ACS ES&T Water

A Light Touch: Solar Photocatalysis Detoxifies Oil Sands Process-Affected Waters Prior to Significant Treatment of Naphthenic Acids

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Cite This: *ACS EST Water* 2024, 4, 1483−1497

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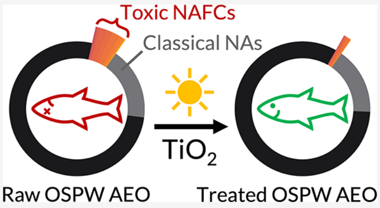


ABSTRACT: Environmental reclamation of Canada's oil sands tailings ponds is among the single largest water treatment challenges globally. The toxicity of oil sands process-affected water (OSPW) has been associated with its dissolved organics, a complex mixture of naphthenic acid fraction components (NAFCs). Here, we evaluated solar treatment with buoyant photocatalysts (BPCs) as a passive advanced oxidation process (P-AOP) for OSPW remediation. Photocatalysis fully degraded naphthenic acids (NAs) and acid extractable organics (AEO) in 3 different OSPW samples. However, classical NAs and AEO, traditionally considered among the principal toxicants in OSPW, were not correlated with OSPW toxicity herein. Instead, nontarget petroleomic analysis revealed that low-polarity organosulfur compounds, composing <10% of the total AEO, apparently accounted for the majority of waters' toxicity to fish, as described by a model of tissue partitioning. These findings have implications for OSPW release, for which a less extensive but more selective treatment may be required than previously expected.

KEYWORDS: *photocatalysis, toxicology, passive treatment, oil sands, naphthenic acids, target lipid model, biomimetic extraction, exposomics, petroleomics*

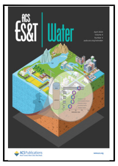
■ INTRODUCTION

Water remediation is a key challenge of environmental reclamation in Alberta's oil sands region. Water is integral to the bitumen mining operation, and from its inception, the oil sands industry has subscribed to a zero discharge practice,[1] storing all process waters on-site in tailings ponds. Nevertheless, freshwater input is still required for bitumen production,[2] which, together with the growth of the industry, has proliferated the volume and footprint of oil sands process-affected water (OSPW) stored, and associated environmental liability.[3] Toxic bitumen-leached organic chemicals,[4−6] recalcitrant to natural attenuation,[7,8] have accumulated in this process-affected water over intensive recycling, presenting a challenge to the industry's obligation to safely return this OSPW to natural watersheds.[9,10] To meet mine closure and reclamation timelines, a water treatment solution may be required.

Toward a Passive Advanced Oxidation Process (P-AOP). Passive treatment approaches, i.e., methods reliant on natural processes and energy sources without the need for significant electrical, chemical, or human interventions, form a mainstay of environmental remediation strategies in the natural resource sector due to their low carbon footprints and favorable treatment economics at scale.[11,12] Many passive systems can also integrate as features of the reclamation landscape: in the oil sands industry, mine closure plans include end pit lakes (EPLs) and treatment wetlands to remediate tailings and OSPW over protracted hydraulic retention time (HRT).[13−17] However, given the known biological recalcitrance of some of the dissolved organics, residual OSPW toxicity may persist through conventional passive treatments.[18−31] Advanced oxidation processes (AOPs), such as ozonation, while being powerful solutions to rapidly degrade organics and detoxify OSPW,[32−36] are not considered passive treatments, given their energy, chemical, and infrastructure requirements, and as such, may be financially impractical. There is an unmet need and technology gap for effective, rapid, and passive OSPW treatments.

The potential for passive operation was a guiding objective of our treatment process design herein.[37] Buoyant solar photocatalysis is a candidate passive advanced oxidation process (P-AOP),[38−41] combining the advantages of the two treatment paradigms typically considered diametric. Photocatalysts, such as TiO$_2$, generate reactive oxidizing species (ROS) under natural sunlight, providing electricity-independent organics treat-

Received: October 6, 2023
Revised: January 25, 2024
Accepted: January 25, 2024
Published: February 23, 2024



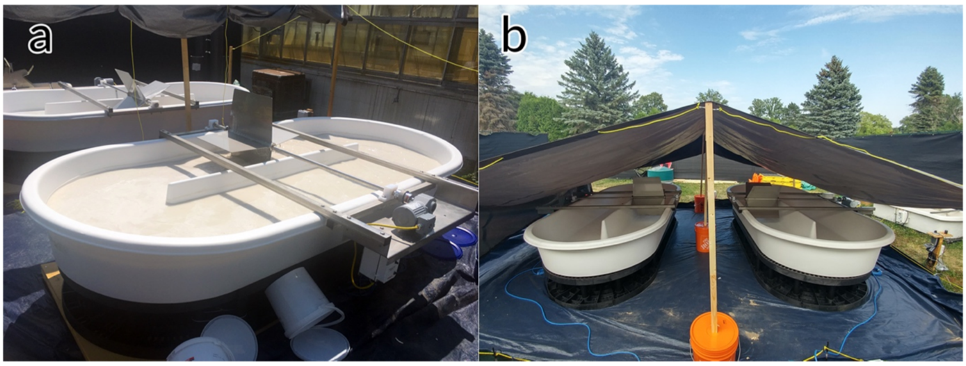


Figure 1. Overview of the outdoor treatment test site and raceway reactors. (a) Solar photocatalytic OSPW treatment is pictured in the foreground, operating with the tarp canopy retracted. (b) The raceway basins are covered by the canopy, with a weather station located to the right of the basins.

ment.[42,43] Buoyant photocatalysts (BPCs), photocatalyst-coated buoyant beads, passively self-separate to the air−water interface, avoiding sunlight exposure limitations from water turbidity[44] and facilitating low-energy catalyst recovery by skimming.[38,39,45]

The second element of our proposal was to use open "raceway" channel pools as hydraulically mixed plug-flow solar treatment reactors to promote radiance and mass transfer to BPCs during the OSPW treatment. Paddlewheels have proven energy efficient at mixing shallow pools for sunlight exposure,[46−49] and raceway pools have been optimized for decades in the aquaculture, biofuel, and wastewater treatment sectors and demonstrated at up to hectares in scale.[50] In this work, we combined paddlewheel mixed recirculating raceway photoreactors with BPCs under batch reaction conditions for semipassive OSPW treatment and as a model of solar photocatalytic treatment under open channel flow more generally; e.g., if mixed instead by natural elevation head loss, the treatment system would be fully passive.

Whole Effluent Toxicity (WET). Evaluating OSPW treatment has been challenging due to the waters' multifaceted toxicity, analytical complexity, and spatiotemporal heterogeneity. OSPWs have diverse toxic effects on aquatic organisms, e.g., acute lethality,[5] genotoxicity,[51,52] developmental deformities,[53,54] immune dysregulation,[55,56] endocrine disruption,[57,58] and behavioral abnormalities.[59,60] This toxicity has been associated with the waters' dissolved organics (especially the acid extractable organics, AEO)—once thought to be primarily naphthenic acids (NAs, with classical formula $C_cH_hO_2^-$), these compounds, now referred to as naphthenic acid fraction components (NAFCs), comprise complex mixtures of millions of unique molecular structures with various functional groups and heteroatom substituents, including but not limited to NAs; analytical characterization of this petroleomic diversity and establishing connections with toxic effects remain active fields of research.[61−64] Complicating matters further is that the chemical and toxicological profiles of OSPWs are not static with time; instead, they are significantly affected by the mined formation, process inputs, and natural weathering in the ponds.[65,66]

For wastewaters comprising this type of complex mixture toxicity, current government policy recommends whole effluent toxicity (WET) as a metric to regulate environmental discharge for the protection of aquatic life.[67,68] It is therefore important that candidate OSPW treatment processes be evaluated within a WET framework. A number of standard toxicological assays have been developed by Environment & Climate Change Canada for WET testing,[69] of which fish assays are among the most acutely sensitive to OSPW organics (and hence were selected for use herein);[4,18,70−72] other WET outcomes may be different. While standardized testing has merit for situating results within a broader environmental and toxicological context, toxicity testing beyond these selected organisms (e.g., with native fauna,[73,74] cell-line assays[75]) remains important for developing a comprehensive assessment of OSPW toxicity.

Previously, we evaluated photocatalytic OSPW treatment performance by analytical water chemistry;[39,42] however, the toxicity implications remained unclear. Here, we studied larger-scale solar photocatalytic treatment of multiple OSPWs toward both analytical chemistry and WET endpoints. Solar photocatalysis detoxified the waters to fish remarkably quickly despite minimal reductions in total dissolved organics concentrations having yet occurred. We found that AEO and NA concentrations were not correlated with WET outcomes; instead, untargeted omics MS analysis suggested organosulfur NAFCs, preferentially photocatalytically treated, apparently accounted for the majority of the OSPW toxicity.

MATERIALS AND METHODS

Materials. Three OSPW samples (~1 m^3 each) were collected into HDPE intermediate bulk containers (IBCs) from active tailings ponds at three different mining operations (different companies) near Fort McMurray, Alberta, Canada, in the summer, 2018, and transported by ground freight to the test site at 43°28′23.9″N 80°33′33.5″W in Waterloo, Ontario, Canada. Immediately upon receipt, samples were transferred into secondary HDPE drums, stored in the dark, and refrigerated at ~4 °C until use (within 2 weeks). BPC powder was provided by H2nanO Inc. (Waterloo, ON) and comprised of TiO_2 particle-coated hollow glass beads described previously.[38,39] Naphthenic acids (technical mixture, SKU 70340) and dichloromethane (DCM, ≥99.9%, HPLC grade) were purchased from Sigma-Aldrich and used as received.

Indoor Simulated Solar UV Photocatalytic Treatment. Photocatalytic experiments were performed in a custom solar UV simulator enclosure, consisting of an array of UVA fluorescent bulbs (Philips F20T12/BL, peak emission ~350 nm) suspended above the samples.[76] The UV intensity was measured to be ~40 W/m^2 with a UVA/B light meter (Sper Scientific, NIST certified calibration), similar to the UV content of the solar spectrum (ASTM G173−03 global tilt).

BPC powder (1.05 g) was added to 210 mL of OSPW in borosilicate glass beakers (6.5 cm I.D., sides wrapped with aluminum foil) and sealed with a UV transparent polyethylene film. Beakers were equilibrated in the dark for ~1 h, then exposed to simulated solar UV while vigorously stirring (PTFE-coated magnetic stir bar). BPCs were separated from OSPW by vacuum filtration (Whatman GF/F, 0.7 μm pore size), and the water was stored in the dark at ∼4 °C until analysis (<24 h).

Outdoor Treatment Site. The outdoor test site was established in a fenced, open-air yard at the University of Waterloo. Two recirculating "raceway" style open-top HDPE basins (MicroBio Engineering, RW3.4, 3.4 m^2 surface area of water exposed, 30 cm maximum depth), including each an integrated paddlewheel (stainless steel, 4 blades, ∼12 × 15.5 inch $l \times w$ each), were used as solar treatment reactors, placed 0.8 m apart under a retractable tarp canopy (used to control sunlight exposure and rain accumulation, Figure 1). Adjacent to the basins at equal height and building offset was an environmental monitoring station, which included a Si pyranometer (Onset Computer Corporation, S-LIB-M003, 300−1100 nm spectral range); a photodiode UV light sensor (Apogee Instruments Inc., SU-100, 250−400 nm spectral range); and 2 temperature sensors (Onset Computer Corporation, S-TMB-M-006, −40 to 100 °C range), each inserted to each basin below the water level. Sensor measurements were recorded at 30-s intervals by a stand-alone, battery-powered data logger (Onset Computer Corporation, H21-USB). A closed, bottom draining tank (HDPE) was also located at the site used for flotation separation of BPCs from treated OSPW samples prior to analysis.

Outdoor Solar Photocatalytic Treatment. Outdoor experiments were conducted between July 17 and September 17, 2018. For each sample of OSPW, a raceway basin was filled to ∼25 cm depth with 650 L of the OSPW pumped directly from refrigerated storage and paddlewheel mixed (8.6 rpm) to equilibrate to ambient temperature while covered by the tarp canopy; three control basins (20 L, HDPE) were also filled and positioned next to the raceway tub. The initial raw OSPW was sampled, after which 3.25 kg BPC powder (premixed with a small portion of the same OSPW to form a slurry) was added to the raceway tub while stirring, forming a lightly mixed BPC layer at the water surface (5 g/L BPC was also added to the dark adsorption control basin).

The test was initiated with the removal of the tarp canopy to expose the water to sunlight. OSPW was continuously paddlewheel mixed (8.6 rpm, water velocity ∼0.17 m/s) throughout the test. After sunset each day, the tub was covered with a tarp canopy overnight until the following morning. Each morning, to compensate for evaporation losses, the water in the tub was topped up with deionized water to the level measured at the previous sampling (net zero dilution) and mixed for at least 1 h to equilibrate prior to sampling. Following completion of the test, the remaining OSPW and BPC were drained from the raceway tub, which was washed prior to testing with subsequent OSPW samples.

Water samples (40 L) were collected from the raceway tub periodically (together with BPCs to maintain a constant BPC concentration in the tub) at cumulative UV doses chosen based on preliminary treatment kinetics determined for each OSPW using the indoor solar UV simulator. Control containers were collected at the same time as the corresponding raceway tub samples. Samples were transferred to a sealed tank (HDPE) and left in the dark indoors at ambient temperature for at least 24 h to allow the BPCs to separate from the OSPW by flotation, after which the treated OSPW was drained and sent for water chemistry analysis and toxicity testing.

Water Chemistry Analysis. AEO_{FTIR}: samples were centrifuged (14k × g, 15 min) and vacuum filtered (Whatman GF/F, 0.7 μm pore size), acid extracted with DCM, and measured by Fourier transform infrared spectroscopy (FTIR, PerkinElmer, Spectrum Two) as previously,[77−79] with minor modifications (viz., the acidified samples were extracted thrice with DCM in a 1:12.5 solvent to sample volumetric ratio, with 80 ± 4% total recovery), using an acid extract from the raw OSPW to prepare the calibration curve. Chemical oxygen demand (COD): samples were filtered (0.2 μm pore size, wwPTFE) prior to analysis (Hach, APHA 5220D). UV_{254}: samples were filtered as described above prior to analysis (BioTek, Epoch).

Conductivity (APHA 2510B), total dissolved solids (TDS, APHA 2540C), total suspended solids (TSS, APHA 2540D), turbidity (APHA 2130B), alkalinity (EPA 310.2), anions by ion chromatography (Br^-, Cl^-, F^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, EPA 300.1), total Kjeldahl nitrogen (TKN, APHA 4500NorgD), total organic carbon (TOC, APHA 5310B), biochemical oxygen demand (BOD, APHA 5210B), total and dissolved metals in water by inductively coupled plasma mass spectrometry (ICPMS, APHA 3030B/6020A), polycyclic aromatic hydrocarbons (PAHs), and alkyl-PAHs by GC/MS (EPA 3510C/8270) were measured by ALS Environmental (Waterloo, ON, Canada), a CALA accredited and ISO 17025 certified laboratory. Samples were preserved and transported on ice to the laboratory.

Biomimetic extraction with solid phase microextraction fibers (BE_{SPME}): samples were completely filled (zero headspace) to each of two VOA vials (40 mL) containing 0.1 mL of H_3PO_4, shipped overnight on ice to ExxonMobil Biomedical Sciences Inc. (EMBSI, Annandale, NJ), and analyzed as previously.[71]

Naphthenic acids and acid extractable organics by mass spectrometry (NAs_{MS} & AEO_{MS}, respectively): samples were acid extracted with DCM according to the same method as for AEO_{FTIR} and shipped as dried extracts overnight on ice to InnoTech Alberta (Vegreville, AB, Canada) for analysis. Analysis was performed using an HPLC Orbitrap Elite mass spectrometer (Thermo Scientific, San Jose, CA). Component separation was performed using an Ultimate 3000 HPLC system (Thermo Fisher Scientific, San Jose, CA) on a C_8 column (150 mm × 3.0 mm, 3 μm particle size; Thermo Fisher Scientific, San Jose, CA) at 40 °C. The flow rate was set at 0.5 mL/min, and an injection volume of 5 μL was used. Mobile phases consisting of (A) 0.1% acetic acid in water/methanol (90/10; v/v) and (B) 100% methanol were employed. The following mobile phase composition was used: 5% B for 1 min, followed by a linear gradient ramp to 90% B at 10 min and to 99% over 5 min and returning to 5% B in 1 min, followed by a 4 min hold prior to the next injection. The eluent was injected directly into an Orbitrap Elite. The Orbitrap was operated under the following conditions: source temperature of 350 °C in electrospray ionization (ESI) mode; sheath, aux, and sweep gas flow at 30, 5, and 5 (arbitrary units), respectively; the capillary temperature at 350 °C; S-Lens RF at 65%; resolving power set to a nominal value of 120,000 at full width half-maximum at m/z 400, and using a full maximum ion time of 200 ms. Mass calibration and tuning were done externally by direct infusion of a standard mixture of caffeine, the peptide MRFA (sequence, Met-Arg-Phe-Ala), and Ultramark 1600 in H_2O/acetonitrile 50:50 (v/v), covering a mass/charge (m/z) of 138−1722. Mass spectral data were collected at 2 full scans per second between 100−1000 m/z using automatic gain control. Data acquisition and analysis were

Table 1. Apparent First-Order Rate Constants (k_{app}) of Photocatalytic AEO_{FTIR} Elimination

	test volume (L)		AEO_{FTIR} treatment rate (equiv. $days^{-1}$)	
OSPW	solar UV simulator	natural sunlight	solar UV simulator	natural sunlight
A	0.21	650	0.18 ± 0.03	0.13 ± 0.03
B	0.21	650	0.19 ± 0.03	0.20 ± 0.02
C	0.21	650	0.09 ± 0.02	0.04 ± 0.01
Leshuk et al., 2018	1	0.5	0.12 ± 0.01[39]	0.26 ± 0.02[38]
Leshuk et al., 2016[a]	0.2	0.2	0.76 ± 0.03[76]	0.68 ± 0.05[42]

[a] Rate constants for treatment with TiO_2 nanoparticle slurries, i.e., not directly comparable to treatment rates with BPCs.

performed using Thermo Xcalibur 2.0 software. Merichem oil was used for the calibration curve for semiquantification of NAs_{MS}; only classical NAs, i.e., with a formula corresponding to $C_cH_hO_2$, were included in the summed NAs_{MS} calculated value.

Whole Effluent Toxicity (WET) Testing. Samples were transported on ice overnight to AquaTox Testing & Consulting Inc. (Puslinch, ON, Canada), a CALA accredited and ISO 17025 certified laboratory; or Bureau Veritas (formerly Maxxam Analytics, Burnaby, BC, Canada), a Standards Council of Canada (SCC) accredited laboratory. Waters were tested for toxicity to rainbow trout (*Oncorhynchus mykiss*, 96 h lethality at 100% v/v sample concentration, EPS 1/RM/13) and fathead minnow (*Pimephales promelas*, 7 d larval growth, and survival at 100% v/v sample concentration, EPS 1/RM/22) according to Environment & Climate Change Canada's reference test methods.

Toxicity Modeling. Statistical analysis was performed in Python 3.9, primarily with the scipy,[80] sklearn,[81] and statsmodels[82] libraries.

Physiologically based quantitative class-activity toxicity modeling was used to study potential mechanisms of photocatalytic OSPW detoxification through an approach inspired by the success of the target lipid model (TLM) in describing the baseline toxicity of petroleum hydrocarbons.[83,84] As in the TLM, internal physiological contaminant concentrations are taken as a better proxy of toxic exposure (dose) than aqueous concentrations, with the bioaccumulation potential estimated from chemical partition coefficients. Unlike the TLM, however, which prescribes a single hazard threshold (critical target lipid body burden, c_l^*) for all chemicals, here this assumption is relaxed to allow different classes of NAFCs to have different toxic potencies (critical thresholds inferred through dose−response fits to experimental WET data), as in recent generalizations of TLM reasoning to other chemical classes (Discussion S1).[84−88] This empirical approach enables unbiased inclusion of multiple (unknown) mechanisms of toxicity under a single framework to better leverage experimental WET data without the requirement for definitive characterization of all molecular structures (a particular challenge for OSPW NAFCs) or elucidation of all mechanisms of toxicity−information burdens typical of theoretical quantitative structure−activity modeling.[88] Physiologically based modeling (PBM) can therefore be considered an extension of the TLM to contexts with incomplete chemical/biological information.

Octanol−water and membrane phospholipid−water partition coefficients (K_{ow} and K_{mw}, respectively) were estimated by MS ionization mode- and heteroatom class-specific regression models fit to published OSPW NAFC partitioning data,[89,90a] with the molecular carbon numbers, double bond equivalents, and oxygen:carbon atomic ratios (o/c) as regressors (e.g., Figures S1−S5 for K_{ow} fits to the O_2^- and OS^+ NAFC classes). K_{mw} could not be reliably estimated for all NAFCs, where measurable partitioning was negligibly low (K_{mw} below detected in the literature data set)—in these cases, K_{mw} was omitted and the components were modeled by K_{ow} alone. This empirical partitioning estimation was preferred to theoretical modeling (e.g., polyparameter linear free energy relationships, ppLFERs, as applied to ionizable organics[71,91]) since exact molecular structures and acid dissociation constants (pK_a) were unknown for most components detected (Discussion S2). The assumptions of this empirical approach are that the detected ions comprised molecular structures similar to those in the reference OSPW[89,90] and that isomeric NAFCs partition together similarly.

Semiquantitative molar concentrations of NAFCs were estimated from MS data by assuming that (a) components were only ionizable in one mode, i.e., ions measured in ± ESI were derived from separate and distinct molecules (implying that compounds that could in actuality be ionized by both modes may have been double counted); and (b) equal response factors for all components, as previously.[92] Each sample's gravimetric AEO_{MS} concentration was estimated from a calibration curve indexed to AEO_{FTIR} concentration (i.e., reference standardization[93,94]); MS intensity was linearly proportional to AEO_{FTIR} (Figure S6), as found previously.[95,96]

Two-compartment physiologically based toxicity models (PBMs) were fit to each toxic endpoint, with NAFC equilibrium concentrations (by MS ionization mode and heteroatom class) in both polar and nonpolar target lipids (determined from aqueous concentrations by K_{mw} and K_{ow}, respectively) input as separate regressors contributing additively to the total body burden. PBMs were fit as generalized linear models (GLMs) by non-negatively constrained logistic regression with elastic net regularization (i.e., both L_1 and L_2 priors, hyperparameters optimized by 5-fold cross-validation), i.e., as

$$\mathrm{logit}(p) = \beta_0 + \sum_{i \neq 0} \beta_i c_i$$

where p is the probability of toxic effect, c_i are the lipid concentrations (mol/L) of i NAFC heteroatomic classes, and β_i are the regression coefficients (with β_0 intercept). A 4:1 storage lipid to phospholipid ratio was assumed for EC_{50} estimation.[90,97,98]

Data and Code Availability. The data, code (Python scripts), and models (K_{ow} and K_{mw} prediction, PBMs) from this study are openly available in Figshare at DOI: 10.6084/m9.figshare.25188662.

■ RESULTS AND DISCUSSION

Preliminary Treatability: Extensive AEO Elimination Possible. Prior to outdoor testing, preliminary OSPW treatability was assessed with an indoor solar UV simulator to estimate the required treatment exposure. For TiO_2 photocatalysts, activated only by UV light, treatment kinetics under artificial UV (with spectral intensity similar to solar UV) typically closely match kinetics under natural sunlight.[42,76]

Rates of organics oxidation and mineralization were similar across the three OSPWs and broadly comparable to previously reported photocatalytic OSPW treatment rates (Figure S7, Table 1). Near complete AEO_{FTIR} elimination was achieved in all OSPWs within a UV dose equivalent to ~2−4 weeks of typical sunlight exposure (Mar. − Aug.) at Fort McMurray, AB. These rates and extents of AEO degradation compare favorably to those reported for treatment wetlands (k_{app} 0.01−0.03 days^{-1},[99] 0−50% removal extent achievable[25,44]) and natural attenuation (half-life ~13 years[8]). Based on these preliminary trials, the sampling program for outdoor testing was designed to be ~15−30 equiv. days of cumulative solar UV exposure.

Fish Toxicity Rapidly Eliminated by Solar Photocatalysis. The as received raw OSPWs were found to be toxic to both rainbow trout (RBT) and fathead minnow (FHM); the RBT appeared to be the more sensitive of the two fish, as previously reported.[100] Surprisingly, the toxicity of the waters appeared to be inversely proportional to the measured NAs and AEO concentrations (Table 2). OSPW A, the most potently toxic, was also the least saline, possibly revealing less recycled, relatively younger process water; fresher OSPWs typically present as more acutely toxic than aged or weathered waters.[57,66,101]

Table 2. Initial Water Characterization of the As-Received Raw OSPWs (Further Characterization Available in Table S2)

parameter	OSPW A	OSPW B	OSPW C
rainbow trout mortality (%)	100	60	100
fathead minnow mortality (%)	92 ± 8	12 ± 13	0
fathead minnow growth inhibition (%)	89 ± 16	28 ± 15	40 ± 9
AEO_{FTIR} (mg/L)	25.3	47.9	32.2
NAs_{MS} (mg/L)	7.5	15.4	7.3
BE_{SPME} (mmol/L)[a]	47.0	43.7	51.1
TOC (mg/L)	45	58	41
COD (mg/L)	150	240	187
TDS (mg/L)	745	2570	2390
conductivity (mS/cm)	1.03	3.59	3.61

[a] BE_{SPME} units: as mmol of 2,3-dimethylnaphthalene per L of PDMS.

All measured toxicity (as per the studied RBT and FHM bioassays) in each OSPW was fully eliminated by the first sample taken from the outdoor photocatalytic treatment trial (Figure 2) within a solar UV dose equivalent to <2 days of typical sunlight exposure (Mar. − Aug.) at Fort McMurray, AB (i.e., <2 "equiv. days"); the waters were likely detoxified at even lower UV doses, although these earlier stages of treatment were unsampled. This result was surprising since the aquatic toxicity of OSPW has been ascribed primarily to the AEO and classical NAs (i.e., O_2^- class by LC-MS),[72,100−102] however, here the initial sharp reduction in acute toxicity to fish was apparently decoupled from the relatively slower elimination of dissolved organics (Figure 2), which were degraded at rates similar to the indoor trial (Table 1). OSPWs were still measured to be toxic in both dark and photolysis controls (treated to an equivalent solar UV dose without a photocatalyst);[b] one dark adsorption control (OSPW mixed with BPCs without sunlight) was detoxified to both RBT and FHM, possibly indicating a role for catalyst surface adsorption in the treatment (Table S3). Following its initial disappearance, the toxicity of the treated waters remained effectively zero at all subsequent samplings (Figure 2), evincing negligible formation of any toxic treatment intermediates or byproducts, at least as per the RBT and FHM assays. Overall, the results are congruent with prior literature suggesting that complete NAs removal or complete mineralization of dissolved organics, while both achievable by solar photocatalysis, would not prove necessary to meet fish WET-based water quality objectives;[25,66,101] indeed, the acute toxicity of the OSPWs to RBT and FHM was fully eliminated without significant change to their AEO concentrations.

AEO and Classical NAs Poorly Correlated with Toxicity. While WET assays are standard tools to evaluate complex wastewaters with mixed or unknown toxicants, they are costly and time-consuming to turnaround results, and lower latency water quality measures may be required for monitoring the OSPW treatment processes. To this end, analytical chemistry metrics could be useful as toxicity surrogates,

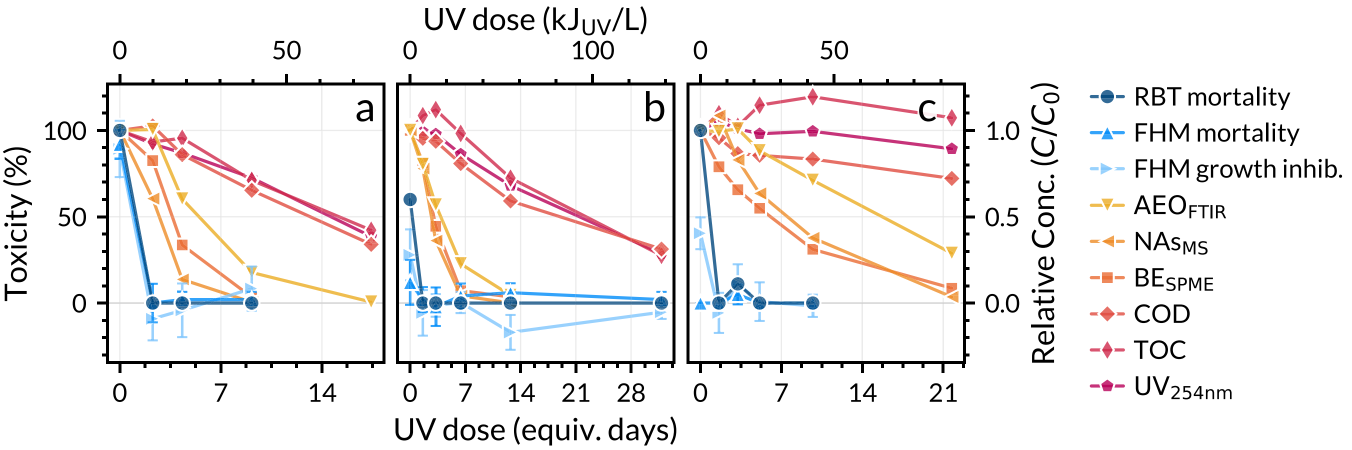


Figure 2. Solar photocatalytic OSPW treatment kinetics in outdoor raceway pools under natural sunlight for OSPWs A−C in (a) to (c), respectively. Elimination of measured toxicity (shades of blue) precedes substantial decreases in the concentration of water chemistry metrics (shades of yellow to red). "Equivalent days" represent the expected treatment time required at Fort McMurray, AB, to accumulate the same solar UV dose to the water (*c.f.* Materials & Methods section). Abbreviations: RBT, rainbow trout; FHM, fathead minnow; inhib, inhibition; equiv, equivalent; and conc., concentration.

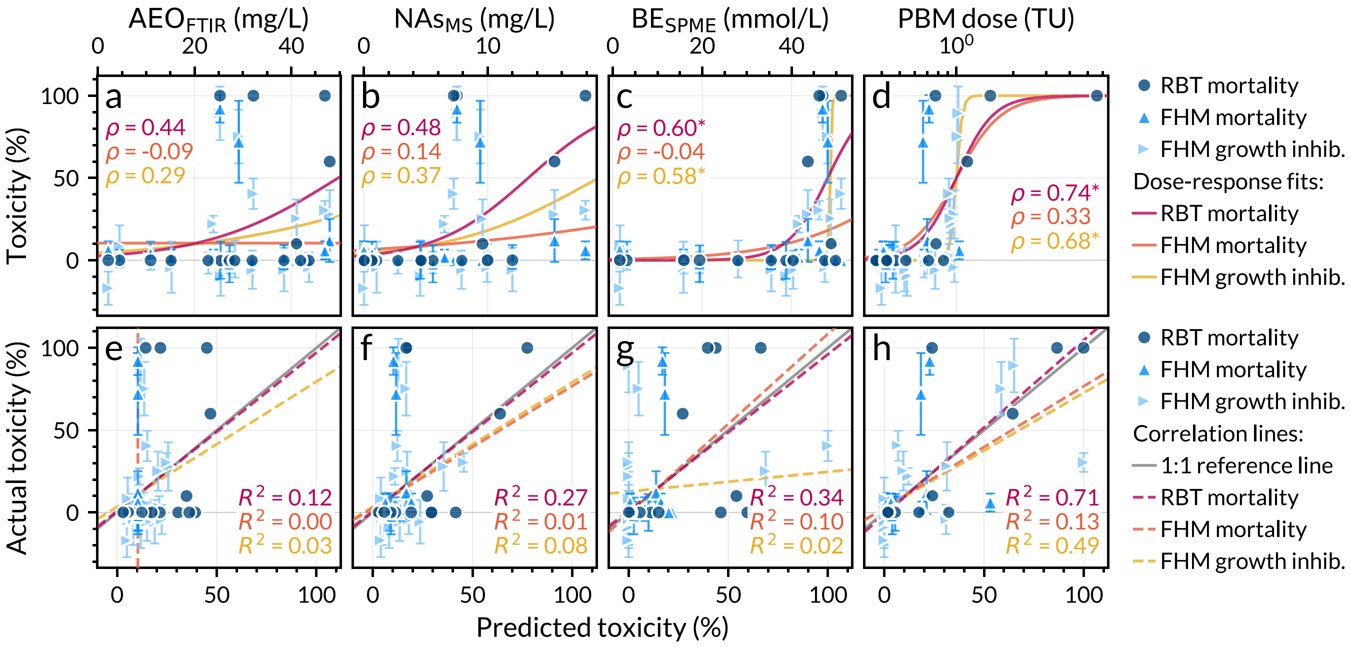


Figure 3. Dose−response correlation analysis between water chemistry metrics (AEO$_{FTIR}$, NAs$_{MS}$, BE$_{SPME}$, and the AEO$_{MS}$-derived PBM dose) and toxicity (data collected from all OSPW treatments). (a−d) Dose−response logistic regression using the indicated water chemistry metric as the toxic dose, with corresponding Spearman rank correlation coefficients (ρ) indicated (higher is better), (*) denoting significant correlations ($p < 0.05$). (e−h) Correlation analysis between experimentally measured toxicity and toxicity predicted by the dose−response models of (a−d), respectively, with coefficients of determination (R^2) indicated (higher is better); in a perfect correlation, the data would fall along the 1:1 reference line. Abbreviations: RBT, rainbow trout; FHM, fathead minnow; and inhib., inhibition.

provided they have a sufficient correlation with WET endpoints. The performance of various water chemistry metrics to predict toxicity was therefore assessed in parallel with the study's WET assays.

Classical NAs (as measured by MS, referred to herein as NAs$_{MS}$) have been extensively studied toxicologically,[24,104,105] and are thought to be among the most toxic constituents of OSPW[100,102] (perhaps surprisingly so, considering NAs are ionized at OSPW pH, limiting bioaccumulation[71,106]). Acid extraction is thus often used to analytically recover a greater proportion of NAs (together with other NAFCs), which are routinely measured as an unresolved mixture by FTIR (referred to herein as AEO$_{FTIR}$).[77−79] More recently, nondepletive acid extraction by SPME fibers has been proposed as potentially more representative of biological exposure (so-called "biomimetic extraction," BE$_{SPME}$) and may be more practical as a rapid passive monitoring tool and toxicity surrogate, avoiding the need for animal testing.[71,107]

Dose−response logistic regression models were fit using these chemistry metrics as the dose and the pooled fish toxicity data (from all 3 OSPWs) as the response (Figure 3). NAs$_{MS}$ and AEO$_{FTIR}$ were not significantly correlated with the WET data: e.g., nontoxic samples were measured with nearly double the concentration of NAs$_{MS}$ or AEO$_{FTIR}$ as acutely lethal samples. The literature also contains examples of nontoxic OSPWs (RBT 96 h LC$_{50}$ > 100% v/v) with AEO$_{FTIR}$ and NAs$_{MS}$ concentrations higher than any of the OSPWs herein (58 ± 14 and 24 mg/L, respectively).[25,108] Similarly, Base Mine Lake (first oil sands EPL, water capped partially with OSPW in 2012) is no longer acutely toxic to RBT and FHM,[30,31] despite NAs$_{MS}$ and TOC concentrations similar to raw OSPWs herein.[20,109] Recent toxicology suggests that classical NAs alone do not fully account for the toxicity of OSPW to fish.[5,18,63,110]

Of the above chemistry metrics, BE$_{SPME}$ had the best correlation with toxicity (Figure 3c,g). The BE$_{SPME}$ EC$_{50}$s estimated herein (48, 64, 49 mmol/L for RBT mortality, FHM mortality, and FHM growth inhibition, respectively) are within the BE$_{SPME}$-based species sensitivity distribution and comparable to the BE$_{SPME}$ LC$_{50}$ (19 mg/L for FHM embryo 4 d survival) derived previously from OSPW AEO exposure,[71] demonstrating the similar performance of the technique in whole OSPWs as with spiked extracts. However, BE$_{SPME}$ may prove to be a conservative predictor for OSPW treatment monitoring (Figure 3g) insofar as BE$_{SPME}$ reports a single aggregate AEO concentration, similar to the AEO$_{FTIR}$ and NAs$_{MS}$ methods, and thus does not account for AEO composition and the differential toxicity of diverse NAFCs.

OSPW Toxicity May be Caused by only a Small Subset of NAFCs. Several hypotheses were considered to explain the incongruence between the analytical chemistry measures of treatment performance described above and the WET outcomes achieved:

1. Unmeasured toxicants may have contributed to measured OSPW fish toxicity. Besides NAFCs, several other potential fish toxicants have occasionally been described in OSPW, both organic (e.g., PAHs, hydrocarbons, phenolics) and inorganic (e.g., ammonia, sulfide, heavy metals).[4,111] ∑PAHs measured in raw OSPWs A and C were below concentrations likely to contribute to the WET assays used (Table S2), and other petroleum compounds would be expected to have partitioned together with the AEO. Significant toxicity from inorganic factors was considered unlikely given toxicity identification evaluations (TIEs) have repeatedly attributed OSPW aquatic toxicity to its dissolved organics;[72,100] further-

more, TKN and dissolved metal concentrations were below levels likely to be toxic (Table S2).

2. OSPW toxicity to fish may arise from an interaction of organic (and inorganic) factors, where mild photocatalysis is sufficient to disrupt this toxic interaction. E.g., dissolved organics can modulate the toxicity of PAHs and heavy metals,[112−114] while the pH and salinity of OSPW significantly lower NAFC toxicity (vs NAFC extracts spiked to freshwater);[18,106,115] alternately, for some compounds, salinity may be a costressor.[116,117] Provided the toxicity results herein could be sufficiently described by independent action (IA) or concentration addition (CA) toxicology, higher-order multifactor interactions were considered less likely. However, interactive toxicity in OSPW remains under research in our laboratory.
3. The principal aquatic toxicants in OSPW may comprise a relatively small subset of NAFCs, unresolved in the aggregate analyses above, and preferentially eliminated early in the treatment (by analogy, photocatalyst selectivity may have treated the toxic "needle" in a mostly benign AEO "haystack"). Chemical structure dictates toxicity, and the composition of OSPW AEO is as important as its concentration in determining toxic effects. Since classical NAs (NAs_{MS}) were poorly correlated with the fish toxicity measured herein (Figure 3b,f), treatment-induced changes to the AEO chemical profile were therefore analyzed by MS (AEO_{MS}) to assess whether alternate NAFC correlates may support this toxic subfraction hypothesis.

Photocatalysis Preferentially Treats Organosulfur and Low-Polarity NAFCs. Chemical omics by untargeted MS is a powerful approach to finding patterns in complex mixtures,[39,118−120] applied here to analyze treatment-induced changes to the OSPW AEO chemical "fingerprints," with a goal to identify candidate toxic NAFCs. Since the sharp drop in the level of toxicity of the OSPW to fish occurred at the start of the treatment, attention was focused on the most significant changes to the AEO_{MS} profiles between the initial (raw) water and first sample point (i.e., t_0 to t_1), which were consistent between OSPWs. The underlying assumption was that NAFCs behaved toxicologically similarly across OSPWs sampled from different sites (i.e., ignoring possible higher-order interactions with the water matrix chemistry), a standard simplification made in the OSPW toxicology literature to enable broadly applicable chemistry-toxicity inference.

The aquatic toxicity of classical NAs is known to be proportional to their molecular weight (MW) and double bond equivalents (DBE);[100,105,121] thus, while their summed concentration (NAs_{MS}) did not correlate with the WET data, we evaluated whether their MW and DBE could account for the toxicity trends. Solar photocatalysis preferentially removed the highest MW and DBE NAs (Figure S8d−f), as previously.[39] However, this trend was not yet evident by the first treatment sample, at least not consistently across OSPWs (Figure S8g,l), and thus unlikely to explain the initial sharp drop in acute toxicity. The search was therefore expanded to include all AEO_{MS} components.

Initial AEO heteroatom class speciation was similar across the OSPWs, predominately from O_2^- to O_4^- (classical, hydroxy-, and dicarboxylic NAs, respectively) in negative ion mode (ESI−), and from O_0^+ to O_3^+ and OS^+ to O_3S^+ in positive ion mode (ESI+), classical NAs comprising only ∼10−20% of the total NAFCs detected in the AEOs (Figure S9a−c). Photocatalytic treatment preferentially eliminated sulfur-containing NAFCs (Figure S9d), as observed previously,[39,42,122] and the classes with significantly reduced abundance from t_0 to t_1 (consistent across OSPWs) were predominately sulfur bearing: S^-, O_2S^-, O_7^-, S^+, OS^+, and O_2S^+ (Figure S9e−h). AEO_{MS} negative ions with nominal mass >280 g/mol and the oxygen:carbon atomic ratio $o/c < 0.15$, together suggestive of low-polarity congeners, also appeared to be preferentially removed by t_1 (Figure S10b,k). AEO_{MS} oxygenation significantly increased over photocatalytic exposure (Figure S10l), although no consistent patterns were evident in the DBE distributions. Together, these MS signatures of photocatalytic selectivity suggested a potential chemical mechanism of OSPW detoxification.

Physiologically Based Model (PBM) Accurately Describes OSPW Toxicity Trends. Based on these MS observations, it was hypothesized that low-polarity NAFCs were among the most acutely toxic components in the OSPWs. While various modes of action (MoAs) have been implicated in the diverse toxic effects of OSPW,[24,51,56,58,123] its acute aquatic toxicity has been attributed to nonspecific narcosis,[6,124,125] the accumulation of low-polarity chemicals to biological lipid compartments, *a.k.a.* baseline toxicity. To evaluate a baseline interpretation of the above WET results, the bioaccumulation potential of all NAFCs in the AEO_{MS}, as represented by their octanol−water partition coefficients (K_{ow}), was first estimated from their molecular formulas by empirical inference models derived from PDMS partitioning of OSPW NAFCs (pH 8.4, Figure S10m−p).[89,90,92] The NAFCs predicted to be the most hydrophobic ($\log K_{ow} > 1$) were also those preferentially eliminated early in the treatment (Figure S10o). From these inferred K_{ow}, together with predicted membrane phospholipid partition coefficients (K_{mw}),[90,92] equilibrium tissue concentrations of NAFCs (body burdens) were estimated (Figure S11a−c), with O_2^-, O_2S^-, NO^+, NO_2^+, OS^+, S^+, O_2^+, and O^+ NAFCs predicted to be the most bioconcentrating−of these, only the O_2S^- and OS^+ classes were significantly depleted by t_1 consistently across OSPWs (Figure S11h).

Beyond only this first treatment interval (t_0 to t_1), to test the above hypothesis against the full data set, combined results (from all 3 OSPWs) were evaluated through the target lipid model (TLM), a model of baseline toxicity. With standard parametrization,[c] the TLM performed similarly to the aggregate chemistry metrics (AEO_{FTIR}, NAs_{MS}, BE_{SPME}, Figure 3), underpredicting the actual fish toxicity of the OSPWs (Figure S12), potentially suggesting greater NAFC bioaccumulation than expected or toxic MoA(s) beyond the baseline. To account for these possibilities and better fit the experimental observations, extended physiologically based modeling was conducted, allowing for variable toxic potency of different NAFC classes. Predicted tissue concentrations by heteroatomic class were input together as toxic doses to regularized logistic regression models and fit to the pooled WET data, with concentration addition (CA) treatment of mixture toxicity. Dose−response correlation and predictive performance of these physiologically based models (PBMs) exceeded those of the aggregate chemistry metrics (AEO_{FTIR}, NAs_{MS}, BE_{SPME}, Figure 3), and PBM fitted estimates of NAFC lipid EC_{50} critical thresholds were comparable to those of baseline petroleum substances for the O_2^- and O_2S^- classes, but lower for the OS^+ class (i.e., suggesting this class to be more acutely toxic, Table

S4).[71,84] In summary, the OSPW fish toxicity data herein were partially consistent with a narcotic MoA, with some NAFCs inferred to be more toxic than this baseline.

In fitting these PBM dose−response curves, cross-validated regularization constrained the regression to estimate only the most significant parameters and enabled the algorithm to drop irrelevant covariates from the models. Only two heteroatomic classes were retained as significant regressors: O_2S^- (likely sulfur-substituted naphthenic acids) and OS^+, the most acutely toxic (Table S4); the algorithm determined classical NAs (O_2^-) unnecessary to describe OSPW toxicity to RBT and FHM. Intriguingly, OS^+ and O_2S^- were also predicted by Morandi et al. to be the two most potently toxic NAFC classes to FHM embryos,[92] and the majority of the OSPW toxicity could be accounted for by only these two classes (Figure 4), suggesting that low-polarity organosulfur NAFCs may be among the principal organic aquatic toxicants in OSPW.

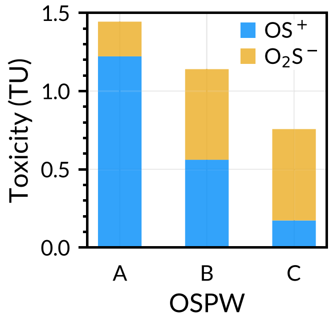


Figure 4. Estimated AEO_{MS} contributions by heteroatomic class to the acute toxicity (RBT mortality, 96 h) of OSPW (in toxic units, TU).

OS^+ NAFCs are Likely Toxic Naphthenic Sulfoxides. It is perhaps unsurprising that the O_2S^- compounds would be correlated with toxicity, presuming they are simply sulfur-bearing NAs, given the extensive literature on NA toxicity. However, OS^+ NAFCs have been relatively less studied, and while this correlation does not necessarily imply toxicological causation, it is prudent to consider whether the ascription of toxicity to these compounds could be plausible.

First, it is proposed that the OS^+ species are probably naphthenic sulfoxides. Considering the relatively low DBE numbers measured for the OS^+ congeners, primarily in the range of DBE 2−5 (Figure S13), these components are unlikely to be (di)benzothiophene derivatives or other polycyclic aromatic sulfur heterocycles (PASHs) but rather oxidized polycyclic aliphatic sulfides.[126−130] By contrast, thiophenic compounds are inefficiently ionized by ESI,[126,131] and hydroxylated sulfides appear in negative ion mode,[132−134] while sulfoxides, as weak bases, are readily detectable as OS^+ ions.[126,130,132,135] Naphthenic sulfoxides have long been recognized as significant polar sulfur constituents of crude oil and, indeed, have been detected in Athabasca bitumen with very similar carbon numbers and DBE profiles as measured herein.[126,132,136,137] Further, a sulfoxide peak at ∼1040 cm^{-1} was found in the AEO_{FTIR} spectra (Figure S15), which was significantly correlated with the OS^+ AEO_{MS} intensity (Figure S16).

Naphthenic sulfoxides are water-soluble[138,139] but, importantly, nonionized at OSPW pH; ionization is known to limit the bioaccumulation and toxicity of NAs.[71,106,140,141] Indeed, OS^+ NAFCs reportedly have among the highest partition coefficients (K_{ow}) of all OSPW organics,[89,90,92] and are readily solvent extracted at the alkaline pH of OSPW;[39,102,110] by contrast, many NAs poorly partition as naphthenate ions.[71,142,143] Nonionic petroleum substances (e.g., hydrocarbons, PAHs, alkylphenols) are known to be up to orders of magnitude more potently toxic than NAs;[84,85,105,144,145] thus, it may not be unreasonable to expect naphthenic sulfoxides to be significant toxicants. Although the above results could be partially described through baseline hydrocarbon toxicity, other possible MoAs were not ruled out: e.g., NAFCs have been shown to be uncouplers of oxidative phosphorylation,[146] an MoA with fish EC_{50}s (∼0.1−1 mmol/kg[88]) comparable to those inferred for OS^+ NAFCs herein; sulfoxide NAFCs may also act to magnify the effects of other toxicants through chemosensitization.[110,147,148]

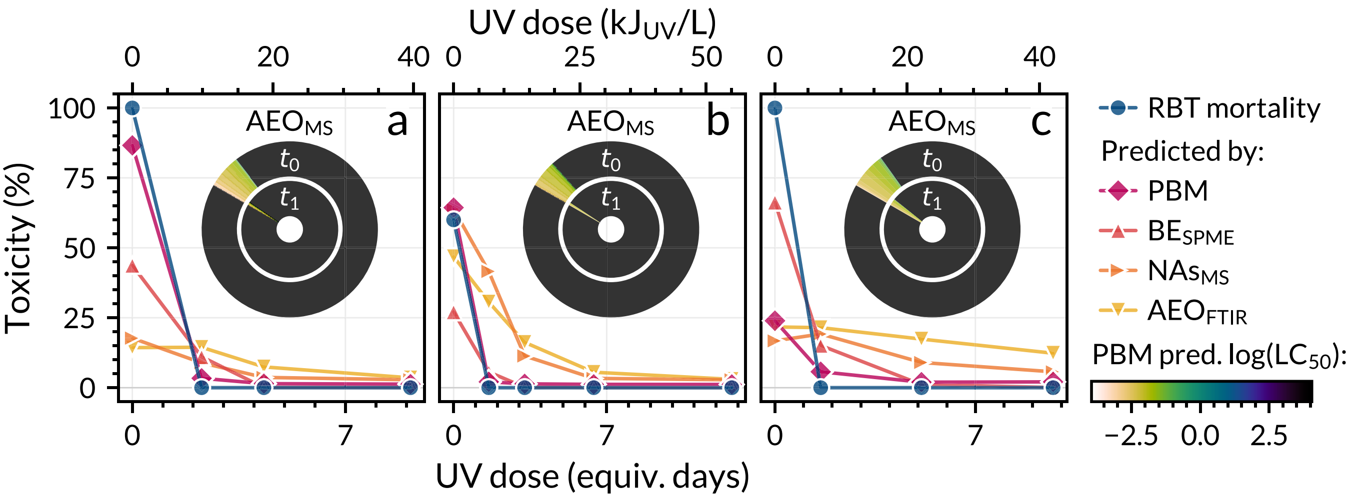


Figure 5. Change in the acute toxicity (RBT mortality, 96 h) of OSPWs A−C in (a−c), respectively, during solar photocatalytic treatment (same data as in Figure 2) and as predicted by the dose−response models (of Figure 3). Insets: pie (donut) plots of all AEO_{MS} measured in the initial raw OSPWs (t_0, measurably toxic) and at the first treated sample (t_1, no measured toxicity), colored according to the PBM-predicted LC_{50} (mmol/L) of each NAFC detected—the model predicted that toxic NAFCs constituted a minority of the AEO_{MS} and that their relative abundance declined due to treatment. Abbreviations: RBT, rainbow trout; equiv, equivalent; and pred., predicted.

Prior TIEs that have attributed OSPW toxicity primarily to classical NAs either (a) were not conducted with whole OSPWs or (b) did not measure positive ion NAFCs.[72,100,102,121] As shown herein and elsewhere,[39,102] OS^+ NAFCs are coextracted and partition together with classical NAs, and it is challenging to analytically separate the two; indeed, even commercial technical mixtures labeled as "naphthenic acids" contain OS^+ components.[149] Unfortunately, since few toxicity studies have analyzed NAFCs by positive ion mode MS, unobserved sulfoxides may have contributed as underlying hidden factors to much of the published OSPW toxicology literature to date.

Photocatalysis Preferentially Treats Toxicity-Correlated NAFCs. Returning to an explanation for the rapid detoxification of the OSPW to RBT and FHM achieved early in the solar photocatalytic treatment despite the minimal reduction in measured (aggregate) concentrations of dissolved organics (Figure 2), the above AEO_{MS}-derived PBM accurately described the sharp drop in toxicity at the start of treatment for OSPWs A and B (Figure 5), although its prediction was worse for OSPW C.[d,e] The PBMs were similarly more accurate than the aggregate chemistry metrics (AEO_{FTIR}, NAs_{MS}, BE_{SPME}) at describing the FHM toxicity trends (Figures S17, S18), although none of these models adequately captured the variance in the FHM mortality data set.

Additionally, the PBM formulation enabled an inferred LC_{50} to be calculated for every component detected in AEO_{MS} (Figure 5 insets). Intriguingly, the model predicted that toxic NAFCs (i.e., those with inferred $\log LC_{50} < 5$) constituted no more than 5−10% by the abundance of the initial AEO_{MS} in the raw OSPWs, dropping to 1−3% by the first treatment sample (t_1); the balance of detected NAFCs were predicted to be toxicologically benign (at least to the selected fish endpoints assayed herein). This PBM description was consistent with the hypothesis that the toxicity of the OSPW to fish is caused by a relatively small subset of NAFCs, preferentially eliminated by photocatalytic treatment.

In summary, a clearer picture of the mechanism of photocatalytic OSPW treatment emerges: highly bioconcentrating organosulfur NAFCs, predicted to be among the principal organic toxicants in OSPW, are rapidly eliminated early in the photocatalytic exposure. Consistently demonstrated photocatalytic degradation selectivity toward sulfur NAFCs[39,42] may be mediated by the unique photocatalytic ROS mixture,[42,122] and may distinguish photocatalysis from other AOP treatments, which do not appear to preferentially remove organosulfur compounds in OSPW (and may even increase the abundance of OS^+ species).[150] Treatment selectivity is also likely advantaged by the adsorption of hydrophobes to the high surface area heterogeneous nanocatalysts, expected to enhance second-order reaction kinetics relative to homogeneous oxidation reactions (i.e., Langmuir−Hinshelwood theory); indeed, treatment with adsorbents (e.g., petroleum coke) has also been demonstrated to detoxify OSPW to RBT.[70,151]

CONCLUSIONS

A "Light Touch" Treatment Detoxifies OSPW. These results serve as a case study demonstrating that only a relatively mild treatment may be required to remove acute and sublethal fish toxicity of OSPW as per standard regulatory WET bioassays without requiring significant reductions in the concentrations of NAs and AEO. Fitted dose−response curves were relatively sharp, so regardless of the mechanistic details of detoxification, significant reductions to these conventional aggregate analytical chemistry measures of dissolved organics proved unnecessary to transform OSPWs from acutely lethal to completely nontoxic to RBT and FHM (according to these specific assays, further investigation of other toxic endpoints is merited). This finding has potentially profound implications for the remediation of the vast quantities of OSPW in the oil sands within practical treatment timeframes.

OSPW Toxicity Poorly Correlated with Standard Water Chemistry Metrics. Poor correspondence between conventional measures of dissolved organics of the OSPW (NAs, AEO, TOC, etc.) and WET outcomes was observed even when comparing the raw OSPWs, calling into question the use of such simplistic metrics as toxicity surrogates. As some of these water chemistry metrics may be under consideration for monitoring the treatment of OSPW for release, the above results give a reason for pause and suggest that WET bioassays may be more protective of aquatic life. OSPWs are incredibly analytically complex chemical mixtures for which identification of chemistry-toxicity correlates remains nascent. BE_{SPME} is a promising development in this direction, and it is suggested herein that low-polarity organosulfur compounds may be associated with fish toxicity; however, more work is needed to validate relevant analytical chemistry thresholds. In so doing, it will be important to research whole OSPWs in addition to isolated organic extracts, as water matrix effects are expected to significantly modulate dissolved organics toxicity. Currently, the scope of the PBM developed here is limited to the results herein; a critical review of the model parameters may provide further insights, and expanding the available partition coefficient data sets is recommended to support more focused applications.

Petroleomics is a Powerful Tool for Toxicology. This work demonstrates the potential of statistical inference over untargeted MS omics as a new approach to environmental toxicology. Such high-level screening could be used to identify promising directions for follow-up targeted TIE and effect-directed analysis (EDA) confirmation; e.g., the results herein suggest further research on naphthenic sulfoxide toxicity may be warranted. Challenges anticipated for such an omics workflow are as follows: (a) highly dimensional data elevates the probability of drawing spurious correlations and (b) inference is only as strong as the analytical basis is comprehensive (i.e., "you don't know what you don't know"). The development of a public repository of toxicity-indexed aquatic MS omics, to which the data herein are an initial contribution, is anticipated to strengthen statistical power. Further extending the analytical basis through alternate extraction methods (e.g., base- and neutral-extractable organics fractions[39,152]) and MS modalities (e.g., APPI,[152,153] GC-MS) could provide complementary insights.[119,120,154] Application of petroleomics to environmental toxicology is an exciting new development with much room for growth (e.g., leveraging recent advances in machine learning[155]).

(Semi)passive Advanced Oxidation for Environmental Remediation. This work also represents the first steps toward the marriage of two conventionally disparate treatment modalities: passive approaches and AOPs. A passive AOP (P-AOP) is a new concept for environmental remediation, where bringing to bear the powerful treatment potential of AOPs has heretofore been impractically expensive. Using natural forces and energy sources, buoyant solar photocatalysis represents the first P-AOP developed for water treatment and may enable treatment outcomes previously inaccessible to conventional passive technologies. In the oil sands, future research should evaluate how buoyant solar photocatalysis can best integrate with existing mine closure plans, such as EPLs and wetlands—in particular, treatment wetlands may be promising to address some of the inorganic challenges in OSPW.[44,156]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.3c00616.

> Theoretical log K_{ow} predictions, water quality characterization and toxicity of control treatments, estimated partition coefficients for NAFCs (Tables S1–S6), and interactive 3D figures (Figures S1 and S2) (ZIP)
>
> Additional discussions on chemical partitioning modeling; 3D interactive figures of modeled partition coefficient fit to empirical data; figures of LC-MS AEO distributions, sulfoxide FTIR peaks, and toxicological model fit to fathead minnow results; tables of OSPW analytical characterization, model predictions, estimated partition coefficients, and LC-MS formula annotations and feature intensities (PDF)

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Funding

This study was funded by a Canadian Oil Sands Innovation Alliance (COSIA) Joint Industry Project (#818992.1) with H2nanO. F.G. acknowledges support from the NSERC Discovery Grant and TERRE-NET. T.M.C.L. gratefully acknowledges stipend support provided by the NSERC Vanier Canada Graduate Scholarship, Ontario Graduate Scholarship, and Mitacs Accelerate Entrepreneur Fellowship.

Notes

The authors declare the following competing financial interest(s): Funding: T.M.C.L., Z.W.Y., B.W., Z.Q.C., D.S., G.L., M.G., S.M., C.S., T.P., A.B., R.G., H.M., T.W., W.Z., D.J.L., A.D.R., and F.G. declare funding support (salaries) from organizations that may gain or lose financially through this publication. A specific role for one of the funders of this work (Canada Oil Sands Innovation Alliance Joint Industry Project #818992:1, including participants Canadian Natural Resources Ltd., Suncor Energy Inc., Syncrude Canada Ltd., Teck Resources Ltd., and Imperial Oil Resources Ltd.) in the decision to publish is declared: majority approval of the Steering Committee was required for public disclosure. Employment: T.M.C.L., Z.W.Y., B.W., Z.Q.C., D.S., G.L., M.G., S.M., C.S.,

T.P., A.B., R.G., H.M., T.W., W.Z., D.J.L., A.D.R., and F.G. declare recent (while engaged in the research project) or present employment by organizations that may gain or lose financially through this publication. Personal financial interests: T.M.C.L., Z.W.Y., and F.G. declare stocks or shares in H2nanO Inc., a company that may gain or lose financially through publication; and inventorship on a patent application whose value may be affected by publication (PCT/IB2017/056505, US16/343,298, assigned to H2nanO Inc., relating to buoyant photocatalysts, their methods of manufacture, and application for water treatment).

■ ACKNOWLEDGMENTS

The authors wish to thank Alberto Pereira (during his tenure at InnoTech Alberta) for his guidance in interpreting the MS data.

■ ADDITIONAL NOTES

[a] The K_{ow} and K_{mw} literature data sets were used as received, i.e., a critical review of these reference partition coefficients was out of the scope of the present work.

[b] This latter result is perhaps unsurprising: while a recent study[103] reported an OSPW sample containing NO_3^- as a "natural photosensitizer," none of the OSPWs here had NO_3^- sufficient to sensitize natural photolysis.

[c] Critical target lipid body burdens (CTLBB) of 47 and 99 μmol/$g_{octanol}$ for acute RBT and FHM toxicity, respectively, and 7.4 μmol/$g_{octanol}$ for subacute FHM (growth inhibition).[84]

[d] Inorganic toxicants or costressors, not captured in the PBM, may have contributed to the toxicity of OSPW C: a comparison to AEO measured (nonspecifically) by BE_{SPME} (Figure S14) indicated that the coverage of the MS analysis was reasonably good, insofar as BE_{SPME} did not suggest the presence of any nonpolar organics that were not already accounted for by the model. Regardless, toxicity arising from any such possible organic–inorganic interactions was also susceptible to rapid photocatalytic elimination.

[e] It must also be acknowledged that toxicity testing is a relatively imprecise tool: interlab variability of 2- to 3-fold is not uncommon.[92]

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