The 2010 Deepwater Horizon incident revealed several critical knowledge gaps on the effects of dispersants on key physical-chemical processes that control the environmental fate and transport of persistent oil components. While studies have been underway to investigate the existence and persistence of dispersed oil in the Gulf Region, little attention has focused on how the dispersed oil has interacted with sediments and the environmental implications of such interactions, despite an unprecedented amount of dispersant being applied as part of spill response efforts. Information is lacking about fundamental properties and behavior of chemically-dispersed oil microdroplets and about the effects of dispersants on the transport and physicochemical transformation of persistent oil compounds. Some key questions remain on: 1) the mechanisms of how oil and oil components are sorbed to and desorbed from relevant sediments and how oil dispersants affect these fundamentals; 2) how dispersant-oil-sediment interactions affect weathering and transport of the oil components; and 3) how these processes are altered in the deepwater environment.

The specific objectives are to: 1) Determine the role and mechanism of model oil dispersants in sorption and desorption of oil components with coastal and deep-sea sediments; 2) Test dispersant-oil-sediment interactions under marine environmental conditions and elucidate the environmental implications; 3) Evaluate the effects of dispersants and sediment sorption on photochemical degradation of persistent oil components; and 4) Determine the contribution of surface-level ozone oxidation to weathering of oil in seawater and sediment, and examine how dispersants and sediment sorption affect the reactions. This study aims to test the following key hypotheses: 1) dispersants can greatly facilitate mass transfer and sorption of oil components to the sediment phase; 2) the dispersant-oil-sediment interactions can greatly alter the physical, chemical and biological availabilities as well as fate and transport of oil components; and 3) the dispersant effects can be more profound under deepwater environmental conditions.
Methods:
The research objectives are achieved by carrying out a series of carefully designed bench-scale laboratory experiments, including sorption and desorption equilibrium and kinetic tests as well as photochemical degradation and ozone oxidation tests in the presence of representative oil dispersants and under simulated Gulf coastal and deepwater environmental conditions. The key research tasks include: 1) Procurement, preparation and analysis of oil, dispersants, sediments and seawater samples; 2) Establishing an information database on related studies; 3) Experimental investigation into effects of dispersants on sediment sorption/desorption of oil/polycyclic aromatic hydrocarbons (PAHs) and effects of oil dispersants on photodegradation and ozonation of oil components; 4) Data analysis and results dissemination.

Products:
Key findings

1) Increasing the dispersant (Corexit EC9500A and Corexit EC9527A) concentration proportionally increases the concentrations of oil alkanes and PAHs in water accommodated oil. However, the dissolution process is selective, and different dispersants disperse different fractions of oil alkanes and PAHs.

2) Corexit EC500A poses contrasting effects on the distribution of oil/PAHs, i.e., it increases dissolution of oil/PAHs in seawater and sediment uptake of oil/PAHs. Overall, increasing the dispersant concentration progressively enhances sediment uptake of oil/PAHs. The presence of the dispersant during desorption results in remarkable sorption hysteresis. Sediment organic matter (SOM) plays key role in sorption of oil dispersants and dispersed oil, and the dispersant effects increase with increasing SOM content.

3) The presence of dispersed oil substantially increases sediment sorption of PAHs.

4) The dual-mode models are able to adequately interpret PAHs sorption isotherms and kinetics.

5) Deepwater conditions reduce solubilization of PAHs and lessen the dispersant effects on PAHs uptake. Sorption of the dispersant on the sediment is favored at higher salinity while inhibited at lower temperature (4 °C).

6) When dispersed oil is subjected to sorption by a loamy sand sediment, n-alkanes of C27-C32 are more favorably taken up by the sediment, though the sorption rate of different n-alkanes is largely comparable.

7) The presence of Corexit EC9500A promotes photodegradation of pyrene, anthracene and 9,10-dimethylantracene due to enhanced formation of superoxide or hydroxyl radicals. Methylated PAHs are more vulnerable to photolysis than their parent PAHs. Higher ionic strength and temperature and lower HA favor pyrene photodegradation.

8) The surface-level ozone plays an important role in degrading alkylated PAHs. Complete hydroxylation of 1-methylfluorene is observed in 22 d, and the presence of 18 mg/L of Corexit EC9500A modestly inhibits the ozonation rate. However, less than 5% of 9,10-dimethylantracene is degraded under the same conditions. Overall, lower molecular
weight $n$-alkanes are more prone to ozone-facilitated hydroxylation than the heavier $n$-alkanes.

9) Both oil and Corexit EC9500A enhance the formation of marine snow (MS). The formation of marine oil snow (MOS) involves the interactions between specific oil components, dispersant, microorganisms, and natural suspended particulate matters. The dispersant not only enhances dissolution of $n$-alkanes (C9-C40) from oil slicks into the aqueous phase, but facilitates sorption of more oil components onto MS. Lower molecular-weight $n$-alkanes (C9-C18) are more favorably partitioned in MOS than in the aqueous phase in the presence of the dispersant.

10) Oil dispersants accelerate the settling velocity of suspended sediment particles. The nonionic surfactants (Tween 80 and Tween 85) are the most important components that enhance aggregation and sedimentation by masking the zeta potential of the sediment particles. While humic acid alone does not show significant effect on sediment settling, combining the dispersant with humic acid shows a synergistic acceleration of the settling velocity. The dispersant effect on sediment settling is insignificant at the deepwater temperature (4 °C). The presence of water accommodated oil accelerates the settling of sediment, and the addition of dispersant greatly increases the uptake of dispersed oil onto sediment.

11) We developed a new technique for measuring the critical micelle concentration (CMC) of surfactants and oil dispersants based on UV absorbance of pyrene as a probe molecule. Compared to conventional methods, the new method is more robust and accurate while easy to use.

12) We developed a straightforward method for measuring oil dispersant concentration in seawater based on the surface tension measurement.

Outreach/Education

1) The PI and PO are organizing a special session focusing on oil-dispersant-sediment interactions at the 2015 Oil Spill and Ecosystem Science Conference.

2) This project has supported more than eight graduate students and two postdocs (One Ph.D. and M.S. student have graduated and one postdoc has completed their term).

3) The PI (Zhao) and GRA (Gong) were invited to attended a BBC press conference at the 245th ACS National Meeting & Exposition (April 7-11, 2013) in New Orleans, Louisiana. The research was reported in the BBC news (http://www.bbc.co.uk/news/science-environment-22075182).

4) A project literature database (http://www.eng.auburn.edu/users/zzc0008/) was established that has attracted more than 628 visits so far.

Publications/Presentations (See complete lists below)

Five papers have been published/accepted in top international journals, and at least ten more journal papers are submitted or in preparation. Eleven conference presentations have been or are slated to be delivered at various international conferences.
Importance to BOEM:
This research resonates with the BOEM’s mission of protecting the environment while ensuring the safe development of the nation’s offshore energy resources. Furthermore, this effort aligns with BOEM’s goal to inform policy decisions by promoting world-class scientific research as it helps fill in a critical information gap regarding how dispersed oil and its components fundamentally interact with sediments and how that may change in a deepwater environment. The results of this study may be used to help prepare Environmental Impact Statements. Specifically, this study offers the following contributions and benefits: 1) understanding the dispersant-oil-sediment interactions will facilitate more accurate estimate of budget, mass balance, and distribution of dispersed oil in various environmental compartments; 2) it will facilitate sounder assessment of the weathering and environmental fate of dispersed oil; 3) understanding effects of dispersants on key transport processes and weathering reactions will aid in more reliable assessment of environmental impacts of the Deepwater Horizon oil spill and future incidents that involve extensive uses of dispersants; 4) it will provide a more complete knowledge base for stakeholders, decision and policy makers, and remediation engineers to make effective remediation management decisions and develop best management practices for possible future dispersant use.

Current Status: It is in the last project year. Most experimental work has been completed, and the team is working on data analyses and publishing the results.

Final Report Due: 11/30/2015

Publications:

1) Gong Y., Zhao X., O’Reilly S.E., Qian, T., Zhao D. (2014) “Effects of oil dispersant and oil on sorption and desorption of phenanthrene with Gulf Coast marine sediments” Environmental Pollution, 185, 240-249.

Conference presentations

1) Gong Y., Zhao X. and Zhao D. (2012) “Effects of oil dispersants on sorption and desorption of polycyclic aromatic hydrocarbons with Gulf Coast marine sediments” invited oral presentation at the 9th International Symposium on Persistent Toxic Substances, October 23-
27, 2012, Miami, Florida, USA.


4) Gong Y., Zhao X., O’Reilly S.E., and Zhao D. (2013) “Effects of oil dispersants and sediment sorption on photodegradation and ozonation of persistent oil compounds in the Gulf Coast ecosystems”. Poster presentation at the 245th ACS National Meeting & Exposition, April 7-11, 2013, New Orleans, Louisiana, USA.


Affiliated WWW Sites: http://www.eng.auburn.edu/users/zzc0008/
Revised Date: January 2015

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