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Polycyclic Aromatic Hydrocarbons Increase in Athabasca River Delta Sediment: Temporal Trends and Environmental Correlates

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Supporting Information

ABSTRACT: The Athabasca River in Alberta, Canada, flows north through an area undergoing extensive bitumen resource extraction and processing before discharging its water and sediments into the Athabasca Delta and Lake Athabasca. Polycyclic aromatic hydrocarbons (PAHs) have been identified as an environmental concern in the region. We analyzed environmental data collected by the Regional Aquatics Monitoring Program and government agencies to determine whether temporal trends exist in the concentration of sediment PAHs in the Athabasca River Delta. We then determined what environmental factors related to the trends in sediment PAH concentrations. Total PAH concentrations in the sediment of the Athabasca River Delta increased between 1999 and 2009 at a rate of 0.05 mg/kg/yr ± 0.02 s.e. Annual bitumen production and mined sand volume, extent of landscape disturbance, and particulate emissions were correlated with sediment PAH concentrations as were total organic carbon in sediment and discharge of the Clearwater River, a major tributary of the Athabasca River. Within four tributaries of the Athabasca River, only the Clearwater River showed a significant correlation between discharge and sediment PAH concentration at their river mouths. Carefully designed studies are required to further investigate which factors best explain variability in sediment PAH concentrations.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of more than 100 organic compounds with fused aromatic carbon rings. They are found or formed in some geologic deposits (petrogenic origin, e.g., in bitumen) and can be created during combustion (pyrogenic origin) or through microbial degradation (diagenic origin). They typically exist as complex mixtures rather than as single compounds. PAHs are hydrophobic and tend to bind to organic matter and small particles in the water column, in sediments, and in soils.[1] PAHs can be found in air as vapors or attached to dust particles.[1] Petrogenic PAHs are characterized by a predominance of C1−C3 alkylated forms of their parent compounds. Pyrogenic PAHs generally have a high concentration of unsubstituted parent compounds and may have elevated concentrations of some PAH species, such as of fluoranthenes/pyrenes from anthropogenic combustion sources and of retenes from wildfires.[2]

PAHs are common contaminants in many ecosystems and can enter the environment along multiple pathways.[1] Releases to air include those from volcanoes, forest fires, combustion, vehicle exhaust, evaporation and outgassing, and stack emissions. Releases to water, soil, and sediment include industrial plant and wastewater treatment plant discharges, precipitation of industrial and natural dust particles, leaks from containers and pipelines, and from seepage through and erosion of PAH-containing materials.[1] Fishes exposed to PAHs can display elevated liver EROD,[3] liver lesions, and damaged DNA.[4] Fish hatching alterations, increases in mortality, spinal malformations, reduced size, cardiac dysfunction, edema, and reduction in the size of the jaw and other craniofacial structures have been observed in fishes exposed to PAHs found in Athabasca sediments.[5−9] PAHs can enter the human body through respiration, eating, drinking, or through the skin. Many PAHs are known or suspected human carcinogens,[1] but there is little toxicity information on the alkylated PAH species that comprise the majority of petrogenic PAHs.

Bitumen extraction and production contribute environmentally significant amounts of PAHs to air, land, and water.[10] Present concentrations of total PAHs in sediments of the lower Athabasca River exceed by a factor of about 2−3 the threshold observed to induce liver cancers in fishes.[11,12] The view of the Alberta Government, the primary agency responsible for environmental management in the region, is that industrial activity is not detectable in the concentrations of PAHs and other contaminants observed in the region.[13,14]

The western Canadian sedimentary basin contains about 2.3 trillion barrels of natural bitumen, 43% of the known global reserve.[15] Roughly 99% of Alberta's known oil reserves are

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contained in bitumen-bearing sands; currently, about 170 billion barrels of bitumen are economically recoverable. Annual bitumen production in the lower Athabasca River region more than doubled from 21.2 M m^3/yr in 1998 to 47.9 M m^3/yr in 2009.[16] Processing of bitumen consumes more energy and produces more CO_2 than does processing of conventional feed stocks (the raw materials processed into useful fuels). Analysis of United States crude feed, processing, yield, and fuel data found that fuel consumption for processing increased by 44 MJ/m^3 for each 1 kg/m^3 increase in density of crude feed stock.[17] At the global scale, a wholesale shift to heavy oil and bitumen feedstock could double or triple refinery emissions and add 1.6 to 3.7 GT of CO_2 to the atmosphere each year.[17]

Critical reviews of the Regional Aquatics Monitoring Program (RAMP) in 2004 and 2010 concluded that the program is unable to measure and assess development-related environmental change.[18,19] The Auditor General of Canada[20] concluded that the federal government has insufficient baseline environmental data to track changes in Athabasca River water quality and environmental health associated with bitumen development, and does not monitor for PAHs. Given inadequate monitoring and that PAHs in the lower Athabasca River may pose an environmental risk,[10,21] it is critical to know whether PAH concentrations are changing and, if so, how and why. The purpose of this Article is to test three hypotheses: (1) There is no temporal trend in sediment PAH concentrations in the Athabasca River Delta (ARD). (2) Variations in sediment PAH concentrations are unrelated to industrial activities. (3) Variations in sediment PAH concentrations are due to variations in river discharge.

STUDY AREA

The study area is located within the boreal forest natural region of northeastern Alberta (Figure 1), upstream and adjacent to Wood Buffalo National Park and the Peace-Athabasca Delta, a Ramsar Wetland of International Significance and a UNESCO World Heritage Site.

Surficial materials range in thickness from ~1 to 140 m and include till, glaciofluvial, glaciolacustrine, lacustrine, eolian, alluvial, and organic deposits.[22] The near surface bedrock includes Devonian Waterways Formation (Fm) carbonates, Cretaceous McMurray Fm bitumen-impregnated sandstone (the source of the bitumen now being exploited in the region), Cretaceous Clearwater Fm shales, Grand Rapids Fm sandstone, and undifferentiated Cretaceous shales.[22] For study area details, see the Supporting Information, Appendix S1.

MATERIALS AND METHODS

Total PAHs in sediment (dry weight, mg/kg, including parent and alkylated forms) are derived from RAMP raw data files (1998−2007) and from RAMP reports[23,24] for 2008 and 2009. For details on data handling and assumptions, see the Supporting Information, Appendix S1. The four sample sites in the ARD were Athabasca−Embarras divergence, Goose Island Channel, Fletcher Channel, and Big Point Channel (stations ATR-ER, GIC, FLC, and BPC), all of them downstream of industry and McMurray Fm bitumen deposits (Figure 1). A parallel analysis of "control" sites, unaffected or little affected by bitumen development, was also conducted that followed the same methods (Supporting Information, Appendix S1). Sediment percent sand, silt, and clay are derived from RAMP raw data files (1998−2007), and from RAMP;[24] total organic carbon in sediment (fall data, dry weight, percent) is derived from RAMP.[24] Sediment total PAH data for the Clearwater (RAMP station CLR-1), Muskeg (MUR-2), Mackay (MAR-1), and Steepbank Rivers (STR-1) were obtained from RAMP to examine the relationship between tributary discharge and tributary PAH concentration. To examine both raw and averaged data, the PAH data were subdivided into three data sets that differed only in degree of averaging, as follows: A (unaveraged raw data, $n = 32$); B (mean of 1, 2, or 4 sites/year; $n = 10$); C (mean of 2 or 4 sites/year; $n = 8$).

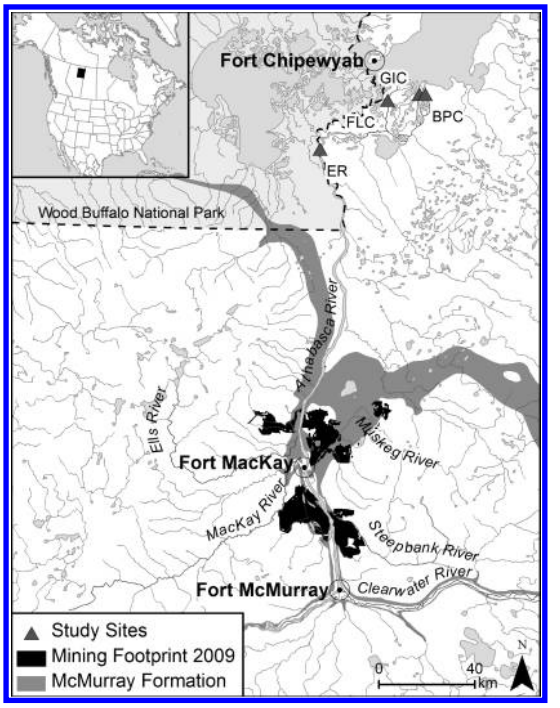

Figure 1. Location of the sediment sites, surficial expression of the McMurray Formation, settlements, and the bitumen mining footprint as of 2009.

Annual bitumen production (m^3) and annual mined sand (m^3) data[16] were summarized from five companies (Suncor Energy Inc., Syncrude Canada Ltd. Mildred Lake, Syncrude Aurora, Shell Albian Sands, and Canadian Natural Resources Ltd. Horizon) within the study area that reported produced bitumen during the period 1997−2009. Mined sand volumes are summarized from the same five companies with the addition of Petro-Canada Fort Hills. Annual $PM_{2.5}$, PM_{10}, and total particulate (TPM) emissions (tonnes/year) for the Alberta "oil sands sector" are from Environment Canada (D. Niemi, Pers. comm., Sept. 2010).

Annual landscape footprints of the bitumen industry within the study area were determined through digitization of industrial disturbances on sequential satellite images in the years 1992, 1999, 2002, 2006, 2008, and 2009. Footprint data were plotted with a spline fit to permit interpolation of footprint values for other years between 1998 and 2009. The footprint values underestimate the true extent of industrial activity because linear features such as roads, pipelines, powerlines, and seismic lines are not included.

Average annual and May−August discharges of the Athabasca River below Fort McMurray (station 07DA001) were determined from Water Survey of Canada data for the period 1997−2009. Athabasca Delta distributary discharges (average

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Table 1. Summary Statistics for Total PAHs in Sediment, Data Normality, Linear Regressions with Time, and Rates of Annual Increase

PAH data set	total PAHs in sediment (dry weight, mg/kg) mean, s.d., *n*	normality (KS test) *p*	linear regression of total PAH with time (*r*, *p*)	rate of annual increase (mg/kg/yr, s.e.)
a	1.352, 0.450, 32	0.259	0.352, 0.048	0.050, 0.024
b	1.318, 0.225, 10	0.564	0.653, 0.040	0.043, 0.018
c	1.352, 0.238, 8	0.525	0.729, 0.040	0.051, 0.020

annual and May−August) were determined from flow split data provided by F. Yusuf (BC Hydro, Pers. comm., Sept. 2010) and Ward et al.[28] Similarly, for rivers that flow through areas that contain bitumen deposits and natural bitumen "seeps", average and maximum annual daily discharge and average May−August daily discharge were determined for the Clearwater River at Draper (station 07CD001), the Muskeg River near Fort Mackay (station 07DA008), the Mackay River near Fort Mackay (station 07DB001), and the Steepbank River near Fort McMurray (07DA006).

Because the PAH data sets were normally distributed (Table 1), as were the annual industrial, landscape, and hydrometric variables (Kolmogorov−Smirnov (KS) tests, *p* ranges from 0.066 to 0.994), parametric statistics were used to examine relationships between variables. The approach used is, of necessity, indirect and correlative and is aimed at assessing trends while providing hypotheses about causation that might be explored in the future.

RESULTS

Temporal Trends in Sediment PAH Concentrations. Sediment PAH concentrations in the ARD increased over the period 1999−2009 (Table 1, Figure 2). The hypothesis that there is no trend in PAH concentration in the ARD is rejected. As of 2009, the mean total PAH concentration was 1.72 mg/kg. The decadal increase in total PAH concentrations of ∼0.50 mg/kg exceeded the estimated error introduced by laboratory procedures of 0.08 mg/kg (Supporting Information, Appendix S1). There was no evidence of a temporal trend in sediment PAH concentration at the control sites (Supporting Information, Appendix S1).

Industrial Activities as Correlates of ARD Sediment PAH Concentrations. Significant correlations of total PAH concentrations with indicators of industrial activity were observed (Table 2). The high correlations of the industrial variables with year indicate that time may serve as a surrogate for industrial activities in the region. Improved correlations between sediment PAH concentrations and industrial factors when the factors are lagged one year suggest that the sediment sampling may track industrial processes and conditions that existed in the year prior to sampling. The hypothesis that sediment PAH concentrations in the ARD are unrelated to industrial activities is rejected.

River Discharge as Correlates of Sediment PAH Concentrations. To test the hypothesis that Athabasca River mainstem discharge is related to sediment PAH concentrations in the ARD, correlations between ARD sediment PAH concentrations were determined for the three PAH data sets and four discharge variables: annual discharge and May−August discharge of the Athabasca River below Fort McMurray in the year of the sediment sample and in the year preceding the sample. There were no significant correlations between ARD sediment PAH concentration and Athabasca River mainstem discharge (Table 3). Similarly, correlations of total PAH concentration and ARD distributary discharge (see footnote to Table 3) were all nonsignificant.

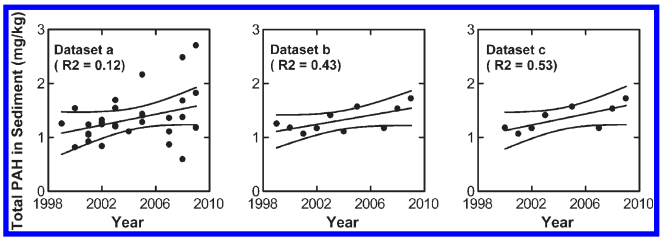

Figure 2. Concentrations of total PAHs in sediment of the ARD. The letters correspond to the data sets of Table 1. The straight lines are linear regressions bounded by 95% confidence intervals; in data set a, seven data points are obscured due to data overlap.

To test the hypothesis that tributary discharge, a surrogate for local runoff, is a correlate of sediment PAH concentrations, correlations of "annual" and May−August discharge for the Clearwater and Muskeg Rivers were determined for ARD mean sediment PAH concentrations. Clearwater River annual and May−August discharge were correlated significantly with mean sediment PAH concentrations in the ARD, whereas Muskeg River "annual" and May−August discharge were weakly correlated ($p \approx 0.075-0.1$) with ARD PAH concentrations (Table 3).

Tributary Discharge and Disturbance in Relation to Total PAHs in Tributary Sediments. To examine the relationship between tributary discharge and total PAH concentration in tributary sediment, correlations between sediment total PAH concentration and average and maximum annual and daily discharge and average May−August daily discharge were determined for the Clearwater, Muskeg, Steepbank, and Mackay Rivers (Table 4). For the Muskeg, Steepbank, and Mackay Rivers, there were no significant correlations between river discharge variables and sediment PAH concentrations. For the Clearwater River, maximum daily discharge was correlated with sediment PAH concentration near its river mouth. The relationship between hydrology and PAH concentration in the Clearwater River watershed may be different from those in the Muskeg, Steepbank, and Mackay Rivers.

Other Physical and Biological Variables as Correlates of Sediment PAH Concentrations. Percentages of sand, silt, and clay were not correlated significantly with total PAH concentration (Pearson correlations, sand %, $r = -0.289$, silt %, $r = 0.287$, clay %, $r = 0.227$, 31 df). Percent total organic carbon in the sediment (fall data) was correlated with both total PAH concentration in the Athabasca River Delta and with time (Table 5).

Normalizing total PAH to total organic carbon explained 34% of the variance in the PAH content of individual stations in the ARD and removed the correlation between year and PAH concentration ($r = -0.166$, df = 31, NS), indicating that both total PAHs and total organic carbon are increasing over time. Total organic carbon in the sediment was not correlated significantly with Athabasca River discharge (mainstem or distributary, annual or May−August discharge,

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Table 2. Pearson Correlations of Annual Industrial Variables with Mean Sediment PAH Concentrations and Time[a]

	correlations (r, p, n)	
annual industrial variable	total PAH	year
bitumen production	0.530, ~0.095, 10	0.956, <0.001, 12
bitumen production, lagged 1 yr	0.614, ~0.046, 10	0.953, <0.001, 12
mined sand	0.527, ~0.096, 10	0.960, <0.001, 12
mined sand, lagged 1 yr	0.627, ~0.041, 10	0.956, <0.001, 12
landscape disturbance footprint	0.674, ~0.024, 10	0.940, <0.001, 13
landscape disturbance footprint, lagged 1 yr	0.698, ~0.018, 10	0.983, <0.001, 12
PM2.5 emissions, oil sands sector	0.684, ~0.021, 10	0.934, <0.001, 14
PM10 emissions, oil sands sector	0.690, ~0.019 10	0.939, <0.001, 14
TPM emissions, oil sands sector	0.690, ~0.019, 10	0.930, <0.001, 14

[a] Data set b reported here; for the same industrial variables, correlations with total PAH in data set a (n = 32) were significant at α = 0.04−0.07, and for data set c (n = 8) were significant at $\alpha \leq 0.05$. For the sake of brevity, the correlation analyses focus on data set b.

Table 3. Pearson Correlations of Total PAH Concentration in Sediment of the ARD with Athabasca, Clearwater, and Muskeg River Discharge

	sediment PAH data set		
discharge parameter[a]	(a) all observations, n = 32 (r, p) [r, p for individual distributaries][b]	(b) annual means, n stations = 1, 2, or 4/yr, n = 10 (r, p)	(c) annual means, n stations = 2 or 4/yr, n = 8 (r, p)
Athabasca R. annual discharge	0.172, 0.347 [0.011, 0.952]	0.281, 0.432	0.386, 0.345
Athabasca R. annual discharge, lagged 1 year	0.270, 0.135 [0.063, 0.734]	0.510, 0.132	0.552, 0.156
Athabasca R. May−August discharge	0.061, 0.741 [-0.058, 0.754]	0.116, 0.750	0.139, 0.743
Athabasca R. May−August discharge, lagged 1 year	0.064, 0.728 [0.055, 0.766]	0.078, 0.831	0.132, 0.756
Clearwater R. annual discharge	0.377, 0.033	0.677, 0.032	0.791, 0.019
Clearwater R. May−August discharge	0.389, 0.028	0.700, 0.024	0.813, 0.014
Muskeg R. March−October discharge	0.289, 0.109	0.513, 0.129	0.541, 0.166
Muskeg R. May−August discharge	0.320, 0.074	0.539, 0.108	0.608, 0.110

[a] For the period 1999−2009, the mean instantaneous discharge of the rivers was: Athabasca 496.1 m^3/s, Clearwater 110.7 m^3/s, Muskeg 5.1 m^3/s. [b] Mainstem discharge adjusted to distributary discharge downstream of the Athabasca−Embarras divergence (station ER) for the FLC, GIC, and BPC stations in the D. data set (e.g., at mainstem flow of 500 m^3/s at Old Fort, FLC receives 12%, GIC receives 41%, and BPC receives 32% of flow; data from acoustic Doppler profiler measurements, F. Yusuf, BC Hydro, Pers. comm., Sept. 2010 and ref 28); all correlations were nonsignificant.

Table 4. Correlations between Annual Sediment Total PAH Concentration in Tributaries and Tributary Discharge[a]

	correlations between total PAH concentration and river discharge (r, n, p)		
river	average annual discharge	maximum annual discharge	average May−August discharge
Clearwater	0.746, 4, 0.254	0.985, 4, 0.015	0.845, 4, 0.155
Muskeg	0.106, 7, 0.821	−0.205, 7, 0.659	−0.175, 7, 0.708
Mackay	−0.010, 5, 0.988	−0.048, 5, 0.939	0.075, 5, 0.904
Steepbank	0.105, 4, 0.895	0.370, 4, 0.630	0.228, 4, 0.772

[a] "Annual" daily instantaneous discharge data for the Muskeg, Mackay, and Steepbank Rivers pertain to the period March 1 to October 31; for the period 1999−2009, the mean instantaneous discharge of the tributaries was: Clearwater 110.7 m^3/s, Muskeg 5.1 m^3/s, Mackay 14.6 m^3/s, Steepbank 6.9 m^3/s.

in the present year or lagged 1 year). The same industrial variables that were correlated with total PAHs in sediment were also correlated with total organic carbon in sediment (Table 5).

DISCUSSION

Temporal Trends in ARD PAH Concentrations. Our conclusion of increasing PAH concentrations in the ARD refutes the statement by the Alberta Government [13] that: "There is evidence that PAH concentrations in [Athabasca River] delta sediments are lower in recent years than historically. This decrease is likely due to drier conditions in the last decade resulting in less erosion from these natural sources." No evidence was provided to support the government's claim of decreasing concentrations of PAHs in ARD sediments, nor was evidence presented to support the view that declining discharge is the driver for the putative decline in sediment PAH concentrations, nor that river discharge has declined over the past decade.

Table 5. Pearson Correlations of Total Organic Carbon in Sediment at the Athabasca River Delta Sites with Total PAH Concentration, Time, and Industrial Variables (n = 32), 1999−2009[a]

	correlations (r, p)
variable	total organic carbon
total PAH concentration	0.582, <0.001
year	0.479, ~0.008
bitumen production	0.418, ~0.018
bitumen production, lagged 1 yr	0.403, ~0.020
mined sand	0.433, ~0.013
mined sand, lagged 1 yr	0.391, ~0.028
landscape disturbance footprint	0.512, ~0.005
landscape disturbance footprint, lagged 1 yr	0.531, ~0.003
PM2.5 emissions, oil sands sector	0.507, ~0.005
PM10 emissions, oil sands sector	0.539, ~0.002
TPM emissions, oil sands sector	0.527, ~0.003

[a] Critical value at α = 0.05: 31 df, 0.344; for the industrial variables, correlations with total organic carbon for data set b (n = 10) were not significant at α = 0.05, but were significant for the data set c (n = 8).

To date, the only published study relevant to temporal trend[25] reported PAH concentrations in sediment cores from Richardson Lake and Lake Athabasca. The trends were inconsistent: total PAH concentrations may have increased modestly with time in Richardson Lake (in the ARD) from 1.53 mg/kg in 1950 to 1.65 mg/kg in 1998 and may have decreased with time in Lake Athabasca from 1.87 mg/kg in 1957 to 1.26 mg/kg in 1998. There is insufficient information to determine whether these differences exceeded variation due to laboratory precision. The single-largest wildfire year in the Peace-Athabasca Delta during the period 1950−2009 took place in 1953, which accounted for 41% of the total area burned in the 60-year period.[26] Postfire deposition of pyrogenic PAHs[2] within these sedimentary basins may have influenced the sediment PAH concentrations at these two sites.

In late 2010, a report[27] considered the question of trend in PAH concentrations in the lower Athabasca River based on RAMP data current to 2009. The review did not present new data or analyze existing data. Instead, it relied upon RAMP[24] to conclude: "The most recent (2009) summary of RAMP data going back to 1997 does not show any consistent evidence of increasing levels in Athabasca River Delta sediment samples over the 12 years of that program." It is noteworthy that such a conclusion would be made in the absence of data analysis both in the review and in its RAMP source (see the Supporting Information, Appendix S2, for a discussion of that report in relation to PAH trends).

Twelve years of industrial development have taken place since the data reported in Evans et al.[25] Industrial activities have increased significantly over the past decade with regulatory approval of new projects and expansion of existing projects. RAMP[28] reported a "historical median" total PAH concentration for the ARD (period 1976−99, which is unfortunately all postindustrial development) of 1.22 mg/kg and concluded that sediments from the lower Athabasca River, including Athabasca Delta, were toxic to several species of invertebrates. In comparison, the 2009 mean PAH concentration in the ARD was 1.72 mg/kg. A threshold of 1 mg/kg of total PAHs in marine sediment for protection of estuarine fish populations has been recommended.[29] Above 1 mg/kg total PAHs, there was a substantial increase in the risk of liver disease, reproductive impairment, and potential effects on fish growth.

Soil erosion from deforested watersheds can increase sedimentation rates and degrade fish spawning and insect habitat.[30] Correlations between PAH concentrations and landscape disturbances such as mined sand and disturbance footprint suggest PAH loading related both to fluvial and to wind erosion.[10] Exposure of unweathered bitumen-bearing deposits and stockpiling of overburden by land clearing and mining should increase runoff of PAHs, total organic carbon, and other compounds. In an upstream/downstream of development analysis of PAH concentrations in the Muskeg River sampled with semipermeable membrane devices,[12] PAH concentrations increased significantly downstream of bitumen mining (p = 0.0005). For the 12 alkylated PAH species, concentrations increased an average 7-fold downstream of development.[12] Recent industrial development such as land clearing has been linked to elevated dissolved PAH concentrations in the Athabasca River that were likely toxic to fish embryos.[10]

Correlations between PAH concentrations and particulate emissions and bitumen production indicate that some PAH loading may be related to industrial activities such as stack emissions, in agreement with the findings of Kelly et al.[10] When those authors compared sites upstream and downstream of development, dissolved PAH concentrations in tributaries to the Athabasca were elevated from 2-fold in winter to 20-fold in summer. In the Athabasca River mainstem, dissolved PAHs increased 1.2−5-fold from upstream to downstream areas (greater effects were observed in the summer). Elevated dissolved PAH concentrations did not persist downstream to the Athabasca Delta and Lake Athabasca in the seasons studied (late winter and midsummer). The authors did not examine PAH loadings delivered on sediments, a potentially significant source of PAH and other contaminants to the delta.

Kelly et al.[31] examined the relationship between industrial particulate deposition and concentrations of 13 priority pollutant elements (PPE) in the Athabasca River. At sites downstream of development (bitumen upgraders, bitumen mining, and land disturbance), including the Athabasca River Delta, concentrations of all PPE except for beryllium and selenium remained elevated above those upstream of development. In melted snow or water collected near or downstream of development, guidelines for protection of aquatic life were exceeded for seven PPE (cadmium, copper, lead, mercury, nickel, silver, and zinc). Over a 4-month winter period in 2008, 11 400 tonnes of airborne particulates, the majority of which were bitumen particles, were deposited within a 50 km radius of the main upgrading facilities. Sources of the particulates included coke and fly ash and dust related to land clearing, mining, and vehicle traffic and roads. Alberta crude bitumen production in 2007 was 1.3 million barrels/day, about three-fourths of which were derived from the lower Athabasca River deposits. Daily production in Alberta could reach 3 million barrels/day by 2020 and 5 million barrels/day by 2030.[32]

PAHs in Relation to Organic Carbon and River Discharge. Total PAH concentration in the sediment of the ARD increased over the past decade, as did total organic carbon. That both total PAHs and total organic carbon increased over the past decade suggests that landscape disturbance within the watershed causes increased loading of both PAHs and organic carbon. Alberta

Environment's explanation [33] for an increase in PAH concentrations in the ARD over the period 2000−2005 was a decrease in sediment organic carbon: "What these data demonstrate is that organic carbon concentrations of the sediments have declined... artificially creating the appearance that PAHs have increased..." Alberta Environment[33] referred to a single RAMP station (ER in the RAMP report[34] and in this Article). In reality, organic carbon at the ER station showed no statistically significant trend over that period, nor did the BPC and FLC sites; organic carbon increased at the GIC station (Pearson $r = 0.93$, $p = 0.02$). The statement that organic carbon declined over the period is without basis.

As the primary agency responsible for environmental management in the region, Alberta Environment has maintained that there is no trend in PAH concentrations in sediment of the Athabasca River Delta, and that variations in sediment PAH concentrations are due to variations in river discharge. The agency writes [clarification by the authors appears in square brackets]: "There is a common misconception that PAH concentrations are increasing in ARD sediments... We have concluded that the pattern [of changes in PAH concentrations] is more consistent with changes in flow and erosion of mineral soils containing globules of oil sand. Flow conditions further support this conclusion because the years 2000 and 2001 were the lowest flow years on record and flows (and hence erosion of natural oil sands) have increased since."[33] The statement that the years 2000 and 2001 were the lowest flow years on record is incorrect; Athabasca River flow was lower in 2002 than in either 2000 or 2001.[26]

The data do not support the notion that Athabasca River discharge is a significant determinant of sediment PAH concentration in the ARD. High discharge on the lower Athabasca River mainstem is not necessarily related to local erosion events. Annually, there are two periods during which high discharge on the Athabasca River is expected. The spring freshet results from melting of the foothills and plains snowpack, whereas the summer freshet is fed by melting of the mountain snowpack.[26] In contrast, above-average local runoff, which may not be reflected in high discharge on the Athabasca River, should be a better predictor of local fluvial erosion and would be modulated by industrial land clearing and mining within each watershed. Finally, during times of high mainstem discharge, deposition rates in the ARD may decline to zero because the increased flow velocities are better able to maintain suspended matter in the water column. In the ARD, channel scouring, rather than deposition, may occur during times of high mainstem discharge.

Headley et al.[35] suggested that runoff-driven erosion events might account for high concentrations of sediment PAHs in the Steepbank and Ells Rivers (Athabasca River tributaries), but there were insufficient data at that time to examine the discharge/PAH hypothesis. Our data indicate that discharge on the Clearwater River is correlated with mean sediment PAH concentrations in the ARD. During high discharge in this tributary, scouring of PAH-bearing materials, and runoff from the disturbed landscape, may contribute higher PAH loads to the Athabasca River. Within the tributaries themselves (Clearwater, Muskeg, Steepbank, and Mackay Rivers), only the Clearwater River showed a significant correlation between discharge and PAH concentrations at their river mouths. Of the four tributaries, the Clearwater River has the highest discharge (Table 4) and the greatest proportion of its banks exposed to McMurray Fm deposits (Figure 1) and is the only tributary without surface bitumen mining. Relationships between PAH loading, disturbance, runoff, storm events, and groundwater movements deserve investigation.

PAH Trends, Industrial Activities, and the Need for Improved Monitoring. The hypotheses of (1) no temporal trend in sediment PAH concentrations in the ARD and (2) that variations in sediment PAH concentrations are unrelated to industrial activities are rejected. The hypothesis (3) that variations in ARD sediment PAH concentrations are due to variations in river discharge is rejected for the Athabasca River mainstem and its distributaries and is not rejected for discharge of the Clearwater River.

Concentrations of PAHs in the sediment of the ARD increased over the period 1999−2009. Measures of industrial activity such as volume of bitumen production and mined sand, extent of landscape disturbance, and particulate emissions also increased over the period and were correlated with sediment PAH concentrations. Total organic carbon in sediment was correlated with sediment PAH concentrations in the ARD.

Given the relationship between industrial activities and PAH releases, the potential toxic effects of PAHs, the increase in sediment PAH concentrations in the ARD over the past decade, and rising bitumen production, concerns over long-term environmental health are exacerbated by inadequate monitoring. In its 2010 review of monitoring programs in the region, Environment Canada[19] concluded that many of the monitoring programs were unable to distinguish bitumen industrial impacts. The inability to measure impacts was often due to poor sampling design (including insufficient spatial or temporal replication), lack of hypothesis testing, undefined or ill-defined baseline conditions, and inadequate analytical capabilities. To determine the factors that affect sediment PAH concentrations, carefully designed studies are required that lie beyond the capability of current monitoring programs and the structure and quality of existing data sets.

■ ASSOCIATED CONTENT

Supporting Information. Further information on the study area, materials and methods, and an analysis of temporal trend in sediment PAH concentrations at control sites (Appendix S1). Background information relevant to evaluation of trends in sediment PAH concentrations (Appendix S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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