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# Effects of Oil Sands Process-Affected Water on Measured Concentrations of Polycyclic Aromatic Hydrocarbons

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**ABSTRACT:** The assessment of the risks and remediation of oil sands process-affected water (OSPW) requires an understanding of possible interactions of naturally occurring surfactants with hydrophobic organic compounds, such as polycyclic aromatic hydrocarbons (PAHs). In this study, the effects of the extractable organic fraction of OSPW (OF-OSPW) on the rate of release and freely dissolved aqueous concentration of several PAHs were investigated using a passive dosing approach, in which a poly-(dimethylsiloxane) (PDMS) film was loaded with the PAHs of interest. The concentrations of PAHs released from PDMS into aqueous solutions were directly proportional to the concentrations of OF-OSPW. PAHs reached equilibrium partitioning 1−4 h faster when the aqueous phase was OF-OSPW than when it was freshwater. Greater concentrations of PAHs were released from PDMS when OF-OSPW was reconstituted in saline water compared to when it was reconstituted in freshwater. The apparent aqueous solubilities of PAHs were greater in intact OSPW than in OF-OSPW. The measured concentrations of PAHs in various aqueous solutions of OSPW and salts correlated with log $K_{ow}$ of PAHs. This might be because of disruption of PAHs sorbed into PDMS. These results suggest that the bioavailability of PAHs can be greater in the presence of more polar organic compounds in OSPW.

**KEYWORDS:** OSPW, PAHs, bioavailability, apparent aqueous solubility, PDMS, surfactant, naphthenic acid
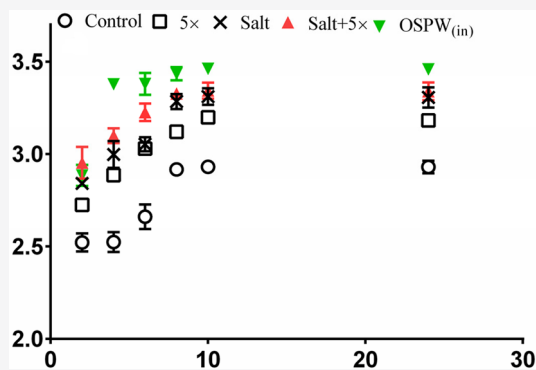
## 1. INTRODUCTION

Extraction of bitumen from surface-mined oil sands deposits in northeastern Alberta, Canada, requires the use of hot, alkaline water to separate bitumen from other unwanted constitutes such as clay, salts, and polar organic compounds. This extraction process results in tailing slurries that comprise process-affected water (OSPW), which contains organic and inorganic chemicals, including salts, and solids such as sand and clay that slowly densify to form mature fine tailings (MFTs)[1] that leave behind an aqueous phase of OSPW. One major challenge facing the surface mining oil sands industry is the release of OSPW back into the environment, which has not been done by industry because of a self-imposed policy of zero discharge.[2] To develop effective strategies for reclamation, remediation, and potential release of OSPW, it is important to understand not only the adverse effects of exposure to OSPW and the chemical composition of OSPW but also the chemodynamics of chemicals in OSPW.[1,2]

Tailings ponds contain a complex mixture of organic and inorganic chemicals. The aqueous phase of OSPW contains a suite of compounds comprised of not only carbon and hydrogen but also heteroatoms of nitrogen, sulfur, and oxygen (NSO),[3,4] including naphthenic acids (NAs),[1] as well as salts and metals.[5] Fine tailings contain nonsoluble organic

contaminants, such as BTX, which includes benzene, toluene, and xylene, humic and fulvic acids, trace metals, asphaltenes, and polycyclic aromatic hydrocarbons (PAHs).[6] Polycyclic aromatic hydrocarbons make up a group of organic chemicals derived from natural and anthropogenic sources that can be distributed across air, soil, and water bodies.[7] Polycyclic aromatic hydrocarbons and their metabolites have been detected in sediments of lakes,[8,9] snowpack,[10] and fish[11] near oil sands mining and upgrading operations. Also, oil sands surface mining and processing at bitumen upgrading facilities contribute to atmospheric deposition of PAHs.[12−17] In oil sands tailing ponds, several PAHs were identified at low concentrations in pore waters.[18−20] Besides mining and upgrading of bitumen, processes such as a natural erosion of geological formations, forest fires, diesel combustion, residential heating, and airborne dust from roads and mining

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operations contribute to concentrations of PAHs in the oil sands region.[15,21]

Natural and industrial sources of bitumen can influence chemistries of surface waters and groundwaters in the oil sands region, which might cause mobilization of polar water-soluble bitumen-derived chemicals into the Athabasca River watershed.[22−24] The water-soluble fraction (WSF) of bitumen contains NAs, which are surfactant-like, acyclic, monocyclic, and polycyclic acids that are defined by the molecular formula $C_nH_{2n+z}O_2$.[1] Organic acids are the most abundant, water-soluble compounds in bitumen, but their solubilities in water depend on pH.[25−28] In addition, bitumen and OSPW contain a suite of basic and neutral heterocyclic/aromatic NSO compounds that are soluble at ambient pH.[4,26,27] OSPW also consists of greater concentrations of inorganic ions such as $Na^+$, $Cl^−$, $HCO_3^−$, and $SO_4^{2−}$, which results in the salinity of OSPW being greater than that of natural surface waters of the region.[5] Because oil sands tailing ponds are a source of PAHs and heteroatomic PAHs, the concentrations of salts and surfactants in tailings ponds might affect the chemodynamics and kinetics of release of PAHs from tailings into the aqueous phase of OSPW.

The sequestration of PAHs in soils and sediments is a function of hydrophobicity, and solubility, which is inversely proportional to molecular mass, strong sorption (affinity), and slow release.[29,30] Lower-mass organic acids, and non-ionic surfactants, can modulate the bioavailability of PAHs by disrupting their sequestration in contaminated soil and sediment and increasing their concentrations in solution.[31−39] Surfactant-enhanced desorption is one method used to enhance the mobilization, bioavailability, and solubilization of PAHs sorbed to particulates in sediments and soils.[40] Although enhancement of the bioavailability of PAHs might be important for remediation of PAHs in contaminated sites, it has been argued that it might increase risks to organisms in aquatic environments by increasing the accessible quantity and chemical activity.[41,42] PAHs and naturally occurring non-ionic and ionic surfactants in bitumen and OSPW might coexist in aquatic environments; however, their interaction is not well understood. Surfactants in OSPW, such as acidic, basic, and neutral, can be released (seepage) into surface waters from deposits of bitumen, and from tailings ponds.[43,44] PAHs from tailings ponds and bitumen and from the transportation of suspended particles can enter aquatic environments such as surrounding bodies of waters.[9,10,13]

Previously, it has been shown that dissolved organic fractions of OSPW extracted at neutral pH enhance the partitioning of the alkylated PAH, retene, from poly-(dimethylsiloxane) (PDMS) to the aqueous phase, resulting in greater bioavailability to embryos of Japanese medaka (*Oryzias lapites*).[45] It is therefore possible that aqueous-phase surfactant micelles and salts in OSPW can increase the aqueous concentrations of hydrophobic organic compounds, such as PAHs, by enhancing desorption from suspended fine tailings. The primary aim of this study was to investigate the effects of the extractable organic fraction of OSPW (OF-OSPW), intact OSPW [$OSPW_{(in)}$], a commercial mixture of NAs, and salinity on the rates of desorption and dissolved concentrations of PAHs loaded into PDMS. The results of this study could lead to an improved understanding of the fates of PAHs in OSPW and in water containing ionic and non-ionic surfactants from OSPW.

## 2. MATERIALS AND METHODS

**2.1. Chemicals.** Acenaphthene (AC), phenanthrene (PH), and pyrene (PY) were obtained from Wellington Laboratories (Guelph, ON). Carbazole (CA), dibenzofuran (DF), dibenzo-thiophene (DT), fluorene (FL), and a commercial mixture of NAs were obtained from Sigma-Aldrich (Oakville, ON). Methanol, ethyl acetate, dichloromethane, and hexane (HPLC-grade) were purchased from Fisher Scientific (Edmonton, AB). Acetic acid was purchased from Sigma-Aldrich. Deionized water was City of Saskatoon municipal water purified using a Milli-Q apparatus. PDMS (aquarium-grade sealant) was purchased from Marineland (Blacksburg, VA). Reconstituted saltwater (saline solution)[46] was used to investigate the influence of salinity on the apparent aqueous solubility of PAHs. The solution was prepared to mimic the salinity and major ion concentrations in OSPW. Briefly, 958 mg/L $NaHCO_3$, 663 mg/L NaCl, 160 mg/L $Na_2SO_4$, 141 mg/L $CaSO_4 \cdot 2H_2O$, 112 mg/L $MgSO_4 \cdot 7H_2O$, and 16.5 mg/L KCl were added to reverse osmosis water.

**2.2. Extraction of the Organic Fraction of OSPW (OF-OSPW).** OSPW was collected from Base Mine Lake in 2015, which is an end-pit lake constructed from the West-In-Pit settling basin that received input of tailings from the main extraction facility (Syncrude Canada, Ltd., Fort McMurray, AB). THe preparation of OF-OSPW was described previously.[28] Briefly, 500 mL of OSPW (pH ~9) was passed through a glass microfiber filter (GF/D 0.47 mm, Whatman) to remove any suspended particulates. Preconcentration of samples was performed in one step using 500 mg of EVOLUTEABN sorbent (Biotage, Charlotte, NC). Before the addition of OSPW, the cartridge was conditioned with 6 mL of methanol followed by 6 mL of ultrapure Milli-Q water (Millipore, Mississauga, ON). Next, 500 mL of OSPW was passed through the cartridge under vacuum at a flow rate of 10−15 mL min⁻¹. Subsequently, cartridges were washed with Milli-Q water and allowed to dry under vacuum for 30 min. The total dissolved organic compounds were eluted in one step with 6 mL of methanol, without use of a vacuum. The eluent was evaporated to dryness under a gentle stream of nitrogen and reconstituted in 500 μL of absolute ethanol. Therefore, the concentration of dissolved organic compounds in the final sample was 1000 times greater than in the original sample of OSPW. The profile of heteroatom classes of this fraction was reported previously.[28]

**2.3. Loading of PDMS with PAHs.** The aqueous apparent solubility of PAHs in this study was estimated using a partition-controlled delivery system of a PDMS film containing the tested compounds.[45,47] Briefly, a mixture of PAHs (individual PAHs combined in one mixture) was prepared as a stock solution that was dissolved in a PDMS solution prepared in a DCM/hexane solvent (15:85), and the solution was sonicated until complete dissolution had been achieved. The final concentration of each PAH in the mixture was 40 μg/mL. The use of the same procedure yielded a negative control that did not contain PAHs. Next, 3 mL of the mixture was transferred into each 20 mL glass vial, and vials were placed in a fume hood until all solvents evaporated. Vials were wrapped in tin foil, and all procedures were conducted in the dark. Then, 15 mL of ultrapure water (freshwater) was added to each vial. Immediately, vials were spiked with either the commercial mixture of NAs at a final concentration of 50 mg/L, OF-OSPW to give final equivalents of 1×, 2.5×, or 5× OF-

**Table 1. Kinetics of the Release into Water of PAHs from PDMS in the Presence of OF-OSPW (1×, 2.5×, and 5×) and a Commercial Mixture of NAs at 50 mg/L**[a]

| | control | | 1× OF-OSPW | | 2.5× OF-OSPW | | 5× OF-OSPW | | NAs | |
|---|---|---|---|---|---|---|---|---|---|---|
| | rate constant (SE) | time for 95% steady state (h) | rate constant (SE) | time for 95% steady state (h) | rate constant (SE) | time for 95% steady state (h) | rate constant (SE) | time for 95% steady state (h) | rate constant (SE) | time for 95% steady state (h) |
| acenaphthene | 0.26 (0.04) | 11.35 | 0.23 (0.04) | 12.78 | 0.30 (0.08) | 9.88 | 0.41 (0.01) | 7.20 | 0.26 (0.04) | 11.18 |
| fluorene | 0.54 (0.05) | 5.48 | 0.69 (0.05) | 4.29 | 0.58 (0.05) | 5.11 | 0.77 (0.13) | 3.87 | 0.68 (0.06) | 4.35 |
| phenanthrene | 0.17 (0.03) | 17.60 | 0.17 (0.04) | 17.51 | 0.15 (0.04) | 19.12 | 0.19 (0.02) | 15.36 | 0.17 (0.04) | 17.41 |
| pyrene | 0.29 (0.04) | 10.04 | 0.28 (0.05) | 10.38 | 0.25 (0.04) | 11.80 | 0.30 (0.02) | 9.75 | 0.28 (0.05) | 10.42 |
| carbazole | 0.20 (0.02) | 14.97 | 0.20 (0.02) | 14.61 | 0.24 (0.02) | 12.08 | 0.24 (0.03) | 12.19 | 0.24 (0.02) | 12.22 |
| dibezofuran | 0.61 (0.05) | 4.91 | 0.59 (0.04) | 5.07 | 0.61 (0.05) | 4.84 | 0.71 (0.10) | 4.18 | 0.58 (0.05) | 5.09 |
| dibenzothiophene | 0.75 (0.09) | 3.97 | 0.78 (0.09) | 3.81 | 0.64 (0.06) | 4.68 | 0.75 (0.09) | 3.98 | 0.75 (0.06) | 3.96 |

[a]Values are the means of three replicates.

OSPW, or reconstituted saline water. For OSPW(in), vials were filled with filtered OSPW instead of ultrapure water, and the experiments were conducted in three replicates. One milliliter of solution was sampled from each vial at 0, 2, 4, 6, 8, 10, and 24 h and stored at −4 °C until analysis.

**2.4. Quantification of PAHs in Solution.** Aqueous concentrations of PAHs were measured in samples taken at 0, 2, 4, 6, 8, 10, and 24 h in the solvent control, OF-OSPW, OSPW(in), and solution of salts. Extraction of PAHs was performed using a liquid−liquid method.[45] Briefly, 1 mL of the aqueous solution at each time point was extracted twice with 0.5 mL of a 1:1 hexane/ethyl acetate mixture. Vials were vortexed and centrifuged at 9000g for 5 min and concentrated under a gentle stream of nitrogen. Next, samples were reconstituted in 100 μL of a nonane/hexane mixture (15:85) and transferred to an autosampler vial fitted with a glass insert. The concentrations of PAHs were determined using an Agilent (Santa Clara, CA) model 7890A gas chromatograph system coupled to an Agilent model 5975C mass spectrometer operated in electron impact ionization mode (EI) with an energy of 70 eV. Using a splitless mode, samples were injected at a volume of 1 μL at an injection port temperature of 280 °C. Chromatographic separation of PAHs was achieved by use of a DB-5MS [60 m × 0.25 mm (inside diameter) × 0.25 μm (film thickness)] fused silica capillary GC column (Agilent). Helium was used as a carrier gas at a constant flow rate of 1.5 mL min⁻¹. The following GC oven temperature program was used: 100 °C for 1 min, increase at a rate of 5 °C min⁻¹ to 190 °C for 2 min, increase at a rate of 20 °C min⁻¹ to 220 °C for 2 min, and increase at a rate of 40 °C min⁻¹ to 300 °C for 4 min. The GC/MS transfer line was maintained at 28 °C. The analysis was performed using selected ion monitoring (SIM), with ions at $m/z$ 166 for fluorene, $m/z$ 167 for carbazole, $m/z$ 168 for dibenzofuran, $m/z$ 184 for dibenzothiophene, $m/z$ 153 for acenaphthene, $m/z$ 178 for phenanthrene, and $m/z$ 202 for pyrene. The limit of detection range was 0.5−2.0 μg/L for PAHs. The concentrations of targeted PAHs in OF-OSPW were lower than the limit of detection.

**2.5. Data Analysis.** The release of PAHs into different aqueous phases was analyzed using a one-compartment model[48] (eq 1)

$$C_{\text{Water}(t)} = C_{\text{Water(eq)}}(1 - \exp^{-k_{\text{Release}}t}) \tag{1}$$

where $C_{\text{Water}(t)}$ (milligrams per liter) is the concentration in water at time $t$, $C_{\text{Water(eq)}}$ (milligrams per liter) is the concentration in water at equilibrium, and $k_{\text{Release}}$ (inverse

hours) is the release rate constant. Data were fitted using the least-squares method using GraphPad Prism 6.07 (GraphPad, San Diego, CA), giving estimates of the appropriate rate constant and equilibrium concentrations. The time to reach 95% steady state was used to quantify the time to reach equilibrium (eq 2).

$$t_{95\% \text{ ss}} = 3/k \tag{2}$$

where 95% ss (hours) is the time to reach 95% of the steady state and $k$ is the release rate constant.

The increment or enhancement ratio $(r)$[34] was used to describe the effects of treatments on the measured concentrations of targeted PAHs in the aqueous phase. Greater values of $r$ show a stronger tendency of treatment to enhance the release of PAHs from PDMS into the aqueous phase. The value of $r$ of each PAH from PDMS was calculated (eq 3).

$$r \ (\%) = (C_b - C_a)/C_a \times 100 \tag{3}$$

where $C_a$ is the desorbed amount of PAH in the control and $C_b$ is the desorbed amount of PAH in treatments. The relationship of PAH increment ratio to log $K_{ow}$ was tested by linear regression; a $p$ value of <0.05 was considered statistically significant.

## 3. RESULTS AND DISCUSSION

**3.1. Kinetics of the Release of PAHs into a Solution of OF-OSPW and Commercial NAs.** Equilibrium concentrations of each PAH, including acenaphthene, fluorene, phenanthrene, pyrene, carbazole, dibenzofuran, and dibenzothiophene, from PDMS to the freshwater control, OF-OSPW, and a commercial mixture of NAs under static conditions were reached in 4−18 h (Table 1). In previous studies, the concentrations of PAHs released from PDMS into water reached equilibrium within 24 h under static conditions.[45,48] The constants for the rate of release and the time to reach a steady state for acenaphthene, fluorene, phenanthrene, pyrene, carbazole, dibenzofuran, and dibenzothiophene in each of the test solutions are summarized in Table 1. Compared to the freshwater control, the time for PAHs to reach 95% steady state decreased in the presence of OF-OSPW but not NAs at 50 mg/L. OSPW contains a complex mixture of naturally occurring acidic and non-acidic heteroatom-containing organic compounds that have surfactant properties.[3,49] Although commercial NAs are not representative of the acid extractable fraction of OSPW, it was tested here to determine if complex mixtures of carboxylic acids enhance the desorption of PAHs.

Compared to OF-OSPW, NAs did not enhance desorption of PAHs. This is probably because OF-OSPW is a complex mixture of anionic, cationic, and non-ionic chemicals representing a mixture of diverse structures, molecular masses, and physicochemical properties, while commercial NAs contain only carboxylic acids. At 1× and 2.5× OF-OSPW, there were no changes in equilibrium concentrations compared to the control. When the concentration of OF-OSPW was increased to 5×, the times to reach the 95% steady state of acenaphthene, fluorene, phenanthrene, pyrene, carbazole, and dibenzofuran decreased by 4.15, 1.61, 2.24, 0.26, 2.78, and 0.73 h, respectively, compared to the control (Table 1), but the time for dibenzothiophene to reach equilibrium did not change.

The release of PAHs from PDMS into each aqueous solution over the course of 24 h is shown (Figures 1–3). The concentrations of acenaphthene, fluorene, phenanthrene, pyrene, carbazole, dibenzofuran, and dibenzothiophene in OF-OSPW increased with time. The greatest calculated $r$ when the aqueous solution was 1× OF-OSPW was 10% for acenaphthene and carbazole, while other PAHs had values of $r$ of <10% (Figure 4A). Values of $r$, when the aqueous phase was 2.5× OF-OSPW, were 24%, 20%, 40%, 39%, 20%, 24%, and 17% for acenaphthene, fluorene, phenanthrene, pyrene, carbazole, dibenzofuran, and dibenzothiophene, respectively (Figure 4B). Values of $r$ of acenaphthene, fluorene, phenanthrene, pyrene, carbazole, dibenzofuran, and dibenzothiophene increased by 51%, 38%, 78%, 86%, 25%, 67%, and 16%, respectively, in 5× OF-OSPW compared to the freshwater control (Figure 4C). The low solubility and high affinity of PAHs for soil or sediment decrease their bioavailability to aquatic organisms. The results of this study showed that dissolved organic compounds in OSPW can increase the concentrations and solubilities of PAHs, as shown previously with retene.[45] The rates of desorption of acenaphthene, dibenzofuran, dibenzothiophene, and fluorene were stable during the sampling period, when the commercial mixture of NAs was the aqueous phase. However, the measured concentrations of PAHs did not increase. Values of $r$ of acenaphthene, fluorene, phenanthrene, pyrene, carbazole, dibenzofuran, and dibenzothiophene from PDMS incubated with the commercial mixture of NAs changed by 5%, 2%, 8%, 8%, −8%, 13%, and 3%, respectively (Figure 4D). The effects of OF-OSPW on the rate of desorption are likely caused by the addition of non-ionic and ionic surfactants at concentrations greater than its critical micelle concentration (CMC), which has been shown to enhance the solubility, rate of release, and bioavailability of slowly desorbing PAHs in soil water.[31,32,35,39] Solutions of a mixture of surfactants increase the solubilization capacity more than solutions of a single surfactant. Furthermore, the desorption capacity of mixtures of anionic and non-ionic surfactants is greater than the desorption capacity of mixtures of anionic and cationic surfactants or cationic and non-ionic surfactants.[50]

The desorption and apparent aqueous solubility of PAHs increased as the concentration of dissolved organics from OSPW increased. When the concentrations of surfactants are lower than the CMC, surfactants occur as individual molecules or monomers and have minimal effects on the solubilities of hydrophobic compounds.[51] Thus, the concentrations of organic compounds in 1× OF-OSPW might not have been sufficient for self-aggregation or formation of micelles that are needed to promote partitioning of PAHs from PDMS.
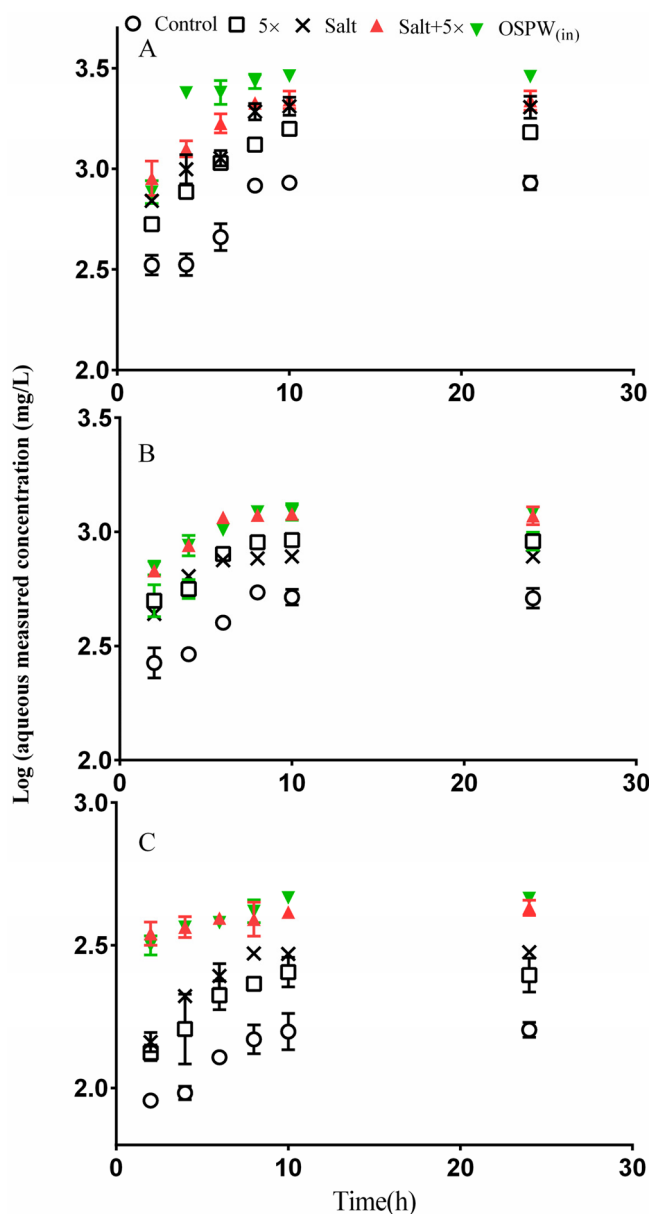


**Figure 1.** Desorption kinetics of (A) phenanthrene, (B) acenaphthene, and (C) pyrene released from PDMS. PAHs were loaded into PDMS and incubated with 5× OF-OSPW, salts, 5× OF-OSPW+salts, and OSPW$_{(in)}$. Values are the means of three replicates.

Although heterocyclic PAHs (NSO) are more polar and more soluble than nonpolar PAHs (homocyclic) because of substitution of one carbon atom with nitrogen, sulfur, or oxygen,[52] the concentrations of carbazole, dibenzofuran, and dibenzothiophene in either of the solutions were not greater than those of non-NSO PAHs. The concentrations of dissolved organic compounds are greater in fresh OSPW than in aged OSPW.[53] Thus, it is expected that micelle formation is more likely to occur in fresh OSPW than in aged OSPW, and that the potential for PAHs to partition to the aqueous phase decreases as OSPW in tailings ponds is diluted and dissolved organics are biodegraded.[39,53]

The organic compounds extracted from OSPW can vary at different pH values,[25,28] which might influence the desorption of PAHs from PDMS to the aqueous phase. It is not known whether the observed effect of OF-OSPW on the solubilities of
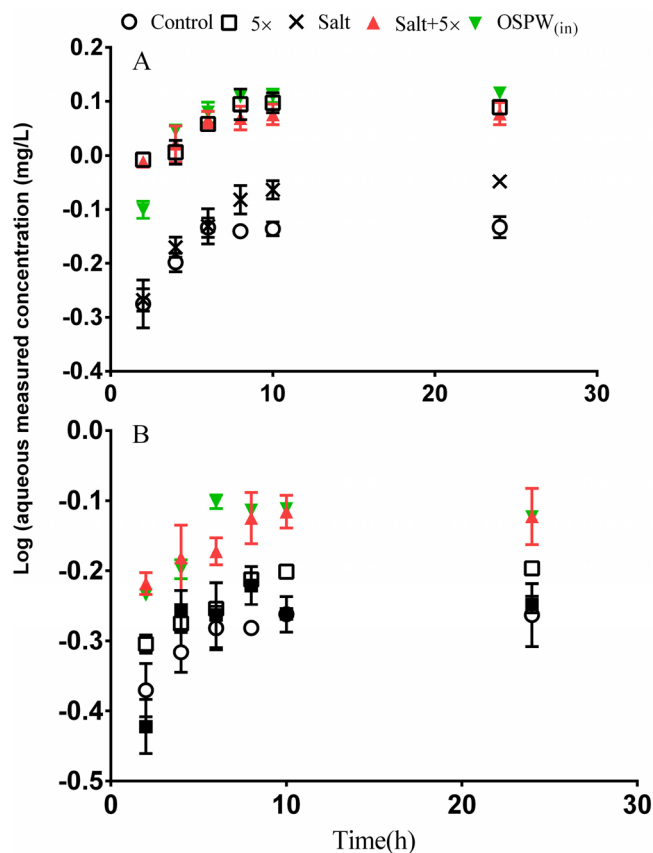
**Figure 2.** Desorption kinetics of (A) dibenzofuran and (B) dibenzothiophene released from PDMS. PAHs were loaded into PDMS and incubated with 5× OF-OSPW, salts, 5× OF-OSPW+salts, and OSPW(in). Values are the means of three replicates.
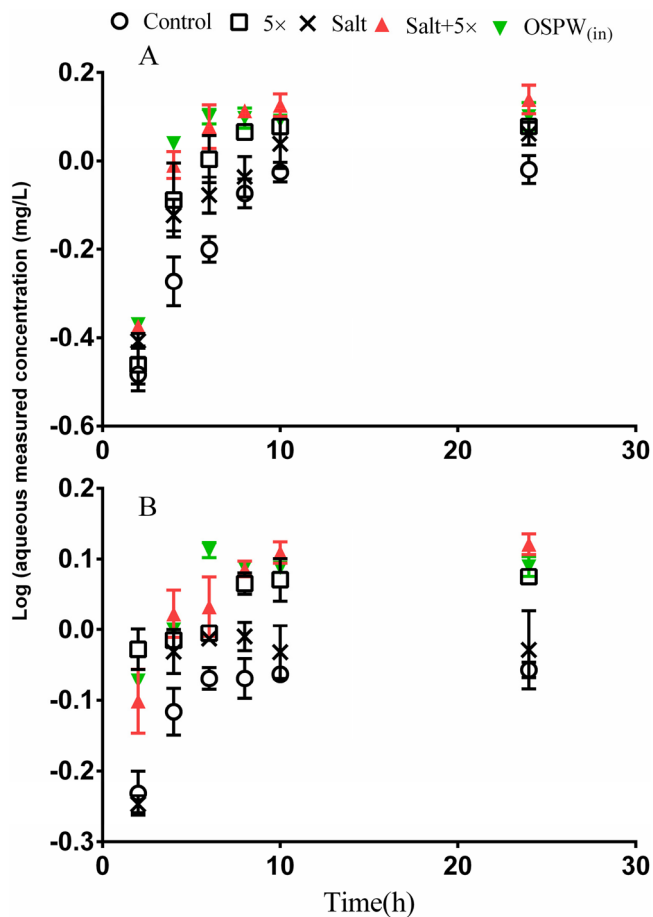


**Figure 3.** Desorption kinetics of (A) carbazole and (B) fluorene released from PDMS. PAHs were loaded into PDMS and incubated with 5× OF-OSPW, salts, 5× OF-OSPW+salts, and OSPW(in). Values are the means of three replicates.

PAHs was due to concentrations of anionic, cationic, or non-ionic surfactants. It has been shown that the pH of OSPW is in the range of 7.7−8.6,[54] which is close to the pH of the total organic extract used in this study. Although in OSPW the concentrations of acid compounds are greater than the concentrations of basic and neutral compounds, it is expected that the extraction method used in this study resulted in concentrations of basic and neutral compounds being greater than the concentration of organic acids in OF-OSPW.[25,28] Therefore, the enhancement of the solubilities of PAHs might be caused by the mixture of dissolved organic compounds (i.e., acidic, basic, and neutral) in OSPW. It has been shown that excess concentrations of organic acids in soil water might decrease the efficiency to dissociate hydrophobic compounds from soil.[36] Given the differences in the chemical structures and properties of organic compounds in OSPW, the extraction of OSPW at pH values similar to those of tailing ponds will provide an environmentally relevant representation of the total organic fraction. The desorption efficiency of PAHs is strongly related to the dissociation forms of organic acids (more ions) in solution, which can be achieved at higher pH values.[36]

**3.2. Effects of OSPW(in) and Salts on the Kinetics of Release of PAHs.** The kinetics of desorption of PAHs from PDMS were influenced by salts, which are present at relatively high concentrations within OSPW.[5] The desorption of PAHs from PDMS differed depending on whether the aqueous phase consisted of salts, salts mixed with 5× OF-OSPW, or OSPW(in) (Figures 1−3). When the aqueous phase consisted of salts

dissolved in freshwater, the measured concentrations of PAHs were slightly increased. The times for PAHs to reach a steady state (equilibrium) when the aqueous phase consisted of salts, salts with 5× OF-OSPW, and OSPW(in) are listed in Table 2. Equilibria of freely dissolved concentrations of acenaphthene, fluorene, phenanthrene, pyrene, carbazole, dibenzofuran, and dibenzothiophene were reached either faster or slower than for the control. For example, pyrene reached 95% of steady state faster by ∼7 h compared to the control in salts with 5× OF-OSPW, while dibenzofuran was slower by approximately 2 h, reaching a steady state in salts compared to the freshwater control (Table 2).

Values of $r$ when the aqueous phase consisted of salts in freshwater were 77%, 15%, 138%, 56%, 20%, 21%, and 3% for acenaphthene, fluorene, phenanthrene, pyrene, carbazole, dibenzofuran, and dibenzothiophene, respectively (Figure 5). The rate of release of PAHs from PDMS into the solution of salts with 5× OF-OSPW was greater than the rate of release into salts or 5× OSPW alone. Values of $r$ when the aqueous solution consisted of salts with 5× OSPW were 129%, 50%, 157%, 167%, 44%, 62%, and 38% for acenaphthene, fluorene, phenanthrene, pyrene, carbazole, dibenzofuran, and dibenzothiophene, respectively (Figure 5). The desorption efficiency of PAHs was enhanced in the presence of OSPW(in), and values of $r$ for acenaphthene, fluorene, phenanthrene, pyrene, carbazole, dibenzofuran, and dibenzothiophene were 136%,
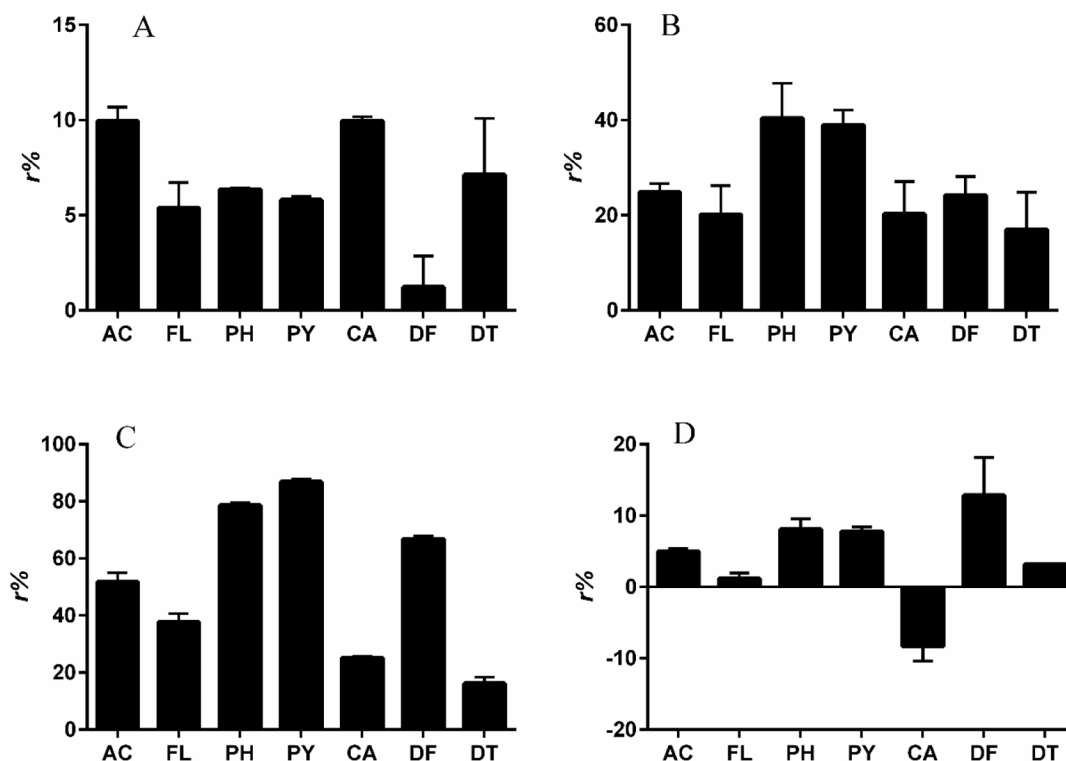
**Figure 4.** Effect of OF-OSPW on the increment ratio ($r$) of PAHs. The effects of (A) 1× OF-OSPW, (B) 2.5× OF-OSPW, (C) 5× OF-OSPW, and (D) NAs on the release of PAHs from PDMS to a water solution measured once concentrations reached a steady state (see the calculation of $r$ in Data Analysis).

**Table 2. Kinetics of Release into Water of PAHs from PDMS in the Presence of Salts, Salts with 5× OF-OSPW and OSPW$_{(in)}$[a]**

| | control | | salts | | salts with 5× OF-OSPW | | OSPW$_{(in)}$ | |
|---|---|---|---|---|---|---|---|---|
| | rate constant (SE) | time for 95% steady state (h) | rate constant (SE) | time for 95% steady state (h) | rate constant (SE) | time for 95% steady state (h) | rate constant (SE) | time for 95% steady state (h) |
| acenaphthene | 0.26 (0.04) | 11.35 | 0.31 (0.06) | 9.51 | 0.39 (0.05) | 7.50 | 0.42 (0.06) | 7.05 |
| fluorene | 0.54 (0.05) | 5.48 | 0.53 (0.09) | 5.60 | 0.43 (0.05) | 6.83 | 0.53 (0.05) | 5.63 |
| phenanthrene | 0.17 (0.03) | 17.60 | 0.17 (0.03) | 16.72 | 0.23 (0.03) | 12.64 | 0.27 (0.04) | 11.00 |
| pyrene | 0.29 (0.04) | 10.04 | 0.30 (0.05) | 9.68 | 0.92 (0.17) | 3.25 | 0.53 (0.07) | 5.58 |
| carbazole | 0.20 (0.02) | 14.97 | 0.21 (0.02) | 13.86 | 0.25 (0.03) | 11.54 | 0.33 (0.54) | 9.08 |
| dibenzofuran | 0.61 (0.05) | 4.91 | 0.41 (0.04) | 7.16 | 0.81 (0.09) | 3.66 | 0.47 (0.01) | 6.38 |
| dibenzothiophene | 0.75 (0.09) | 3.97 | 0.59 (0.07) | 5.07 | 0.78 (0.12) | 3.79 | 0.64 (0.06) | 4.67 |

[a]Values are the means of three replicates.

40%, 237%, 188%, 32%, 77%, and 37%, respectively (Figure 5). The solubilization of PAHs by surfactants can be enhanced in saline solutions. It has been shown that mixed micelles of surfactants were more stable in the presence of salts, and the solubility of pyrene and desorption from soil in mixtures of saline anionic and non-ionic surfactants were greater than in a nonsaline solution.[35] Although salts in OSPW have been shown to be toxic to aquatic organisms,[46] the effects of salts in OSPW on solubility enhancement of PAHs have never been investigated. The concentrations of Na$^+$, Cl$^-$, and HCO$^{3-}$ in OSPW from Base Mine Lake are greater than in freshwater but lower than in pore water of fluid fine tailings (FFT).[55] The concentrations of PAHs were greater when the aqueous phase was a mixture of salts and a 5× OF-OSPW solution compared to concentrations in either OF-OSPW or the saline solution, alone. Additionally, the increment ratio of desorption of PAHs was almost identical when the aqueous phase consisted of OSPW$_{(in)}$ or salts with 5× OF-OSPW. Because the organic compounds and inorganic ions coexist in OSPW, these observations suggest that the salinity of OSPW is a critical component affecting desorption of PAHs from tailings by surfactants.

**3.3. Correlations between the Enhancement Ratio and $K_{ow}$ of Targeted PAHs.** There was a weak positive correlation, but not statistically significant ($p > 0.05$), between the enhancement ratio of PAHs in different aqueous phases and the octanol–water partition coefficient ($K_{ow}$) (Figure 6). The coefficients of determination ($r^2$) from the regression analysis obtained for 5× OF-OSPW, salts with 5× OF-OSPW, OSPW$_{(in)}$, and salts were 0.43, 0.50, 0.41, and 0.10, respectively (Figure 6). Except for dibenzothiophene and fluorene, PAHs with larger $K_{ow}$ values showed greater rates of desorption and measured concentrations.

## 4. CONCLUSION

The results of this study demonstrated that dissolved organic compounds in OSPW alone or in mixture with salts can enhance the release of PAHs from a solid medium of PDMS
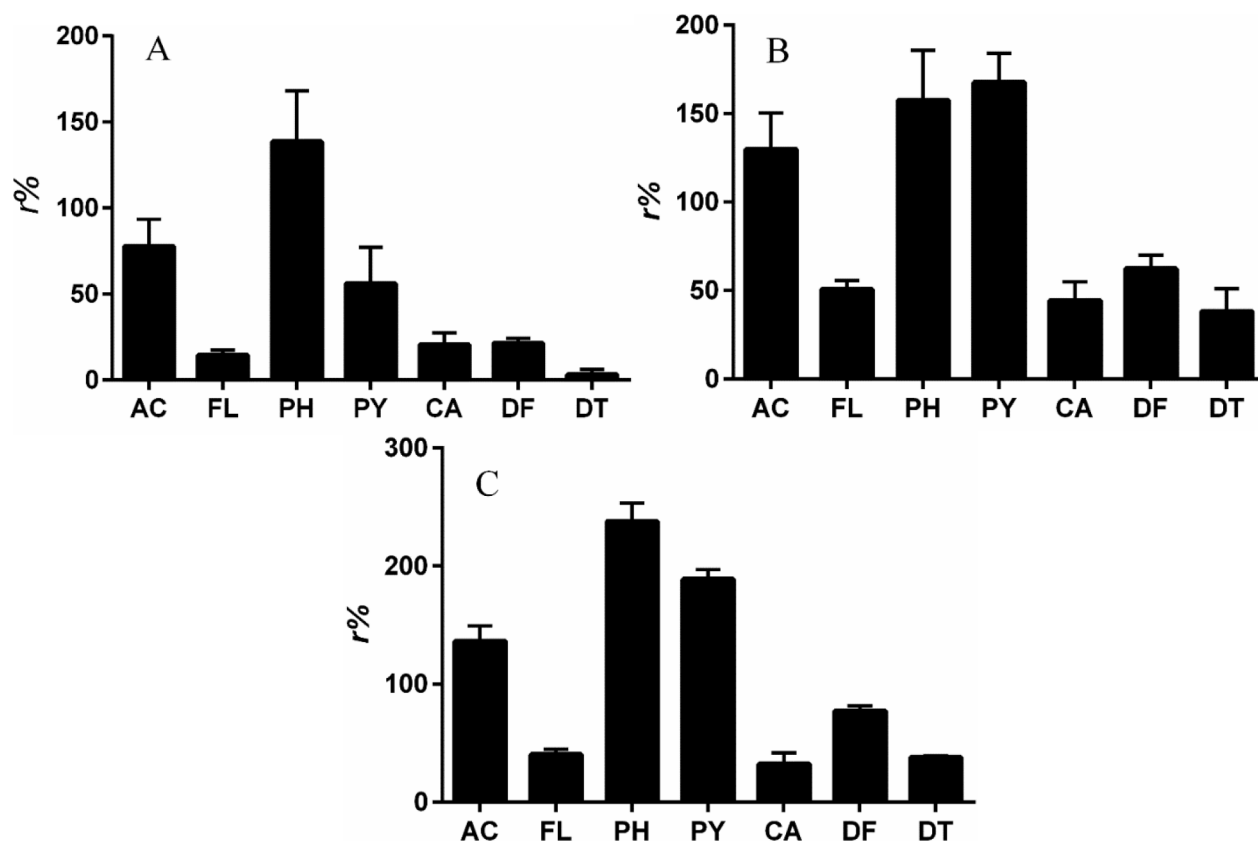
**Figure 5.** Effect of OF-OSPW on the increment ratio ($r$) of PAHs. The effects of (A) salts, (B) salts with 5× OF-OSPW, and (C) OSPW$_{(in)}$ on the release of PAHs from PDMS to a water solution were measured once concentrations reached a steady state (see the calculation of $r$ in Data Analysis).
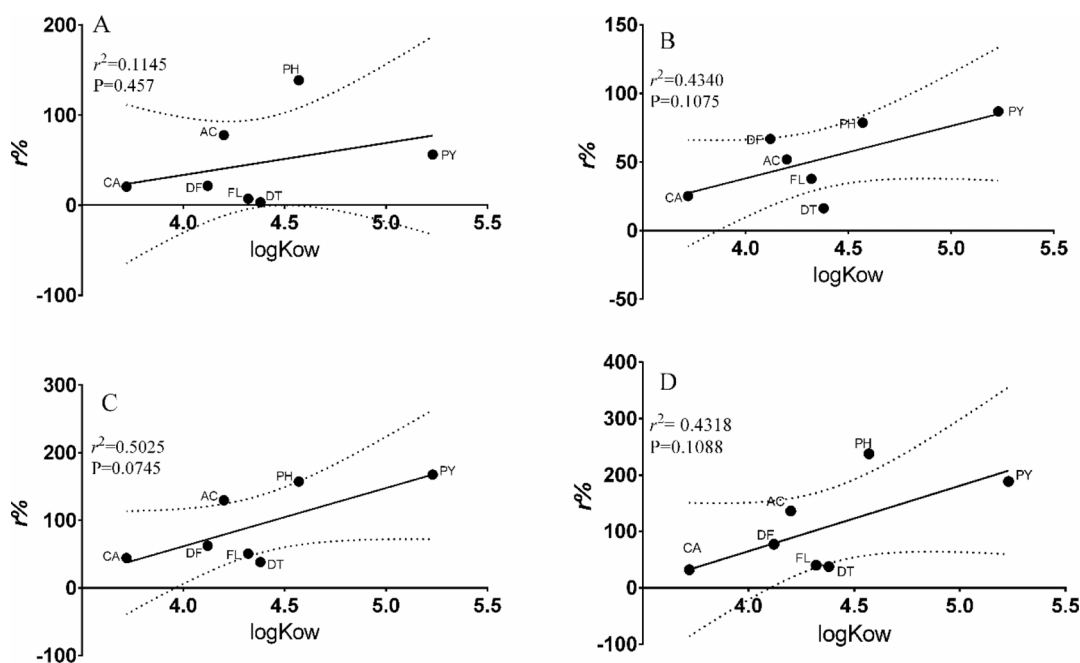


**Figure 6.** Regression analysis of (A) salts, (B) 5× OF-OSPW, (C) salts with 5× OF-OSPW, and (D) OSPW$_{(in)}$ of the measured concentrations of PAHs loaded into PDMS, and log $K_{ow}$. Values indicate the enhancement ratio ($r$) at 24 h of PAHs. The solid line indicates the regression, with associated correlation values displayed in each plot.

into the aqueous phase. This suggests that the concentrations of PAHs in the aqueous phase of OSPW could increase as

PAHs partition from fine tailings. Future ecological risk assessment and strategies for remediation of OSPW should

consider the effects of surfactants and salts on the bioavailability of hydrophobic organic compounds, such as PAHs, which could result in increased risks of the exposure of aquatic organisms to PAHs.

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### Notes

The authors declare no competing financial interest.

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