- 1 Photocatalytic Treatment of Diverse Contaminants of Potential Concern
- 2 in Oil Sands Process-Affected Water
- 3
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- 14

15 Abstract

16

Oil sands process-affected water (OSPW), generated by surface mining in Canada's oil 17 sands, require treatment of environmentally persistent dissolved organic compounds before 18 release to the watershed. Conventional chemical and mechanical treatments have not proved 19 20 suitable for treating the large quantities of stored OSPW, and the biological recalcitrance of some 21 dissolved organics may not be adequately addressed by conventional passive treatment systems. 22 Previous work has evaluated photocatalytic treatment as a passive advanced oxidation process 23 (P-AOP) for OSPW remediation. This work expands upon this prior research to further characterize the effects of water chemistry on the treatment rate and detoxification threshold. 24 25 Under artificial sunlight, buoyant photocatalysts (BPCs) detoxified all OSPW samples within 1 26 week of treatment time with simultaneous treatment of polycyclic aromatic hydrocarbons, 27 naphthenic acid fraction components (NAFCs), and un-ionized ammonia. Overall, these results 28 further demonstrate passive photocatalysis as an effective method for treatment of OSPW 29 contaminants of potential concern (COPCs).

30 Synopsis

Photocatalytic treatment was demonstrated as an effective method to reduce oil sands process water toxicity within 1 week of equivalent sunlight exposure. Photocatalysis effectively removed potentially toxic compounds including naphthenic acid fraction components and polycyclic aromatic hydrocarbons to non-toxic levels.

- 35
- 36 Keywords

- 37 photocatalysis, passive treatment, naphthenic acids, oil sands, polycyclic aromatic
- 38 hydrocarbons, toxicology

39 Highlights

- Buoyant photocatalysts (as a passive advanced oxidation process) were used to treat whole
 effluent toxicity in OSPW.
- Photocatalysis showed effective treatment of additional contaminants of potential concern,
 including polycyclic aromatic hydrocarbons, un-ionized ammonia, and naphthenic acid fraction
 components.
- 45 3. Solar dose of 1-7 days shown to eliminate acute toxicity to fathead minnow and rainbow trout46 species.
- 47

48 1.0 Introduction

- 49 Bitumen production from oil sands surface mining is water intensive.¹ The water used in this process,
- 50 called oil sands process-affected water (OSPW), is recycled and retained on site under a zero discharge
- 51 policy, which has led to a significant increase of tailings ponds across the oil sands region.² The
- 52 government has proposed developing water quality criteria for treated OSPW discharge to the
- 53 environment.³ While these release guidelines are pending, the toxicity of OSPW, and associated
- 54 contaminants of potential concern (COPCs), are slower to attenuate naturally than the rate at which
- 55 fresh OSPW is accumulated from bitumen production.^{4–7} A water treatment solution may therefore be
- 56 required to responsibly manage OSPW inventories into the future.
- 57 For wastewaters comprising complex mixtures of COPCs such as OSPW, current guidelines recommend
- 58 whole effluent toxicity (WET) as the basis for discharge criteria for the protection of aquatic life;⁸ WET
- 59 has also been a focus of regulatory policy development for treated OSPW release.³ OSPWs are
- 60 contaminated by both organic (*e.g.*, petroleum hydrocarbons, such as polycyclic aromatics, PAHs;
- 61 naphthenic acid fraction components, NAFCs) and inorganic (*e.g.*, trace elements, suspended solids)
- 62 COPCs, and it remains unclear the extent to which they contribute additively or interactively to the
- 63 waters' toxicity. To develop mechanistic understanding, it is therefore important that candidate OSPW
- 64 treatment solutions be evaluated not only for WET endpoints, but also for their treatment performance
- 65 toward multiple COPCs.
- 66 Considering the vastness of the challenge, passive treatment processes *i.e.*, methods reliant on natural
- 67 processes, without the need for power, chemical inputs, sophisticated infrastructure, or human
- 68 intervention have been considered the most practical solutions for OSPW remediation.⁹ However,
- 69 conventional passive treatment approaches, such as end pit lakes (EPLs) or constructed treatment
- 70 wetlands (CTWs), require protracted hydraulic retention times (HRTs) and volumes to address the
- 71 recalcitrance of NAFCs to biodegradation.^{10–12} Biological treatment systems are also inherently
- challenged by the toxicity of OSPW.^{13,14} As for abiotic methods, Syncrude recently piloted a treatment
- 73 process based on filtering OSPW through waste petroleum coke, however, while this approach reduced
- 74 dissolved organics concentrations, the treatment mechanism was based on equilibrium sorption rather
- 75 than contaminant degradation.^{15–17}
- 76 Recently we proposed solar photocatalysis with buoyant photocatalyst beads as a passive advanced
- 77 oxidation process (P-AOP) for OSPW treatment, and demonstrated the capabilities of this technology to

- rapidly detoxify OSPW, and transform and eliminate NAFCs at rates exceeding conventional passive
- 79 processes.¹⁸ Building on this prior work, to support further technology assessment, here we investigated
- 80 (a) the feed sensitivity of solar photocatalysis in terms of the spatiotemporal variability of OSPWs from
- 81 different mine operators, and (b) its treatment capacities towards additional OSPW COPCs not
- 82 previously studied, such as PAHs and inorganics.
- 83

84 2.0 Methods

85 2.1 Photocatalysis Experiments

Photocatalytic treatment experiments were performed using industrial samples of OSPW from two 86 87 different oil sands mine operators near Fort McMurray, AB, Canada, sampled from active tailings ponds 88 in 2022 and delivered in HDPE intermediate bulk containers (IBCs) by ground freight to Toronto, ON, 89 Canada, referred to herein as OSPWs A and B. Two samples of OSPW Sample A were examined, Sample 90 A-1 having undergone natural aging during storage, resulting in a decreased initial toxicity but otherwise 91 similar water chemistry to a fresh Sample A-2. Experiments were performed in a custom high-density 92 polyethylene tank with a lengthwise internal baffle to create a circulating flow path with a UV exposed 93 area of 3.2 m² (Figure S1 & S2). The reactors were filled with 800 L of OSPW for each test, corresponding 94 to an initial operating depth of 25 cm. The reactor volume was circulated and mixed with a centrifugal 95 pump (Vevor 1.5 hp, 12.5 m max. head lift), with the inlet located in the bottom of the raceway and two 96 outlets positioned in opposite corners. Each outlet was equipped with an eductor (BEX, T3MP K, 1") to aid 97 in the water circulation motive force and continuous mixing of the slurry to disperse the treatment 98 materials in the OSPW. Buoyant photocatalyst (BPC) particles (TiO₂ coated hollow glass beads, previously 99 characterized in literature,^{19,20} provided by H2nanO Inc.) were added at a dose of 10 g/L.

- To simulate solar UV exposure, the reactor tank was positioned 3 ft underneath a custom-manufactured overhead frame equipped with 6 × 1.5 ft l × w UV lamps (Solarc SolRx, F72T12/BL/HO UV-A bulbs). UVlight intensity was measured daily using a handheld UVA/UVB light meter (Sper Scientific, 850009). UV intensity readings were collected at 6 locations 1 inch above the water level. Evaporation was accounted for by monitoring the liquid level in the raceway pond over the length of the study and adding an equivalent volume of de-ionized water as required to balance evaporative losses.
- Samples were taken at UV doses corresponding to 0, 1, 2, 4, 7, and 14 equivalent days for Sample A and 0, 2, 4, 7, 14, and 30 equivalent days of solar UV exposure for Sample B. "Equivalent days" (equiv. days) herein refers to the expected exposure duration (treatment time) required at Fort McMurray, AB, Canada
- to accumulate the same solar UV dose to the water (May Sept. average).
- 110 Controls were performed using the same OSPW samples and catalyst dose but in 20 L HDPE buckets. 111 Controls include a photolysis control (+UV, -BPC), an adsorption control (-UV, +BPC), and a dark control (-112 UV, -BPC). All controls were performed under the same ambient conditions as the photocatalytic 113 treatment experiment.

114 **2.2 Analytical Methods**

Whole effluent toxicity (WET) testing was performed by Aquatox Testing & Consulting (Puslinch, ON,Canada) according to the standard Environment Canada bioassays for rainbow trout (RBT) 96-h lethality

at 100% effluent concentration (EPS 1/RM/13) and fathead minnow 7-day lethality and growth inhibition

at 100% effluent concentration (EPS 1/RM/22). These standard bioassays are the basis of provincial water quality guidelines for the protection of aquatic life and are the regulatory basis for waters containing complex mixtures of compounds,^{21,22} such as OSPW. Additional details for each bioassay are in the accompanying Supporting Information.

Acid-extractable organics (AEOs), comprising classical NAs, oxy-NAs ($C_nH_{2n+z}O_x$, where x >2), and other acid and neutral organics, have been conventionally correlated with OSPW toxicity. AEOs were analyzed using Fourier transform infrared spectroscopy (FTIR), correlating the IR carbonyl bond absorbance to mg/L AEO concentration through comparison to a reference standard (Naphthenic Acid technical mixture, product number 70340, Sigma-Aldrich) AEO-FTIR was analyzed according to updated methods proposed in literature²³ (details provided in Supporting Information).

- 128 Chemical oxygen demand (COD) measurements were performed according to the standard method²⁴ using the low-range COD reagents provided by Hach (Method 8000). Total ammonia was measured using 129 130 an adapted method from literature²⁵ using Hach reagents and method 10023. Total organic carbon was analyzed using the Standard Method 5310B by ALS Laboratories (Waterloo, ON, Canada). UV_{254nm} 131 absorbance was used to estimate the relative concentration of dissolved aromatic or UV-absorbing 132 133 organics in OSPW following a prefiltration step using a 0.45 µm PTFE filter (VWR Canada). The UV/Vis 134 spectral absorbance of the samples was measured using a plate reader spectrophotometer (Tecan Infinite 135 M Plex Plate Reader) and a 96-well microplate, and compared to a deionized water blank (Millipore, \geq 18 136 MΩ·cm).
- Polycyclic aromatic hydrocarbon (PAH) analysis was performed by the Centre for Oil & Gas Research and
 Development (COGRAD) at the University of Manitoba in Winnipeg, MB. Samples were extracted and
 analyzed by gas chromatography tandem mass spectrometry (GC-MS-MS) according to COGRAD's
 previously published analytical methods for polycyclic aromatic hydrocarbons (PAHs), alkylated PAHs, and
 halogenated PAHs.^{26,27}
- - BE-SPME is a recently established analytical method for assessing the bioavailable organics in a sample.^{28–}
 ³⁰ Depending on chemical properties such as molecular weight, charge, polarity, and hydrophobicity,
 - 144 various chemicals may partition to biological tissues to a greater or lesser extent. The principle of
 - 145 biomimetic extraction (BE) is to simulate the bioaccumulation of compounds to biological lipid tissues
- through the use of a synthetic, biomimetic lipid-like substrate (*i.e.*, a passive sampler, typically a PDMS-
- 147 coated solid phase microextraction [SPME] fiber), where the concentration of compounds in this substrate
- 148 can be quickly and easily measured using standard analytical chemistry techniques. BE-SPME analysis was
- 149 performed by ExxonMobil Biomedical Sciences Inc. (EMBSI) in Annandale, New Jersey, U. S. A. according 150 to the previously reported method ^{30,31}
- to the previously reported method.^{30,31}
- Liquid chromatography mass spectrometry (LC-MS) analysis was used in this project to develop a more 151 152 comprehensive understanding of the various classes of naphthenic acid fraction compounds (NAFCs) in 153 the as-received OSPW samples, as well as the treatment's differential effect on these various classes. 154 Samples for LC-MS analysis were acid-extracted with dichloromethane according to the same method as 155 the AEO_{FTIR} analysis above and sent to InnoTech Alberta (Vegreville, AB, Canada) for analysis (Supporting 156 Information). Additional samples were analyzed through the University of Toronto BioZone MS facility 157 (method detailed in Supporting Information) and processed using an open-source workflow (Figure S3). A 158 comparison of the LC-MS analysis datasets is presented in the Supporting Information.

- 159 Trace elements were analyzed via inductively coupled plasma mass spectrometry (ICP-MS) according to
- 160 Standard Methods 3030B/6020A by ALS Laboratories (Waterloo, ON, Canada). Aqueous ammonia was
- 161 measured as nitrogen, according to the salicylate TNT method using the high-range reagents provided by
- 162 Hach (Method 10031). Total nitrogen was measured according to the persulfate digestion method using
- the reagents provided by Hach (Method 10072).

164 **3.0 Results and Discussion**

165 **3.1 Raw OSPW Characterization**

- The as-received OSPW samples were evaluated for the initial water chemistry and toxicity before treatment testing. Both samples caused RBT mortality and FHM growth inhibition upon delivery, as summarized in Table 1, with statistically significant mortality and growth inhibition, subsequently targeted for elimination through photocatalysis treatment of the dissolved organics. Notably, Sample A-1 had a lower initial toxicity than Sample A-2. This is hypothesized to have occurred from the natural aging of potentially toxic compounds in Sample A-1, whereas Sample A-2 had not undergone this aging procedure. Despite the reduced toxicity, Sample A-1 had similar levels of both acid-extractable organics (AEO-FTIR)
- and BE-SPME compounds, indicating that only a small fraction of these parameters may contribute to
- 174 overall OSPW toxicity.
- 175 In addition to toxicology, the samples were analyzed for various water chemistry parameters, detailed in
- 176 Table S1, to evaluate the contributions of additional COPCs to detoxification kinetics and whole effluent
- 177 toxicity (WET). The primary potential toxicants detected in each OSPW sample were the AEO and NAFCs.
- 178 OSPW Sample B also had ammonia concentrations at potentially toxic concentrations (5.2 mg/L as N).
- 179 None of the other potential toxicants measured (such as PAHs, F1-F4 hydrocarbons, reduced sulfur
- 180 compounds, VOCs, BTEX, SVOCs, phenols) besides AEO/NAFCs were present in detectable or significant
- 181 concentrations to influence toxicity. Notably, both OSPW samples contained detectable initial alkyl-PAH
- 182 concentrations but at levels well below the acute toxicity thresholds.
- Comparing the present OSPW samples to those previously studied¹⁸ (sampled earlier from the same locations), the earlier OSPW samples had much stronger toxicity to fathead minnow, despite lower levels of AEOs and BE-SPME compounds. This may be due to the elevated levels of classical naphthenic acids (represented by the NA_{MS} measurement), although as shown in previously,¹⁸ classical NAs are not always
- 187 reliably correlated with OSPW toxicity.
- Table 1. Initial toxicological profile and water chemistry of oil sands process affected water (OSPW) samples prior to
 treatment testing.

		This Work			Leshuk et al. (2023) ³²	
Parameter	Unit	Sample A-1	Sample A-2	Sample B	Sample A	Sample B**
Rainbow Trout (RBT) Mortality	%	20	100	100	100	100
Fathead Minnow (FHM) Mortality	%	0	8	73	92 ± 8	0

FHM Growth Inhibition	%	19	25	91	89 ± 16	40 ± 9
Acid-Extractable Organics via FT-IR (AEO _{FTIR})	mg/L	44	40	67	25.3	32.2
Naphthenic Acids, Speciated, via Mass Spectrometry (NAs _{MS})	mg/L	N/A	0.708	0.416	7.5	7.3
Bio-mimetic Extraction via Solid Phase Micro- Extraction (BE _{SPME})	nmol/L	59.1	57	86	47.0	51.1
Polycyclic Aromatic Hydrocarbons (PAHs) & Alkyl PAHs	ng/L	1285*	2256*	4237*	N/A	N/A
Ammonia	mg/L as N	n.d	n.d.	5.0	N/A	N/A

^{*}Predominately alkyl-PAHs, esp. C4-naphthalene [†]and dibenzothiophenes

191 **Specified as "OSPW C" in Leshuk et al. (2023)³²

192

3.2 Photocatalytic Treatment Rapidly and Reproducibly Detoxifies OSPW

193 Photocatalysis treatment successfully eliminated RBT mortality and FHM mortality and growth inhibition 194 effects in all OSPW samples within ~1 week of simulated solar UV, despite the increased organics concentrations, salinity, and NH₃ concentration in Sample B. The treatment thresholds are determined by 195 196 the first sampled dose with no significant inhibition effect, as determined by RBT and FHM bioassay 197 standard methods and accredited laboratory results analysis. The UV dose required for detoxification for 198 all samples are summarized in Table 2. Notably, despite a lower initial RBT mortality, Sample A-1 and A-2 required similar UV doses for detoxification, demonstrating the reproducibility of photocatalysis for OSPW 199 detoxification. Compared to past treatment results on OSPWs from the same sources,¹⁸ similar solar UV-200 201 light doses were required for Sample A (≤ 2 equivalent days), further validating the reproducibility of 202 photocatalytic OSPW detoxification. Also of note, these results further demonstrate that OSPW 203 detoxification is achievable prior to significant changes to bulk/composite measures of dissolved organics, 204 such as AEO-FTIR, COD, and TOC (Table S1); these parameters continue to show poor correlation with 205 WET outcomes. Similar UV doses were required under outdoor natural solar UV¹⁸ and indoor simulated solar UV (this work). Sample B required a greater UV dose to detoxify in the work than was found 206 207 previously. Notably, in the present work, Sample B contained levels of ammonia above the acute toxicity 208 threshold to RBT, possibly contributing to the increased UV dose required for toxicity elimination. Toxicity 209 from naphthenic acids was likely treated in ≤ 2 equivalent days based on the results of Sample A.

Table 2. UV dose thresholds for RBT and FHM toxicity elimination to below significant effect (as determined by third
 party accredited labs) in treated OSPW samples.

Sample	Unit	RBT Mortality	FHM Mortality	FHM Growth Inhibition
Sample A-1	kJ/L	≤4.3	n/a†	n/a
	Equiv. Days	≤0.98	n/a†	n/a
Sample A-2	kJ/L	≤4.5	≤8.8†	≤8.8
	Equiv. Days	≤1.0	≤2.0†	≤2.0
Sample B	kJ/L	17.3 – 35.9	≤17.3	≤17.3
	Equiv. Days	4.0-8.3	≤4.0	≤4.0

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^tLow initial FHM mortality was observed for the raw as-received Sample A (3% and 8% respectively).

213 The photocatalytic treatment data for Sample A-1, Sample A-2, and Sample B are shown in Figure 1. 214 Photocatalysis successfully eliminated the acute toxic effects in Sample A-1 and Sample A-2 within 4.5 kJ/L 215 of artificial solar UV dose, or the equivalent of 1 day of solar treatment. For Sample A-1, AEO-FTIR and BE-216 SPME were treated by 70% and 94%, respectively with a UV dose of 60.7 kJ/L, or the equivalent of 2 weeks 217 of solar UV treatment. For Sample A-2, AEO-FTIR and BE-SPME were treated by 74% and 93%, 218 respectively, demonstrating replicable organics treatment in both Sample A-1 and A-2 despite the 219 differing initial WET. Additionally, while these results demonstrate that significant treatment of AEO-FTIR 220 and BE-SPME compounds is reproducible via photocatalysis, it is also demonstrated that full treatment of 221 these parameters is not needed to eliminate WET.

222 For Sample B, photocatalysis successfully eliminated the acute toxicity effects within 17.3 kJ/L of artificial 223 solar UV dose (4 equivalent days of sunlight) and eliminated the acute toxicity for RBT within 17.3-35.9 224 kJ/L (4-8 days solar equivalent). AEO-FTIR and BE-SPME were treated by 71% and 89% respectively, with 225 a UV dose of 129.9 kJ/L, or the equivalent of 30 days of solar UV treatment. However, as with Sample A-1 226 and A-2, neither parameter required this level of treatment to pass the target WET bioassays. Of interest, 227 both BE-SPME datasets increased briefly as toxicity decreased. While not present in Sample A-1 or Sample A-2, Sample B contained an initial ammonia concentration above the RBT and FHM LC50,^{33,34} which likely 228 229 contributed to the initial RBT and FHM toxicity. The ammonia present in the Sample B OSPW may be 230 present from bitumen upgrading operations and is expected to differ based on the OSPW source. Through

photocatalytic oxidation, the ammonia concentrations were reduced to non-toxic levels after 4-8
 equivalent days of solar UV, and 99.6% were eliminated after 30 equivalent days.





Figure 1 – Photocatalytic elimination of Sample A OSPW acute toxicity toward rainbow trout (RBT), acute & chronic
 toxicity toward fathead minnow (FHM), acid-extractable organics measured by FTIR (AEO-FTIR), BE-SPME, chemical
 oxygen demand (COD), PAHs and alkyl-PAHs (sum), and ammonia (total, as N).

237 When compared to controls (dark, adsorption, and photolysis), it is shown that the treatment of the 238 toxicity in OSPW is driven by photocatalysis for both OSPW samples, as shown in Figure S6. Both the 239 adsorption control and the photocatalysis treatment experiments demonstrated initial rapid detoxification for RBT in Sample A, indicating that the adsorption of potentially toxic compounds by the 240 241 buoyant photocatalyst materials may be an important factor. A key advantage of heterogenous 242 (particulate) photocatalysis over other oxidation treatment processes is that both adsorption and 243 oxidation effects occur simultaneously – photocatalysts can be viewed as self-regenerating adsorbents. 244 However, this result was not observed in Sample B, potentially due to the elevated levels of un-ionized 245 ammonia present. Notably, all samples not exposed to the photocatalyst materials remained acutely toxic to RBT. 246

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3.3 Non-Classical Naphthenic Acids Correlated with Toxicity Treatment Trends

248 LC-MS analysis of NAFCs and NAs during the treatment of Sample A-2 is presented in Figure 2 and Figure 249 3. The most notable change in the heteroatom class distribution during treatment is the preferential 250 elimination of N- and S-containing NAFCs (Figure 2), as observed previously,²⁰ with potential implications 251 for understanding the toxicity of OSPW: the rapid drop in fish toxicity in the first day of treatment was correlated with a drop in the N- and S-containing NAFCs, and uncorrelated with classical NAs.¹⁸ While 252 OSPW toxicity has been ascribed primarily to classical NAs,³⁵ this conclusion may have derived from 253 254 analytical limitations (e.g., early literature seldom measured positive-ion mode MS) – recent research 255 has suggested that non-classical NAFCs (especially OS⁺ compounds) may be among the principal

256 toxicants in OSPW.^{36–38} Indeed, there are examples reported of non-toxic OSPW with high

- 257 concentrations of classical NAs,^{39,40} and OSPWs remaining acutely toxic despite virtually complete
- 258 removal of classical NAs.⁴¹ Herein, non-classical NAFCs correlated with OSPW toxicity, consistent with
- 259 results found previously.¹⁸ The CHO– distribution shifted to a higher mean oxygen number during
- 260 treatment, while the CHO+ concentrations, especially O₂ to O₄ were relatively unchanged from t0 to t5,
- as observed previously;²⁰ these CHO+ components are considered to be hydroxylated intermediates
- 262 formed from photocatalytic oxidation of other NAFCs. Photocatalytic elimination of classical NAs was
- pronounced, with a clear shift of the distribution to lower carbon and DBE numbers (Figure 3), as
- observed previously,²⁰ indicating preferential degradation of the most biologically recalcitrant molecular
- 265 structures.



266 267 Figur

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Figure 2 – NAFC heteroatomic class distributions before (t_0 , as-received OSPW), after (t_5 , 14 equiv. days UV exposure) photocatalytic treatment of Sample A, and after (t_5 , 30 equiv. days UV exposure) photocatalysis treatment of Sample B, measured by LC-MS in both ionization polarities (ESI +/-).

270 LC-MS analysis of NAFCs and NAs during the treatment of Sample B is presented in Figure 2 and Figure 3. 271 The initial distribution of NAFCs in Sample B was different from that of Sample A-2, e.g., a greater 272 abundance of CHO vs. CHNOS components in ESI+. The distribution of classical NAs in the as-received 273 Sample B (Figure 3) was also markedly different from Sample A-2, with a relatively much smaller cluster 274 at C 14-20, DBE 7-8, with a greater proportion of smaller NAs at $c \le 10$. This lower initial distribution of NA 275 molecular weight may explain why the relative NA concentration (C/C_0) did not decrease as much as 276 observed in prior work, since low molecular weight NAs can be formed during treatment from the 277 decomposition of larger molecular weight NAFCs²⁰; smaller and simpler NA molecular structures are 278 known to be more biodegradable, and more easily eliminated through secondary natural aging processes.

This also may explain the decreasing trend in toxicity during the first week of treatment in Sample B: larger and more hydrophobic NAFCs were being degraded, but the total NA concentration (including NA intermediates in the sum) did not change as extensively. A stronger decrease in the concentration of dicarboxylic NAs (O₄- components) was observed from treatment, and like the Sample A-2 and prior results,¹⁸ a preferential elimination of N- and S-containing compounds in ESI+. Overall, for both Sample A-2 and Sample B, non-classical NAFCs exhibited the strongest correlation with OSPW toxicity trends and

285 were preferentially treated via photocatalysis.



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287Figure 3 – Distribution of classical NAs (O_2^- formulas only) in (a, b) Sample A2, and (c, d) Sample B OSPWs both (a,288c) before (t_0 , as-received OSPW) and (b,d) after photocatalytic treatment (t_5 , 14 or 30 equiv. days UV exposure for289Samples A2 and B, respectively), as measured by LC-MS.

290 **3.4 Photocatalysis Effectively Treats Polycyclic Aromatic Hydrocarbons**

The photocatalytic treatment data for the (alkyl-)PAH concentrations for Samples A and B are shown in Figure 4. While the initial (alkyl-)PAH concentrations are well below the acutely toxic level in these OSPW samples, they are a concern in a broader environmental context^{42,43} as a persistent and bioconcentrating toxicant. For Sample A-2, ≥90% of the most abundant and toxic (alkyl-)PAHs were removed within 2 weeks of treatment under equivalent solar UV. For Sample B, photocatalysis removed ~60% of the most abundant and (alkyl-)PAHs within 4 days of treatment and ~90% within 30 days. Both OSPW samples demonstrate the efficacy of photocatalysis for effective passive treatment of PAHs. The removal efficacy may be weakly dependent on the PAH partition coefficient ($\log K_{ow}$), seen in Figure 5 (Sample A) and Figure 6 (Sample B). Photocatalysis provides effective treatment of all PAHs tested, even for less water-soluble PAHs that are poorly treated in OSPW treatment wetlands.⁴⁴.



301



Figure 4 – Photocatalytic treatment data for the most abundant (alkyl-)PAH compounds in a) Sample A and b)
 Sample B.







Figure 5 – OSPW Sample A polycyclic aromatic hydrocarbon removal efficacy by photocatalytic treatment as a function of the PAH partition coefficient. TU = toxic units, *i.e.*, PAH concentrations normalized to each their respective LC50 (96 h rainbow trout), as calculated by the TLM from PAH K_{ow} data.



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3.5 Additional Trace Elements Removed via Photocatalysis

314 Previous studies investigating photocatalytic treatment of OSPW have focused on WET and organics removal¹⁸⁻²⁰. In this study, trace elements in the OSPW were monitored during photocatalysis, and 315 decreasing concentrations were observed for cobalt, manganese, nickel, strontium, and uranium (Figure 316 317 S7). However, it is unlikely that these elements contributed significantly to the WET. Manganese 318 treatment has previously been shown to occur via oxidative precipitation⁴⁵, while treatment of the other 319 metals may occur due to adsorption onto the catalyst. Photocatalysis may offer benefits for additional contaminants of potential concern (*i.e.* V and Se) through photocatalytic reduction^{46,47} or oxidative pre-320 321 treatment of As.⁴⁸ While these elements were present in OSPW at trace levels close to the lower detection 322 limits, these results demonstrate the potential of photocatalysis to simultaneously treat trace metals 323 during OSPW detoxification.

324 **3.6** Treatment of Ammonia Correlated with Toxicity Decrease

Notably, Sample B contained initial levels of un-ionized ammonia (0.87 mg/L) above the reported 96-h LC50 value for rainbow trout^{33,49}, likely contributing to the WET for OSPW Sample B. Throughout the photocatalytic treatment of Sample B, the decrease in WET was correlated to corresponding decreases in the ammonia concentration, suggesting that ammonia may be a contributor to the toxicity of OSPW B. These results also demonstrate effective photocatalytic removal of ammonia during detoxification treatment. Initial and final total nitrogen measurements of Sample B were 6.6 and 2.7 mg/L, respectively, suggesting that a portion of ammonia was volatilized during treatment and the remainder oxidized via

- 332 photocatalysis. The conversion of ammonia to N₂ via photocatalysis has also been reported previously.⁵⁰
- 333

4.0 Implications for OSPW Detoxification via Photocatalysis

Buoyant photocatalysis has been rigorously tested in an indoor setting under simulated solar UV, achieving OSPW detoxification for rainbow trout and fathead minnow in less than 1 week of treatment time across 3 water sources, consistent with treatment results from prior studies.¹⁸ Notably, non-classical NAFCs correlated with the WET and were preferentially treated via photocatalysis; complete NAFC elimination was not required to achieve WET detoxification. Additional COPCs, including PAHs and unionized ammonia, were also significantly removed using photocatalysis, where the aqueous ammonia concentration also correlated with OSPW toxicity.

- 342 Given the promising performance of passive photocatalysis, further testing for simultaneous treatment of
- 343 COPCs, both organic and inorganic, in an operational environment for extended periods is recommended.
- 344 Overall, buoyant photocatalysts have demonstrated rapid and consistent elimination of adverse effects
- on aquatic species from OSPW, achieving industry objectives for passive OSPW treatment.

346 **5.0 Acknowledgement**

- The authors gratefully acknowledge the technical review and discussion of the manuscript by
 Pascale St-Germain (Imperial Oil Ltd.).
- 349

350 **6.0 Author information**

T.M.C.L., Z.W.Y., and F.G. declare ownership stakes in H2nanO Inc., a company with financial
 interest in the subject matter of this work, as well as inventorship on a BPC patent application
 (PCT/IB2017/056505, US16/343,298) assigned to H2nanO. The other authors declare no potentially
 competing conflicts of interest.

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356 **7.0 Supporting Information**

The supporting information contains diagrams of the apparatus used for the treatment
 experiments, detailed analytical methods descriptions, additional raw water chemistry, and additional
 PAH treatment data.

360

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