Legacy of a half century of Athabasca oil sands development recorded by lake ecosystems

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The absence of well-executed environmental monitoring in the Athabasca oil sands (Alberta, Canada) has necessitated the use of indirect approaches to determine background conditions of freshwater ecosystems before development of one of the Earth's largest energy deposits. Here, we use highly resolved lake sediment records to provide ecological context to ∼50 y of oil sands development and other environmental changes affecting lake ecosystems in the region. We show that polycyclic aromatic hydrocarbons (PAHs) within lake sediments, particularly C1-C4–alkylated PAHs, increased significantly after development of the bitumen resource began, followed by significant increases in dibenzothiophenes. Total PAH fluxes in the modern sediments of our six study lakes, including one site ∼90 km northwest of the major development area, are now ∼2.5–23 times greater than ∼1960 levels. PAH ratios indicate temporal shifts from primarily wood combustion to petrogenic sources that coincide with greater oil sands development. Canadian interim sediment quality guidelines for PAHs have been exceeded since the mid-1980s at the most impacted site. A paleoecological assessment of *Daphnia* shows that this sentinel zooplankter has not yet been negatively impacted by decades of high atmospheric PAH deposition. Rather, coincident with increases in PAHs, climate-induced shifts in aquatic primary production related to warmer and drier conditions are the primary environmental drivers producing marked daphniid shifts after ∼1960 to 1970. Because of the striking increase in PAHs, elevated primary production, and zooplankton changes, these oil sands lake ecosystems have entered new ecological states completely distinct from those of previous centuries.

atmospheric deposition | Cladocera | contaminants | environmental stressors | paleolimnology

Bituminous oil sands in northern Alberta and Saskatchewan comprise 97% of Canada's proven oil reserves. They represent the world's third largest reserves (1) and are a significant North American economic driver, with a staggering growth trajectory. In 1980, oil production was 100,000 barrels per day. Production today is ∼1.5 million barrels per day and is projected to increase by 150% (to 3.7 million barrels per day) between 2010 and 2025 (2). With stakeholders having polarized views on Canada's oil sands development, attention is fixated on the region because of environmental and perceived public-health concerns, as well as the significant economic benefits and evolving governmental macroeconomic and energy policies. Environmental concerns result primarily from the industrial activities associated with surface mining, in situ recovery, and upgrading of bitumen. Collectively, these industrial activities yield significant landscape disturbance and habitat loss (3, 4) and add to the controversy regarding water quantity and quality issues (5). The potential and realized emissions of pollutants (6, 7), including greenhouse gases (8) and mercury (9), are also contentious. Some of the controversy results from a lack of systematic environmental monitoring of industrial activities before the establishment of the industry-funded Regional Aquatics Monitoring Program (RAMP) in 1997. Furthermore, weaknesses highlighted by scientific reviews of RAMP, in its inability to recognize effects on freshwaters (10–12), leads to additional criticism by some stakeholders.

A paradox exists between the pace and scale of oil sands development after ∼1980 and the claims that development has minimal or no detectable impacts and that contaminants result mainly from natural sources (13). Of particular concern are the atmospheric loadings and distributions of contaminants associated with oil sands surface-mining and processing activities (6, 7, 14, 15), many of which are carcinogens and rank in the top 10 hazardous substances on the US Agency for Toxic Substances and Disease Registry (16). Polycyclic aromatic hydrocarbons (PAHs) are one such example, with natural and anthropogenic pathways to ecosystems (17). PAHs are a diverse group of organic compounds with multiple aromatic rings and are produced by the incomplete combustion of fossil fuels and biomass. They are relatively insoluble in water and bind to organic particles in the water column, persist in lake sediments, occur in complex mixtures, and have the potential to impact aquatic organisms at several trophic levels, particularly in the presence of other stressors (18–21). With similar properties to PAHs, the sulfur-containing dibenzothiophenes (DBTs) are a related class of aromatic compounds. C1-C4– alkylated PAHs and DBTs are both recognized as prominent components of Athabasca oil sands bitumen (6, 22).

Almost two decades of environmental monitoring within the oil sands region has failed to establish background concentrations of highly toxic contaminants. RAMP data of PAH measures in Athabasca River Delta sediments showed increases of ∼30% between 1999 and 2009 and yet no significant increases in PAHs from control sites (15). Others have challenged these findings. For example, based on three lake sediment records within well-understood hydrological settings ∼200 km north of the major development area, natural erosional processes in regional rivers were identified as the key vector of PAH delivery to sediments in seasonally flooded Athabasca Delta lakes (14). Analysis of PAHs in dated sediment cores from western Lake Athabasca and Richardson Lake in the Athabasca Delta also found no increases in total PAHs from the ∼1950s to 1998 (23). The lack of consensus among the few temporal-focused PAH studies to date, and the shortcomings of oil sands monitoring programs to adequately recognize the deposition patterns of atmospheric contaminants (6, 7), leave justifiable cause for concern as to the ecological implications of oil sands development. Establishment of background PAH concentrations and historic loadings is essential and would allow the impacts of development, including industrial PAH contributions, to be compared with the natural range in variability and composition of these contaminants in lake sediments from the region.

As noted repeatedly in previous assessments of the impacts of the Alberta oil sands operations, insufficient monitoring data

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and a poor understanding of predevelopment conditions have hampered attempts to determine the scope of pollution from oil sands development (11). Near the bitumen upgraders (Fig. 1), high atmospheric deposition of PAHs from upgrader emissions was recognized only recently by a March 2008 snowpack spatial survey (6). PAHs may also enter freshwaters by additional pathways, including atmospheric deposition from forest fires, localized wind-blown dust from active surface-mining areas (6), and erosion and transport of bitumen-rich sediments by flowing waters (14, 23). In lieu of the paucity of monitoring data and the focus of previous studies using highly mobile river sediments, we use paleolimnological techniques to reconstruct PAH loadings, aquatic primary production, and zooplankton (Cladocera) assemblage shifts archived in a strategically selected set of study lakes. *Daphnia*, our focal zooplankton indicator, is an established model organism used worldwide in toxicology assessments and represents a promising indicator for understanding multiple environmental stressors, including contaminants (24). We use highly resolved paleolimnological records dating to at least the mid-19th century to examine trends in atmospheric PAH deposition from five lakes near upgrading facilities and mining operations north of Fort McMurray, Alberta (Fig. 1 and Table S1). Additionally, to detect a wider signal of contaminant loading, a sediment core from remote Namur Lake, ~90 km northwest of the upgrading facilities and outside of the recently identified zone of high atmospheric PAH deposition (6), was analyzed for PAHs. Our data reveal that oil sands development has increased the delivery of PAHs and DBTs to near-field and remote lake ecosystems in the Athabasca oil sands region to well-above "natural," predevelopment levels (Figs. 1 and 2). The persistent, decades-long PAH loadings have also occurred during a period of substantial 20th century climatic changes (Fig. S1). Collectively, our temporal insights, coupled with findings from spatial contaminant surveys (6, 7), leave little doubt of the unprecedented increases of PAHs and the overarching influences of recent climatic changes on northeastern Alberta's lake ecosystems.

Results

PAH and DBT Trends. Total (Σ)PAH concentrations in sediment cores from five lakes within a 35-km radius of major upgrading facilities and from remote Namur Lake (i.e., our most distant site) have all increased from the mid-20th century to modern times (Fig. 1). All sediment records showed significant (Mann–Kendall trend test, all $P < 0.05$) increases in ΣPAH concentrations. The timings of increased ΣPAH and DBTs in lake sediments from "natural" background levels began at the ^{210}Pb-estimated years of 1966 ± 5.7 (SE) and 1972 ± 5.3 (SE), respectively. This is defined by a highly significant breakpoint ($P < 0.0001$) in each standardized time series (Fig. 2 *B* and *C*). When expressed as ΣPAH flux (nanograms per square centimeter per year), temporal flux trends were similar to those of ΣPAH concentration, except at SW22 (Fig. S2*A*). ΣPAH enrichments of modern sediments from stable background levels ranged between ~2.5 and 23 times (Table S2). Total DBT enrichments over the same time period ranged between ~2.6 and 57 times (Table S2). Breakpoints based on the standardized flux data (Fig. S2 *B* and *C*) occurred about two decades later than those breakpoints identified using standardized concentration data (Fig. 2 *B* and *C*).

None of the six cores presented here revealed ΣPAH trends similar to trends observed in remote lakes in north-central North America, where maximum PAH deposition typically occurred during the mid-20th century and has declined toward modern times (Table S3). The three lakes east of the Athabasca River generally showed exponential-like increases in ΣPAH concentrations with time, whereas sites to the west, including Namur Lake, showed more variable ΣPAH time series (Fig. 1). Generally, ΣPAH concentrations at the eastern sites showed low variance between ~1950 and 1980, and at ~1980, ΣPAH concentrations increased sharply toward modern times. Nevertheless, all six sites exhibited highly significant ΣPAH increases toward modern times (Fig. 1). Notably, maximum concentrations and fluxes of unsubstituted PAHs from our six study lakes were within the range typical of remote lakes but substantially lower than lakes in urbanized catchments (Table S3). For example, unsubstituted PAH concentrations in the upper sediment intervals from Albertan lakes within tens of kilometers of coal-fired power plants and extensive agricultural and residential developments (25) were about one order of magnitude greater than maximum concentrations recorded by our study lakes, with the exception of NE20.

C1-C4–alkylated PAHs and DBTs predominated in all sediments, representing 55–88% and 1.4–17% of the ΣPAHs, respectively (Table S2). DBTs were more prominent in the eastern sites (3.6–17% of ΣPAHs) compared with the western sites (1.7–8.9% of ΣPAHs). Notably, concentrations of alkylated PAHs and DBTs in our lake sediments were much lower than those reported for alluvial and bank sediments of the Athabasca River (6, 22). For example, total alkylated PAHs ranged from 7.2 to 216,000 $\mu g \cdot g^{-1}$ in alluvial sediments (22). Only sediment concentrations from NE20 approached the lower end of this range. Because bitumen is generally under ~10–50 m of overburden, it is not a direct PAH source to our study lakes with small, undisturbed catchments. In contrast, high-energy flowing waters, such as the Athabasca River and its tributaries within the McMurray Formation, likely integrate PAHs within their sediments from erosional processes of a landscape rich in bitumen (14). However, with the surface-mining footprint increasing from ~40 ha in 1974 to ~71,500 ha in 2010 (9), unweathered bitumen in the form of dust particles may become an important source of PAHs to lake ecosystems near surface-mining areas.

PAH ratios comparing pre-~1960 sediment intervals and lake surface (modern) sediment intervals were examined to assess PAH sources (Fig. S3). Ratios of retene (RET) to total unsubstituted PAHs and to total C1-C4–alkylated PAHs were higher in pre-~1960 sediments than in the modern sediments in all six lakes (Fig. S3 *A* and *B*). This indicates a greater proportion of wood combustion and terrestrial plant inputs compared with recent times (26). Namur exhibited the least change in these ratios (30% and 16% for RET/total unsubstituted PAHs and RET/total C1-C4–alkylated PAHs, respectively) compared with the other lakes. Pre-~1960 sediments generally showed anthracene/(phenanthrene + anthracene) [ANT/(PHE+ANT)] ratios >0.1 and fluoranthene/(pyrene + fluoranthene) [FLA/(PYR+FLA)] ratios near or >0.5 (Fig. S3 *C* and *D*). These ratio values are indicative of mainly wood-combustion sources of the unsubstituted PAHs (27). Indeno[*1,2,3-cd*]pyrene/(indeno[*1,2,3-cd*]pyrene + benzo[*g,h,i*]perylene) [IP/(IP + BghiP)] ratios in pre-~1960 sediments from NE20, NW35, and SW22 were ~0.5 (Fig. S3*E*) and characteristic of grass or wood combustion (26), whereas modern sediments generally showed IP/(IP + BghiP) ratios <0.5, except for SW22 and Namur. The 1,7-dimethylphenanthrene (MePH)/(1,7 + 2,6-MePH) ratios were >0.7 in pre-~1960 sediments from four of five lakes (Fig. S3*F*), also implying wood-combustion sources (26).

Ratios of unsubstituted PAHs in modern sediments indicated greater petrogenic influence in NE20, NE13, SE22, and NW35 [i.e., FLA/(PYR+FLA) <0.4], coinciding with increased PAH deposition. The relative amounts of alkylated PHEs, chrysene (CRY), and DBTs are considered reliable indicators of petroleum hydrocarbon sources and weathering (28). C2-DBT/C2-CRY ratios showed higher values in the modern sediments of all lakes, except Namur (Fig. S3*G*). Modern C3-DBT/C3-PHE ratios ranged from ~1.1–2.5 and, compared with the pre-~1960 values, were higher in all six lakes (Fig. S3*H*). C3-DBT/C3-PHE ratio values of ~2–3 are characteristic of alluvial and river bank sediments in the development area (22). Collectively, the C3-DBT/C3-PHE and C2-DBT/C2-CRY ratios, along with other indicators of combustion sources, suggest a shift to petrogenic and unweathered alkylated PAH sources in the modern sediments of our five lakes proximate to the major oil sands development area. In the case of Namur Lake, the limited difference between most

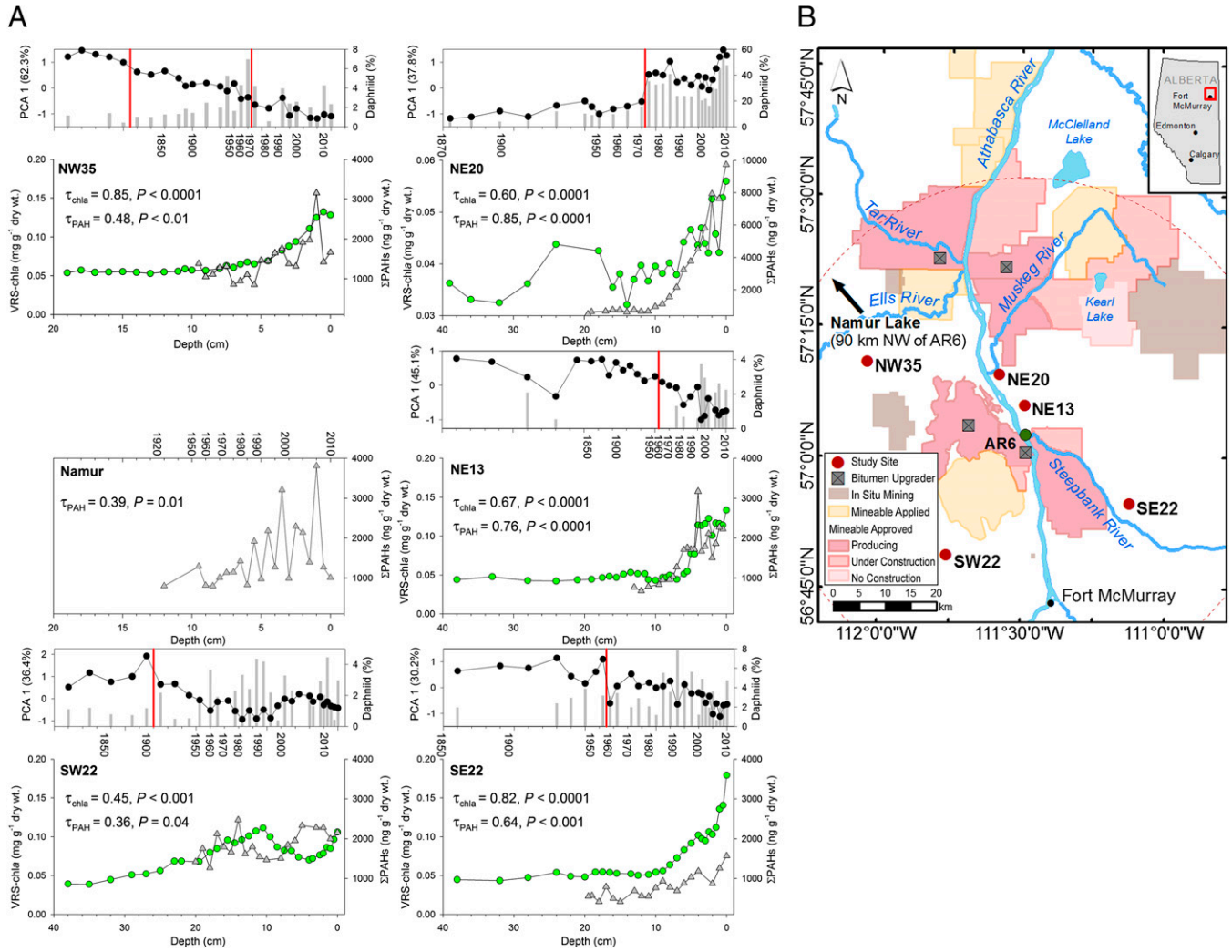

Fig. 1. (*A*) Stratigraphies of visible reflectance spectroscopy (VRS) chlorophyll *a* inferences (green circles), total PAH concentrations (gray triangles), daphniid abundances (gray bars), and principal components analysis scores of cladoceran assemblages (black circles). Modeled ages based on ^{210}Pb dating are plotted. The vertical lines (red) represent assemblage zone boundaries (*SI Text*). A Mann–Kendall nonparametric trend test assessed the significance of the VRS-chla and ΣPAH time series. (*B*) Location of the five study sites near the major development area. Namur Lake is to the northwest. The dashed line shows a 50-km radius surrounding site AR6 (6). Spatial data of industrial operations were acquired from the Energy Resource Conservation Board. Winds are generally from the southwest and southeast (http://windatlas.ca/en/maps.php).

diagnostic ratios comparing the pre-~1960 and modern sediment intervals suggests less influence from petrogenic sources than our other study lakes.

VRS-Chl*a* Reconstructions. Lake primary production (i.e., reconstructions of chlorophyll *a* and its breakdown products as inferred by visible reflectance spectroscopy: VRS-chl*a*) increased substantially, especially in the post late-1970s sediments (Figs. 1*A* and 2*A*). All sediment records examined (Namur Lake was not analyzed for VRS-chl*a* because of lack of sediment) showed highly significant increasing trends in VRS-chl*a* (all $P < 0.001$). The ^{210}Pb-estimated year of 1978 ± 4.8 (SE) was recognized as a highly significant breakpoint in the standardized time series (r^2= 0.63; $P < 0.0001$). VRS-chl*a* inferences from SW22 increased much earlier (~1900) than at the other lakes and also showed a decreasing trend between ~1990 and recent times. Although the Namur Lake sediment record lacked VRS-chl*a* measurements, diatom-based inferences from this lake indicated greater primary production that began at ~1900 and accelerated after ~1990 (29). Thus, the pattern observed at Namur Lake is generally consistent with our other five study lakes.

Cladoceran Assemblages. Principal components analysis (PCA) axis 1 sample scores reflected the dominant shifts in the cladoceran assemblages, capturing ~30–62% of the variation (Fig. 1*A*). Two significant assemblage zones were recognized at all sites, except NW35, where three significant zones were delineated (Fig. 1*A* and Fig. S4). Generally, the timings of shifts in axis 1 scores were consistent with the placement of zone boundaries. Primary zone boundaries occurred during the ~1960–1970s for all sites except SW22, where the boundary occurred at ~1900. The eastern sites demonstrated relatively stable axis 1 scores for at least a century of lake history until the ~1960–1970s, after which *Daphnia* increased at the expense of *Alona* and/or *Chydorus*. At SW22, axis 1 scores were generally stable until the zone boundary at ~1900. From ~1900 to modern times, axis 1 scores mainly decreased and generally reflect increased abundances of *Bosmina* and *Daphnia*. At NW35, there was a directional trend in axis 1 scores that began near the earliest zone boundary (Fig. 1*A*). This reflects a shift in the pelagic assemblage from *Bosmina*- to *Daphnia*-dominated (Fig. 1*A* and Fig. S4).

Daphniids increased as a percentage of the cladoceran assemblage between about the mid-1900s and modern times at all sites (Fig. 1*A* and Fig. S4), despite the low quantity of pelagic

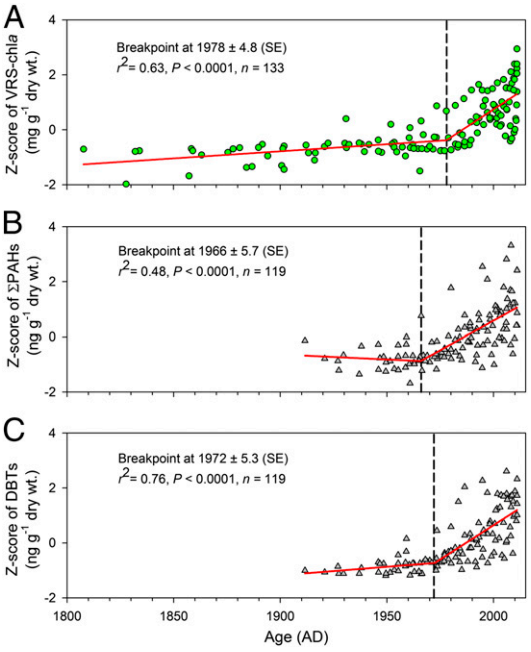

Fig. 2. Standardized values (Z scores) of visible reflectance spectroscopy (VRS) chlorophyll *a* inferences from the five lakes proximate to major oil sands operations (*A*). Standardized values (Z scores) of total PAH concentrations (*B*) and total DBT concentrations (*C*), from our six study sites. Two-segmented, piecewise linear regression models identify the timings of breakpoints (*SI Text*).

habitat in these shallow lakes. The magnitudes of the daphniid increase varied depending on the dominance of *Bosmina*, *Alona*, and/or *Chydorus* in each sediment record. NE20 showed, by far, the largest daphniid increase beginning at ~1970. At NE13 and SE22, daphniids became more frequent and abundant in the most recent assemblage zone, delineated at ~1960. Daphniids never exceeded ~4% and 8% abundance at NE13 and SE22, respectively. At the western sites, daphniids increased in abundance in the post mid-1900s sediments. Between the mid-1900s and modern times, daphniids tripled and doubled their average abundance at NW35 and SW22, respectively; however, abundances remained low.

Discussion

Focused environmental monitoring of oil sands aquatic ecosystems did not exist before the establishment of RAMP in 1997 through industry funding. Furthermore, before 2000, Canada's mandatory National Pollutant Release Inventory (NPRI) did not require industrial facilities to report PAH emissions. Therefore, indirect monitoring, provided by our paleolimnological approach, is the only method available for establishing background conditions of PAHs before extensive development of the oil sands began. Together, the historic timings of PAH increases measured from our lake sediments (Fig. 1), including the temporal shifts in characteristic PAH ratios suggesting more petrogenic sources (Fig. S3), and the results of a spatial PAH deposition survey (6) provide compelling science-based evidence that local industrial activities are important contributors of PAHs to aquatic ecosystems in the Athabasca oil sands region. Additionally, lakes to the east of the Athabasca River record particularly striking contaminant increases, consistent with the prevailing winds blowing across local upgrading facilities and surface-mining areas. Atmospheric depositions of PAHs from upgrader emissions and/or unweathered bitumen in the form of dust particles from surface-mining areas are now likely a major source of PAHs entering regional aquatic ecosystems. Industry's role as a decades-long contributor of PAHs to oil sands lake ecosystems is now clearly evident.

PAH concentrations and fluxes from our lake sediment records have increased markedly since the ~1960–1970s, coinciding with over four decades of oil sands development (Fig. 2 and Fig. S2). This temporal pattern is also evident at remote Namur Lake and suggests that PAHs from oil sands operations are delivered outside of the 50-km zone of high-PAH deposition identified by a March 2008 snowpack spatial survey (6). Of the few regional sites investigated that potentially reflect atmospheric PAH deposition, PAD 18 (~200 km north of the major development area) in the Athabasca River Delta shows a strong decrease in PAHs since the early 1800s (14). The modern lake sediments presented here now record average ΣPAH and DBT concentrations and fluxes that greatly exceed "natural" levels of the early-to-mid–20th century. However, given these temporal trends, maximum PAH concentrations and fluxes from our study lakes, except NE20, are generally comparable to other remote lakes and much lower than absolute values from lakes within more urbanized catchments, including three Albertan lakes influenced by localized coal and gasoline combustion sources of PAHs (Table S3). Canadian interim sediment quality guidelines (CISQGs), which are available for 13 specific PAHs (30), are currently exceeded for seven compounds [i.e., phenanthrene, pyrene, benz(*a*)anthracene, chrysene, benzo(*a*)pyrene, dibenz(*a,h*)anthracene, 2-methylnaphthalene] at NE20, the site receiving the highest deposition of PAHs through time. Sediment concentrations of five PAHs at NE20, including 2-methylnaphthalene, benz(*a*)anthracene, chrysene, benzo(*a*)pyrene, and dibenz(*a,h*)anthracene, have exceeded CISQGs for about two decades.

It is increasingly apparent that the compounding effects of anthropogenic stressors have the potential for extraordinary impacts to northern lake ecosystems (31–33). There is no doubt that lakes in northeastern Alberta also experience other stressors coincident with the effects of industrial-scale oil sands mining and processing operations. For example, Fort McMurray annual air temperatures have increased by ~1.65 °C since 1960 and show a significant increase since the early 1900s (Fig. S1). Climatic observations also confirm decadal-scale patterns in annual precipitation. These patterns are consistent with other regional observations over the past ~100 y (34). In northern Alberta, shifts in flood regime and an increase in the number of closed-drainage lakes during the 20th century are unprecedented over the last millennium and signify a shift in the region's hydrology in response to climatic changes (34, 35). In addition, the oil sands industry is an obvious point source of atmospheric emissions of key components of acidic precipitation, including sulfur and nitrogen oxides (3, 36, 37), although Alberta's carbonate-rich soils provide some buffering capacity.

Although our findings demonstrate that oil sands development leads to greater PAHs in regional lake ecosystems, the ultimate driver of increased primary production within our study sites beginning in the late 1970s is likely an outcome of multiple environmental factors. As a consequence of climate warming, the physical processes that lakes experience can be altered. Longer ice-free season and enhanced thermal stability, coupled with higher surface-water temperatures and the redistribution of nutrients within the water column, contribute to greater algal production within many lake ecosystems (38, 39). Paleolimnological studies from a suite of lakes in Alberta (29, 36) and the adjacent Northwest Territories (40) record notable shifts in lake primary production, influenced to some degree by climatic control. Despite the acidification potential of emissions from upgrading facilities, diatom-based analyses of 20 acid-sensitive lakes in northern Alberta (29, 36) showed evidence of acidification at only one site. To date, the overall pattern emerging from paleolimnological studies conducted in the greater oil sands region, including data presented here, is that 20th century biotic assemblages (i.e., cladocerans, diatoms) and other sediment measures (i.e., VRS-chl*a*, C:N) reflect greater lake primary production and higher alkalinity (29, 36). If climate warming enhances limnological conditions favorable to some algal species, such as cyanobacteria (38), then internal phosphorus loading during anoxia may

exacerbate the already-enhanced nutrient conditions of relatively productive Albertan lakes that thermally stratify (29, 41). Indeed, enhanced lake primary production attributable to recent climatic warming is under way in the greater Athabasca oil sands region.

The ultimate ecological consequences of decades-long increases in aquatic primary production, coupled with greater PAH loadings to lakes in the oil sands region, are unknown and require further assessment. Sediments within oil sands deposits from downstream portions of the Athabasca, Ells, and Steepbank rivers, and a wastewater pond, were toxic to early developmental stages of common forage fish native to northern Alberta (i.e., *Catostomus commersoni*, *Pimephales promelas*), and PAH concentration and composition contributed to the effects (19, 20). Other native forage fish (i.e., *Perca flavescens*, *Cottus cognatus*, *Semotilus margarita*) compared between reference and exposed sites within the oil sands region displayed lower levels of gonadal steroids in response to PAHs, although robust relationships between steroid hormone reductions and gonadal development were not detected (42, 43). Although some linkages between PAH exposure and the health of sentinel fish species are evident, less is known regarding the potential effects of PAH exposure to other members of aquatic ecosystems. Our paleolimnological analysis reveals an overall increase in occurrences (NE13 and SE22) and relative abundances (all sites) of *Daphnia* beginning at ~1960s to 1970s (Fig. 1 and Fig. S4). Surprisingly, this daphniid shift is most obvious at NE20: the lake experiencing the greatest modern PAH loadings at ~23-times background levels and the only site to exceed CISQGs. It does not appear that the elevated concentrations of PAHs and likely other contaminants, such as metals (7), have thus far had observable negative effects on *Daphnia* populations. Beginning in the late 1970s, climate-induced shifts in algal primary production appear to have trumped the potential effects of historic contaminant loadings on key algal grazers such as *Daphnia* (Figs. 1 and 2). Furthermore, lake trophic status often correlates negatively with contaminants in some lake biota, possibly because of the lipid content and growth rate of phytoplankton, in combination with greater sedimentation of organic matter as a result of increased algal biomass and shifting algal species composition (44, 45).

The effects of contaminants such as PAHs on the biota of lakes undergoing shifting ecological status highlights the complexity of predicting biological response to multiple environmental stressors. We assume that time periods with higher sedimentary concentrations of PAHs reflect lake conditions when water-column PAH concentrations were also greater, thus increasing biological exposure to both dissolved and particle-associated PAHs. *Daphnia* demonstrate potential to bioaccumulate PAHs from aqueous solution by several orders of magnitude (46). Despite this, our paleoenvironmental results reveal *Daphnia* abundance trends that are unexpected given the empirical evidence from laboratory-based experiments examining *Daphnia* response to PAHs. Laboratory studies using *Daphnia magna* neonates demonstrate that interactions involving some PAHs and environmental factors, such as UV-light penetration (18) and dissolved metal (i.e., Cu) concentrations (21), have the potential to amplify PAH toxicity. Within lake ecosystems experiencing climatic changes, allochthonous dissolved organic carbon (DOC) inputs may decrease in response to shifts in catchment hydrology, or in extreme cases, drought-like conditions, which are processes that are already occurring in the Athabasca oil sands region (34, 35). Decreased DOC in the water column can result in increased water transparency allowing greater UV-B penetration (47, 48) and possibly amplifying PAH toxicity but decreasing persistence (18). Conversely, humic acids can reduce the phototoxicity and bioaccumulation of specific PAHs (49). Despite the potential of photo-induced toxicity negatively impacting *Daphnia*, we suspect that daphniids are showing increased success in response to changes in regional climate that have increased aquatic primary production (i.e., the food resource of *Daphnia*). Environmental change driving both shifts in the physical and chemical conditions of aquatic ecosystems, coupled with modern sedimentary PAH concentrations several-fold greater than "natural" background levels, warrants much further research consideration. Nevertheless, considering predictions of future climate warming and accelerating oil sands development, there exists great potential for Athabasca oil sands ecosystems to experience marked changes in their function and ecological organization.

Conclusions

Analyses of sediment cores from five lakes near major oil sands operations and remote Namur Lake demonstrate that modern ΣPAH concentrations and fluxes, including DBTs, are well above "natural," predevelopment levels. Coincident with increased PAH deposition after the ~1960s to 1970s, lake ecosystems must now also contend with 20th century climatic changes, which are contributing to increased aquatic primary production and marked cladoceran assemblage shifts. *Daphnia*, a sentinel zooplankter, has not yet exhibited decreases in relative abundance associated with increased PAH loadings through time, despite potential toxicity enhancement of PAHs by other stressors. Rather, climate-driven primary production increases may have trumped some effects of oil sands-derived PAHs on at least *Daphnia* populations. Nonetheless, several striking PAH trajectories recorded in sedimentary profiles reflect the decades-long impacts of oil sands development on lake ecosystems, including remote Namur Lake. This temporal PAH pattern was not recognized previously by industry-funded oil sands monitoring programs. We conclude that lake sediments in the Athabasca oil sands region register a clear PAH legacy with the pace and scale of industrial development of the region's tremendous bitumen deposits.

Materials and Methods

Lake-sediment cores were obtained from the center of five small, shallow lakes with undisturbed catchments near oil sands operations north of Fort McMurray, Alberta (Fig. 1*B* and *SI Text*). Remote Namur Lake, outside of the ~50-km radius surrounding site AR6, where high atmospheric PAH deposition was identified (6), was also cored. Approximate ages of the sediments were determined by standardized dating procedures at the laboratories of Flett Research using ^{210}Pb, ^{137}Cs, and ^{226}Ra radioisotopic techniques and the constant rate of supply model (50) (Fig. S5).

PAH analysis of lake sediments was conducted by AXYS Analytical Services using their method MLA-021 (*SI Text* and Table S4), which is based on US Environmental Protection Agency (EPA) Methods 1625B and 8270C/D. Each sample was defrosted and homogenized by manual stirring. A weighed subsample was then dried with anhydrous, powdered Na_2SO_4. The dried subsample was spiked with 16 perdeuterated surrogate PAH standards and Soxhlet extracted with dichloromethane (DCM) for 18 h. A second subsample was then oven dried to determine moisture content. The extract was then concentrated to ~2 mL and exchanged into hexane for cleanup. The extract in hexane was fractionated on a silica column with pentane for the first discard fraction and dichloromethane for the second PAH fraction. The PAH fraction was subjected to Alumina cleanup using hexane for the first discard fraction and DCM for the second PAH fraction. This extract was analyzed, after concentration and addition of recovery standards, by low-resolution mass spectrometry (LRMS) using an RTX-5 capillary GC column. The LRMS was operated at a unit mass resolution in the electron impact (EI) ionization mode using multiple ion detection acquiring at least one characteristic ion for target analytes and surrogate standards. Concentrations of PAHs were calculated using the isotope dilution method of quantification. Total PAHs (ΣPAHs) represented the sum of 46 analytes (i.e., 17 unsubstituted PAHs, 24 C1-C4–alkylated PAHs, and 5 DBTs). Further details on quantification and quality assurance are provided in *SI Text*.

Trends in lake primary production were estimated from sedimentary chlorophyll *a* concentrations using visible reflectance spectroscopy (VRS-chl*a*; *SI Text*). This method is ground-truthed by paleolimnological studies (51) and captures the spectral signatures between 650 and 700 nm of HPLC-derived chl*a*, chl*a* isomers, and associated breakdown products (52). To recognize effects of oil sands development and other environmental stressors on biota, crustacean zooplankton (Cladocera) assemblages were analyzed. Cladocera are key algal grazers positioned centrally in aquatic food webs (53). Additionally, cladoceran assemblages respond strongly to local, environmental gradients rather than predation- or dispersal-related factors (54). Standard guidelines for processing, counting, and enumerating cladocerans were

followed (55, 56). The numerical techniques of indirect ordination and constrained clustering summarized the main variation in the cladoceran assemblage data through time (*SI Text*).

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