Environmental Science & Technology

Article

pubs.acs.org/est

Profiling Oil Sands Mixtures from Industrial Developments and Natural Groundwaters for Source Identification

Richard A. Frank,[†] James W. Roy,[†] Greg Bickerton,[†] Steve J. Rowland,[‡] John V. Headley,[§] Alan G. Scarlett,[‡] Charles E. West,[‡] Kerry M. Peru,[§] Joanne L. Parrott,[†] F. Malcolm Conly,[§] and L. Mark Hewitt*[,†]

[†]Water Science and Technology Directorate, Environment Canada, 867 Lakeshore Road, Burlington, Ontario, Canada L7R 4A6

[‡]Petroleum and Environmental Geochemistry Group, Biogeochemistry Research Centre, University of Plymouth, Drake Circus, 5 Plymouth PL4 8AA, U.K.

[§]Water Science and Technology Directorate, Environment Canada, 11 Innovation Boulevard, Saskatoon, Saskatchewan, Canada, S7N3H5

Supporting Information

ABSTRACT: The objective of this study was to identify chemical components that could distinguish chemical mixtures in oil sands process-affected water (OSPW) that had potentially migrated to groundwater in the oil sands development area of northern Alberta, Canada. In the first part of the study, OSPW samples from two different tailings ponds and a broad range of natural groundwater samples were assessed with historically employed techniques as Level-1 analyses, including geochemistry, total concentrations of naphthenic acids (NAs) and synchronous fluorescence spectroscopy (SFS). While these analyses did not allow for reliable source differentiation, they did identify samples containing significant concentrations of oil sands acid-extractable organics (AEOs). In applying Level-2 profiling analyses using electrospray ionization high resolution mass spectrometry (ESI-HRMS) and comprehensive multidimensional gas chromatography time-of-flight mass spectrometry (GC × GC-TOF/MS) to samples containing appreciable AEO concentrations, differentiation of natural from OSPW sources was apparent through measurements of O_2:O_4 ion class ratios (ESI-HRMS) and diagnostic ions for two families of suspected monoaromatic acids (GC × GC-TOF/MS). The resemblance between the AEO profiles from OSPW and from 6 groundwater samples adjacent to two tailings ponds implies a common source, supporting the use of these complimentary analyses for source identification. These samples included two of upward flowing groundwater collected <1 m beneath the Athabasca River, suggesting OSPW-affected groundwater is reaching the river system.

1. INTRODUCTION

The Canadian oil sands region contains an estimated 168.6 billion barrels of recoverable bitumen,[1] accounting for 97% of Canada's petroleum reserves and ranking Canada third globally in terms of domestic oil reserves.[2] Recent studies investigating the loading of inorganic and neutral organic compounds have identified significant aerial depositions of priority pollutants[3,4] associated with mining activities. These results, combined with recent calls for a greater understanding of the potential environmental impacts resulting from industrial development of the oil sands,[5−7] have catalyzed the implementation of a new Canada−Alberta Joint Oil Sands Monitoring Program (JOSMP[8]).

One of the objectives of the JOSMP is to evaluate the nature and extent of the possible migration of contaminants associated with mining developments to regional aquatic ecosystems.[5,7] The proximity of several large containment structures (e.g., tailings ponds) containing oil sands process-affected water (OSPW) to the Athabasca River and its tributaries provides an obvious focus for this investigation. Process-affected waters contain complex mixtures of neutral and polar organic compounds, in addition to dissolved metals and major ions (e.g. Na, Cl, SO_4, HCO_3).[9] Of significance are the acid-extractable organics (AEOs), which include naphthenic acids (NAs). These are attractive from a monitoring perspective because they have demonstrated acute[10,11] and sublethal[12] toxicity.[13] Furthermore, their enhanced water solubility makes them prime candidates for possible migration beyond containment structures via groundwater, which is important given the zero-discharge policy for surface water releases within mining lease licenses. Advancements in analytical techniques including electrospray ionization high resolution mass spectrometry (ESI-HRMS) and comprehensive multidimensional

Received: January 10, 2014
Accepted: January 21, 2014

 © XXXX American Chemical Society dx.doi.org/10.1021/es500131k | Environ. Sci. Technol. XXXX, XXX, XXX−XXX

gas chromatography time-of-flight mass spectrometry (GC × GC-TOF/MS) have shown that mixtures of oil sands-derived AEOs include compounds containing aromatic rings,[14−16] other multiple oxygenated acid species, and sulfur- and nitrogen-heteroatoms.[17−22]

Several studies have shown or suggested leakage of OSPW into groundwater and migration of OSPW-affected groundwater away from impoundments.[23−27] Numerical modeling[23,24] estimated leakage from the base of one impoundment and dyke at <75 L s^{-1} (about 0.1% of the lowest daily Athabasca River flow recorded, 75 m^3 s^{-1}).[28] A plume of OSPW-impacted groundwater has also been mapped to extend approximately 500 m away from another nearby impoundment.[25,26] In these studies, a variety of geochemical and organic signatures have been employed[24,26,29] in attempts to track potential leakage, including: bicarbonate,[24,30] sodium,[30] the sodium to chloride ratio, the water type as indicated by its position on a Piper plot, boron, ammonium,[25,26] and various measures of AEOs (including by Fourier transform infrared spectroscopy (FTIR), ESI-MS, synchronous fluorescence spectroscopy (SFS[16,31])). Although advanced analytical and chromatographic techniques such as ESI-HRMS,[19,32] APPI-HRMS[33,34] and GC × GC-TOF/MS[31,35−37] have provided breakthroughs in the identification of classes within OSPW-derived AEO mixtures, there has been minimal progress differentiating the similar, but less-studied, AEO mixtures present in the natural background waters within the McMurray Formation.[19] Given the large areas requiring monitoring under the JOSMP, it is important to establish whether a unique chemical profile of OSPW exists that could be employed to identify and track OSPW-affected groundwater and surface waters.

Recent attempts to profile industrial and natural waters from the oil sands region have begun to indicate potential chemical markers for successful differentiation. For example, a 2011 pilot study[38] at one tailings impoundment used ESI-HRMS and ^{13}C isotopic signatures of the carboxylic acid functional groups in NAs for profiling. This study, and a related study[39] that compared ^{13}C isotopic signatures between OSPW, monitoring wells, unprocessed oil sand and Athabasca River water, illustrates the potential of these techniques for differentiation. To date, the most complete study used liquid-chromatography (LC)-ESI-TOF/MS to profile oil sands AEOs in lakes, the Athabasca River and some of its tributaries, and pore water (e.g., potentially discharging groundwater) collected from the Athabasca River.[27] Although this investigation indicated that similarities in surface water compositions of two tributaries and OSPW were suggestive of seepage, the clustering of OSPW and pore water sites following principal components analysis made differentiation difficult. Consequently, the application of more specific analytical techniques was recommended. Furthermore, it is important to note that a systematic investigation, beyond proof-of-concept, examining the range of naturally occurring bitumen-derived AEO, lacking any possible OSPW influence, has yet to be conducted.

The objective of the present study was to identify chemical components that could distinguish OSPW-affected groundwater from natural groundwater containing bitumen-derived AEOs within the McMurray Formation. The first part of the study involved application of Level-1 analyses consisting of assessing geochemistry (major ions, Na, B, NH_4), total AEO concentrations, and the presence/absence of maxima in a SFS profile characteristic of oil sands mono- and diaromatic NAs, to two different OSPW containments and a broad variety of natural groundwater samples. Level-2 analyses, consisting of advanced separation and ESI-HRMS techniques, were then applied to differentiate bitumen-derived AEO mixtures originating from OSPW from those naturally present in groundwater in the oil sands region. In the second part of the study, both Level-1 and 2 analyses were applied to groundwater samples collected adjacent to two tailings ponds to determine whether their chemical profiles resembled those of natural or OSPW sources.

2. MATERIALS AND METHODS

2.1. Sample Collection. For the first part of the study, duplicate samples of OSPW were collected from each of two tailings ponds from different oil sands developments between September 20 and 25, 2009 (OSPW 1, 2; Figure 1). Far-field groundwater samples (15−20 mL) were collected from 20 sites. One groundwater seep sample collected in the Joslyn Creek catchment was obtained on October 19, 2010, directly from groundwater discharging to the surface at the seepage face. The remaining 19 were collected using a stainless steel drive-point system[40] at depths of 30−120 cm below the streambed of the Athabasca River and associated tributaries (Ells River, Steepbank River) between May and October 2010. Far-field was defined in this study as >1 km upstream or downstream from any tailings pond, given the likely dominance of groundwater flow perpendicular to the Athabasca River. Level-1 analyses of these samples included the assessment of geochemical parameters (defined below), total AEO concentrations (referred to in the Results as [NA] and determined by low resolution ESI-MS), and expected maxima in an SFS profile associated with suspected mono- and diaromatic acids.[31] Far-field samples containing appreciable amounts of NAs (>5 mg L^{-1}) and both OSPW samples were selected for detailed profiling by ESI-HRMS and GC × GC-TOF/MS. For the second part of this investigation, a total of seven near-field samples (<200 m from an OSPW containment) were collected near two tailings ponds. Two samples were collected from Site A: an interceptor well and a monitoring well. In addition, five samples were collected from Site B: an interceptor well, a monitoring well, and three drive-point groundwater samples along the western shore of the Athabasca River. On-development interceptor and monitoring wells (4.8−39.0 m depths) were sampled June 22−23, 2010, while drive point samples were collected as noted above. All near-field samples underwent Level-2 analyses for comparison with OSPW and far-field samples with appreciable NAs, in addition to Level-1 analyses. Locations of the near- and far-field samples selected for AEO profiling are presented in Figure 1.

2.2. Geochemical Analysis. Measured geochemical parameters comprised anions (including chloride, sulfate, and nitrate) analyzed by ion chromatography, major cations (including sodium and calcium) analyzed by direct aspiration using an inductively coupled argon plasma system,[40] and ammonium analyzed by spectrophotometry using a phenolhypochlorite reagent (absorbance measured at 640 nm). Samples were also analyzed for a suite of trace metals (including boron) at Environment Canada's National Laboratory for Environmental Testing (NLET) (Burlington, ON) using Inductively Coupled Plasma-Sector Field Mass Spectrometry.[41] Samples were categorized into different water types according to the relative balances of major ions as depicted on a Piper plot, which is a graphical technique commonly applied in groundwater studies.[24,27]

2.3. Synchronous Fluorescence Spectroscopy (SFS). Analysis by SFS was performed using a Perkin-Elmer Luminescence spectrometer LS50B and data collection was controlled

dx.doi.org/10.1021/es500131k | Environ. Sci. Technol. XXXX, XXX, XXX−XXX

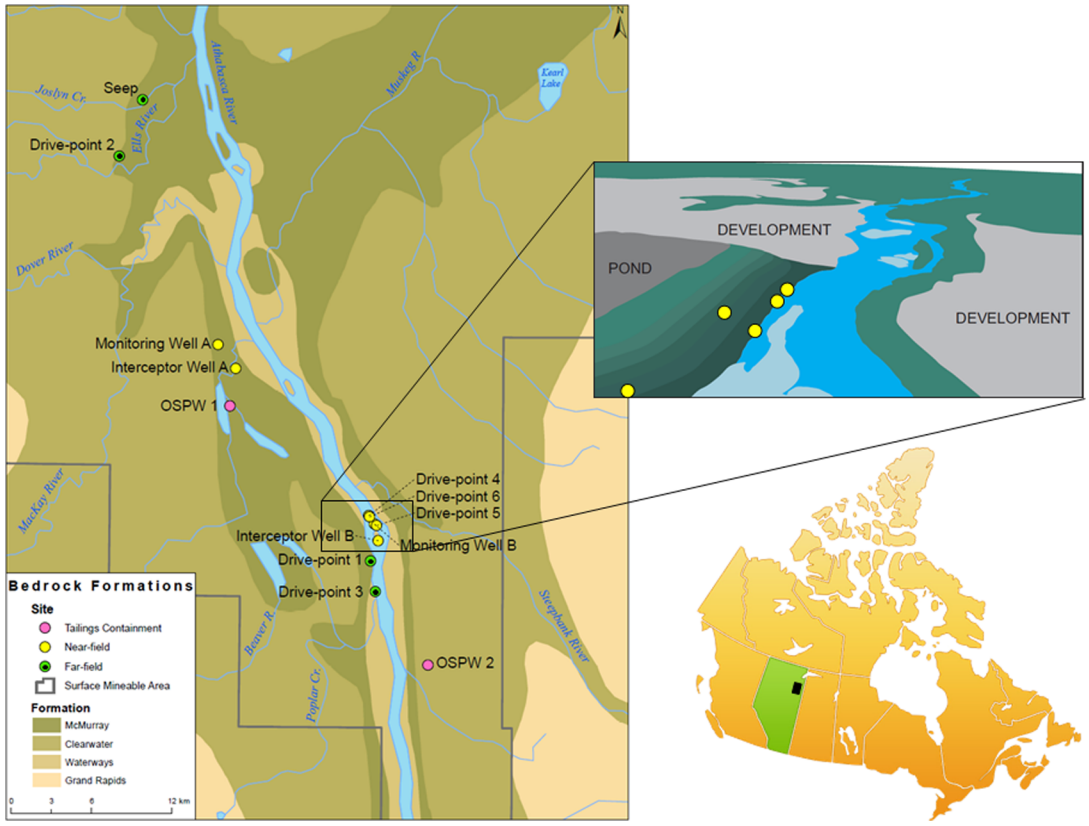

Figure 1. Map depicting sampling locations of OSPW, Near-field and Far-field locations prioritized for Level-2 profiling. Inset depicts close-up of area illustrating locations of Site B Near-field drive-points, interceptor and monitoring wells.

by FL Winlab 3 software (Perkin-Elmer, Norwalk, CT) as previously described.[16] The expected maxima for an SFS oil sands NA profile are at 282, 320, and 333 nm.[16,31] In this investigation, samples that exhibited maxima at 282 and 320 nm above a signal intensity of 100 were identified as positive for this profile.

2.4. Sample Preparation for Detailed Profiling. Prior to analysis by ESI-HRMS and GC × GC-TOF/MS, all samples were extracted by solid phase extraction (SPE) to remove residual salts and to concentrate polar organics. For each 15-mL sample, a 200 mg styrene divinylbenzene, Isolute ENV+ SPE cartridge (Biotage, Charlotte, NC) was conditioned with 10 mL of acetonitrile followed by 10 mL of milli-Q water at a flow rate of approximately 5 mL min^{-1}. Each sample was acidified to pH 2 using 12 M HCl, and drawn through the SPE cartridge at a flow rate of approximately 1 mL min^{-1}. The adsorbed AEOs were eluted into 12-mL glass scintillation vials using 7 mL of acetonitrile at 1 mL min^{-1}. Each extract was subsequently evaporated to dryness under a stream of N_2, assessed by constant weight, and reconstituted in 3.0 mL of acetonitrile. This 3.0 mL extract volume was partitioned into 1-mL aliquots and a single aliquot was examined by ESI-HRMS and, after conversion to the methyl esters, a second aliquot by GC × GC-TOF/MS.

2.5. Infusion-Electrospray Ionization Mass Spectrometry. Low resolution ESI-MS analyses[32] for NAs were conducted with a Quattro Ultima (Waters Corp., Milford, MA) triple quadrupole mass spectrometer equipped with an ESI interface operating in negative-ion mode. The MS conditions were set as follows: source temperature 90 °C; desolvation temperature 220 °C; cone voltage setting 62 V; capillary voltage setting 2.63 kV; cone gas (N_2) flow rate 158 L h^{-1}; desolvation gas (N_2) flow rate 489 L h^{-1}. The multiplier was set at 650 V and full scan mass spectra were acquired in the m/z range 50−550. Samples (5 μL) were loop injected by use of a Waters 2695 separations module with 50:50 acetonitrile/water containing 0.1% ammonium hydroxide as the eluent at 200 μL min^{-1}.

Level-2 AEO profiling of sample extracts using ESI-HRMS was performed on a LTQ Orbitrap Velos mass spectrometer (Thermo Fisher Scientific, San Jose, CA) using electrospray ionization in negative ion mode. ESI source conditions were as follows: heater temperature was set to 50 °C, sheath gas flow rate was set to 25 (arbitrary units), auxiliary gas flow rate was set to 5 (arbitrary units), spray voltage set to 2.90 kV, capillary temperature was set to 275 °C and the S lens RF level was set to 67%. Samples were analyzed in full scan with an m/z range of 100−600, at a resolution set to 100 000 using the lockmass of m/z 212.07507 $[M\text{-}H]^-$ of *n*-butyl benzenesulfonamide. Resulting NA concentrations were determined by comparison to a predefined 5-point regression ($R^2 > 0.989$) of OSPW-derived NAs at known concentrations (initially quantified by FTIR). Xcalibur version 2.1 software (Thermo Fisher Scientific San Jose, CA) was used for data acquisition, instrument operation, and quantitative data analysis. Class distributions were determined using acquired accurate mass data and Composer version 1.0.2 (Sierra Analytics, Inc. Modesto, CA) with an average mass error for all classes of approximately 1 ppm, with an O_2 mass error of 0.065 ppm.

2.6. GC × GC-TOF/MS. Extracts selected for Level-2 AEO profiling by GC × GC-TOF/MS were evaporated to dryness under a stream of N_2, methylated by refluxing for 90 min at 70 °C with boron trifluoride-methanol (2 mL; Aldrich, Poole, UK), back-extracted into hexane (2 × 1 mL) and concentrated under a stream of N_2 to 50 μL. Conditions for analysis were essentially as described previously.[36] Briefly, analyses were conducted using

dx.doi.org/10.1021/es500131k | *Environ. Sci. Technol.* XXXX, XXX, XXX−XXX

Table 1. Level-1 Analyses for OSPW and Natural (Far-field) Groundwater Samples, Collected from the Shore of Rivers in the Oil Sands Area of the Athabasca River Watershed[a]

Associated surface water body	Sample type	Water type	Na:Cl (molar)	[Na] (mg L^{-1})	[B] (μg L^{-1})	[NH_4] (mg L^{-1})	[NA] (mg L^{-1})	SFS OSPW profile?
	OSPW 1	saline	2.5	636	2275	28.40	54	Y
	OSPW 2	saline	1.0	287	3164	1.30	60	Y
Athabasca R.	Drive-point 1	saline	1.7	1577	4040	0.84	48	Y
Ells R.	Drive-point 2	n/a	n/a	n/a	n/a	0.91	27	Y
Athabasca R.	Drive-point 3	fresh	1.4	1.8	68.7	0.18	<DL	N
Joslyn Cr.	Seep	fresh	22.6	6	15	n/a	4	N
Athabasca R.	Drive-point 7	sulfate	1.84	182	577	<DL	26	Y
Athabasca R.	Drive-point 8	fresh	1.80	52.6	126	16.2	20	N
Athabasca R.	Drive-point 9	saline	1.13	713	1620	0.57	33	Y
Athabasca R.	Drive-point 10	fresh	<DL	<DL	90.6	1.03	7	Y
Athabasca R.	Drive-point 11	fresh	0.76	4.3	66	0.17	4	Y
Athabasca R.	Drive-point 12	fresh	2.05	4.9	77.5	3.00	4	N
Ells R.	Drive-point 13	fresh	10.28	119	384	0.41	4	N
Ells R.	Drive-point 14	fresh-alkaline	11.91	135	435	0.03	5	N
Ells R.	Drive-point 15	sulfate	11.84	594	695	0.03	4	N
Ells R.	Drive-point 16	alkaline	2.40	680	1340	1.44	10	Y
Steepbank R.	Drive-point 17	fresh	6.62	3.4	126	0.17	5	n/a
Steepbank R.	Drive-point 18	fresh	0.00	<DL	67.2	0.09	5	n/a
Steepbank R.	Drive-point 19	fresh	0.00	<DL	77.7	0.07	4	n/a
Steepbank R.	Drive-point 20	fresh	2.96	4.8	217	0.04	n/a	n/a
Steepbank R.	Drive-point 21	fresh	0.00	<DL	125	<DL	6	n/a
Steepbank R.	Drive-point 22	fresh	0.00	<DL	204	0.03	n/a	n/a

[a]Y, observed. N, not observed. n/a, bitumen in sample prevented analysis for Drive-point 2; SFS not conducted for Drive-points 17−22; insufficient sample for NAs for Drive-points 20, 22. <DL, values less than method detection limit of 0.01 mg L^{-1} for Na; 3 mg L^{-1} for NAs; 0.02 mg L^{-1} for NH_4.

an Agilent 7890A gas chromatograph (Agilent Technologies, Wilmington, DE) equipped with a Zoex ZX2 GC × GC cryogenic modulator (Houston, TX) interfaced with an Almsco BenchToFdx time-of-flight mass spectrometer (Almsco International, Llantrisant, UK) operated in positive ion electron ionization mode and calibrated with perfluorotributylamine. The scan speed was 50 Hz, the first-dimension column was 50 m × 0.25 mm ×0.40 mm VF1-MS (Varian, Palo Alto, CA), and the second-dimension column was 2.5 m × 0.15 mm ×0.15 mm VF-17MS (Varian). Three μL of sample were injected in a splitless mode at 300 °C. The initial temperature of the oven (40 °C) was held for 1 min and then increased at 2 °C min^{-1} to 325 °C and held for 10 min. The modulation period was 4 s, the transfer line temperature was 280 °C, and the ion source temperature was 300 °C. Helium was used as the carrier gas at a constant flow rate of 0.8 mL min^{-1}. Subsequent data processing was conducted using GCImage v2.1 (Zoex).

3. RESULTS AND DISCUSSION

3.1. Profiling OSPW versus Natural Groundwaters. Differentiation between the 2 OSPW and the 20 natural groundwater (far-field) samples was first attempted in the Level-1 analyses that included geochemical data, total NAs, and the presence/absence of the SFS NA profile (Table 1). The SFS profiles of OSPW from the two mining operations studied (Figure 2) were consistent with those obtained in previous analyses.[16,31] Concentrations of total NAs in the OSPW samples were 54 and 60 mg L^{-1}, consistent with values previously reported for OSPW.[42] In previous studies,[24,29] 30 mg L^{-1} and 40 mg L^{-1} were used as the lower NA concentration limit to identify OSPW-affected water. However, one study[43] identified OSPW with NA concentrations below 10 mg L^{-1}.

Of the 14 far-field samples analyzed by SFS, 7 had spectral profiles similar to those of OSPW, although Drive-points 7 and 11 differed in that they exhibited lower signal intensities at 282 nm and elevated signal intensities at 320 and 345 nm (SI Figure S1). While the majority of the far-field samples in the current study had lower NA concentrations than OSPW (<10 mg L^{-1}), Drive-point 2, on the Ells River, contained 27 mg L^{-1} and 4 samples from an area along the Athabasca River where the McMurray Formation outcrops at the river edge (near Drive-point 1; Figure 1) ranged from 20 to 48 mg L^{-1}. Generally, appreciable NA concentrations corresponded with the presence of the SFS profile for OSPW, and vice versa, but there were a few exceptions which are currently under investigation: Drive-point 11 had a positive SFS profile and NA concentration of 4 mg L^{-1}, and Drive-point 8 had a negative SFS profile and a NA concentration of 20 mg L^{-1} (Table 1). The occurrence of an SFS profile similar to that observed for OSPW in many far-field samples with appreciable NA concentrations illustrates that these parameters are effective at identifying the presence of bitumen-derived AEOs, however they alone cannot be used to indicate whether these AEOs are originating from natural or OSPW sources.

A full description of the geochemical comparisons between far-field groundwater and OSPW is provided in SI Geochemistry. Briefly, analysis of the geochemical data showed that the ranges of most parameters (Na, B, and NH_4 concentrations, Na:Cl ratio) from the 20 far-field samples encompassed those for OSPW in this study (Table 1). When plotted on a Piper Plot (Figure 3A), the far-field samples plotted across all water types (alkaline, saline, sulfate, fresh), whereas the OSPW samples in general were commonly of alkaline or saline water type.[24,25,29,43] These results are consistent with previous conclusions that geochemical parameters alone cannot broadly distinguish OSPW

dx.doi.org/10.1021/es500131k | Environ. Sci. Technol. XXXX, XXX, XXX−XXX

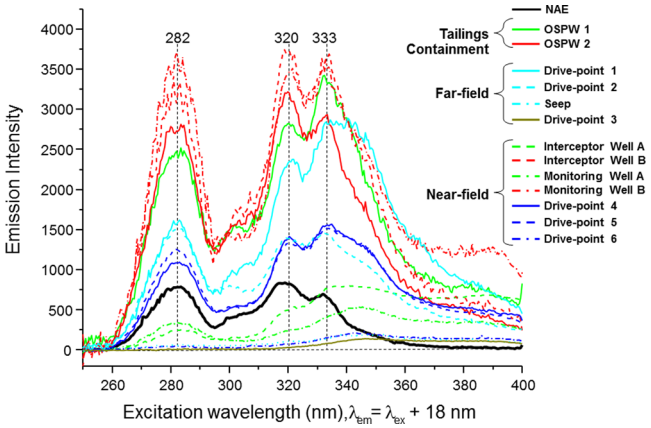

Figure 2. Spectra from synchronous fluorescence spectroscopy (SFS) for Near-field, and Far-field samples, as well as for a naphthenic acid extract (NAE) isolated from "fresh" OSPW.

from bitumen-influenced natural groundwaters in the oil sands region.

Due to the qualitative nature of the data obtained from the SFS analysis, a rigorous principal component analysis could not be performed to assess the ability of the entire Level-1 analyses to distinguish OSPW from natural groundwaters. However, it is clear (Table 1; SI Geochemistry & SI Figure 1) that OSPW tends to be elevated in concentrations of Na, B, NH_4, and NA, as well as the characteristic SFS spectra for suspected oil sands aromatic organic acids). Several of the far-field samples (Drive-points 1, 9, and 16) have a similar composition, especially when considering dilution effects on OSPW-affected groundwater. Thus, while a combination of the Level-1 parameters does not provide a universal indicator for OSPW migration, they have been found to be useful as site-specific tracers (i.e., tracking known plumes)[26] where information on local groundwater chemistry and flow systems is available.[43]

The Level-1 analyses did, however, reveal multiple significant sources of naturally occurring bitumen-derived AEOs (Table 1). The Level-2 analyses then focused on profiling the complex AEO mixtures present in OSPW and natural sources by utilizing these new sources of natural AEOs from different hydrogeological settings. Drive-points 1 and 2 exhibited two of the highest NA concentrations and signal intensities of the SFS profile (Figure 2). The Drive-point 1 sample was collected from the top of the limestone layer in an area where bitumen-containing sands were exposed at the bank of the Athabasca River, and also had elevated levels of B and Na, as well as a saline-alkaline water type. The sample from Drive-point 2 was collected along the Ells River near an area designated for future oil sands mining development, but where no activities existed at the time of sampling. The extracted groundwater contained bituminous globules (note: filters clogged immediately preventing the collection of samples for major ion determinations). In this same general area, but on the smaller tributary of Joslyn Creek, a natural groundwater seep sample (Seep) was collected that also contained bituminous globules, but did not exhibit the SFS NA profile (Figure 2) and had low Na, B, and NA concentrations (fresh water type). Finally, the Drive-point 3 sample was collected off of the McMurray Formation and had low Na, B, and NA concentrations (fresh water type), and no SFS signature.

Level-2 analysis by ESI-HRMS of the AEO containing far-field samples provided relative contributions of various ion classes via heteroatom histograms (Figure 4), including those assigned to

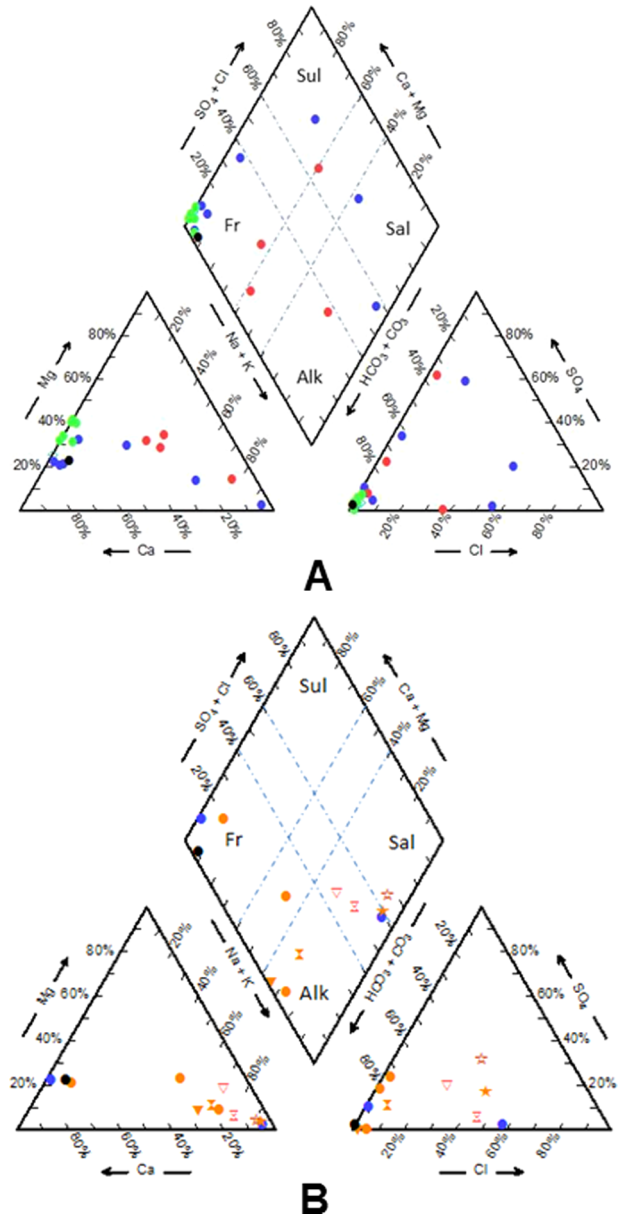

Figure 3. (A) Piper plot of major ions for natural far-field groundwater samples (>1 km from a tailings pond) collected along the Athabasca River (blue), Steepbank River (green), Ells River (red) and Joslyn Creek (black; seep) in the oil sands area. (B) Piper plot of major ions from the samples selected for Level 2 analyses, except for Drivepoint 2, separated by symbol type: OSPW (stars), interceptor wells (hourglass), on-development monitoring wells (triangle), and off-development drive-point or seep samples (circles); and by site/location: Site A samples in red outline; Site B samples in orange; background groundwater along Athabasca in blue; Joslyn Creek in black. Diamonds are divided (by dotted lines) into water type sections: Fr, fresh; Sul, sulfate; Sal, saline; Alk, alkaline (Hunter, 2001).

O_x, O_xS_y, N_xO_y, and $N_xO_yS_z$ species. For comparison purposes, the responses for all species were assumed to be the same in Figure 4, understanding that this assumption is not valid as ion-suppression and matrix effects are known to be prevalent for ESI-MS analyses of such complex mixtures. Furthermore, as authentic standards were not available for the thousands of components revealed by HRMS, these data are considered semi-quantitative. The O_x species in particular are of much interest as this group contains the classical NAs (O_2 components)

dx.doi.org/10.1021/es500131k | Environ. Sci. Technol. XXXX, XXX, XXX−XXX

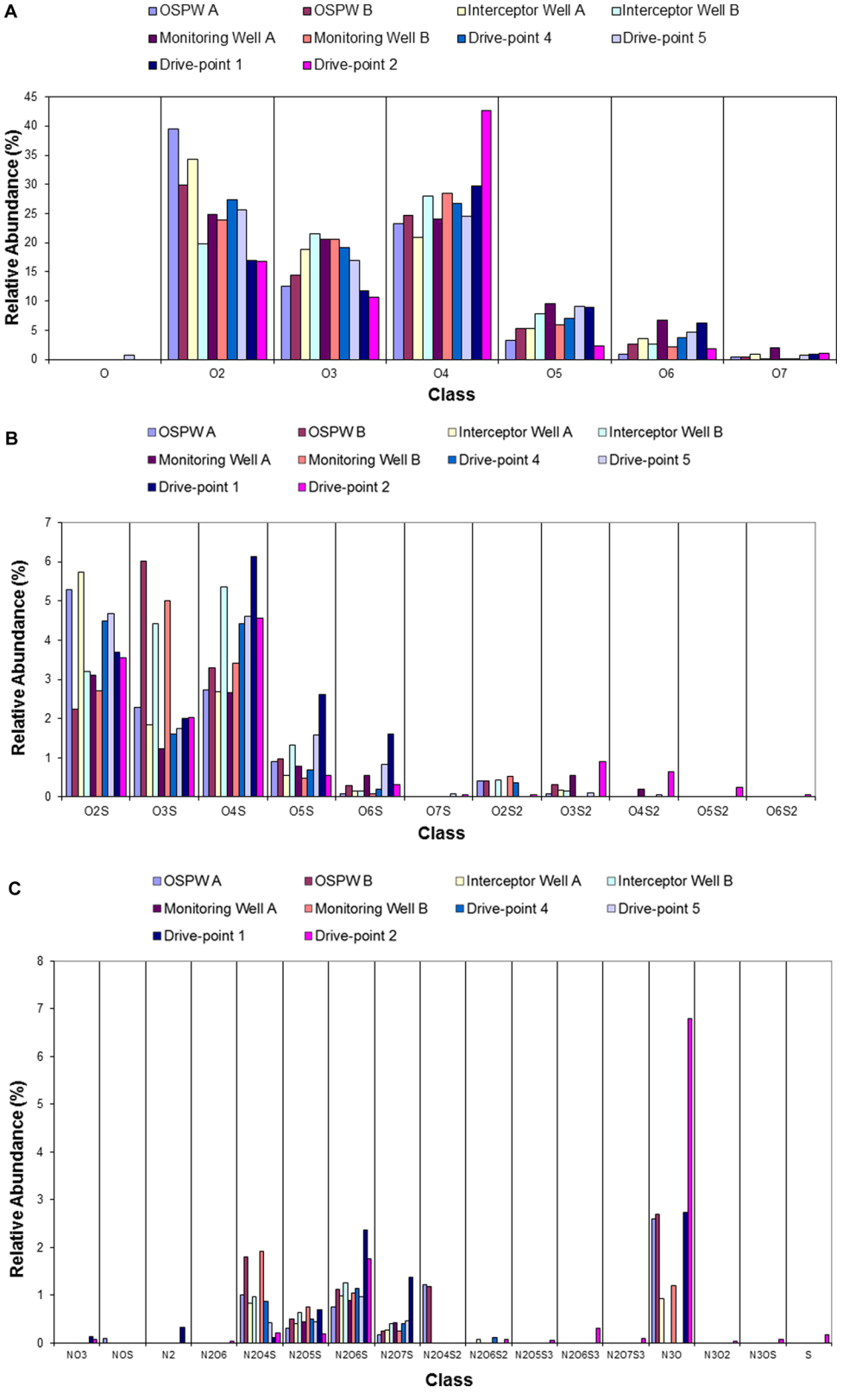

Figure 4. Level-2 HRMS speciation profiles for samples representative of On-development, Near-field, and Far-field samples.

along with higher oxidized hydroxyl acids (O_3 species), dicarboxylic acids (O_4), and possibly humic, fulvic, or weathered acids (O_{5-7}).

All far-field samples with detectable concentrations of NAs (Drive-points 1 and 2) were dominated by O_x heteroatoms, with notable observations concerning ratios of O_2:O_4 containing ion classes (Table 2; Figure 4a). OSPW samples 1 and 2 had O_2:O_4 ratios of 1.69 and 1.21, respectively, however, Drive-points 1 and 2 differed whereby the O_2:O_4 ratios were the lowest observed at 0.57 and 0.40, respectively (Table 2).

dx.doi.org/10.1021/es500131k | *Environ. Sci. Technol.* XXXX, XXX, XXX−XXX

Table 2. Summary of Level-1 and Level-2 data for all OSPW, Near-field and Select Far-field Samples[a]

		Level-1						Level-2	
		Water type	Na:Cl (molar)	[Na] (mg L^{-1})	[B] (μg L^{-1})	[NA] (mg L^{-1})	SFS OSPW Profile?	HRMS O_2:O_4	GC × GC-TOF/MS Monoaromatic acids?
									Family A / Family B
Tailings containment	OSPW 1	saline	2.5	636	2275	54	Y	1.69	7/7 / Y+
	OSPW 2	saline	1.0	287	3164	60	Y	1.21	7/7 / Y+
Far-field	Drive-point 1	saline	1.7	1577	4040	48	Y	0.57	1/7; peak #5 / Y
	Drive-point 2	n/a	n/a	n/a	n/a	27	Y	0.40	2/7; peaks #1,5 / Y
	Drive-point 3	fresh	1.3	2	69	<DL	N		0/7 / N
	Seep	fresh	22.6	6	15	4	Y		0/7 / N
Near-field Site A	Interceptor Well	saline	1.7	631	1230	60	Y	1.65	4/7; peaks #1,3−5 / Y+
	Monitoring Well	alkaline	2.7	549	743	30	Y	1.04	5/7; peaks #1−5 / Y+
Near-field Site B	Interceptor Well	alkaline	7.8	272	1469	39	Y	0.71	4/7; peaks #1−4 / Y
	Monitoring Well	alkaline	33.0	359	1640	43	Y	0.84	5/7; peaks #1−5 / N
	Drive-point 4	alkaline	14.0	300	1620	50		1.02	7/7 / Y+
	Drive-point 5	alkaline	18.0	61	1380	55	Y	1.04	5/7;peaks #1−5 / Y+
	Drive-point 6	fresh	5.8	16	170	5	N	0.92	0/7 / N

[a]Y, Observed for SFS, both Family B monoaromatic acids by GC × GC-TOF/MS at correct m/z and GC retention times. Y+ indicates enriched signal for Family B acids. N, Not observed for SFS or Family B monoaromatic acids at correct m/z and GC retention times. n/a, bitumen in sample prevented analysis. <DL values less than method detection limit of 0.01 mg L^{-1} for Na; 3 mg L^{-1} for NAs. O_2:O_4 ratios cannot be reported for NA <5 mg L^{-1}.

Ratios of O_xS ion classes, among others, have previously been proposed as useful diagnostic markers for OSPW in surface waters using Fourier transfer ion cyclotron resonance mass spectrometry (FTICR-MS).[19] In the current investigation, the increased prevalence of O_2 over O_4 species in OSPW samples and the reversal in the natural far-field samples appeared to be similarly reflected in the O_2S:O_4S ratios at these sites (Figure 4B), however the trend was less consistent. Although the sample set in this investigation only included two samples each of the anthropogenic and natural sources that contained appreciable concentrations of NAs, the diagnostic potential observed for the O_2:O_4 ratio is nevertheless consistent with suggestions from previous work using ESI-HRMS[19,33,38] and supports use of this ratio in tracking OSPW.

Qualitative analysis by GC × GC-TOF/MS focused on two groups of well-resolved acids previously suggested to be monoaromatic steroidal-type acids,[31] using base peak or characteristic ions (Family A m/z 145; Family B m/z 237, 310). Analysis of the two OSPW samples revealed strong signal intensities for both families, consistent with previous analyses of NAs extracted from OSPW by GC × GC-TOF/MS.[31] Seven distinct Family A members were identified by retention times (R1 ± 0.1 min, R2 ± 0.2 s) that were used in profiling (Peak 1: R1−113.2 min, R2−2.8 s; Peak 2: R1−114.2 min, R2−2.6 s; Peak 3: R1−117.0 min, R2−3.0 s; Peak 4: R1−118.7 min, R2−3.0 s; Peak 5: R1−120.3 min, R2−3.1 s; Peak 6: R1−122.9 min, R2−2.4 s; Peak 7: R1−123.5 min, R2−2.4 s) and two distinct Family B compounds were similarly identified (m/z 237: R1−106.2 min, R2−1.4 s; m/z 310: R1−106.5 min, R2−1.5 s) (Figure 5). In contrast, Drive-points 1 and 2, the far-field samples with appreciable NA concentrations and SFS signal intensities approximating OSPW (Figure 2; Table 2), exhibited only 1 or 2 of the 7 Family A isomers, and comparably minimal signals for Family B. The remaining two far-field samples (Drive-point 3 and Seep) lacked any signal for both families under the conditions used (Table 2). Acids with structures similar to those of Families A and B are suspected as contributors to the 282 nm maximum in the SFS profile,[31] however, the present results indicate that different monoaromatic acids are contributing to the SFS profiles within the far-field samples. While lack of authentic reference compounds and limited sample volumes in the present study precluded definitive identifications of these acids, their potential as tracers of OSPW migration is certainly indicated. Work is underway to better characterize the structures of these compounds and to establish their relevance for monitoring migration of OSPW.

3.2. Profiling Groundwaters near Tailings Ponds. The Level-2 profiling analyses were then applied to a series of groundwater samples collected near two previously studied tailings ponds, to determine if their profiles more closely resembled OSPW or natural bitumen-derived AEOs. Samples were collected from near-field on-development interceptor and monitoring wells near tailings ponds A and B, as well as from shallow drive-points along the bank of the Athabasca River, within 200 m of tailings containment B (Figure 1). Although it cannot be assumed that any of these samples contain OSPW, they were collected in areas where previous studies have suggested OSPW impacts on local groundwater (Site A;[26] Site B [24]) as determined by Level-1 analyses similar to those employed in this study.

Analysis by ESI-HRMS of the two Site A samples revealed O_2:O_4 ratios of 1.65 and 1.04 for Interceptor well A and Monitoring well A, respectively, closely resembling the 1.29 and 1.61 ratios measured for OSPW (Table 2; Figure 4A). The somewhat lower ratio for the Monitoring well, as well as a lower NA concentration (Interceptor well A: 59.8 mg L^{-1}; Monitoring well A: 29.7 mg L^{-1}) indicates that the sample may have contained a mixture of OSPW and natural groundwater-derived NAs. Moreover, all Site A samples fell within a similar zone on a Piper plot (intermediate between alkaline and saline; Figure 3B).

dx.doi.org/10.1021/es500131k | Environ. Sci. Technol. XXXX, XXX, XXX−XXX

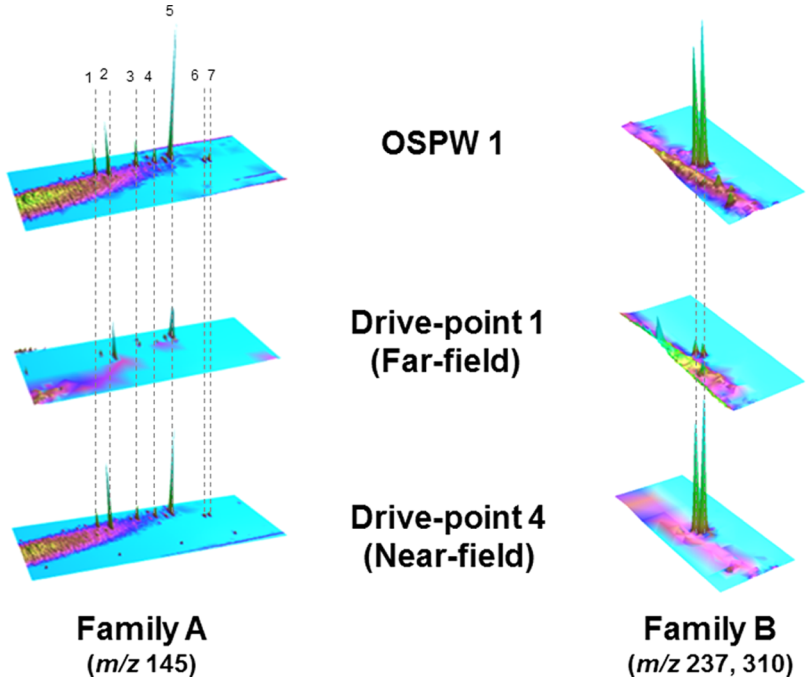

Figure 5. GC × GC-TOF/MS ion chromatograms for selected samples from OSPW, Far-field (Drive point 1) and Near-field (Drive-point 4) sites. Shown are the monoaromatic m/z 145 (Family A) and m/z 237 and 310 (Family B) ions; refer to Experimental for exact retention times.

Analysis by GC × GC-TOF/MS of the interceptor and monitoring well samples from Site A revealed 4 and 5 of the 7 diagnostic m/z 145 isomers (Family A), respectively, and enriched signal intensities for the m/z 237 and 310 ions (Family B) for both samples (Table 2). Qualitatively, both on-development samples were identical, with the exception of peak 2, which was absent from Interceptor well A. This, together with the enriched intensities of Family B ions, is consistent with both of the OSPW samples and contrasts with all of the far-field samples. Collectively, the Level-1 and Level-2 analyses all demonstrate a close similarity between these two Site A samples and OSPW, as opposed to the natural far-field groundwater. Consequently, both samples likely contain differing proportions of OSPW, with greater dilution from other water sources in Monitoring well A.

Consistent with both OSPW samples (and near-field Site A samples), GC × GC-TOF/MS analysis revealed that most of the Site B near-field samples exhibited enriched Family B aromatic acid signal intensities. With the exception of Drive-point 6, all Site B near-field samples consistently contained at least 4 out of the 7 Family A isomers, with peaks 6 and 7 being absent from all but one sample. It is worth noting that Drive-point 4 was the only non-OSPW sample of this study where all 7 Family A isomers were detected. There were no detectable signals for either ion Family for Drive-point 6 (Figure 5), suggesting it was not affected by OSPW. Furthermore, Level-1 analyses for this sample showed very low Na, B, and NA concentrations, no SFS signal, and a fresh water type (Table 2), in contrast to OSPW, supporting this contention. Monitoring well B was an exception where Family B ions were not detected, and while Interceptor well B exhibited these ions, they were at much lower intensities than both OSPW and near-field samples containing appreciable concentrations of NAs.

Level-2 profiling by ESI-HRMS of Site B near-field samples was also consistent with OSPW. Drive-points 4 and 5 had appreciable NA concentrations and O_2:O_4 ratios near 1.0, compared to 1.2 for Site B OSPW. The Interceptor and Monitoring well samples for Site B exhibited O_2:O_4 ratios of 0.71 and 0.84, respectively (Table 2; Figure 4A). These values, although lower than other near-field and OSPW samples, were greater than the two far-field samples with appreciable NA concentrations. It is important to understand that water collected in interceptor wells may emanate from a variety of sources (e.g., OSPW seepage, natural groundwater, surface runoff, etc.) that are mixed in unknown proportions with temporal fluctuations. It is therefore expected that interceptor systems will have a broad range of values that should lie between the range described by OSPW and the natural far-field samples.

When comparing the HRMS data for all Level-2 analyses, several trends are evident. First, the AEO profiles for O_2 and O_4 species are skewed to the left (OSPW influence) and right (natural bitumen-derived) respectively, whereas the profiles for the O_3, O_5, O_6, and O_7 components are bell shaped (Figure 4A). Although the rationale for these differences is not established, the relative abundances of the species may be linked to differences in the primary sources of these component classes. The relative abundances of the higher O_x species ($x > 4$; Figure 4A) were generally lower (<10%) compared to the levels of the O_2 and O_4 species (15−40%), and are likely indicative of the presence of weathered NAs and natural humic and fulvic acids. A complementary trend to that observed for the O_x species is also apparent for the O_xS_y species (Figure 4B), in which the profiles for the O_2S and O_3S species are skewed to the left (OSPW influence) whereas the O_4S, O_5S, O_6S, and O_4S_2 species are skewed to the right (natural bitumen-derived). These O_xS_y species are believed to contain natural surfactants, and possibly industrial additives, and warrant further investigation for their diagnostic utility as previously suggested.[19] While the profiles for the N-containing heteratomic species (Figure 4C) illustrate that some species classes are enriched (i.e., N_2O_4S, N_2O_6S, and N_3O), their application for source differentiation is unclear at present. Finally, although the O_2:O_4 ratio for the Drive-point 6 sample of 0.92 is suggestive of the influence of OSPW, the low NA concentration

dx.doi.org/10.1021/es500131k | Environ. Sci. Technol. XXXX, XXX, XXX−XXX

(4.8 mg L^{-1}), coupled with the lack of detectable Family A and B acids and a fresh water type strongly indicates this is not the case and illustrates the importance of utilizing the Level-1 and 2 techniques in complement.

The results from the Level-2 analyses of the Site B groundwater samples containing appreciable concentrations of NAs (all samples except Drive-point 6, as noted above) are generally supported by the Level-1 analysis. All had elevated concentrations of B (1400−1600 μg L^{-1}) and NAs (39−55 mg L^{-1}) in a range similar to OSPW (Table 2), as well as exhibited the SFS signal characteristic of NAs. All were of similar water type (alkaline or alkaline-fresh), and Na concentrations were elevated, with the exception of the sample from Drive-point 5. Note that complete support for all of the Level-1 analyses was not expected, given the results on geochemical variation in background groundwater samples from this study, as previously discussed.

The chemical profiles of the Drive-point 4 and 5 samples more closely resembled those of OSPW than any of the far-field samples, particularly in the presence and distributions of the Family A and B acids. Previous work has relied on less definitive tracers, such as total NA concentrations and major ions,[24−26] or attributed differences in the chemical profiles of surface waters to groundwater inputs when the groundwater samples themselves did not exhibit an OSPW influence.[27] The fact that the sample from Drive-point 6 (not resembling OSPW) was collected within ∼100 m of Drive-point 4 (strongly resembling OSPW), illustrates the inherent variability in groundwater geochemistry that can be expected given the convergence of local and regional flow systems along this river valley, where groundwaters with varying geochemical evolutions and characteristics may be encountered and combined with the potential localized effects of tailings structures and oil sands development. As such, future monitoring activities should give careful consideration to spatial replication of sampling in areas that may have highly variable and heterogeneous flow paths.

To investigate the potential for false-negatives, three samples (Far-field: Drive-point 3 and Seep; Near-field: Drive-point 6) were selected for detailed profiling. Rationale for their selection included that they exhibited lower concentrations of bitumen-derived AEOs ([NA] $\leq$ 5 mg L^{-1}), an absence of the characteristic SFS spectra for oil sands organic acids, and a "fresh" water type, in addition to the following: Drive-point 3 is located off of the McMurray Formation; the Seep sample contained bituminous globules, similar to Drive-point 2; and the proximity of Drive-point 6 to Drive-points 4 and 5 that exhibited bitumen-derived AEOs. Level-2 profiling confirmed that these three samples do not contain bitumen-derived AEOs, validating the absence of false negatives. Subsequent attempts to apply multivariate statistics to the differences reported in Table 2 were precluded by the qualitative data provided by the SFS and GC × GC-TOF/MS analyses.

3.3. Study Implications. The present investigation demonstrates that SFS, ESI-MS, and several geochemical analyses (Level-1 analyses) should not be used in isolation or in combination as a universal indicator of OSPW-affected groundwater, as these were unable to reliably differentiate OSPW from natural groundwaters containing bitumen-derived AEOs. However, data from ESI-HRMS and GC × GC-TOF/MS profiles (Level-2 analyses) for both sources appeared consistent within each source type, and different between them. Given the relatively small sample volumes utilized here for the Level-2 analyses (15−20 mL), these methodologies on their own likely would not enable conclusive differentiation of OSPW from all natural groundwater sources. However, the profiles provided by these methods, used in complement with the Level-1 analyses, collectively indicated that differentiation of sources was possible. This was highlighted by the Level-2 profiles of Drive-points 4 and 5 more closely resembling those of OSPW than any of the far-field samples, particularly in the presence and distributions of the Family A and B acids. The resemblance between the AEO profiles from OSPW and from 6 groundwater samples adjacent to two tailings ponds implies a common source, supporting the use of these complimentary analyses for source identification. These samples included two of upward flowing groundwater collected <1 m beneath the Athabasca River, suggesting OSPW-affected groundwater is reaching the river system. While profiling AEO mixtures from the Athabasca River was outside the groundwater focus of this study, the tools developed herein should provide this capability. Ongoing work with larger sample volumes is aimed at confirming and improving the diagnostic utility of the compound classes identified in this study.

■ ASSOCIATED CONTENT

Supporting Information

Figure S1 includes synchronous fluorescence spectra of all far-field samples. Geochemical criteria have been developed from past studies for differentiating OSPW from natural groundwater, these are briefly discussed and applied to the samples collected in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (905)319-6924; fax: (905)336-6430; e-mail: mark.hewitt@ec.gc.ca.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank William Govenlock, Jody Klassen, Ryan Levitt, Jason Miller, and Kirsten Nickel (Environment Canada-Edmonton); Jim Syrgiannis (Environment Canada-Regina); Andrew Basha and Bill Streeton (Environment Canada-Calgary); and Ruth Vanderveen, Katherine French, André Talbot, Amanda Malenica, Charles Talbot and John Voralek (Environment Canada-Burlington), for providing field, technical, and logistical support. We thank Susan Brown, Pamela Collins, and Jerry Rajkumar (Environment Canada-Burlington) for inorganic analyses. Access to the Athabasca River was graciously provided by Northland Forest Products (Fort McMurray, Alberta). A special appreciation is extended to the Fort McMurray offices of Alberta Environment and Sustainable Resource Development and the Water Survey of Canada for logistical support. A portion of the funding for the GC × GC-TOF/MS instrumentation was kindly provided by the European Research Council (project OUTREACH, Grant number: 228149 to SJR). Disclaimer: The views in this paper are only held by the authors and are not representative of the official policy of the authors' individual affiliations.

■ REFERENCES

(1) *ST98-2012 Alberta's Energy Reserves 2011 and Supply/Demand Outlook 2012−2021*; Energy Resources Conservation Board, 2012; p 290.

(2) *Upstream Dialogue—The Facts on Oil Sands*; Canadian Association of Petroleum Producers, 2012; p 64.

(3) Kelly, E. N.; Schindler, D. W.; Hodson, P. V.; Short, J. W.; Radmanovich, R.; Nielsen, C. C. Oil sands development contributes elements toxic at low concentrations to the Athabasca River and its tributaries. *Proc. Natl. Acad. Sci.* **2010**, *107* (37), 16178−16183.
(4) Kelly, E. N.; Short, J. W.; Schindler, D. W.; Hodson, P. V.; Ma, M.; Kwan, A. K.; Fortin, B. L. Oil sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries. *Proc. Natl. Acad. Sci.* **2009**, *106* (52), 22346−22351.
(5) Dillon, P.; Dixon, D. G.; Driscoll, C.; Giesy, J. P.; Hurlbert, S.; Nriagu, J. *Evaluation of Four Reports on Contamination of the Athabasca River System by Oil Sands Operations*; Water Monitoring Data Review Committee—Prepared for Government of Alberta, 2011; p 55.
(6) Kindzierski, W.; Jin, J.; Gamal El-Din, M. *Review of Health Effects of Naphthenic Acids: Data Gaps and Implications for Understanding*, Oil Sands Research and Information Network, OSRIN Report No. TR-20; University of Alberta, School of Energy and the Environment: Edmonton, Alberta, 2012; p 43.
(7) *Environmental and Health Impacts of Canada's Oil Sands Industry*; Royal Society of Canada Expert Panel, 2010.
(8) *Joint Canada/Alberta Implementation Plan for Oil Sands Monitoring*; Environment Canada and Alberta Environment, 2012; p 27.
(9) Allen, E. W. Process water treatment in Canada's oil sands industry: I. Target pollutants and treatment objectives. *J. Environ. Eng. Sci.* **2008**, *7*, 123−138.
(10) Frank, R. A.; Kavanagh, R.; Burnison, B. K.; Arsenault, G.; Headley, J. V.; Peru, K. M.; Solomon, K. R. Toxicity assessment of generated fractions from an extracted naphthenic acid mixture. *Chemosphere* **2008**, *72*, 1309−1314.
(11) Scarlett, A. G.; Reinardy, H. C.; Henry, T. B.; West, C. E.; Frank, R. A.; Hewitt, L. M.; Rowland, S. J., Acute toxicity of aromatic and non-aromatic fractions of naphthenic acids extracted from oil sands process-affected water to larval zebrafish. *Chemosphere* **2013**, *93*, 415−420.
(12) Reinardy, H. C.; Scarlett, A. G.; Henry, T. B.; West, C. E.; Hewitt, L. M.; Frank, R. A.; Rowland, S. J., Aromatic naphthenic acids in oil sands process-affected water, resolved by GC × GC-MS, only weakly induce the gene for vitellogenin production in zebrafish (*Danio rerio*) larvae. *Environ. Sci. Technol.* **2013**, *47*, 6614−6620.
(13) FTFC. Clark hot water extraction fine tailings. In *Advances in Oil Sands Tailings Research*; FTFC (Fine Tailings Fundamentals Consortium): Alberta Department of Energy, Oil Sands and Research Division; Edmonton, AB, Canada, 1995; Vol.*I*.
(14) Frank, R. A.; Fischer, K.; Kavanagh, R.; Burnison, B. K.; Arsenault, G.; Headley, J. V.; Peru, K. M.; Van Der Kraak, G.; Solomon, K. R. Effect of carboxylic acid content on the acute toxicity of oil sands naphthenic acids. *Environ. Sci. Technol.* **2009**, *43* (2), 266−271.
(15) Jones, D.; West, C. E.; Scarlett, A. G.; Frank, R. A.; Rowland, S. J. Isolation and estimation of the 'aromatic' naphthenic acid content of an oil sands process-affected water extract. *J. Chromatogr., A* **2012**, *1247*, 171−175.
(16) Kavanagh, R.; Burnison, B. K.; Frank, R. A.; Solomon, K. R.; Van Der Kraak, G. Detecting oil sands process-affected waters in the Alberta oil sands region using synchronous fluorescence spectroscopy. *Chemosphere* **2009**, *76*, 120−126.
(17) Barrow, M. P.; Headley, J. V.; Peru, K. M.; Derrick, P. J. Data visualization for the characterization of naphthenic acids within petroleum samples. *Energy Fuels* **2009**, *23*, 2592−2599.
(18) Bataineh, M.; Scott, A. C.; Fedorak, P. M.; Martin, J. W. Capillary HPLC/QTOF-MS for characterizing complex naphthenic acid mixtures and their microbial transformation. *Anal. Chem.* **2006**, *78*, 8354−8361.
(19) Headley, J. V.; Barrow, M. P.; Peru, K. M.; Fahlman, B.; Frank, R. A.; Bickerton, G.; McMaster, M. E.; Parrott, J.; Hewitt, L. M. Preliminary fingerprinting of Athabasca oil sands polar organics in environmental samples using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Rapid Commun. Mass Spectrom.* **2011**, *25*, 1899−1909.
(20) Headley, J. V.; Peru, K. M.; Fahlman, B.; Colodey, A.; McMartin, D. W. Selective solvent extraction and characterization of the acid extractable fraction of Athabasca oil sands process waters by Orbitrap mass spectrometry. *Int. J. Mass Spectrom.* **2013**, *345*−*347*, 104−108.
(21) Headley, J. V.; Peru, K. M.; Mohamed, M. H.; Frank, R. A.; Martin, J. W.; Hazewinkle, R. R. O.; Humphries, D.; Gurprasad, N. P.; Hewitt, L. M.; Muir, D. C. G.; Lindeman, D.; Strub, R.; Young, R. F.; Grewer, D. M.; Whittal, R. M.; Fedorak, P. M.; Birkholz, D. A.; Hindle, R.; Reisdorph, R.; Wang, X.; Kasperski, K. L.; Hamilton, C.; Woudneh, M.; Wang, G.; Loescher, B.; Farwell, A.; Dixon, D. G.; Ross, M. S.; Dos Santos Pereira, A.; King, E.; Barrow, M. P.; Fahlman, B.; Bailey, J.; McMartin, D. W.; Borchers, C. H.; Ryan, C. H.; Toor, N. S.; Gillis, H. M.; Zuin, L.; Bickerton, G.; McMaster, M. E.; Sverko, E.; Shang, D.; Wilson, L. D.; Wrona, F. J., Chemical fingerprinting of oil sands naphthenic acids in environmental samples—A review of analytical methods. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2013**, *48*, 1145−1163.
(22) Smith, D. F.; Schaub, T. M.; Kim, S.; Rodgers, R. P.; Rahimi, P.; Teclemariam, A.; Marshall, A. G. Characterization of acidic species in Athabasca bitumen and bitumen heavy vacuum gas oil by negative-ion ESI FT-ICR MS with and without acid-ion exchange resin prefractionation. *Energy Fuels* **2008**, *22*, 2372−2378.
(23) Ferguson, G. P.; Rudolph, D. L.; Barker, J. F. Hydrodynamics of a large oil sand tailings impoundment and related environmental implications. *Can. Geotechnol. J.* **2009**, *46*, 1446−1460.
(24) Hunter, G. P. Investigation of groundwater flow within an oil sands tailings impoundment and environmental implications. University of Waterloo, 2001.
(25) MacKinnon, M. D.; Kampala, G.; Marsh, B.; Fedorak, P. M.; Guigard, S., Indicators for assessing transport of oil sands process-affected waters. In *Bringing Groundwater Quality Research to the Watershed (Proceedings of GQ2004 International Conference of Groundwater Quality)*, Thomson, N. R., Ed.; IAHS Press, 2005; Vol. *297*, pp 71−80.
(26) Oiffer, A. A. L.; Barker, J. F.; Gervais, F. M.; Mayer, K. U.; Ptacek, C. J.; Rudolph, D. L. A detailed field-based evaluation of naphthenic acid mobility in groundwater. *J. Contam. Hydrol.* **2009**, *108*, 89−106.
(27) Ross, M. S.; dos Santos Pereira, A.; Fennell, J.; Davies, M.; Johnson, J.; Sliva, L.; Martin, J. W. Quantitative and qualitative analysis of naphthenic acids in natural waters surrounding the Canadian oil sands industry. *Environ. Sci. Technol.* **2012**, *46*, 12796−12805.
(28) Athabasca River below McMurray. In *Environment Canada Water Level and Stream Flow Statistics*, Water Survey of Canada Station 07DA001; January 1957 to December 2011, 2013.
(29) Baker, K. M. Identification of process water in a surficial aquifer at Syncrude's Mildred Lake Site; University of Waterloo, 1999.
(30) Kasperski, K. L. A review of properties and treatment of oil sands tailings. *AOSTRA J. Res.*, **1992**, *8*, 11−53.
(31) Rowland, S. J.; West, C. E.; Jones, D.; Scarlett, A. G.; Frank, R. A.; Hewitt, L. M. Steroidal aromatic "naphthenic acids" in oil sands process-affected water: Structural comparisons with environmental estrogens. *Environ. Sci. Technol.* **2011**, *45*, 9806−9815.
(32) Headley, J. V.; Peru, K. M.; Armstrong, S. A.; Han, X.; Martin, J. W.; Mapolelo, M. M.; Smith, D. F.; Rogers, R. P.; Marshall, A. G. Aquatic plant-derived changes in oil sands naphthenic acid signatures determined by low-, high-, and ultrahigh-resolution mass spectrometry. *Rapid Commun. Mass Spectrom.* **2009**, *23* (4), 515−522.
(33) Barrow, M. P.; Peru, K. M.; Fahlman, B.; Hewitt, L. M.; Frank, R. A.; Headley, J. V. Beyond naphthenic acids: Environmental fingerprinting of water from natural sources and the Athabasca oil sands industry using atmospheric pressure photoionization Fourier transform ion cyclotron mass spectrometry. *Environ. Sci. Technol.* **2014**, *(currently in review)*.
(34) Barrow, M. P.; Witt, M.; Headley, J. V.; Peru, K. M. Athabasca oil sands process water: Characterization by atmospheric pressure photoionization and electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. *Anal. Chem.* **2010**, *82*, 3727−3735.
(35) Rowland, S. J.; Scarlett, A. G.; Jones, D.; West, C. E.; Frank, R. A. Diamonds in the rough: Identification of individual naphthenic acids in oil sands process water. *Environ. Sci. Technol.* **2011**, *45*, 3154−3159.
(36) Rowland, S. J.; West, C. E.; Scarlett, A. G.; Ho, C.; Jones, D. Differentiation of two industrial oil sands process-affected waters by

two-dimensional gas chromatography/mass spectrometry of diamondoid acid profiles. *Rapid Commun. Mass Spectrom.* **2012**, *26*, 572−576.
(37) Rowland, S. J.; West, C. E.; Scarlett, A. G.; Jones, D.; Frank, R. A. Identification of individual tetra- and pentacyclic naphthenic acids in oil sands process water by comprehensive two-dimensional gas chromatography-mass spectrometry. *Rapid Commun. Mass Spectrom.* **2011**, *25*, 1198−1204.
(38) Ahad, J. M. E.; Pakdel, H.; Savard, M. M.; Calderhead, A. I.; Gammon, P. R.; Rivera, A.; Peru, K. M.; Headley, J. V., Characterization and quantification of mining-related naphthenic acids' in groundwater near a major oil sands tailings pond. *Environ. Sci. Technol.* **2013**, *47*, 5023−5030.
(39) Ahad, J. M. E.; Pakdel, H.; Savard, M. M.; Simard, M.-C.; Smirnoff, A. Extraction, separation, and intramolecular carbon isotope characterization of Athabasca oil sands acids in environmental samples. *Anal. Chem.* **2012**, *84*, 10419−10425.
(40) Roy, J. W.; Bickerton, G. A proactive screening approach for detecting groundwater contaminants along urban streams at the reach-scale. *Environ. Sci. Technol.* **2010**, *44*, 6088−6094.
(41) *SOP 2003 - Standard Operating Procedure for the Analysis of Dissolved, Extractable and Total Trace Metals in Water by "Direct Aspiration" or "In Bottle Digestion" Inductively Coupled Plasma-Sector Field Mass Spectrometry (ICP-SFMS)*; NLET2008.
(42) Clemente, J. S.; Fedorak, P. M. A review of the occurrence, analyses, toxicity, and biodegradation of naphthenic acids. *Chemosphere* **2005**, *60*, 585−600.
(43) Gibson, J. J.; Birks, S. J.; Moncur, M.; Yi, Y.; Tattrie, K.; Jasechko, S.; Richardson, K.; Eby, P. *Isotopic and Geochemical Tracers for Fingerprinting Process-Affected Waters in the Oil Sands Industry: A Pilot Study*; Oil Sands Research and Information Network, University of Alberta, School of Energy and the Environment, Edmonton, AB, OSRIN Report No. TR-12: 2011; p 109.