

1 Title: Profiling oil sands acid extractable organic mixtures from industrial developments and
2 natural groundwaters using high resolution mass spectrometry and comprehensive two
3 dimensional gas chromatography-mass spectrometry

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9 **Supporting Information for Manuscript**

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11 **SI Geochemistry**

12 In this section, a more thorough investigation is presented of the use of geochemical
13 properties to distinguish natural groundwater from groundwater affected by oil sands process
14 water (OSPW). Various criteria have been developed from past studies and these are briefly
15 discussed and applied to the OSPW and background samples collected in this study. The
16 rationale for using these specific properties is discussed in the main manuscript and will not be
17 repeated here.

18 The geochemical composition of OSPW has generally been reported as being dominant
19 in sodium and bicarbonate, with varying degrees of chloride (Baker, 1999; Gibson et al., 2011;
20 Hunter, 2001; MacKinnon et al., 2005). The composition can vary over time and between the
21 various tailings ponds. Thus, it typically plots in the lower portion of the diamond on a Piper
22 diagram (Hunter, 2001), a region commonly classified as alkaline, or in the right region
23 (MacKinnon et al., 2005), classified as saline, or in between those two (Baker, 1999; Gibson et
24 al., 2011). The two OSPW samples collected for this study fit this pattern, being saline (but still
25 ~ 40% bicarbonate) (Figure 3B). Natural groundwater samples were predominantly fresh, as has
26 been reported for shallow groundwater in previous work (MacKinnon et al., 2005); however, one
27 or more of these samples plotted in each of the other three regions of a Piper plot (Figure 3A),
28 indicating that geochemical composition is not perfectly diagnostic of OSPW.

29 For sodium (Na) concentration as a distinguishing geochemical marker for OSPW, Baker
30 (1999) applied criteria of < 30 mg/L for natural groundwater and < 150 mg/L to indicate OSPW.
31 Hunter (2001) applied these conditions: over 1000 mg/L indicates natural saline groundwater, <
32 10 mg/L indicates background groundwater, and > 40 mg/L is possibly groundwater affected by

33 OSPW. The Na concentrations for our two OSPW samples were about 290 and 640 mg/L, which
34 fits with the above criteria. Of note, OSPW reported by MacKinnon et al. (2005) had a Na
35 concentration of about 900 mg/L, which is close to the criteria for natural saline groundwater
36 (Hunter, 2001). The Na concentrations for background groundwater samples in this study ranged
37 from < detection limit to nearly 1600 mg/L (Table 1). This variability encompasses the full range
38 of criteria, which also demonstrates that Na alone cannot be broadly applied to distinguish
39 OSPW impacts.

40 For applying the sodium to chloride (Na:Cl) molar ratio as an OSPW indicator, Hunter
41 (Hunter, 2001) applied the following conditions: background groundwater was generally about 1
42 for limestone and < 5 for sands; while a ratio >15 indicated OSPW affected groundwater. No
43 other criteria for Na:Cl have been reported. The 2 OSPW samples in this study had low Na:Cl
44 (2.5 and 1.0), and would have been classified as natural groundwater. Our natural groundwater
45 samples had ratios ranging between 0 and 22 (Table 1); thus covering both natural and OSPW-
46 affected Na:Cl categories. Thus, the use of Na:Cl is not supported by this data.

47 Specific criteria for boron (B) have not been suggested; however, (MacKinnon et al.,
48 2005) reported elevated levels, around 2.5 mg/L, in OSPW, compared to surface aquifer
49 groundwater at around 0.12 mg/L. Our two OSPW samples had B at 2.3 and 3.2 mg/L, similar to
50 that reported above for OSPW. However, several of the natural groundwaters were at similar or
51 greater (up to 4 mg/L; Table 1) levels.

52 Finally, ammonium concentrations in OSPW have been reported at ~ 10 mg/L
53 (MacKinnon et al., 2005) and > 15 mg/L (Hunter, 2001), with natural groundwater having lower
54 values. Ammonium for our 2 OSPW samples ranged broadly between 1.3-28.4 mg/L. Nearly all

55 natural groundwater samples had levels below 3 mg/L, with one exception, at 16 mg/L (Table 1).

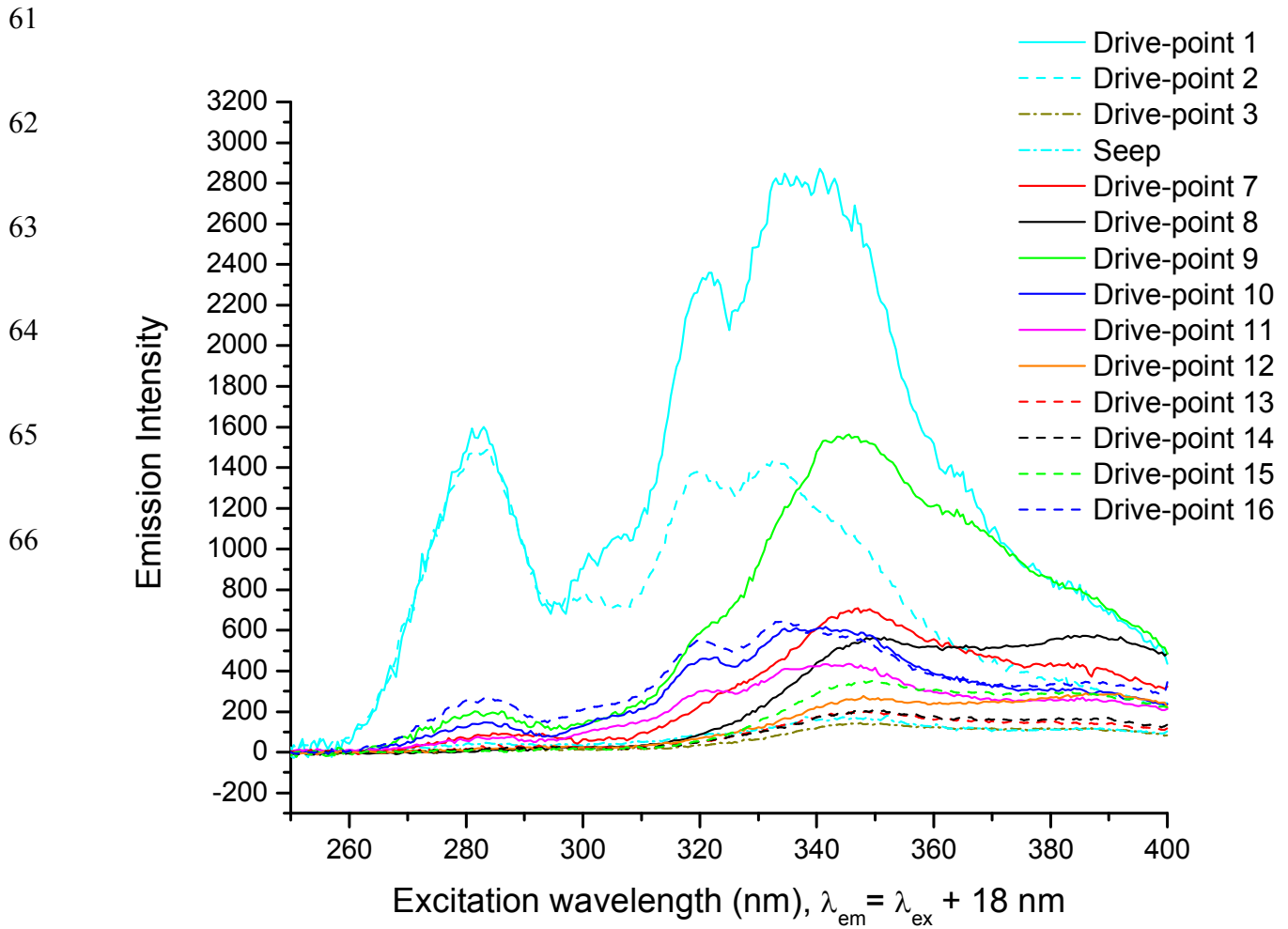
56 These findings indicate ammonium also cannot be applied singly to distinguish natural from

57 OSPW-affected.

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59 **SI Figure 1**

60 Spectra from synchronous fluorescence spectroscopy (SFS) for analyzed Far-field samples.



67 **References**

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