UNIVERSITY OF MIAMI (RSMAS):

"Resolving chemical properties and extent of crude oil dispersant distribution in the Deepwater Horizon Oil Spill"

Rod G. Zika and Daniel Riemer

SCIENCE ACTIVITIES

1) General Summary

Narrative (1 pages maximum): Please provide a brief overview of the project and goals supported during the conduct of this project. Be sure to highlight any 'lessons learned' that could be applied to other/future oil spill related projects (e.g., management, data support, logistics, etc.). Listing accomplishments against project activities, objectives and milestones in bulleted form is acceptable.

This project is designed to follow the transformation and distribution of the crude oil and the applied dispersants in the impacted region of the Gulf of Mexico and the projected path of the oil plume, using a novel fluorescent technique combined with computer modeling.

This study focused on the Macondo crude source oil (as reference) in developing a fluorescence-based monitoring tool for PAH after the deepwater Horizon Oil spill in the Gulf. Some of our accomplishments are as follows:

- Identified seven types of fluorophores that can potentially be used as a tracer of selected PAHs from the Deepwater Horizon oil spill
- Identified a fluorophore that might be of use to trace the dispersant in the water column
- Identified similarity of selected fluorophores with authentic PAH standards
- Identified elevated crude oil fluorescence located west of the southwest Florida Shelf during the October 3-13, 2011 research cruise. Elevated sea surface crude oil fluorescence was also observed near the DeSoto Canyon.

Compared to recently published data, use of excitation-emission fluorescence spectroscopy is a simple technique to monitor fluorescent compounds in oil spills. However, in order to resolve the derived fluorescent components, correlation of components with mass spectroscopic measurements is necessary.

Currently, we are still working on some of the large datasets obtained during the research cruise. The next step of this work is to determine the efficacy of EEM and PARAFAC analysis in distinguishing the Macondo crude oil from other crude oils (e.g., Arabian Crude, North Slope Crude, South Louisiana Crude) by correlating it with the GC-MS analysis. A quantitative approach of estimating crude oil in the water column using the derived fluorescent components will be worked on.

It is also recommended that fixed sampling stations be established in order to determine changes of the oil components distribution in the water column. Establishing a standard method using fluorescence methods for monitoring is a simple and cheaper means for long-term measurement in the Gulf of Mexico.

2) Results and scientific highlights

Narrative (2 pages maximum): This should be a summary of significant results (positive and negative) and conclusions during the conduct of this project. Listing science results and highlights in bulleted form is acceptable. In each case, please explain the impact of the result.

We evaluated the use of excitation and emission matrix (EEM) fluorescence and parallel factorial analysis (PARAFAC) modeling techniques for monitoring crude oil components in the water column. Four of the seven derived PARAFAC loadings were associated with the Macondo crude oil components. The other three components were associated with the dispersant, an unresolved component and colored dissolved organic matter (CDOM). The fluorescence of the associated benzene and naphthalene-like components of crude oil components exhibited a maxima at ~1200 m. Fluorescence measurement observed abundance of naphthalene-like enriched fluorescent component northeast from the wellhead. The benzene-like/arene-like component was more abundant south and southwest near the blowout well compared to the naphthalene-like component. Mechanisms that govern this spatial variability are unknown and needs further investigation.

On the other hand, the fluorescence of the associated benzene-like component exhibited a maximum at ~1100 m at the south and southwest stations. The maximum fluorescence of the component associated with the dispersant (i.e., Corexit EC9500A) was also observed at the same depth. The plume observed at this depth was attributed to the dispersed crude oil from the Deepwater Horizon oil spill. Results demonstrate use of EEM and PARAFAC use to monitor simultaneously selected crude oil groups, dispersant and humic-like components in the water column. This can have an impact in an effective monitoring of true oil components and distribution in the water column using fluorescence methods.

The maximum fluorescence of the component associated with the dispersant (i.e., Corexit EC9500A) was observed at the same depth. The plume observed at this depth was attributed to the dispersed crude oil from the Deepwater Horizon oil spill. Results demonstrate use of EEM and PARAFAC to simultaneously monitor selected PAH fluorescent, dispersant and humic-like components in the oil spill region in the Gulf of Mexico.

Form the October 3-13, 2011 research cruise. The potential hydrocarbon levels of the hydrocarbon in seawater in the Gulf of Mexico were monitored using fluorescence sensors (Figure 1). The oil fluorescence near the DeSoto Canyon was more elevated than the fluorescence near the Deepwater Horizon site. This is indicative of possible oil northeast transport from the 2010 Deepwater Horizon oil spill location. There is also an observed elevated oil fluorescence west of the southwest Florida Shelf. CDOM fluorescence showed similar fluorescence in the same stations (not shown). Because of this result, the presence of oil in this sampling track cannot be confirmed. The collected seawater samples using multi-dimensional fluorescence and GC-MS will confirm the source and composition of any oil present in these sampling sites.

We already have optimized the GC-MS in the lab and have analyzed selected PAH composition of the Macondo source crude and other crude oils. We will use these standardized profile to calibrate and calculate PAH concentrations in seawater samples that were likely contaminated with the spilled Macondo crude oil.

We also have analyzed the Corexit EC9500A profile and determined potentially the compounds that are responsible for its fluorescent property. Knowing these conjugated compounds will allow us to develop a possible standard that can be used for quantitatively estimating Corexit directly in seawater using fluorescence technique.

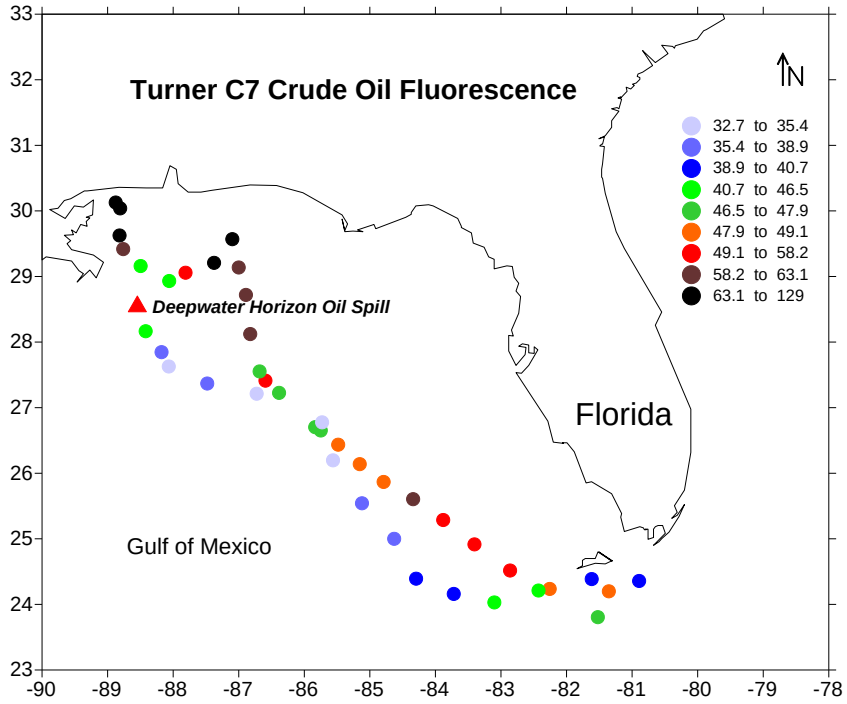

Figure 1. Elevated crude oil fluorescence located west of the southwest Florida Shelf. Elevated sea surface crude oil fluorescence was also observed near the DeSoto Canyon.

Ship or Platform Name	**Class** (if applicable)	**Chief Scientist**	**Objectives**	**Dates**
R/V Walton Smith		Wilson Mendoza	Collect water samples from Miami to the Deepwater Horizon Oil spill site	October 3-13, 2011

3) Peer-reviewed publications, if planned (Note: a special section will focus on student and post-doctoral publications)

   a. *Published, peer-reviewed bibliography (Copies of the papers are requested)*
   b. *Manuscripts submitted or in preparation (Please note target journal, and anticipated date of publication or submission)*

Manuscript submitted:

Wilson G. Mendoza, Daniel Riemer, Rod Zika (submitted). Application of fluorescence and PARAFAC to assess vertical distribution of subsurface hydrocarbons and dispersant during the Deepwater Horizon oil spill. *Journal of Environmental Monitoring* (Royal Society of Chemistry Publishing)

Expected publication: April-June 2013

4) Presentations and posters, if planned (Please provide copies of each) (Note: a special section will focus on student presentations)

Title	Presenter	Authors	Meeting or Audience	Abstract published (Y/N)	Date
Tracking of the Deepwater Horizon hydrocarbons and the dispersant in the Gulf of Mexico using EEM and PARAFAC modeling Copy of abstract (see link): http://www.sgmeet.com/osm2012/viewabstract2.asp?AbstractID=10073	Wilson G Mendoza	Rod Zika, Daniel Riemer	Ocean Sciences Salt Lake, Utah	Y	2/23/2012

5) Other products or deliverables

Please list (for example: maps, models, tools) and indicate where they can be located/obtained.

Maps of the October 3-13 R/V Walton Smith research cruise
Contact: Wilson Mendoza (wgmendoza@ucsd.edu)

6) Data

Please provide a spreadsheet indicating the metadata and ancillary information on the location and status of the archived samples. Also, indicate if there are any issues with respect to data archiving schedule and plan. If you have a lot of metadata, representative samples will suffice. This will all be incorporated into the GoMRI database at some point in the future.

We can provide a spreadsheet of our metadata until we analyzed and correlated the fluorescence components derived from PARAFAC modeling with the GC-MS data.

Contact: Wilson Mendoza (wgmendoza@ucsd.edu)

PARTICIPANTS AND COLLABORATORS

7) Project participants

Please list the participants of your project, their role(s) and contact information. No personal information will be released.* ***Note: Student/educational information will be collected elsewhere in this report****.*

** We understand one person may fulfill more than one role; please list all applicable roles using the following standardized titles: Principal Investigator, Co-Principal Investigator, Scientific Participant, Technician, Lab Assistant, Administrative Support.*

First Name	Last Name	Role in Project	Institution	Email
Rod	Zika	PI	UM (RSMAS)	rzika@rsmas.miami.edu
Daniel	Riemer	Co-PI	UM (RSMAS)	driemer@rsmas.miami.edu
Wilson	Mendoza	Graduate student/Postdoc	UM (RSMAS)	wmendoza@rsmas.miami.edu
Lilian	Custals	Research Technician	UM (RSMAS)	lcustals@rsmas.miaim.edu

MENTORING AND TRAINING

8) Student and post-doctoral participants

Please list the student participants of your project, their educational role, and other information. No personal information will be released.

First Name	Last Name	Post-doc / PhD / MS / BS	Thesis or research topic	Institution	Supervisor	Expected Completion year
Wilson	Mendoza	PhD	Application of 3D-Fluorescence and PARAFAC Modeling in Marine DOM Investigations	UM (RSMAS)	Rod Zika and Daniel Riemer	May 2012
Wilson	Mendoza	Postdoc		UM (RSMAS)	Rod Zika and Daniel Riemer	June-Dec 2012

9) Student and post-doctoral publications, if planned

a. Published, peer-reviewed bibliography (Copies of the papers are requested)
b. Manuscripts submitted or in preparation (Please note target journal, and anticipated date of submission or publication)

1. Wilson G. Mendoza, Daniel Riemer, Rod Zika (submitted). Application of fluorescence and PARAFAC to assess vertical distribution of subsurface hydrocarbons and dispersant during the Deepwater Horizon oil spill. *Journal of Environmental Monitoring* (Royal Society of Chemistry Publishing)
Expected publication: April-June 2013

2. Mendoza, Wilson G., "Application of 3D-Fluorescence and PARAFAC Modeling in Marine DOM Investigations" (2012). *Open Access Dissertations.* Paper 753.
http://scholarlyrepository.miami.edu/oa_dissertations/753

10) Student and post-doctoral presentations and posters, if planned (Please provide copies of each)

Title	Presenter	Authors	Meeting or Audience	Abstract published (Y/N)	Date
Application of 3D-Fluorescence and PARAFAC Modeling in Marine DOM Investigations http://scholarlyrepository.miami.edu/oa_dissertations/753	Wilson Mendoza	Wilson Mendoza	Dissertation defense UM(RSMAS)	N	May 2012

11) Images

Please attach high-resolution images and provide details including a description of the image, location, credit, date, etc. Of note: Image may be used in FIO or GoMRI promotions, so please make sure you have rights to use the image.

Image 1. CTD/Rosette deep water cast. Seawater samples were collected in 1 liter glass bottles. (FIO-BP R/V Walton Smith Cruise; Oct 3-13, 2011; photo credit: Marlena Skrobe).

Image 2. We monitored surface and water column physical and chemical seawater profiles (FIO-BP R/V Walton Smith Cruise; Oct 3-13, 2011; photo credit: Marlena Skrobe).

Image 3. Collection of water samples from the Niskin bottles
(FIO-BP R/V Walton Smith Cruise; Oct 3-13, 2011; photo credit: Marlena Skrobe).

13) Continuing Research

If you are continuing this research under another grant, please include granting authority and title of award and a very brief synopsis (2-3 sentences).

There is no current funding, however as time permits we are working on our data archives in preparation of additional publications.