Letter of intent: Did the Macondo 252 oil spill results in large scale perturbations of the NGoM ecosystem structure and function?

# Oil spill hydrocarbons enhancing microbial respiration and summer hypoxia in the Mississippi Bight*

*) Phase 1 of this GRI/BP proposal was part of a larger effort "Monitoring and Assessment of Potential Impacts of Oil Contamination on Coastal and Marine Ecosystems in the northern Gulf of Mexico". Participants in a subsection of that proposal kept to activities and deliverables stipulated in the original proposal, and these are the preliminary results reported here.

**Lead-PI: Kjell Gundersen; Co-PIs: Karen M. Orcutt, Stephan Howden**
Institution: The University of Southern Mississippi, Department of Marine Science
Duration: January 1st – December 31st, 2011 (12 months); Budget: $187,760
Cluster 1 – Observe (60%); Cluster 2 – Understand (40%)

**INTRODUCTION** – The Gulf of Mexico region provides approximately half the amount of total U.S. production of crude oil, natural gas, and has a major part of the commercial seafood landings (NOAA 2008, http://gulfofmexicoalliance.org/pubs_links/welcome.html). Stressors to the region include population growth causing a growing seasonal hypoxia on the LATEX shelf and in other regions (Rabalais et al. 2007, Estuaries & Coasts 30: 753–772), harmful algal blooms (e.g. Stumpf et al. 2003, Harmful Algae, 2: 147-160), tropical cyclone impacts, and coastal subsidence (Shinkle & Dokka 2004, NOAA Tech. Rpt. NOS/NGS 50, 67pp). Ecosystem metabolism, driven by available organic and inorganic nutrients, is an important end-point indicator for water quality and health of estuarine systems. Generally, when consumption of oxygen exceeds the rate of DO production, hypoxia (<2mgDO/L) or even anoxic (no oxygen) conditions may develop. The daily budget of net primary productivity (netPP) and respiration (RESP) in the Mississippi Sound (Fig.1) shows that there is a delicate balance between autotroph production and heterotroph consumption in coastal waters off Mississippi. Another threat to environmental health and productivity in the northern Gulf of Mexico region manifested itself with the Deepwater Horizon event (April-August, 2010) leading to a discharge of more than 200 million gallons of crude oil (plus a significant amount of chemical dispersants) into the environment. Crude oil components are polycyclic aromatic hydrocarbons (PAH) and the higher molecular weight compounds are toxic to living organisms (Collins et al. 1998, Regul. Toxicol. Pharmacol. 28:45-54). Lower molecular weight PAH compounds are utilized by microbial communities as a source of carbon. Catabolism of PAH (by the enzyme dioxygenase) requires oxygen and is one of the major pathways of eliminating hydrocarbon pollutants from the environment (Cerniglia 1984, In: Petroleum Microbiology [RM Atlas, ed.], MacMillan Publishing). Therefore, biodegradation of hydrocarbons derived from oil spills may increase the rate of heterotrophy further exacerbating the balance between netPP and RESP into the negative.

Since the oil spill event itself appeared to have a low impact on netPP and RESP in the MSound, we propose to expand the field incubations further offshore (NGI st.8 and the Chandeleur Sound) to reach areas that had a higher influx of crude oil during the event. We hypothesize that traces of sedimented crude may still have an impact on benthic netPP and RESP and, during vertical mixing of the water column, this may also impact water column production and consumption of oxygen. Furthermore, oil may also impact the water column through seepage/diffusion from surrounding salt marshes that are still heavily loaded with crude residue.

The broader regional impact of this study will give us a better understanding of the biological response by micro-plankton to hydrocarbons derived from a long term oil spill event. The proposed work will support regional environmental monitoring and develop scientific assessment tools. Knowledge of biogeochemical parameters controlling hypoxia in this region will help resource managers determine targets set for "dead zone" reductions on the LA and MS shelf. Our work will further regional coordination to reduce hypoxia in the GOM providing a critical link between man-made hydrocarbon spillage, nutrient concentrations and nutrient loading on temporal and spatial scales.

**PRELIMINARY RESULTS** – Field results of netPP and RESP are shown with oil-in-water (OIW) determinations (Fig.1) from Henderson Point in the Mississippi Sound (MSound). We found an inverse relation between OIW and RESP, but the measured rates of netPP and RESP never exceeded expected seasonal variability. The OIW concentrations we measured in the western MSound never exceeded 5 ppm (range 2.4-4.9 ppm) during the study period (Fig.1, not all stations shown). In comparison, the MARPOL Convention requires that oil tanker effluent water does not exceed 15 ppm**. It appears that OIW concentration in the western MSound never exceeded environmentally significant levels during our sampling. The student in charge of DNA determinations of PAH dioxygenase (not paid by this grant) was called in for Coast Guard duty (August-November this year) and will process the molecular samples in December. Dioxygenase samples were collected from NGI stations 2, 5 and 8 prior to, throughout and after the oil spill event this year and will be analyzed by quantitative PCR. (qPCR).

(**) http://www.bsh.de/en/Marine_data/Environmental_protection/MARPOL_Convention/Discharge.pdf

**METHODS** – Further proposed work will take place in conjunction with the monthly NGI transect cruises and the time-series core data from this program will be used to support the work in this proposal (Tab.1). These activities adds approximately 15 min to the time spent on each of the selected NGI stations and, as such, does not add significant time to each of the time-series stations. Additional incubations and samples will be collected twice from a selected site in the Chandeleur Sound by a ship-of-opportunity, where significant amounts of oil were observed during the oil spill event.

Data Collection – The work will be expanded to include 3 selected stations where netPP and RESP will be measured in-situ using optode DO sensor technology (Aanderaa Instruments, Norway) in surface waters and at the sediment-water interphase using a bell jar. Further sampling of OIW (TD500D hydrocarbon analyzer) and DNA for PAH dioxygenase (Ni Chadhain et al. 2006, Applied Environmental Microbiology 72:4078-4087) will be done from surface waters and the benthic sediment (Tab.1).

Adaptive sampling – From a selected site in the Chandeleur Sound, additional incubations and samples (same as on each NGI station visit) will be collected during the field period. This work is depending on access to ships-of-opportunity and other environmental sampling done in the shallow (<10 m) regions closer to the Horizon platform site, where significant amounts of oil were observed during the oil spill event. The additional site will be visited at least twice during the sampling period.

Data archival, data analysis & interpretation – All the data generated in this project will be made available through the data archives generated by the Northern Gulf Institute (NGI) at USM. In-situ incubation data (netPP and RESP) will be used to compute the seasonal significance of daily biological DO production and consumption in the water column and in sediments of the MSound, MS Bight and in the Chandeleur Sound. Biological production and consumption of DO is missing in the NGI core data sets and hence, these measurements will greatly compliment local hydrography and the calculated air-sea exchange and gas diffusion estimates (the only current tools available) used to evaluate seasonal hypoxia in the region. Combined with specific environmental parameters (OIW and the dioxygenase gene) the proposed work will also provide metrics of the significance of remaining oil in shelf waters NE of the Horizon platform and in local MS waters.

Collaborators & complimentary, ongoing, funded programs – The proposed continuation of our work is expanding the field sampling to include more offshore stations and a separate benthic oxygen consumption component. This activity will compliment current collaborators within the NGI program at USM (Dr. Rakocinski, GCRL) and a number of potential collaborators identified within the GRI/BP phase1 initiative (e.g. Drs. Brunner & Yeager). Coastal surface current measurements and trajectory analysis generated in two companion proposals (Dr. Howden – Coastal Observation Platform in Support of Characterization of Oil Extent and Transport; Dr. Nechaev – Implementing and Advanced Algorithm for Monitoring the Surface Circulation in the Northern Gulf of Mexico) will provide the necessary context for sampling stations selected and greatly aid us in our dissolved oxygen assessments of the water column (gas diffusion versus biological modifications of DO). The proposed study will also be supported by results from a number of ongoing programs: The NASA GSRP Fellowship awarded to Ryan Vandermeulen (Dr. Gundersen – Nutrient Criteria and Primary Productivity Driving Ocean Color Distribution Observed by Remote Sensing in the Mississippi Bight) and the NGI initiative granted to DMS at USM (Dr. Howden – Monitoring and Assessment of Coastal and Marine Ecosystems in the Northern Gulf).

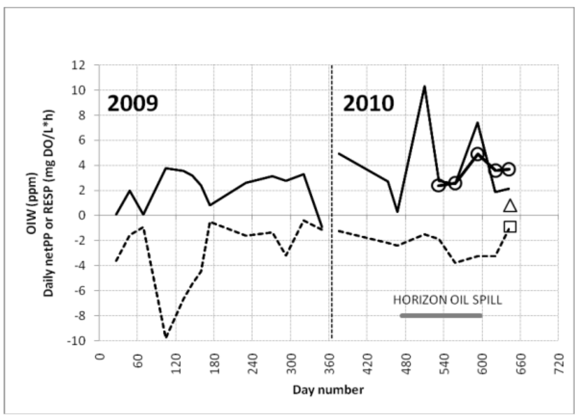


Figure 1 – Net primary productivity (Net PP; whole line) and respiration (RESP; broken line) in surface waters at Henderson Point in the Mississippi Sound, from January 2009 to October 2010. For comparison, netPP (open triangle) and RESP (open square) in October 2010 from NGI st.5, immediately south of Cat Island, is also shown to demonstrate the low productivity (but equally high respiration) outside the barrier islands.
Oil-in-Water concentrations (OIW; open symbols) were measured in surface waters from June-October. The duration of the Horizon oil spill event (grey horizontal bar) lasted approximately 4 months.

Table 1 – Overview of samples collected during monthly visits to the Mississippi Bight region (NGI transect) and the proposed monthly monitoring parameters (surface waters and the benthos).

| | |
|---|---|
| Water samples: | Sensor profiles: |
| Salinity (S) | SeaBird (S, T, DO) |
| Dissolved Oxygen (DO) | In-Situ (Troll 9500) Turbidity, pH |
| Nutrients (NO3, NO2, NH4, PO4, SiO3) | Optics FL3 (Chl-a, CDOM, Phycoxanthin) |
| HPLC pigments | Optics BB9 (Turbidity back-scatter) |
| Chl-a (total fluorescence) | Optics AC9 (Absorbance, Attenuation) |
| Trace Metals | |
| Dryweight (TPM), DOC, DON | |
| | |
| Surface waters + benthic sediment (this study): | |
| DO incubations (Aanderaa optode) | PAR water column profiling + daily surface |
| Dryweight (TPM), Chl-a (total fluorescence) | Nutrients (NO3, NO2, NH4, PO4, SiO3) |
| DNA for PAH dioxygenase (qPCR) | OIW, total PAH (Turner Design TD500D) |