Oil sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries

Erin N. Kelly[a], Jeffrey W. Short[b], David W. Schindler[a,1], Peter V. Hodson[c], Mingsheng Ma[a], Alvin K. Kwan[a], and Barbra L. Fortin[a]

[a]Department of Biological Sciences, University of Alberta, Edmonton, AB, Canada T6G 2E9; [b]Oceana, 175 South Franklin Street, Suite 422, Juneau, Alaska 99801; and [c]Department of Biology and School of Environmental Studies, Queen's University, Kingston, ON, Canada K7L 3N6

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For over a decade, the contribution of oil sands mining and processing to the pollution of the Athabasca River has been controversial. We show that the oil sands development is a greater source of contamination than previously realized. In 2008, within 50 km of oil sands upgrading facilities, the loading to the snowpack of airborne particulates was 11,400 T over 4 months and included 391 kg of polycyclic aromatic compounds (PAC), equivalent to 600 T of bitumen, while 168 kg of dissolved PAC was also deposited. Dissolved PAC concentrations in tributaries to the Athabasca increased from 0.009 μg/L upstream of oil sands development to 0.023 μg/L in winter and to 0.202 μg/L in summer downstream. In the Athabasca, dissolved PAC concentrations were mostly <0.025 μg/L in winter and 0.030 μg/L in summer, except near oil sands upgrading facilities and tailings ponds in winter (0.031–0.083 μg/L) and downstream of new development in summer (0.063–0.135 μg/L). In the Athabasca and its tributaries, development within the past 2 years was related to elevated dissolved PAC concentrations that were likely toxic to fish embryos. In melted snow, dissolved PAC concentrations were up to 4.8 μg/L, thus, spring snowmelt and washout during rain events are important unknowns. These results indicate that major changes are needed to the way that environmental impacts of oil sands development are monitored and managed.

airborne deposition | oil sands processing | water contamination | hydrocarbons | oil sands mining

The Alberta oil sands consist of water, sand, and bitumen, a heavy and viscous hydrocarbon, that is recovered by surface mining or by in situ steam injection. To produce crude oil, bitumen must be extracted with hot water and upgraded by using heat, pressure, and catalysts (1). Production of bitumen increased from 482,000 to 1.3 million barrels per day from 1995 to 2008 (2, 3). The area disturbed by mine operations was 530 km^2 in 2007, and the area of tailings ponds surpassed 130 km^2 in 2008 (1, 4). Oil sands production by both mining and in situ methods will increase rapidly, with projected output ranging from 2.0 to 2.9 million barrels per day by 2020 (5).

Some residents of downstream Fort Chipewyan are convinced that the oil sands industry is responsible for higher than expected cancer rates (6). However, government, industry and related agencies, relying in part on the joint Regional Aquatic Monitoring Program (RAMP), report that effects are minimal, that natural sources cause elevated contaminant concentrations in the Athabasca and its tributaries (7), and that human health and the environment are not at risk from oil sands development (8–10), see *Controversy Background Information* in *SI Text*.

Since 1997, the RAMP, funded by industry and directed by a multistakeholder committee, has monitored aquatic ecosystems near the oil sands development (11). However, it lacks scientific oversight, and a peer review severely criticized its ability to detect effects (12). RAMP data are not publicly available, and the methods used to analyze, interpret, and report the data are not entirely transparent.

We conducted an independent, detailed, and accessible assessment of the loadings of polycyclic aromatic compounds (PAC) to the north-flowing Athabasca River, its tributaries, the Athabasca Delta, and Lake Athabasca (Fig. 1). In February to March and June to August 2008, we sampled water using polyethylene membrane devices (PMDs). In March, the accumulated snowpack was sampled at most sites. Athabasca River sites were selected upstream and downstream of oil sands mining and processing activity. Upstream and downstream sites near oil sands development are directly exposed to erosion of the McMurray geologic formation (McMF), where most oil sands occur (13).

Three sites along each of four impacted tributaries were selected using 2006 Landsat imagery. The first was located upstream of oil sands development and the McMF, the second midstream within the McMF but upstream of mining activity, and the third near stream mouths at the confluence with the Athabasca, downstream of development and downstream or within the McMF. Comparable sites were chosen on two reference tributaries unaffected by industry. In the summer, additional stream mouth sites, with and without upstream development, were included to increase statistical power.

After sampling, 2008 Landsat imagery revealed marked changes in the extent of oil sands development since 2006. Some tributary sites could be compared as planned, but some midstream and stream mouth sites unaffected in 2006 were affected by new development in 2008. To assess the impacts of this new development, the change in development between 2006 and 2008 was categorized visually from Landsat imagery as nil–small (N-S) and medium–large (M-L). This gave four classes of new development: midstream/N-S, midstream /M-L, stream mouth /N-S, and stream mouth /M-L. To compare the relative importance of natural erosion and mining on PAC mobilization, PAC concentrations in water were regressed against the proportion of the catchment within the McMF, overall land disturbance, and land disturbed by oil sands mining in 2008. These comparisons were made for all tributaries combined and separately for the Athabasca.

Samples were analyzed for PAC (sum of parent and alkylated homologues of two-, three- and four- ring polycyclic aromatic hydrocarbons + dibenzothiophene). Melted snow was analyzed for the mass of particulate and associated PAC retained on 0.45-μm glass fiber filters and for dissolved PAC in filtrate. Because PMDs accumulate only dissolved PAC from water (14), equivalent water concentrations were calculated from PAC concentrations in PMDs,

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[1]To whom correspondence should be addressed. E-mail: d.schindler@ualberta.ca.

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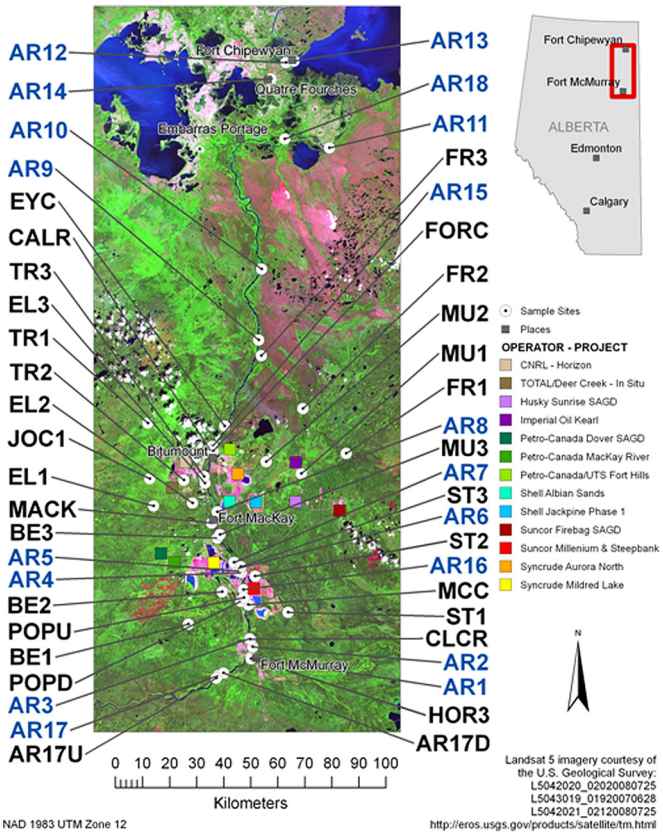

Fig. 1. Study Area Map. Sites: blue, Athabasca River; black, tributaries (AR17U, unnamed creek; AR17D, unnamed creek; HOR, Horse River; CLCR, Clarke Creek; POP, Poplar Creek, BE, Beaver River; ST, Steepbank River; MCC, McLean Creek; MACK, MacKay River; EL, Ells River; JOC, Jocelyn Creek; MU, Muskeg River; FR, Firebag River; FOR, Fort Creek; TR, Tar River; CALR, Calumet River; EYC, Eymundson Creek; 1, upstream; 2, midstream; 3, stream mouth). Landsat 5 image is a false color composite, where blue is water, green is vegetation, and pink is nonvegetated and/or developed areas. Squares represent existing and approved oil sands projects.

assuming equilibrium between PMDs and ambient water concentrations after ≈30-day deployment. Further details are provided in *Methods* and *Analytical and Statistical Method Details* in *SI Text*.

Results

Particulates and PAC in Snow. Substantial deposition of airborne particulates was discovered within 50 km of the Suncor and Syncrude upgrading facilities, near AR6 (Fig. 2 and Fig. S1). Particulate deposition exponentially declined from 19 g/m^2 at AR6, near the upgrading facilities, to <0.35 g/m^2 at sites >50 km distant (particulates = $10.6 \times e^{-0.0714*x}$ g/m^2, x = km from AR6, $r^2 = 0.71$, $P < 0.0001$, $n = 23$; Fig. S2*A*). Integrating over a 50-km radius indicates deposition of 11,400 metric T of particulates during ≈4 months of snowfall.

Most particulates collected at AR6 consisted of oil sands bitumen. An oil slick formed on the surface of melted snow (Fig. S3), and the PAC distribution was similar to the four oil sands samples, i.e., dominated by dibenzothiophenes, phenanthrenes/anthracenes, fluoranthenes/pyrenes, and benzanthracenes/chrysenes (Fig. S4 *A* and *B*). Compared with the oil sands, PAC in the snow particulates were slightly enriched in naphthalenes and unsubstituted four- to five-ring PAC, suggesting admixture with volatile and combustion-derived PAC [i.e., dominated by less-substituted four or more-ring PAC (15)]. Using a measured mean ratio of 0.000649 ± 0.000168 (see *Analytical and Statistical Method Details* in *SI Text*) for total PAC to bitumen in oil sands, the 0.414 mg of PAC per gram of particulate in AR6 snow was equivalent to 64% bitumen.

The proportion of PAC in snow particulates declined rapidly with distance from AR6, indicating that bitumen was deposited closer to the source than particulates (Fig. 3). Measured PAC deposition declined exponentially (PAC = $1.06 \times e^{-0.130*x}$ mg/m^2, $r^2 = 0.76$, $P < 0.0001$, $n = 23$; Fig. S2*B*) from 7.87 mg/m^2 at AR6, near the upgrading facilities, to 0.011 mg/m^2 or less at sites over 50-km distant. This is equivalent to deposition of 391 kg of PAC within a 50-km radius of AR6 over 4 months, or 600 T of bitumen. Deposition of PAC declined significantly more rapidly with distance from AR6 than particulates (t test, $P < 0.01$), suggesting association of bitumen PAC with heavier or denser particles.

Dissolved PAC in the filtrate from melted snow also declined with distance from AR6 (Fig. 3), and were dominated by fluorenes, dibenzothiophenes, and phenanthrenes/anthracenes, consistent with partitioning into air or water of more volatile and soluble PAC in bitumen (Fig. S4*C*). Dissolved PAC deposition declined exponentially with distance from AR6 (dissolved PAC = $0.148 \times e^{-0.0691*x}$ mg/m^2, $r^2 = 0.59$, $P < 0.0001$, $n = 23$; Fig. S2*C*), with a similar decay constant (−0.0691) as particulates (−0.0714; $P > 0.8$). Integrating over a 50-km radius gives 168 kg of dissolved PAC accumulated during 4 months. Dissolved PAC concentrations in

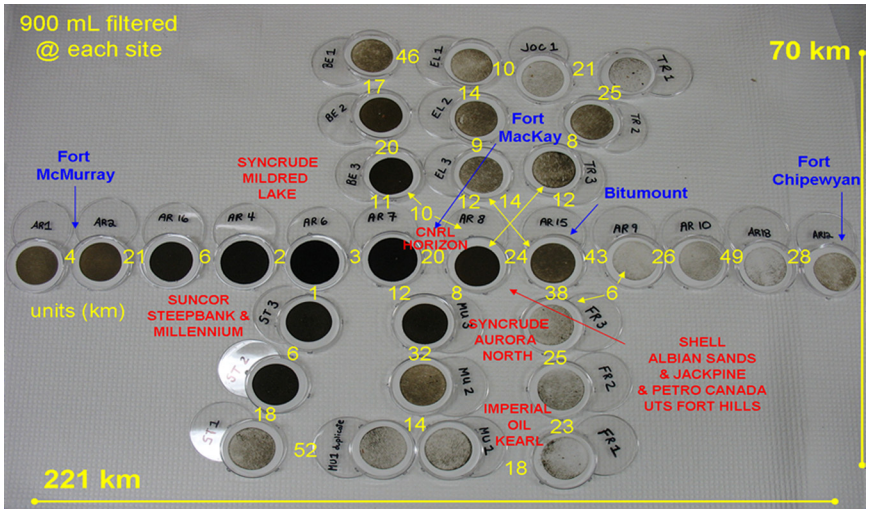

Fig. 2. White 0.45-μm Whatman GF/F filters after 900 mL of melted snow from each site was filtered. Yellow, distance between sites; blue, communities; red, existing and approved surface mining projects.

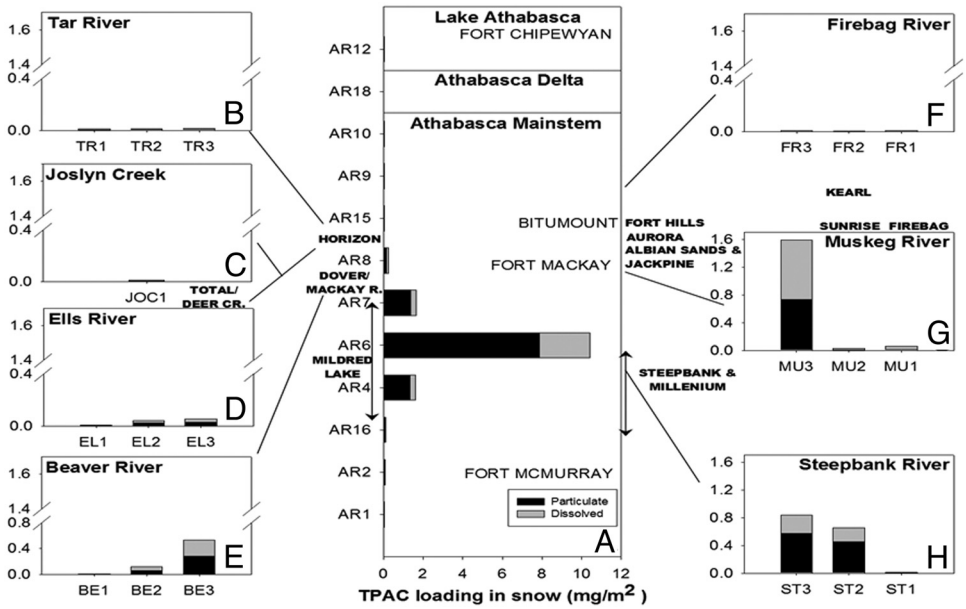

Fig. 3. Particulate and dissolved PAC loading (mg/m^2) in accumulated snowpack, March 2008. (*A*) Athabasca River, Athabasca Delta, and Lake Athabasca. (*B*) Tar River. (*C*) Joslyn Creek. (*D*) Ells River. (*E*) Beaver River. (*F*) Firebag River. (*G*) Muskeg River. (*H*) Steepbank River. Bolded font indicates existing and approved projects (Syncrude: Mildred Lake and Aurora, Suncor: Millennium, Steepbank and Firebag In-situ, Petro Canada Dover-MacKay River In-situ, Husky Oil Sunrise In-situ, TOTAL/Deer Creek In-situ, Shell: Albian Sands/Muskeg River and Jackpine, CNRL: Horizon, Imperial Oil: Kearl, Petro Canada/UTS: Fort Hills). Mildred Lake spans AR16 to AR7, whereas Steepbank and Millennium span AR16 to AR6, as indicated by arrows. Upgrading facilities are near AR6.

melted snow declined from 4.8 μg/L at AR6 to <0.27 μg/L at sites >50 km away, and exceeded 0.7 μg/L at 9 of 10 sites within 22 km of AR6.

PAC in Tributaries. Dissolved PAC concentrations in the six tributaries sampled during winter and summer mostly increased from upstream to downstream and were greater in summer than winter (Fig. 4*A*). Mean concentrations increased from 0.009 μg/L at upstream sites in both winter and summer to 0.023 ± 0.0059 μg/L and 0.202 ± 0.160 μg/L at stream mouth sites, respectively, similar to melted snow. Differences among sites along tributaries were highly significant (two-way ANOVA, ln

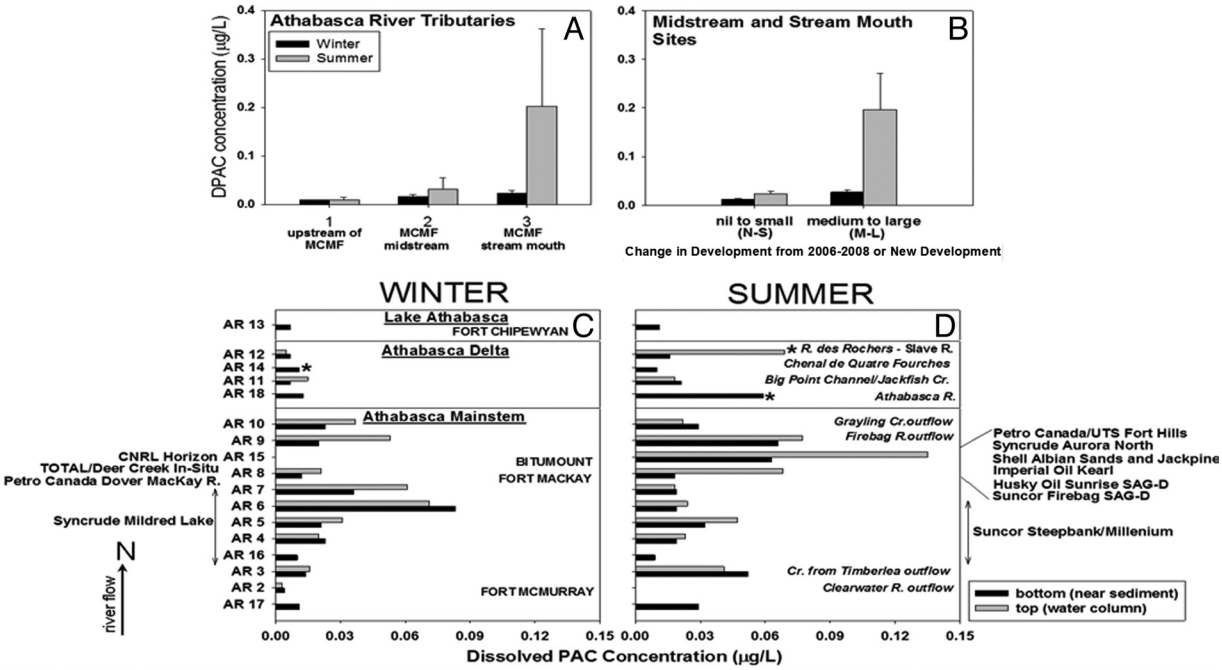

Fig. 4. Estimated winter and summer dissolved PAC concentrations (μg/L). (*A*) Tributaries. (*B*) Midstream and stream mouth tributary sites in relation to ''new'' development (change in development from 2006 to 2008), $n = 5$–8. Athabasca River, Athabasca Delta, and Lake Athabasca (*C*) Winter. (*D*) Summer. * indicates samples contaminated by diesel fuel (see *Analytical and Statistical Method Details* in *SI Text*), not included in calculations; McMF, McMurray Formation; N, north. Error bars are standard error of the mean.

transformed, $P = 0.004$), but not between seasons ($P = 0.91$). The power to detect seasonal differences was low ($\beta = 0.05$), so a seasonal effect could not be discounted. The greater trend of increasing PAC downstream in summer compared with winter (Fig. 4*A*) was nearly significant (interaction $P = 0.095$) at only moderate power ($\beta = 0.30$).

This analysis included all upstream, midstream, and downstream tributary sites, regardless of development. Almost all development was near the stream mouth on some tributaries, with insignificant development near midstream or upstream sites. Analyzing only these tributaries, no significant increase in PAC concentrations between upstream and midstream sites was found (Fig. S5*A*). Thus, when development was insignificant, flow of water through the McMF did not significantly affect PAC concentrations, indicating that natural sources are not solely responsible for increased concentrations of PAC midstream or at stream mouths.

Increasing PAC concentrations from upstream to downstream in the tributaries (Fig. 4*A* and Fig. S5*A*) could reflect increasing contributions from natural erosion of the McMF, greater disturbance from development, or both. Little of the variability in summer PAC concentrations of tributaries was explained by the proportion of McMF, total surface land disturbance, or oil sands mining disturbance in watersheds ($r^2_{\mathrm{McMF}} = 0.009$, $r^2_{\mathrm{disturbance}} = 0.003$, $r^2_{\mathrm{oil\ sands}} = 0.000$; $P > 0.69$, $df = 19$).

In contrast, when midstream and stream mouth sites were grouped, PAC concentrations were strongly associated with new land disturbance or mining activity expansion from 2006 to 2008. Mean PAC concentrations increased 2-fold from 0.012 ± 0.0012 at N-S sites to 0.027 ± 0.0052 μg/L at M-L sites in winter, and 8-fold from 0.024 ± 0.0055 to 0.197 ± 0.0738 μg/L in summer (Fig. 4*B*). Season and disturbance effects were highly significant (two-way ANOVA, ln transformed, $P < 0.004$), and the season and disturbance interaction was nearly significant ($P = 0.065$, $\beta = 0.36$). The power to detect the seasonal effect was $\beta > 0.85$, much greater than for the previous test ($\beta = 0.05$). Comparing only midstream or stream-mouth sites leads to essentially the same conclusions (Fig. S5 *B* and *C*). Thus, seasonal differences in PAC concentrations are likely real, and increased PAC concentrations in both winter and summer result from land disturbance by oil sands development between 2006 and 2008.

Approximately 75% of PAC homologues accumulated by PMDs deployed at the M-L sites consisted of three-ring PAC, dominated by alkyl-substituted dibenzothiophenes, phenanthrenes/anthracenes and fluorenes, with the remainder mostly four-ring PAC including alkyl-substituted fluoranthenes/pyrenes and benzanthracenes/chrysenes and negligible naphthalenes (Fig. S4*D*). Enrichment of three-ring PAC in PMDs compared with oil sands (Fig. S4*A*) is consistent with greater solubility of three- vs. four-ring PAC. The near absence of naphthalenes in PMDs is also consistent with low concentrations of these PAC in bitumen (Fig. S4*A*).

Athabasca River, Athabasca Delta, and Lake Athabasca. Dissolved PAC concentrations were usually low at most sites on the Athabasca River, Athabasca Delta, and Lake Athabasca, but often greater during summer (Fig. 4 *C* and *D*). In winter, concentrations were mostly <0.025 μg/L, except at sites near oil sands upgrading facilities and tailings ponds which ranged from 0.031 to 0.083 μg/L (Fig. 4*C*). In summer, PAC concentrations in the Athabasca were usually <0.030 μg/L. Upstream and within oil sands development, concentrations were unrelated to the proportion of McMF, total surface land disturbance, and oil sands mining disturbance ($r^2_{\mathrm{McMF}} = 0.137$, $r^2_{\mathrm{disturbance}} = 0.006$, $r^2_{\mathrm{oil\ sands}} = 0.085$; $P > 0.33$, $df = 8$). However, immediately downstream of new development, concentrations ranged from 0.063 to 0.135 μg/L (Fig. S6).

Discussion

The increased deposition of particulates and PAC in snow close to the Suncor and Syncrude upgrading facilities clearly implicates them as sources and corresponds to a similarity between patterns of PAC congeners in particulates and oil sands (Fig. S4 *A* and *B*). The enrichment of snow particulates by the more volatile PAC and by five-ring PAC (e.g., benzo[a]pyrene) is typical of PAC volatilized by heat or particulates produced by combustion. The dominance of oily material in snow from AR6 also suggests a separate organic bitumen phase in stack emissions that is present as droplets larger and less buoyant than average particulates, and precipitates near the source. Alternatively, the heavier particles might be bitumen-contaminated dust eroded by wind from mine sites (Fig. S7), but this was inconsistent with the high organic content of particulates near AR6. Although mining can mobilize dust, deposition would likely be localized and site-specific, and further study is needed to establish detailed loadings.

The similar deposition patterns of particulates and dissolved PAC in melted snow (Fig. S2 *A* and *C*) suggests that dissolved PAC did not leach from particulates, but was scavenged from the atmosphere. Snow samples were filtered within an hour of thawing, leaving little time for PAC dissolution. More likely, PAC dissolved in the snowmelt were readily desorbed from non-bitumen particulates or scavenged from vapor-phase PAC by ice nuclei in plumes of condensing steam from stack emissions, as occurs with metals (16).

The oil sands industry is a known source of air pollutants. Snow surveys in 1978 and 1981 identified elevated metal deposition via flyash particulates 25 km north and south, and 10 km east and west of Suncor and Syncrude upgrading facilities (16, 17). In 1978, 96% of particulates were deposited within 25 km of the stacks (17), but PAC deposition was not measured. From 2005 to 2007, the mean annual release of particulates measured by Suncor and estimated by Syncrude (stack and fugitive emissions) was 6037 ± 927 T (18). In contrast, during the 4 months before sampling in 2008, emissions were almost twice as large at 11,400 T and contaminated an area nearly 2-fold larger, with only ≈60% of particulates falling within a 25-km radius. Assuming similar deposition rates during the year implies a total annual particulate deposition of ≈34,000 T. This is nearly five times current reported emissions, and similar to annual deposition rates of 32,594 T in 1978 (19), before precipitators were installed. The discrepancy may be due to dust from mining (Fig. S7) or somewhat elevated loading estimates that were based on a circle around AR6, despite somewhat greater particulate deposition north/south of upgrading facilities than east/west (16). The close association of deposition with proximity to the upgrading facilities suggests that they are the primary source.

Airborne PAC from oil sands development conveys a considerable burden to the surrounding watershed. Historical stack discharges of particulates rich in aluminum (Al) (16, 17), and a strong correlation between Al and PAC concentrations in snow ($r = 0.94$, $P < 0.001$), suggest that large amounts of particulate PAC have been discharged since the onset of oil sands production in the 1960s. If deposition rates are constant throughout the year, the estimated annual release of PAC is now ≈1,200 kg associated with ≈1,800 T of bitumen particulates, and another 500 kg of dissolved PAC. This amount of bitumen released in a pulse would be equivalent to a major oil spill, repeated annually.

Given that particulate deposition rates in the 1970s before installation of stack precipitators (19) were as great as today, this situation has likely persisted for 30–40 years. As a result, current background PAC concentrations in surface soils, vegetation, snow, and runoff over a broad area of boreal forest may be greater than true background concentrations contributed naturally by oil sands in the region. Although RAMP collects snow for hydrologic monitoring (11), pollutant concentrations are not reported. In the early 1980s, snow sampling was recommended in northeastern Alberta and adjacent areas of Saskatchewan and the Northwest Territories to assess the effects of air emissions from expanding oil sands development (16, 17). The absence of such a program has made it progressively more difficult to separate pollution inputs

from rising background contamination. With more oil sands development projects approved and proposed, including new and expanded upgrading facilities, the increased deposition of airborne PAC will further raise regional "background" concentrations.

Tributaries impacted by oil sands development indicate a second major flux of PAC to receiving waters. Recent disturbances (new roads, deforestation, encampments, exploration, mining) expose and distribute fresh bitumen to wind and soil erosion and enhance bitumen transport to surface waters, which leach out the most available PAC. The lack of correlation between PAC concentrations in water and the extent of older development suggests that disturbed areas eventually stabilize. However, the lack of correlation may also reflect increasing background PAC concentrations. At sites distant from upgrading facilities and unaffected by land disturbance, the regional background of total dissolved PAC in surface waters is ≈0.015 μg/L, closely comparable with concentrations in remote Canadian Arctic rivers (20). In contrast, at the most impacted stream mouths, PAC concentrations were 10- to nearly 50-fold greater (e.g., EL3, PAC = 0.682 μg/L), similar to concentrations toxic to fish embryos [as low as 0.4 μg/L (21)]. The PAC in oil sands, snow, and water were dominated by homologues of three-ringed alkyl phenanthrenes, alkyl dibenzothiophenes, and alkyl fluorenes, PAC most closely associated with embryotoxicity of crude oil (22, 23). Embryos of fathead minnows (*Pimephales promelas*) and white sucker (*Catostomus commersoni*), species native to the Athabasca watershed, showed higher rates of mortality, reduced rates of growth, and signs of pathology typical of PAC toxicity when exposed to as little as 0.01–0.1 μg/L of alkyl phenanthrene in oil sands leachates (calculated from refs. 24 and 25). PAC can also limit fish production through endocrine disruption. Compared with reference fish, gonads of slimy sculpin (*Cottus cognatus*) and pearl dace (*Margariscus margarita*) collected near active oil sands processing were less capable of synthesizing sex steroids (26). PAC may contribute to a greater prevalence of abnormal juvenile and adult fish captured in the Athabasca near and downstream of oil sands mining (11, 27).

During spring, the snowmelt pulse could increase PAC concentrations in tributaries to those toxic to both aquatic and terrestrial organisms (28, 29). Dissolved PAC would be immediately available to biota but particulate PAC may be taken up by filter feeders or partition into water for uptake by fish across gills. Residual particles may also accumulate on the forest floor with organic material or in underlying soils, causing PAC to leach more gradually into surface waters, adding to the overall PAC burden.

Of the 24 fish species resident in the Athabasca and its tributaries (30), 19 spawn in the spring or early summer (31). Embryos of these species are likely present when PAC concentrations are greatest. If located in shallow tributaries receiving PAC-enriched snowmelt, embryos may also experience photo-enhanced toxicity (32). Newly hatched whitefish embryos exposed to sublethal concentrations of retene (alkyl phenanthrene) died when coexposed to visible and UV light (33). Toxicity may also increase if PAC and metals associated with oil sands act synergistically, as observed for *Daphnia magna* (34).

Dissolved PAC did not persist as far as the Athabasca River Delta and Ft. Chipewyan, at least during the seasons sampled. However, PAC-contaminated sediments in the Athabasca Delta and Lake Athabasca (35, 36) are consistent with long-range atmospheric and fluvial transport of particulate PAC. Our sampling did not include the intervening spring snowmelt, which would release a pulse of PAC up to 50 km from oil sands upgrading facilities into nearby tributaries and the Athabasca. Although this should increase PAC concentrations in tributaries, it might not be detected in the main stem because of high-volume dilution by uncontaminated snowmelt from areas upstream of oil sands mining. PAC may also be removed from the water column by microbial degradation and adsorption to organic matter that settles out of the water column (37). These dilution and removal processes likely account for declining concentrations of dissolved PAC as the Athabasca flows to Lake Athabasca and Fort Chipewyan.

Conclusions

Due to substantial loadings of airborne PAC, the oil sands industry is a far greater source of regional PAC contamination than previously realized. Despite previous recommendations (17), there is no apparent detailed monitoring of PAC fluxes via wet and dry deposition in the winter or summer, when similar or greater contributions are likely. Monitoring of air, the snowpack, spring snowmelt, and summer rain and vegetation is essential to identify and control sources of PAC and their potential environmental and human health impacts. A second important source of PAC is landscape disturbance. Surprisingly, impacts are related primarily to recent disturbance (<2 y), which suggests that revegetation or erosion controls mitigate long-term loadings.

Controls on waterborne PAC are critical because concentrations at tributary mouths and at one site on the Athabasca are already within the range toxic to fish embryos. However, the impacts on the Athabasca ecosystem of mining wastewater, snowmelt, or contaminated groundwater remain enigmatic due to high seasonal variability of flow and dilution capacity.

Our study confirms the serious defects of the RAMP (12). More than 10 years of inconsistent sampling design, inadequate statistical power, and monitoring-insensitive responses have missed major sources of PAC to the Athabasca watershed. Most importantly, RAMP claims that PAC concentrations are within baseline conditions and of natural origin have fostered the perception that high-intensity mining and processing have no serious environmental impacts. The existing RAMP must be redesigned with more scientific and technical oversight to better detect and track PAC discharges and effects. Oversight by an independent board of experts would make better use of monitoring resources and ensure that data are available for independent scrutiny and analyses. The scale and intensity of oil sands development and the complexity of PAC transport and fate in the Athabasca watershed demand the highest quality of scientific effort.

Methods

Study Design. Seventeen sites were chosen on the main stem Athabasca, the Delta, and Lake Athabasca, from south of Fort McMurray (upstream of development) to Fort Chipewyan (downstream of development) (Fig. 1). The Athabasca River is exposed to the McMF 50 km upstream of Fort McMurray and is present within its banks to Eymundson Creek (38).

Tributaries draining from the east (Steepbank, Muskeg, and Firebag Rivers) and west (Beaver, Ells, and Tar Rivers), including reference rivers (Firebag and Ells Rivers) and those impacted by oil sands development (Steepbank, Muskeg, Beaver, and Tar Rivers), and the Horse River stream mouth, were sampled in winter and summer (Fig. 1). Nine other stream mouth sites (AR17down, AR17up, Clarke, Poplar, McLean, Fort, and Eymundson Creeks and MacKay and Calumet Rivers) were sampled only in summer.

GIS analyses were performed by using ArcGIS 9 ArcMap version 9.2 (39), to delineate catchments, extract disturbance and geologic data, and calculate distances between AR6 and other snow sampling sites (see *Analytical and Statistical Method Details* in *SI Text* for details).

Field Sampling. In March, snow was collected from 12 sites on the Athabasca River, Athabasca Delta, and Lake Athabasca and from 19 tributary sites. Samples were collected close to the middle of the river, and replicated at MU1. At each site, the depth and weight of five snow cores were recorded to calculate snow density, snow water equivalents, and PAC areal deposition rates. For PAC, an integrated sample of the snowpack was melted and vigorously stirred, and a subsample (775–4,000 mL) was filtered through a 0.45-μm muffled Whatman GF/F filter. The filter was frozen, and the filtrate was decanted, spiked with a suite of perdeuterated hydrocarbon surrogate standards in 0.5 mL of acetone, shaken, extracted twice with 100 mLl of DCM, and stored at −20 °C.

PMDs were deployed in the Athabasca and its tributaries for ≈30 days to passively monitor dissolved PAH in summer and winter and provide a time-integrated measure of dissolved PAH (14). PMDs were cleaned by sonication successively with dichloromethane (DCM), put in DCM-cleaned metal holders,

wrapped in DCM-rinsed aluminum foil and stored in heat-sealed Ziploc bags at −20 °C. At 12 locations on the Athabasca River and the Horse River mouth, two PMDs were deployed per site, near the river bottom and in surface water. One PMD was deployed near the river bottom at the five other Athabasca sites, and all tributary sites. PMDs were retrieved by using global positioning system coordinates and a metal detector (winter). Replicate PMDs were deployed within 500 m at sites where PAC were assumed to be high (MU3) or low (EL1). One trip blank and five field blanks, handled like deployed PMDs, were included with winter and summer samples.

Oil sands samples were collected in summer from the Syncrude lease area, the east and west bank of the Athabasca River north of Bitumount, and underwater at the mouth of the Steepbank River. All samples were frozen.

Laboratory. PAC were measured at the University of Alberta Biogeochemical Analytical Laboratory by using an Agilent 6890N gas chromatograph coupled to a 5975 inert XL mass selective detector and 7683B injector (modified refs. 14 and 40). Detailed methods and instrument and method detection limits are presented in *Analytical and Statistical Method Details* in *SI Text* and Table S1, respectively.

Analytical and Statistical Methods. Details of QA/QC, contamination by diesel fuel, PAC source identification, estimation of aqueous PAC concentrations and PAC deposition calculations are provided in *Analytical and Statistical Method Details* in *SI Text*.

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