Assessing Natural Resource Damages Resulting from the BP Deepwater Horizon Disaster

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NATURAL RESOURCE DAMAGE ASSESSMENT (NRDA) FOR SARASOTA BAY ECOSYTEM:

APPROACH FOR ADDRESSING POTENTIAL IMPACTS FROM THE *DEEPWATER HORIZON* OIL SPILL

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I SUMMARY AND SIGNIFICANCE OF RESEARCH

The National Aquarium, in collaboration with Mote Marine Laboratory and Johns Hopkins University, is conducting a comprehensive study designed to ensure that pre- and post-*Deepwater Horizon* oil spill impact status of Sarasota Bay is documented as rigorously as possible. This will enable scientists to demonstrate causality between the release of oil and injured resources and/or lost human use of those resources and services.

The first phase of this research will provide vital information needed to evaluate the status of this sensitive aquatic environment before potential contamination by the Deepwater Horizon Gulf of Mexico oil spill. Oil from the BP Deepwater Horizon oil disaster has spread significantly from the ruptured well-head and impacted numerous coastal communities in four different states so far with further significant damage expected. The National Aquarium, which provided seed funding for this research in Sarasota Bay, developed an approach in conjunction with its partners which could be used in other Gulf coast regions to ensure a consistent data set for all threatened areas.

It's critical to gather robust, baseline information about the current state of any aquatic ecosystem that may ultimately be impacted by this oil disaster. This ecosystem-based approach, which includes the deployment of sophisticated petroleum contaminant samplers, will help to ensure that important long-term natural resource damages can be properly evaluated. Without a well thought-out experimental design, findings may have an unacceptably high level of uncertainty.

Implementation of this study's experimental design will make it possible to reduce the level of uncertainty and, therefore, increase the ability to predict the magnitude and extent of impacts to the Sarasota Bay habitat and biota. Research scientists from Mote Marine

Laboratory are collecting and analyzing samples from approximately 50 locations throughout Sarasota Bay. Sampling to obtain baseline information began on June 28, 2010 and will continue for a number of months.

Analysis of these samples will begin in a few weeks and a schedule for obtaining additional data will depend on the likelihood of oil entering this ecosystem. Sediment, water found in sediment (called porewater) and the overlying water are being analyzed using integrative water quality samplers called semi-permeable membrane devices (SPMDs) to mimic the bioaccumulation of organic contaminants found in oil over time. These devices will provide quantitative and qualitative information on petroleum contamination.

Mote is also collecting bottom dwelling organisms (e.g., clams) and taking blood and tissue samples from spotted eagle rays and bottlenose dolphins. All of these samples will be analyzed for levels of petroleum before the spill and, if necessary, after the oil impacts the Bay. This all-inclusive effort is necessary since the consequences to Sarasota Bay could include substantial long-term damage to beaches, inlets, estuaries, salt marshes and the organisms residing there.

Researchers at Johns Hopkins University's Center for Contaminant Transport, Fate and Remediation will use this empirical evidence to develop mathematical bioaccumulation models. These models will demonstrate how contaminants in oil move through the food chain and accumulate in marine plant and animal tissues. Understanding the relationship between levels of organic contaminants in water and in fish and dolphins will give government agencies a powerful tool to quantify natural resource damages. These models will also provide insights into how humans will be impacted if exposed to contaminated seafood.

Scientists from the National Aquarium Conservation Center have been instrumental in developing the experimental design for this research and will continue to play a key role in the interpretation, characterization and communication of the study's findings.

In addition to determining levels of petroleum in water, sediment and biota, bioassays and toxicological studies will be conducted to assess damages to natural resources. Tests will include typical short term 3-5 day acute toxicity tests, as well as, an assessment of chronic impacts on long-term exposures (e.g., pulsed as to replicate the continuing delivery of Deepwater Horizon oil into the gulf).

This type of independent, in depth, site-specific research should probably be considered for other Gulf coast areas which have been, or are likely to be, impacted by the BP spill.

II INTRODUCTION

This scope of work has been prepared to assess natural resource damages to the south west Florida Gulf coast that could result from the Deepwater Horizon oil spill. Oil from this spill has spread significantly from the ruptured well-head and impacted numerous coastal communities in four different states so far with further significant impacts expected. The consequences to south west Florida could include substantial long-term damage to beaches, inlets, estuaries and salt marshes, either from floating oil sheen, mousse, tar balls residual oil slicks, and/or from subsurface oil and dispersed oil-containing water masses.

These insults could occur not only on the west coast of Florida, but if and when the oil from the spill reaches the Gulf Loop Current, the impacts may be felt in the Florida Keys, up the east coast of Florida and beyond to Georgia, the Carolinas, Virginia and Maryland. In anticipation of this exposure, it is critical to understand the current status of the fragile ecosystems within these potentially impacted areas.

III LESSONS LEARNED FROM THE EXXON VALDEZ SPILL

While valuable lessons have been learned from the Valdez spill regarding short-term effects on the ecosystem, long-term population effects on the organisms within those affected areas are not well documented. According to a review of long-term response to the Valdez spill (Peterson et. al, 2003), chronic exposures persist years after an oil spill particularly in sediments. These persistent toxic effects were evident in fish, sea otters and sea birds over the years due to mortality, lower growth rates, decreased reproduction and compromised immune function.

Indirect effects on communities were substantiated, as well, from the exposure to oil and were considered as important as direct trophic interactions (Peterson et. al, 2003). Probably one of the most important lessons learned from the Exxon Valdez spill was a significant change in standard paradigms regarding oil ecotoxicology.

Previously Accepted Models:

a) Oil on shorelines will be rapidly degraded microbially and by exposure to the sun.

b) Oil effects on fish are short term in nature and are restricted to 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, a short-term response.

d) Only the short-term mortality from exposure to oil is important for anticipated losses to submerged aquatic vegetation and invertebrates.

The emerging appreciation:

a) Oil degradation depends upon each unique environment and therefore contamination could occur for years.

b) Long-term exposure of fish embryos shows population level consequences through impaired growth, deformities, reduced reproduction and behavioral changes.

c) Effects of oil exposure on marine mammals and sea birds will compromise health and reproduction, and magnifies environmental stressors with severe consequences.

d) Clean-up attempts (either physical or chemical) can be more damaging than the oil itself by interfering with the strong biological interactions of the cascade of communities, thereby delaying recovery.

There is now an opportunity to apply what has been learned from past oil spill tragedies. Support now exists for the inclusion of a range of physiological, biochemical, and histopathological evaluations of toxicity, facilitated by rapid development of molecular tools to assess sub-lethal effects (NRC, 2002). It is now acknowledged that there is a significantly important cascade of indirect effects on oil exposed ecosystems. These effects need to be assessed thoroughly for understanding impacts to the communities from delayed, chronic and indirect effects of petroleum contamination in the marine environment. By knowing this information and advancing the predictive capacity of ecology, a more confident model of long-term, delayed effects of stressors though ecosystem-based frameworks can be created (Peterson, et. al, 2003).

IV ASSESSING AND PRESERVING SARASOTA BAY

The Sarasota Bay is located on the southwestern coast of Florida, spreading across two counties, Manatee and Sarasota. The bay is characterized by stretches of barrier islands such as Siesta Key and Longboat Key. It is a coastal lagoonal system formed by a necklace of barrier islands to the west and the mainland of Manatee and Sarasota Counties to the east.

This coastal lagoon, with its unique ecological character of small embayments, tidal tributaries and small creeks, coves, inlets and passes, is bounded by Anna Maria Sound to the north and stretches all the way to just north of the Venice Inlet, which serves as its southern boundary. More than 1,400 different native species of plants and animals inhabit the 445 square mile Bay area, 56 miles long with an average depth of 6.5 feet.

Sarasota Bay is made of a series of smaller bays or embayments. Each of these embayments is unique from one another. They differ in overall size, shape and water depth, shoreline features, habitat and sediment characteristics. These unique characteristics lead to differences in water circulation, freshwater inputs, nutrient loads, as well as other consequences for health and vitality. Because of these differences, each embayment must be analyzed and managed independently from the others at the same time recognizing their connectivity (Sarasota Bay Estuary Program, 2010).

This special ecosystem is a small, subtropical estuary currently classified as an outstanding Florida water body and an estuary of national significance. The region is home to a wide variety of marine life, including dolphins, manatees, black mullet, red drum, spotted sea trout, snook, blue crab, stone crab and bait shrimp, oysters, clams, loggerhead turtles, as well as, spotted eagle rays.

However, devastating impacts could occur which significantly alter the biodiversity and integrity of the Sarasota Bay ecosystem as a result of the Deepwater Horizon oil spill. The three main passes (Big Sarasota, New, and Longboat) leading from the Gulf into the Bay will expose the sensitive environments to potential oiling from the spill. Seagrass habitats are among some of the most important habitats in Florida's estuarine environments, indispensable for the role they play in nutrition cycling, primary production, sediment

stabilization and habitat for juvenile and adult finfish and shellfish. Oil from the spill could impact all facets of this and all other habitats with significant long-term effects.

V THREATS TO SARASOTA BAY

Recently**,** concerns have arisen regarding the impact to all flora and fauna residing in the Sarasota Bay area from the *Deepwater Horizon* oil spill. As of July 17, 2010, government estimates of South Louisiana Crude oil in the Gulf from the *Deepwater Horizon* well spill range from 50 million gallons to 145 million gallons. In addition, it has been estimated that BP has used 1.8 million gallons of oil dispersants in the Gulf of Mexico aquatic ecosystem.

At this point, there is no clear prognosis of the toxicity both lethal and sub-lethal, on different organisms in the Gulf environment from these chemical releases. As the oil leak continues, and as more dispersant is applied in an effort to mitigate some of the effects of the spill, there are rapidly escalating concerns over the potential environmental impact on a wide range of plants and animals which rely on the Gulf.

There will be two types of exposure on Gulf organisms from this oil spill. The first is from acute effects which are short term in duration and may have limited impact, or they may have long-term population or community level impacts depending on the timing and duration of the spill and the numbers and types of organisms affected (NRC 2002).

The second exposure is chronic or long-term exposure in which organisms are constantly exposed to low levels of petroleum concentration over a period of at least two years or longer (NRC 2002). Under this latter scenario, it is likely that organisms will be affected at

least the length of a generation or even longer. For long-lived and particularly sensitive species, such as the spotted eagle ray, this may have significant consequences.

The impacts of oil spills on subsurface aquatic populations are difficult to measure, and are usually estimated from counts of mortalities observed immediately afterwards. However, individuals suffering from sublethal effects may not be counted among the number of mortalities, despite potential impacts on the individuals' probability of surviving and reproducing. These impacts, which are normally difficult to measure, would be most profound in populations exposed during early developmental stages (Rosenthal & Alderdice 1976).

Some impacts identified (e.g. NRC 2002) that can occur in the marine environment include: 1) biochemical and cellular; 2) organismal, including the integration of physiological, biochemical and behavioral responses; 3) population, including alterations in population dynamics; and 4) community, resulting in alterations in community structure and dynamics.

Sublethal effects from oil exposure can take the form of reduced growth rates or fertility (alteration of gametes), or increased mortality in larvae and juvenile stages. They can disturb communication between individuals or between them and the environment, causing, for example, an alteration in their migratory behavior. They can also lead to stunted growth, either through a loss of appetite or a reduction in their capability of transforming food into energy. Finally, they can produce various physiological or behavioral changes. These changes can generate a reduction in resistance to stress and the capacity to find or consume food (Heintz, et.al. 2000). The exposure of marine organisms to sites with elevated PAH loads is therefore a cause for concern.

VI STRATEGY FOR ASSESSING OIL CONTAMINATION SARASOTA BAY

Sample matrices

We propose a comprehensive approach to defining the existing petroleum levels in Sarasota Bay. By understanding and documenting the current conditions of the Bay, we can determine qualitatively and quantitatively changes resulting from the *Deepwater Horizon* oil spill and predict possible impacts to the Bay environment and organisms. This plan proposes to collect petroleum level data from pore-water, water column, sediments and selected spotted eagle rays and bottlenose dolphins along with benthic organism filter feeders such as clams and sea-grasses. Once the data from these different matrices are determined, petroleum contamination bioaccumulation and biomagnification models will be developed to demonstrate how these organic pollutants are transported through the food chain.

The proposed method for assessing and water column petroleum concentrations is using a semi-permeable membrane device (SPMD) which was developed by Huckins et al. (1990, 1993) to mimic the bioaccumulation of organic contaminants without the limitations of using bivalves. The SPMDs consist 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 1). 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 levels over the entire time



Figure 1. SPMD in deployment housing.

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 2). 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.

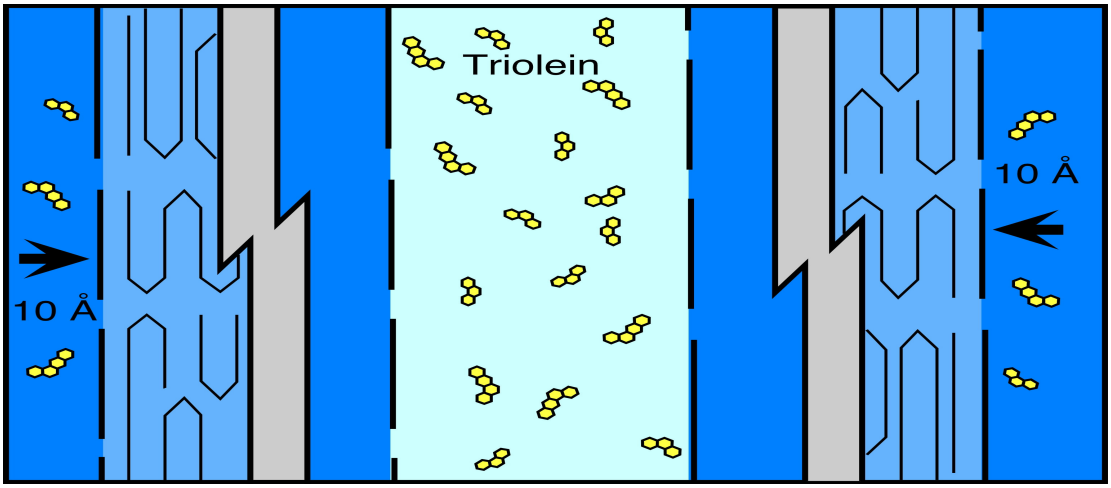


Figure 2. Exploded View of SPMD Device

The SPMDs will be deployed in approximately 50 sampling locations (Figure 3). These locations will be beneath the sediments for assessing pore water and in the water column for measuring petroleum compounds for a period of three weeks before recovery and petroleum analysis. Bivalves and sea grasses will be collected from the same or nearby areas for petroleum level evaluation and compared with the data obtained from the SPMDs. Additionally, tissue and blood samples will be taken from spotted eagle rays and bottlenose dolphins. These matrices will also be analyzed for petroleum contamination. Once petroleum concentration measurements have been obtained for the pore-water, water column, sediments, bivalves, sea grasses, spotted eagle rays and dolphins, the information will be used to develop a model of bioaccumulation for these toxic organics.

VII ANALYTICAL METHODS

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. Sulfur interferences are removed from the extracts following EPA Method 3660B using tetrabutylammonium (TBA) hydrogren sulfite reagent. Samples are then analyzed for polycyclic aromatic hydrocarbons (PAHs) on an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass selective detector (EPA Methods 8260B and 8080). Total petroleum hydrocarbons (TPHs) are analyzed and quantified on a Varian 3800 GC using a Flame Ionization Detector (FID). 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.

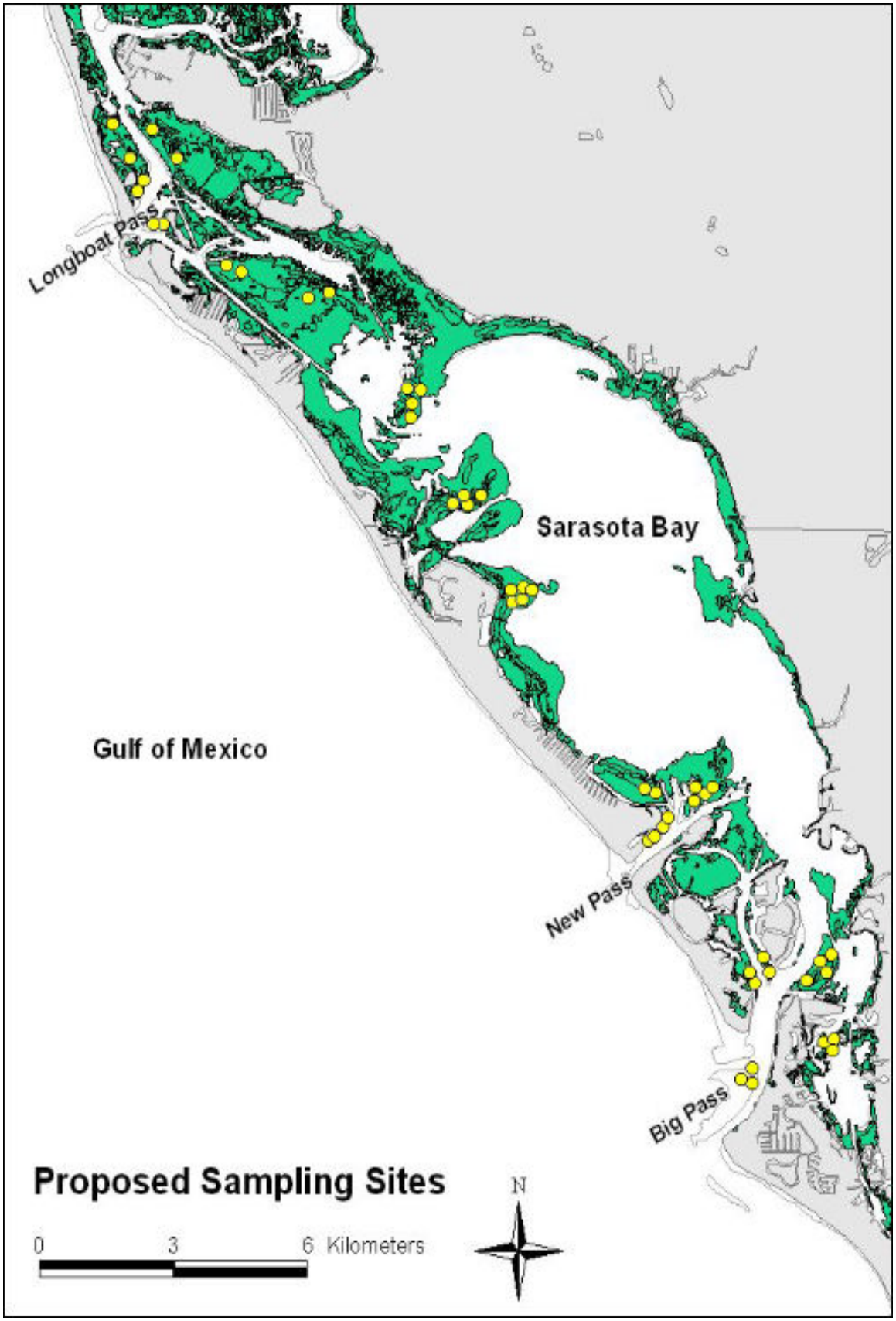


Figure 3. Sampling Site Locations in Sarasota Bay for SPMD deployments, sea grasses and bivalves.

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.

There will be a total of 100 triplicate SPMDs deployed in Sarasota Bay for a period of three weeks. We anticipate approximately 25 spotted eagle ray samples of both blood and tissue, and we will be analyzing dolphin tissue opportunistically. All samples will be extracted and analyzed according to standard methods and using gas chromatography-mass spectrometry for 57 parent and homolog polycyclic aromatic hydrocarbons.

VIII DEVELOPMENT OF BIOMARKERS

There is a critical need to use biomarkers for both exposure and effects of various stressors or stressor pathways. First, they empirically assess effects of a stressor, rather than simply allowing scientists and managers to acknowledge that an organism has been exposed to something potentially, but not necessarily, harmful. Second, many biomarkers are extremely sensitive, allowing scientists to document the onset of harmful effects long before the critical stage is reached.

Some of these biomarkers can be used to determine impacts on fertility potential of exposed organisms, assess negative consequences on immune function and ascertain possible DNA damage. While knowing contaminant levels in the environment is useful, understanding bioaccumulation pathways and residence times of various contaminants is critically important. It is determining the long-term costs of exposure to contaminants which is ultimately the aspiration of all environmental health investigations.

IX MODEL FOR BIOACCUMULATION OF ORGANIC CHEMICALS IN BENTHIC ORGANISMS

Hydrophobic organic compounds [1](HOCs) 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 in aquatic environments. Total HOCs in sediments have often used to estimate the accumulation of HOCs to benthic organisms using equilibrium partitioning theory (Blermann, 1990).

The theory utilizes thermodynamic relations between the POC in sediment and lipids in organisms to estimate the distribution of HOCs. The theory leads to the following biota-sediment accumulation factor (*BSAF*) as a measure of the HOC's bioaccumulation potential (McFarland, 1984):

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

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 HOCs concentrations have been developed which correspond with observed bioaccumulation of HOCs in biota (Lampert, 2010). The $BSAF_{sediment}$ can be updated by a direct measurement of porewater HOCs using an *in-situ* passive sampler, such

[1] Such as Polycyclic Aromatic Hyrdrocarbons (PAHs), Polychlorinated Biphenyls (PCBs), Polychlorinated dibenzodioxins (or simply dioxins), Dichloro-diphenyl-trichloroethylene (DDT), Perfluorinated surfactants including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS).

as a Semi-Permeable Membrane Device (SPMD). The corresponding equation for $BSAF_{porewater}$ is as follows:

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

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 HOCs to sediments (Karickhoff et al., 1979):

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

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 HOCs in sediments, while $BSAF_{sediment}$ can be a useful bioaccumulation indicator in areas where SPMD cannot be deployed.

X MODEL FOR BIOMAGNIFICATION OF HOCs IN FOOD WEBS OF THE SARASOTA BAY ECOSYSTEM

HOCs tend to be biomagnified through trophic transfer resulting in higher concentrations of HOCs in predator organisms compared to their prey (Gray, 2002). To assess the biomagnification of HOCs in foodwebs of the Sarasota Bay ecosystem, 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. A similar approach was recently used in the Sarasota Bay foodwebs to study biomagnification of perfluoroalkyl compounds (Houde et al., 2005). Since the foodwebs in Sarasota Bay are not yet affected by the BP oil spill, the model above employs a steady state *BMF* as the ratio of the lipid normalized chemical concentrations in the whole bodies of the predator and prey, respectively.

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 (Morrison et al., 1997; Fraser et al., 2002; Serrano et al., 2003; 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).

The timeline is short for assessing the conditions before the oil spill to form a baseline for any future changes that could happen if the oil spill impacts the Sarasota Bay. Therefore, the equations above will be employed for this rapid response study. If the oil spill should impact the Sarasota Bay and transient dynamics of the *BMFs* are observed, the more sophisticated and mechanistic biomagnification models will be considered for future modeling efforts.

Considerations for the experimental design to facilitate the modeling

- In assessing biomagnification of HOCs, it will be necessary to normalize the chemical concentrations in whole fish by the lipid content of the fish. Body concentrations of organic compounds vary with lipid content, and thus in order to compare across species, normalization to uniform lipid content will be necessary (Gray, 2002).

- Appropriate relationships, approaches or calibrations are necessary to estimate the porewater HOCs concentrations from the SPMD measurements.

- A previous study (Houde et al., 2005) quantified the trophic levels in the Sarasota Bay ecosystem using stable isotope analysis (^{15}N). Based on this analysis, the following species are recommended for target species to be sampled in this effort: zooplankton, sheepshead (*Archosargus probatocephalus*), pigfish (*Orthopristis chrysoptera*), pinfish, striped mullet and spotted seatrout**.**, spotted eagle ray and dolphin**.** In addition, sediments and benthic organisms, such as crab and shellfish, are recommended to be sampled for evaluating the *BSAF*.

- A sample size of between 10 and 15 is recommended for appropriate statistical analysis.

XI Budget

The costs of sampling, analysis, developing bioaccumulation and biomagnification models, interpreting data and preparation of reports related to pre-existing conditions in Sarasota Bay

will be approximately $200,000. The National Aquarium has provided the funds for this 1st phase of the project.

In the event that oil from the BP spill enters this aquatic ecosystem, there will be the need to have additional phases for this research which may last over an extended period of time. If needed, acute and chronic toxicity testing would also increase the costs of this research.

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