

Divergent Transport Dynamics of Alkylated versus Unsubstituted Polycyclic Aromatic Hydrocarbons at the Air–Water and Sediment–Water Interfaces at a Legacy Creosote Site

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Cite This: *ACS EST Water* 2025, 5, 146–155



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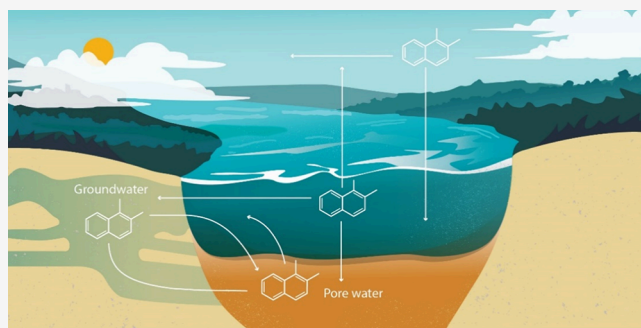
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ABSTRACT: Alkylated polycyclic aromatic hydrocarbons (PAHs) are abundant constituents of many PAH mixtures and contribute to risk at contaminated sites. Despite their abundance, the movement of alkylated PAHs remains understudied relative to unsubstituted PAHs. In the present study, passive sampling devices were deployed in the air, water, and sediments at 11 locations across multiple seasons to capture spatial and temporal variability in the abundance and movement of alkylated PAHs at a Brownsfield creosote site in Oregon, USA. Freely dissolved concentrations of 18 alkyl homologous series were quantified by gas chromatography–triple quadrupole mass spectrometry. Alkylated PAHs were consistently more abundant than unsubstituted PAHs in all sampled media (sum PAH and APAH concentrations 43–96% alkyl PAHs). Models of diffusive and advective flux revealed abundant 2 and 3-ring alkyl PAHs exhibited seasonal differences in movement, particularly across the air–water interface. The novel application of these methods to freely dissolved alkylated PAH homologues revealed that, in many instances, alkylated PAHs, particularly C3 and C4 homologues, moved in the opposite direction as unsubstituted PAHs across both the air–water and sediment–water interfaces. These findings reinforce the need to characterize alkylated PAHs and seasonal variability and can inform future sampling at contaminated sites.

KEYWORDS: *advective flux, diffusive flux, passive sampling, brownsfield site*



INTRODUCTION

Alkylated polycyclic aromatic hydrocarbons (APAHs) are an important but insufficiently characterized class of chemicals responsible for driving human and ecological risk in many exposure situations. Alkylated PAHs are frequently the most abundant constituents of Polycyclic Aromatic Compound (PAC) mixtures at contaminated sites.¹ PAC mixtures in crude oil, diesel, and coal are rich in alkylated PAHs relative to unsubstituted PAHs as result of their formation temperatures through petrogenic processes.² PAC mixtures in the environment are subject to differential transportation and degradation processes, called weathering, that preferentially deplete the unsubstituted PAHs as a result of their increased volatility, aqueous solubility, and biodegradation. The abundance of APAHs in petrogenic source material and their relative resistance to weathering makes them particularly important at Brownsfield sites where PAC mixtures may remain for decades after release.

In addition to their abundance, the characterization of alkylated PAHs can provide critical lines of forensic evidence in source apportionment. While PACs are present in the

environment in complex mixtures, the relative abundance of APAHs and particular structures of varying stability can allow differentiation of sources and degrees of weathering. In their 2001 paper, Stout et al. developed forensic ratios based on samples of known origin, subsequently used to differentiate urban runoff and creosote in several other studies.³ Yunker et al. (2002) used a variety of forensic ratios to parse sources of PACs in a large river basin impacted by a variety of natural and anthropogenic sources. The utility of APAHs in source apportionment remains an important rationale for their measurement.^{2,4}

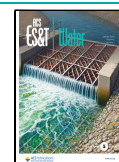
One challenge to the investigation of APAHs is the multitude of isomers. Each homologous series (isomers with the same number of alkyl carbons relative to the parent

Received: August 8, 2024

Revised: December 9, 2024

Accepted: December 11, 2024

Published: December 23, 2024



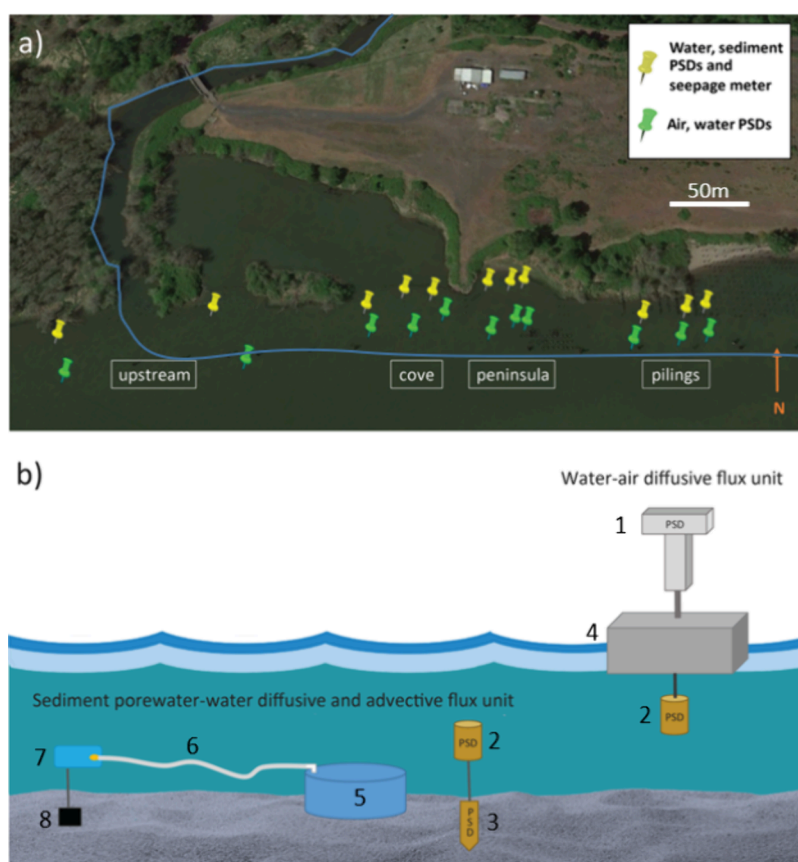


Figure 1. (A) Sampling locations from left to right: Upstream, Cove Upstream, Cove Western, Cove Central, Cove Eastern, Peninsula Western, Peninsula Central, Peninsula Western, Shore Western, Shore Eastern, Pilings. Yellow points reflect sediment porewater–water diffusive and advective flux units while green points show locations of water–air diffusive flux units. Approximate site boundaries indicated with blue line. (B) Passive samplers housed in deployment devices for air (1), water (2) and sediment porewater (3). Seepage meter consisted of a bottomless cylinder (5) connected with plastic tubing (6) to a hydration bladder (7) anchored by a weight (8). Reproduced with permission from Ghetu et al. (2024).¹

molecule) contains from two to several hundred isomers.⁵ As a result of the lack of analytical standards for the thousands of isomers, there is limited data available to characterize the toxicity of individual APAHs. Despite these challenges, a variety of fractionation, and modeling approaches have implicated alkylated PAHs in toxicity to fish and benthic invertebrates in a variety of contaminated sites and spills.^{6–8} While critical knowledge gaps remain, it is understood that incorporating alkylated PAHs in ecological risk assessment is essential.^{9–11}

While historically neglected in human health risk assessment, there is growing recognition of the toxic potential of alkylated PAHs to human health.^{12–15} While their abundance alone would warrant recognition, in some cases alkylated derivatives are more toxic than their respective parent compounds.^{16,17} Experimental evidence in animal models suggests several alkylated PAHs are carcinogens and mutagens, in some cases more potent than their respective parent compounds, 7–12-dimethylbenz[a]anthracene and 5-methyl chrysene being two frequently cited examples.^{17–19}

A principle challenge in assessing the distribution and movement of chemical mixtures at contaminated sites is conducting sampling that captures the spatial and temporal dynamics inherent to complex environmental systems. Utilizing recent advancements in analytical capabilities for the measurement of alkylated PAHs, the present study reports the results of an extensive passive sampling campaign with high

spatial and temporal resolution at a Brownsfield creosote site. The use of passive samplers allowed for measurement of the freely dissolved, bioavailable fraction, generating data with direct relevance to the exposure of human and ecological receptors.^{20,21} Building on a recently published paper by Ghetu et al. describing the movement of unsubstituted PAHs at the same site, the focus of this study was to investigate the occurrence and behavior of alkylated PAHs.²² While, previous studies have reported fluxes of alkylated PAH homologous series through particle deposition, less is known about the diffusive movement of alkylated PAHs.^{23–26} To the authors' knowledge, this study represents the first description of air–water and sediment–water exchange of freely dissolved alkylated PAH homologous series. The principle objectives of this study were to 1) demonstrate the application of passive sampling and models of diffusive and advective flux to APAH homologous series, 2) identify differences in the behavior of APAHs relative to their unsubstituted parents, 3) evaluate spatial and temporal patterns of APAH concentrations and fluxes, and 4) identify driving factors of chemical movement.

MATERIALS AND METHODS

Materials and Reagents. Solvents used for cleaning (isopropanol) and extraction (hexanes) of low-density polyethylene passive samplers were Optima grade (Fisher Scientific) or better. Deuterated internal standards were purchased from CDN Isotopes. Analytical standards were

purchased from the US National Institute of Standards and Technology (NIST), Chiron, Sigma-Aldrich, Accustandard and Santa Cruz Biotechnology. Additive free low-density polyethylene was sourced Brentwood Plastics Ltd. Type one ultrapure water was provided by a Milli-Q 18M-ohm/cm reverse osmosis filter system (Millipore).

Study Area. Located on Scappoose Bay, a tidal estuary near the confluence of Multnomah Channel and the Columbia River, the former Pope and Talbot site was used as a wood treatment facility from 1912 to 1960 (Figure 1).²⁷ Release of materials during facility operations resulted in creosote treated wood debris and subsurface contamination with creosote nonaqueous phase liquid (NAPL). Remedial investigation at the site describe unacceptable risk to human and ecological receptors, particularly from APAHs and creosote NAPL.²⁸ Separate cleanup sites, Boise Cascade Mill and St Helens Fiberboard Plant, lie up and down river, respectively. The site is divided into priority action areas with the present study focused on the western, in-water, portion of the site where the majority of historic operations took place. Discontinuous pockets of creosote NAPL exist throughout the study area associated with both NAPL seeps and creosote contaminated wood debris.

Passive Sampler Preparation and Extraction. Passive samplers were constructed as described in Anderson et al. (2009).²⁹ Briefly, one-meter strips of low-density polyethylene (LDPE) tubing were precleaned by three rounds of dialysis in hexanes prior to drying and storage at $-20\text{ }^{\circ}\text{C}$. Two LDPE strips from each cleaning batch were extracted and analyzed by mass spectrometry to verify lack of contamination. Prior to deployment LDPE strips were infused with isotopically labeled performance reference compounds (PRCs) to enable quantification of in situ sampling rates. During construction, quality control samples were created which followed field deployed samplers through all stages of laboratory processing. Additionally, three PRC infused LDPE strips from each batch were used to measure predeployment concentrations of PRCs. Samplers were stored in amber glass jars at $-20\text{ }^{\circ}\text{C}$ prior to field deployment and transported to and from the laboratory in coolers. Previous work has demonstrated transport stability under these conditions.³⁰ Field and trip blanks were used on each deployment/retrieval to evaluate contamination through field deployment/retrieval and transport, respectively.

Upon return to the laboratory, passive samplers were briefly cleaned with dilute hydrochloric acid, type one water, and isopropanol to remove biofouling. Immediately prior to extraction, samplers were spiked with deuterated surrogates (naphthalene-d₈, acenaphthylene-d₈, phenanthrene-d₁₀, fluoranthene-d₁₀, chrysene-d₁₂, benzo[a]pyrene-d₁₂ and benzo[ghi]perylene-d₁₂). Each passive sampler was extracted by two rounds of dialysis in *n*-hexane. Extracts were combined, concentrated under a stream of ultrapure nitrogen (TurboVap, RapidVap) to 1 mL, and stored in amber glass vials.

Field Deployment. Passive samplers and seepage meters were deployed at 11 locations across three discrete sampling periods as described in Ghetu et al. 2024.²² Briefly, samplers were deployed along an approximately 400m section of shoreline. Passive samplers were housed in metal deployment devices to protect samplers from physical damage and UV light as described previously.^{31,32} Sediment porewater passive samplers consisted of a single strip of LDPE housed in a steel sediment probe. In the surface water five strips of LDPE were deployed in a steel cage. Air samplers were housed in a

sheet metal box with an open bottom. See Figure S1 for a detailed depiction of sampling apparatus. Sediment probes were driven into the sediment flush with the sediment-water interface, sampling an approximate depth of (5–25 cm). Sediment probes were codeployed with surface water samplers. Air samplers were mounted to Dockblocks© floating platforms 1m above the water and paired with surface water samplers suspended 1m below the surface (Figure 1B). At one location, Peninsula Western, triplicate samplers were deployed in the air and water. Platforms were deployed on an anchor allowing for movement with tides at sufficient depth to ensure apparatus did not contact sediment or disturb sediment porewater samplers. Deployment periods averaged 30 days and spanned September–November, 2019 and November – December 2020.

Seepage meters were used to measure advective flows between surface and sediment porewater (referred to as porewater hereafter) using a previously established design.^{33–35} Seepage meters utilized a bottomless cylinder formed from a 32 cm section of a steel 55-gallon drum, connected to a hydration bladder by plastic tubing. Seepage meters were placed 5–10 cm into the sediment, forming a seal across the sediment-water interface. After 24 h of equilibration preweighed bladders with known volumes of water were connected to the tubing. After 24 h of exchange the bladders were removed and changes in water volume were measured. Water exchange volumes are provided in Table S2.

Chemical Analysis. Samples were analyzed for 18 homologous series of alkylated isomers using the methods described by Ghetu et al. (2021).³⁶ Each alkyl series (ex. C₁-naphthalenes, one additional carbon relative to parent molecule) represents between two and several hundred individual isomers.¹⁰ Analysis was performed using an Agilent 7890B gas chromatograph (GC) and Agilent 7000C triple quadrupole mass spectrometer (MS/MS) with a J&W Select PAH column (30m x 0.25 mm x 0.15 μm). Deuterated surrogates were used as internal standards for targets with similar physicochemical properties. A full list of targets and internal standards is available in Supporting Information (Tables S2, S3). Instrument performance was verified at the beginning and end of each run and every 10–15 samples with a calibration check using Standard Reference Material (SRM) 1991 (National Institute of Standards and Technology). Solvent blanks were analyzed every 10–15 samples and at the beginning and end of each run. Four matrix spikes were prepared by addition of SRM 1991 to passive sampler extracts. Four duplicate sample aliquots were analyzed. In all cases, check standards, matrix spikes and duplicate samples met laboratory data quality objectives (within 30% of nominal or relative percent difference less than 30%). Low concentrations of alkylated PAHs detected in a laboratory processing blank were subtracted from field sample concentrations (Table S4).

Unsubstituted PAHs corresponding to alkyl series (naphthalene, fluorene, phenanthrene, anthracene, dibenzothio-phenene, fluoranthene, pyrene, chrysene, and triphenylene) are drawn from previously published analysis of these samples by GC-MS/MS on the same instrument using the methods described by Anderson et al. (2006).^{22,37}

Modeling and Data Analysis. Freely dissolved concentrations (C_{free}) in air, water and porewater were calculated from passive sampler extract concentrations using the empirical uptake model and PRC derived in situ sampling rates as described in detail elsewhere²⁰ (Equations S2–S11).

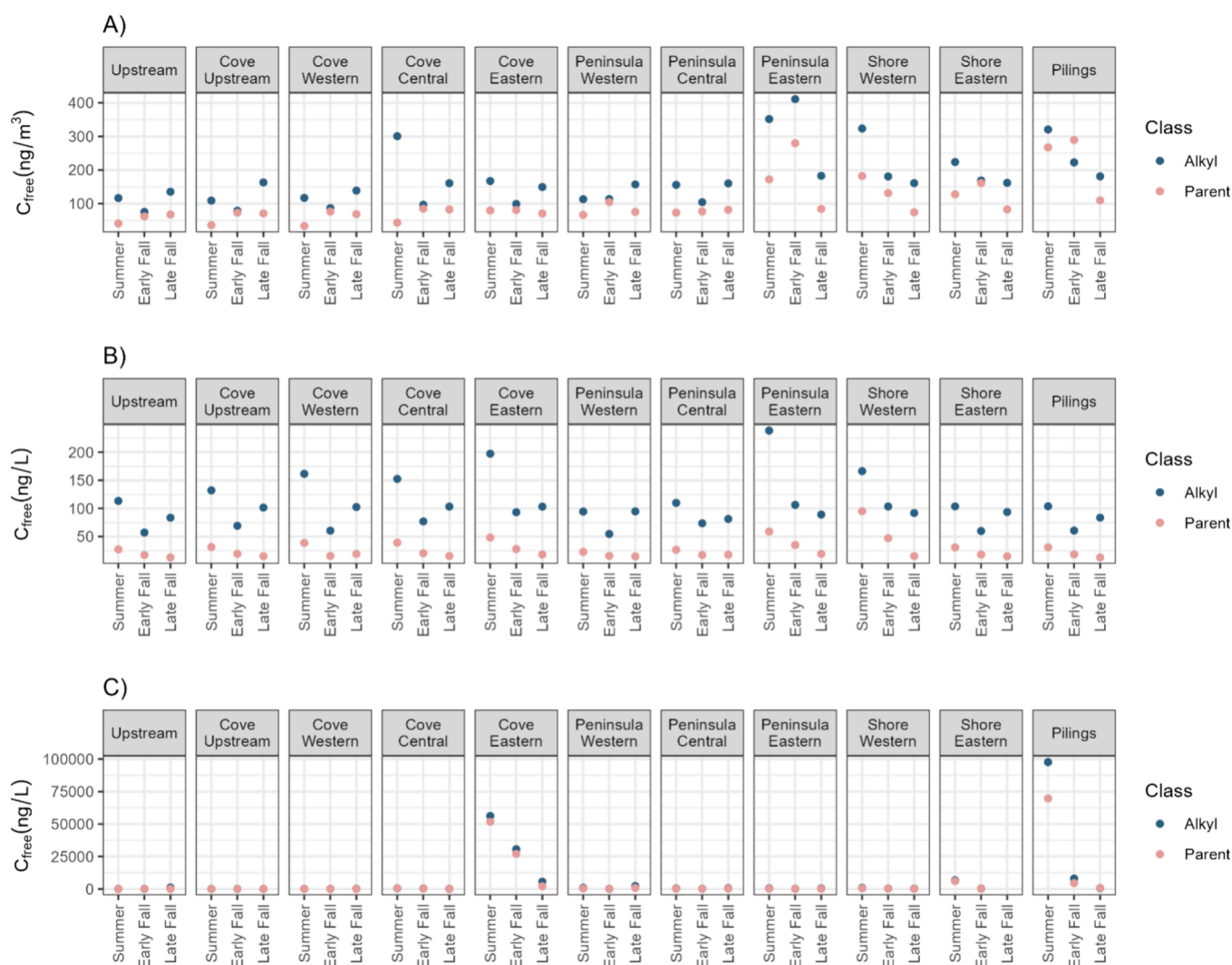


Figure 2. Freely dissolved (C_{free}) sum PAH and APAH concentrations in air (A), surface water (B), and sediment porewater (C). In all cases, the alkylated PAHs were more abundant than unsubstituted PAHs, in some cases by greater than an order of magnitude.

Diffusive flux (F_x) was calculated using derivations of Fick's first law, scaling the concentration gradient ($\frac{dC}{dx}$) between two environmental compartments by a compound-specific mass-transfer coefficient (D), derived from the properties of the compound and site specific conditions (eq 1).³⁸

$$F_x = -D \left(\frac{dC}{dx} \right) \quad (1)$$

Diffusive flux between air and water was calculated using the Whitman two-film model described in detail elsewhere.^{39,40} Diffusive flux across the sediment-water interface was calculated following the methods described in Fernandez et al. (2014).⁴¹ Advective flux between porewater and water was determined using the methods described in Ghetu et al. (2024).²² A detailed description of flux calculations is available in Supporting Information (Equations S12–S19). Uncertainty in reported fluxes arising from measurement variability and parameter uncertainty was calculated using propagation of error as described in detail elsewhere^{22,42} (Equation S20). Uncertainty in the mass transfer velocities and Henry's law constants were represented by an assumed relative standard deviation (RSD) of 30% and 50%, respectively. Based on

previous studies evaluating the variability of seepage meter measures, uncertainty in advective flows was assumed to be 20% (RSD).^{34,43,44} Propagation of error calculations demonstrated uncertainty in flux estimates around 30% (RSD) for diffusive flux and 20–30% for advective flux. Calculations, statistical analyses and data visualization were performed in Microsoft Excel and statistical software, R.^{45–47}

RESULTS AND DISCUSSION

Concentrations in Air, Water, and Porewater. Freely dissolved concentrations of PACs in all matrices were predominantly composed of alkylated PAHs, particularly two and three ring compounds (Figure 2, Figure S2), comprising 78%–96% of the total measured PAC concentrations. Surface water and porewater concentrations also reflected a high proportion of naphthalenes but additionally contained a higher proportion of three ring compounds phenanthrene, anthracene, fluorene and their alkylated derivatives compared to air (Figure S2).

Porewater concentrations were more spatially heterogeneous than surface water and air concentrations in all seasons. Porewater concentrations at Cove Eastern and Pilings were elevated relative to other locations, with sum PAH and APAH

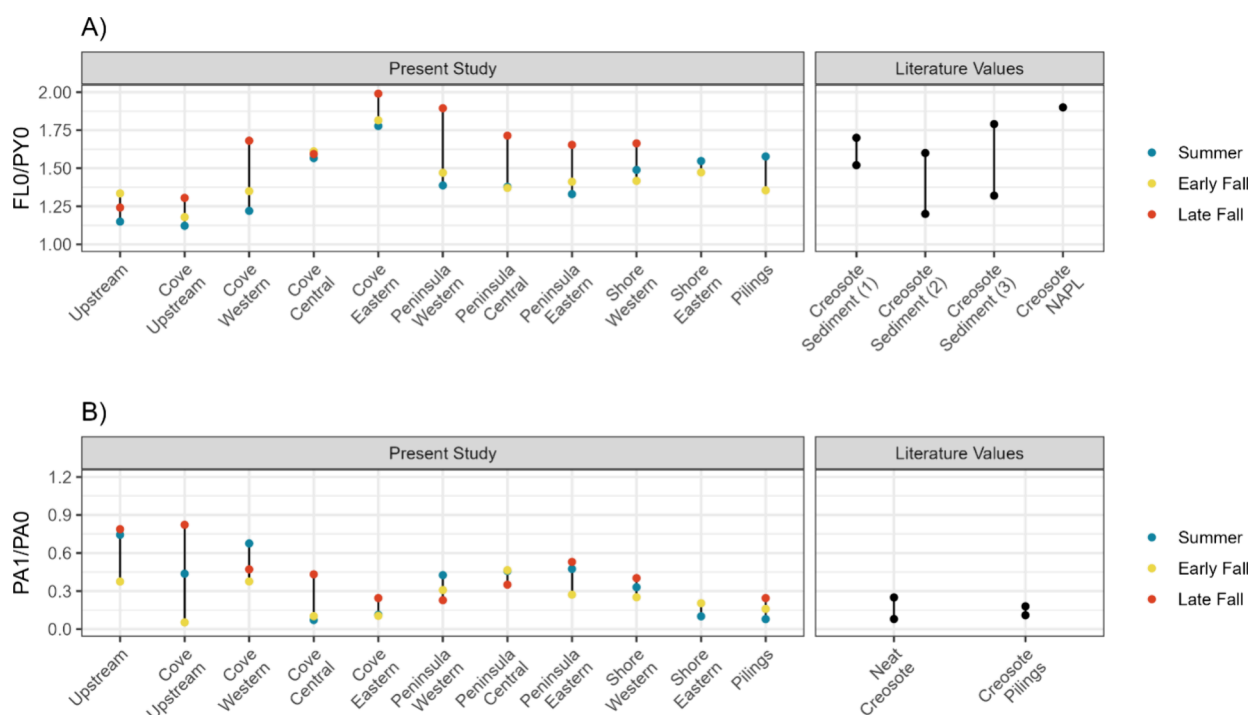


Figure 3. (A) Sediment porewater ratios of fluoranthene over pyrene compared to literature reported values and NAPL from an upland monitoring well at the present study location.^{3,28,51,52} Urban runoff exhibits lower values of FLO/PY0. (B) C1 – phenanthrenes + anthracenes over unsubstituted phenanthrenes + anthracenes. Low values indicate definitive creosote signature, while other PAH sources exhibit higher ratios.^{1,4}

concentrations 1–3 orders of magnitude higher than other locations in summer (Figure 2). Porewater concentrations at Cove Eastern were consistently greater than an order of magnitude larger than the adjacent site, Cove Central, less than 20m away, reflecting the highly localized nature of creosote contamination at the site. Temporal changes in environmental concentrations were most pronounced in sediment porewater at Cove Eastern and Pilings, decreasing by 2 orders of magnitude at Pilings. In all matrices, sum PAC concentrations were most similar between locations in late fall. Generally, surface water concentrations decreased from summer to late fall by as much as a factor of 2.

Interpretation of Porewater Concentrations. While the composition of creosote depends on the production method, 2–4 ring PAHs are known to be particularly abundant constituents.^{3,48} The abundance of low molecular weight (2–3 ring) PAHs and APAHs in the porewater in the present study, likely reflects the composition of creosote. Weathering enriches alkylated PAHs relative to the parent molecules as a result of their lower volatility, aqueous solubility and susceptibility to microbial degradation.⁴⁹ Brenner et al. (2002) investigated the composition of creosote NAPL subject to various degrees of weathering.⁴⁹ Sediment cores collected around the Wykoff-Eagle Harbor Superfund Site demonstrated that while unsubstituted PAHs were more abundant than alkylated homologues in unweathered NAPL, weathering resulted in a higher proportion of alkyls than the parent molecule.⁴⁹ Their investigation found that sediments containing creosote subject to extensive weathering exhibited higher concentrations of 3 and 4 ring APAHs than naphthalene and its derivatives. In contrast to sediments, groundwater impacted by creosote is typically enriched with lower molecular weight, more water-soluble compounds. Scherr et al. (2016) described the dissolution of weathered creosote in groundwater using

empirical and modeling approaches and reported naphthalene to be more abundant than PAHs with three or more rings in subsurface NAPL.⁵⁰ Additionally, they reported adjacent aqueous concentrations were substantially enriched in naphthalene and its alkylated homologues relative to the NAPL source material. The predominance of low molecular weight APAHs in porewater in the present study likely reflect dissolution of more mobile PAHs in groundwater adjacent to the NAPL plume, or creosote wood debris.

A variety of forensic ratios have been applied to PAHs and APAHs to determine contributions of source materials to PAC mixtures in the environment. The ratio of fluoranthene to pyrene, applied by Stout et al. (2001) at the Wykoff-Eagle Harbor creosote Superfund site, was used to evaluate the influence of creosote on the PAC mixtures measured in porewater.³ Previous studies have demonstrated both the utility and the stability of these ratios across broad concentration ranges and degrees of weathering.^{1,4,51} Applying this ratio, and others, demonstrated that all sampling locations reflected a creosote signature to varying degrees (Figure 3, Figure S3). The strongest creosote signatures were associated with locations with high porewater concentrations and release from porewater. Cove Eastern samples consistently reflected a stronger creosote signature than other locations (Figure 3). Pilings also exhibited a strong creosote signal in many of the forensic ratios. Cove Eastern is in close proximity to a subsurface NAPL plume described in the site's remedial investigation while Pilings lies under the former transfer table dock, an area with extensive creosote treated wood debris. The Upstream location exhibited ratios with the weakest creosote signature, reflecting a smaller input from creosote than Cove Eastern and Pilings.

Air–Water Exchange. In all instances, flux across the air–water interface was principally comprised of naphthalene and

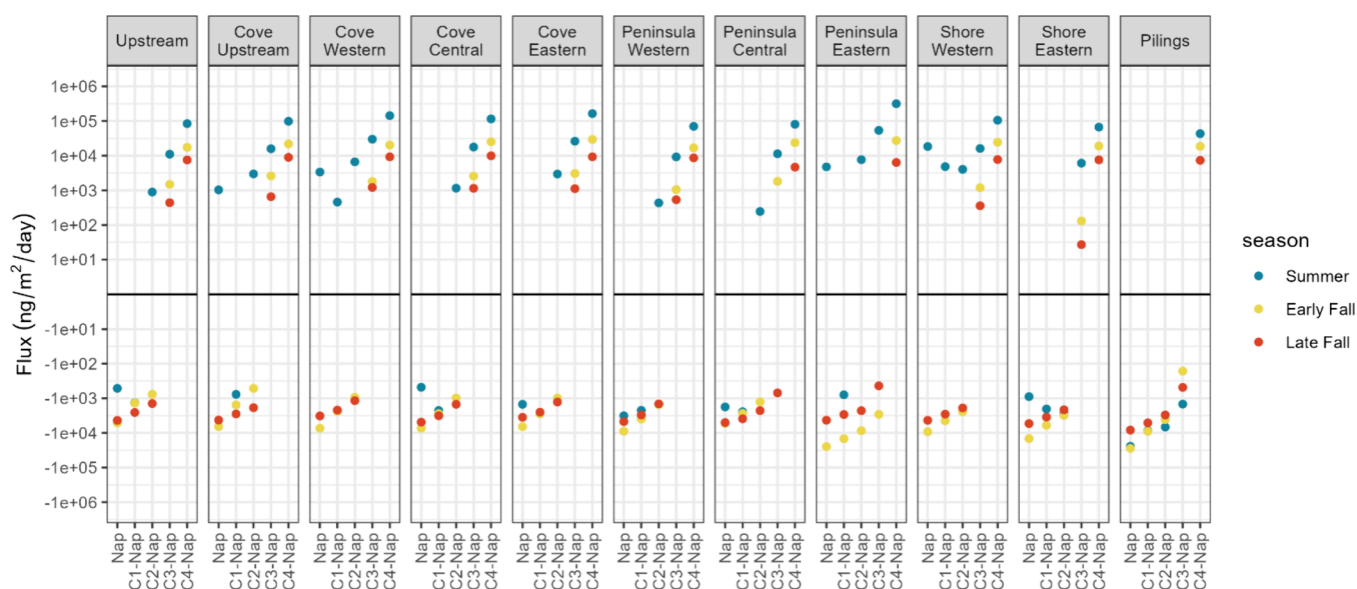


Figure 4. Air–water exchange of naphthalene and alkylated homologues which constituted a high proportion of total flux (median: 92%). Values presented on a base 10 logarithmic scale. Negative values reflect deposition to surface waters while positive values indicate release to atmosphere. Fluxes of remaining PAHs and propagation of error results are available in the [Supporting Information](#).

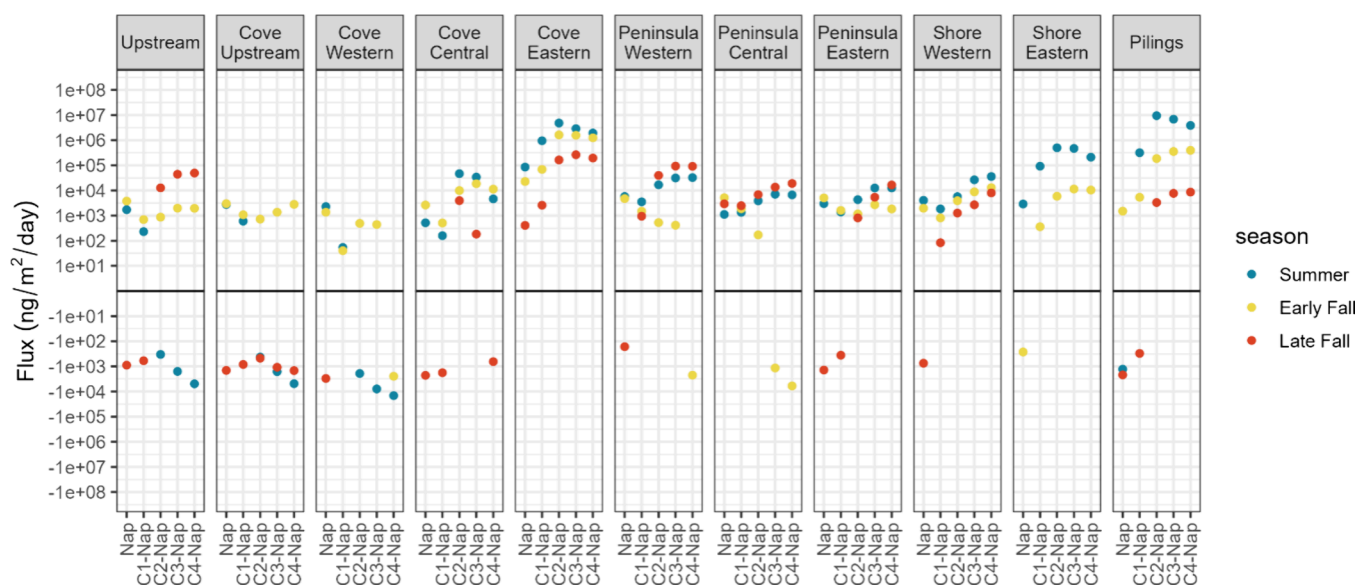


Figure 5. Diffusive sediment–water exchange of naphthalene and alkylated homologues which were large contributors to total fluxes (median: 40%). Values presented on a base 10 logarithmic scale. One porewater sampler was lost in late fall at Shore Eastern. Negative values reflect deposition to porewater while positive values indicate release to surface water. Fluxes of remaining PACs and propagation of error results are available in the [Supporting Information](#).

its alkylated derivatives (76%–94%, median: 92%, [Figure S4](#)). In all cases C4-naphthalenes were volatilizing from surface waters at high magnitudes relative to other compounds ([Figure 4](#), [Table S6](#)). Surface water concentrations of C4-naphthalenes were greater than C1–C3 naphthalenes in all cases. As a result of these elevated surface water concentrations, C4-naphthalenes exhibited larger magnitudes of volatilization driven by the large concentration gradient between surface water and air. In summer, surface water was primarily a source of PAHs and APAHs to the atmosphere. In contrast, in late fall the magnitudes of volatilization and deposition were similar to one another. At many locations, the parent compound was in deposition while some or all alkylated homologues were in release. These difference in behavior between parents and

APAHs result from differences in their abundance and physicochemical properties. Previous studies at this site and another creosote site indicated limited volatilization of PAHs, even in summer, with sum PAH magnitudes of volatilization less than 3×10^3 ng/m²/day and often substantially lower.^{22,31} In the present study, the addition of hundreds of alkylated isomers results in a very different characterization of air–water exchange, demonstrating high rates of volatilization, particularly in summer ([Figure 4](#)).

Air–water fluxes of alkylated and unsubstituted PAHs were more strongly correlated with water concentrations than air, suggesting temporal shifts in water concentrations had a greater impact on flux than changes in air concentrations (Pearson's $r = 0.96$ and 0.7 , respectively, p -values < 0.001). In

addition to the influence of decreasing water concentrations, temperature-driven shifts in volatility played a large role in the decreased volatilization in cooler months (SI Figure S5). Air–water fluxes were more variable across seasons than across locations. These findings reinforce the need to consider seasonality when assessing chemical movement across the air–water interface and the limitations of generalizing findings from a limited time period. While air–water fluxes decreased by as much as an order of magnitude from summer to late fall, atmospheric concentrations were less variable suggesting that volatilization from surface water at the site has little influence on atmospheric concentrations.

Porewater–Surface Water Exchange. Advective Flux. Similar to the data previously reported for unsubstituted PAHs, advective flux of alkylated PAHs was a minor contributor to overall movement across the sediment–water interface, in all cases contributing less than 2% of the total flux.²² The predominance of diffusive flux over advective flux is a result of the low measured advective flows (Table S1).

Diffusive Flux. Naphthalenes represented 11% – 66% of the total diffusive flux across the sediment–water interface within each location/time (median: 40%). Other major contributors to total porewater fluxes included phenanthrenes and anthracenes (median: 28%, min–max: 18–41%), fluorenes (median: 15%, min–max: 7%–32%), and fluoranthenes and pyrenes (median: 12%, min–max: 1%–34%). Higher proportions of three and four ring PAHs in release from porewater were observed in late fall when the magnitude of flux was substantially lower and consequently represent a small cumulative input relative to alkylated two and three ring PAHs.

Flux across the sediment–water interface was spatially heterogeneous with larger fluxes observed at Cove Eastern and Pilings, corresponding to elevated porewater concentrations. These locations typically exhibited sum PAH fluxes greater than an order of magnitude higher than other locations with the exception of late fall when differences between sites were less pronounced (Figure 5). At these two locations alkylated and unsubstituted PAHs were consistently in release while other locations experienced either release and deposition or solely deposition. Both Cove Eastern and Pilings displayed a consistent decreasing magnitude of release across the three time points. This pattern of decreasing release is reflected in decreasing surface water concentrations throughout the site. These findings implicate the role of diffusive release from porewater in two locations on mediating surface water concentrations site-wide. In contrast to the consistent release from porewater at Cove Eastern and Pilings, other locations exhibited more complex patterns of deposition and release, with overall magnitude generally decreasing from summer to fall.

In many cases, C2–C4 alkyl derivatives moved in the opposite direction of the parent compound further supporting the assertion that alkylated PAHs often behave differently than their unsubstituted parents. Porewater fluxes were highly correlated with porewater concentrations and uncorrelated with surface water concentrations reflecting the role of porewater in dictating magnitude and direction of fluxes rather than variability in surface water concentrations (Figure S6, Pearson's $r = 1$, p -value < 0.001 and $R = 0.06$, p -value = 0.07, respectively). While we observed a clear relationship between locations with high porewater concentrations and high release from porewater, the overlying surface water concentrations at Cove Eastern and Pilings were not elevated relative to other

sites. This likely reflects the hydrologic complexity of this waterbody, subject to thorough mixing through fluctuating tides, river flow and wave action.

Few papers have reported concurrent measures of diffusive flux across the air–water and sediment–water interfaces.^{31,32} Using the same methodology as the present study, Minick and Anderson (2017) assessed chemical movement between air, water and porewater in the Portland Harbor Superfund Site including the McCormick and Baxter creosote site post-remediation. They reported atmospheric deposition as a greater input of low molecular weight PAHs to surface water than release from porewater. Their interpretation was that contemporary atmospheric inputs outweighed legacy inputs from porewater following remediation. In the present study, conducted prerediation, porewaters were a larger source of low molecular weight PAHs to surface water, particularly at Cove Eastern and Pilings (Figure S7). As in the present study, Minick and Anderson reported heterogeneous fluxes across the sediment–water interface with two locations reflecting releases 2 orders of magnitude higher than other locations. These consistent findings underscore the spatial heterogeneity of sediments and the need for extensive sampling to adequately characterize porewater concentrations and fluxes.

CONCLUSIONS

The measurement of hundreds of alkylated isomers in the present study reflects a previously unreported advancement to our understanding of diffusive flux at creosote sites. The novel finding that in many cases, across both the air–water and sediment–water interfaces, parent PAHs moved in one direction while alkylated derivatives moved the opposite direction demonstrates important differences in their behavior. These data motivate the importance of measuring both parents and alkylated PAHs at contaminated sites and demonstrate the potential limitations of assuming alkylated PAHs behave the same as their unsubstituted parent compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsestwater.4c00737>.

Photos and descriptions of sampling apparatuses, detailed equations for calculation of freely dissolved concentrations and diffusive and advective fluxes, measured advective flows, GC-MS/MS method parameters, supporting graphics, and tables with all measured concentrations and fluxes (PDF)

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I.L.M. performed data curation, formal analysis, investigation, software, visualization, writing—original draft, and writing—review and editing. C.C.G. performed conceptualization, data curation, formal analysis, investigation, methodology, and writing—review and editing. R.P.S. performed data curation, formal analysis, investigation, software, and writing—review and editing. L.G.T. performed conceptualization, investigation, methodology, and writing—review and editing. P.D.H. performed conceptualization, investigation, and writing—review and editing. K.A.A. performed conceptualization, funding acquisition, methodology, project administration, resource gathering, supervision, and writing—review and editing. CRediT: **Ian Moran** data curation, formal analysis, investigation, software, visualization, writing - original draft, writing - review & editing; **Christine C. Ghetu** conceptualization, data curation, formal analysis, investigation, methodology, writing - review & editing; **Richard P. Scott** data curation, formal analysis, investigation, software, writing - review & editing; **Lane G. Tidwell** conceptualization, investigation, methodology, writing - review & editing; **Peter D. Hoffman** conceptualization, investigation, writing - review & editing; **Kim A. Anderson** conceptualization, funding acquisition, methodology, project administration, resources, supervision, writing - review & editing.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the National Institute of Environmental Health Sciences (NIEHS) award numbers P42 ES016465, P30 ES030287 and T32 ES007060. This content is solely the responsibility of the authors and does not represent the official views of the NIEHS or NIH. We wish to

thank Cascadia Associates, LLC. (GeoEngineers Inc.) and The Port of Columbia County for access to the site and site history. We extend a special thanks to Jessica Scotten, Emily Bonner and Kaci Graber for their help in the field with gear deployment and retrieval. We thank Clarisa Caballero-Ignacio, Caoilinn Haggerty and Kaci Graber for their help with gear preparation and sample processing. Additionally, we thank D. James Minick for assistance with conceptualization and study design

ADDITIONAL NOTE

¹Reprinted from Science of the Total Environment, Vol 912, Christine C. Ghetu, Ian L. Moran, Richard P. Scott, Lane G. Tidwell, Peter D. Hoffman, Kim A. Anderson, Concurrent assessment of diffusive and advective PAH movement strongly affected by temporal and spatial changes, 168765, Copyright (2024), with permission from Elsevier

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