Title

Waste containment ponds are a major source of secondary organic aerosol precursors from oil sands operations

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Abstract

The surface mining and bitumen extraction of oil sands (OS) generates over one million barrels of heavy oil each day in the Alberta Oil Sands Region of Canada. Recent observations suggest

that emissions from OS development contribute to secondary organic aerosol (SOA) formation, but the chemical composition, mass fluxes, and sources of those emissions are poorly delineated. Here, we simulated OS extraction and used comprehensive two-dimensional gas chromatography to quantify and characterize direct air emissions, bitumen froth, residual wastewater, and tailings components, ultimately enabling fate modeling of over 1,500 chromatographic peaks simultaneously. During the non-ice cover season, tailings ponds emissions contributed 15,000 - 72,000 metric tonnes of hydrocarbon SOA precursors, translating to 3,000 - 13,000 tonnes of SOA, whereas direct emissions during the extraction process itself were notably smaller (960 ± 500 tonnes SOA yr^{-1}). These results suggest that tailings pond waste management practices should be targeted to reduce environmental emissions.

Introduction

The Athabasca Oil Sands Region (AOSR) in Alberta, Canada is home to the world's largest oil sands (OS) deposit, with 1.84 trillion bbl in reserve¹. Wastewater generated as part of OS extraction has accumulated to nearly one billion cubic meters and contains fine tailings, residual bitumen, organic acids, solvents, and salts. This OS process water (OSPW) has demonstrated toxicity to aquatic life²⁻⁶, and "zero-discharge" policies necessitate its transfer to tailings ponds⁷ (lined, open pits covering 220 km² of the AOSR⁸). Residual hydrocarbons volatilizing from storage ponds (volatile organic compounds, VOCs) could contribute to secondary organic aerosol (SOA) formation via atmospheric transformation⁹⁻¹⁰ of organic molecules into particulate matter, and both VOCs and SOA have impacts on human health and climate¹¹⁻¹². Indeed, recent field-based estimates suggested SOA formation rates from all OS operations in the remote AOSR were on par with major metropolitan areas¹³. However, qualitative chemical characterization and quantitative apportionment among various OS processing steps are lacking¹⁴, limiting strategic reduction and management of SOA precursor emissions.

Several investigators have measured ambient concentrations of hydrocarbons in local air samples near tailings ponds¹⁵⁻¹⁷ and subsequently modeled air-water transfer¹⁸⁻¹⁹, but these studies are inherently influenced by other ambient sources (e.g., fuel combustion or wood burning). Similarly, direct field measurements of bitumen hydrocarbons released from OS upgrading facilities are difficult to obtain due to access restrictions. The approach used to process OS depends both on the depth of the deposit and adhesion of the oil to the sand carrier. Ores in the AOSR are water-wet (i.e., there is a layer of water between the sand carrier and the bitumen), and heat or mechanical agitation with hot water can liberate the sand-associated

bitumen²⁰. For deep deposits, *in situ* extraction techniques such as steam-assisted gravity drainage (SAGD) can be deployed²¹. However, for shallow deposits, *ex situ* extraction approaches are needed. Such surface mining and hot water bitumen extraction accounts for over 1 million bbl d⁻¹ of Canadian production (i.e., 46% of Canadian OS production in 2018)²². Following surface extraction, OS ore is combined with hot water, occasionally alkalized via NaOH addition, and mechanically agitated with aeration to enhance bitumen removal and floatation, creating a froth that can be collected for further refinement. Stripping of some organic compounds into the gas phase is inherent to this aeration strategy, and this represents a potentially large, yet unquantified, source of SOA precursors during OS extraction (i.e., direct processing emissions) in the volatile, intermediate-volatility, and semivolatile organic compound ranges, defined here as VOC ($n\text{C}_2\text{-}n\text{C}_{12}$), IVOC ($n\text{C}_{13}\text{-}n\text{C}_{19}$), and SVOC ($n\text{C}_{20}\text{-}n\text{C}_{26}$), respectively²³. Ultimately, post-processing emissions of SOA precursors occur when the residual wastewaters generated by the extraction are removed to open containment ponds that are in active exchange with the atmosphere (i.e., indirect emissions).

Strategic reductions in environmental impacts associated with OS production require knowledge of the relative size and composition of each of these source terms. Furthermore, the chemical character of the volatilized and water-soluble compounds from or in OSPW must be identified to predict SOA formation and potential impacts to aquatic systems. Indeed, Tokarek et al.²⁴ emphasized the urgency of this need and the paucity of data, especially in the IVOC and SVOC ranges, where source and compound-specific information is severely limited^{14, 25}.

Here, we modified an industry-accepted, laboratory-scale OS hot water extraction simulator to enable closed-system collection of bitumen hydrocarbons across resulting process media (i.e., air, froth, OSPW, and tailings) (see Supporting Information (SI) Figure S1). The

qualitative chromatographic composition and quantitative fate of each peak was determined using comprehensive two-dimensional gas chromatography (GC×GC), providing estimates of *direct* emissions from OS extraction processing from hot water extraction. Leveraging chromatographic retention parameters, we estimated molecular equilibrium partitioning descriptors (e.g., air-water and water-solid partitioning constants) for over 1,500 peaks simultaneously, allowing calculation of the total *indirect* emissions to the atmosphere from waste storage ponds during non-ice-cover months. Finally, chemical-class specific SOA formation yields were used to determine the total SOA production from direct extraction and indirect post-processing OS emissions. Coupled with the qualitative chromatographic profile information presented here, these results could enable both better tracking of OS-derived hydrocarbon sources to the atmosphere and inform targeted emissions mitigation strategies.

Methods

Samples. OS samples were purchased from the Oil Sands Sample Bank at Alberta Innovates Technology Futures (now Innotech Alberta; innotechalberta.ca). Samples used in this study were high grade, as determined by the producer, and received in 10-L pails. Note that high-, medium-, and low-grade samples were available for analysis, but only one grade was analyzed in replicate in order to reduce computational complexity. In 2019, 100% of oil sands processed in Canada met the requirements for “high grade” (greater than 10% bitumen content). Further, Innotech reported that the sample reflects an effort to homogenize the heterogeneous sources of high grade OS (i.e., it is not single source). Our subsample of this bulk sample was homogenized and stored in glass jars under refrigeration in the dark.

Batch extraction unit. A benchtop batch extraction unit (BEU; SI Figure S1) was fabricated by the Gibbs Machine Shop at Yale University from 316 stainless steel following

designs by Syncrude²⁶. Note the BEU design is commonly used to simulate the industrial-scale hot water extraction process²⁷⁻³⁴. The BEU design was modified to include a cap and sampling port for which a polyurethane foam (PUF) filter could be installed to collect air emissions. The impeller was powered by a variable speed drill press.

Oil sand extraction. Once the BEU reached a temperature of 75 °C, 500 g of raw oil sand ore was added with 200 mL of 75 °C Milli-Q water. The lid was closed, pre-cleaned PUF filters and housing attached, and the impeller was set to 600 rpm with 7 mL s⁻¹ airflow from an ultra-zero air tank. Following industry guidance²⁶, after 10 minutes, the lid was opened and approximately 1 L of 80 °C Milli-Q water was added to bring the bitumen froth close to the top of the BEU walls. The lid was then closed, and the impeller was set to 600 rpm for 10 minutes with no airflow. Afterwards, the froth was skimmed from the top of the water and stored in 250-mL amber jars. Separation of the bitumen from the sand particle was enhanced after more water was added after the initial agitation and aeration phase (simulating hydrotreatment). For this final extraction, the impeller operated at 780 rpm with 3.9 mL s⁻¹ airflow for 5 minutes, as recommended. The remaining froth was skimmed and collected, and the remaining water and coarse tailings were collected separately and stored in pre-combusted amber jars. Some residual froth remained on the walls of the BEU and impeller, accounting for the 3% discrepancy in recovered hydrocarbons compared to the raw ore extract. Duplicate samples, each analyzed in duplicate, were processed to calculate hydrocarbon recovery. Finally, the PUF filters were immediately removed and packed into accelerated solvent extraction (ASE) cells for processing.

Dean – Stark hydrocarbon extraction. Approximately 20 g of solid sample (raw ore, froth, or coarse tailings) were add to a cellulose Soxhlet extraction thimble and refluxed with toluene for at least 24 hrs until the solvent was colorless when in contact with the thimble. Any

water that had refluxed and collected in the trap was drained and volumetrically measured. The extraction solvent was subsequently concentrated via rotary evaporation and the final extract was stored below 0°C until analysis.

OSPW separation. Oil sands produced water (OSPW) was centrifuged at 4,000 rpm for 60 min in borosilicate glass centrifuge tubes. The aqueous layer was decanted into a separatory funnel and acidified with 50% v/v HCl to pH below 2 to prevent formation of an emulsion in preparation for liquid-liquid extraction. The remaining solid fraction, defined as the fluid fine tailings (FT), was dried overnight at 100°C under vacuum before accelerated solvent extraction.

Liquid – liquid extraction of OSPW. The sample was extracted three times with toluene using gentle agitation for several minutes to prevent emulsion formation. The two phases were allowed to separate for at least three hours. The organic fractions were combined and dried with Na₂SO₄ and concentrated via rotary evaporation to approximately 1 mL.

Accelerated solvent extraction of polyurethane foam (PUF) and fine tailings (FT). PUF filters were extracted three times with dichloromethane (DCM) at 1,500 psi with 10-minute static holds at 100°C. FT samples were extracted three times with toluene under the same conditions. All extracts were concentrated via rotary evaporation to approximately 1 mL. Note that PUF filters are not quantitative for compounds lower than *n*C₆ equivalent volatility, which is a suitable limitation as our study range is *n*C₉-*n*C₂₅.

Comprehensive two-dimensional gas chromatography (GC×GC). Analysis was performed on a LECO Pegasus 4D using both time-of-flight (TOF) mass spectrometric detection and flame ionization detection (FID). Sample extracts were analyzed in duplicate. For the TOF analysis, the primary column was a Restek Rxi-1ms (60m x 0.25mm x 0.25 um) and the secondary column was a BPX-50 (2m x 0.1mm x 0.1um). Samples were injected in splitless

mode with an inlet temperature of 300°C and 1 mL min⁻¹ helium carrier gas. The oven temperature program was held static at 50 °C for 15 min, ramped to 315 °C at 1.75 °C min⁻¹ and held for 30 min for a total run time of 196 min, while the secondary oven and modulator were offset 5 °C and 15 °C, respectively. The modulator was programmed to alternate a 1-sec hot pulse and 5-sec cryogenic focus for a total modulation period of 12 sec. The TOF scanned across 35 – 500 mass units at 50 spectra sec⁻¹ at a detector voltage of 1641 and 70 eV ionization, with a source temperature of 230 °C.

GC×GC-TOF-MS was used for all tentative hydrocarbon identification. Peak identification was delineated using the mass spectrometer and ChromaTOF software. In particular, individual peaks within the range of *n*C₇-*n*C₄₀ were designated if they met the following criteria: baseline offset of 0.5 (through the middle of the noise), a signal to noise (S/N) ratio of 25, expected peak width of 30s (1st dimension) and 0.2s (2nd dimension), with a minimum S/N ratio of 6 for subpeaks within in the single chromatographic feature. We note that the total number of annotated peaks (e.g., outside the *n*C₇-*n*C₂₅) was higher than 1500, and each peak may represent more than one compound, even with the exceptional resolving power of the multidimensional chromatography.

The FID analysis used the same oven temperature program and primary and secondary columns, with an additional deactivated guard column (0.1 m x 0.1 mm) between the secondary oven and the FID. The modulator was programmed to alternate a 3-s hot pulse and 7-s cryo focus for a total modulation period of 20 s. The FID was set to 300 °C with H₂ of 45 mL min⁻¹, 450 mL min⁻¹ air, and 45 mL min⁻¹ He makeup, with a data collection rate of 50 Hz. GC×GC-FID was used for total petroleum hydrocarbon (TPH) quantification. TPH in a *n*-alkane volatility range of *n*C₇-*n*C₄₀ was reported for bulk hydrocarbon quantification of raw materials (raw OS, froth,

OSPW, tailings), and the nC_9 - nC_{25} volatility range was quantified and reported for emissions modeling (see SI for details).

An Iraq light crude oil was analyzed via the same GC×GC-FID program as the oil sand extraction fractions in order to create a rapid classification method to apply to all samples. Regions were drawn on the two-dimensional chromatogram using LECO's ChromaTOF software for all eluting 1) alkanes, 2) single ring aromatic compounds, 3) PAHs, and 4) other compounds using reference standards to confirm elution space. These classifications, applied to the peaks detected in the oil sands samples, guided the SOA yield calculations for the direct extraction emissions and the tailings ponds mass transfer modeled emissions. Heteroatom-containing compounds commonly found in oil sands were not separately distinguished in this compound classification approach and the effects of this are discussed in the Supplemental Information; briefly, whereas the retention index preserves the partitioning behavior, the main impact of unforeseen heteroatoms will manifest in the assigned SOA-formation potentials.

Tailings pond emissions model. A two-film boundary layer model (Equation 1) was used to predict mass transfer rates of each individual peak qualitatively identified by GC×GC-MS and quantified by GC×GC-FID (using duplicate analyses of OSPW from duplicate BEU extractions; see SI for quantification details), where environmental partitioning parameters were estimated from chromatographic retention times as described below.

Mass transfer for each peak was calculated as:

$$Mass\ Flux_{water} = -v_{i,aw} \left(C_{i,w} - \frac{C_{i,a}}{K_{i,aw}} A_w \right) \quad \text{Equation 1}$$

where C_{ia} and C_{iw} are the concentrations of a compound, i , in the air and water, respectively, A_w is the surface area of the water, K_{iaw} is a compound i 's air-water dimensionless partitioning coefficient, and $v_{i,aw}$ is the air – water transfer velocity defined by:

$$\frac{1}{v_{i,aw}} = \frac{1}{v_{i,w}} + \frac{1}{v_{i,a}K_{i,aw}} \quad \text{Equation 2}$$

$$v_{i,a} = \frac{D_{i,a}}{\delta_a} \text{ and } v_{i,w} = \frac{D_{i,w}}{\delta_w} \quad \text{Equation 3}$$

where $v_{i,a}$ and $v_{i,w}$ are the air- and water-mediated transfer velocities, respectively; $D_{i,a}$ and $D_{i,w}$ are molecular diffusivities in air and water, respectively; and δ_a and δ_w are the stagnant film thickness of air and water, respectively.

To account for hydrocarbon sorption to tailings particles, we adjusted the compound concentrations according to the fraction of a compound i in the aqueous phase, f_{iw} :

$$f_{i,w} = \frac{1}{1 + K_{i,d} \frac{M_s}{V_w}} \quad \text{Equation 4}$$

where V_w is the volume of water, M_s is the total mass of solids, and $K_{i,d}$ is the sediment-water partition coefficient defined by:

$$K_{i,d} = K_{i,oc} * f_{oc} \quad \text{Equation 5.}$$

Here, $K_{i,oc}$ is defined as the organic-carbon-water partitioning coefficient for a compound i (calculated following Nabi et al. ³⁶, as described below) and f_{oc} is the fraction of organic carbon (0.0027±0.0003, n=3; measured by Interek Labs, Whitehouse, NJ).

Molecular diffusivities in air and water were corrected for assumed field temperatures adapted from *Parajulee and Wania* (2014) (SI Table S1)^{18, 35}. Tailings pond surface area, OSPW volume, and solids fraction were found in the literature (see Table S4)^{8, 38} Finally, we developed

the model under two modes: an *active* pond was assumed to have a constant input of fresh material (i.e., C_{iw} was continuously refreshed based on the composition of the OSPW), whereas an *inactive* pond had a single input every month with no additional volume withdrawal or replenishment (i.e., C_{iw} is allowed to be depleted monthly). These two modes were intended to capture the range of realistic operating conditions for tailings ponds in the field.

Calculation of partitioning parameters based on the GC×GC retention space. Briefly, using a column configuration of a primary hydrophobic stationary phase coupled to a secondary polar stationary phase, the equilibrium partitioning constants for air-water and water-solid partitioning can be modeled directly from the retention profile³⁶⁻³⁷ (i.e., the retention index is a measure of a compound's physicochemical behavior; separations in the first dimension are based on vapor pressure while separations in the second dimension are based on polarity). Thus, the parameters $K_{i,aw}$ and $K_{i,oc}$ were estimated following Nabi et al.³⁶ for each chromatographic feature, while $D_{i,a}$ and $D_{i,w}$ were calculated based on molecular weight³⁵, also derived using GC×GC. This approach has been demonstrated by others for obtaining partitioning parameters of compounds with volatilities between nC_9 – nC_{25} , and we limit application of the technique to that same range to avoid extrapolation error.

Reported Uncertainty. Uncertainty in the results presented here are attributed to sample analysis, compound partitioning property estimation models, and SOA formation factors. Uncertainty in analytical results of sample hydrocarbon content are due to duplicate Dean-Stark solvent extractions (solid samples), duplicate accelerated solvent extractions (air emission PUF filters), and duplicate liquid-liquid extractions (OSPW). All extracts were analyzed in duplicate via GC×GC-FID for quantification. Uncertainty due to the property estimation models was bound by the 95 percent confidence interval from the Nabi et al. (2014) model output. Additional

uncertainty in reported emissions is from SOA formation factors adapted from Gentner et al. (2012) (SI Table S2)³⁹. Finally, the standard error on SOA emissions from ponds captures the wide range of operating modes for new OSPW inputs to the tailings ponds: an *active* pond was assumed to have a constant input of fresh material, whereas an *inactive* pond had a single input monthly with no additional volume withdrawal or replenishment.

Results and Discussion

Raw oil sand characterization

Duplicate bulk analysis from the Dean-Stark extractions indicated that the high-grade raw OS ore averaged 9-10% w/w bitumen, 4-5% water, and 85-86% w/w solids. The chemical character of the OS bitumen was remarkably complex, more than a typical crude oil. Specifically, there was a high degree of branched and cyclic alkanes and aromatic hydrocarbons (Figure 1), reflective of a heavily bio-processed petroleum. Despite the unparalleled resolving power of GC×GC, linear *n*-alkanes and the isoprenoids (i.e., pristane and phytane) were not independently resolved (even using methods that successfully resolved these compounds in an Iraq light crude oil; Figure 1b). Efforts to enhance separation via silver-impregnated silica gel preparative chromatography⁴⁰ were unsuccessful. Furthermore, *n*-alkanes were below detection in soft-ionization mass spectrometric analyses (e.g., gas chromatography-atmospheric pressure chemical ionization-quadrupole time-of-flight mass spectrometry (GC-APCI-QTOF-MS⁴¹)), consistent with previous OS characterization with heavy biodegradation⁴². The total mass of hydrocarbon in the *n*C₉-*n*C₂₅ volatility range was 13.5 ± 0.9 g kg_{ore}⁻¹ (n=2), including the IVOCs-SVOCs that may act as critical SOA precursors. (This range is amenable to partitioning

parameter estimation³⁶). Less volatile hydrocarbons (nC_{26} - nC_{40}) were also detected in the raw bitumen ($3.6 \pm 0.5 \text{ g kg}_{\text{ore}}^{-1}$, $n=2$).

Figure 1. Two-dimensional GCxGC-FID chromatograms of the oil sand batch extraction unit fractions. These show similar elution patterns of the hydrocarbons in the (A) raw ore and the (C) froth once water is removed, while the (D) OSPW and (E) FT profiles differ based mainly on the water-soluble components. The air emissions contain nearly all alkanes (branched and cyclic) with a small amount of heteroaromatic compounds as tentatively identified by the GCxGC-TOFMS analysis. A reference (B) crude oil analyzed with the same GCxGC method indicates baseline resolution of the petroleum hydrocarbons; baseline resolution of the saturated hydrocarbons was not possible in the OS samples. Note here that the secondary axis scales are identical, and that the color scale in each panel is optimized for best viewing and the max intensity does not correspond to the same mass abundance by flame ionization detection (FID) in each panel.

Fate of extracted hydrocarbons

To determine the fate of bitumen hydrocarbons throughout the extraction process, we built a representative bench-scale batch extraction unit (BEU) following industry guidance²⁶, modified to collect emissions from aeration on polyurethane foam (PUF) filters⁴³⁻⁴⁴. We defined resulting fractions as direct air emissions, OSPW, froth (i.e., product), and fine tailings (SI Figure S1). As required by the Alberta Energy Regulator for a 10% w/w OS ore, we were able to recover up to 88% of the total hydrocarbon content was recovered in the product froth (see SI Figure S2)⁴⁵, where the chemical distribution was similar to the raw oil chromatographic fingerprint (Figure 1) and the majority of hydrocarbons were in the C₉-C₂₅ range.

The remaining hydrocarbon mass was in products that will ultimately be discharged to the environment or containment systems: 5.3 ± 1 % and 3.5 ± 1 % total hydrocarbon mass was associated with the coarse tailings (CT) and fine tailings (FT), respectively; 0.17 ± 0.1 % was in the OSPW; and 0.3 ± 0.2 % was directly emitted to the atmosphere (SI Figure S3; remaining 3% losses to BEU components). Due to acidification of the aqueous phase of the centrifuged OSPW prior to liquid-liquid extraction, the hydrocarbon content reported here reflects the behavior of protonated compounds and is potentially greater than expected in the field (e.g., due to reduced water solubility of non-ionic species).

There was a broad range in the polarity and hydrophobicity of organic materials associated with tailings (Figure 1e). CT are heavier sand particles that rapidly settle during bitumen separation and remove their hydrocarbon burden with them, whereas FT fractions are stable during transport to containment ponds and have very long settling times (e.g., 10 years to consolidate to 44% solids⁷), allowing for equilibration with the aqueous OSPW. The distinction between fully dissolved (Figure 1d) and colloid-associated organic matter is sometimes neglected in OS wastewater studies^{19, 46}, but it is critically important for (a) estimates of total

biological exposure and (b) accurate estimation of indirect, post-processing emissions from tailings ponds.

Direct emissions during hot water extraction

Air emissions generated in the hot water extraction process emitted directly to the atmosphere⁴⁷ amounted to $35 \pm 0.7 \text{ mg kg}_{\text{ore}}^{-1}$; 0.3% of the $\text{C}_9 - \text{C}_{25}$ hydrocarbons in the extractable bitumen (Figure 1 and S3, Table S3). These hydrocarbons include branched and cyclic alkanes, as classified by the GC×GC retention space, that accounted for 98% of the total mass of air emissions, predominantly ranging in *n*-alkane equivalent volatility of $\text{C}_9 - \text{C}_{14}$ (Figure 2a). The regions designated as single- and multi-ring aromatic compounds (including parent, alkylated, and heteroatom-containing compounds) accounted for 1.8 and 0.6% of total hydrocarbons measured in the air emissions sample, respectively, with a small portion of unclassified material (0.08% “other;” see SI Figure S4).

Figure 2. Emissions and potential SOA from hot water extraction. (A) The volatility distribution of hydrocarbon emissions from the hot water extraction process shows the most volatile components of the oil sands ore are lost to the atmosphere, and the emission composition is primarily alkanes (branched and cyclic). Error bars represent standard deviation on duplicate measures from duplicate extractions of high grade ore. (B) The SOA yield from the emissions generated during the hot water extraction is dominated by alkanes, with a relatively larger contribution coming from one ring aromatic compounds and PAHs. Error bars capture analytical uncertainties and those uncertainties associated with the SOA formation factors (see Table S2).

While the direct emissions represented only a small fraction of the total bitumen hydrocarbons, the large mass of OS ore mined and processed in the AOSR (8.30×10^8 metric tonnes in 2018⁴⁸) could translate to $28,600 \pm 600$ metric tonnes of emitted hydrocarbons each year (78 ± 2 tonnes d^{-1}) (Table 1). These compounds are largely IVOCs and some SVOCs, which are not typically measured in the AOSR explicitly and may have been previously unaccounted. Recent efforts to measure SOA precursors this region observed large contributions in the IVOC range, citing surface mining and tailing ponds as potential sources, but the methods deployed were not able to interrogate SVOC contributions. Earlier measurements have focused on specific VOCs (e.g., benzene, ethylbenzene, toluene, and xylenes) from integrated sources⁴⁹⁻⁵⁰ or have simulated emissions via thermal desorption from a low-grade, weathered bitumen rock in the absence of an aqueous phase¹³. Taken together, the IVOC and SVOC emissions reported here provide the first qualitative and quantitative description of this important processing source over this volatility range.

Table 1. Estimated hydrocarbon and SOA emissions from oil sands extraction and tailings ponds. Ranges reflect incorporation of all uncertainties described in the methodology.

	Hydrocarbons (tonnes d^{-1})	Secondary Organic Aerosol (tonnes d^{-1})
Extraction Emissions (this study)	76 - 80	1.4 - 3.9
Modeled Tailings Ponds Emissions (this study)	70 - 340	14 - 60

Liggio et al. (2016) deposition corrected SOA	--	55 - 101
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Indirect post-processing emissions from tailings ponds

To estimate the transfer of OS-derived hydrocarbons to the atmosphere from waste containment ponds, we applied a two-film boundary layer model³⁵ and calculated total mass flux to the atmosphere from AOSR tailings storage ponds. In order to develop this estimate, the critical environmental partitioning parameters of the more than 1,500 detected chromatographic features present in OSPW extracts were estimated from their retention indices in the two-dimensional gas chromatogram^{36, 51}. Prediction statistics for $\log K_{i,aw}$ and $\log K_{i,oc}$ were generally good using the 79-compound nonpolar training set of Nabi et al.³⁶ ($r^2 = 0.86$, $rmse = 0.51$; $r^2 = 0.96$, $rmse = 0.32$, respectively). Hydrocarbons sorbed to FT and dissolved within OSPW have the opportunity to outgas during the non-ice cover months (from April to October¹⁸) (SI Table S1), and total mass fluxes were estimated to be $41,000 \pm 11,000$ (mean ± 1 sd) metric tonnes (nC_9 - nC_{25}) over the modeled 7-month period (191 ± 50 tonnes per day of non-ice cover) (Table S5). For context, the total anthropogenic VOC emissions in Los Angeles are 960 ± 140 tonnes per day⁵². Somewhat remarkably, these indirect emissions from the waste containment practices are on the same order of magnitude as the direct emissions from the OS processing itself.

Uncertainty in the modeled flux (reported as a range) is partially due to the partitioning property estimation, using the 95% confidence intervals for the estimated partitioning parameter for each peak, uncertainty in SOA yields, as well as experimental error and analytical replicates (see methodology). Furthermore, the apparently large error also captures the wide range of operating modes for new OSPW inputs to the tailings ponds: an active pond was assumed to have a constant input of fresh material, whereas an inactive pond had a single input with no additional volume withdrawal or replenishment.

Accounting for sorption equilibrium to the tailings particles (Equations 4-5) reduced water-to-air transport by 37-64% total mass (compared to volatilization without considering sorption), depending on the sorptivity of the compound. Functionally, this means that the organic burden remaining on the tailings can act as a sink, thereby removing a substantial amount of dissolved-phase hydrocarbons. To determine this, the measured hydrocarbon concentration in the aqueous and tailing-associated phases (Figure 3a) and the sorption equilibrium-corrected $f_{i,w}$ (aqueous fraction of a compound i (Figure 3b)), were used to estimate the total mass flux from the tailings ponds (Figure 3c). For example, $f_{i,w}$ for a non-polar, lower-volatility compound was on the order of 10^{-8} , indicating the compound would be fully associated with tailings particles (Figure 3b). For the majority of OS-extracted organic compounds, the mass load associated with tailings was greater than 90%, where $f_{i,w}$ decreased with lower volatility (i.e., later first dimension retention times) and lower polarity (i.e., earlier second dimension retention time) (Figure 3b). Accordingly, mass fluxes (Figure 3c) were greatest for compounds that had relatively low aqueous solubilities (e.g., low polarity) and moderate volatility *and* were present in both the FT and aqueous OSPW (i.e., had sufficient abundance to outgas).

Figure 3. Individually modeled peaks detected in the two-dimensional chromatogram. (A) The chromatographic composition and calculated abundance of the hydrocarbons in the OSPW and FT applied to the assumed tailings pond volume (SI Table S4). **(B)** Calculated f_{iw} (Eq. 4) reveal a pattern of decreasing water fractional abundance as compounds become less volatile (eluting later in the first dimension) and less polar (eluting earlier in the second dimension), which is the expected pattern within the two-dimensional chromatogram. The f_{iw} was used to adjust the measured water concentration before applying the mass transfer model. **(C)** The results of the model for the hydrocarbons in the two samples show mass transfer rates from the tailings ponds to the atmosphere on the order of kilograms per day for the most volatile (early first dimension retention time (RT)) and least water soluble (early second dimension RT) compounds. Note that all uncertainties are described in detail in the SI and the “Reported Uncertainty” section of the methods.

For the most abundant compounds, cumulative losses to the atmosphere could be over 500 kg in a single month (e.g., July; Figure 4), where compound-specific mass transfer rates could reach up to 100 kg d⁻¹ for the total surface area of tailings ponds (220 km²; translating to

fluxes of $39 \text{ g m}^{-2} \text{ s}^{-1}$). Nevertheless, based on f_{oc} (fraction of organic carbon) measurements ($0.20 \pm 0.03\%$) and predicted organic carbon sorption partition coefficients ($\log K_{oc}$ 2.2 to 10.5), the sorptive potential of individual compounds (i.e., K_{id}) detected in the OSPW to FT particles were as high as $10^9 \text{ m}^3 \text{ kg OC}^{-1}$. That is, the existence of the FT waste stream, and the residual organic carbon on those FT particles, is functionally reducing the flux of organic chemicals to the atmosphere from post-processing sources.

Figure 4. Total cumulative hydrocarbon emissions for the month of July. Calculations using the two-film mass transfer model show the evolution of over 1,500 chromatographic features simultaneously, plotted relative to 1st and 2nd dimension retention times (R.T.) in comprehensive two-dimensional gas chromatography.

This is the first study that calculates bitumen-derived hydrocarbon emissions from tailings ponds on a peak-specific and compound class-specific basis over a broad volatility range. Previous studies have evaluated the influence of tailings ponds emissions on individual PAHs in

413 AOSR air samples through mass transfer models¹⁸⁻¹⁹. For example, Galarneau et al. (2014)
414 combined field measurements with flux calculations and concluded that loadings from tailings
415 ponds to the atmosphere is as high as 1,069 kg yr⁻¹ for 13 priority PAHs¹⁹. Furthermore, they
416 found that the loading was dominated by lower molecular weight PAHs like phenanthrene and
417 pyrene. Similarly Parajulee and Wania (2014) demonstrated through modeling efforts that
418 tailings ponds contribute a significant load of PAHs through volatilization (1×10^6 kg of
419 phenanthrene and 3.6×10^5 kg pyrene over the course of a 42-year modeling period) and noted
420 that larger PAHs with lower air-water partitioning coefficients contribute less to tailings ponds
421 emissions as they are sequestered by the solid particles¹⁸. While not directly comparable, these
422 findings are within the same order of emissions found from our partitioning model (e.g., $5,430 \pm$
423 17×10^3 kg yr⁻¹ total PAHs). Others have measured air quality around tailings ponds, testing for
424 VOCs⁵⁰ only, finding levels up to 2-4 times the background values. Recent lab-simulated
425 studies²⁵ aerated tailings pond samples for some unstated period of time, measuring volatile
426 species. In comparison with our work, these studies suggest that failure to account for IVOCs
427 and SVOCs may lead to large underestimates in SOA formation potential. The modeling effort
428 presented here provides an estimate of local hydrocarbon emissions without measurement
429 interference from other sources (e.g., combustion) and does so using robust direct measurements,
430 chemical equilibrium, and mass transfer principles. Combining these laboratory-derived
431 predicted emissions for each compound and SOA formation parameters for specific compound
432 classes³⁹ enables estimation of field-based air quality impacts, such as the formation of OS-
433 associated SOA. While it is important to note that the results presented here are specific to our
434 experiments and extrapolated to the larger OS wastewater domain, the approach is one that can

be applied across practitioners studying mass transfer of hydrocarbons in tailings pond field studies and beyond.

Secondary organic aerosol formation

Liggio et al.¹³ recently estimated 55 – 101 metric tonnes SOA d⁻¹ due to OS operations in the AOSR. That work represented an important first estimate for the region via aircraft measurements. Here, we sought to quantify specific emissions pathways of SOA precursors to inform targeted reduction from OS extraction process and waste management. To calculate SOA formation potential, we applied previously-reported SOA yields for a NO_x-present regime (1 – 15 ppb NO_x) with OH-initiated oxidation chemistry and organic aerosol (OA) loadings of 10 ug m⁻³, based on field observations of OA and NO_x downwind of OS operations^{13, 39}. SOA precursors were separated into four compound classes (alkanes, single-ring aromatic compounds, PAHs, and ‘other’) across equivalent n-alkane volatility ranges (Figure S4), and previously determined SOA yields³⁹ were applied to each bin. Since SOA yields for the ‘other’ compound class are not specified, this class was assigned either a conservative or high SOA yield (i.e., of the alkane group or the PAH group, respectively) to determine a potential SOA range.

SOA formation from hot water extraction (i.e., “direct”) emissions was approximately 1.15 ± 0.55 mg SOA kg_{ore}⁻¹, with uncertainty reflecting the analytical measurement and SOA formation factors³⁹ (Figure 2b). The majority of SOA resulted from alkane precursors (74%) due to their large mass fraction, while single-ring aromatic compounds and PAHs contributed 15% and 11%, respectively (Figure 2b). The relative contribution of single-ring and PAH compounds to the total SOA is disproportionately high compared to their minor abundance (2.2% total; Figure 2a) due to their higher SOA yields (SI Table S2). Applying the conservative and high yield estimates to the ‘other’ compound class had a modest effect on overall SOA precursor

contribution (0.01 and 0.07%, respectively), as the “other” compound mass fraction is small relative to total hydrocarbon emissions. Extrapolating these SOA formation potentials to the total ore processed by surface mining and hot water extraction in 2018 (8.30×10^8 metric tonnes), direct emissions in the AOSR could account for up to 960 ± 500 (mean ± 1 sd) metric tonnes SOA annually (2.6 ± 1.4 tonnes d^{-1} , a minor fraction of the total estimated by Liggio et al.¹³; Table 1; Figure 2).

In comparison, SOA yields applied to the modeled hydrocarbon emissions from the tailings ponds within the AOSR resulted in 7250 ± 4900 (mean ± 1 sd) metric tonnes SOA over the 7-month period (33 ± 23 tonnes d^{-1}), capturing uncertainty in the analytical measurement, the predicted K_{aw} and K_{oc} , and SOA yields (but excluding uncertainty associated with extrapolating a lab measurement to the field implicit in the approach). This is a striking result: the direct emissions from OS hot water extraction are responsible for as little as 1% of total SOA formation, whereas emissions from tailings ponds are an order of magnitude larger. Note that organic compounds from waste containment ponds represent a larger source of SOA potential than OS processing itself due to the chemical composition of the OSPW and the tailings: these wastewater constituents have much higher compound-class specific SOA yields. From the waste containment ponds, the largest contributions of SOA were from single-ring aromatic and PAH precursors (49% and 42%, respectively) compared to alkanes (8%) and remaining ‘other’ compounds (1.0 – 4.0%). Taken together, we estimate that SOA formation potential from both hot water extraction emissions and tailings ponds emissions could be in the range of 3,700 – 14,000 metric tonnes SOA annually (Table 1).

Limitations. Importantly, we acknowledge that there are clear limitations to the model presented here and its extrapolation to a large, field system. First, in hot-water processing of OS ore, chemical additions such as organic diluents or pH adjusters⁵³ will affect both the hydrocarbon recovery in the froth (thereby influencing residual hydrocarbon discharged to tailings ponds) and contribute to hydrocarbon emissions from the extraction itself (e.g., adding naptha-based diluents to the hot-water extraction units would likely increase VOC emissions). In tailings ponds, a host of physicochemical processes can affect the total mass and transfer rate of outgassed hydrocarbons. For example, biological transformation of residual hydrocarbons in OSPW from indigenous microbiota will change the chemical composition of over time⁵³ and should be explored experimentally, *in situ*. Furthermore, photooxidative processes reduce the organic burden by transformation of aromatic hydrocarbons⁵⁴ and degradation of naphthenic acids⁵⁵. These processes will change OSPW composition and the fate of individual compounds therein. Additionally, the presence of surface slicks and surfactants (e.g., naphthenic acids) in tailings ponds will generally decrease air-water mass transfer velocities through two mechanisms: (1) physically limiting diffusion and (2) hydrodynamic dampening of the water surface³⁵. In modeling mass transfer with a slick present, the film-water partitioning coefficient ($K_{i,f/w}$) is required³⁵, but this varies as a function of thickness. Lacking these field-measurements, we neglect these impacts in our model and encourage future study on the topic. Similarly, we reiterate that our laboratory simulation of a relatively small number of high-grade oil sands samples (duplicate extractions, each with duplicate analysis) only provides a first estimate that does not capture the potentially broad variability seen in the field system.

Implications and mitigation strategies. Primary separation vessels with open tops allow the ventilation of OS-derived hydrocarbons ⁴⁷ (less than 1% of the total extractable ore), and these emissions could be mitigated with simple control technologies such as wet scrubbing, activated charcoal filtration units, or catalysis. A larger source of hydrocarbon emissions with higher SOA yields comes from wastewater storage in tailings ponds, which represent a more formidable engineering challenge due to their vast size and distributed nature. Nevertheless, the partitioning calculations presented here indicate that sorption of the dissolved hydrocarbons to FT particles bears heavy influence on the total emissions from the tailings ponds. Complimentarily, emissions reductions through *in situ* sorption technologies may be viable mitigation strategies. For example, due to the hydrophobic nature of the majority of the material in the OS extracts and residual OSPW, activated carbon amendments could reduce atmospheric release. Further, but yet to be demonstrated, these same amendments may help encourage flocculation of the otherwise stable fine tailings, whose long settling rates currently limit reuse of the fluid and challenge long-term management of the ponds. The multiphase analyses presented here provide a route to estimate the mass flux of hydrocarbons detected in the OSPW and FT from the water to the atmosphere for hundreds of chromatographic features simultaneously. Though limited to bench-scale extractions, this approach can be directly translated to field-scale systems with proper assumptions. Similar analyses may be useful for future evaluation of treatment strategies where direct over-pond measurements are limited. Indeed, as air sampling campaigns are often challenged to identify individual emission pathways uniquely, emissions estimations from hot water extraction and modeled tailings ponds are crucial to understanding the air quality impacts and identifying opportunities for improved pollution prevention strategies.

Supporting Information Available Quantification and standards, SOA formation factors, processing of “other” compound class, and model parameters.

Conflict of Interest Statement The authors declare no conflicts of interest.

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