

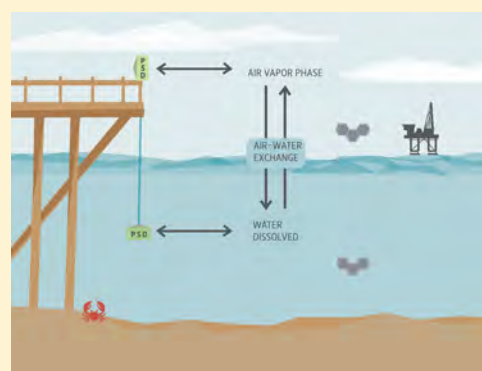
Polycyclic Aromatic Hydrocarbon (PAH) and Oxygenated PAH (OPAH) Air–Water Exchange during the Deepwater Horizon Oil Spill

Lane G. Tidwell, Sarah E. Allan, Steven G. O’Connell, Kevin A. Hobbie, Brian W. Smith, and Kim A. Anderson*

Environmental and Molecular Toxicology Department, Oregon State University, ALS 1007, 2750 SW Campus Way, Corvallis, Oregon 97331, United States

S Supporting Information

ABSTRACT: Passive sampling devices were used to measure air vapor and water dissolved phase concentrations of 33 polycyclic aromatic hydrocarbons (PAHs) and 22 oxygenated PAHs (OPAHs) at four Gulf of Mexico coastal sites prior to, during, and after shoreline oiling from the Deepwater Horizon oil spill (DWH). Measurements were taken at each site over a 13 month period, and flux across the water–air boundary was determined. This is the first report of vapor phase and flux of both PAHs and OPAHs during the DWH. Vapor phase sum PAH and OPAH concentrations ranged between 1 and 24 ng/m³ and 0.3 and 27 ng/m³, respectively. PAH and OPAH concentrations in air exhibited different spatial and temporal trends than in water, and air–water flux of 13 individual PAHs were strongly associated with the DWH incident. The largest PAH volatilizations occurred at the sites in Alabama and Mississippi in the summer, each nominally 10 000 ng/m²/day. Acenaphthene was the PAH with the highest observed volatilization rate of 6800 ng/m²/day in September 2010. This work represents additional evidence of the DWH incident contributing to air contamination, and provides one of the first quantitative air–water chemical flux determinations with passive sampling technology.



INTRODUCTION

The explosion of the Deepwater Horizon (DWH) oil rig on April 20, 2010 led to the release of approximately 4.1 million gallons of oil into the Gulf of Mexico.¹ Between April 28 and July 19, 411 in situ burns were undertaken to remove oil from the water surface.² An additional nonmechanical response included the application of 2.1 million gallons of chemical dispersants at the wellhead and to off-shore surface waters which likely increased the freely dissolved fraction of the oil constituents.^{3,4} Crude oil released from the Macondo 252 well during the DWH incident contained an estimated 3.9% of polycyclic aromatic hydrocarbons (PAHs) by weight.⁵ PAHs are chemicals of concern in oil, and their fate and transport in the environment is an important component of understanding potential impacts from spills.

Whereas PAHs have been widely studied for many decades, oxygenated polycyclic aromatic hydrocarbons (OPAHs) are an emerging contaminant of concern. Interest in OPAHs has increased in the past decade due to their presence in the environment coupled with the toxicity of some OPAHs.^{6,7} Individual OPAHs consist of one or more oxygen atoms attached to an aromatic ring structure that may also contain other chemical groups.⁸ Formation of these compounds through both biotic and abiotic mechanisms could be expected during the DWH incident, especially through photo-oxidation of PAHs in air and waters.^{6,9}

Low-density polyethylene (LDPE) passive sampling devices (PSDs) have been used in water and air to assess time-integrated environmental concentrations of many dissolved and vapor phase contaminants, respectively, including PAHs and OPAHs.^{10–12} Air sampling is often focused on determining the concentration of particulate-bound chemicals; however, exposure to the PAH vapor phase has been shown to account for up to 86% of the cancer risk from inhalation exposure.^{13–15} Vapor-phase PAHs are by definition unbound to particulates which means this atmospheric fraction is respirable and bioavailable. Similarly, the dissolved fraction of contaminants in water is bioavailable for passive uptake by organisms.^{10,16} In addition to being biologically relevant, the gas-phase and dissolved concentrations of chemicals are the fractions that flux from one environmental compartment to another.^{17–19}

PSDs are ideally suited for flux measurements since they specifically sequester the dissolved-water phase and air-vapor phase fractions. Generally, great effort is required to acquire the dissolved water fraction including multiple filtration steps and solid phase cleanup(s).²⁰ Additionally, the filtered water is only operationally defined as dissolved, as any particles smaller than

Received: August 6, 2014

Revised: November 17, 2014

Accepted: November 20, 2014

Published: November 20, 2014



Figure 1. (A) Sampling locations along the Gulf of Mexico. (B) Samplers deployed off piers at each sampling site. (C) Air sampling cage affixed to pier in Gulf Breeze, FL.

the filter are also extracted. The PSDs employed are not subject to filter bias due to their lipophilic carbon polymer design and average pore size of 10 Å that characterize diffusion samplers.¹¹ Until recently, investigation of flux using PSDs has only assessed the overall direction of flux based on the air–water partition compound coefficients (K_{aw}), or through concentration gradients measured in both air and water samples.^{21,22} To the authors' knowledge there are only two reports of measuring the actual magnitude of PAH flux using PSDs, and a separate investigation of flux targeting a different chemical class.^{23–25}

The air–water flux of PAHs is an important factor in understanding the fate of spilled oil.²⁶ Though air and water quality monitoring were conducted during the DWH oil spill, no studies to the authors' knowledge have reported on flux of PAHs and OPAHs across the air–water boundary. In this study, we present the air–vapor phase PAH and OPAHs at coastal sites in Louisiana, Mississippi, Alabama, and Florida prior to, during, and after shoreline oiling. Spatial and temporal trends for individual PAHs and OPAHs were examined during 13 months. We also address the data gap of aromatic hydrocarbon flux during episodic events. Using PSDs for quantitative flux assessment is a developing technological advancement in environmental chemistry, and this work is the first to quantitatively measure flux during an environmental disaster.

MATERIALS AND METHODS

Sample Collection. Sampling was performed at four coastal sites: Grand Isle, Louisiana (LA); Gulfport, Mississippi (MS); Gulf Shores, Alabama (AL); and Gulf Breeze, Florida (FL) (Figure 1A and B). Air and water samples were collected concurrently during 12 sampling events from May 2010 to June 2011; sampling durations for flux assessment ranged from 3 to 41 days (see Supporting Information (SI) Table 1 for specific dates).¹⁶

Stainless steel air sampler cages that allowed for air circulation while minimizing sampler exposure to water, particulate depositions, and UV (Figure 1C) were deployed concurrently with water cages described previously.¹⁶ A total of five PSDs were deployed in each air or water cage. Air samplers were located between 1 and 5 m above the water surface and were directly above water samplers.¹⁶ Approximately 1-m-long PSDs were constructed from LDPE tubing, and were fortified

with deuterated PAH performance reference compounds (PRCs) for water or air sampling rate calculations. A list of PRCs can be found in SI List 1. PRCs spanned a range of K_{oa}/K_{ow} s similar to the target analyte PAHs and OPAHs, and the most similar PRC was used for quantification (SI List 1). OPAHs were quantified using PAH PRCs; any biases generated from this approach are conservative since PAHs have slightly higher K_{oa}/K_{ow} s than the analogous OPAHs.^{27–30} Detailed PSD conditioning, construction, cleanup, and extraction is described in Anderson et al. 2008.³¹ PSDs were transported in sealed polytetrafluoroethylene (PTFE) airtight bags. Samples were stored in the laboratory at 4 °C until extraction within 2 weeks of receipt.

Sample Processing and Chemical Analysis. All solvents used were Optima grade or better (Fisher Scientific, Pittsburgh, PA), and standards were purchased at purities $\geq 97\%$. All five PSDs from each cage were extracted as a composite representing a single sample in order to increase analytic sensitivity. PAH and OPAH in PSDs were extracted by dialysis with *n*-hexane detailed in Anderson et al.;³¹ use of *n*-hexane for extraction of OPAH is explained in O'Connell et al.³² Extracts were stored in amber glass vials at -20 °C until instrumental analysis.

PAH and OPAH analysis used an Agilent 5975B gas chromatograph–mass spectrometer (GC-MS) with an Agilent DB-5MS column (30 m \times 0.25 mm \times 0.25 μ m) in electron impact mode (70 eV) using selective ion monitoring (SIM). PAH GC parameters are detailed in Allan et al.,¹⁶ and OPAH parameters are detailed in O'Connell et al.¹² Six and nine point calibration curves for PAHs and OPAHs, respectively, had correlation coefficients >0.98 for all target analytes. A list of measured analytes is provided in SI Lists 1 and 2.

Quality Control. Quality control (QC) samples accounted for over 30% of the total number of samples analyzed and included the following: PSD construction blanks, field and trip blanks for each deployment and retrieval, postdeployment cleaning blanks, and laboratory reagent blanks. Extraction surrogates were added to all samples immediately prior to extraction, and concentrations were surrogate corrected. All compounds were below detection limits in all blank QC samples. Mean extraction surrogate recoveries were 52.5% (range 37–113) for naphthalene-D8, 67.8% (range 53–116) for acenaphthylene-D8, 80.1% (range 77–113) phenanthrene-D10, 97.8% (84–118) for fluoranthene-D10, 105% (86–139)

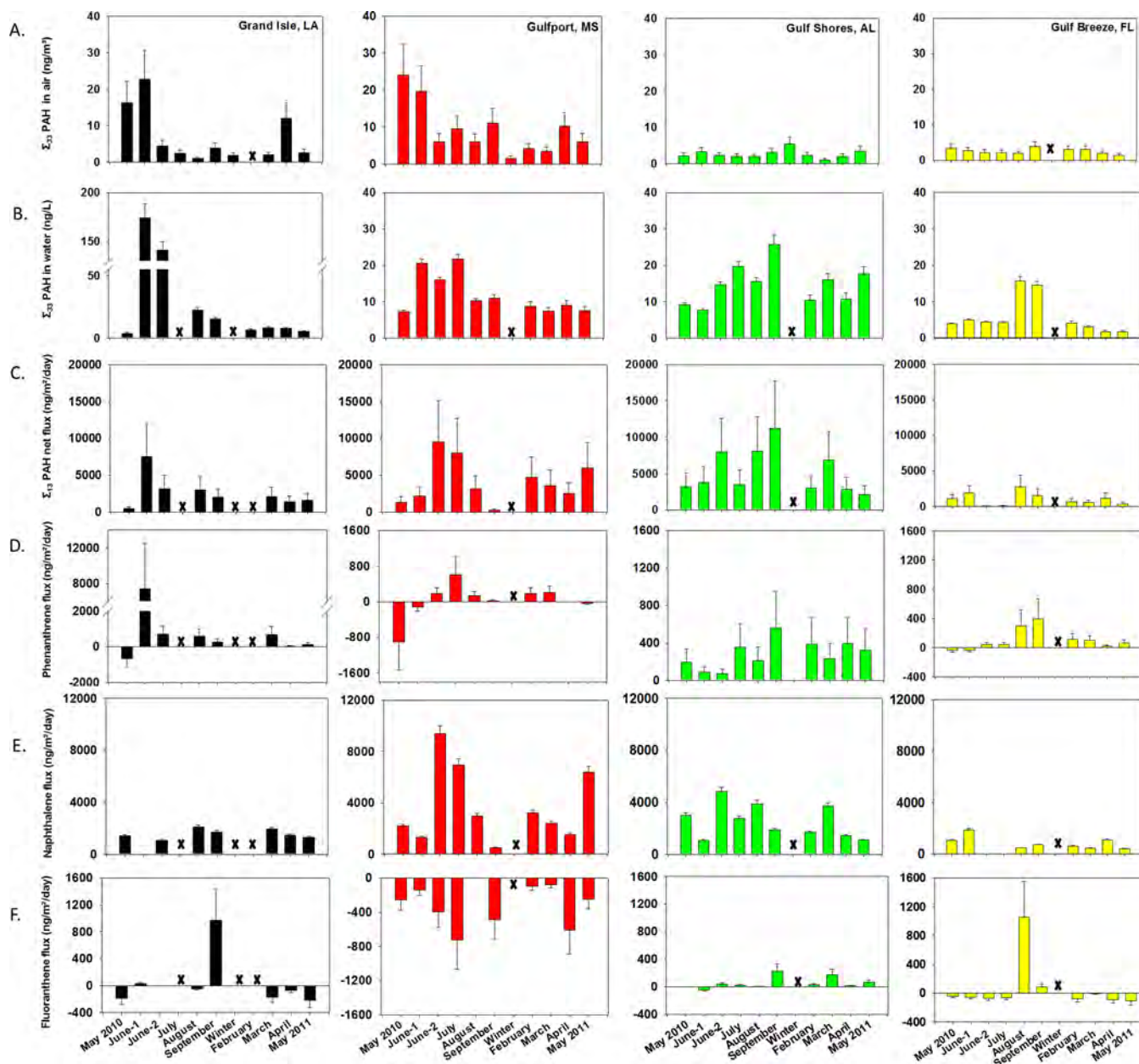


Figure 2. (A) Σ_{33} PAH vapor phase concentrations in air. (B) Σ_{33} PAH dissolved concentrations in water.¹⁶ (C) Σ_{13} PAH net flux. (D) Phenanthrene flux. (E) Naphthalene flux. (F) Fluoranthene flux. Error bars represent the calculated 95% confidence interval based on pooled variance from a replication study.

for chrysene-D12, 80.5% (68–90) for benzo(a)pyrene-D12, 66.7% (50–85) for dibenzo(g,h,i)perylene-D12, 66% (44–80) for 1,4-naphthalenequinone-D8, 104% (80–140) for 9-fluorenone-D8, and 96% (60–150) for 9,10-anthraquinone-D8.

Air–Water Flux Calculation. Environmental vapor concentrations were determined using an empirical uptake model with sampling rates derived by measuring PRC loss as described by Huckins et al. and others.^{11,27,29,33} Details and formulas are presented in the SI. Previously published water concentrations were used for calculation of PAH flux and are described in detail in Allan et al.¹⁶

The exchange of chemicals between air and water at the interface can be described as the movement of a chemical from the bulk phase, followed by transport across the thin films of each phase into the receiving compartment. The Whitman two film model is used to calculate this movement:

$$F = K_{ol} \left(\frac{C_w - C_a}{H'} \right) \quad (1)$$

where F is the flux ($\text{ng}/\text{m}^2 \text{ day}^{-1}$), the total mass-transfer rate coefficient is K_{ol} (m/day), and C_w and C_a are the dissolved and vapor phase concentrations in the water and air, respectively.^{17,18} H' , in this case, is a compound-specific temperature-corrected Henry's law value, and can be calculated using eq 2:

$$H' = \frac{H}{RT} \quad (2)$$

where R is the ideal gas constant ($8.2057 \times 10^{-5} \text{ m}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$) and T is the temperature in Kelvin. Air and water temperatures were collected hourly using temperature loggers co-located with PSDs at each sampling site. The average temperature over each deployment was calculated and used for

assessment of the temperature-corrected Henry's law values. The total mass transfer coefficient in eq 1 can be calculated according to eq 3:

$$\frac{1}{K_{ol}} = \frac{1}{k_a H'} + \frac{1}{k_w} \quad (3)$$

where k_a is the air side mass transfer coefficient and k_w is the water side mass transfer coefficient. Average wind speed over the course of the deployment was calculated from NOAA data published on the tides and currents web interface.³⁴ Published diffusivity values for 13 PAHs were used to calculate Schmidt values as inputs for mass transfer coefficients.³⁵ An estimate of OPAH flux was performed on 7 OPAHs, using PAH analogue diffusivity values, and are considered semiquantitative as a result. Details of the calculations are further described in Johnson and Bamford et al.^{36,18} Flux was only assessed when the compound was detected in both environmental compartments. PSD concentrations represent a time-weighted average concentration, therefore the net flux for each sampling period is the time-weighted average flux over the sampling duration. Using PSDs to assess the time-weighted flux provides an alternative new way to characterize movement of chemicals over a time period. PSD flux is especially well suited to applications where episodic changes and releases are important to capture and characterize. Assigning additional uncertainties to mass transfer coefficients derived from average values was determined to be an overly conservative approach. As a result, the error bars present on the flux figures in Figures 2 and 4 represent the pooled variance of the flux from an $n = 12$ replication study performed in the Gulf of Mexico during this study.

Data Modeling. Differences between sites and between sampling times were assessed using Wilcoxon rank-sum tests, and differences were considered significant at a probability value of $p \leq 0.05$. Confidence intervals were calculated from a Gulf of Mexico air and water replication study performed using $n = 12$ PSDs and represents the pooled variance.³⁷ The average percent difference between SUM PAH replicates in water and air at each site were 18 and 41, respectively. Principal component analysis (PCA) was used to explore changes in chemical profiles of samples; a specific description can be found in the SI. Analytes in the PCA below detection limits were assigned a value of one-half the limit of detection, information on detection limits can be found in SI Table 3.

RESULTS AND DISCUSSION

Vapor PAHs in Coastal Air of Four Gulf Coast States.

Prior to shoreline oiling at LA, the measured $\sum_{33\text{air}}\text{PAH}$ at this site was 16 (± 5) ng/m³. This increased to 23 (± 7) ng/m³ the following month when there was visible shoreline oiling (Figure 2A). The June-1 sampling event was significantly greater ($p \leq 0.04$) than sampling periods later in summer 2010. $\sum_{33\text{air}}\text{PAH}$ concentrations tended to increase earlier than PAH concentrations in water (Figure 2B from Allan et al.¹⁶), which could be due to faster atmospheric transport, as well as contributions from in situ burn events.^{38,39}

At MS, the May 2010 and June-1 $\sum_{33\text{air}}\text{PAH}$ were significantly above all other sampling times ($p < 0.05$). The May 2010 and June-1 maximum concentrations observed in air are similar to the LA site. Although Middlebrook et al. did not measure PAHs (except naphthalene) their bulk organic carbon measurements, taken at concurrent time points with the June-1

sampling, are consistent with our high $\sum_{33\text{air}}\text{PAH}$, providing converging lines of evidence that the DWH incident had tangible impacts on near-shore Gulf of Mexico air.⁴⁰

The temporal trend of bioavailable PAHs at the AL site was different from that of LA and MS sites (Figure 2A). The $\sum_{33\text{air}}\text{PAH}$ concentrations were generally ≤ 2 ng/m³. The highest observed $\sum_{33\text{water}}\text{PAH}$ was in September at 25 (± 2) ng/m³; the highest measured $\sum_{33\text{air}}\text{PAH}$ concentration was during the winter.¹⁶ High wind events and continued near-shore cleanup activities were observed during those sampling periods (SI Table 2) and the air PAH trend observed is consistent with a recirculation/suspension of contaminated waters/sediments and some volatilization. Other possible explanations include increased local inputs such as marine traffic or other oil sources.

The coastal air at FL had an initial $\sum_{33\text{air}}\text{PAH}$ concentration of 4 (± 1) ng/m³. A trend of decreasing $\sum_{33\text{air}}\text{PAH}$ from May 2010 through August was observed, but was not statistically different from other sampling periods ($p = 0.7$). The FL air $\sum_{33\text{air}}\text{PAH}$ are about 8-fold less than those observed in LA or MS in May 2010 and June-1.

All sites taken together displayed a temporal pattern of increases in the maximum air PAH concentrations occurring earlier at the western sites and later in the eastern locations. This could be explained by the distance of the sites from the wellhead, in addition to in situ burns and air currents in the Gulf of Mexico.^{40,41} The sites at LA and MS were most heavily impacted in May and June 2010. A similar trend was observed in water samples.¹⁶ Dispersion and aging of oil and oil chemicals could also explain this trend; if DWH were a primary source of PAHs during this time period, then a decrease of vapor phase PAH would be expected.^{42,43}

Comparing Gulf of Mexico Air PAHs to Literature

Values. The vapor-phase $\sum_{33\text{air}}\text{PAH}$ concentrations in this study ranged between 2 and 23 ng/m³, and are similar to vapor-phase $\sum_{13}\text{PAH}$ concentrations of 3.06 and 24.1 ng/m³ recorded in the coastal metropolitan region of Kozani and the rural region of Petrana Greece, respectively.⁴⁴ A 2006 study near a petroleum industry harbor in Belgium found $\sum_{16}\text{PAH}$ vapor phase concentrations to range between 15 and 135 ng/m³ during different seasons, overlapping with the measured PAHs in this study.⁴⁵ Conversely, very high vapor phase concentrations were observed in the inland metropolitan region of Alexandria Egypt, with $\sum_{42}\text{PAH}$ concentrations ranging between 390 and 990 ng/m³.⁴⁶ The highest individual PAH contributions to the total PAH load in this study were phenanthrene and 2-methyl phenanthrene (SI Figures S1 and S2), which are similar to other studies of vapor-phase PAHs at petroleum impacted sites or areas of moderate urbanization.^{44,45}

PAH Air–Water Exchange. Predicting the fate of PAHs during environmental disasters includes characterizing the exchange of PAHs across the air–water boundary.^{18,20} Whereas many fate models for the DWH oil spill assumed volatilization was an important transfer and fate mechanism, this pathway has not been directly quantified.²⁶ Air–water exchange (flux) of 13 PAHs was determined at the four sites over a 13-month period that spanned the DWH incident (Figure 2C–E). $\sum_{13}\text{PAH}$ net flux was positive; meaning volatilization of PAHs from the water to the air occurred at all sampling sites and all time points during this investigation. The greatest $\sum_{13}\text{PAH}$ net flux to air occurred at MS and AL, observed during June-2 at 9570

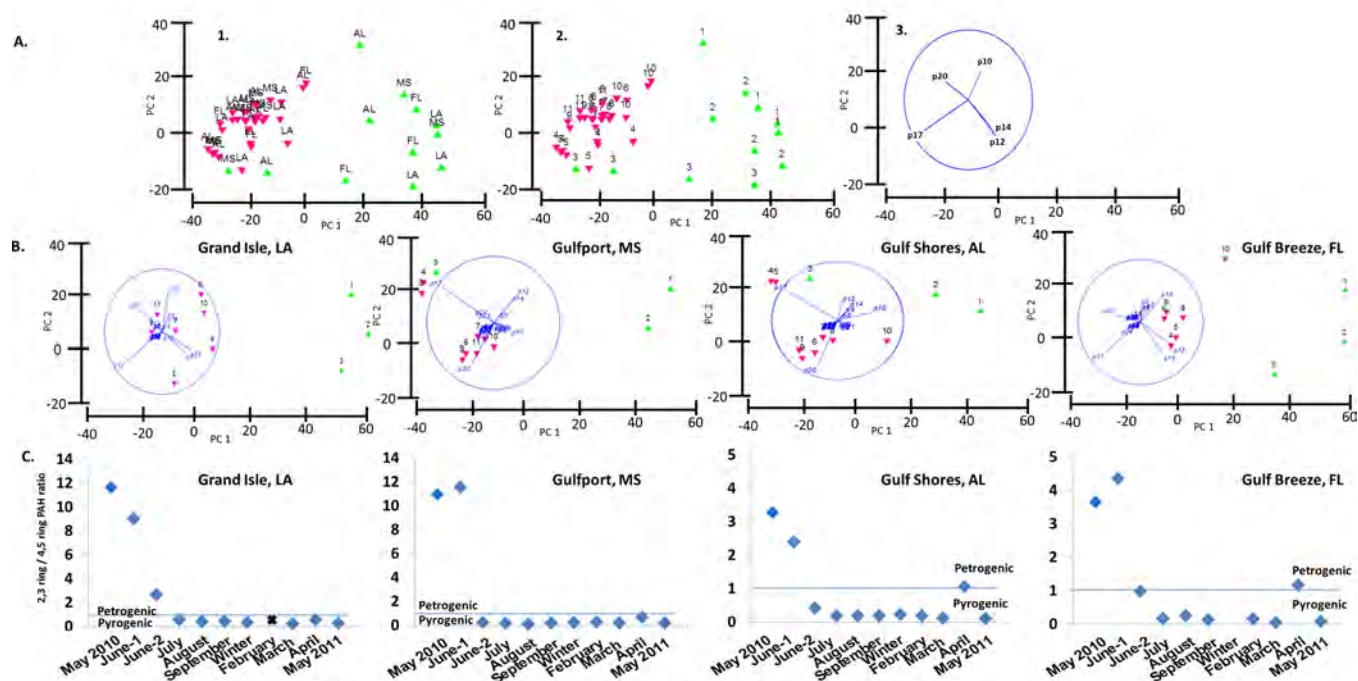


Figure 3. (A) Principal component analysis (PCA) plots. Green and red triangles represent samples prior to, and after, the well head was capped, respectively. A1 is labeled by state, A2 is labeled by events numbered 1–10 (representing May 2010–May 2011), and A3 are PAH vectors (p20 = pyrene, p17 = fluoranthene, p14 = 1-methylphenanthrene, p12 = 2methylphenanthrene, p10 = phenanthrene). (B) Individual state PCA plots. (C) Ratio of 2–3 ring/4–6 ring PAHs for each site during each sampling event.

(± 5000) ng/m²/day, and September at 11 200 (± 6000) ng/m²/day, respectively.

The \sum_{13} PAH flux to air peaked at LA in June-1, at 7600 (± 4000) ng/m²/day. After the DWH in situ burns stopped and the well head was capped, the \sum_{13} PAH flux generally decreased at those sites. Interestingly, ten months after the peak (i.e., June-1) \sum_{13} PAH flux volatilization was about 6-fold lower at the LA site, but flux of PAHs from water to air was still 2.5-fold greater than observed in May 2010 prior to shoreline oiling. This may be due to the continuing influence of DWH oil in this area. The FL \sum_{13} PAH net flux, volatilization, was significantly less ($p = 0.05$) than that at the three other sites.

Individual PAHs showed more variability in flux direction and magnitude than the net PAH flux. The greatest volatilization at MS and AL was naphthalene at 9370 (± 600) and 4850 (± 300) ng/m²/day during the June-2 sampling event. The largest individual PAH volatilization at LA was phenanthrene at 7390 (± 5000) ng/m²/day in June-1 and the largest deposition was -665 (± 400) ng/m²/day in May 2010. The shift of flux from deposition to volatilization for phenanthrene is an important indicator of increased dissolved PAH levels in water rather than decreased vapor-phase PAH levels in air. In 1999, Bamford et al. found that local inputs from an urban setting to surface waters resulted in similar degassing events, indicating that local sources such as industrial activities, or an oil spill in this case, may strongly influence the flux of PAHs.¹⁸ Phenanthrene and fluoranthene underwent the largest observed single PAH deposition events at MS and AL at a rates of -905 (± 600) ng/m²/day in May 2010 and -45.5 (± 20) ng/m²/day in June-1, respectively (Figure 2D and 2F).

Few other relevant studies are available for comparison of individual PAHs, but a study in a heavily industrialized harbor in Taiwan showed phenanthrene to be undergoing deposition

during 19 of the 22 sampling time points.¹⁹ Additionally, another study reported the observed mean annual flux of phenanthrene along the southern coastline of Singapore to be -457 (± 490) ng/m²/day.⁴⁷ A third investigation shows phenanthrene in deposition phase for all but one observation in Lake Erie and Lake Ontario,²³ and a fourth investigation of PAH flux found phenanthrene to be in or near equilibrium for all sites with detectable levels of phenanthrene in both air and water.²⁵ All of these studies illustrate that the typical trend for phenanthrene is deposition under many environmental conditions, however, we found during the DWH incident along the coast of the Gulf of Mexico phenanthrene was volatilizing. The change from deposition to volatilization of phenanthrene at LA, MS, and FL sites give strength to the supposition that the influx of hydrocarbons from the DWH incident changed the direction of phenanthrene flux well after visible oil was gone. The AL site did not shift from deposition to volatilization as observed at the other three sites and does not exhibit the characteristic phenanthrene deposition observed in other flux investigations.^{19,23,47} However, there was an increase in volatilization later in the study showing that a perturbation of the steady-state flux at this site occurred. Continuous volatilization of phenanthrene at AL might be explained by the local marine and residential activities which were in close proximity. The proximity of residential and marine activity at AL may have introduced phenanthrene directly to the water through runoff or marine engine use and maintenance. Sources such as local residences and other anthropogenic activities have been shown to affect PAH air–water dynamics.^{18,23}

PAH Chemical Profiles and Source Modeling. Principle component analysis (PCA) using air data in profile form was used to produce score and loading plots, shown in Figure 3A.

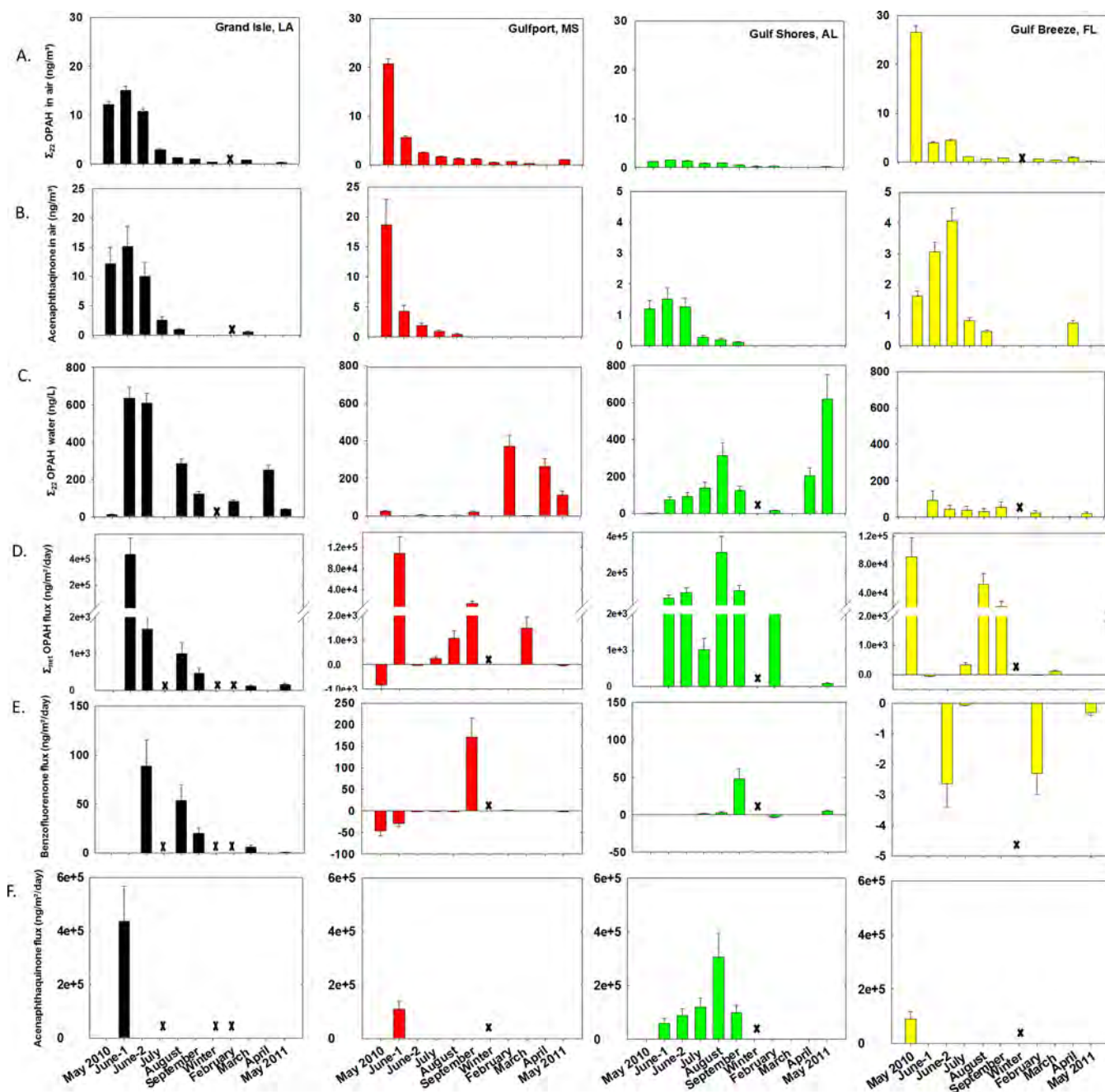


Figure 4. (A) Σ_{22} OPAH vapor phase concentrations in air. (B) Acenaphthenequinone vapor phase concentrations in air. (C) Σ_{22} OPAH dissolved concentrations in water. (D) Σ_{22} OPAH net flux. (E) Benzofluorenone flux. (F) Acenaphthenequinone flux. Error bars represent the calculated 95% confidence interval based on pooled variance from a replication study.

The two score plots differ only by the choice of deployment time or state labels. PCA was also performed on individual state air data, as seen in Figure 3B. The score plots show good delineation between precap and postcap and also give a clear time trajectory for the first five sampling events, where the first samples taken in each state have the majority of the variability explained by PC1. As the sampling progressed after the DWH incident, p12 (1-methylphenanthrene) and p14 (2-methylphenanthrene) variability and percent contribution decreased until sampling events 6–10 (September–May 2011) show little to no difference between site or deployment in terms of PAH profile (Figure 3). Furthermore, postcap sampling events 4–10 (July–May 2011) show less intrasample variation than precap

observations, suggesting the homogeneity of postcap samples consistent with a single episodic event (Figure 3). Postcap sampling periods of July and August (labeled as 4 and 5) show a transitional behavior which is most apparent when looking at PCA graphs for individual states (Figure 3B). The loading plot in Figure 3A shows precap samples have relatively high percentages of the alkylated PAHs compared to the parent PAHs, labeled as p12 (1-methylphenanthrene) and p14 (2-methylphenanthrene) and are consistent with a petrogenic source (see SI Figure S2).^{48,49} In contrast, the postcap samples tend to have high percentages of the parent PAHs consistent with pyrogenic sources, such as pyrene labeled as p20.^{48,49}

Figure 3C shows source ratios enriched in 2- and 3-ring PAHs compared to 4- to 6-ring PAHs in May and June-1 at all sites, consistent with a petrogenic source.^{50,51} Ratios with values greater than 1 are indicative of a petrogenic source.⁵¹ The alkylated-PAH versus parent PAH profiles are dominantly also petrogenic in June-1 at LA. In urban environments, no single source was expected; this was consistent with our observations of mixed alkylated profiles observed later in 2010 and 2011.

Oxygenated Polycyclic Aromatic Hydrocarbons in Air and Water. Few OPAH concentrations in air and water have been quantified using PSDs.¹² Oxygenated hydrocarbons were reported during the DWH incident using active sampling techniques; however, the specific oxygenated analytes were not identified.⁵² OPAHs detected in DWH crude oil were identified in both water and air samples (SI Table 4). During this study 11 OPAHs were quantified, five of those OPAHs were detected in most of the samples (SI Figure S3). The most abundant OPAHs in air during the DWH incident were acenaphthenequinone, benzofluorenone, 9,10-anthraquinone, and 9-fluorenone (Figures 2A–C and SI S3). Over the course of the study, the OPAHs with the highest concentrations in water were phenanthrene-1,4-dione, and acenaphthenequinone in LA, MS, and AL, while 1,4-anthraquinone was the largest contribution in water at FL (SI Figure S3). Sum OPAHs at LA peaked in June-1 in air and water, $\sum_{22\text{air}}\text{OPAH}$ 15.1 (± 1) ng/m³ and $\sum_{22\text{water}}\text{OPAH}$ 635 (± 60) ng/L. Unlike PAHs, the $\sum_{22\text{air}}\text{OPAH}$ remained elevated in the June-2 sample, after which a decrease of 10–15 fold was observed. However, water concentrations of phenanthrene-1,4-dione 257 (± 40) ng/L, and acenaphthenequinone 185 (± 30) ng/L remained elevated at LA through May 2011.

$\sum_{22\text{water}}\text{OPAH}$ concentrations at the MS site were less than 25 ng/L for the first six sampling periods (Figure 2C). The most frequently observed was benzofluorenone (SI Figure S3). $\sum_{22\text{water}}\text{OPAH}$ concentrations were elevated in February, April, and May 2011 at concentrations of 369 (± 60), 262 (± 40), and 112 (± 20) ng/L respectively, $p < 0.05$, when compared to the other 5 sampling events for each of these observations. In each instance, acenaphthenequinone had the greatest contribution to the $\sum_{22\text{water}}\text{OPAH}$. Conversely, $\sum_{22\text{air}}\text{OPAH}$ at MS was significantly higher in May 2010 at 20 (± 1) ng/m³ than in all subsequent sampling times ($p = 0.01$). Similar to LA, the OPAH that contributed the most to MS $\sum_{22\text{air}}\text{OPAH}$ was acenaphthenequinone. The high concentrations of OPAHs in air in May 2010 suggest that air quality may have been impacted by the DWH before shoreline oiling was observed. Also, given the proximity of this site to urban and industrial activities, it is also important to consider possible impacts from local sources. Increased levels of OPAHs in Gulf of Mexico waters during later sampling in 2011 may be evidence of the continuing transformation of PAHs in the system into OPAHs.

The $\sum_{22\text{air}}\text{OPAH}$ levels at AL were approximately 20-fold less than the highest concentrations observed at LA or MS. The highest $\sum_{22\text{air}}\text{OPAH}$ at AL was during June-1 sampling at 1.5 (± 1) ng/m³, and concentrations gradually decreased throughout the study to a minimum of 0.19 (± 0.1) ng/m³ in May 2011 (Figure 4A). OPAHs in water were minimal at the onset of sampling and peaked during the last sampling event. The lowest $\sum_{22\text{water}}\text{OPAH}$ concentration at AL, 2.2 (± 0.5), was observed during May 2010 and the highest $\sum_{22\text{water}}\text{OPAH}$, 617 (± 100) ng/L, was recorded during May 2011.

The highest concentration $\sum_{22\text{air}}\text{OPAH}$ observed during the study was measured at FL in May 2010 at level of 26 (± 2) ng/m³; this observation was significantly different from all other samples ($p < 0.05$) (Figure 4A). The high concentration is largely due to acenaphthenequinone and 1,4-anthraquinone (Figure 4B, SI Figure S3). Due to short atmospheric half-lives and multiple formation pathways, positively identifying sources of OPAH is an ongoing research question. The potential for May 2010 $\sum_{22\text{air}}\text{OPAH}$ at this site to be affected by factors other than DWH is likely. $\sum_{22\text{water}}\text{OPAH}$ concentrations in FL reached a peak concentration of 92 (± 50) in June-1, a value nominally six times lower than the highest observed concentration at the LA site (Figure 4C). Unlike the other three sites, waterborne OPAH in Gulf Breeze, FL showed little temporal variation during the course of this research.

In a study in southern France, the highest combined gas and particle OPAH values observed were nominally 50 to 65% less than the highest concentrations observed in FL and MS, respectively.⁵³ The high concentrations of vapor-phase OPAHs observed during May 2010 are much higher than what has been previously characterized in typical urban settings.⁵³ A study in Texas showed elevated vapor phase levels of benz[a]-anthracene-7,12-dione during the summer, which was proposed to be a result of temperature-dependent partitioning between the particle-bound and vapor-phase OPAHs.⁵⁴ Although similar meteorological conditions occurred during this study, the OPAH levels actually decreased dramatically during the summer. This observation lends support to the idea that elevated levels were due to a specific input(s) disrupting typical environmental conditions, and not simply a shift in partitioning between the vapor and aerosol phase.^{55–57} A study performed in Oregon on the Willamette River in the Portland Harbor Superfund site found dissolved OPAH concentrations in water ranging from 6 to 50 ng/L.³² This observation by O'Connell et al. is nominally 12 times lower than the highest water value reported here.³² The May 2010 event yielded OPAHs 10–20 fold higher at the LA, MS, and FL sites compared to sampling events later in the study. The consistently low levels of OPAHs in air after June 2010 are different from the PAH temporal profile where increases were observed in April 2011 in both LA and MS. Although toxicity of OPAHs is not thoroughly known, early evidence suggests development toxicity may be the same or higher for some OPAHs than the parent PAH.⁷ Therefore, OPAHs appear to be an important consideration as part of the transport, weathering, and ecosystem health during environmental disasters.^{9,52}

OPAH Air–Water Exchange. To the authors' knowledge this is the first report of OPAH flux. Direction and approximate magnitude for the OPAH flux is shown in Figure 4D–F. Unlike PAHs, where the net flux was consistently volatilization during the study, $\sum_7\text{OPAH}$ flux underwent repeated periods of deposition and volatilization at both MS and FL. LA and MS had the largest magnitude of volatilization in June-1 and August, respectively. Large $\sum_7\text{OPAH}$ volatilization at all four sites was primarily driven by the movement of acenaphthenequinone from water to air. MS underwent a change from net deposition to net volatilization between May 2010 and June-1, primarily attributable to acenaphthenequinone. Benzofluorenone flux at each site was of significantly lower magnitude than acenaphthenequinone; however, benzofluorenone was found to be of a very transient nature, undergoing volatilization in LA, deposition in FL, and changed from deposition to volatilization in MS. The nature of the dynamic movement between

environmental compartments and the observed magnitudes indicate further investigation is warranted. The extremely high magnitude of OPAH flux to the atmosphere concurrent with the DWH incident shows that OPAHs as well as PAHs need to be assessed for environmental fate and transport when assessing the long-term impacts of an environmental disaster.

■ ASSOCIATED CONTENT

📄 Supporting Information

Figures that present the full characterization of PAH and OPAH chemical profiles and PAH flux for all samples. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kim.anderson@orst.edu. Phone: 541-737-8501. Fax: 541-737-0497.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was supported in part by awards P42 ES016465 and the associated Analytical Chemistry Facility Core, P30 ES000210, and R21 ES020120 from the National Institute of Environmental Health Sciences. The content is solely the responsibility of the authors and does not necessarily represent the official views of the NIEHS or the National Institutes of Health. We appreciate valuable help from Alan Bergmann, Ricky Scott, Gary Points, and Glenn Wilson. We thank Grand Isle State Park, Gulfport Harbor, Bon Secour National Wildlife Refuge, and Gulf Shores National Seashore. Gulf Shores National Seashore permits: GUI-2010-SCI-0022, GUI-2011-SCI-0042. Bon Secour National Wildlife Refuge permits: 10-011, 11-002. Grand Isle State Park permit issue dates: May 18, 2010 and May 18, 2011.

■ REFERENCES

- (1) Camilli, R.; Di Iorio, D.; Bowen, A.; Reddy, C. M.; Techet, A. H.; Yoerger, D. R.; Whitcomb, L. L.; Seewald, J. S.; Sylva, S. P.; Fenwick, J. Acoustic measurement of the Deepwater Horizon Macondo well flow rate. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *109*, 20235–20239.
- (2) Aurell, J. *Aerostat Sampling of PCDD/PCDF Emissions from the Gulf Oil Spill in Situ Burns*; Diane Publishing: Darby, PA, 2010.
- (3) Kujawinski, E. B.; Kido Soule, M. C.; Valentine, D. L.; Boysen, A. K.; Longnecker, K.; Redmond, M. C. Fate of dispersants associated with the Deepwater Horizon oil spill. *Environ. Sci. Technol.* **2011**, *45* (4), 1298–1306.
- (4) National Research Council. *Oil Spill Dispersants: Efficacy and Effects*; National Academy of Sciences: Washington, DC, 2005.
- (5) Reddy, C. M.; Arey, J. S.; Seewald, J. S.; Sylva, S. P.; Lemkau, K. L.; Nelson, R. K.; Carmichael, C. A.; McIntyre, C. P.; Fenwick, J.; Ventura, G. T. Composition and fate of gas and oil released to the water column during the Deepwater Horizon oil spill. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *109*, 20229–20234.
- (6) Lundstedt, S.; White, P. A.; Lemieux, C. L.; Lynes, K. D.; Lambert, L. B.; Oberg, L.; Haglund, P.; Tysklind, M. Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites. *Ambio* **2007**, *36* (6), 475–485.
- (7) Knecht, A. L.; Goodale, B. C.; Truong, L.; Simonich, M. T.; Swanson, A. J.; Matzke, M. M.; Anderson, K. A.; Waters, K. M.; Tanguay, R. L. Comparative developmental toxicity of environmentally relevant oxygenated PAHs. *Toxicol. Appl. Pharmacol.* **2013**, *271*, 266–275.

- (8) Wischmann, H.; Steinhart, H. The formation of PAH oxidation products in soils and soil/compost mixtures. *Chemosphere* **1997**, *35* (8), 1681–1698.

- (9) Layshock, J. A.; Wilson, G.; Anderson, K. A. Ketone and quinone-substituted polycyclic aromatic hydrocarbons in mussel tissue, sediment, urban dust, and diesel particulate matrices. *Environ. Toxicol. Chem.* **2010**, *29* (11), 2450–2460.

- (10) Sower, G. J.; Anderson, K. A. Spatial and temporal variation of freely dissolved polycyclic aromatic hydrocarbons in an urban river undergoing superfund remediation. *Environ. Sci. Technol.* **2008**, *42* (24), 9065–9071.

- (11) Huckins, J. N.; Petty, J. D.; Booi, K. *Monitors of Organic Chemicals in the Environment: Semipermeable Membrane Devices*; Springer: New York, 2006.

- (12) O'Connell, S. G.; Haigh, T.; Wilson, G.; Anderson, K. A. An analytical investigation of 24 oxygenated-PAHs (OPAHs) using liquid and gas chromatography–mass spectrometry. *Anal. Bioanal. Chem.* **2013**, 1–12.

- (13) Ramírez, N.; Cuadras, A.; Rovira, E.; Marcé, R. M.; Borrull, F. Risk assessment related to atmospheric polycyclic aromatic hydrocarbons in gas and particle phases near industrial sites. *Environ. Health Perspect.* **2011**, *119* (8), 1110.

- (14) Tsai, P.-J.; Shieh, H.-Y.; Lee, W.-J.; Lai, S.-O. Characterization of PAHs in the atmosphere of carbon black manufacturing workplaces. *J. Hazardous Mater.* **2002**, *91* (1), 25–42.

- (15) Liu, Y.; Tao, S.; Dou, H.; Zhang, T.; Zhang, X.; Dawson, R. Exposure of traffic police to polycyclic aromatic hydrocarbons in Beijing, China. *Chemosphere* **2007**, *66* (10), 1922–1928.

- (16) Allan, S. E.; Smith, B. W.; Anderson, K. A. Impact of the Deepwater Horizon Oil Spill on Bioavailable Polycyclic Aromatic Hydrocarbons in Gulf of Mexico Coastal Waters. *Environ. Sci. Technol.* **2012**, *46*, 2033–2039.

- (17) Baker, J. E.; Eisenreich, S. J. Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air–water interface of Lake Superior. *Environ. Sci. Technol.* **1990**, *24* (3), 342–352.

- (18) Bamford, H. A.; Offenber, J. H.; Larsen, R. K.; Ko, F. C.; Baker, J. E. Diffusive exchange of polycyclic aromatic hydrocarbons across the air–water interface of the Patapsco River, an urbanized subestuary of the Chesapeake Bay. *Environ. Sci. Technol.* **1999**, *33* (13), 2138–2144.

- (19) Fang, M.-D.; Lee, C.-L.; Jiang, J.-J.; Ko, F.-C.; Baker, J. E. Diffusive exchange of PAHs across the air–water interface of the Kaohsiung Harbor lagoon, Taiwan. *J. Environ. Manage.* **2012**, *110*, 179–187.

- (20) Gustafson, K. E.; Dickhut, R. M. Distribution of polycyclic aromatic hydrocarbons in southern Chesapeake Bay surface water: evaluation of three methods for determining freely dissolved water concentrations. *Environ. Toxicol. Chem.* **1997**, *16* (3), 452–461.

- (21) Prest, H.; Jacobson, L.; Huckins, J. Passive sampling of water and coastal air via semipermeable membrane devices. *Chemosphere* **1995**, *30* (7), 1351–1361.

- (22) Lohmann, R.; Dapsis, M.; Morgan, E. J.; Dekany, V.; Luey, P. J. Determining Air–Water Exchange, Spatial and Temporal Trends of Freely Dissolved PAHs in an Urban Estuary Using Passive Polyethylene Samplers. *Environ. Sci. Technol.* **2011**, *45* (7), 2655–2662.

- (23) McDonough, C. A.; Khairy, M. A.; Muir, D. C.; Lohmann, R. The significance of population centers as sources of gaseous and dissolved PAHs in the lower Great Lakes. *Environ. Sci. Technol.* **2014**, *48*, 7789–7797.

- (24) Lohmann, R.; Klanova, J.; Kukucka, P.; Yonis, S.; Bollinger, K. Concentrations, Fluxes, and Residence Time of PBDEs Across the Tropical Atlantic Ocean. *Environ. Sci. Technol.* **2013**, *47* (24), 13967–13975.

- (25) Lohmann, R.; Klanova, J.; Pribylova, P.; Liskova, H.; Yonis, S.; Bollinger, K. PAHs on a west-to-east transect across the tropical Atlantic Ocean. *Environ. Sci. Technol.* **2013**, *47* (6), 2570–2578.

- (26) Ramseur, J. L. *Deepwater Horizon Oil Spill: The Fate of the Oil*; Congressional Research Service, Library of Congress: Washington, DC, 2010.
- (27) Bartkow, M. E.; Jones, K. C.; Kennedy, K. E.; Holling, N.; Hawker, D. W.; Müller, J. F. Evaluation of performance reference compounds in polyethylene-based passive air samplers. *Environ. Pollut.* **2006**, *144* (2), 365–370.
- (28) Booij, K.; Smedes, F.; van Weerlee, E. M. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. *Chemosphere* **2002**, *46* (8), 1157–1161.
- (29) Huckins, J. N.; Petty, J. D.; Lebo, J. A.; Almeida, F. V.; Booij, K.; Alvarez, D. A.; Cranor, W. L.; Clark, R. C.; Mogensen, B. B. Development of the permeability/performance reference compound approach for in situ calibration of semipermeable membrane devices. *Environ. Sci. Technol.* **2002**, *36* (1), 85–91.
- (30) Söderström, H. S.; Bergqvist, P.-A. Passive air sampling using semipermeable membrane devices at different wind-speeds in situ calibrated by performance reference compounds. *Environ. Sci. Technol.* **2004**, *38* (18), 4828–4834.
- (31) Anderson, K.; Sethajintanin, D.; Sower, G.; Quarles, L. Field trial and modeling of uptake rates of in situ lipid-free polyethylene membrane passive sampler. *Environ. Sci. Technol.* **2008**, *42* (12), 4486–4493.
- (32) O'Connell, S. G.; McCartney, M. A.; Paulik, L. B.; Allan, S. E.; Tidwell, L. G.; Wilson, G.; Anderson, K. A. Improvements in pollutant monitoring: Optimizing silicone for co-deployment with polyethylene passive sampling devices. *Environ. Pollut.* **2014**, *193*, 71–78.
- (33) Bartkow, M. E.; Huckins, J. N.; Müller, J. F. Field-based evaluation of semipermeable membrane devices (SPMDs) as passive air samplers of polyaromatic hydrocarbons (PAHs). *Atmos. Environ.* **2004**, *38* (35), 5983–5990.
- (34) NOAA. http://tidesandcurrents.noaa.gov/station_retrieve.shtml?type=Meteorological%20Observations. NOAA, 2013.
- (35) G.S.I. Environmental Chemical Properties Data Base. <http://www.gsi-net.com/en/publications/gsi-chemical-database.html> (accessed 02/10/14).
- (36) Johnson, M. A. A numerical scheme to calculate temperature and salinity dependent air-water transfer velocities for any gas. *Ocean Sci.* **2010**, *6* (4), 913–932.
- (37) Matzke, M. M.; Allan, S. E.; Anderson, K. A.; Waters, K. M. An approach for calculating a confidence interval from a single aquatic sample for monitoring hydrophobic organic contaminants. *Environ. Toxicol. Chem.* **2012**, *31* (12), 2888–2892.
- (38) Lehr, B.; Bristol, S.; Possolo, A. *Oil Budget Calculator—Deepwater Horizon, Technical Documentation: A Report to the National Incident Command*; Coastal Response Research Center: Durham, NH, 2010.
- (39) Leifer, I.; Lehr, W. J.; Simecek-Beatty, D.; Bradley, E.; Clark, R.; Dennison, P.; Hu, Y.; Matheson, S.; Jones, C. E.; Holt, B. State of the art satellite and airborne marine oil spill remote sensing: Application to the BP Deepwater Horizon oil spill. *Remote Sens. Environ.* **2012**, *124*, 185–209.
- (40) Middlebrook, A. M.; Murphy, D. M.; Ahmadov, R.; Atlas, E. L.; Bahreini, R.; Blake, D. R.; Brioude, J.; de Gouw, J. A.; Fehsenfeld, F. C.; Frost, G. J. Air quality implications of the Deepwater Horizon oil spill. *Proc. Natl. Acad. Sci. U. S. A.* **2011**, *109*, 20280–20285.
- (41) Allen, A. A.; Jaeger, D.; Mabile, N. J.; Costanzo, D. The Use of Controlled Burning during the Gulf of Mexico Deepwater Horizon MC-252 Oil Spill Response. In *International Oil Spill Conference Proceedings (IOSC)*; American Petroleum Institute: Washington, DC, 2011; p abs194.
- (42) Brubaker, W. W.; Hites, R. A. OH reaction kinetics of polycyclic aromatic hydrocarbons and polychlorinated dibenzo-p-dioxins and dibenzofurans. *J. Phys. Chem. A* **1998**, *102* (6), 915–921.
- (43) Jones, K. C.; De Voogt, P. Persistent organic pollutants (POPs): State of the science. *Environ. Pollut.* **1999**, *100* (1), 209–221.
- (44) Terzi, E.; Samara, C. Gas-particle partitioning of polycyclic aromatic hydrocarbons in urban, adjacent coastal, and continental background sites of western Greece. *Environ. Sci. Technol.* **2004**, *38* (19), 4973–4978.
- (45) Ravindra, K.; Bencs, L.; Wauters, E.; De Hoog, J.; Deutsch, F.; Roekens, E.; Bleux, N.; Berghmans, P.; Van Grieken, R. Seasonal and site-specific variation in vapour and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. *Atmos. Environ.* **2006**, *40* (4), 771–785.
- (46) Khairy, M. A.; Lohmann, R. Field validation of polyethylene passive air samplers for parent and alkylated PAHs in Alexandria, Egypt. *Environ. Sci. Technol.* **2012**, *46* (7), 3990–3998.
- (47) He, J.; Balasubramanian, R. The exchange of SVOCs across the air-sea interface in Singapore's coastal environment. *Atmos. Chem. Phys. Discuss.* **2009**, *9*, 13235–13269.
- (48) Larsen, R. K.; Baker, J. E. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: A comparison of three methods. *Environ. Sci. Technol.* **2003**, *37* (9), 1873–1881.
- (49) Wang, Z.; Stout, S. *Oil Spill Environmental Forensics: Fingerprinting and Source Identification*; Academic Press: Waltham, MA, 2010.
- (50) Blumer, M.; Youngblood, W. Polycyclic aromatic hydrocarbons in soils and recent sediments. *Science* **1975**, *188* (4183), 53–55.
- (51) Zhang, W.; Zhang, S.; Wan, C.; Yue, D.; Ye, Y.; Wang, X. Source diagnostics of polycyclic aromatic hydrocarbons in urban road runoff, dust, rain and canopy throughfall. *Environ. Pollut.* **2008**, *153* (3), 594–601.
- (52) Aeppli, C.; Carmichael, C. A.; Nelson, R. K.; Lemkau, K. L.; Graham, W. M.; Redmond, M. C.; Valentine, D. L.; Reddy, C. M. Oil Weathering after the Deepwater Horizon Disaster Led to the Formation of Oxygenated Residues. *Environ. Sci. Technol.* **2012**, *46* (16), 8799.
- (53) Albinet, A.; Leoz-Garziandia, E.; Budzinski, H.; Villenave, E. Polycyclic aromatic hydrocarbons (PAHs), nitrated PAHs and oxygenated PAHs in ambient air of the Marseilles area (South of France): Concentrations and sources. *Sci. Total Environ.* **2007**, *384* (1–3), 280–292.
- (54) Wilson, N. K.; McCurdy, T. R.; Chuang, J. C. Concentrations and phase distributions of nitrated and oxygenated polycyclic aromatic hydrocarbons in ambient air. *Atmos. Environ.* **1995**, *29* (19), 2575–2584.
- (55) Albaigés, J.; Bayona, J. M.; Fernandez, P.; Grimalt, J.; Rosell, A.; Simó, R. Vapor-particle partitioning of hydrocarbons in Western Mediterranean urban and marine atmospheres. *Microchim. Acta* **1991**, *104* (1), 13–27.
- (56) Cincinelli, A.; Bubba, M. D.; Martellini, T.; Gambaro, A.; Lepri, L. Gas-particle concentration and distribution of *n*-alkanes and polycyclic aromatic hydrocarbons in the atmosphere of Prato (Italy). *Chemosphere* **2007**, *68* (3), 472–478.
- (57) Eiguren-Fernandez, A.; Avol, E. L.; Thurairatnam, S.; Hakami, M.; Froines, J. R.; Miguel, A. H. Seasonal influence on vapor-and particle-phase polycyclic aromatic hydrocarbon concentrations in school communities located in Southern California. *Aerosol Sci. Technol.* **2007**, *41* (4), 438–446.