

Supplementary Information: PAH and OPAH Flux during the Deepwater

Horizon Incident

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This article is a corrected form of Tidwell *et al*, which was originally published in 2015, DOI: 10.1021/es503827y.¹ Vapor phase PAH and OPAH measured concentrations in air were corrected, as were the air-water flux mass exchange rates. Corrections were made due to the detection of an honest calculation error found in the original manuscript. Errors resulted from using incorrect units of the ideal gas constant and improper cell linkages in the spreadsheet that was used to adjust air concentrations for sampling temperature. The original article was retracted by the authors.² This version of the article presents corrected versions of all of the original analyses and discussions.

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Table 1: Sampling events and durations

May 2010	May 10-13, 2010
June-1	June 8-11, 2010
June-2	June 11-July 7, 2010
July	July 7-August 5, 2010
August	August 5-September 8, 2010
September	September 8-October 13, 2010
Winter	October 13, 2010 – February 9, 2011
February	February 9-March 15, 2011
March	March 15-April 25, 2011
April	April 25-April 29, 2011
May 2011	April 29-June 8, 2011

Table 1: Sampling deployment times varied throughout the study due to scientific and logistical considerations including degree of nearshore and shoreline oil, travel, weather, and site accessibility. Because performance reference compounds were used to determine *in situ* uptake rates to calculate water and air concentrations, a wide range of deployment times were feasible and data from different deployment periods are directly comparable.

List 1: 33 PAH analyte method compounds

naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, 1,6-dimethylnaphthalene, acenaphylthene, acenaphthene, fluorene, dibenzothiophene, phenanthrene, 1-methylphenanthrene, 2-methylphenanthrene, 3,6-dimethylphenanthrene, anthracene, 2-methylanthracene, 9-methylanthracene, 2,3-dimethylanthracene, 9,10-dimethylanthracene, flouanthene, pyrene, 1-methylpyrene, retene, benz[a]anthracene, chrysene, 6-methylchrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene and dibenzo[a,l]pyrene.

Deuterated performance reference compounds (PRC): fluorene-D10, p,p'-DDE-D8, and benzo[b]fluoranthene-D10. Maximum differences between PRC log k_{ow} and target PAH and OPAH log k_{ow} in water samples was 1.2 and 2.8 respectively.

The deuterated surrogate recovery standards: naphthalene-D8, acenaphthylene-D8, phenanthrene-D10, fluoranthene-D10, pyrene-D10, benzo[a]pyrene-D12 and benzo[g,h,i]perylene. Perylene-D12 was used as the instrumental internal standard.

List 2: 22 OPAH analyte method compounds

6H-benzo[cd]pyreneone, 1,4-phenanthrenedione, 1,4-benzo[c]phenanthrenequinone, 9-fluorenone, 9,10-anthraquinone, 1,9-benzanthrone, benzo[a]pyrene-1,6-dione, benzo[a]pyrene-7,8-dione, 1,4-benzoquinone, chromone, 9,10-phenanthrenequinone, 5,12-naphthacenequinone, benz[a]anthracene-7,12-dione, xanthone, 1,2-naphthoquinone, 1,4-naphthoquinone, perinaphthenone, pyrene-4,5-dione, aceanthrenequinone, benzo[a]fluorenone, 1,2-acenaphthenequinone, 2-ethyl-9,10-anthraquinone, cyclopenta[def]phenanthrenedione.

Deuterated surrogate recovery standards: 9,10-anthraquinone-D8 and 9-fluorenone-D8. The internal standard was 2-fluoro-fluorenone- ^{13}C .

Air concentration calculation.

Environmental vapor phase air concentrations were determined using an empirical uptake model with sampling rates derived by measuring PRCs loss as described in Huckins *et al.* 2006.³ PRCs allow for an accurate assessment of *in situ* uptake rates for a wide range of analytes under environmental conditions including variable wind speeds, temperatures and humidity levels.⁴⁻⁶ The uptake calculation makes no assumptions about the analyte being at equilibrium or in the linear uptake range, we used this model for air and water calculations for all compounds. PRCs all share similar physical chemical properties with the analytes of interest in this study and spanned a range of log K_{oa} values from 6.58 to 10.35.⁵ Maximum differences between PRC log k_{oa} and target PAH and OPAH log k_{oa} in air samples was 2.9 and 0.72 respectively. This extrapolation is quite modest and well supported by the PRC literature.³⁻⁴ Air concentrations of PAHs and oxygenated PAHs (OPAHs) were determined by:

$$C_a = \frac{N_{analyte}}{V_s K_{sa} (1 - \exp(-\frac{R_s t}{V_s K_{sa}}))} \quad \text{Eq. S1}$$

Where C_a is the air concentration, $N_{analyte}$ is the mass of the compound of interest present in the sampler, V_s is the sampler volume, K_{sa} is the sampler-air partition coefficient and is calculated for each target analyte and PRC using a regression based on individual octanol-air partition coefficients (K_{oa}), R_s is the compound specific sampling rate, and t is the duration of sampling. The sum of the vapor phase air concentrations of all 33 PAH analytes considered in this study are denoted as $\sum_{33\text{air}} \text{PAH}$. The sum of the vapor phase air concentrations and dissolved phase water concentrations of all 22 OPAH analytes considered in this study are denoted as $\sum_{22\text{air}} \text{OPAH}$ and $\sum_{22\text{water}} \text{OPAH}$. The sampling rates of the PRCs were determined by using equation S2.

$$R_s = - \frac{\ln(\frac{N}{N_0})}{t} K_{sa} V_s \quad \text{Eq. S2}$$

Where N_0 and N is the amount of PRC at the beginning and ending of sampling respectively. The sampling rate R_s for individual analytes were calculated based on the R_s of the PRC with the most similar K_{oa} . By employing eq 3 from Huckins et al. 2006, α values can compensate for compound-specific adjustments between the PRC and the target analyte.

$$R_{s,target\ analyte} = R_{s,PRC} * \frac{\alpha_{analyte}}{\alpha_{PRC}} \quad \text{Eq. S3}$$

In equation S3, α is a class of compounds specific modifier. Equation S4 was used to calculate α for both target analytes and PRCs:

$$\log \alpha = 0.0130(\log K_{oa})^3 - 0.3173(\log K_{oa})^2 + 2.244(\log K_{oa}) \quad \text{Eq. S4}$$

In Huckins et al., equation S4 uses K_{ow} .⁷ K_{oa} was used in this study to estimate air concentrations instead of water concentrations. A compound specific sampler-air partition coefficient (K_{sa}) at the reference temperature (298 K) was calculated for each PRC and target analyte (PAH and OPAH), using equation S5:

$$K_{sa(298)} = \frac{K_{sw} \times R \times 298}{K_{aw}} \quad \text{Eq. S5}$$

In equation S5, K_{sw} is the sampler-water partition coefficient, K_{aw} is the Henry's law constant in $\text{atm} \cdot \text{m}^3 \cdot \text{mol}^{-1}$, R is the ideal gas constant in $\text{m}^3 \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, and 298 K is the reference temperature used in this study. K_{sw} was calculated using equation S6, from Huckins et al.⁷:

$$\log K_{sw} = a_0 + 2.321(\log K_{ow}) - 0.1618(\log K_{ow})^2 \quad \text{Eq. S6}$$

In equation S6, $a_0 = -2.61$ for PAHs.⁷ Environmental temperature-specific K_{sa} values ($K_{sa(T)}$) were calculated using an approach described in Khairy et al.⁸ This approach uses a modified Van 't Hoff

equation to adjust each analytes K_{sa} for the temperature during the sampling period. Equation S7 is the modified Van 't Hoff equation used in this study:

$$K_{sa(T)} = K_{sa(298)} \times e^{\frac{\Delta H_{vap}}{R} \times (\frac{1}{T} - \frac{1}{298})} \quad \text{Eq. S7}$$

In equation S7, ΔH_{vap} is the enthalpy of vaporization, T is the average temperature during each deployment at each site in K, 298 is the reference temperature in K, and R is the ideal gas constant in $\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. ΔH_{vap} values for the target PAHs and OPAHs were calculated using Equation S8:

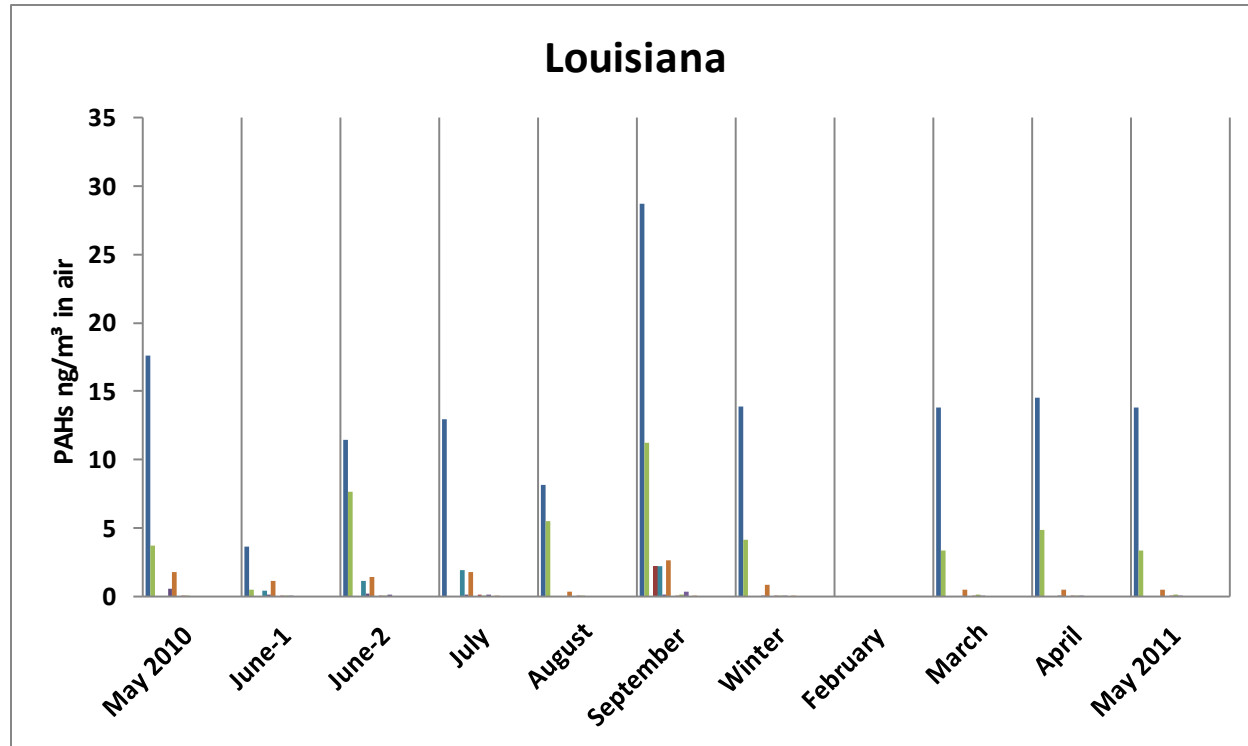
$$\Delta H_{vap} = 69.354 - 9.3891 \times \log P_L \quad \text{Eq. S8}$$

In equation S8 P_L is the subcooled liquid vapor pressure. This equation is a relationship between $\log P_L$ and ΔH_{vap} that was reported by Khairy et al.⁸ It uses empirically-derived ΔH_{vap} from Roux et al.,⁹ and $\log P_L$ that were estimated using Equation S9:

$$\log P_L = 8.52 - 0.054 \times MW \quad \text{Eq. S9}$$

In equation S9 MW is the molecular weight. This equation is a relationship between $\log P_L$ and MW that was empirically derived by Ma et al.¹⁰

Figure S1: Individual PAH concentrations



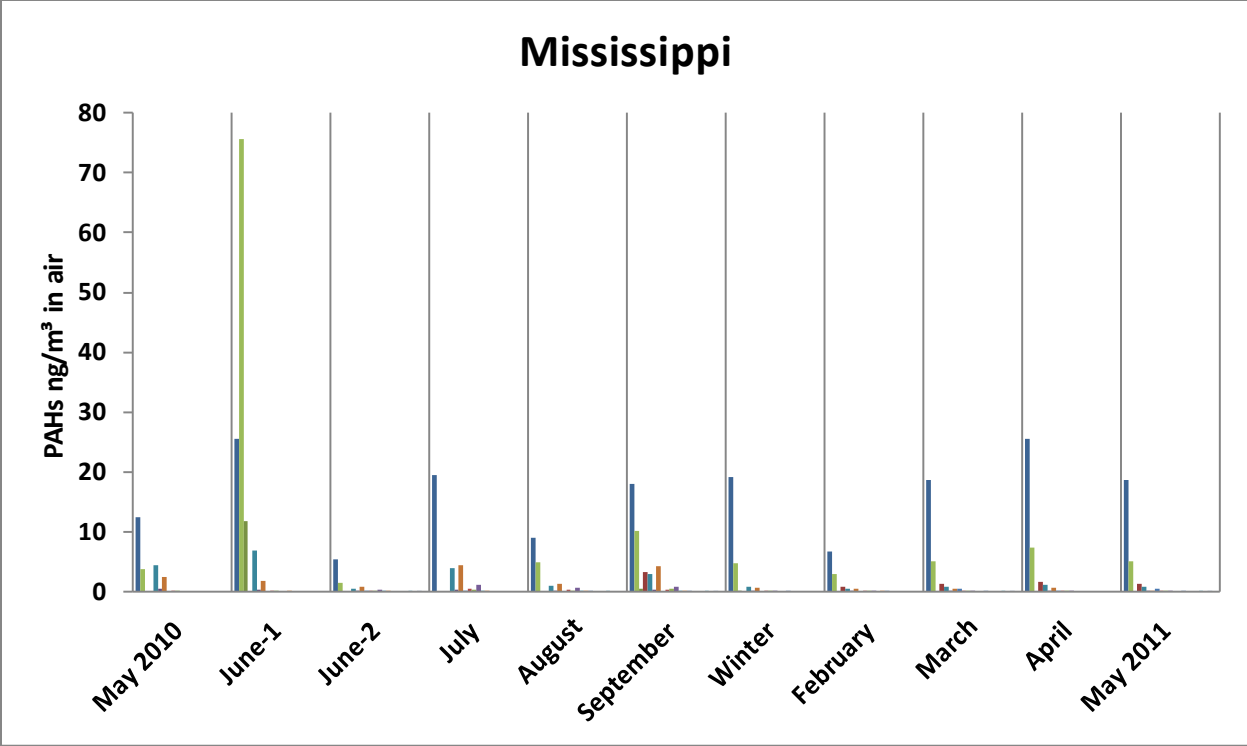
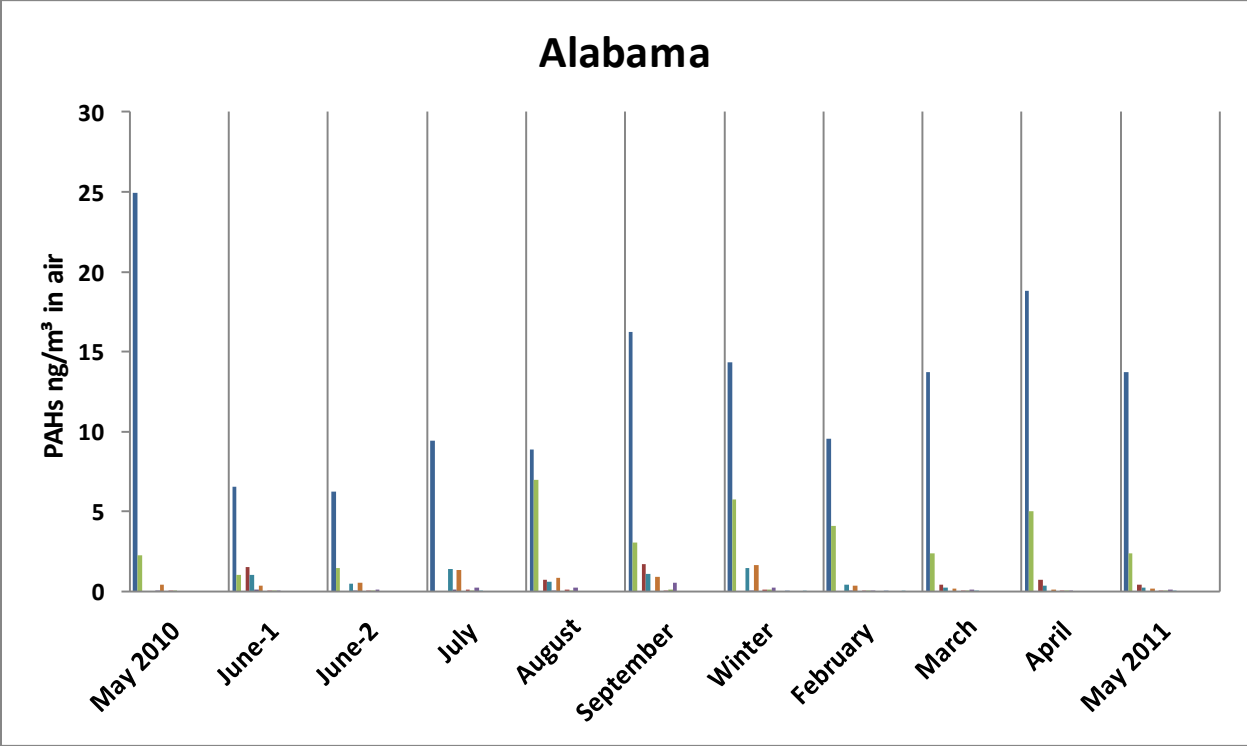


Figure S1 continued: Individual PAH concentrations



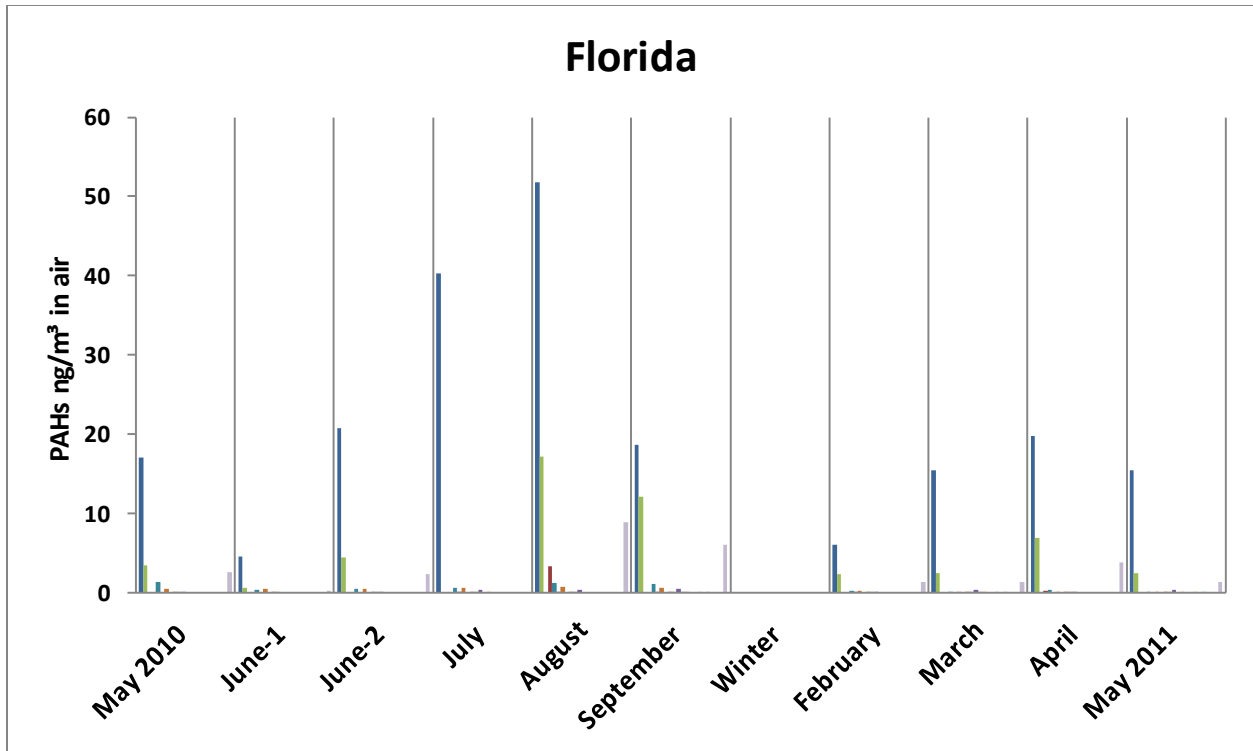


Figure S1 continued: Individual PAH concentrations



Figure S1: Individual parent PAH concentrations at four sampling sites across all time points in the Gulf of Mexico.

Figure S2: Selected PAH alkylation profiles

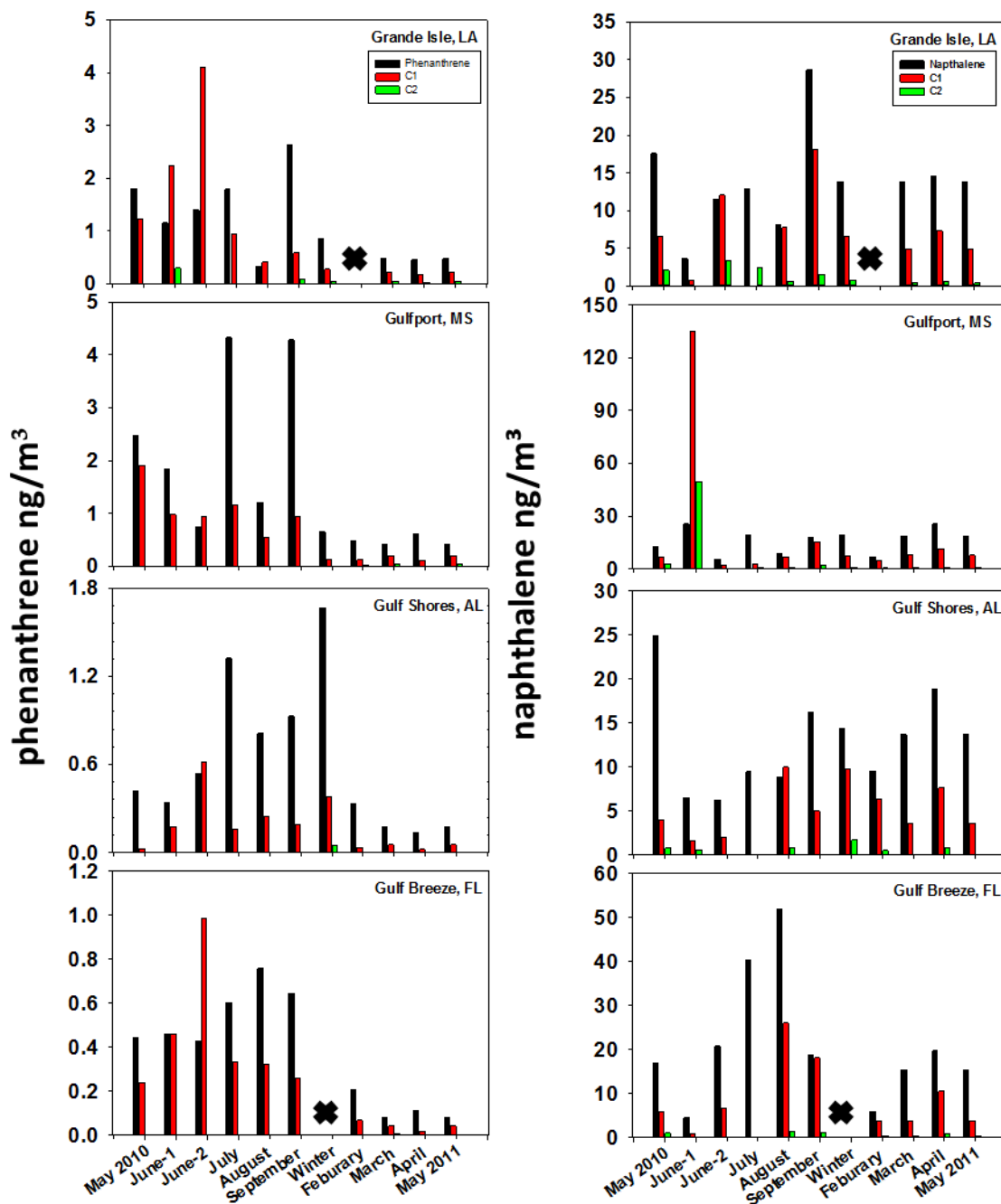


Figure S2. Alkylation profiles of phenanthrene and naphthalene. Profiles are predominantly mixed. Evidence of petrogenic signature of phenanthrene in Grand Isle, LA during June-1 sampling.

Figure S3: Individual OPAH concentrations

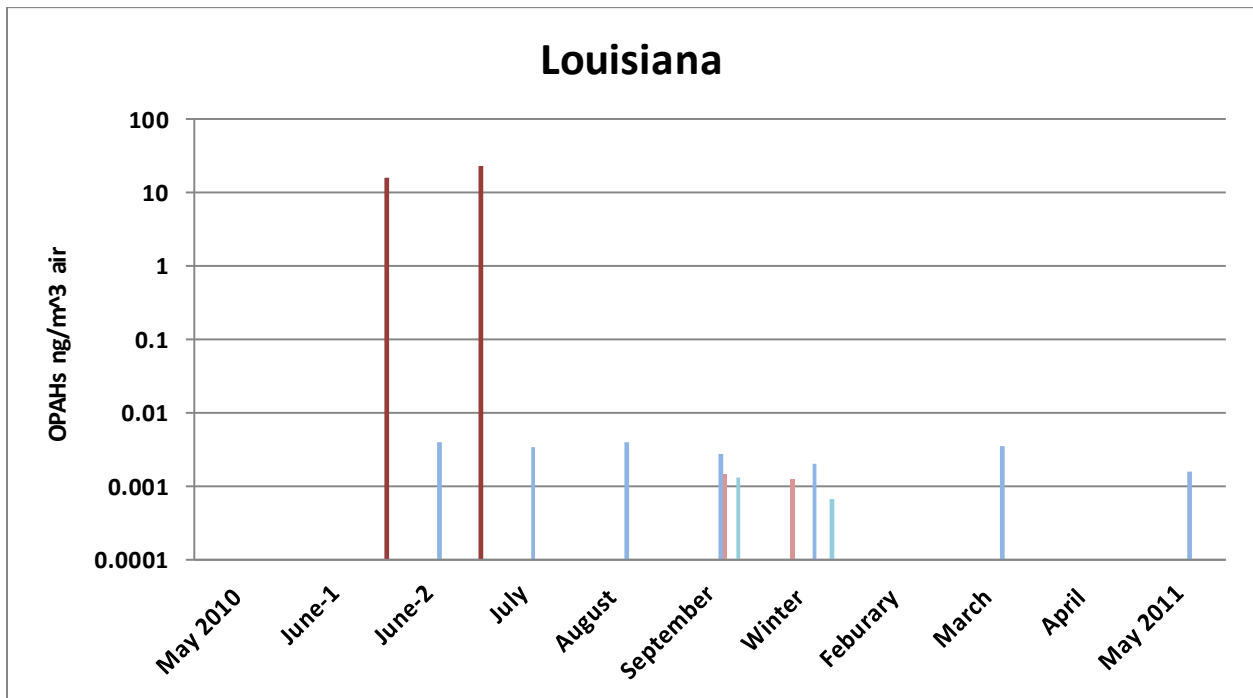
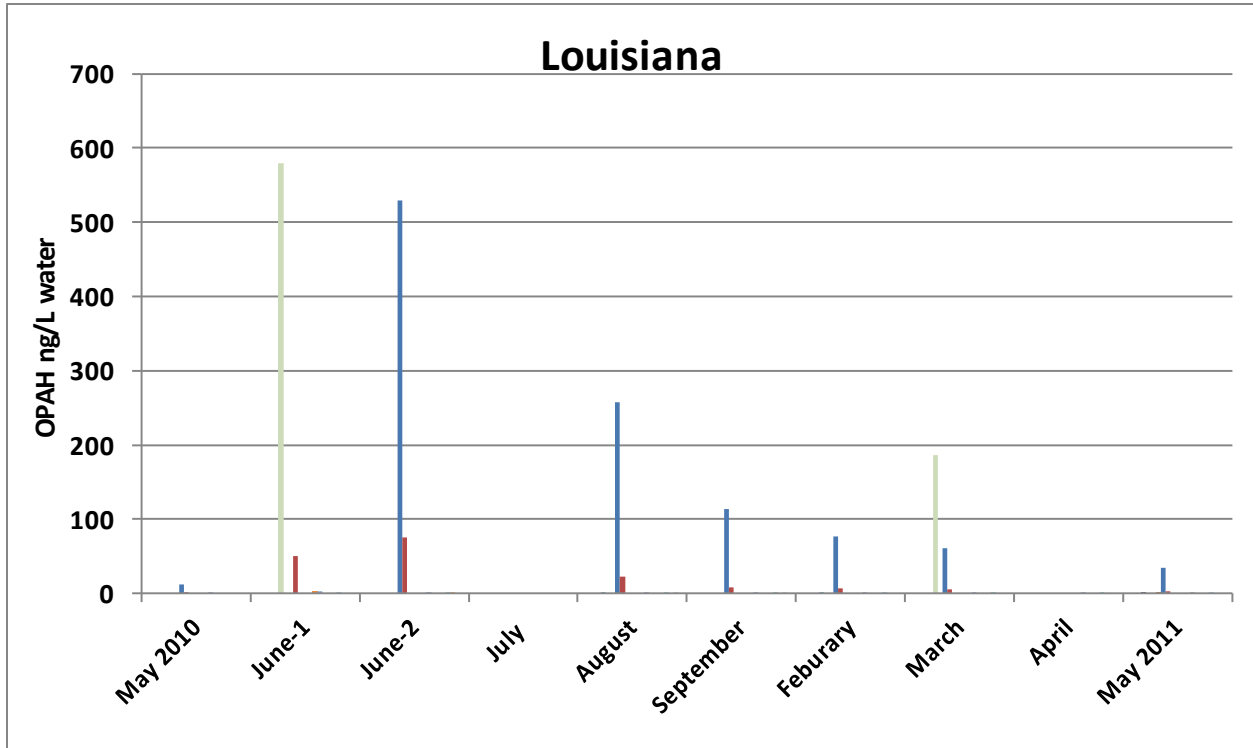


Figure S3: Individual OPAH concentrations

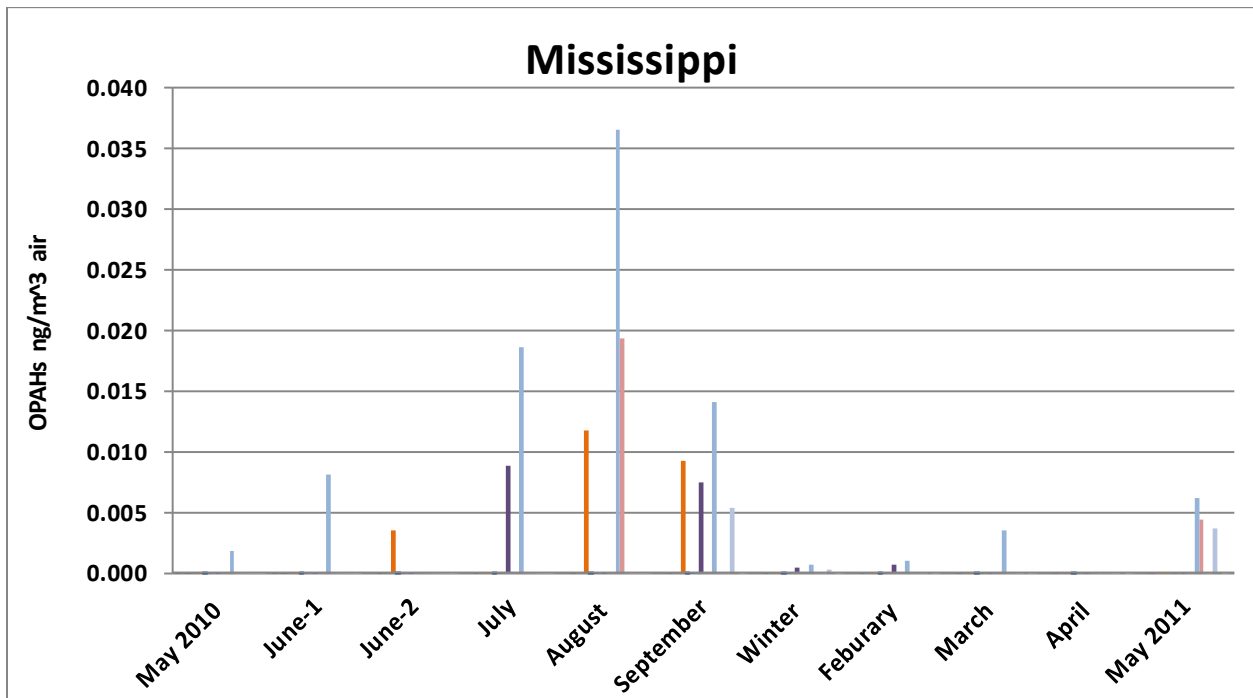
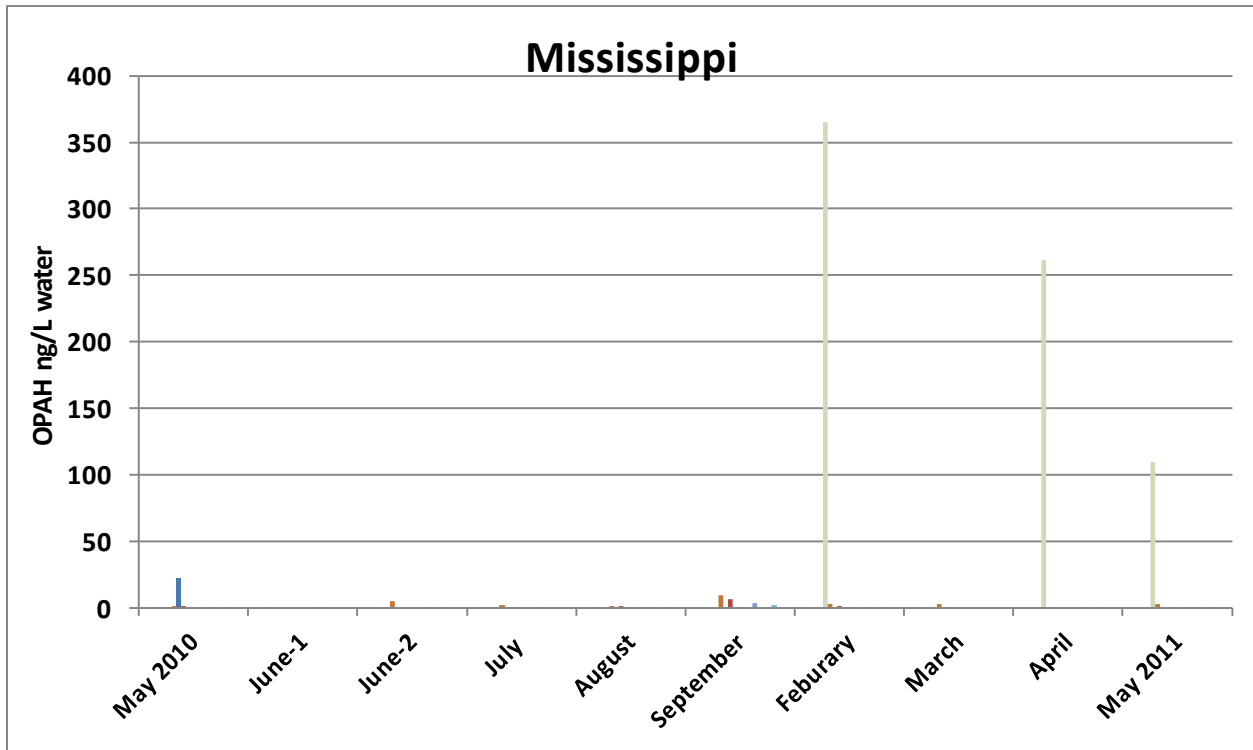


Figure S3 continued: Individual OPAH concentrations

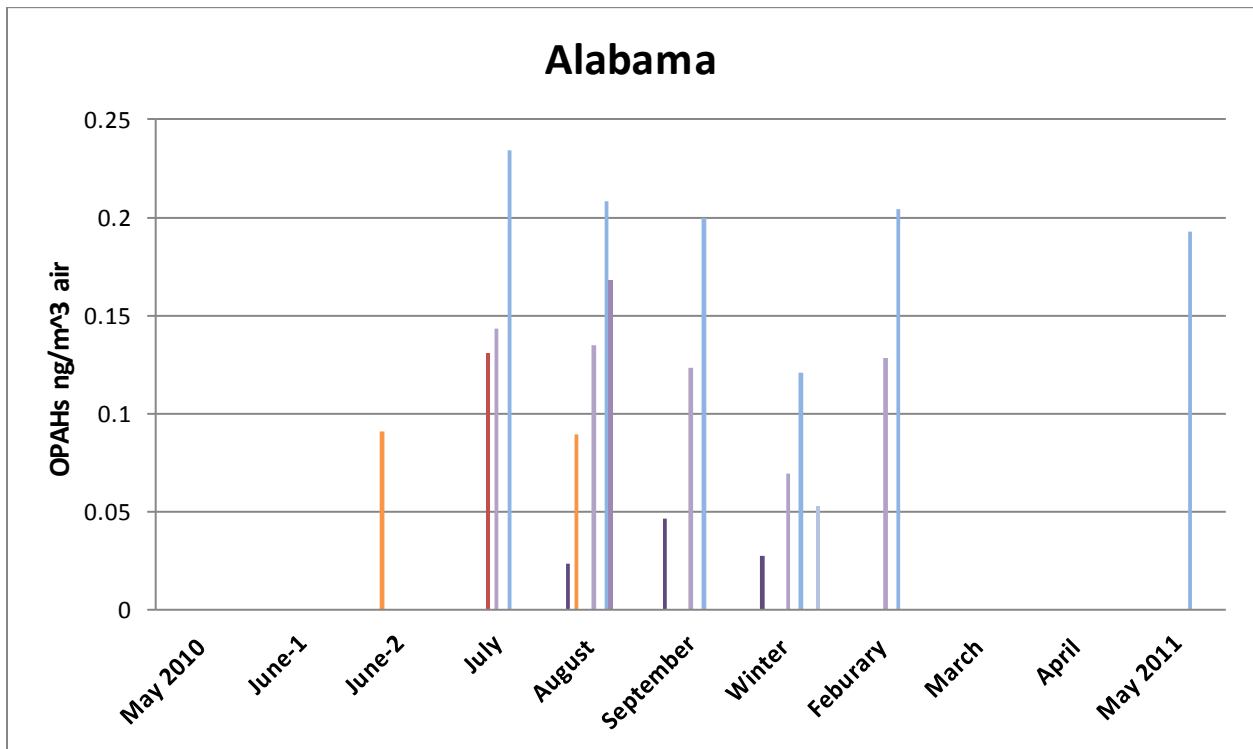
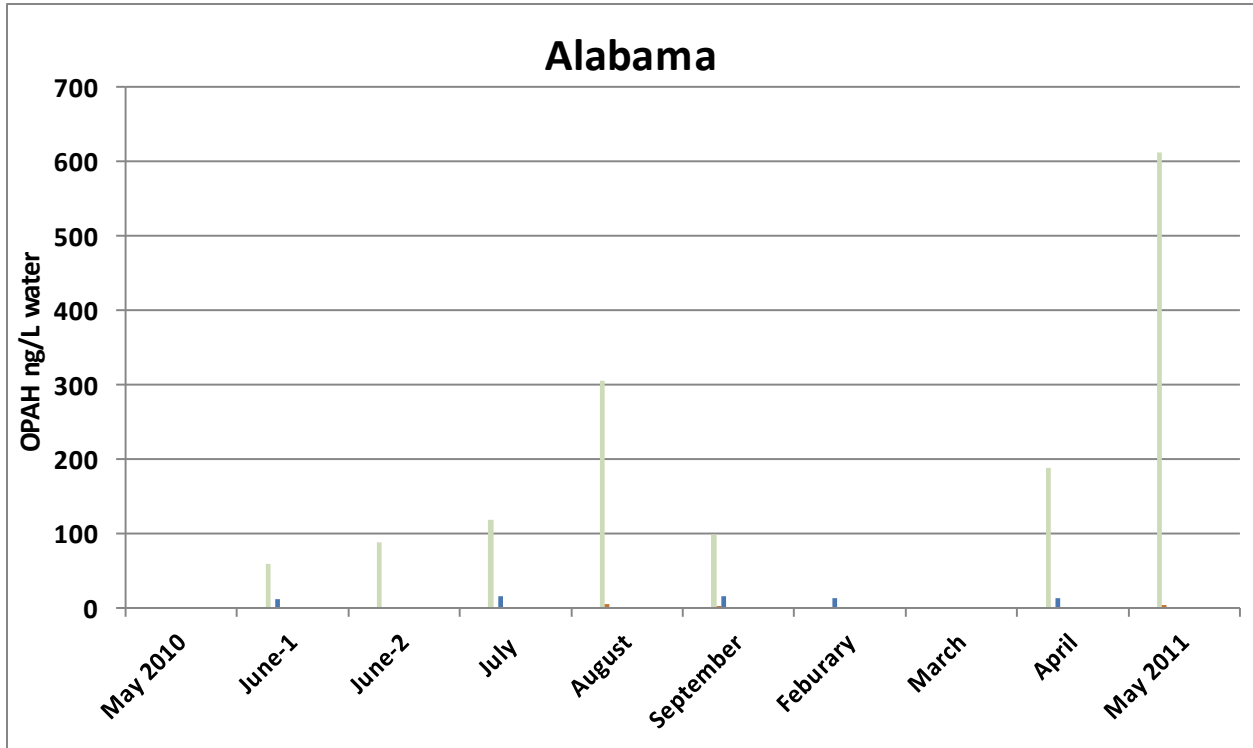


Figure S3 continued: Individual OPAH concentrations

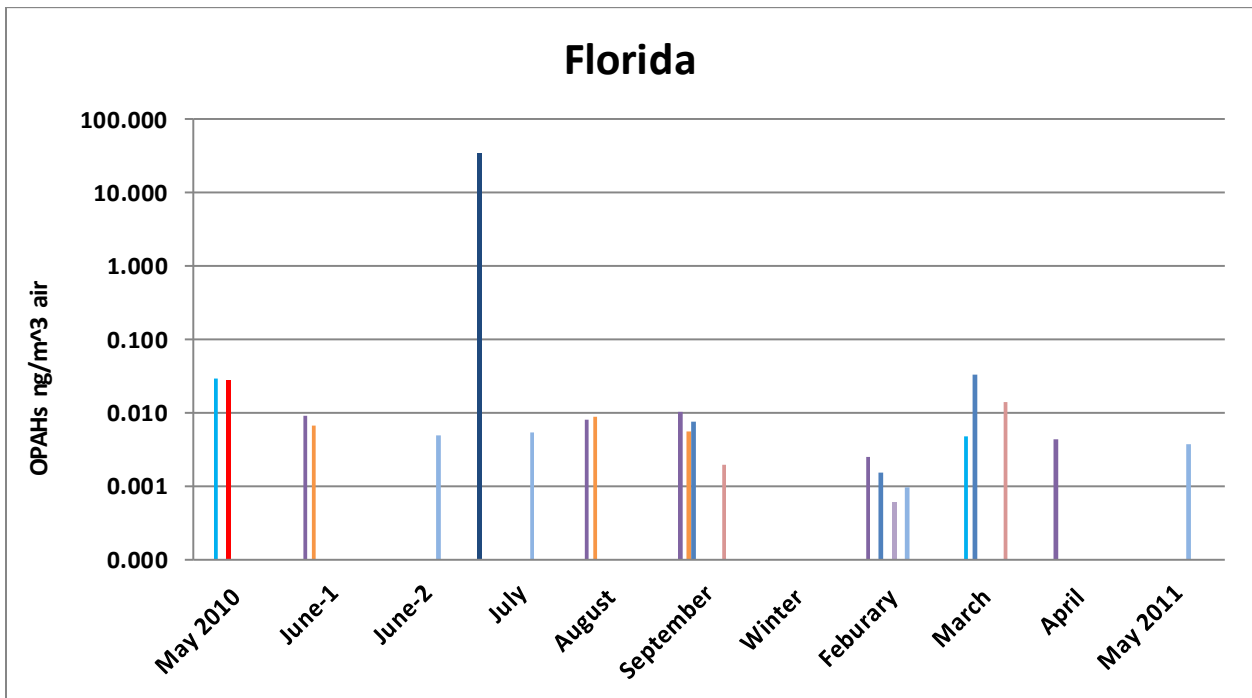
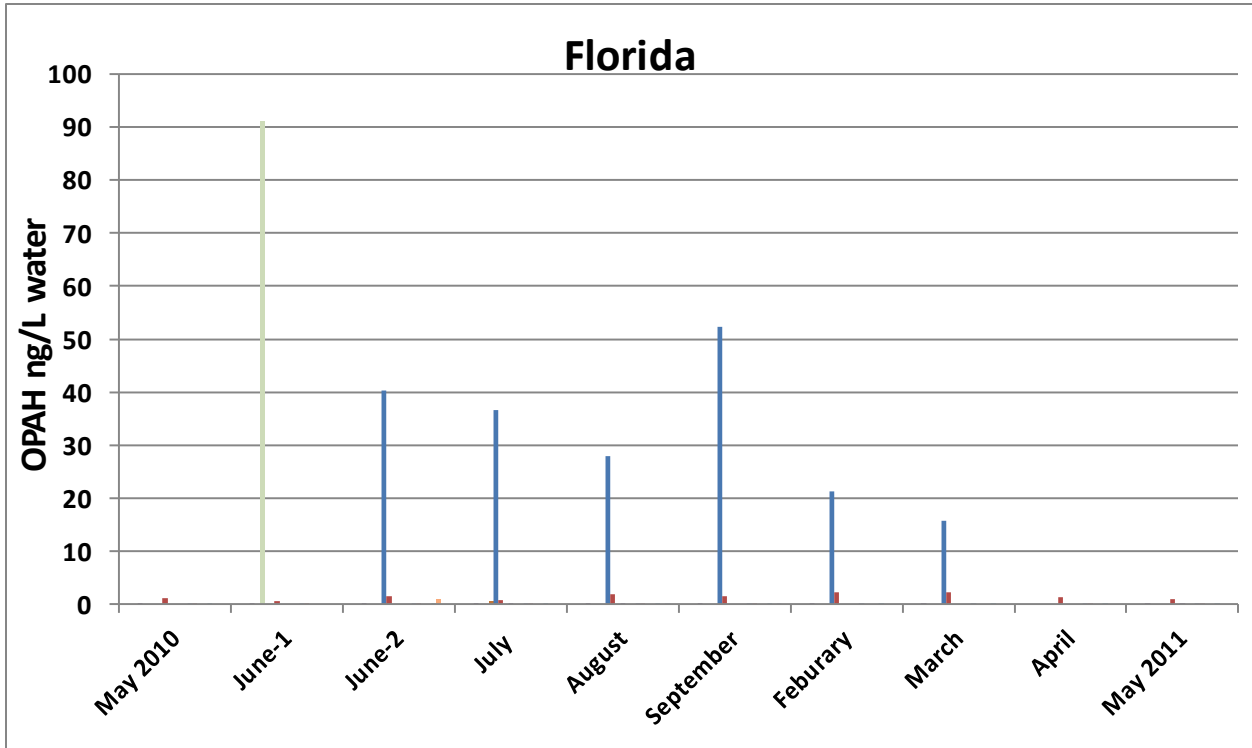


Figure S3 continued: Individual OPAH concentrations



Figure S3: Individual OPAH in air and water concentrations for four sampling sites across the Gulf of Mexico.

PCA explanation

PCA using profile data was performed using PRIMER-E version 6.1.13. Profile analyte data express the percent contribution of each analyte to the total for each sample. PCA is a multi-variant variable reduction technique where principal components (PCs) are calculated as combinations of the original variables to express the maximum total variation with a few uncorrelated PCs. This modeling approach has been applied to many PAH fingerprinting and allocation studies.^{11, 12} Assessment of samples using this approach allowed for recognition of spatial and temporal trends in the chemical profile of Gulf of Mexico air that were not elucidated by other data analysis tools. PCA loading vector plots show the direction of increase of the individual analytes, as percentages, in terms of the first two principle components.

Table 2: Sampling date, sampling location, air ng/m³, water ng/L, temperature Kelvin average(min,max), wind speed meters/second average(min,max) water side mass transfer coefficient, air side mass transfer coefficient, total mass transfer coefficient, flux, flux variance.

Table 3: Instrumental detection limits

Compound Name	LOD	LOQ
Naphthalene	0.066	0.328
2-Methylnaphthalene	0.078	0.391
1-Methylnaphthalene	0.093	0.465
1,6-Dimethylnaphthalene	0.177	0.883
Acenaphthylene	0.260	1.302
Acenaphthene	0.104	0.519
Fluorene	0.160	0.799
Dibenzothiophene	0.064	0.322
Phenanthrene	0.126	0.632
Anthracene	0.137	0.685
2-Methylphenanthrene	0.188	0.942
2-Methylanthracene	0.226	1.131
1-Methylphenanthrene	0.153	0.765
9-Methylanthracene	0.126	0.628
3,6-Dimethylphenanthrene	0.071	0.355
2,3-Dimethylanthracene	0.200	0.998
Fluoranthene	0.159	0.795
9,10-Dimethylanthracene	0.135	0.674
Pyrene	0.112	0.562
Retene	0.639	3.195
1-Methylpyrene	0.100	0.502
Benz(a)anthracene	0.275	1.377
Chrysene	0.281	1.407
6-Methylchrysene	0.334	1.669
Benzo(b)fluoranthene	0.136	0.678
Benzo(k)fluoranthene	0.284	1.419
Benzo(e)pyrene	0.130	0.649
Benzo(a)pyrene	0.299	1.496
Indeno(1,2,3-c,d)pyrene	0.339	1.697
Dibenz(a,h)anthracene	0.332	1.658
Benzo(ghi)perylene	0.211	1.056
Dibenzo(a,l)pyrene	0.632	3.162
1,4 Naphthoquinone-D6	0.32	1.6
2-Methyl-1,4-naphthoquinone-d8	0.42	2.1
9-Fluorenone-D8	0.18	0.91
9,10-Anthraquinone-d8	0.65	3.2
1,4 Benzoquinone	0.49	2.4
Chromone	0.89	4.4
1,4 Naphthoquinone	0.45	2.3
1,2-Naphthoquinone	36	179
9-Fluorenone	0.20	1.0
Xanthone	0.38	1.9
Acenaphthenequinone	11	57
Perinaphthenone	0.89	4.4
Phenanthrene-1,4-dione	0.86	4.3
9,10-Anthraquinone	1.5	7.7
1,4-Anthraquinone	5.6	28
4H-cyclopenta[def]phenanthren-4	0.21	1.0
9,10-phenthrenequinone	6.90	34.5
2-Ethylanthraquinone	0.35	1.8
Benzofluorenone	0.45	2.3
Benzanthrone	0.78	3.9
Aceanthracenequinone	27	133
Pyrene 4,5 dione	11	57
7,12-benz[a]anthracenquinone	0.85	4.2
Benzo[c]phenanthrene-[1,4]quinone	1.7	8.5
5,12-Naphthacenequinone	1.3	6.3
Benzo(cd)pyrenone	1.1	5.7

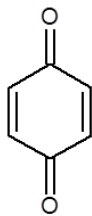
Table 3: Instrumental limits of detection and quantitation for PAH and OPAH using GC/MS

Table 4: Concentrations of OPAH in crude oil

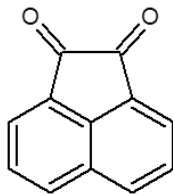
Deep Water Horizon GoM Oil OPAHs								
Sampling site	OPAH	concentration in crude oil ng/mL	Concentration in water ng/L May 2010	Concentration in air ng/m ³ May 2010	Concentration in water ng/L June-1	Concentration in air ng/m ³ June-1	Concentration in water ng/L June-2	Concentration in air ng/m ³ June-2
MC252	Phenanthrene-1,4-dione	138.1	X	X	X	X	X	X
	9,10-Anthraquinone	155.3	X	X	X	X	X	X
	Benzofluorenone	67.9	X	X	X	X	X	X
LA	Phenanthrene-1,4-dione	X	12.2	BDL	BDL	BDL	529.9	BDL
	9,10-Anthraquinone	X	0.8	BDL	49.7	BDL	75.1	BDL
	Benzofluorenone	X	BDL	BDL	3.2	BDL	2.0	0.007
MS	Phenanthrene-1,4-dione	X	22.2	BDL	BDL	BDL	BDL	BDL
	9,10-Anthraquinone	X	1.3	BDL	BDL	BDL	BDL	BDL
	Benzofluorenone	X	BDL	0.002	0.1	0.008	0.2	0.004
AL	Phenanthrene-1,4-dione	X	BDL	BDL	11.7	BDL	BDL	BDL
	9,10-Anthraquinone	X	1.1	BDL	0.8	BDL	1.1	BDL
	Benzofluorenone	X	BDL	BDL	0.1	BDL	0.1	BDL
FL	Phenanthrene-1,4-dione	X	BDL	BDL	BDL	BDL	40.4	BDL
	9,10-Anthraquinone	X	0.98	BDL	1.4	BDL	2.4	BDL
	Benzofluorenone	X	0.02	BDL	0.1	BDL	0.1	0.004

Table 4: OPAH concentrations in crude oil sample MC252 (NIST SRM 2779) collected May 21, 2010 at the site of the Deepwater Horizon (DWH) oil rig.¹³ Dissolved OPAH concentrations in water, OPAH vapor phase concentrations in air. Sample analyzed by methods defined in O’Connell et al 2013.¹⁴

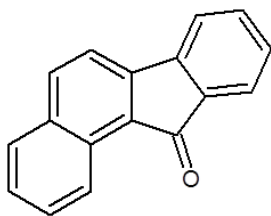
Figure S4: OPAH structures



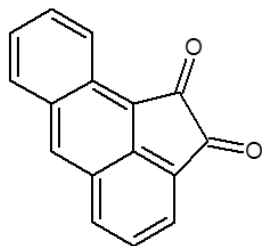
1,4-Benzoquinone



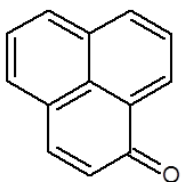
Acenaphthenequinone



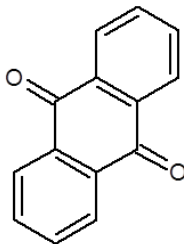
Benzofluorenone



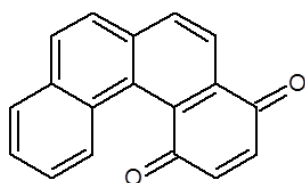
Aceanthracenequinone



Perinaphthenone



Anthraquinone



Benzo(c)phenanthrene(1,4)quinone

Figure S4. OPAHs that were assessed for air water exchange.

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