Title: Evaluating changes in fluorescence EEM and size spectra during the degradation of oil and dispersant

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Cluster: UNDERSTAND

Introduction

During the unprecedented oil spill in the northern Gulf of Mexico between April and July 2010, about $8x10^8$ liters of crude oil and $\sim 7x10^6$ liters of dispersant were released into the water column in the Gulf of Mexico. However, the fate, transport, and ecological and biogeochemical consequences of oil components and dispersant in the Gulf of Mexico are largely unknown. In many recent oil spill research projects including those funded through the NSF-RAPID and GRI-BP, fluorescence excitation-emission matrix (EEM) techniques and CDOM measurements have been used to examine the fate, transport and transformation of oil components in the Gulf of Mexico in addition to direct determination of total hydrocarbon and its speciation. Quantitative understanding of the fate of oil and dispersant in the water column requires detailed knowledge of the chemical speciation of oils during their degradation. Nevertheless, how optical properties and fluorescence EEM spectra of oil components change during their degradation is poorly understood, but is indispensable to better use of fluorescence EEM techniques and other optical properties for oil fingerprinting and tracing the fate and transport in the water column. Therefore, in addition to field observations, controlled laboratory experiments is sorely needed to provide new insights into a better understanding of the fate and transport of dispersant and oil in the water column as oil and dispersant undergo photochemical and microbial degradation.

Through a recent research project funded by NGI-BP, we have shown that the dispersant, nonylphenol ethoxylate, used during the oil spill event has unique fluorescence EEM spectra, which are distinct from oil components, and could be used to trace the fate and transport of the dispersant in the water column. In addition, dispersant is a surfactant that could form droplets and react with natural organic matter, potentially altering the size distribution or phase partitioning of organic matter between dissolved, colloidal and particulate phases in the water column. However, these physicochemical and biogeochemical processes are largely unknown, and the laboratory experiments will provide highly complimentary data in addressing the fate, transport, and toxicity, as well as impacts and consequences of dispersant and oil in the water column.

Understanding the degradation rate of dispersant and oil as well as their accompanying changes in optical properties is extremely important not only to field observations using fluorescence EEM technique, but also to the modeling studies and the application of remote sensing and ocean color in the monitoring of oil and dispersant from the space. Results from our proposed laboratory studies should also provide much needed information to evaluating the effects of dispersant on marine organisms and ecosystems.

Objectives

- To investigate the effect of oil and dispersant on the size distribution of marine organic matter among dissolved and particulate phases in the water column through control laboratory experiments. These will include the effect of oil, or dispersant, or the mixture of oil and dispersant.
- To examine the variations in fluorescence EEM spectra and other optical properties during the degradation of oil and dispersant under natural photochemical and microbial environmental conditions.
- To examine whether fractionation exists during oil degradation, and the inter-relationship between degradation rate and stable carbon isotopic composition, aromaticity, and molecular weight. We expect that there will be a fractionation in stable carbon isotopic composition, aramaticity, and molecular weight of organic matter.

Our working hypotheses are

1) The dispersant and oils from the Deepwater Horizon spill should be selectively degraded, both microbially and photochemically, resulting in a shifting in optical properties of the residual dispersant and oil. This information in return can be used to trace the fate and transformation of oil and dispersant in the water column using fluorescence EEM and optical measurements through both field sampling and remote sensing techniques.

2) The addition of dispersant and oil in the water column will significantly alter the size distribution, especially in the colloidal size range, resulting in more large-size colloids and the coagulation of colloidal particles. However, during degradation, the large-size oil and dispersant should be preferentially decomposed, casing a shifting in the size spectra as degradation proceeded.

3) Oil components with lighter stable carbon isotopic composition should be preferentially decomposed leaving the oil components with heavier isotopic ration in the solution. In addition, the preferential decomposition of oils with lighter isotopic ration should resulting in a measurable isotopic composition change in the dissolved inorganic carbon pool.

Approach

Size fractionation techniques including flow field-flow fractionation, ultrafiltration and microfiltration will be used to examine the effect of oil and dispersant on the size spectra of natural marine organic matter collected from the northern Gulf of Mexico. The particulate phase will be separated through a >0.4 μm filter. The <0.4 μm filtrate or the traditionally defined dissolved phase will be size fractionated either on a centrifugal ultrafiltration or the flow field flow fractionation system to provide a size spectrum of the dissolved phase. Different filter types will also be compared to examine the potential filtration artifact when dealing seawater contaminated with oil and dispersant.

Control laboratory experiments will be conducted to investigate the degradation of oil and dispersant under natural environmental conditions. Samples with different treatments will be exposed to natural sunlight in a water bath to maintain a relatively constant temperature. Variations in temperature will be recorded in a device. Time series samples will be taken for the measurements of dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), particulate organic carbon (POC), UV-vis absorbance, fluorescence EEM spectra, and to calculate the specific UV absorbance (SUVA) and spectral slope values.

Concentrations of DOC and DIC will be measured using a Shimadzu TOC analyzer on an acidified and a unacidified water sample, respectively. Concentrations of POC will be measured using an elemental analyzer.   Stable isotopic composition will be measured through the stable isotope facilities at UV Davis. The aromaticity will be derived from measured SUVA values and the molecular weight will be derived from measured spectral slope values.

Data collected from our proposed laboratory experiments will be used 1) to estimate the degradation rate based on changes in fluorescence intensities, 2) to determine the interrelationship between degradation of oil and dispersant and fluorescence EEM spectra, optical properties, and stable isotopic composition, and 3) to determine whether there is a significant fractionation in organic composition (aromaticity and molecular weight), fluorescence Ex/Em characteristics, and stable carbon isotopic composition. Results from these laboratory experiments will be very useful in interpreting field observations and help with field sampling strategies.

Approximate Cost (Budget)

Overall project cost: $52,757

       Total salary and Benefits: $24,862

       Materials and Supplies: $8,000

       Travel: $2,800

       Others: $3,000

       Facility use: $3,270

       Indirect Cost: $10,825