TRACING THE INTRUSION OF THE GOM-2010 OIL SPILL ON COASTAL AND MARINE FOOD WEBS WITH NATURAL ABUNDANCE RADIOCARBON (^{14}C) AND STABLE ISOTOPES (^{13}C, ^{15}N & ^{34}S)

A collaborative project
Florida State University and Florida A&M University
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SCIENCE ACTIVITIES

1) General Summary

The Deepwater Horizon oil spill in the northern Gulf of Mexico (GOM) was a large-scale tracer release. The isotopic signature of the carbon entering the marine environment from the spill provides a means of tracing the immediate and long term effects of the spill on coastal food webs. Understanding the extent of incorporation and the assimilation pathways allows us to trace the long-term effects of the spill on coastal ecosystems.

Living biomass is imprinted with a $\Delta^{14}C$ signature which is set by carbon fixation from atmospheric CO_2. This living biomass has slightly greater radiocarbon content than "modern" due to nuclear weapons testing in the 1950's and 1960's which produced an abundance of ^{14}C in the atmosphere. Currently this value is around +106% of modern, but it can vary locally in coastal waters due to variation in the importance of terrestrial inputs or upwelling of older deeper water including contributions from sediments. The carbon added from the oil spill will be free of radiocarbon inputs or 0% modern.

Our project is to investigate the near-term effects of the spill on Gulf coast ecosystems, with a particular emphasis on the food web dynamics that support major fisheries in the Gulf by using ^{14}C (radiocarbon) and ^{13}C, ^{15}N & ^{34}S to (1) trace the oil, its derivatives, as well as dispersants and methane through coastal and offshore food webs, and (2) evaluate spill-associated shifts in the structure and function of these food webs. Our plan is to examine the isotopic signatures of surface sediments, dissolved inorganic carbon and dissolved and particulate organic carbon in the water column, algae, seston, and consumer organisms across an impact gradient along the Gulf coast from Florida to Louisiana. Results of plankton studies are reported in Chanton, Cherrier et al., (2012).

This grant has currently supported 2 FAMU graduate students thesis/dissertation research: Judith Sarkodee-Adoo (M.S.) and Tiffany Baskerville (Ph.D). Ms. Sarkodee-Adoo has completed her MS degree and is currently employed in New York at Queens College, CUNY. Ms. Baskerville will defend her dissertation prospectus at the end of the fall 2012 semester. Both students have made excellent progress with their research and both have presented their data at national meetings. Ale Mickel was an undergraduate who also worked on the project while at FSU. She is working part time as a lab assistant. Tyler Mauney, and Alex Harper are greaduate students at FSU who worked on this project. Ms. Harper finished her MS degree in the Spring of 2012 and has gon on for a PhD.

2) Results and Scientific Highlights

Carbon isotopes provide a powerful tool for tracing oil into marine food webs. We have employed natural stable and radio carbon isotope abundances to observe oil across two potential impact gradients: coastal and offshore. The coastal gradient included sites in: Barataria Bay, LA;

Pensacola Bay, FL; and Apalachicola Bay, FL ranging from heavily to negligibly impacted. The offshore gradient consisted of sites along a cruise transect off the Florida shelf, across Desoto Canyon, and out to the Deepwater Horizon site. $\Delta^{14}C$ and $\delta^{13}C$ signatures of animal tissues were evaluated along with respective potential prey items. Other vectors were evaluated (DIC, DOC, POC) to determine the route by which the oil may have entered the food web.

1. The isotopic composition of DIC (dissolved inorganic carbon) represents the influences of ecosystem respiration in addition to atmospheric exchange. Atmospheric exchange will yield values with modern $\Delta^{14}C$ signature, +30 to +40‰. We have defined this value with measurements of surface DIC from un-impacted Bays. In impacted estuaries, we observed ^{14}C and ^{13}C depleted carbon in the DIC (Figure 1). Barataria Bay represents an impacted Bay while Pensacola Bay and Apalachicola Bay are un-impacted. Pensacola Bay and Apalachicola Bay samples were not different from surface water DIC in the open Gulf.

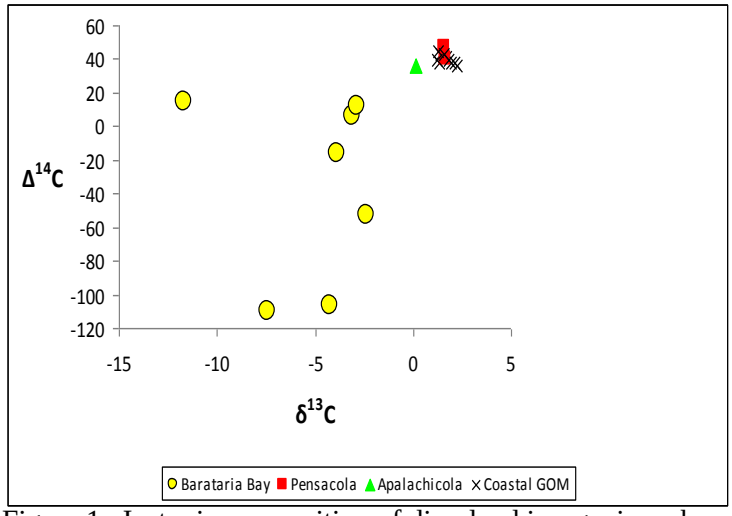

Figure 1. Isotopic composition of dissolved inorganic carbon in surface waters.

We have also examined the composition of DIC in the deep Gulf (Figure 2), which varies from surface values of +40‰ to as low as -100‰ at depth, approaching 1000 radiocarbon years old. It is not known to what extent this deep DIC is due to respiration of petro-carbon associated with the oil spill, but over time we will continue to monitor it to see if it becomes more enriched in 14C.

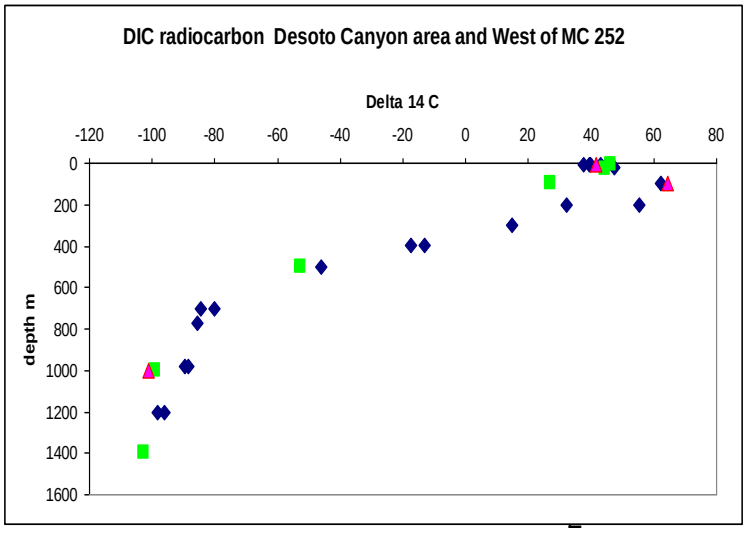

Figure 2. DIC isotopic composition at various sites in the Gulf shows respiration of older carbon at depth. As no such profiles were measured before the oil spill, it is not know to what extent this profile is due to respiration of petro-carbon and natural gas associated with the spill but continued measurements will shed light on this question.

Particulate organic matter at depth in the Gulf was depleted in ^{13}C and ^{14}C, suggesting its origin from oil spill carbon (Figure 3 and 4). The $\delta^{13}C$ of the POC was as negative as -37‰ suggesting a methane based carbon input as suggested by Chanton, Cherrier et al., (2012) for petro inputs phytoplankton (see also Graham et al., 2011).

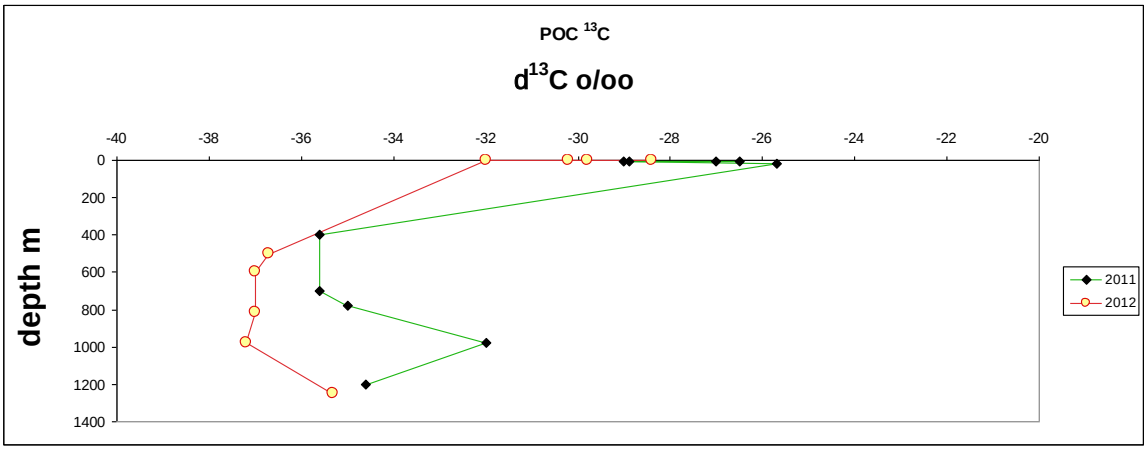

Figure 3. The $\delta^{13}C$ of POC in the Desoto Canyon transects in 2011 and 2012 suggests an input from methane carbon.

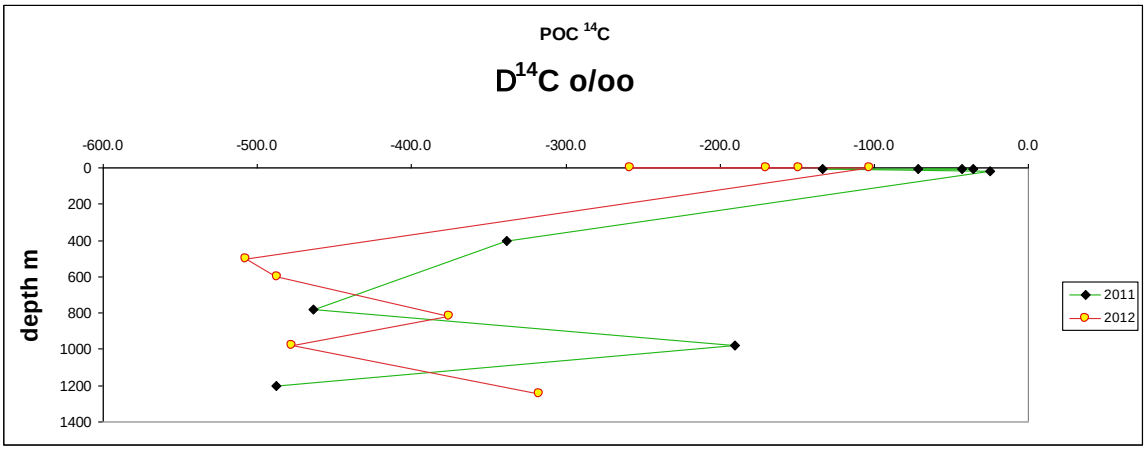

Figure 4. The $\Delta^{14}C$ of POC was significantly depleted in radiocarbon, consistent with the input of fossil carbon approaching 50%. The most depleted values were -500‰ consistent with half of the carbon entering the POC with a value of -1000‰.

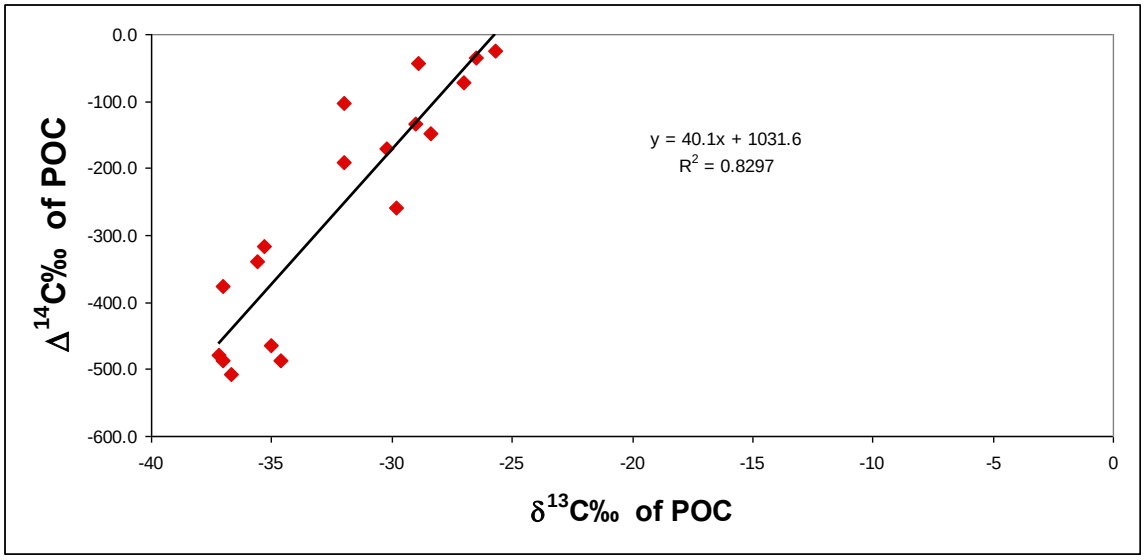

Figure 5. Correlation between ^{13}C and ^{14}C in the POC suggests a fossil methane input with a $\delta^{13}C$ value of about -51‰.

Interestingly, as for plankton (see Chanton, Cherrier et al., 2012), there was s significant correlation between $\delta^{13}C$ and $\Delta^{14}C$ of the POC (Figure 5). When the equation fit to the data was solved for the $\delta^{13}C$ input that would results in radiocarbon dead POC (-1000‰) a very methane like value of -51‰ was obtained. Crespo-Medina et al., (in prep) reported a methane $\delta^{13}C$ value for Macoando methane of -56‰.

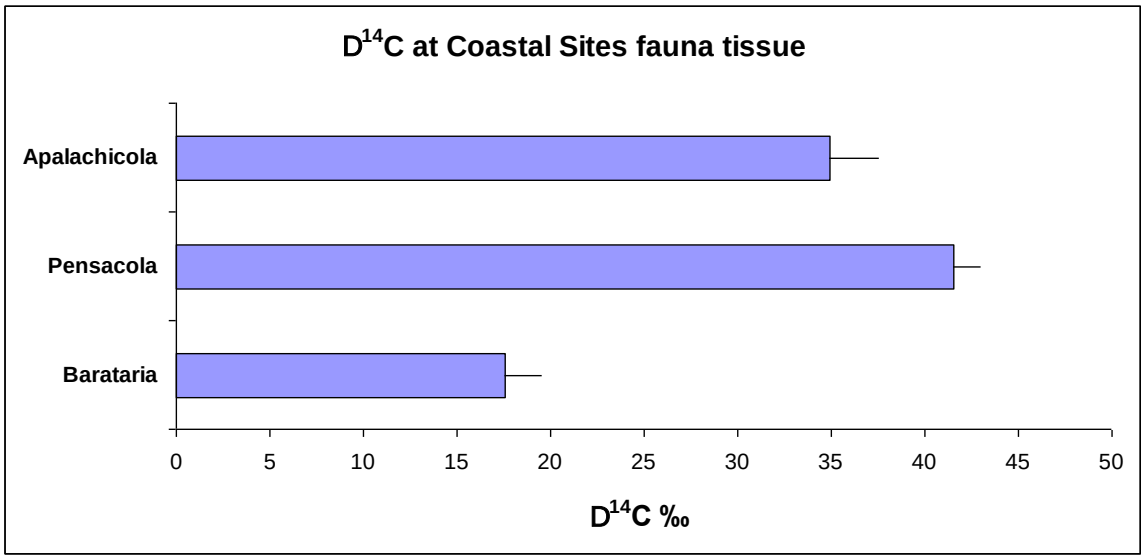

Figure 6. Radiocarbon values of coastal fauna.

We observed radiocarbon depletion in coastal fauna in Barataria Bay (Figure 6) but this was not observed in fauna in Pensacola Bay or in Apalachicola Bay or in offshore fauna (data not shown).

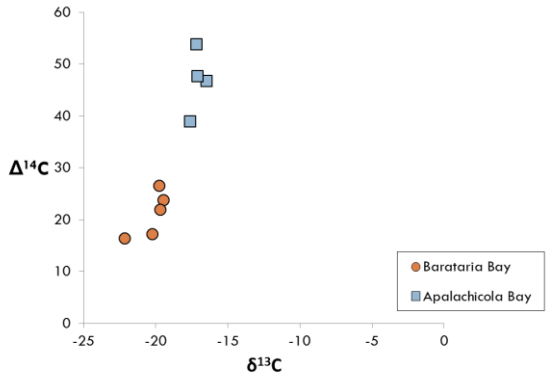

Figure 7. $\Delta^{14}C$ vs. $\delta^{13}C$ values for Hardhead catfish *Ariopsis felis* taken from Barataria Bay (●) and Apalachicola Bay (■).

To evaluate these differences in more detail, carbon isotopic compositions of animals residing in heavily impacted Barataria Bay were compared to animals in a reference site that received little or no oiling, Apalachicola Bay, FL. Specifically, $\Delta^{14}C$ and $\delta^{13}C$ signatures of Hardhead catfish *Ariopsis felis* tissues were evaluated along with potential vector sources (i.e. dissolved inorganic carbon and sediment organic carbon) to determine the route by which oil may have entered the GOM food web. Fish, invertebrates, DIC, and SOC samples from Barataria Bay, LA were all depleted in ^{14}C relative to those from Apalachicola Bay FL. ^{14}C values of Barataria Bay Hardhead catfish ranged from 16 ‰ to 26‰ while those collected in Apalachicola Bay ranged from 39‰ to 54‰ (Fig. 7). Using a dual isotope-three source mixing model we estimate that in Barataria Bay, oil contributed between 6 to10% and 1 to 12% of the observed ^{14}C-SOC and ^{14}C-DIC signals, respectively. Using these vectors, we again used these mixing models and found that as much of 22% of the Barataria Bay catfish carbon could be accounted for by the oil contaminated vectors. These results indicate that oil intrusion into this coastal ecosystem is traceable to the macrofauna level using natural carbon isotope abundances.

References

Chanton, J.P. J. Cherrier, R.M. Wilson, J. Sarkodee-Adoo, S. Boseman, A. Mickle, and W.M. Graham. 2012. Radiocarbon indicates that carbon from the Deepwater Horizon Spill entered the planktonic food web of the Gulf of Mexico, Environmental Research Letters, accepted for special issue.

Crespo-Medina, M, C. D. Meile, K. S. Hunter, A.-R. Diercks, V. L. Asper, J. P. Chanton, V. J. Orphan, A. M. Shiller, J. J. Battle[1], D.-J. Joung, R. M. W. Amon, A. Bracco, J. P. Montoya, T. A. Villareal, A. Vossmeyer, A. M. Wood[1], and S. B. Joye. The rise and fall of methanotrophy following a deepwater oil-well blowout. In prep for Science.

Graham, W.M. R. H Condon, R. H Carmichael, I. D'Ambra, H. K Patterson, L. J Linn and F. J Hernandez Jr. Oil carbon entered the coastal planktonic food web during the Deepwater Horizon oil spill. Environ. Res. Lett. 5 (2010) 045301 (6pp) doi:10.1088/1748-9326/5/4/045301

Cruises & field expeditions

Ship or Platform Name	**Class** (if applicable)	**Chief Scientist**	**Objectives**	**Dates**
Coastal sampling		Sarkodee-Ado	Collect coastal fauna	April 2011
Weatherbird		Cherrier	Collect offshore plankton, POC, , sediments, DIC	May 2011
Weatherbird		Chanton	Collect offshore plankton, POC, , sediments, DIC	May 2012

2) 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)

Chanton, J.P. J. Cherrier, R.M. Wilson, J. Sarkodee-Adoo, S. Boseman, A. Mickle, and W.M. Graham. 2012. Radiocarbon indicates that carbon from the Deepwater Horizon Spill entered the planktonic food web of the Gulf of Mexico, Environmental Research Letters, accepted for special issue.

Chanton, J., J. Cherrier, S. Bosman, A. Mickel, S. Joye, C. Brunner, J. Sarkodee-Adoo, D. Hollander. Sediment Radiocarbon analysis of the Gulf Oil Spill, in prep for Deep Sea Research.

Crespo-Medina, M, C. D. Meile, K. S. Hunter, A.-R. Diercks, V. L. Asper, J. P. Chanton, V. J. Orphan, A. M. Shiller, J. J. Battle[1], D.-J. Joung, R. M. W. Amon, A. Bracco, J. P. Montoya, T. A. Villareal, A. Vossmeyer, A. M. Wood[1], and S. B. Joye. The rise and fall of methanotrophy following a deepwater oil-well blowout. In prep for Science.

Sarkodee-Adoo, J., Cherrier*, J., Chanton, J.P. Tracing Oil Intrusion into Epibenthic Fish in Coastal Louisiana Using Natural ^{14}C and ^{13}C Abundances. in prep for submission to DSR

Baskerville, T. J. Cherrier, J. Chanton, J. Sarkodee-Adoo Tracing insitu hydrocarbon utilization using natural carbon isotope abundances.

3) 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
TRACING THE DEEPWATER HORIZON OIL SPILL INTO FAUNA ALONG COASTAL AND OFFSHORE CONTAMINATION GRADIENTS IN THE GULF OF MEXICO USING NATURAL ^{14}C	Judith Sarkodee-Adoo[1]	Jennifer Cherrier,; Jeff Chanton	ALSO/ Ocean Science, Salt Lake City, Utah.	Y	2012
Biogeochemical Radiocarbon Analysis of the Gulf Oil Spill:	J. P. Chanton	J. Cherrier, J. Sarkadee-Adoo, S. Joye, D. Hollander, W.Graham, C. Brunner, S. Bosman, A. Mickel.	AGU fall meeting, San Francisco.	Y	2012

4) Other products or deliverables

5) Data

Reporting on data is done separately through communications with Harte Research Institute; however, 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.

Samples are archived at Florida State University and data are being prepared for input to Harte Institute.

PARTICIPANTS AND COLLABORATORS

6) Project participants

Please list the participants of your project, their role(s) and contact information. This includes some personal information that we will hold closely and for limited purposes. We ask for demographic data – relating to gender, race, and citizenship – so that we can: gauge whether the GoMRI program is fairly reaching and benefiting everyone regardless of demographic category; ensure that those in under-represented groups have the same knowledge of and access to programs, meetings, vacancies, and other research and educational opportunities as everyone else; and we can monitor involvement of international investigators. We will use the demographic data for statistical purposes only. Submission of demographic data is voluntary, but basic data such as name, contact information, and role in the project is required. 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	Gender	Race	Citizenship
Jennifer	Cherrier	PI	famu	jcherrier@fsmu.edu	F	W	USA
Alejandra	Mickle	undergraduate	FSU	ale_mickle@hotmail.com	F	H	USA
Judith	Sarkodee-Adoo	Graduate student	FAMU	jsarkodeeadoo@gmail.com	F	AA	USA
Samantha	Bosman	tech	FSU	sbosman@fsu.edu	f	w	canada
Jeff	Chanton	PI	FSU	jchanton@fsu.edu	M	w	usa
Tiffany	Baskerville	Graduate student	FAMU	tbaskerville04@yahoo.com	f	aa	usa
Alex	Harper	Graduate student	FSU	arh03c@fsu.edu	f	w	usa

MENTORING AND TRAINING

7) Student and post-doctoral participants

Please list the student participants of your project, their educational role, and other information. This includes some personal information that we will hold closely and for limited purposes. We ask for demographic data – relating to gender, race, and citizenship – so that we can: gauge whether the GoMRI program is fairly reaching and benefiting everyone regardless of demographic category; ensure that those in under-represented groups have the same knowledge of and access to programs, meetings, vacancies, and other research and educational opportunities as everyone else; and we can monitor involvement of international investigators and students. We will use the demographic data for statistical purposes only. Submission of demographic data is voluntary, but basic data such as name, contact information, and research area is required. No personal information will be released.

First Name	Last Name	Post-doc / PhD / MS / BS	Thesis or research topic	Institution	Supervisor	Expected Completion year	Gender	Race	Citizenship
Judith	Sarkodee-Adoo	Graduate student	FAMU	jsarkodeeadoo@gmail.com	F	AA	USA	Judith	Sarkodee-Adoo
Tiffany	Baskerville	Graduate student	FAMU	tbaskerville04@yahoo.com	f	aa	usa	Tiffany	Baskerville
Alejandra	Mickle	BS	none	FSU	na	2011	f	w	usa
Alex	Harper	Graduate student	FSU	arh03c@fsu.edu	f	w	usa		

8) 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)
   c.

   Sarkodee-Adoo, J. J. Cherrier, J., J. Chanton. Radiocabon tracing of the Macando Oil spill. Submission planned for December 2012, for Biogeochemistry.

9) 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
TRACING THE DEEPWATER HORIZON OIL SPILL INTO FAUNA ALONG COASTAL AND OFFSHORE CONTAMINATION GRADIENTS IN THE GULF OF MEXICO USING NATURAL ^{14}C	Judith Sarkodee-Adoo[1]	Jennifer Cherrier,; Jeff Chanton	ALSO/ Ocean Science, Salt Lake City, Utah.	Y	2012
Assessing the Impact of the Deepwater Horizon Oil Spill on Indigenous Bacterial Communities: A Biogeochemical and Molecular Approach	Tiffany Baskerville	Sarkodee-Adoo, J., Jeffrey, W., Chauhan, A., Chanton, J. and J. Cherrier	GRI meeting in New Olreans, January 2013.	N	

10) Images

Please attach high-resolution image and provide details including a description of the image, location, credit, date, etc. Of note: Image may be used in GoMRI promotions, make sure you have rights to use the image. Note: GoMRI will establish a Flicker site to share these images through the GoMRI website and with media and the public.

Images have been submitted to main GoMRI website through Tracy Ipolito.