps (isoscapes, limnoscapes) captures the enormous spatial and temporal variation in lake water balances and water chemistry across the delta, which closely track shifts in hydroclimatic conditions. The maps also inform that concentrations of key indicator metals of oil sands development (Ni, V) remain within the range of natural variation that existed before 1920.

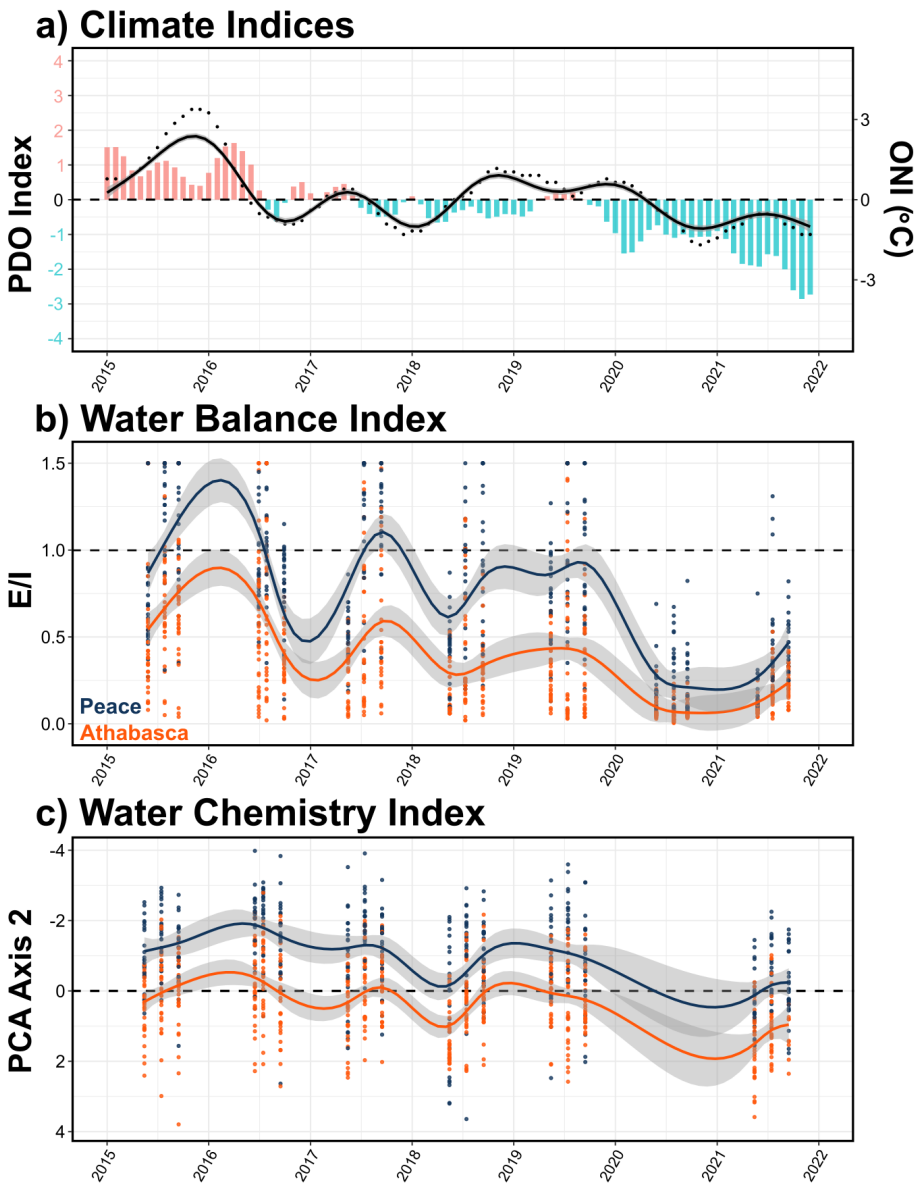


Fig 10. The Pacific Decadal Oscillation (PDO) Index is represented as a 3-month running mean of the sea surface temperature (SST) anomalies and is coloured based on whether the values are positive (pink) or negative (blue). The Oceanic Niño Index (ONI) is represented by a 3-month running mean of SST anomalies in the Niño 3.4 region and is displayed as black-filled points along with a GAM-estimated trendline ($k=13$). Lake E/I ratios (Water Balance Index) and PCA axis 2 scores (Water Chemistry Index) are colour-coded based on whether the lakes are located in the Peace (blue) or Athabasca (orange) sectors and GAM-trendlines ($k=13$) are presented to summarize temporal patterns of the index scores at each sector. PDO data were retrieved from: <https://www.ncei.noaa.gov/pub/data/cmb/ersst/v5/index/ersst.v5.pdo.dat>. ONI data were retrieved from: <https://www.ncei.noaa.gov/access/monitoring/enso/sst>.

The monitoring approach and the knowledge gained during this study may be useful to evaluate the effects of mitigative actions and environmental stewardship decisions that are currently under consideration by the WBNP Action Plan. These include strategic releases of water from the W.A.C. Bennett Dam to enhance flooding of the delta's perched lakes when hydroclimatic conditions are favourable for ice-jam formation, and the installation of weirs at key locations within the PAD to raise the water plane of the open-drainage network [53]. These actions are intended to counteract effects of Peace River flow regulation which are widely considered to reduce the frequency of ice-jam floods and lower water levels in the PAD [32, 34, 112]. Systematic monitoring of the 60 lakes for water isotope composition and water depth variation will be critical to inform about the success of these mitigative actions on hydrological processes influencing lake water balances. Also, legislation to permit the release of treated wastewater from oil sands leases into the Athabasca River is currently in development to mitigate an overabundance of mine wastewater and enable mine reclamation and closure [124]. Threats posed by release of treated mine wastewater have been identified as a serious and growing concern for Indigenous Peoples in the region and other stakeholders at the PAD [50, 51]. We suggest the metal concentrations in the surface sediment and periphytic biofilm samples collected in 2017 and 2018 can contribute to benchmarks that can be compared to similarly and systematically collected samples after treated wastewater is released to evaluate if, and when, contamination of lakes in the PAD occurs as an outcome of this legislation.

We recognize that the research phase was intensive, and the sampling regime may present some challenges to maintain. The PAD, however, is an internationally renowned landscape that is deserving of a world-class long-term integrated hydrology – water quality –

contaminants aquatic ecosystem monitoring program. Below we present four key recommendations for operationalizing the methodology during a transition from research to monitoring. If followed, we suggest this has the potential to contribute positively towards many goals stipulated in the WBNP Action Plan [53] and generate valuable knowledge towards nearly half (8) of the 17 recommendations issued by the Joint World Heritage Center / International Union for Conservation of Nature's most recent Reactive Monitoring Mission report [51; p. 4–6]. These include:

WHC/IUCN Recommendation 2: Complete hydrodynamic modelling and ELOHA (environmental flows assessment) tools that are essential to understanding the current hydrology (i.e., existing condition) of the Peace River and the PAD, the natural, pre-Bennett Dam baseline condition, the impact of climate change, and the feasibility of benefits to be derived from proposed water control structures and strategic flow releases on the OUV of the property.

WHC/IUCN Recommendation 3: Construct and repair water control structures in the PAD (such as the planned weir at Dog Camp) only after modelling and environmental flows tools have been completed, allowing an understanding of the benefits to the PAD, potential interactive effects and downstream impacts.

WHC/IUCN Recommendation 5: Urgently establish a sound decision-making mechanism allowing for key corrective actions to be taken in terms of ecological flow releases and potentially water control structures to protect the OUV of the property.

WHC/IUCN Recommendation 6: Before 2026, decide on a set of concrete mitigation measures including ecological flow releases and the construction of required water control structures to correct the impacts of the W.A.C. Bennett Dam and other alterations of the hydrology of the PAD, including increased impacts from climate change, and agree on operational strategies and interjurisdictional protocols for the implementation of the adopted mitigation measures as well as a budget sufficient for their implementation.

WHC/IUCN Recommendation 7: Urgently and before the end of 2024, conduct an independent systematic risk assessment of the tailings ponds of the Alberta Oil Sands region with a focus on risks to the PAD, and submit the report of this assessment to the World Heritage Centre, for review by IUCN, in accordance with Paragraph 172 of the Operational Guidelines.

WHC/IUCN Recommendation 8: Re-evaluate and adapt (as needed) collaborative, systematic, science-based monitoring of oil sands impacts on the Athabasca River and PAD to ensure sufficient parameters, sampling design, and protocols are employed to detect impacts. Long-term monitoring and syntheses of long-term data will be essential to establishing baselines, detecting changes, and communicating impacts.

WHC/IUCN Recommendation 9: Before 2026, develop a clear, consensus-based strategy consistent with precautionary principles for the reclamation of tailing ponds, including the treatment and disposal of OSPW, which guarantees protection of the Athabasca River's and PAD's water quality and avoids any impacts on the OUV of the property.

WHC/IUCN Recommendation 13: Ensure that the innovative Integrated Research and Monitoring Programme developed under the Action Plan, which is integrating indigenous knowledge with western science, is standardized and sustained over time in order to understand trends and dynamics in response to various pulse (e.g., ice-jam flooding) and press (e.g., climate change) disturbances that affect the OUV of the PAD and across WBNP.

To maximize knowledge generation towards the WHC/IUCN recommendations, below we present four key monitoring recommendations and present opportunities to reduce the frequency at which some types of samples are collected to reduce costs while minimizing the loss of information. Based on our scientific expertise and experience, the scope and scale of the long-term monitoring cannot be substantially reduced beyond our four monitoring recommendations without compromising the ability to achieve the recommendations detailed in [51].

Monitoring Recommendation #1: A substantial number of well-dispersed lake and river sampling sites is essential for long-term monitoring of status and trends in the Peace-Athabasca Delta.

Results obtained during the research phase have demonstrated marked variation of lake water balance over space and time at the PAD in response to shifts in meteorological conditions, river discharge and water levels in the open-drainage network. To inform about change over time in status and trends across the broad gradients and discern the cause(s), we advocate that a long-term monitoring program maintain sampling at the full suite of 60 lakes and 9 river sites. This is important because effects of Peace River flow regulation, consumptive water use by oil sands development, climate change and point-source contaminant releases to the rivers can be expected to exert different effects on lakes depending on their geographic location, position along the hydrological connectivity gradient, and proximity to the Peace and Athabasca rivers. Moreover, monitoring records will be needed from a substantial number of lakes spanning the hydrological gradients of both sectors of the delta to quantify the effects of strategic water releases from the W.A.C. Bennett Dam on the water balance of perched lakes

and evaluate the effectiveness of the planned weirs on water levels of open-drainage lakes, which are mitigative actions in development within the WBNP Action Plan [53], and to determine if accidental spills and any future releases of treated wastewater from upstream oil sands leases contaminate lakes via input of Athabasca River water [51]. Success of the mitigative actions and policy changes, and effects of accidental spills cannot be adequately evaluated if only a few lakes are monitored long-term.

Display of the monitoring data as time series of maps (isoscapes, limnoscapes) is highly informative and effectively communicates the responses of lakes to a range of audiences, including rightsholders, stakeholders and decision-makers. The geospatial interpolation used to generate the maps, however, could become untenable if the number of sites monitored is reduced substantially [141]. For the maps generated from the 60 lakes in the PAD, the Moran's I statistic, a metric that quantifies the association of values among nearby sites and is used to determine if there is significant spatial autocorrelation, was almost always sufficiently strong to permit use of geostatistical interpolation (S12 Table). However, low geospatial autocorrelation becomes an issue if the density of sites is reduced because uncertainty of predictive surface models (like those used in the isoscapes and limnoscapes) increases to a point where geostatistical interpolation cannot be used.

When operationalizing the sampling for a long-term monitoring program, there may be opportunity to improve upon the spatial distribution of the 60 lake sites for geospatial interpolation. For example, the density of sites could be increased in the northwestern portion of the Peace sector to avoid interpolation across substantial areas where we did not obtain measurements. It might be tempting to reduce the density of lakes in the northeastern portion of the Peace sector to achieve this, but three main distributary channels are situated in the northeastern portion, which are important transportation routes. The density of lakes is also low across the central portion of the PAD, but most of the lakes there are ephemeral, which means gaps in data will be frequent because water samples cannot be obtained when they desiccate. Nonetheless, the 60 lakes sampled during 2015-2021 capture exceptionally well the broad gradients of hydrological processes influencing lake water balance and water chemistry, and the monitoring program can benefit from the information provided by the multi-year

datasets already acquired. Moreover, paleolimnological analyses have been completed at nearly half the lakes, which provides a strong foundation of knowledge on the range of natural variation, and status and trends in hydroecological conditions and concentrations of substances of concern at multidecadal to centennial timescales prior to the monitoring records (e.g., [37, 86, 91]). For these reasons, we strongly advocate that monitoring should be continued at the same set of sites as in the research phase.

Monitoring Recommendation #2: We recommend that sampling for water isotope composition be conducted systematically at seasonal intervals every year and water depth data loggers be deployed every year.

Sampling for water isotope composition and lake depth variation at the 60 lakes and 9 river sites forms the foundation of the integrated aquatic ecosystem monitoring framework presented here because knowledge of hydrological processes informs the interpretation of results from the Water Chemistry and Contaminants Monitoring components. For example, a shift in water chemistry and contaminant metrics can be interpreted as caused by input of river floodwaters if the hydrological metrics identify the lake was flooded recently versus by climatic processes and atmospheric pathways if the hydrological metrics identify the lake was not recently flooded. Many of the important hydrological processes play out at seasonal time scales. This includes ice-jam floods and snowmelt runoff in spring, and open-water floods, rainfall runoff and evaporation during summer and fall. Seasonal sampling for water isotope composition effectively captures the influence of these processes on lake water balances, and continuous depth measurements throughout the open-water season delineates the most influential processes and ensures important events are not missed when they occur between the three seasonal water sampling campaigns. Every time a water sample is collected, we recommend that measurements of conductivity and turbidity be recorded using a handheld multiparameter water quality device (e.g., YSI instrument), because this information is easy to obtain and can be used to help distinguish if recent input of water originated from river flooding or precipitation (e.g., [58-60]). The information gathered by this suite of measurements has strong potential to enhance other monitoring efforts conducted by Parks Canada Agency and the local Community-Based Monitoring programs, such as muskrat and bison surveys and

measurements of ice thickness to safeguard winter travel, because water depth and hydrological process affect all components of the delta.

Monitoring Recommendation #3: We recommend systematic water chemistry surveys be performed at 3-year intervals, and opportunistically after widespread flooding of perched lakes.

Water samples for water chemistry analysis must be refrigerated during the time between collection and lab analysis, which presents logistical challenges for remote locations such as the PAD because samples must be shipped by air transportation to a distant city and local staff must be adequately trained. Currently, analytical costs are also about ten-fold higher for water chemistry than for water isotope composition. Thus, we recommend that water chemistry surveys to be conducted systematically at 3-year intervals in spring, summer and fall at all 60 lakes and 9 river sites, and opportunistically at all sites after widespread flooding of perched lakes to quantify the influence of floodwaters on water chemistry. An additional potential application is detection of an increase in salinity and ionic content at perched lakes that could occur, under flood conditions, from release of treated and untreated oil sands wastewater to the Athabasca River [142].

Monitoring Recommendation #4: We recommend systematic surface sediment surveys be performed annually at Mamawi Lake, and opportunistically at all 60 lakes after widespread flooding of perched lakes.

The uppermost 1 cm of sediment in lakes in the PAD often contains materials that have deposited over a period of more than one year. Consequently, annual sample collection is unwarranted at all lakes. We advocate for systematic annual sampling at Mamawi Lake where distributary flow of the Athabasca/Embarras River is constant and sedimentation rates are rapid to foster ability for early detection of enrichment of concentrations of substances of concern (e.g., Ni and V) that could arise from releases of wastewater from upstream oil sands mining and processing operations. This should be augmented by opportunistic sampling at all 60 lakes after widespread flooding of perched lakes to quantify the influence of floodwaters on concentrations of substances of concern and assess for river pollution. Widespread flooding of

perched lakes typically occurs in spring, which is when contaminants from industrial activities are released from winter snowpacks and delivered as a pulse downstream [143, 144]. Surface sediment collection after widespread spring flooding, thus, is an ideal time to maximize detection of contamination, should it occur. Knowledge of metal concentrations in surface sediment samples also can be used to ‘fingerprint’ which river supplied the floodwaters (i.e., Peace River vs. Athabasca River) via use of a Bayesian mixing model [145]. Distinguishing the source of floodwater and sediment is important in the PAD because concentrations of several substances of concern are naturally higher in Peace River sediment (e.g., [92]). Moreover, assessment of enrichment relative to ‘pre-release’ baseline concentrations in sediment supplied by the Peace River can serve as an ‘experimental control’ to disentangle future changes attributable to regional processes affecting both rivers (e.g., climate-induced change to river flow regimes, regional land-use changes) versus releases of oil sands wastewater into the Athabasca River only.

We recommend at least 50-100 grams of wet sediment be obtained from each lake so analyses of metal(loid)s and PACs can be performed. Analyses of PACs is expensive (currently \$CAD 400-500 per sample); thus, we recommend that the more cost-effective analysis of metal(loid)s be performed on all samples. If enrichment factors for Ni or V exceed the 1.5 threshold of ‘minimal enrichment’ at several lakes (as determined by stakeholders), we advocate that this should trigger analysis of the more hazardous PACs.

We do not recommend inclusion of systematic collection of periphytic biofilms in the Contaminants Monitoring component of a long-term monitoring program because concentrations of Ni and V currently are sufficiently low that analytical uncertainties exert strong influence on estimates of enrichment factors. Instead, periphytic biofilms could be collected opportunistically when Ni and V enrichment factors exceed the 3.0 threshold of ‘moderate enrichment’ in surface sediment samples to inform about concentrations at the base of aquatic food webs when contamination of river-supplied sediment becomes apparent.

Concluding Thoughts

The PAD is the largest inland freshwater boreal delta on Earth. Its ecological, historical, and cultural significance has been recognized nationally and internationally. Stakeholders and rightsholders have long identified that this unique northern freshwater landscape must be protected yet concerns continue to abound over the potential downstream consequences of hydroelectric production, oilsands development and climate change. To address these concerns, we envisioned over a decade ago to undertake extensive research to inform an aquatic ecosystem monitoring framework using approaches capable of assessing changes in hydrological conditions, water quality, and sources and distribution of contaminants in lakes of the PAD. Implementation of a long-term monitoring program is urgently required and herein lies the foundation. Through our multi-faceted and multi-disciplinary approach, which builds upon decades of collective hydroecological and contaminants research experience in the PAD and elsewhere, we have furnished stakeholders with informative tools and metrics to safeguard the natural and cultural heritage of the PAD now and in the future.

Supporting Information

S1 Table. Site IDs, local names and geographic coordinates of the 60 lake and 9 river monitoring sites in the Peace-Athabasca Delta. Coordinates are reported in decimal notation and latitude/longitude (degrees, minutes, seconds).

S2 Table. Raw water isotope compositions and lake evaporation-to-inflow (E/I) ratios for 60 lakes and 9 rivers in the Peace-Athabasca Delta during 2015-2021. Each year is recorded on different sheets.

S1 Text. Isotope framework and stable isotope mass balance modelling of lake water balance in the Peace-Athabasca Delta

S3 Table. Parameters associated with two isotope frameworks (2015-2019; 2020-2021) for the Peace-Athabasca Delta.

S4 Table. Moran's I statistics, z-scores and p-values for the geostatistical maps (isoscapes, limnoscapes) presented in Figures 4 and 6 of the manuscript. Values of Moran's I that are bolded with an asterisk are not significant at $\alpha = 0.05$.

S5 Table. Hourly lake depth (m) measurements in 2018-2021. Each year is separated by sheets.

S6 Table. Lake-level variation categories for each of the 60 lakes in the Peace-Athabasca Delta during 2018-2021. S = stable, D = drawdown, GR = gradual rise, SR = sharp rise, as defined in [60].

S7 Table. Water chemistry measurements of 60 lakes and 9 rivers made in spring, summer and fall of 2015-2019 and 2021. Each year is on a separate worksheet.

S8 Table. *In situ* measurements of specific conductivity and turbidity obtained in spring of 2020 (sheet 1) and 2021 (sheet 2) and the flood status designation for each lake.

S9 Table. Pre-1920 baseline sediment metal (Al, Ni, V) concentrations organized by sites in the Athabasca sector and Peace sector of the Peace-Athabasca Delta.

S10 Table. Concentrations and enrichment factors of Al, Ni, V in lake surface sediment and periphyton biofilm samples obtained at lakes in the Athabasca sector and Peace sector in 2017 and 2018.

S11 Table. Eigenvectors and correlation coefficients for the water chemistry variables along axis 1 and axis 2 for the Principal Component Analysis (PCA) shown in Figure 5 of the manuscript.

S1 Figure. Violin plots comparing the distributions of the water chemistry variables among open-drainage lakes, flooded perched lakes and non-flooded perched lakes during spring, summer and fall of 2015-2019. Horizontal gray bars show the interquartile range of values for the flowing river sites.

S12 Table. PCA axis 1 and 2 sample scores associated with Figure 5.

Acknowledgements

The authors respectfully acknowledge that the field research was conducted on Treaty 8 territory – the traditional and ancestral lands of the Athabasca Chipewyan First Nation, Mikisew Cree First Nation and Fort Chipewyan Métis Nation (FCMN). We also acknowledge that our institutions (University of Waterloo and Wilfrid Laurier University) are situated on the Haldimand Tract, land that was granted to the Haudenosaunee of the Six Nations of the Grand River, and are within the territory of the Neutral, Anishnaabe and Haudenosaunee Peoples. We extend our deepest respect to all First Peoples for their past and present contributions to these lands and offer these acknowledgements as acts of reconciliation between Indigenous and non-Indigenous Peoples of Canada. LKN was supported by an NSERC Alexander Graham Bell Scholarship (Master's), Weston Family Awards in Northern Research (Master's, Doctoral), an

NSERC Postgraduate Scholarship (Doctoral), and a Queen Elizabeth II Graduate Scholarship in Science and Technology. The research was supported by grants to RIH and BBW from Natural Sciences and Engineering Research Council of Canada's (NSERC) Collaborative Research and Development [RDPJ47399-14 to RIH and BBW; with contributing research contracts from BC Hydro (059786), CNRL (059508), Suncor (059510) and AMERA (16-0022)], Discovery [2016-03630 to RIH, 2017-05462 to BBW] and Northern Research Supplement programs [2016-305405 to RIH, 2017-391558 to BBW], Canada Foundation for Innovation [Innovation Fund 33661 to BBW], the Polar Continental Shelf program of Natural Resources Canada [617-15, 634-15, 637-17, 624-17, 640-18, 641-19, 643-19, 636-20 to RIH and BBW], the Northern Water Futures program of Global Water Futures [no grant number, to BBW], and Polar Knowledge Canada's Northern Scientific Training Program [to LKN, CRR, TJO, CAMG, MLK, AI]. Funding sources had no role in the study design or decision to publish this article. We also thank the Environmental Isotope Laboratory at the University of Waterloo and the Biogeochemical Analytical Service Laboratory at the University of Alberta and ALS Canada Ltd. (Waterloo and Vancouver locations) for sample analyses. We extend our profound appreciation for the logistical and fieldwork assistance provided by Wood Buffalo National Park (especially Queenie Gray) throughout the project, and for the fieldwork assistance provided by members of the MCFN and ACFN Community-Based Monitoring Programs in 2015-2016 and 2020-2021. We also thank the many students who participated in 16 field sampling campaigns during 2015-2019, and Robert and Barbara Grandjambe of Fort Chipewyan for their hospitality, knowledge sharing and cherished moments that have become unforgettable memories.

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