Significant Spatial Variability of Bioavailable PAHs in the Water Column and Sediment Porewater in the Gulf of Mexico One Year After the Deepwater Horizon Oil Spill

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INTRODUCTION

After the Deepwater Horizon oil spill in 2010, one of the major responses of federal and regulatory agencies tasked with assessing natural resource damages has been the collection of water and sediment grab samples and their analysis for PAH concentrations. The water PAH levels are then directly compared to benchmark values, such as the final chronic value (FCV) derived from the National Water Quality Criteria (WQC) guidelines. The PAH levels in sediment porewater were estimated from the sediment PAH concentrations using equilibrium partitioning theory (USEPA, 2003), then compared to the benchmarks assuming porewater PAH concentrations best estimate toxicity and bioavailability. Most of the grab samples revealed concentrations below the analytical detection limits, so the assumption was made that there are insignificant damages to the natural resources from the released PAHs (http://www.epa.gov/BPSpill).

However, conventional grab sampling techniques have several limitations in detecting part-per trillion (ng/L) concentrations of PAHs. In addition, PAH values below non-detect and predetermined benchmark values doesn't mean that PAHs are absent or present at levels which are not harmful. The benchmarks are meant to be used for screening purposes only. They are not regulatory standards, site-specific cleanup levels, or remediation goals, and only help the public understand the condition of the environment as it relates to the oil spill. Although various microorganisms can degrade oils (Atlas and Hazen, 2011), we have observed long-term effects of oil spill on our environments (Reddy et al., 2002) and aquatic organisms (Peterson et al., 2003). Low chemical concentrations of oil in the water column can show sublethal toxicities, such as alterations in genome expression and tissue morphology (Whitehead et al., 2011). Persistent effects of toxicant exposures were evident in certain species of fish and sea birds and in sea otters, with a notable and persistent decline in some species over the years due to increased mortality, lower growth rates, decreased reproduction and compromised immune function.

For better quantification of the chronic damages to the natural resources in the Gulf of Mexico (GOM) in-situ passive samplers were deployed and analyzed in the BP oil spill impacted area through a collaborative effort between Johns Hopkins University, National Aquarium Conservation Center, Mote Marine Laboratory, University of Texas at Austin, and Texas Southern University. In-situ passive samplers are effective in measuring time-integrated sub ng/L levels of PAHs in water (Lohmann and Muir, 2010; Allan and Harman, 2011). In addition, the samplers can effectively characterize the risks of the released PAHs during an oil spill (Reible, 2010) by measuring freely dissolved form which are considered to be more bioavailable. Hence, in the present study, the passive sampler data were used to monitor the risk associated with PAHs potentially released from the BP oil spill accident.

STUDY AREA AND SAMPLING ACTIVITIES

- 1st sampling activity: 25 locations in Barataria Bay, LA from May to June, 2011
- 2nd sampling activity: 40 locations in Chandelier Island, LA; Cat Island, Ship Island, Horn Island, Petit Bois Island, MS; Dauphin Island, Mobile Bay; AL, Pensacola Bay, Perdido Bay; FL.

MATERIALS AND METHODS

SPMDs (Semipermeable membrane devices), PDMS (Polydimethylsiloxane), PE (Polyethylene)

- 1st sampling activity (Barataria Bay,): SPMDs in overlying water and sediment
- 2nd sampling activity (coastal areas in LA, MS, AL, FL): SPMDs in overlying water, PDMS in sediment, PE samplers in both overlying water and sediment

Deployment Procedure

Laboratory fabrication → Transportation to sites → Deployment/ Retrieval → Back to lab and sampler process → Analyses

GC-MS analysis for PAHs in PE and SPMDs

- PAHs were extracted in hexane and analyzed using GC (Agilent, 6890) equipped with a capillary column (Agilent, DB-5MS; 25 m ×, 0.25 mm ID, 0.25 μm film thickness) and a mass selective detector (Agilent, 5973).

HPLC analysis for PAHs in PDMS fiber (vertical profilers)

- All fibers were removed from the sampling devices and cut to 2 cm segments
- PAHs were extracted in acetonitrile and analyzed using High Performance Liquid Chromatography (HPLC) and fluorescence detector according to via SW-846 Method 8310

CONVERTING PASSIVE SAMPLER DATA TO DISSOLVED CONCENTRATIONS

PE and SPMDs (kinetic approach using performance reference compounds) (Anderson et al., 2008)

- $k_{e,PRC} = -\frac{\ln(N_{PRC}/N_{0,PRC})}{t}$
- $R_{s,PRC} = V_s K_{sw} k_{e,PRC}$
- $R_{s,target} = \alpha_{target} \times avg\left(\frac{R_{s,PRC}}{\alpha_{PRC}}\right)$
- $\log K_{sw\ PRC\ SPMD} = -2.61 + 2.321\left(\log K_{ow}\right) - 0.1618\left(\log K_{ow}\right)^2$
- $\log K_{sw\ PRC\ LDPE} = 0.972 \times \left(\log K_{ow}\right) - 0.13$
- $\log\alpha = 0.013\left(\log K_{ow}\right)^3 - 0.3173\left(\log K_{ow}\right)^2 + 2.244\ \log K_{ow}$

$k_{e,PRC}$ = the PRC's release rate constant (day[-1]), N_{PRC} = the measured amount of the PRC after the exposure period (ng samplers[-1]), $N_{0,PRC}$ = the measured amount of the PRC at the beginning of the exposure period (ng samplers[-1]), t = the exposure period, $R_{s,PRC}$ = the PRC sampling rate (L day^{-1}), V_s = the PE/SPMD volume (L[3]), $K_{sw,PRC}$ = the PRC's LDPE or SPMD-water partitioning coefficient (L L^{-1}), $k_{e,PRC}$ = the PRC's release rate constant (day[-1]), $R_{s,target}$ = the sampling rate of the target analyte (L day^{-1}), $R_{s,PRC}$ = the PRC sampling rate (L day^{-1}), α_{target} = the target analyte compound-specific effect α_{PRC} = the PRC compound specific effect, K_{ow} = octanol-water partition coefficient (Huckins et al., 2006).

PDMS fiber (equilibrium approach) (Reible, 2010)

- $C_{ff} = \frac{A \times RSF_{PAH} \times V_{solvent}}{L_{fiber} \times V_{ffiber} \times K_{PDMS-W}}$

A=HPLC response integration area, RSF_{PAH} = response factor from standard curve unique to each PAH, $V_{solvent}$ = volume of solvent used to extract fiber (mL), L_{fiber} = the length of fiber sample (cm), V_{fiber} = specific volume of fiber (cm[3]), K_{PDMS-W} = fiber-water partition coefficient unique to each PAH (Reible, 2010)

RESULTS

Result 1

1. Water quality parameters suggested that the waters in Barataria Bay and in coastal areas were brackish water (salinity=8.4±2.4) and salt waters (salinity=25 ppt), respectively.
2. The waters were well oxygenated.

		Temp (°C)	pH	Salinity (ppt)	DO [a] (mg/L)
Barataria Bay May 14-15, 2011	AVG (SD) [a]	26.3 (1.3)	8.4 (0.4)	8.4 (2.4)	7.0 (0.9)
	Range	24.0-28.9	7.6-9.2	3.2-11.5	5.7-9.3
Coastal Areas and Barrier Islands, Sep 26-27, 2011	AVG (SD)	28.3 (0.8)	8.4 (0.2)	24.8 (2.5)	7.7 (1.2)
	Range	26.1-29.7	8.2-9.1	18.6-28.9	5.6-10.3
Coastal Areas and Barrier Islands, Oct 23-24, 2011	AVG (SD)	20.5 (0.7)	8.4 (0.2)	26.7 (2.3)	8.4 (1.0)
	Range	19.3-22.5	8.2-8.8	22.4-30.2	7.1-10.4

AVG: average, SD: standard deviation, DO: dissolved oxygen

Result 2

1. Sampling rates at log Kow=5 (representative Kow of PAHs)
2. Sampling rates determined in Barataria Bay showed wider ranges (more variability) compared to those determined in other coastal areas suggesting that Barataria Bay has more complex environmental settings.
3. The complex shorelines of Barataria Bay are considered to lead more variability of water mixing in Barataria Bay and the observe sampling results further confirmed the empirical expectation.
4. The sampling rates of overlying water were 2-4 larger than those of sediment porewater and this was due to mass transfer resistance in sediments.

Result 3

1. The average (range) total PAH concentrations in the overlying water and sediment porewater of the coastal areas were 0.36 (0.05-1.11) ng/L and 1.03 (0.03-5.58) ng/L, respectively.
2. The average (range) total PAH concentrations in the overlying water and sediment porewater of the wetland areas were 14.1 (1.4-72.9) ng/L and 19.7 (3.3-107.4) ng/L.
3. The PDMS profilers deployed in the coastal areas didn't show any vertical profiles of PAH levels in the sediment porewaters from surface to 60 cm below.
4. Generally, PAH concentrations in Barataria Bay were one or two orders of magnitude higher than those in coastal areas.
5. PAH concentrations in sediment porewater were generally higher than those in overlying water.

Result 4

1. Example of PAH distribution pattern in sediment porewater of Barataria Bay.

In some locations, alkylated PAHs concentrations were higher than those of non-alkylated suggesting potential higher toxicity.

Result 5

1. To consider the differences of individual PAH toxicity (high molecular weight PAHs tend to be more toxic than low molecular weight PAHs), the toxic unit (TU) is calculated as follows assuming the PAH toxicities are additive (USEPA, 2003).

- $TU = \sum \frac{C_{PAH}}{FCV_{PAH}}$
- $\log_{10} FCV = -0.945 \times \log_{10} K_{ow} + \log_{10} 2.24$

C_{PAH} = the dissolved concentrations of individual PAH (μmol/L); FCV = the final chronic value (FCV) (μmol/L).

2. The highest TU was 0.088 in a sediment porewater of Barataria Bay suggesting that the potential toxicity of PAHs in the sampling locations were very low.

REFERENCES

Allan, I.J., Harman, C., 2011. Environ Sci Technol 45, 6233-6234.
Anderson, K.A., Sethajintanin, D., Sower, G., Quarles, L., 2008. Environ Sci Technol 42, 4486-4493.
Atlas, R.M., Hazen, T.C., 2011. Environ Sci Technol 45, 6709-6715.
Huckins, J.N., Petty, J.D, Booij, K., 2006. Springer, New York
Lohmann, R., Muir, D., 2010 Environ Sci Technol 44, 860-864.
Peterson, C.H., Rice, S.D., Short, J.W., Esler, D., Bodkin, J.L., Ballachey, B.E., Irons, D.B., 2003. Science 302, 2082-2086.
Reddy, C.M., Eglinton, T., Hounshell, A., White, H.K., Xu, L., Gaines, R.B., Frysinger, G.S., 2002. Environ Sci Technol 36, 4754-4760.
Reible, D. 2010. Environ Sci Technol 44, 5685-5686.
Reible, D.D. (2010) SPME/PDMS Calibration Study. Final Report to Northwest Division Seattle District US ArmyCorps of Engineers, April 2010.
USEPA, 2003. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms PAH mixtures. U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Atlantic Ecology Division : Mid-Continent Ecology Division, Western Ecology Division, Narragansett, RI, Duluth, MN, Newport, Or.
Whitehead, A., Dubansky, B., Bodinier, C., Garcia, T.I., Miles, S., Pilley, C., Raghunathan, V., Roach, J.L., Walker, N., Walter, R.B, Rice, C.D., Galvez, F., 2011. Proc Natl Acad Sci USA.