Assessment and source-modeling of bioavailable polycyclic aromatic hydrocarbons in Gulf of Mexico coastal waters before, during and after the Deepwater Horizon oil spill

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BACKGROUND

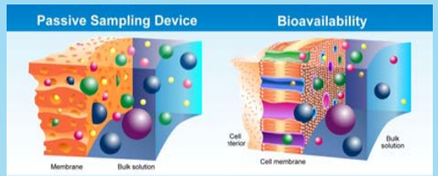
Following the fatal explosion of the Deepwater Horizon oil rig on April 20th, 2010 an estimated 4.4 million barrels of oil spilled into the Gulf of Mexico until the well was finally capped on July 15th(1). Additionally, an estimated 2.1 million gallons of dispersant were applied at the ocean surface and wellhead between May 15th and July 12th(2).

Crude oil contains polycyclic aromatic hydrocarbons (PAHs), a group of compounds which can be toxic and carcinogenic to humans and wildlife. PAHs can persist in the environment even after visible oil has been removed and the application of dispersants to oil has been shown to make PAHs more bioavailable (3, 4).

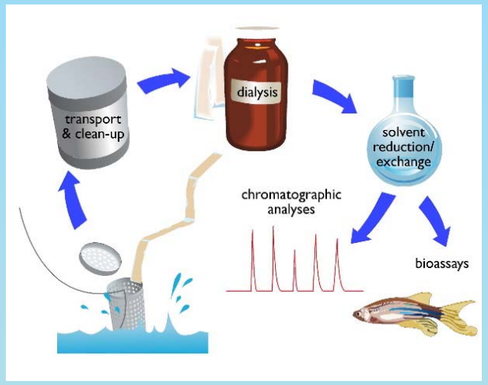
Passive sampling devices (PSDs) mimic chemical uptake by biomembranes by sequestering the freely dissolved fraction of lipophilic contaminants during an environmental exposure. PSDs can provide a time weighted average of the concentration of bioavailable chemicals. Chemical data from PSDs can be used to assess potential exposure, as well as to model chemical sourcing, transport and fate (5).

Objectives: 1) Assess the impact of the Deepwater Horizon oil spill on bioavailable PAHs at coastal sites in the Gulf of Mexico. 2) Apply forensic chemistry source modeling techniques to elucidate sources of bioavailable chemicals of concern that were observed before, during and after the oil spill.

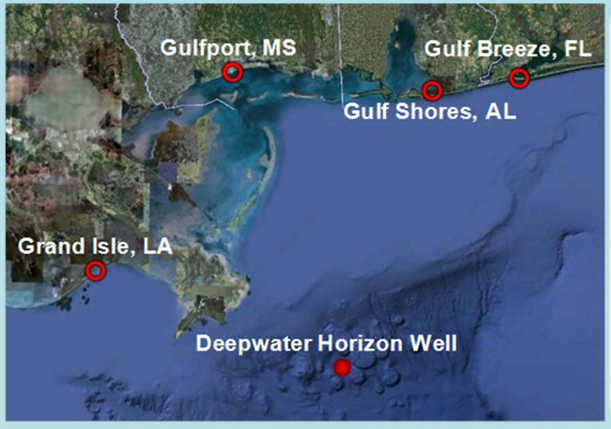
METHODS



Passive Sampling Devices (PSDs) sequester and concentrate the bioavailable fraction of chemicals.



Sampling and Chemical Analysis: Low-density polyethylene tubing PSDs, were spiked with performance reference compounds (PRCs) and deployed in the water column. PSDs were extracted and analyzed by GC-MS for 33 PAH compounds. Water concentrations were calculated based on PRC diffusion rates(5).

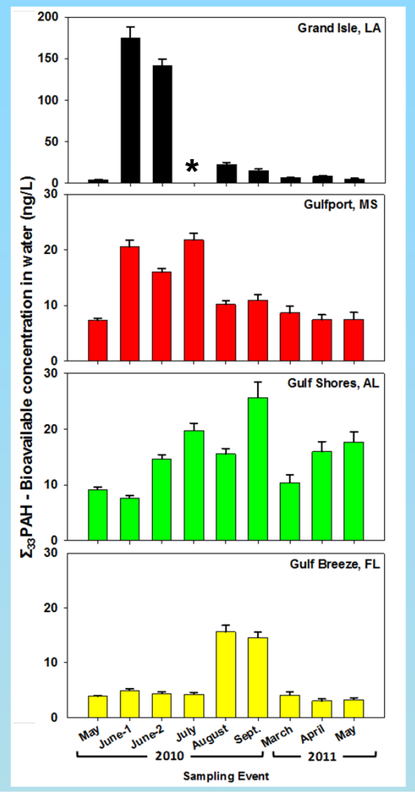


Sampling Design:

- PSDs were deployed from piers in shallow coastal waters
- The first sampling event, in May, 2010, was completed prior to shoreline oiling at any of the sites
- Nine sampling events were carried out between May, 2010 and May, 2011
- The site at Grand Isle, LA was heavily oiled in June and July, 2010
- The site at Gulfport, MS was visibly oiled in June and July, 2010
- The sites in Gulf Shores, AL and Gulf Breeze, FL are located at the mouths of Mobile Bay and Pensacola Bay respectively

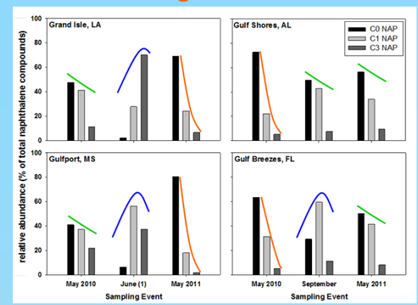
RESULTS

Bioavailable PAHs in water



Spatial and temporal variations in Bioavailable PAHs: Bars represent PSD measured bioavailable concentrations of sum 33 PAHs (Σ_{33} PAH) in water. Error bars are 95% confidence interval. Note Y axis scale change on LA graph. Asterisk indicates no data.

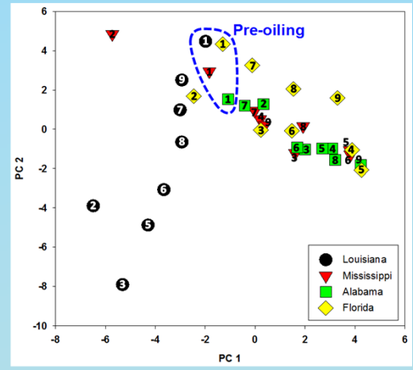
Source-modeling



Relative abundance of unsubstituted and alkyl- PAHs: Naphthalene profiles from samples obtained pre-oiling, during maximum observed Σ_{33}PAH and a year after the oil spill. A high relative abundance of unsubstituted PAH, compared with the alkyl-PAH (C1 and C2) indicates a primarily pyrogenic source (orange line). A high relative abundance of the alkylated PAHs indicates a primarily petrogenic source (blue line). Samples with approximately equal relative abundances are a mix of petrogrenic and pyrogenic sources (green line).

Temporal changes in PAH assemblage types:

- LA and MS: mixed pyro/petrogenic in May, 2010, petrogenic signatures in June, 2010 and pyrogenic in May, 2011
- AL: pre-oiling pyrogenic profile replaced by a mixed source signature in September, 2010, continued mixed pyro/petrogenic signature in May, 2011
- FL: pyrpgenic in May, 2010, petrogenic in September, 2010, mixed pyro/petrogenic signature in May, 2011



Principal component analysis (PCA) of PAH chemical profiles: Principle component 1 and 2, represent 49% of the variability in the data set. Data were normalized to avoid a magnitude bias. States are differentiated by symbols and the numbers indicate the sampling events in chronological order. There is no month 4 sample for Louisiana. Data from samples taken prior to shoreline oiling, are enclosed by a dotted line labeled 'Pre-oiling'.

Temporal changes in PAH chemical profiles:

- All sites had similar chemical profiles prior to oiling
- PAH chemical profiles at LA changed during oiling (months 2 and 3) and showed a progressive return to the pre-oiling profile after the spill (months 5-9)
- Samples from MS and FL showed temporal changes in chemical profile that were not clearly associated with oiling events
- Samples from AL showed similar chemical profiles in months 1, 2 and 7, which coincided with lower Σ_{33}PAH concentrations. Samples from months 3, 4, 5 and 6, as well as 8 and 9 grouped closely, separated from the pre-oiling profile, and coincided with elevated Σ_{33}PAH concentrations.

Conclusions

- The concentration of bioavailable PAHs increased over 40 fold above pre-oiling levels during June in LA. Other sites showed 3-5 fold increases at one or more time points.
  - Maximum concentrations were observed at different times at the four sites and showed a west-to-east temporal trend.
  - The concentration of bioavailable PAHs measured in March, 2011 was not significantly different than pre-oiling levels at any of the sites.
  - A return to elevated concentrations of PAHs was observed at the site in AL in April and May, 2011.
- Changes in PAH assemblage types and chemical profiles coincide with observed increases in bioavailable PAH concentrations, indicating a significant input from a unique petrogenic source, which is consistent with knowledge of the impacts of the Deepwater Horizon oil spill.

ACKNOWLEDGEMENTS AND REFERENCES

This project was supported in part by award numbers P42 ES016465 and the associated Analytical Chemistry Facility Core, P30 ES000210 and R21 ES020120 from the National Institute of Environmental Health Sciences. Steven O'Connell was supported in part by NIEHS Training Grant Fellowship T32 ES007060 from the National Institutes of Health. The content is solely the responsibility of the authors and does not necessarily represent the official views of the NIHS or the National Institutes of Health. We would like to thank Grand Isle State Park, Bon Secour National Wildlife Refuge and Gulf Shores National Seashore.

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