Status of the Deepwater Horizon Natural Resource Damage Assessment

Written Testimony of
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Testimony before the Senate Committee on Environment and Public Works
Subcommittee on Water and Wildlife
Washington, DC

July 28, 2011

Submitted on June 23, 2011

Attached please find the written testimony of Erik Rifkin, PhD.

QUANTIFYING CHRONIC DAMAGES TO NATURAL RESOURCES IN THE GULF RESULTING FROM THE BP SPILL:

AN INDEPENDENT STUDY

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June 28, 2011

PREFACE

Approximately one year ago (July 27, 2010), the National Aquarium was given the opportunity to provide the Senate Subcommittee on Water and Wildlife written and oral testimony at a hearing on "Assessing Natural Resource Damages Resulting from the BP *Deepwater Horizon* Disaster". At that time, we emphasized the importance of independent research when attempting to quantify potential chronic damages to natural resources in the Gulf resulting from exposure to petroleum from the BP spill. The rationale for this view was, and still is, based on the concern that the NRDA process is not using a methodological approach which adequately measures small quantities of petroleum contaminants which could have chronic impacts on aquatic biota.

More specifically, the National Aquarium's testimony, and the testimony of the other independent researchers on the panel, suggested that passive diffusers be used to measure low levels of petroleum in order to accurately characterize ecological risks. Since the last hearing, the National Aquarium Conservation Center (NACC), in collaboration with Mote Marine Laboratory and Johns Hopkins University, has conducted research designed to provide concerned government agencies and others with data necessary to quantify chronic damages to natural resources in the Gulf. The findings from this independently funded study will be readily available to interested parties, including Gulf communities directly impacted by this oil spill.

Our research involves the deployment of sophisticated petroleum contaminant samplers, developed by the USGS, called semi-permeable membrane devices (SPMDs). These devices function as "virtual" fish and provide unparalleled, time integrated data on levels of petroleum contaminants in the water column and sediment porewater (interstitial water found in sediment) necessary for assessing potential chronic impacts. Data will be integrated into bioconcentration and bioaccumulation models in order to more clearly understand the fate and transport of petroleum contaminants in aquatic organisms.

By using SPMDs, we were able to obtain empirical data on levels of individual PAHs (organic pollutants found in petroleum) in the water column and porewater in areas impacted by the BP spill. Our findings support the contention that data obtained from SPMDs, when incorporated into bioconcentration models, will provide a far more accurate assessment of the nature and extent of chronic damages in the Gulf than the standard approach of collection and analysis of grab samples of water and sediment.

The ramifications of our findings should not be underestimated. The ability to measure levels of potentially toxic PAHs in the water column and sediment porewater at specific sites is a necessary prerequisite to accurately quantifying chronic damages to natural resources.

Following the July 27, 2010 Senate Subcommittee hearing, a meeting was arranged with representatives from EPA so that we could share our preliminary findings with the Agency and obtain advice and guidance from their research scientists. At our meeting and in subsequent discussions, EPA scientists supported the use of passive diffusers to monitor levels of PAHs in the water column, sediment and sediment porewater. They acknowledged the benefits of these devices to measure low concentrations of contaminants which, because of bioconcentration, could result in adverse impacts.

A meaningful NRDA must be able to incorporate robust data into economic models in order to accurately quantify chronic damages and injury to natural resources in the Gulf. In light of our findings, there are reasons to give serious consideration to expanding the use of passive diffusers in impacted areas of the Gulf as soon as possible. This will increase our ability to assess causality between the release of oil and injured resources and/or lost human use of those resources and services.

We look forward to the opportunity to provide you with an update of our findings.

I Goals and Objectives

This independent research involves the use of passive samplers to monitor PAH concentrations in water, sediment porewater and sediment in the Gulf of Mexico in order to quantify site-specific, chronic damages to natural resources. The research team consists of three institutions: the National Aquarium Conservation Center (NACC) (Baltimore, MD), Johns Hopkins University (Baltimore, MD) and Mote Marine Laboratory (Sarasota, FL.).

Our goal is to use passive samplers, such as semi-permeable membrane devices (SPMDs) and polyethylene (PE) tubing, to monitor the PAH concentrations in water and sediment porewater respectively, impacted by the *Deepwater Horizon* oil spill. These passive samplers are considered to be an innovative approach in measuring time integrated ng/L levels in situ.

The monitoring results will be archived and shared with all interested stakeholders, researchers and regulators. Our plans are to incorporate the measured values into mathematical models to study bioconcentration and bioaccumulation of PAHs in the Gulf of Mexico ecosystem impacted by the oil spill.

In addition, the measured PAH levels in water and sediment porewater can be used as base line concentrations, which will assist other researchers in conducting a variety of bioassays designed to assess the sublethal toxicity of PAHs and to generate new benchmarks for evaluating possible chronic damages.

II Summary Description of the Proposed Work

We propose a comprehensive approach to characterizing the existing petroleum (PAHs) levels in oil spill impacted areas in the Gulf of Mexico. We will collect data on petroleum levels (specifically focused on PAHs and their homologues) from the water column, sediment porewater, and sediments. In addition, sediment dwelling benthic organisms which comprise the basis of the foodweb and commercially important organisms, such as redfish, shrimp, oysters, and finfish, will be collected and analyzed to measure bioaccumulated PAHs. The proposed monitoring study particularly suggests using passive samplers, such as semi-permeable membrane devices (SPMDs) and lipid free polyethylene (PE) tubing to measure time integrative PAHs in water and sediment porewater in-situ [1].

Although grab sampling has been traditionally used in this NRDA, that method of sampling provides information on the concentrations of PAHs only during one point in time or a relatively brief interval of time, which is in marked contrast to the exposure duration of most organisms. Moreover, grab sampling methods suffer from potential problems with sample preservation, and the method quantification limits are not adequate for the analysis of environmentally relevant (ng/L) levels of PAHs in water. These relatively low levels of quantification are especially needed for assessing the chronic damages to the natural resources in the Gulf of Mexico.

These difficulties can be minimized by using SPMDs and lipid free PE tubing which can provide a more time integrative measure and improve the ability to detect the low concentrations of PAHs in aqueous environments. The SPMD is one of the most studied and widely used passive sampler for determining water column concentrations [2], and the research team has experience and data sets on PAH occurrence from the use of SPMDs in the Gulf of Mexico, which were obtained with seed funding from the NACC.

SPMDs have severe limitations for measuring sediment porewater concentration, so lipid free PE tubing will also be used to better estimate porewater PAH concentrations [3, 4]. It is important to know sediment porewater PAH levels as they are a better indicator of the bioavailable fraction of PAHs than total sediment concentrations [5].

The passive samplers will be deployed in aquatic environments for several weeks, and PAHs will accumulate in the adsorbing materials of the devices. The samplers will be retrieved and be transported to the laboratory to extract and determine the accumulated PAHs using analytical instruments, such as GC-MS. The water and sediment porewater PAH concentrations can be estimated from the accumulated PAHs with strict QA/QC, such as estimation of sampling rates using performance reference compounds (PRCs) and mathematical models considering ancillary parameters, such as temperature, dissolved organic carbon and salinity.

III The Value of the Obtained Data

After the Deepwater Horizon oil spill, one of the primary responses from federal and state regulatory agencies, for the natural resource damage assessment, has been collecting water and sediment grab samples and analyzing concentrations of PAHs. The water PAH levels have been directly compared to benchmarks, such as the final chronic value (FCV) derived from the National Water Quality Criteria (WQC) guidelines [6]. The PAH levels in sediment porewater were estimated from the sediment PAH concentrations using equilibrium partitioning theory (EqP) [7, 8]. These values were then compared to the benchmarks, assuming that porewater PAH values are the best estimate of toxicity and bioavailability. So far, most of the grab samples have revealed concentrations below the analytical detection limit, so the assumption is made that there are insignificant damages to the natural resources from the released PAHs [9].

However, 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.

We have learned valuable lessons from the Exxon Valdez spill with regard to long-term effects on the populations of aquatic organisms [10]. 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. We observed significant residual oil in the Barataria Bay (LA) from the oil spill during our recent field experiment in May 2011(see Figure 1).

For more accurate quantification of the chronic damages to the natural resources in the Gulf of Mexico, it is necessary to monitor the PAH levels in a more robust way rather than continuing to collect grab samples and reporting non-detect (ND) values. The data obtained from the passive samplers can be used in a variety of ways in quantifying chronic damages to the Gulf of Mexico ecosystems. For example, the bioaccumulation and toxicity of PAHs to benthic organisms can be updated by a direct measurement of porewater PAHs using the passive sampling techniques [5]. The data can further be used to evaluate biomagnification of PAHs through trophic transfer using process based bioaccumulation models [11].

In addition, the values can be used as a baseline concentration to conduct both acute and chronic toxicity studies involving the shellfish and finfish species that are important to the Gulf of Mexico, as well as using the Zebrafish model. Hence, the data we will obtain can be used to evaluate the site and species responsive to a variety of toxic thresholds of PAHs in the Gulf of Mexico ecosystem. We anticipate that several other research institutions will conduct toxicity tests to study organisms' physiological processes at the cellular level (genes and their transcripts and expression products, such as proteins and hormones) and whole animals. Such toxicity tests will provide us with information on the effects of dispersed oil on early developmental processes, muscle/skeletal development, growth, immune systems and reproductive processes.

IV. General Work Plan

We have deployed our passive sampler (SPMDs) and collected organisms with seed funding from the NACC in a few locations, such as Terrebone Bay (LA), Barataria Bay (LA), Jose Bay (MS), Perdido Bay (FL), and Cotton Bayou (AL), to measure PAH levels in water and sediment porewater. The locations of these past sampling efforts are delineated in Figure 2.

Additional funding will allow us to conduct a more comprehensive study in the areas sampled and provide a much more accurate assessment of natural resource damages.

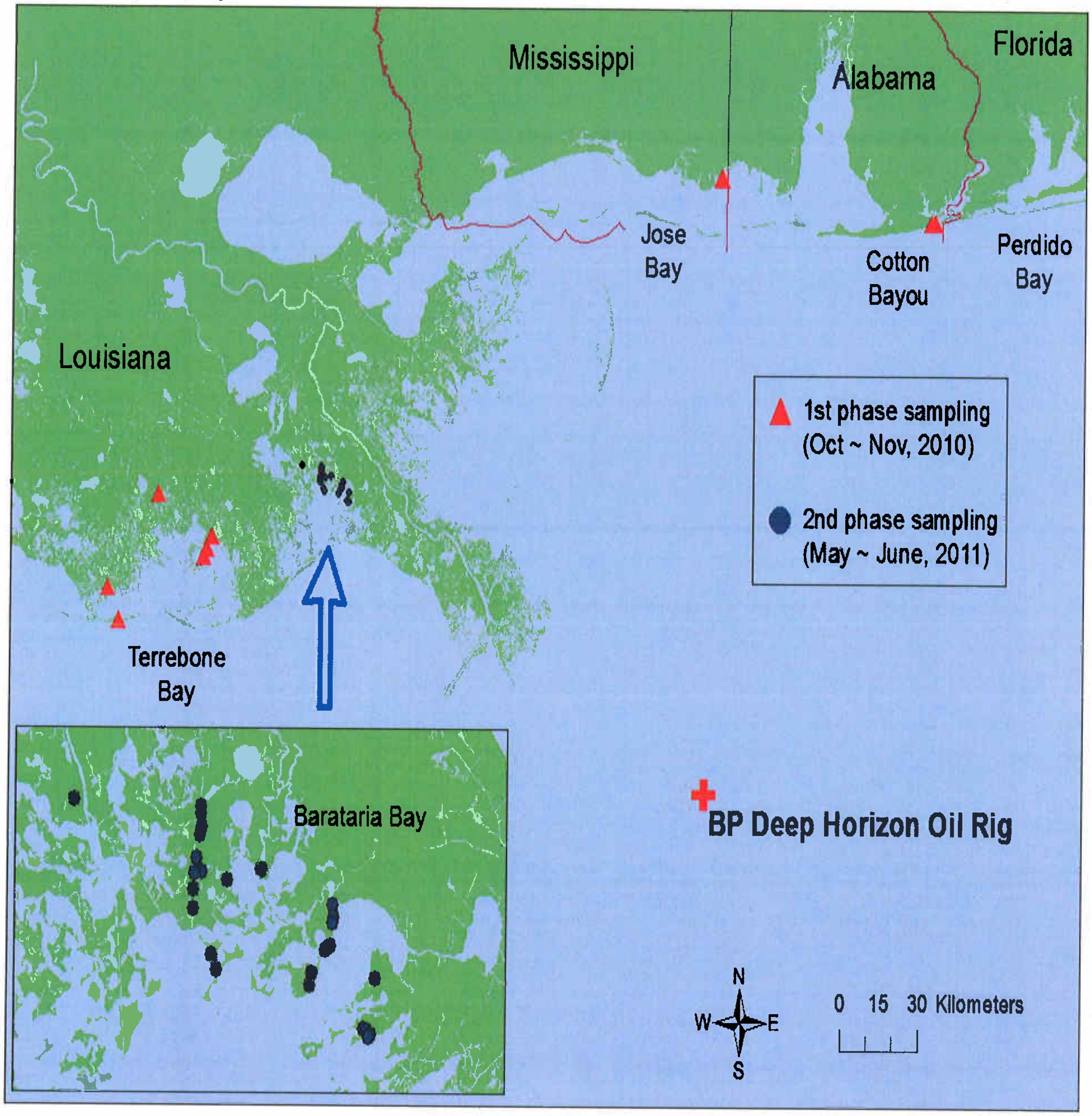
We envision an additional 50 sampling locations including several impacted commercial and recreational fishing zones.

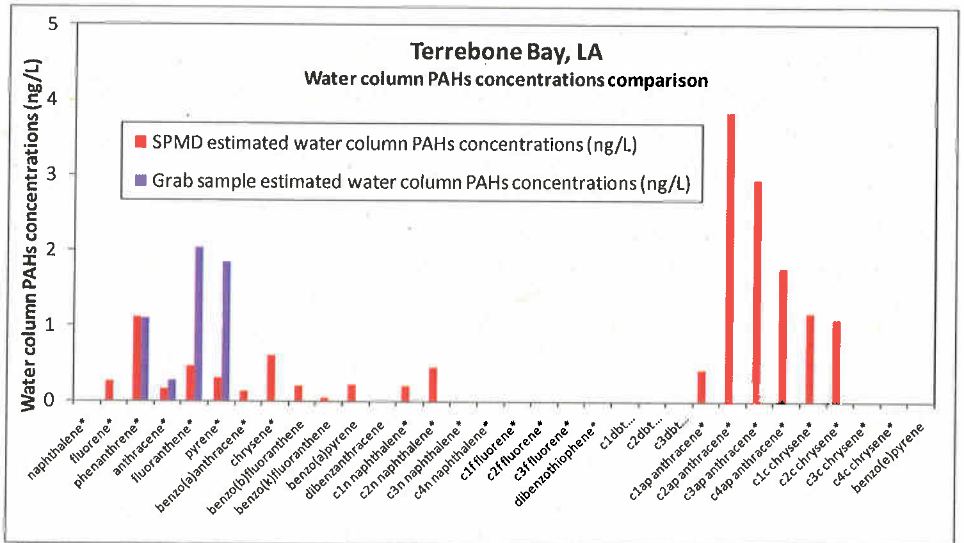
Our team has expertise in risk communication. We plan to meet with local community groups located in the Gulf of Mexico area that have been impacted by the oil spill to communicate our findings and obtain their feedback. We will hold similar meetings with EPA and other interested stakeholders. To assist with public outreach, we will work with the Baltimore Aquarium to develop an exhibit on the Gulf of Mexico oil spill.

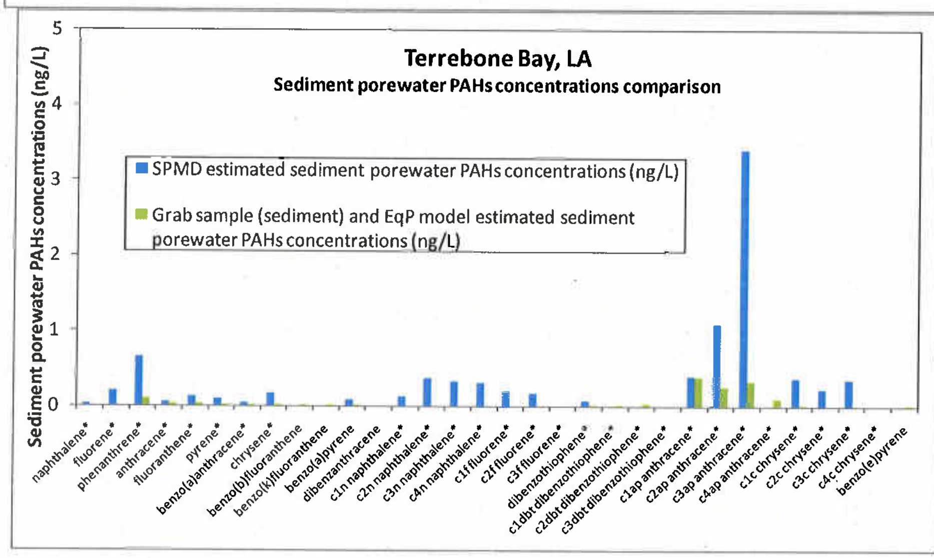
We have already been monitoring PAHs for the past year with NACC seed funding in more than 40 locations in the Gulf of Mexico, which are shown in Figure 2. Some of the preliminary data on the PAH concentrations are available in Figure 3. Generally, SPMDs showed far greater sensitivity in measuring 'ng/L' levels of dissolved PAHs in the water column and sediment porewater than grab sampling techniques. Once the data from these different matrices are determined, a model of bioavailability and bioaccumulation will be developed for petroleum contamination. We have the capability to develop process and probability based mathematical models to better understand the underlying processes and to synthesize and interpret experimental observations.

Figure 1. Weathered visible oils in Barataria Bay, Louisiana. The pictures were taken during the 2nd phase passive sampler (SPMDs) deployment and sediment/water grab sampling for PAH analysis (May 14th – 15th, 2011).

Figure 2 (below).




Terrebone Bay, LA
Water column PAHs concentrations comparison
SPMD estimated water column PAHs concentrations (ng/L)
Grab sample estimated water column PAHs concentrations (ng/L)
Water column PAHs concentrations (ng/L)
0
1
2
3
4
5
naphthalene*
fluorene*
phenanthrene*
anthracene*
fluoranthene*
pyrene*
benzo(a)anthracene*
chrysene*
benzo(b)fluoranthene
benzo(k)fluoranthene
benzo(a)pyrene
dibenzanthracene
c1n naphthalene*
c2n naphthalene*
c3n naphthalene*
c4n naphthalene*
c1f fluorene*
c2f fluorene*
c3f fluorene*
dibenzothiophene*
c1dbt...
c2dbt...
c3dbt...
c1ap anthracene*
c2ap anthracene*
c3ap anthracene*
c4ap anthracene*
c1c chrysene*
c2c chrysene*
c3c chrysene*
c4c chrysene*
benzo(e)pyrene


Terrebone Bay, LA
Sediment porewater PAHs concentrations comparison
SPMD estimated sediment porewater PAHs concentrations (ng/L)
Grab sample (sediment) and EqP model estimated sediment porewater PAHs concentrations (ng/L)
Sediment porewater PAHs concentrations (ng/L)
0
1
2
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fluoranthene*
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chrysene*
benzo(b)fluoranthene
benzo(k)fluoranthene
benzo(a)pyrene
dibenzanthracene
c1n naphthalene*
c2n naphthalene*
c3n naphthalene*
c4n naphthalene*
c1f fluorene*
c2f fluorene*
c3f fluorene*
dibenzothiophene*
c1dbt dibenzothiophene*
c2dbt dibenzothiophene*
c3dbt dibenzothiophene*
c1ap anthracene*
c2ap anthracene*
c3ap anthracene*
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c1c chrysene*
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benzo(e)pyrene

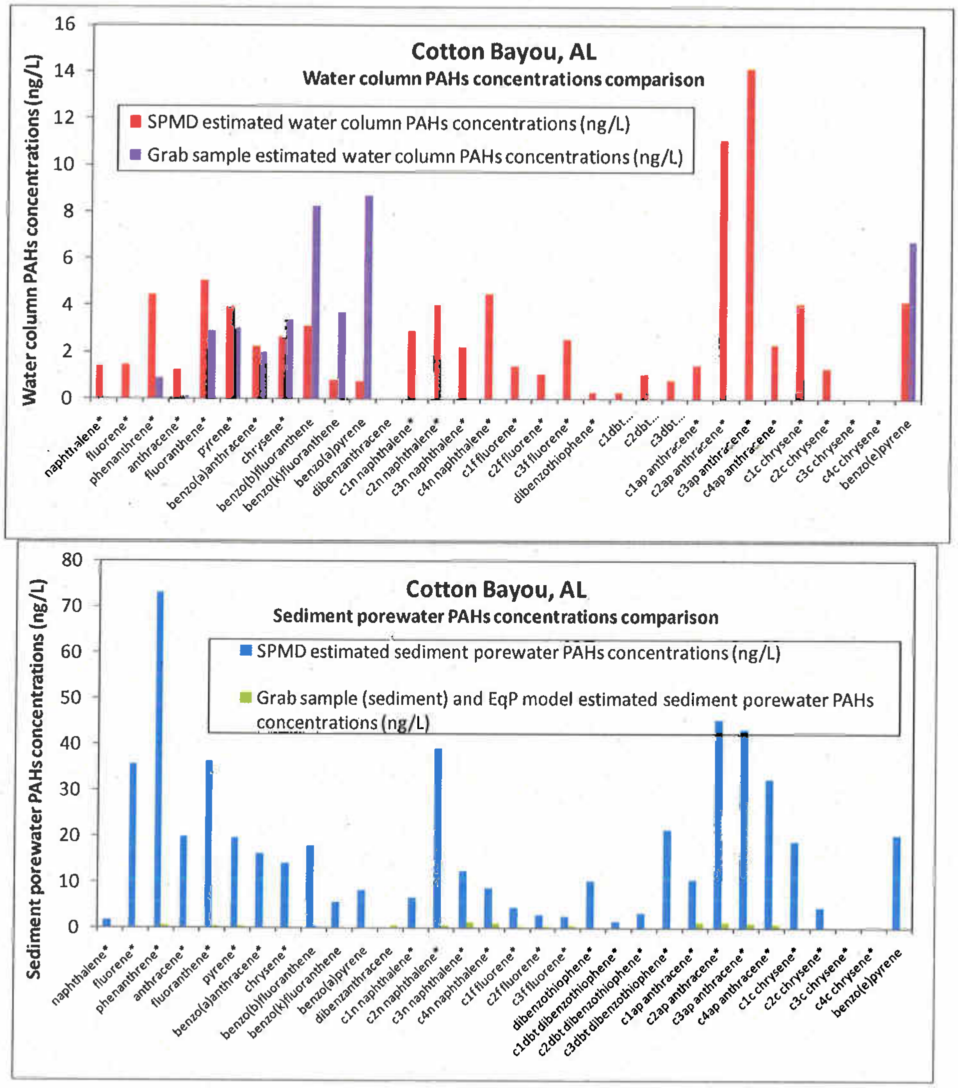

Figure 3. Comparison of PAH concentrations estimated by SPMDs and grab samples in water column and sediment porewater. The models described in Huckins et al. (2006, [2]) were used to estimate water concentrations from SPMD data. Sediment porewater PAH levels for the grab sampling technique were estimated from measuring PAH concentrations in sediment and applying equilibrium partitioning model (q_s=f_{oc} K_{oc} C_{aq}), where q_s is the sediment phase PAH concentration, f_{oc} is organic carbon fraction (~ 1 %), K_{oc} is the organic carbon partition coefficient (log K_{oc} = 0.903 log K_{ow} + 0.094, Baker et al., 1996. Water Environ Res.

V Background

When BP's Deepwater Horizon (DWH) oil platform exploded on 20 April, 2010, it catalyzed the most extensive oil spill response in United States history. That response has largely been governed by the provisions of the Oil Pollution Act of 1990 (OPA-90). OPA-90, in turn, was triggered and shaped by the consequences of the Exxon Valdez oil spill in March 1989, which was the largest US oil spill up until that time.

The response to DWH was substantial, but not without controversy. Although federal agencies charged with responding to the DWH disaster, as well as BP, have suggested that the spill was handled effectively and that short and long-term consequences have largely been mitigated, evidence suggests that chronic ecological impacts still remain.

The Deepwater Horizon oil spill had significant adverse consequences for certain coastal habitats and communities. Reports of those consequences vary considerably, depending on the source. That inconsistency is certainly frustrating to the people living in coastal communities whose health and livelihoods have been affected, but the frustration is exacerbated by a lack of transparency and meaningful involvement of those very communities.

Although scientists and managers learned valuable lessons from the Exxon Valdez spill with regards to short-term effects on the ecosystem, people are still trying to understand long-term population effects on the organisms within those affected areas. Peterson et al. 2003 reviewed the long-term effects of the Valdez spill and noted that chronic exposures persist years after an oil spill, particularly in sediments. Persistent effects of toxin 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.

Indirect effects on communities in Prince William Sound were also substantiated from the exposure to oil and were considered as important through direct trophic interactions. Probably one of the most important lessons learned from the Exxon Valdez spill was a significant change in perceptions regarding oil ecotoxicology.

The old paradigms included the beliefs that:

a) oil on shorelines will be rapidly degraded microbially and by exposure to the sun;
b) oil effects on fish are short term and arise from only the volatile fraction of oil;
c) impacts on birds and marine mammals occur solely through coating of fur and feathers resulting in hypothermia, smothering, drowning or ingestion of oil. No long term effects occur; and
d) submerged aquatic vegetation and invertebrates will be affected in the short term due to mortality from exposure to oil.

The emerging appreciation is quite different and includes the following:

a) oil degradation rates depend upon conditions in specific environments and biologically meaningful contamination may occur for years or decades;
b) long-term exposure of fish embryos can have population level consequences through impaired growth, deformities, reduced reproduction and behavioral changes;
c) effects of oil exposure on marine mammals and sea birds may compromise health and reproduction, and synergistically magnifies effects of other environmental stressors with severe consequences; and
d) clean-up attempts (physical or chemical) can be more damaging than the oil itself by interfering with biological interactions within communities, thereby delaying recovery.

VI. Details of Approach:

Traditional approaches approved by the EPA and the NRDA process to sampling environments affected by oil have involved analysis of water column samples (by simply using a water grab sample) and sediments (using a grab sampler that fails to distinguish between contaminants in pore water, where they are most available to benthic organisms, and contaminants bound to sediments themselves).

The experimental design for this project will result in a reduction of uncertainty when quantifying chronic damages (e.g., risks, impacts) to natural resources which have occurred as a result of exposure to BP oil (Figure 4). There is currently a lack of consensus, when using generic ecotoxicological benchmarks, on what organisms should be protected and what level of protection should be achieved. Although EPA and other agencies provide broad guidelines for the assessment of benchmark endpoints, specific endpoints are not identified. Benchmarks cannot be validated for all sites and situations. They can be defended only in terms of regulatory precedent.

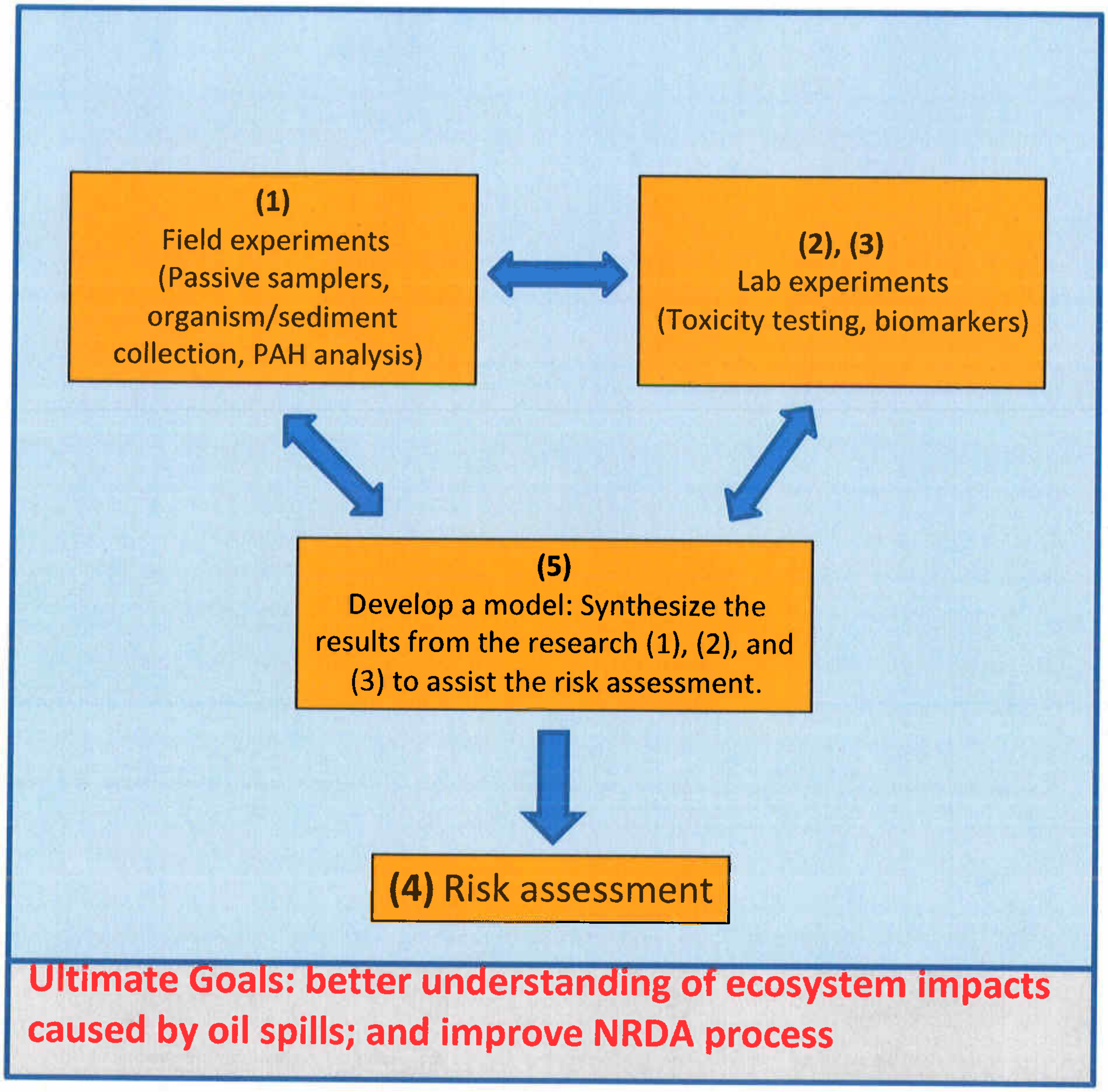

Figure 4 provides a simple flow diagram summarizing the scientific research that would form the underpinnings of our proposed study.

A. Sampling:

We have initiated a more comprehensive approach to defining the existing and future petroleum levels in Barataria Bay and nearby areas. In addition to the traditional sampling, we have already sampled the water column and pore water in those locations using passive diffusers (SPMD's; see below) to collect data on petroleum levels (specifically focused on PAHs). We plan to continue and expand our sample collecting for two more years; we will once again focus on sampling pore-water, the water column, sediments and selected fish, shrimp and benthic filter feeders such as oysters. The precise locations of samples and the range of species to be sampled will be determined in discussions with leaders of the community partners representing fishing organizations. Once the data from these different matrices are determined, a model of bioavailability and bioaccumulation will be developed for petroleum contamination (see below).

The primary proposed method for assessing water column petroleum concentrations is using a semi-permeable membrane device (SPMD) which was developed by Huckins et al. (1990, 1993) to mimic the bioconcentration of organic contaminants without the limitations of using bivalves. The SPMD consists of thin, low-density polyethylene lay-flat tubing filled with 1 g of triolein, a naturally occurring lipid material, and sealed at the ends, with a total surface area of 400 cm^2 placed in a protective housing (Figure 5). When placed in aquatic environments, the SPMD mimics the bioconcentration process of aquatic animals based upon the comparability of its octanol/water partition coefficient, since this membrane device collects hydrophobic organic pollutants from the surrounding area and integrates the

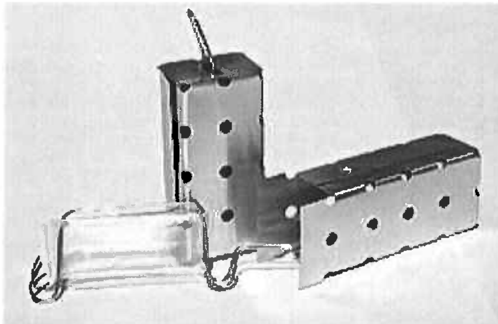
Figure 5. SPMD in deployment housing.

levels over the entire time of exposure (Palowitch 1994, Ellis et el. 1995, Gale 1998). This technique passively replicates the partitioning and accumulation potential found in sentinel organisms while providing consistent availability of a pollution monitoring device without the impediments associated with using live organisms. Possible metabolization and depuration, bias in absorption of contaminants, size, age and sex-related differences influencing body burden and site-to-site variations among bivalves, particularly in highly polluted areas, diminish the utility of using sentinel organisms as ubiquitous monitors in environmental assessment (Buhler and Williams 1989, Prest et al. 1992). Chiou (1985) demonstrated that for a wide variety of organic compounds, a close correlation exists between triolein-water equilibrium partition coefficients (K_{tw}) and octanol-water equilibrium partition coefficients (K_{ow}). The partition coefficient, K, is analogous to the partitioning that occurs from an aqueous phase to an organic solvent in liquid-liquid extraction processes:

$$K = \frac{[\text{analyte in organic solvent}]}{[\text{analyte in water}\}}$$

In the case of the partitioning coefficient K_{tw}, the organic solvent is triolein; for K_{ow}, the organic solvent is octanol. It has been shown that a compound's K_{tw} should closely approximate its K_{ow} (Chiou 1985). Since K_{ow} values are large for hydrophobic organic contaminants, the capacity of triolein-containing SPMDs to accumulate these contaminants is correspondingly large (Huckins et al. 1993).

The low-density polyethylene, used to make SPMDs, and gill membranes appears to exhibit similar steric exclusion limits with respect to the uptake of hydrophobic organic contaminants (Lebo et al. 1992). The pore size of the membrane is approximately 10 angstroms, thus excluding contaminants with a larger diameter (Figure 6). Analytes that fall below this size exclusion limit pass through the SPMD and accumulate in the triolein lipid interior of the membrane, and can then be easily extracted and analyzed. By using a sorbent that mimics the lipid/water partitioning that occurs in sentinel organisms, this new tool may potentially provide a consistent and reproducible pollution monitoring method that would overcome several of the disadvantages of using living organisms.

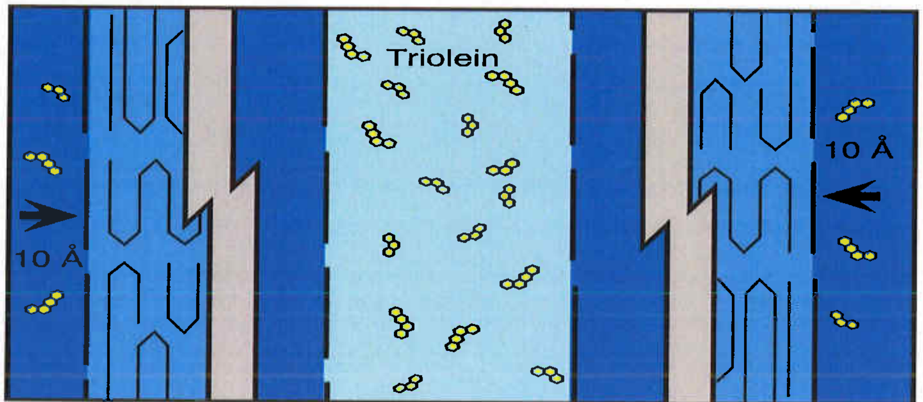

Figure 6. Exploded view of SPMD

All samples will be extracted and analyzed according to standard methods and using gas chromatography-mass spectrometry for ~70 parent and homolog polycyclic aromatic hydrocarbons. We will also conduct analyses for chemicals indicative of the use of Corexit dispersants. Sediment and tissue samples are extracted by pressurized fluid extraction (PFE) according to EPA Method 3545A. Briefly, sediment samples are ground with anhydrous sodium sulfate and packed into a 33mL stainless extraction steel cells. Samples are extracted using a 50% mixture of methylene chloride and acetone using a Dionex 300 ASE system. Samples will be further purified using gel permeation chromatography (GPC). Samples are then analyzed for PAHs on an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass selective detector (EPA Methods 8260B and

8080). Analyte separation is achieved using a HP-5MS column (30m x 0.250mm x 0.250um; J&W Scientific) with ultrahigh-purity helium as the carrier gas.

After recovery from the field, the SPMDs will be sent to the manufacturer for dialysis and the extracts will be sent back to Mote Marine Laboratory for analysis. A non-exposed SPMD will be retained for both field and lab blanks and analyzed for possible background contamination. All extracts will be analyzed as above.

Additional sediments will be collected with a grab sampler, sieved through a 2mm sieve and stored in glass jars, on ice until analysis.

B. Model Development

PAHs tend to be strongly associated with particulate organic carbon (POC) in sediments, hence sediments have been considered to be a long term source of contaminants after oil spill. Total PAHs in sediments is often used to estimate the bioaccumulation of PAHs to benthic organisms using equilibrium partitioning theory (EqP) (Blerman, 1990). With the EqP, the toxicity of PAHs can be estimated using the narcosis theory and the final chronic value (FCV) derived from the National Water Quality Criteria (WQC) guidelines (USEPA, 2003).
In the proposed modeling study, the bioaccumulation factors and toxicity will be estimated using the data obtained from the field and laboratory experiments.

New FCV will be evaluated based upon sub-lethal toxicity tests. Porewater PAH levels in sediments will be directly estimated from a passive sampler (using PEs) rather than estimating PAHs from total sediment concentrations. From the study, the site specific PAH bioconcentration factors and toxicity in the GOM ecosystems will be evaluated. Since field collected data are likely to have uncertainties, probability based modeling approaches, such as Monte Carlo Simulation, will be conducted to better evaluate and assess the parameters. The values will be compared with current 'Equilibrium Partitioning'.

<u>Bioaccumulation of PAHs</u>

The EqP theory utilizes thermodynamic relations between the POC in sediment, porewater, and lipids in organisms to estimate the distribution of PAHs (Blerman, 1990). The EqP leads to the following biota-sediment accumulation factor (*BSAF*) as a measure of the PAH bioaccumulation potential (McFarland, 1984):

$$BSAF_{sediment} = \frac{q_{lipid}}{q_{oc}} = \frac{q_{organism} / f_{lipid}}{q_{sediment} / f_{oc}} \quad (1)$$

Here q_{lipid} represents the contaminant lipid-phase concentration of the organism, q_{oc} is the contaminant concentration in the sediment organic matter, $q_{organism}$ is the contaminant concentration in the organism, $q_{sediment}$ is the contaminant concentration in sediment, f_{lipid} is the lipid fraction of the organism, and f_{oc} is the organic carbon fraction in sediment.

More recently, porewater PAH concentrations have been correlated with observed bioaccumulation of PAHs in biota (Lu et al., 2011). The $BSAF_{sediment}$ can be updated by a direct measurement of porewater PAHs using an *in-situ* passive sampler.. The corresponding equation for $BSAF_{porewater}$ is as follows:

$$BSAF_{porewater} = \frac{q_{organism} / f_{lipid}}{K_{oc}\, C_w} \quad (2)$$

Here K_{oc} is the organic carbon partition coefficient and C_w is the porewater concentration. Equation (2) can be derived from equation (1) using the following empirical linear adsorption model for the partitioning of PAHs to sediments (Karickhoff et al., 1979):

$$q_{oc} = f_{oc} K_{oc} C_w \quad (3)$$

Here f_{oc} is the fraction of organic carbon in the sediments. The partition coefficients (K_{oc}) can be estimated from octanol-water partition coefficients (Karickhoff 1981) and empirical correlations (Schwarzenbach et al., 2003). Our hypothesis is that the $BSAF_{porewater}$ will be a better estimate of the bioavailability and bioaccumulation of PAHs in GOM sediments, while $BSAF_{sediment}$ can be a useful bioaccumulation indicator in areas where passive samplers cannot be deployed.

Biomagnification of PAHs

Typically, organisms in high trophic levels (fish, mammals) seem to be able to eliminate PAHs quickly,hence no significant bioaccumulation or biomagnification have been observed in such organisms. However, a previous study showed that alkylated PAHs which are elevated in fresh oil can significantly change the bioaccumulation of PAHs to fish (Jonsson et al., 2004).

To assess the biomagnification of PAHs from fresh spilled oil in foodwebs of the GOM, the following biomagnification factor (*BMF*) for each organic compound will be evaluated from the data collected from the site.

$$BMF = \frac{q_{predator} / f_{lipid,predator}}{q_{prey} / f_{lipid,prey}} \qquad (4)$$

Here $q_{predator}$ represents the contaminant concentration in the predator, q_{prey} is the contaminant concentration in the prey, $f_{lipid,\ predator}$ is the lipid fraction of the predator, and $f_{lipid,\ prey}$ is the lipid fraction of the prey. In addition to the simplistic approach described above, there exist several fugacity based bioaccumulation models, such as biomass conversion, digestion or gastrointestinal magnification, micelle-mediated diffusion, and fat-flush diffusion (Fraser et al., 2002; Kelly et al., 2004). The models are highly mechanistic and require many more input parameters (10 to 20 variables) and much more complex characterization studies. The models consider competing rates of chemical uptake from the gastrointestinal tract and other potential chemical elimination routes, such as respiration, gill ventilation, urinary excretion, metabolism, and growth dilution (Kelly et al., 2004). If comprehensive data could be obtained from field and laboratory experiments, more sophisticated and mechanistic biomagnification models will be used.

Toxicity model

PAHs present as a mixture in environments and the toxic effects of PAHs are generally considered to be additive. Hence, the estimation of PAH toxicity should be based upon the individual concentration of PAHs measured in environmental matrix. The approach outlined in USEPA (2003) will be applied to evaluate the toxicity of dispersed oil (PAHs) in GOM using the data obtained from the field and laboratory experiments. Water column and sediment porewater PAHs including alkylated homologues levels will be estimated from the passive sampling devices. The new final chronic values (FCVs) evaluated in toxicity experiments will be used as follows.

$$TPR = \sum \frac{C_{PAH}}{FCV_s} \quad (5)$$

where *TPR* is the toxic potency ratio of PAH mixtures in environments, C_{PAH} are the individual PAH concentrations measured by passive sampler, *FCVs* are the toxicity threshold of individual PAHs evaluated in the toxicity test. If TPR is greater than 1 in the GOM, the environment may be still under toxic conditions to the organisms. Or if TPR is less than 1, the GOM environment would not be toxic to the organisms.

The development and application of mathematical models helps researchers to understand the underlying processes occurring beyond observation, to predict future behaviors, and to assist decision makers. The proposed mathematical modeling approach incorporates bioaccumulation and toxicity models which are currently being used by USEPA to assess the risk associated with PAH levels measured in water column and sediments. Hence, the approach will be updated by the proposed field and laboratory experiments. Furthermore, by conducting probability based modeling approaches, the uncertainties beyond field and laboratory experiments will be more adequately addressed. We believe that current research will be of value to EPA and other agencies when developing sediment benchmarks in the future.

C. Risk assessment

The primary objective of this Ecological Risk Assessment (ERA) will be to conduct a comparative analysis between: 1) protocols used to quantify chronic damages to natural resources currently used under the formal NRDA process; and 2) our experimental design which uses empirical data from passive diffusers to obtain water-column values for PAHs and bioconcentration and bioaccumulation modeling. These water column values can then be used to conduct a variety of bioassays designed to assess casualty between exposure and impacts.

ERA is a scientific approach used to determine the possible impacts of human activities on the environment. The EPA defines ERA as "the process that evaluates the likelihood that adverse ecological effects are occurring, or may occur, as a result of exposure to one or more stressors". In this context, the stressors are constituents of petroleum released as a result of the BP oil spill in the Gulf – more specifically PAHs.

The ERA process generally runs parallel to human health risk assessment. The ecological problem and the hazards need to be identified. The ecological effects then need to be correlated with exposure to contaminants and/or levels of habitat destruction, and dose-response relationships need to be determined. From all of this information, ecological risks are characterized along with major assumptions and uncertainties.

Risk managers then consider scientific conclusions from the ERA alongside policy judgments, economic ramifications, legal issues, and social concerns. They try to balance these different factors to recommend a course of action. The description of the ecological risk assessment and management process sounds reasonable on paper. The ERA process seems analytical; it appears to be grounded in sound scientific principles. But applying these ideas in a real world isn't simple.

The difficulties begin with the formulation of the problem. What ecological unit should we analyze? There is no standard procedure for assessing ecological risk. It should be noted that the use of a ERA framework for assessing effects of oil spills is applicable to the injury assessment component of Natural Damage Resource Assessment (NRDA). Central to the ERA process is the assessment of exposure, the critical component linking the release of oil to the assessment of effects. A release of petroleum may not, in itself, equate to an effect on a natural resource. The presence of residual petroleum hydrocarbons does not imply either availability to living organisms or injury to a biological resource.

As mentioned above, there is no standard practice to conduct ERAs rather, assessments are addressed on a site-by-site basis. Further, there is no clear relationship between body burdens of PAHs and effects, due to the metabolism of PAHs by many organisms at various levels of the food web, and hence tissue residues are seldom used as a determinant for quantifying risks for these contaminants. Exposure and effects measurements are most often assessed in the benthos, where sublethal toxicity may be observed. Water column, sediment or interstitial (pore) water measures of PAHs are used to quantify exposure while toxicity to benthic organisms is applied as a measure of effects. In some instances, benthic community composition and condition are used to assess effects.

Sediment quality guidelines including empirical (Long et al., 1995; Field et al., 2002) and consensus (Swartz, 1999; MacDonald et al., 2000) approaches as well as the mechanistic equilibrium partitioning sediment benchmarks (ESBs) (U.S. EPA, 2003, 2005) are also used as complementary and predictive tools for assigning risk. In a few rare cases, photo-enhanced toxicity caused by PAHs has also been used to assess risk. To determine the exposure invertebrates experience in contaminated sediments it is necessary to measure or predict the concentrations of bioavailable PAHs. For hydrophobic organic contaminants like PAHs, under equilibrium conditions, the interstitial (pore) water concentration of

PAH is the most accurate indicator of the bioavailable exposure concentration. The interstitial water concentration can be measured empirically or predicted by using equilibrium partitioning (EqP).

In a sediment system, the predominant phases involved in EqP include the sediment organic carbon and dissolved phase (i.e., interstitial water). Based on EqP, theoretically, if the sediment concentration of PAH and concentration of sediment organic carbon are known, the interstitial water concentration of PAH can be predicted. Because the interstitial water concentration of PAH is the primary exposure concentration, knowing this concentration allows for an assessment of potential risk to benthic invertebrates. However, as previously mentioned, there is considerable uncertainty in characterizing ecological risks. There is a lack of consensus, when using generic ecotoxicological benchmarks, on what organisms should be protected and what level of protection should be achieved.

The NRDA protocol supports the use of benchmark values as the basic determinant for whether concentrations of PAHs (and other organic contaminants) constitute an ecological risk. However, benchmarks cannot be validated for all sites and situations. They can be defended only in terms of regulatory precedent. Benchmarks are not criteria or standards and while EPA and other agencies provide broad guidelines for the assessment of benchmark endpoints, specific endpoints are not identified.

The current NRDA protocol for determining whether concentrations of PAHs are potentially problematic has considerable, and perhaps an unacceptable level of, uncertainty. Of particular concern is the use of grab water and sediment samples to determine if PAH values are above or below a predetermined benchmark.

A Final Chronic Value (FCV) for PAHs derived using the National Water Quality Criteria (WQC) Guidelines are generally used as the toxicity endpoint. This value is intended to be the concentration of a chemical in water that is protective of the presence of aquatic life. This value does not consider the antagonistic, additive or synergistic effects of other sediment contaminants in combination with PAH mixtures or the potential for bioaccumulation and trophic transfer of PAH mixtures to aquatic life, wildlife or humans.

The general PAH water and sediment benchmark calculations use a measured concentration from a water or sediment grab sample (ug/l) x an alkylation multiplier to derive an alkyl adjusted concentration (ug/l). This value is divided by either an acute potency divisor (ug/l) or a chronic potency divisor (ug/l) to arrive at an acute or chronic potency ratio. This sum of these ratios is termed the Equilibrium Partitioning Sediment Benchmark Toxic Unit (EESBTUFCV). Freshwater or saltwater sediments containing <1.0 EESBTUFCV of the mixture of applicable PAHs are acceptable for the protection of benthic organisms, and if the EESBTUFCV is greater than 1.0, sensitive benthic organisms may be unacceptably affected.

The grab sampling method makes it difficult to detect contaminants in the water because they are present in very low concentrations. Further, porewater concentrations are modeled using the equilibrium partitioning approach. The absence of site-specific empirical porewater values adds another level of uncertainty to the equation. Therefore, the result is that measured concentrations of PAHs in water and sediment are generally characterized as non-detect (ND). By definition, if the measured PAH concentration is generally ND, the acute and/or chronic EESBTUFCV will rarely exceed 1 – therefore, implying no toxicity to benthic invertebrates is expected to occur.

However, simply because PAH values are below a predetermined benchmark value doesn't mean PAHs are not present or present at a level which is potentially problematic. There are currently accepted protocols for sampling the water column and sediment pore water which can readily detect low concentrations of PAHs. This is critically important because it has been demonstrated that PAHs bioconcentrate and bioaccumulate in the tissues of fresh water and marine organisms over time at levels orders of magnitude higher than concentrations found in the water column or porewater.

By using passive diffusers (e.g., SPMDs and PEs) unparalleled, time integrated data on low concentrations of PAHs in the Gulf can be obtained (refer to explanation of SPMDs above). These empirical values can then be converted to water column concentrations and placed in the appropriate bioconcentration and bioaccumulation models so that bioconcentration and bioaccumulation throughout the food chain can be calculated in a variety of marine organisms (refer to modeling section). Armed with this information, bioassays can be conducted to determine if exposure to specific PAHs (and other petroleum contaminants) is causally related to damages.

The use of passive diffusers and water column models will significantly reduce the level of uncertainty in characterizing damages and impacts to natural resources in the Gulf. This approach allows for the use of empirical data obtained at the impacted site to assess ecological risks and provide a more robust data set to be used in quantifying chronic impacts to this aquatic ecosystem. Consideration should be given to incorporating this experimental design in the formal NRDA process.

Ecological risks will be characterized subsequent to the completion of the field experiments (passive samplers, sediment/organism collection and PAH analysis) laboratory experiments (toxicity testing, biomarkers) and development of water column and bioconcentration and bioaccumulation models. Observed concentrations of PAHs in aquatic organisms and results obtained from bioconcentration models will be compared to bioassay results on chronic toxicity in the peer reviewed literature (e.g., reproductive and immune changes, DNA alterations and so on). This site specific, empirical data on potential impacts on indigenous Gulf flora and fauna will allow a comparison with results obtained from water and sediment grab sampling used in conjunction with ecological benchmarks. The results should reduce the level of uncertainty when quantifying chronic damages from exposure to oil from the BP spill.

Once the ecological risks are characterized, this information will be presented to interested members of the impacted community. The information will be in a format which will be readily understood by individuals without a scientific or medical background. Information communicated to the public will include, but not necessarily limited to, the following: rationale for the experimental design; use of benchmarks to assess ecological risks; limitations in using benchmarks; results from using passive diffusers; a comparative analysis of both methods (in the context of assessing risks); an assessment of whether site-specific empirical data from passive diffusers are of additional value in quantifying chronic damages, are useful as markers of exposure or neither. This data and information will include graphs and illustrations.

D. Outreach

The National Aquarium will engage Gulf Coast community members in the process of developing and communicating the results of a robust scientific study aimed at reducing the uncertainties when determining chronic effects of contaminants from the BP Oil Spill on Gulf Coast ecosystems. They will work with community leaders from the beginning to create a communications strategy that will inform citizens, trustees, policy makers, federal agencies, etc. on the intent, direction and results of our studies. Easy to digest materials will be created to help the community partners interpret the scientific data and create audience-appropriate resources to communicate findings. This could be in the form of printed materials, workshops/meetings, videos, interactive website applications, small exhibits, etc., - according to the specifications defined by the community partners.

Zoos and aquariums have both the capacity and the responsibility to increase public awareness of these issues and to implement conservation programs. To that end, the National Aquarium is active in marine research and conservation across many ecosystems and habitats around the world. They work to connect the public to the environmental challenges around us, beyond an individual species. More than 1.6 million people each year visit their venues in Baltimore and in Washington, DC. By interacting with their living collections of more than 16,000 animals, people make emotional connections that open them up to learning how to preserve and protect the aquatic world. Through each of their exhibits and through science-based education programs, they teach people respect for animals and the environment, and inspire them to take action to preserve aquatic habitats.

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