

Comment on “Profiling Oil Sands Mixtures from Industrial Developments and Natural Groundwaters for Source Identification”

Frank et al. 2014¹ presented a case study on fingerprinting acid extractable organic compounds in oil sands process-affected water (OSPW). The study compared near-field groundwater (<200 m from a tailings pond) with tailings pond OSPW and far-field groundwater (>1 km from any tailings pond) to evaluate impact of OSPW on near-field groundwater. The paper proposed using O₂:O₄ ratios as one of series tests that could be diagnostic indicators to identify OSPW impact. While the results of the small data set presented in the paper may suggest the potential of O₂:O₄ ratios, this correspondence aims to provide evidence of broad variability of O₂:O₄ ratios in OSPW and environmental waters in the region, raising caution on the usage of O₂:O₄ ratios. In addition, we do not think the selection of the OSPW2 in the study is an appropriate end-member for source identification at near-field site B.

We first compiled O₂:O₄ results available in the literature and from our own industrial projects. The ranges in O₂:O₄ ratios for OSPW, groundwater and surface water samples differed greatly between various data sets (Figure 1). More importantly, different O₂:O₄ characteristics of OSPW in comparison with background samples are revealed according to individual data sources. Based upon two OSPW samples (OSPW1 and OSPW2) and two far-field samples (Drive-point1 and Drive-point2), Frank et al,

suggest that OSPW can be distinguished from natural background (i.e., far-field groundwater) by higher O₂:O₄ ratios in OSPW.¹ The far-field drive-point samples were selected to be representative of natural background containing bitumen-derived organics based on NA concentrations and SFS profiles. Therefore, relatively high O₂:O₄ ratios in near-field site A are presented as evidence of impact from OSPW. However, relatively higher O₂:O₄ ratios were observed in natural background (i.e., rivers and lakes) compared to OSPW in some studies^{2,4,5} (Figure 1). There is also an investigation that shows significant overlap in O₂:O₄ ratios between OSPW and natural background³ (Figure 1). Inconsistent patterns when comparing OSPW to natural background in different studies warrants further study on the O₂:O₄ ratios and other compound class ratios.

We note that the data we compile are from studies using different profiling and sample pretreatment techniques (refer to captions in Figure 1 for details), that may account for some of the variability in O₂:O₄ ratios. However, using only the results from AITF-led projects, all of which used consistent analytical protocols, systematic differences in OSPW, groundwaters and surface waters are evident (Figure 1). While these groupings are intriguing, we feel that it is premature to advocate the usage of O₂:O₄ ratios as part of diagnostics before a standardized

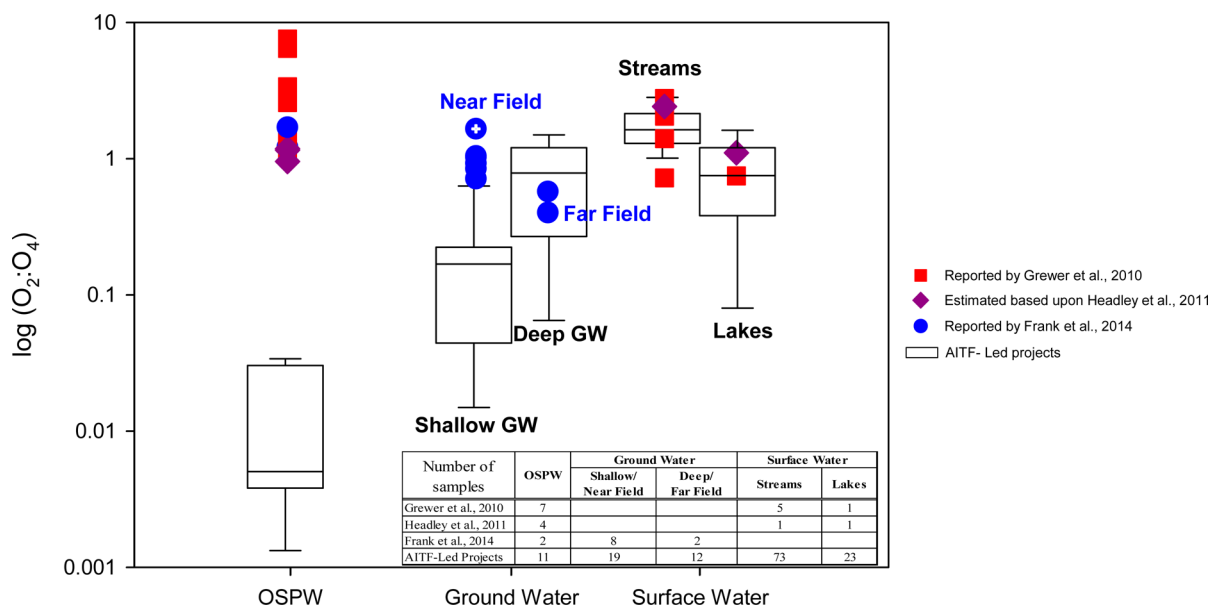


Figure 1. Summary of O₂:O₄ ratios from multiple studies. Inset table provides numbers of sample from various sources. Data source include Frank et al. (2014),¹ Headley et al. (2011),² Grewer et al. (2010)³ and AITF-Led projects.^{4,5} Frank et al. (2014) employed HRMS after solid phase extraction (SPE) with acetonitrile; Headley et al. (2011) used FT-ICR MS after SPE with methanol; Grewer et al. (2010) analyzed by FT-ICR MS after liquid-liquid extraction (LLE) with DCM; while AITF-led projects were acquired by FT-ICR MS after LLE with EA-DCM. Results from Headley et al. (2011) are estimated based upon figures, because no tables were reported. The two samples from near-field site A in Frank et al., 2014, which are suggested as OSPW-impacted groundwater samples, are highlighted with a white cross within the solid circles. Results from AITF-Led projects are summarized by box plots because of relative large number of samples.

procedure to report O₂:O₄ ratios (as well as other compound class ratios based upon organic profiling) are established.

Second, given the broad variability of organic characteristics in OSPW, the evaluation and identification of contaminant sources in near-field groundwater have to be performed at a site-specific scale. At site A, the closest tailings pond was available for characterization (OSPW1). However, the OSPW2 was from a tailings pond, which is highly unlikely to impact near-field groundwater at either sites (see Figure 1, Frank et al., 2014¹). The paper used these two OSPW samples to develop diagnostic indicators of OSPW, and identified OSPW-impacted near-field groundwater based on the presence or absence of these indicators. While we realize there are difficulties in obtaining OSPW samples, we think the limited number of OSPW samples, plus lack of consideration of physical locations, do not give sufficient representation to identify sources of contamination at a site-specific scale. This is particularly concerning at site B where the most likely OSPW source has not been included in the study.

Overall, the paper presents arguments for using chemical characterization, especially O₂:O₄ ratios, to identify and evaluate contamination in groundwater in the Athabasca oil sands region. Although the paper makes a significant effort to identify potentially useful chemical characteristics for source identification, the evidence is not conclusive. There is an urgent need to standardize the analytical protocol to facilitate accumulation and integration of data over time. There is also a need to develop more comprehensive data sets that capture the range and variability of organics present in natural and industrial waters across the region to improve our understanding of the processes that control and potentially alter organic labeling.

Yi Yi^{*,†,§}

John Gibson^{†,§}

Jean Birks^{‡,§}

Jun Han^{||}

Christoph H. Borchers^{||,⊥}

[†]Alberta Innovates – Technology Futures, Victoria, British Columbia Canada

[‡]Alberta Innovates – Technology Futures, Calgary, Alberta Canada

[§]Department of Geography, University of Victoria, Victoria, British Columbia Canada

^{||}University of Victoria – Genome BC Proteomics Centre, Victoria, British Columbia Canada

[⊥]Department of Biochemistry and Microbiology, University of Victoria, Victoria, British Columbia Canada

AUTHOR INFORMATION

Corresponding Author

*Phone 250 483 3291; email: yiyi@uvic.ca.

Notes

The authors declare no competing financial interest.

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