Deep Spill 2

Technical Science Plans and Supporting Explanations

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Mission Statement

On April 20, 2010, a catastrophic event in the Gulf of Mexico left the Macondo well flowing without control into its surrounding waters. Large volumes of crude oil and natural gas began to be released into the environment.

While there has been and continues to be much tragedy to the communities, the flora and the fauna of the Gulf of Mexico, this accidental emission of hydrocarbons into the environment provides a rare opportunity to capture critical raw data about such large and turbulent emissions, and to perform scientific experiments to deepen our knowledge of these hydrocarbon events.

This scientific mission was developed to address a wide range of critical scientific hypotheses that can only be tested during the actual spill. If we do not seize the moment, then irreplaceable scientific knowledge will be lost to humanity and our response to future accidents greatly diminished.

BP and its partners are working to stop the flow of the hydrocarbons. While our research team fully supports that effort, *BP*'s urgency in its efforts requires any research on the Macondo well flow to begin as soon as possible.

With urgency in mind, this plan has been developed in great haste. The project was broken into subprojects, and each sub-project was assigned to world-class, experienced leaders of science and research missions. This document details the scientific research and experiment procedures to be employed. All of the proposed experiments build on previously published research, and integrate numerous governmental, industrial, and academic institutes, laboratories, and communities.

Given the extensive planned experiments, procurement planning has been accomplished in parallel. Now, the key remaining challenge for the team is to find sufficient capital resources to make this scientific mission possible.

On June 10, 2010, Congressman Markey wrote a letter to BP in support of funding an effort to study the well emissions. Three weeks later, as of July 1, 2010, the Deep Spill 2 Team has heard absolutely nothing from BP. During this period the attached study was developed. The Deep Spill 2 scientific research mission remains unfunded, and the window of opportunity to capture potentially life saving and environmentally critical learning is tightening.

- Ira Leifer, Rick Coffin, and the Deep Spill 2 Team

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Overview

Thorough evaluation of the oil distribution on Macondo well failure is necessary to plan remediation and predict the time for significant environmental impact. Recent data from the Macondo incident includes studies on natural seepage, and theoretical concerns suggest highly complex hydrocarbon pathways in the environment, which are dependent on diverse chemical and physical parameters on a wide range of depth, length, and time scales. Deep Spill 2-EMT will identify these pathways in the near field (10 km, daytime scale) through collection of multiply redundant, direct and indirect measurements. Data analysis including modeling will elucidate the underlying driving mechanisms for the oil partitioning and transport.



Figure 1 – (Top) Image of riser pipe oil-gas plume during an oil-droplet plume expulsion event. CDOG numerical model simulation of a deep-sea oil-gas plume. (Bottom) Plume velocimetry of uncapped well pipe flow. MODIS satellite image of oil slick extending from Louisiana to Florida coastlines.

Deep Spill 2 will test a wide range of hypotheses regarding underlying chemical and physical processes. Because the chemical and physical processes are interdisciplinary and interlinked, Deep Spill 2 is a consortium experiment drawing on an extremely broad range of experience with researchers whose careers have focused on oil and gas in the oceanic environment.

Deep Spill 2 will elucidate the underlying mechanisms governing the partitioning of the seabed hydrocarbon flux into distinct environmental compartments from the seabed to the atmosphere.

Deep Spill 2 will provide the data critical for numerical model validation – a key goal of Deep Spill 1, and demonstrate monitoring capabilities. Validated numerical models are a critical component to facilitate appropriate spill response planning both for the current Macondo incident as seabed well emissions change over time and for future spill response planning.

Response Relevance

The primary and immediate study benefit of Deep Spill 2 for responders and planners will be to greatly increase the safety of responders, both in knowing the emission variability through demonstrating a monitoring/ warning system and to understand the partitioning of volatile components in the water column and atmosphere. Data from the later will provide the ability to warning for surface responders regarding air quality (based on validated spill models).

Second, data and insights from this study will aid responders through improved planning of containment strategies, from the cap and collection system, to where to put and_place booms and skimmers, to identifying where near-surface oil is drifting, and to improve that coordination planning in-between all parties.

Importantly, by understanding not only *where* oil is being transported in the environment, but *why* (model validation), responders will be better able to assess what ecosystem levels (species and groups of species) are at greatest risk from the toxic and carcinogenic actions of the more volatile components of the petroleum, and therefore be better positioned to assess and respond to potential cascading consequences to the marine, coastal, avian, life, and human health.

Scientific hypotheses to be tested in the Deep Spill 2 Experiment

This planning requires a broad range of field expertise and addresses a range of science issues in the deep ocean that have remained unaddressed to date. The following is a list of hypothesis that will be addressed in this study. Details on how the team addresses these hypotheses are presented in the subsequent project sections.

Hypothesis 1:	As the plume rises in the water column, detrainment / entrainment rates are strongly influenced by currents.
Hypothesis 2:	Enhanced plume fluid detrainment occurs at depths of strong stratification, or current shear, with enhanced oil droplet and dissolved hydrocarbon components.
Hypothesis 3:	Observed hydrate flake formation and detrainment correlates with enhanced plume detrainment.
Hypothesis 4:	Plume growth during the acceleration phase depends on entrainment rates and is related to total flux.
Hypothesis 5:	Flux varies with external and internal factors including earth tides, and deep-sea water temperature.
Hypothesis 6:	Hydrate flake formation and detrainment is dependent on water temperature.
Hypothesis 7:	Surface feature derived velocities based on image correlation velocimetry are related to peak and mean plume fluid velocities in a manner that can be calibrated.
Hypothesis 8:	Surface feature divergence and vorticity based on image correlation velocimetry can be related to plume turbulence characteristics
Hypothesis 9:	Sonar data can monitor the effect of currents, decreasing buoyancy due to dissolution, stratification, and the loss of plume coherency on plume dynamics.
Hypothesis 10:	Oil droplet concentrations will be greatest in the deep plumes near the well head and will decrease with distance due to sedimentation, rising, dissolution, and decomposition.
Hypothesis 11:	Water column oil droplets and dissolved hydrocarbons are correlated (with a temporal offset) to the extent that droplet dissolution is an important mechanism for oil dissolution.

Hypothesis 12: Droplet interaction with marine snow is an important loss mechanisms leading to droplet sedimentation.

- Hypothesis 13: The oil output from the source is constrained by mass exchange within the water column through the vertical rise of the plume.
- Hypothesis 14: Increased methane fluxes are correlated with anoxia at greater depths, and thus will have an ecosystem impact. Simultaneously, iron mobility in the reduced form, and therefore also the associated phosphorous, will increase and cause enhanced productivity at the shallower depths.
- Hypothesis 15: Droplet interaction with marine snow is an important loss mechanisms leading to droplet sedimentation
- Hypothesis 16: Oil released from the Macondo Well will enter the ocean C cycle via the marine dissolved organic material (DOM) pool.
- Hypothesis 17: The ultraviolet fluorescence (UVF) of oil is similar to, but distinct from the background natural UVF of dissolved organic material (DOM) and these signals can be separated in an array of Excitation Emission Matrix Spectroscopy (EEMS) using a statistical model.
- Hypothesis 18: Oil near the Macondo Well site, primarily originates from the well with a spatial distribution and flux determined by a combination of dispersion, hydrate flake detrainment, and interaction with marine snow and currents.
- Hypothesis 19: Methane serves as a proxy for estimating the petroleum flow out of the Macondo Well.
- Hypothesis 20: Elevated gas fluxes, associated with the Macondo Well oil flow, influence the oil transport and fate through the water column.
- Hypothesis 21: Increased gas flux to the water column elevates the water column hypoxic and anoxic conditions.
- Hypothesis 22: Oil sedimentation rates are directly related to water-column particle loading, hydrate flake formation, and correlate with seabed sediment deposition through the intermediary of current transport.
- Hypothesis 23: With increasing distance, the chemical composition of sedimented oil will more closely relate to oil component fractionation higher in the water column.
- Hypothesis 24: Gas fractionation within the plume due to bubble processes leads to spatially distinct aqueous n-alkane plumes.
- Hypothesis 25: Aqueous higher molecular weight n-alkanes exhibit a spatial distribution that correlates with dissolved PAH and other high molecular weight oil components, unlike lighter n-alkanes, such as methane.

- Hypothesis 26: Oil globules are dispersed within the mixed layer, with a depth distribution related to mixing processes wind and wave development in the case of natural dispersion and suspension processes.
- Hypothesis 27: Most of volatile loss from seabed flow is due to (solubility-driven) dissolution, rather than vapor pressure evaporation. Thus, slick evaporative losses are both lower and chemically distinct from those due to weathering over time for the same oil if spilled at the sea surface.
- Hypothesis 28: Oil advection by winds and currents in a massive oil spill is unique from a conventional oil spill due to wide-scale alteration of the ocean-atmosphere boundary by the extensive oil slick.
- Hypothesis 29: Thickness categories of floating oil layers can be distinguished by comparing satellite SAR with visible wavelength data (e.g. MERIS, MODIS).
- Hypothesis 30: The types and rates of crude oil weathering and degradation differ between oil on the sea surface and oil in the water column.
- Hypothesis 31: In the absence of photo-oxidation, subsurface degradation will follow a different pathway from surface oil with different intermediate compounds.
- Hypothesis 32: Sub-surface degradation of oil may exacerbate oxygen demand in an already oxygen limited environment.
- Hypothesis 33: Due to the depth of the spill, volatile components in the atmosphere are shifted towards higher molecular weight, less soluble components compared to a conventional oil spill.
- Hypothesis 34: Photo-degradation of older, drifting surface oils cause distinct atmospheric composition over slick portions with freshly surfaced versus older oils, while oil component photolysis leads to smog precursors.
- Hypothesis 35: Winds advect significant quantities of volatile oil components over land.
- Hypothesis 36: Numerical modeling in tandem with detailed water column data will allow investigation of the underlying physical processes.

Schedule and Minimal Lead Times

Initially, the timeline was envisioned as occurring over a period of three weeks prior to arrival on site; however, despite the study proposal having been submitted in mid-June in response to concerns voiced in a letter by Congressman Markey to BP on June 10, 2010, the team has not heard from BP. Given the *hoped for early containment* of the Macondo spill, a compressed timeline has been developed. Should circumstances occur that (as has happened repeatedly, again and again), BP's containment plan slips, the additional time would be used to secure better quality data (i.e., more), allowing a far better understanding to be developed of the ongoing spill processes. A prototype schedule is provided below.

Minimum Lead Time Timeline

Day 0	Team Activation
	Technical support team activation
	Negotiations for vessel and ROV contracts
	Supplier notification for critical instrument procurement
Day 1	Subcontracts in place
Day 2	Procurement contracts for vessels and ROVs in place
	Activation of technical support (ROV integration) teams
Day 2	Critical instrument and supply procurements
	Laboratory testing of <i>in-place</i> equipment
Day 3	Next-day arrival of critical instrument procurements and supply.
	Laboratory testing/integration of <i>in-place</i> and procurement equipment
Day 3	Arrival of remaining critical instrument procurements
	Laboratory testing/integration of <i>in-place</i> and procurement equipment
Day 4	Equipment shipping to Gulf of Mexico
-	Travel to Gulf of Mexico
Day 5	Equipment loading on boat (Team Shift 1).
	Shipboard testings and ROV system integration (Team Shift 2)
Day 6	Transit from Port to Site (13 hours)
	Integration and shipboard testing
Day 7	Test deployments (not at site)
	Well-site area work (5 hours)
	Surface and upper water column work from boat 2, surfacing area (several kms
	downcurrent from surface vessels)
	Mid to upper water column, one km to several km downcurrent of surface site
Day 8	Repeat day 7 for entire water column
Day 9-10	Upper and mid water column studies
	Retrieve seabed monitoring ROV
Day 11-14	Surface slick studies. Downcurrent plume and seabed studies. Atmospheric
	studies. Mixed layer studies
Day 15	Boat travels from port
	Shipboard debriefing meeting

Day 16	Demobilize
Day 17	Return to home institutions
Day 20	Mission summary teleconference
Day 28	Preliminary draft reports
Day 40	Full reports
Day 60	Discussion Meeting

The original mission plan includes 5 days for a Santa Barbara Coal Oil Point Seep Field mission to test protocols. The planned seep field component (not in the Minimum Lead Time Schedule) adds six days at Day 4.

Scientific Background

The evolution and fate of hydrocarbons from a seabed blowout are complex for shallow seas. In deep-sea systems this evaluation is more difficult due to the high-pressure regime, which includes the presence and formation of hydrates, and changes in ocean current velocity and stratification. Moreover, the largest previous deepwater blowout field study [*Chen and Yapa*, 2002; *Johansen et al.*, 2001; *Johansen*, 2003; *Johansen et al.*, 2003; *Zheng et al.*, 2002] was for flows that are a fraction of the emissions of the Macondo incident.

In the original Deep Spill experiment, the main objective was to obtain data for verification and testing of numerical models for simulating accidental releases in deep waters. In addition, studies were aimed at testing equipment for monitoring and surveillance, and evaluation of safety aspects of deep-sea gas and oil spills. During releases from 844 m water, discharges of oil and water were at rates of $1 \text{ m}^3/\text{min}$ and natural gas discharges of $0.6 \text{ m}^3/\text{s}$ and lasted for 40 or 60 minutes for a total of 4 discharges. Gas bubble and diesel droplet size distributions at formation were large, ~1-2 mm radius with some oil globules to cm diameter, orders of magnitude larger than appear to be formed in the Macondo spill. Echo sounder images showed bubbles rising in a long pulse, during periodic boat overpasses, requiring ~20 minutes to transit the water column (~30 cm/s) with an apparent velocity decrease as the bubbles neared the thermocline. Modeling efforts with the Comprehensive Deepwater Oil and Gas blowout model captured the main features of the plume during its rise and advection by currents [*Chen and Yapa*, 2002].



Figure 1. Echosounder image during Deep Spill crude oil and LNG discharge June 29, 2000. Time in HH:MM. from [*Johansen et al.*, 2001].

However, many important questions remain – there was, for example, no sonar evidence of hydrate flake formation in Deep Spill 1, a phenomena observed associated with the Macondo incident (*Asper*, 2010, *unpublished observation*), while the effect of hydrate skins on bubble hydrodynamics was elucidated only recently (*Rehder et al.*, 2009). As a result, understanding of the key processes occurring in the Macondo spill incident based on the data from the Deep Spill experiment are limited. Unfortunately, the original Deep Spill experiment never was repeated.

Observations from the Macondo incident suggest a range of additional complex processes. These include the formation of hydrate flakes and extensive submerged oil globules floating in the mixed layer, extensive underwater deep sea oil plumes, a general absence of surfacing bubble plume, and rapid variability in emission rate and at times oil to gas ratio.

Some of these observations suggest plume processes associated with fluid detrainment are important. Further, studies of natural seepage [Solomon et al., 2009] and engineered plumes [Leifer et al., 2009] confirmed that strong stratification, such as at the thermocline/pycnocline, leads to large-scale plume fluid loss or detrainment, a phenomenon identified in the laboratory as distinct to two phase flows – bubbles [McDougall, 1978]. Upwelling flows associated with seep bubble plumes are effective at fluid transport including of water enhanced with elevated concentrations of dissolved gases [Leifer et al., 2000; Leifer et al., 2009] as well as marine particles which would include oil droplets. Detrainment leads to deposition of these droplets as well as enhanced dissolved natural gas and oil components into layers first identified in Leifer and Judd [2002], also known as intrusions [Lemckert and Imberger, 1993].

Other marine phenomena can lead to enhanced plume detrainment and a hydrocarbon flux to the surrounding ocean. For example, currents play an important role. Thus, in recent (June 2010) ROV tests in the Coal Oil Point seep field, under slack current conditions, dye injections demonstrated that seabed fluid was transported across the thermocline and reached the sea surface. In contrast, for conditions earlier in the day under strong current conditions, no dye reached the sea surface. Laboratory studies show significant bifurcation of the plume where it consists of bubbles of different size [*Socolofsky et al.*, 2002]. In contrast, field studies of large natural mega seepage (> 10^6 L/dy) show some size segregation of bubbles, but not bifurcation, which correlated with detrainment of upwelled detritus (smaller bubbles in the downcurrent side of the plume where marine particle concentrations were greater [*Leifer et al.*, 2009].

Moreover, the oil spill flow is persistent, allowing the formation of large-scale flow patterns. Research in lake destratification [*McGinnis et al.*, 2004; *Wüest et al.*, 1992] suggests these can be important. Persistence also means that data can be acquired on these processes stochastically, unlike transient phenomena.

Based on these site observations as well as insights from field studies of natural oil and gas seepage, and theoretical concerns, seven key depth zones are proposed where distinct processes govern the fate of seabed hydrocarbons from the Macondo Well (**Fig. 2**). Within these depth zones, the primary changes in the composition of the plume with time are associated with hydrates (formation, dissociation), hydrocarbon dissolution, and plume entrainment (plume growth) and detrainment. Details of these processes are hypothesized to be distinct in each of the depth zones. For example, hydrate-related processes only occur in the deep sea within the hydrate stability field, although they persist to somewhat shallower due to time required for hydrate dissociation.





Zone 7 Benthic-water interface

There are natural processes of deposition and sedimentation of organic material from the upper mixed layer photic zone to the deep sea and benthos – marine snow and conversion of dissolved organic material to particulate organic material, which settles. The processes are complex, only partially understood, and include biological cycling. In the case of a large oil gas plume, droplet detrainment in the deep sea leads to a plume of dispersed oil droplets, which diffuse towards the seabed (against their slight buoyant rise), that also interact with sinking marine snow (organic particles and detritus), leading to seabed deposition. As a result, the oil deposition to the sediment's upper layers, provides an integrated record of the portion of the total emissions detrained in the deep sea.

Zone 6 – Deep-sea plume

Unlike natural gas plumes at shallow depths, in the deep sea, hydrate (water-methane crystals stable at low temperature and high pressure) formation can strongly affect plume behavior [*Sauter et al.*, 2006]. Key initial plume processes are the acceleration phase when there is rapid plume growth and entrainment absent detrainment, which approaches quasi steady state behavior after a distance of tens of plume diameter length scales – e.g., [*Greinert et al.*, 2006; *McGinnis et al.*, 2004; *Milgram*, 1983], in steady state, plume entrainment and detrainment are balanced, and the driving buoyancy flux changes slowly due to bubble gas exchange, negligible hydrostatic pressure changes, and phase (hydrate) changes. Dissolution losses are small because of hydrate skins [*Rehder et al.*, 2009]. Also, hydrate bubble skins separate the methane from the fluid, preventing rapid formation of hydrate crystals. Summer 2009 observations (*Leifer, Kastner, Solomon, MacDonald*, 2010, unpublished)

during the HyFlux mission tracked intermediate size bubbles (1 - 3 mm radius) at MC118 (~1000 m, near the Macondo well site) across most of the water column, only losing them near the mixed layer. Their survival is best explained by hydrate skins, although oiliness likely also played a role [*Leifer and MacDonald*, 2003]. Despite multiple repeat bubble plume following experiments, there were no observations of spontaneous hydrate flake formation. Thus, the underlying mechanism behind the observed formation of hydrate-like particles in the deep sea remains unknown.

During the initial acceleration phase, and possibly into the steady state phase, rapid and potentially significant bubble growth occurs due to desorption of natural gas from the oil.

In general, in the deep sea, changes in the water column are slow and subtle; leading to general steady state plume behavior (*Solomon et al.*, 2009). However, relatively abrupt changes associated with for example, deep loop currents, can be observed. In the schematic, this is illustrated by a current shear, which leads to an intrusion in the hydrate stability field (HSF). Observations (*Asper*, 2010, unpublished) suggest increased hydrate particles with height above the seabed until several hundred meters altitude. This could result from progressively greater work required by the plume against the stratification (density gradient) leading to progressively greater detrainment, or could also have sharp characteristics due to the effect of water-column changes. There also is significant evidence for a deep-sea plume of oil (*Samantha Joye*, 2010, pers. comm.), which could be related in part to hydrate processes, as well as bubble plume processes.

There have been some deep-sea studies in the vicinity of the well site. The *R/V Brooks McCall* conducted field sampling during 4, EPA cruises May 8- 25, during which ~230,000 of dispersants were applied. Oil transit to the surface as ~3 hours (~10 cm/s), implying the flux is not gas-driven across the entire water column. Rosette samples and standard Seabird suite measurements showed peak fluorescence at 1000 m (to 34 ppm) correlated with CDOM data while LISST data suggested small oil droplets. No analysis was performed to distinguish between natural and wellsite emissions.

Zone 5 – Deep to mid-water column (above Hydrate Stability Field)

In the absence of water column changes, the dominant evolution of the plume in the mid water column arises from bubble dissolution and fluid mixing with the ambient water column. Due to the buoyancy flux loss from bubble dissolution (mid-water hydrostatic pressure changes are relatively minimal, as is air uptake), the plume is increasingly unable to support the upwelling flow with gradually increasing detrainment. Total dissolution is feasible if the bubbles are small enough, however, sonar and direct ROV evidence suggests bubbles can survive against dissolution during transit of the mid-water column.

Zone 4 Upper mid water-column

If there are current shear in the upper portion of the mid water column, plume coherency can be lost leading to plume dissipation, i.e., as in *Sauter et al.* [2006] for the Hakon Mosby mud Volcano at 1000 m. Because this is an oil-gas plume, the result would be to strand vast oil quantities mid water-column, likely as a cloud of dispersed droplets. The cloud then would rise slowly towards the sea surface (oil's buoyancy force is orders of magnitude less than that of bubbles).

Should strong coherent bubble plumes reach the thermocline, they may instigate downdrafts into the upper mid water column zone. Specifically, a bubble plume that reaches the

thermocline does significant work upwelling cooler, denser, deeper water against the strong density gradient (stratification). As a result, massive plume detrainment is probable [*McDougall*, 1978]. If the detrained water is sufficiently higher density than local ambient, the detrained fluid, instead of forming a horizontal intrusion, can form strong downwelling jets, which will advect oxygen rich water downwards.



Figure 3. One AVIRIS flight line on 17 May 2010, superimposed over MODIS satellite data of oil slick. Upper right shows band ratio (550 nm to 650 nm) with false color. Lower right shows focused in area. Dark brown patches are freshly surfaced oil based on analysis. Images here courtesy Eliza Bradley, UCSB.

Zone 3 Thermocline and mixed layer

For a bubble plume, the thermocline represents a significant challenge due to the rapid stratification at the base of the mixed layer. Here, massive plume detrainment is highly likely [*McDougall*, 1978], which, coupled with common current shear, likely leads to plume disruption. Sonar observations often show bubble plumes disappearing abruptly at the thermocline or levels of current shear, e.g., [*MacDonald et al.*, 2002] for bubbles rising from 550 m. Observations in the Coal Oil Point seep field have shown that bubble plumes tend to self-organize into clouds or boils with time scales comparable to the wave period [*Leifer et al.*, 2009]. This was observed not just for natural seep emissions, but also for engineered bubble plumes with constant flow rates.

Moreover, surface remote sensing observations based on analysis of data from the Airborne Visual InfraRed Imaging Spectrometer (AVIRIS) flown aboard the ER2 [*Clark et al.*, 2010], indicate that oil reaches the surface not as a stream or plume, such as is commonly observed in shallow seeps, like in the Coal Oil Point seep field, but as large boils. Specifically, several kilometers to the SE of the incident site (Fig. 3), down current, large patches of oil are observed with very low water content (oil in non-sheen slicks almost always is in the form of an emulsion – a mixture of tiny oil and water droplets), and spatial patterns distinct from most of the scene oil which has high water content [*Clark et al.*, 2010, in review]. The best explanation is that these are patches of freshly surfaced oil and their spatial distribution suggests that the transport mechanism in the upper water column is as boils. Further, surface observations (*Asper*, 2010, *MacDonald*, 2010) indicate that from a boat, it is very difficult to see the surfacing of fresh oil revealed in the remote sensing data.

Other observations with sonar suggest significant oil is submerged in the shallow subsurface (*Maillard*, 2010, unpublished), which matches visual observations (*Asper*, 2010, unpublished). These oil globules (to tens of centimeters) and oil droplets (sub millimeter) are affected by surface mixing processes related to wind stress, turbulence, wave breaking, currents, and interaction with algae and density stratification due to fresh water lensing from the Mississippi outflow – at MC118, we measured salinities of 20 ppt or lower, summer 2010 in the upper few tens of centimeters. Here, also, weathered sinking oil (or tar balls) also may be found.



Figure 4. Major processes affecting oil spills during the initial period after the spill. After [Leifer et al., 2006]

Zone 2 Sea surface

Spilled crude oil changes due to numerous processes, shown schematically in Fig. 4, including advection from currents and winds, wave and current compression (into wind rows or narrow slicks), spreading and surface diffusion, flocculation and dissolution into the water column, evaporation, as well as photochemical and biological degradation [*NRC*, 2003]. Spreading is a process whereby oil tries to maximize its surface area, and is distinct from diffusion. Both increase the oil slick dimensions, while Langmuir circulations (wave compression in Fig. 4) narrow the slick [*Lehr and Simecek-Beatty*, 2000], as do convergence zones due to current sheer, which are common in coastal waters. Both wind and currents cause slick advection and may be in different directions. Biochemical degradation occurs on a time scale of days to weeks, while the other processes mentioned can be significant on a time scale of hours or less.

Changes in chemical composition are important because different components have different toxicity. [*Labelle and Danenberger*, 1997; *Riazi and Al-Enezi*, 1999]. For example, among the n-alkanes, the more volatile compounds are more toxic [*Engelhardt*, 1987]. Also, very low Volatile Organic Hydrocarbon (VOH) concentrations have been shown to cause nervous system effects if inhaled (a danger to marine mammals) and gill damage to fish for VOH exposure at the ppb level has been documented [*Spies et al.*, 1996].

Many of these processes depend upon sea state [*Delvigne*, 1987], oil slick film thickness [*ASCE*, 1996], meteorology and currents. For example, wind creates turbulence that increases

evaporation, while dissolution is affected by turbulence in the water from wind stress, waves, and wave breaking. Understanding oil evolution is further complicated by the numerous components in petroleum, each with its own chemical (e.g., evaporation and diffusion rates, etc.) and physical properties [*NRC*, 2003].

Chemically, oil slicks where there are multiple sources can be complex in terms of stages of weathering. Fresh oil can become intermixed with more aged oil, although the two tend not to become intimately mixed barring wave action (boat wakes, etc). In addition, while volatilization occurs on hour time-scales for thin sheens and slicks [*Leifer et al.*, 2006], where oil is in thick emulsions, slicks, or tarballs, evaporation proceeds far more slowly. In addition, while volatilization is highly efficient for lighter alkanes (decane, C10 and lighter) – as well as photolysis of larger molecules into lighter volatile components, dissolution is much less efficient than volatilization, Thus, oil at the base of an emulsion or slick loses volatile components at far slower rate. Also, volatilization from a thick emulsion becomes a two-step process; diffusion of the components through the oil to the surface followed by volatilization. Thus, thick emulsions will preserve their volatile components better than thin emulsions or sheens.

The fraction of oil that is volatile is important not only for reasons of toxicity, but also because many key oil physical properties (viscosity, density, diffusivity, etc.,) are altered as the oil chemical characteristics shift. Thus, the physical properties, which depend on the oil's chemical composition, affect the spatial distribution of the oil under natural advective and dispersive forces.

For example, wind causes oil advection; however once the wind passes from clear water to an oil slick, the change in the ocean surface boundary condition to immobile (from mobile) and the loss of capillary waves due to oil damping, shifts the wind profile such that momentum transfer to the oil at the sea surface is greatly decreased. As a result, oil slicks "bunch up" under the effect of wind. Countering this force is Fahy gravitational spreading, where the oil attempts to minimize its thickness. As a result, a thin sheen typically is observed to the upwind side of an oil slick line spreading against the advective force of the wind. The extent of this spreading thin oil depends on the oil viscosity, thus as oil weathers; the upcurrent sheen will spread less (but be thicker). In contrast, on the down wind side of the oil slick line, spreading works in tandem with wind advection to create a far more extensive thin spreading oil slick.

Although these processes suggest that oil slick lines should dissipate, in reality, slicks tend to accumulate at current sheers, which may or may not be bathymetrically induced, for example, Langmuir circulation windrow [*Lehr and Simecek-Beatty*, 2000] create convergence zones.

Zone 1 – Atmosphere

Volatile oil components enter the atmosphere and are advected by winds and diffuse by turbulence. The balance of components entering the atmosphere depends significantly on the extent of dissolution during transit of the water column. For a deep spill, these dissolution

losses can be significant. Photochemistry also can play a role as photo-dissociation transforms higher molecular weight components into lighter, more volatile components...

Preliminary analysis of gulf air samples showed significant higher carbon number alkanes and aromatics present while the lower carbon oil components were missing. This would be consistent with significant volatile component water-column dissolution. Total hydrocarbon (non-methane) loads were high, > 2 ppm, which is very unusual (*Blake*, 2010, unpublished), and has significant health implications (manuscript in prep). These observations were confirmed during a mid June NOAA flight (*David Parrish*, NOAA, 2010, personal comm.).

Macondo Well Site

The focus of this study is the plume of hydrocarbons escaping at the seabed and rising through the water column and drifting downcurrent in the immediate environs of the well site. Due to currents (small, but not negligible), within a few hundreds of meters (Zone 5) above the seabed, the study will have shifted away from the immediate well site vicinity. Evidence of freshly oil surfacing several kilometers down current (Fig. 3) suggests the second boat (surface and mixedlayer activities) will be kilometers distant from the well site, while the primary boat will only conduct studies close to directly above the well for the deepest few hundred meters.



Figure 5. Seepage (red and yellow column) mapped by Thomas Jefferson, and Gordon Gunter (purple cylinders), using echo-locators along with CTD stations showing high fluorescence (brown, green, and white spheres). Deep Water Horizon well site is in the background (Red cylinders) and the spatial distribution of bottom following reflectors is represented by orange lines. From [Smith et al., 2010], Figure 20.

This general area of Mississippi canyon is known for natural seepage (e.g., MC118, the hydrate observatory) due to faults providing migration pathways from the reservoir to the seabed. Evidence of seepage [*Smith et al.*, 2010] is provided in fisheries echo sounder data (Fig. 5), which can locate (but not quantify) seepage. Studies will assess carefully the relative contribution of seepage in the vicinity of the Macondo Well site.

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Non-Technical Materials

A Description of Deep Spill 2

On June 10, 2010, Congressman Edward Markey, Chairman of the Select Committee on Energy and Commerce, wrote a letter to BP requesting their support and funding for Dr. Ira Leifer to lead an experiment to improve the scientific data related to the Macondo Well spill. Since that date, Dr. Leifer has assembled an outstanding team of researchers with literally centuries of experience in the study of hydrocarbons in the ocean to fulfill Congressman Markey's request. The team has made careful and detailed plans to complete the mission, and continues to refine mission plans while remaining on standby for confirmation of schedule and budget.

The Deep Spill 2 experiment is a unique and critical opportunity to observe a major oil and natural gas catastrophe as it happens, to improve scientific understanding of the behavior of hydrocarbons released at high volumes at deep depths, and to provide analysis to better secure the safety of the workers supporting the on-going well capping efforts and to better secure the general environmental safety for the Gulf of Mexico during the capping efforts.

The results of the Deep Spill 2 data and reports will be useful for both preventing future blowout catastrophes (including during relief well drilling) and for advancing the technologies and capabilities to respond to such future deep-sea blowout events. Data and reports will be made publicly available after review by the Quality Review Board to aid science and safety planning. Although engineering continues to advance and improve fundamental safety, no design will ever be completely safe from catastrophic failure, thus it is vitally critical that science seizes this unfortunate opportunity to ensure the best science and technology are available to ameliorate any future catastrophe.

If the current opportunity were to be lost, it would be highly unethical to later attempt to artificially reproduce a similar sized subsea spill for safety planning. Thus, it is very important to capture the current moment for scientific advancement.

Historical experiments to study deep-sea hydrocarbon spills have been necessarily limited to comparatively smaller volumes, such as the 750 barrel controlled release, authorized for the original Project Deep Spill in June 2000, or just gas. Such limited hydrocarbon releases, while scientifically important, leave many critical unanswered questions. Further advancements to safety and environmental protection require the data that only can be obtained from genuinely large hydrocarbon spills. Unfortunately, the Macondo spill provides precisely these necessary conditions for immediate observation.

The critical data to be collected during Deep Spill 2 will be unavailable for observation or forensic-style reconstruction once the well is capped – the turbulent flow and the reality of the mass and dynamics of the hydrocarbon emissions *will be lost permanently if not immediately measured*.

An analogy can be made to tornado study and catastrophe prevention. It is clearly insufficient only to study devastated areas after the conclusion of a tornado attack. It is critical to observe tornados as they occur, to observe their energy and capabilities. Similarly, Deep Spill 2 will observe and measure the hydrocarbon "cyclone" as it leaves the well, mapping the oil and gas flows through the ocean, so that future planners will be able to model better potential deep sea blow outs and provide for better environmental and worker safety planning. The Deep Spill 2 team is committed to advancing our knowledge of these rarely observed large-scale catastrophes.

The goals of Deep Spill 2 are:

- to collect an accurate and well-designed data set in the environment near the spill of the hydrocarbon emissions,
- to demonstrate that a top-notch research team can be assembled quickly, trained, and deployed to a well site catastrophe,
- to establish a public data set for future research and development into human and environmental safety for offshore drilling and exploration, and
- to reduce the range of measurement uncertainty on the flow of hydrocarbons from the well.

The Deep Spill 2 will take place at sea, close to the Macondo well site. The team will charter two research vessels, the Geodetic and Seaprobe I for simultaneous plume and near field measurements. The Seaprobe I has a full chemical laboratory on-board to support the team onsite. Both vessels will support ROV and diving activities.

The primary focus of Deep Spill 2 is where are the Macondo well hydrocarbons going in the ocean (and atmosphere) and at what rates. The team will perform experiments to determine the hydrocarbon fluxes from the well (Mass in) and between the plume and environment (Mass out) in seven different depth zones. Providing redundancy in flux measurements. In this regards, we are repeating the 2009 HyFlux experiment (July 2009, Gulf of Mexico, ~10 km from Macondo site) at a more detailed level through additional measurements. Comparison of Mass In and Mass Out for each depth zone provides independent confirmation of the measurements and identifies fluxes to the environment.

The Deep Spill 2 team will utilize a range of established and ground-breaking technologies to achieve these measurements.

- The team will complete the world's first mass-balance study of an active subsea eruption at such depth and at such huge volumes as is occurring at the Macondo well site. The previous record is a measurement at only 844 meters, and of ~750 barrels of oil. Macondo is leaking many, many times that volumes at a depth significantly deeper. The scale difference is hugely significant for scientific understanding and modeling, and the depth difference is critical because of the role of hydrates
- The team will introduce subsea-monitoring technologies to enable real-time remote monitoring of large 3D volumes for emissions.

- The team will use a variety of ROV robotic vessels to perform a variety of sampling and observational activities. The team will perform chemical studies on water and hydrocarbon samples from the well site area guided by in situ observations.
- The team will capture high quality video of specific utility for scientific analysis rather than the incidental video previously produced from the Macondo well site. This will enable more precise video analysis.
- Establish continuity with the important work of the Technical Flow Rate Team through team member direct and indirect involvement.

In more technical terms, key scientific questions to be answered by Deep Spill 2 are:

- 1. What are the oil and gas fluxes, where each phase has distinctly different transport velocities over a range of time and spatial scales?
- 2. What is the oil loss to the water column?
- 3. What is the methane loss to the water column?
- 4. What is the contribution from natural seep oil and methane?
- 5. What is the total oil loss of volatiles due to dissolution versus evaporation?
- 6. What fraction of the mid-water and surface oil is in the form of tar balls from previous emissions and from natural sources?
- 7. Can the results of the above experiments be united in rigorous modeling?

The Deep Spill 2 team is composed from America's leading experts in oceanography, chemistry, engineering, subsea surveillance, and environmental sciences. The Deep Spill 2 roster of experts are drawn from the Naval Research Laboratory's Marine Biogeochemistry Section, the SCRIPPS Institute of Oceanographic Studies, subsea sonar detection staff from Reson Sonar, Inc., and SRI international, and academic scientists from Clarkson University, UC Irvine, UC Santa Barbara, North Carolina State University, University of Southern Mississippi, Purdue, and University of Washington.

The Deep Spill 2 team is as well prepared for this mission as any team could be prepared including literally centuries of at sea fieldwork experience. The team's professional experiences include participation in the original MMS Project 377 "Deep Spill" experiment, on Exxon Valdez Incident research teams, on the USGS/NOAA Technical Flow Rate Team, on the recent NOAA scientific cruises investigating the subsea oil plumes, on the NASA remote sensing missions to observe the Macondo spill from high altitudes and space, and on other recent cruises to examine the seabed and natural emissions near the Macondo well site. Many team members are either directly involved or collaborating actively with other researchers in the Gulf of Mexico, which will ensure integration of study results and provide opportunities for synergistic measurements.

The Deep Spill 2 team also draws directly upon the wider community support under the Quality Review Board, which will provide advice on the experiment design and data analysis. For example, several DOE Computational Fluid Dynamics teams have contributed measurement suggestions to improve data utility to important numerical modeling efforts. The Deep Spill 2 team also is reaching out to the broader oceanographic through conference presentations and other means to develop synergistic collaborations.

Useful links:

Congressman Markey's Letter to BP:

Press Release: http://markey.house.gov/index.php?option=content&task=view&id=4020&Itemid=125

Letter: http://globalwarming.house.gov/files/LTTR/06-10-10McKayDirectMeasure.pdf

MMS Website materials on Project 377 "Deep Spill" Summary: <u>http://www.mms.gov/tarprojects/377.htm</u>

Additional relevant links:

Hyflux Project - <u>http://www.netl.doe.gov/technologies/oil-</u> gas/FutureSupply/MethaneHydrates/projects/DOEProjects/MH_05638HYFLUX.html

Deep Spill 2 FAQs

The high quality of the research team for Deep Spill 2

Is this a UCSB-only project?

The science team is broadly composed from 9 universities, 2 governmental agencies, and 15 independent scientists. The Quality Review Board brings an additional 12 independent researchers who will evaluate and critique the efforts of Deep Spill 2.

Is the team small and inexperienced?

This is one of the largest and most senior staffed research cruises ever developed to study hydrocarbon venting in the deep seas. The team represents a significant fraction of the marine hydrocarbon research community. This team is well experienced with hydrocarbons in the marine environment and embodies literally centuries of at-sea-experience across a range of critical disciplines.

Are only academic researchers involved in this project?

The team includes a variety of non-academic team members from the Naval Research Laboratory (NRL), Scripps, US Geologic Survey, and industrial partners, with other top government scientists and international scientists drawn for the Quality Review Board.

What is the Quality Review Board's (QRB) function?

The QRB will provide constructive critiques of the experiment and analysis to improve data quality, and to ensure that data collected can be leveraged properly. Each QRB member will be able to contribute unedited commentary on concerns that the science team will address or to which they will provide a scientific response. In short, the QRB provides a quality control process for Deep Spill 2.

Deep Spill 2 will not disrupt safety of current oil spill response and containment efforts

Does the experiment require a free flowing well?

Not at all. All mission objectives can be accomplished with the current containment system in place. Current overflow from the containment system provides enough flowing hydrocarbons to provide for a full scientific study.

Will the experiment interfere with current containment efforts?

This project will offer very little disturbance to the current containment efforts. Most of the experimental tasks will be performed kilometers away from the wellsite. Most "close to plume" activities can be performed above and away from the actual cap.

Will this experiment drain BP resources away from the oil-spill response?

No, the team will bring and provide for its own boats, research equipment, staff, and other supplies. Both boats are scientific research vessels, and include support for ROVs and on-board

laboratories. The experimental teams are preparing equipment and back-up equipment, and they are all bringing sufficient staff to replace and repair on the fly. The experiment's budget factors in costs for all of this planning.

Are the technologies planned for deployment in Deep Spill 2 immature or risky?

All the experiments use published or proven technologies.

Is Deep Spill 2 safe for the scientists and for personnel at the Macondo site?

Safety is our number one priority. Many team members have worked in the COP seep field, where *unflared* methane emissions can be comparable to the Macondo flaring, and oil (with volatiles) emissions can reach 1000 bpd, and where safety is always at the forefront. Other team members have worked at the Macondo site. The team has the experience and motivation to adapt experimental protocols to ensure safe operations.

The Deep Spill 2 team is ready to go

Will this project require long preparation?

Project planning and procurement are already underway. All of the team members are very experienced at bringing missions together quickly. With funding, the team can be ready to go in a very short period of time. The whole project can be completed before 100% containment is achieved sometime mid-July.

Will this be a mad dash project?

Extensive planning, both logistical and scientific, has been on going for weeks. Further, the experimental builds upon Deep Spill 1 and HyFlux 2009, the later of which studied natural seep methane fluxes near the incident site (lead HyFlux team members are team members). "Wet run" practice efforts also were completed in the Coal Oil Point seep field, offshore UCSB in mid June, 2010.

What is the budget?

The budget for Deep Spill 2 is \$8.4M USD. This is based on the urgency of the timeline for planning and procurement, a procurement environment already stressed by the on-going spill response, and includes budgeting for staff, 2 research vessels, primary equipment and redundancy planning, and ROV costs. This compares well against the original MMS Project 377 "Deep Spill", which was budgeted at approximately \$2.5M USD in 2000 dollars, and was far less comprehensive in scope and was completed with significantly less urgency.

Deep Spill 2 is about science and to improve future engineering and safety

Is this experiment only about the well flow rate?

The experiment is about science and for future engineering and safety. The study will provide critical data to answer the basic questions:

- *Where* do the hydrocarbons go?
- What fraction goes where?

• *Why* do the hydrocarbons partition as observed?

What is the benefit of the experiment to modelers?

Currently, CFD models are required to use theoretical considerations for hydrate thermodynamics, an area of active research and discovery. Data from the experiment will validate and/or improve the models, allowing them to be used with confidence for future spills, contingency planning, and thus support environmental and industrial safety.

What is the scientific strategy?

We divide the ocean into 7 depth layers with measurements in each layer using different approaches. In each layer, we perform separate mass balance experiments (hydrocarbons in and hydrocarbons out).

How many experiments are going to be conducted?

There are currently 10 experiments planned for Deep Spill 2.

Can the results of Project 377 "Deep Spill" and Deep Spill 2 be integrated?

There are plans to integrate the results of the 16 experiments in a singular model. The project team includes the same lead numerical modeler from the original Project Deep Spill, so that information learned from the two experiments can be bridged.

How will the team prepare for the experiments?

This is how the team will prepare for the experiment:

- 1. Onshore laboratory calibrations and instrument acquisition, followed by
- 2. "wet run" test experiments in a shallow natural seep field, and then
- 3. a full-scale test in the Gulf of Mexico.

What are the research questions to be answered by the ten experiments?

- 1. What are the oil and gas fluxes, and their diffusion rates, in the plume?
- 2. How do plume-edge feature-velocimetry and interior plume velocities relate?
- 3. How does the plume interact with currents and stratification?
- 4. What is the conversion and detrainment rate of oil bubbles into hydrate flakes?
- 5. What is the methane (buoyancy) loss to the water column?
- 6. What is the oil loss to the water column from mixing and detrainment?
- 7. What is the contribution from natural seep hydrocarbons? (MC252 is in a natural seepage area)
- 8. What is the oil volatilization from surface slicks?
- 9. What is the surface and near surface tar ball flux?
- 10. What fraction of the tar balls comes from natural seepage?
- 11. What is the tar ball formation time-scale?
- 12. What is the total loss of volatiles due to dissolution?

Will the results of Deep Spill 2 be made public?

Simple answer – Yes! The data will be made public, and the research generated from this project will be published in peer-reviewed journals with serious effort to collaborate with and leverage on going research projects in the Gulf of Mexico.

DETAILED TECHNICAL PLANS

In the following technical discussion, sub projects are organized according to Mass In (well emissions) and mass fluxes throughout the water column and environment from the seabed towards the sea surface and from shorter to longer length scales. Each section details the specific and measurements that the team leader will conduct to address specific hypotheses.



Science Question: What are the oil and gas fluxes (and diffusion rates) in the plume?

QUANTIFYING OIL and GAS PLUME FLUX

and FATE by TRACER DYE

Team Leader: Ira Leifer, University of California, Santa Barbara, CA.

OBJECTIVE

To make direct measurement by repeat fluorometric dye injections of known fluorescein dye quantities of plume advective flow by visualization and fluorometry, repeated at key depths throughout the water column. The dye is a tracer of fluid motions that can be mapped by fluorometry.

HYPOTHESES

- Hypothesis 1: As the plume rises in the water column, detrainment / entrainment rates are strongly influenced by currents.
- Hypothesis 2: Enhanced plume fluid detrainment occurs at depths of strong stratification, or current shear, with enhanced oil droplet and dissolved hydrocarbon components.
- Hypothesis 3: Observed hydrate flake formation and detrainment correlates with enhanced plume detrainment.

METHOD BACKGROUND and SUMMARY

Rising bubble plumes power fluid flows (the upwelling flow) that transport CH₄ and nutrientrich waters (*Leifer and Judd*, 2002; *Leifer et al.*, 2009), as well as bacteria and zooplankton (*Jeuthe* 2009). As bubbles rise in a plume, they entrain and vertically transport deeper waters towards the sea surface. In a stratified fluid-the ocean-this uplifts deeper, cooler and denser, oxygen-depleted, water against a density gradient (*Leifer et al.*, 2009). After the initial acceleration phase (*Leifer* 2009), this leads to a steady loss of transported fluid into currents (*Adams and Socolowsky* 2002); however, where the rising plume encounters a rapid density change (the thermocline) massive detrainment can occur (*MacDougall*, 1978), creating horizontal intrusions of deposited fluid (*Leifer et al.*, 2009). Intrusions can contain denser water than ambient, which tends to sink. Dye injection fluid motion tracking (Fig. 1) has been used to quantify upwelling flows in the marine environment (*Leifer et al.*, 2009; *Grimaldo et al.*, 2010); however, salinity and temperature (i.e., density) also can be used to determine upwelling flows if the plume entrainment rate is known. Specifically, the work of the plume against a density gradient provides an additional method for estimating the buoyancy flux. Furthermore, for known fluorescein injection rates, fluorometric measurements provide an approach to derive diffusion rates and turbulence characteristics within the plume, and in conjunction with sonar derived plume size, entrainment rates.



Fig. 1. Upwelling flow measured by dye injection for engineered bubble plumes from [*Leifer et al.*, 2009]. Dye release study using ROV injection in the Coal Oil Point seep field, June 2010.

DETAILED METHODOLOGY

- Dye is injected into the plume from an ROV at a known rate or a known quantity (Fig. 1), either by pump or hydraulic through a heated metal tube to shield instruments from oil fouling.
- Sampling in the plume at hydrate depths is accomplished by a modified bubble blocker approach (as in *Leifer et al.*, 2003), where a heated tube directs fluid out of the plume and in front of a fluorometer to prevent oil fouling. At shallower depths, where the plume is less intense, direct fluorometric measurements can be made in the plume.
- In situ fluorometry provides guidance for sampling for methane and other natural gas components, dissolved oil, and based on known injection rates and calibrated concentrations, fluxes from the plume to the water column at different depths
- Dye injection studies occur at a range of depths spanning the water column.
- Complementary fluid flow measurements will be performed, including an array of heated propeller flow meters and an array of hot wire anemometers will be used to profile velocity structures in the flow at several specific heights.

KEY BROADER IMPACTS

Improved understanding of the governing processes of the fate of oil and natural gas in the deep sea and shallow sea, including plume entrainment and detrainment rates and turbulence measurements in the plume for use in validating numerical models (CFD and otherwise) of the

complex flow. Also, to validate velocimetry measurements by image correlation to improve the interpretation of analysis by the Technical Flow Rate Group of ROV video data. Direct measurements of fluid detrainment rates and plume energy loss from hydrate flake formation.

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Science Question: What are the plume entrainment rates and temporal variability in plume buoyancy fluxes?

QUANTIFYING GAS PLUME FLUX by SCANNING MULTIBEAM SONAR

Team Leader: Ira Leifer, University of California, Santa Barbara, CA.

OBJECTIVE

Direct monitoring of plume growth and dimensions by scanning multibeam sonar. Sonar data analysis in conjunction with fluorometric data will allow plume processes to be characterized. Based on calibrating sonar return with direct flux measurements, near seabed fluxes can be monitored while ROV studies are occurring at shallower depths.

HYPOTHESES

- Hypothesis 1: Plume growth during the acceleration phase depends on entrainment rates and is related to total flux.
- Hypothesis 2: Flux varies with external and internal factors including earth tides, and deep-sea water temperature.
- Hypothesis 3: Hydrate flake formation and detrainment is dependent on water temperature.

METHOD BACKGROUND and SUMMARY

A scanning multibeam-sonar (*Leifer et al.*, 2010a) will monitor plume activity as well as suspended particulates (hydrate crystals, oil droplets) to characterize quantitatively, temporal emission variability, and builds upon single beam sonar studies of seepage (*Leifer et al.*, 2010b). The multibeam operates in vertical fan mode, scanning a complete 3D volume up to 100-m radius, as fast as 10° s⁻¹. The scanner is cabled to the sea surface for real-time data display allowing real-time adjustment of sonar parameters, e.g., range, gain, ping rate, etc., and scanner parameters, including speed, angular limits, etc.). True direction is recorded by a digital compass at 10 Hz. 4D (time-varying) allowing mapping of all scatterers in the scan volume with 20 to 50 cm spatial precision or better, based on range setting (Fig. 1).

Other published multibeam sonar bubble studies use a technically far simpler, horizontal swath (*Greinert and Nützel*, 2004; *Nikolovska et al.*, 2008). Unfortunately, a horizontal swath has severe calibration problems. Specifically, field calibration data (Fig. 1A) shows that sonar return increased with height above the seabed for air bubbles despite a slight predicted decrease in bubble volume from air outgassing. This increase in sonar return with height above the seabed arises from plume expansion and the multiple acoustic pathways in the plume leading to increased attenuation and scattering out of the plume as well as to delayed sonar ping return in a dense plume. This multipath return process decreases as the plume density decreases. Our flux calibration incorporates bubble plume growth; however, this requires 3D visualization.

Algorithms that identify structural orientation and persistence are based on techniques developed for particle velocimetry (*Leifer et al.*, 2010a), enabling automated analysis, and current profile derivation (from plume tilt) for comparison with ADCP data. ADCP data and current-induced horizontal plume displacement allows derivation of vertical bubble velocity and thus gas flux.



Fig. 1 A). Field sonar rotator calibration data for controlled bubble flows during a COP seep field deployment at Shane Seep (22 m). B) Sonar-scanner data (10-min average) from 2009 Siberian Arctic deployment, showing spatial distribution of seepage bubbles and a school of fish.

DETAILED METHODOLOGY

- Sonar rotator is seabed deployed using an ROV with data communication via the ROV fiber optic umbilical. Scan rate and limits, range, gain, can be controlled remotely or set to repeat. Rotator includes a hydrophone to acoustic
- Noise reduction filtering is in the theta-omega-range space.
- Turbulence structures in the four dimensional sonar data are tracked with correlation velocimetry.

KEY BROADER IMPACTS

Demonstration of an approach to monitor seabed leakage and derive fluxes for large emissions flows, comparable to blowout conditions (the approach has been demonstrated for typical seepage systems). The system also has the capability to observe hydrate flake formation and advection.

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Science Question: How do plume-edge feature-velocimetry and interior plume velocities relate?

QUANTIFYING PLUME HYDROCARBON FLUXES by IMAGE CORRELATION

Team Leader: Steve Wereley, Ph.D., Dept. of Mechanical Engineering, Purdue University, IN.

OBJECTIVE

To derive surface velocities from high quality video images with known size scales of the oil gas plume issuing from the Macondo Well site, for comparison with direct fluid dynamics measurements at a range of depths spanning the water column.

HYPOTHESES

- Hypothesis 1: Surface feature derived velocities based on image correlation velocimetry are related to peak and mean plume fluid velocities in a manner that can be calibrated.
- Hypothesis 2: Surface feature divergence and vorticity based on image correlation velocimetry can be related to plume turbulence characteristics.

METHOD BACKGROUND and SUMMARY

The oil flow from the top of the Blow Out Preventer (BOP) is classified (in fluid mechanics jargon) as a buoyant, immiscible two-phase jet with different physical properties from the ambient fluid into which it is issuing. *Panton* (2005) provides an excellent discussion of the physics of jet behavior. The more complicated physics of immiscible jet behavior is discussed by the classic paper of *Hayworth and Treybal* (1950). Analysis of a crude oil/gas jet in seawater is especially difficult because crude oil is opaque. Consequently it is not possible to see interior jet motions with conventional flow visualization experiments. Oil spill videos only show the outer surface of the oil/gas jet as it flows into the seawater. Although this is a distinct limitation of video analysis, it is offset by the convenience of video analysis.

The recent work of the Flow Rate Technical Group (FRTG) relied on just such video imaging to reach its conclusion on the oil spill flow rate. Generally, the FRTG approach relied on optical feature tracking. Several of the group members used Particle Image Velocimetry (PIV) algorithms which usually cross-correlate small regions of a particle-laden flow in order to extract the velocity of the flow. However, because few observable particles are carried by the flow, this approach would be more properly classified as correlation-based feature tracking in which motion of (evolving) vortex structures are tracked. This approach relies on analysis of features
that are observable at the oil/water interface, introducing complexity into the analysis, including assumptions about how visible structure motion relates to the mean and peak jet velocity.

DETAILED METHODOLOGY

- During the time period when dye based flow velocity measurements are being made, video will be recorded. This will allow comparison of the image analysis flow calculations and the dye tracking experiment. Several different algorithms will be used.
- Particle Image Velocimetry algorithms are well accepted and common. However, they have several drawbacks. In particular, they rely on spatially-averaged cross correlations to calculate velocity. This inherently selects a certain feature size to be tracked.
- Another approach is called Optical Flow which relies on iteratively solving the complex equations of fluid motion to determine the most likely flow that matches with the apparent motion of the turbulent structures on the outside of the jet. This approach has no windowing effects but is computationally expensive.
- A third approach to be used is a temporal cross-correlation on a pixel by pixel basis (*Crone*, 2008). This option also has some drawbacks, most notably that the direction of the flow must be assumed in order to calculate the speed of the flow.
- All three optical flow tracking methods (and others not mentioned herein) will be compared to the dye tracking experiments to determine the most accurate algorithm for computing the relationship between the visible motion of the outer flow structures of the and the average speed of the jet to be determined. There is no other way to determine this parameter besides an experiment such as this.

KEY BROADER IMPACTS

Determination of the relationship between surface feature velocities and interior plume velocities and turbulence statistics, will allow analysis of video data for future oil spills to determine oil flow rates to guide numerical models and response from day one rather than after one or more months have elapsed.

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Science Question: How does the plume interact with currents and stratification?

SONAR TRACKING of HYDROCARBON PLUMES in the WATER COLUMN

Team Leader: Bruce Luyendyk and Doug Wilson, Dept. of Geologic Sciences, University of California, Santa Barbara, CA.

OBJECTIVE

Use water-column multibeam data to monitor the buoyancy flux from the plume throughout the water column. Sonar returns are calibrated based on in situ measurements. Data is compared with shipboard Acoustic Doppler Current Profiler data, and CTD casts.

HYPOTHESIS

Hypothesis 1: Sonar data can monitor the effect of currents, decreasing buoyancy due to dissolution, stratification, and the loss of plume coherency on plume dynamics.



Figure 1. Oblique view from above looking northwest at the Coal Oil Point seep field distribution and underlying geologic structure showing faults, Monterey Formation (MF) and Rincon Formation (RF). From *Leifer et al.* (2010).

METHOD BACKGROUND and SUMMARY

Sonar data has been used to quantify bubble flux based on sonar return (*Hornafius et al.* 1999; *Quigley et al.*, 1999) and related to migration through subsurface geologic structure (*Leifer et al.*, 2010). However, for a number of reasons including multiple acoustic pathways, the effect of

bubble size, and acoustic interaction with structures in the seep bubble plumes, direct calibration is critical. For example, sonar return has been calibrated for seep field bubble emissions based on direct flux buoy measurements (*Washburn et al., 2005*). In this study, direct flux measurements will be used to calibrate sonar return.

DETAILED METHODOLOGY

- Multibeam sonar data will be collected during shipboard transects over the bubble plume. Sonar return values are multi-pass gridded [W H F Smith and Wessel, 1990] by first averaging all normalized σ within each grid cell at a coarse resolution grid of 80 m. Empty grid cells were filled by a harmonic interpolation algorithm. Data is analyzed in a series of depth windows, each of which is calibrated by the direct flow measurements.
- Bubble plumes are strongly affected by currents and stratification, which will be determined from ADCP data and CTD casts. Changes in plume character (structure sizes, bubble velocities, and plume coherency) will be related to water column changes.

KEY BROADER IMPACTS

Sonar approaches require *in-situ* calibration, it provides a capability for remote monitoring of emissions. Data can be used to monitor plume dynamics or changes in emission related to internal and external processes, such as earth tides, or loop currents which affect hydrate dynamics.

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Science Question: What is the conversion and detrainment rate of oily bubbles oily droplets, and hydrate flakes?

QUANTIFYING OIL WATER COLUMN DROPLETS

Team Leaders: Vernon Asper and Arne Diercks, University of Southern Mississippi, MS.

OBJECTIVE

To map size and distribution of oil droplets (dispersion) and hydrate particles throughout the water column using a visual approach for comparison with sediment trap data, passive tracer data, and sensed oil and PAH levels.

HYPOTHESES

- Hypothesis 1: Oil droplet concentrations will be greatest in the deep plumes near the wellhead and will decrease with distance due to sedimentation, rising, dissolution, and decomposition.
- Hypothesis 2: Water column oil droplets and dissolved hydrocarbons are correlated (with a temporal offset) to the extent that droplet dissolution is an important mechanism for oil dissolution.
- Hypothesis 3: Droplet interaction with marine snow is an important loss mechanisms leading to droplet sedimentation.

METHOD BACKGROUND and SUMMARY

Preliminary results from studies near the wellhead have indicated the globules of oil are visible both near the surface and in layers (clouds, plumes) at depths below ~1,000m. Near the surface, oil often forms very large aggregates, some exceeding meter length scale) with most on the order of centimeter size. Surface oil globules extend to at least 20 m depths and probably far below that but little is known about their formation, sinking/rising characteristics, or ultimate fate. The deeper oil layers also contain large aggregates; however, most of the oil appears to be dispersed in millimeter sized droplets. The layers also appear to contain substantial methane hydrate crystals, at least in the samples acquired in close proximity to the release site, suggesting enhanced aqueous methane levels.

A series of optical instruments will be deployed in conjunction with other sensors to study these aggregates, layers, globules, and possibly hydrate crystals. These techniques have traditionally been applied to the study of "marine snow" organic aggregates but the similarity between the oil aggregates and these well-studied aggregates is so striking that results likely will be comparable *(Honjo et al., 1984, Asper et al, 1992, Asper and Smith 2003).*

DETAILED METHODOLOGY

- The main system consists of a digital camera that is positioned to acquire images of a lighted "slab" of illumination. This "slab" is produced by twin Deep Sea Power and Light parabolic, collimated strobe lights the face each other and produces a 7.5 cm thick illuminated volume.
- The Insite Pacific "Scorpio" camera photographs this volume using a zoom setting and distance separation to yield a field of view that is 22 x 15 cm, yielding a usable sample volume of 2.5 liters.
- The 3.2 megapixel sensor in the camera yields a resolution of less than 100 microns, allowing excellent discernment of the objects in the illuminated volume, their size, and their concentration in either number/liter or volume/liter.
- The optical system is completely self-contained and does not require a conductive cable to operate, allowing it to be used on any vessel with a cable of at least 0.25" in diameter and long enough to reach the depths of interest. In order to record the depths at which the images are acquired, a Seabird Seacat CTD is attached to the frame.
- A Sequoia LISST particle size sensing instrument will measure very small particles and oil droplets. Fluorometry of the water flow in conjunction with ground reference sampling will enable discrimination between marine snow and oil droplets.
- Other sensors to be deployed will measure CH₄, CO₂, and PAH, and a second Seacat to record control signals. These sensors all are commercially available and most are included in one or more of the Federal guidelines for oil monitoring in both the near and far fields.
- This combined system will provide a comprehensive sampling system for monitoring the abundance, size distribution and location of oil droplets and globules throughout the water column spanning sizes from micrometer to centimeter scales.

KEY BROADER IMPACTS

Improve our understanding of the processes that govern the fate of oil as dispersions in the deep sea and shallow sea, including plume detrainment and the role of hydrate flakes and crystals and their persistence.

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Science Question: What is the methane (buoyancy) loss to the water column?

SURVEY of PLUME MASS OUTPUT FLUX

Team Leaders: Miriam Kastner and Evan Solomon, SCRIPPS and U. Washington

OBJECTIVE

To compute a mass balance for the oil/gas plume, not only do the input fluxes need to be measured at the Macondo wellhead, but output fluxes need to be quantified in the water column and at the sea surface. A major component of the output flux is plume detrainment and mass exchange within the water column as the oil and gas rise. Our goal is to constrain these output fluxes by detailed water column sampling via ROV and CTD/rosette both adjacent to the plume as well as at down-current and across-current locations. A comprehensive suite of analyses including temperature, salinity, oxygen, methane, C₂-C₅ alkanes, DOC, δ^{13} CH₄, δ^{13} C-DIC, and DO¹⁴C will be performed on water samples.

HYPOTHESES

- Hypothesis 1: The source oil output is constrained by mass exchange within the water column and the vertical rise of the plume.
- Hypothesis 2: Increased methane fluxes are correlated with anoxia at greater depths, and thus will have an ecosystem impact. Simultaneously, iron mobility in the reduced form, and therefore also the associated phosphorous, will increase and cause enhanced productivity at the shallower depths
- Hypothesis 3: The combined effects of greater production of organic matter and its enhanced preservation at depth should provide a positive feedback for hydrocarbons formation

METHOD BACKGROUND and SUMMARY

We have applied this approach to constrain plume detrainment, water column oxidation, and hydrocarbon fluxes to the atmosphere at the GC 185 cold seep (~280 km away from the spill site) and at the MC 118 seep site (~8 km away from the oil spill; *Solomon et al.*, 2009a; 2009b). These comprehensive datasets on the background conditions in the northern Gulf of Mexico and the impact of natural hydrocarbon seepage at MC 118 will be of critical importance in evaluating the water column impact of the deepwater oil spill.

The C_1 - C_5 and DOC concentrations trace the oil lost to the water column, the DO¹⁴C is used to distinguish the DOC from the oil spill, natural hydrocarbon seeps, and background seawater, and

the δ^{13} C analyses provide an estimate of the amount of hydrocarbon oxidation in the water column (e.g., *Solomon et al.*, 2009; *Kessler et al.*, 2006; *Grant and Whiticar*, 2002; *Valentine et al.*, 2001). The δ^{13} C profiles in conjunction with the oxygen profiles measure the impact and control of the oil spill on the local biosphere (benthic and water column).



Fig. 1. Methane concentrations associated with a seep bubble plume from 550 m (hydrate zone) showing strong evidence of deep-sea detrainment and thermocline detrainment, consistent with bubble plume theory. Detrainment layers associated with the Macondo spill are hypothesized to correlate with elevated oil levels in the water. From *Solomon et al.* (2009a).

DETAILED METHODOLOGY

- Temperature, salinity, and oxygen measured during CTD downcasts and ROV dives help identify areas of detrainment. Assuming it takes ~2 hours to deploy and sample a hydrocast at ~1 km depth, we anticipate the 24 full water-column hydrocasts to take 2 days to complete. We plan 8 full water column profiles (~18 depths each) via hydrocast down current from the plume and 16 casts across current from the plume to constrain the spatial distribution of these parameters and fully constrain the output flux. Additional hydrocasts will focus on sampling the thermocline where plume detrainment is expected to be the most intense.
- Samples will also be collected during ROV dives, which is likely to take 3-4 days based on similar sampling during the Hyflux expedition. All of the water column samples will also be sub-sampled by other research groups on the team. We plan to collect full water column profiles from ROV dives both adjacent to and down current from the Macondo well.
- In total, ~500 samples will be collected and analyzed for C_1 - C_5 and DOC concentrations, T, S, and oxygen. A subset of these samples will be analyzed for $\delta^{13}C$ -CH₄, $\delta^{13}C$ -DIC, and DO¹⁴C.
- Niskin bottles on rosettes and the ROV are then collected and the water is measured for these components to trace and quantify mass fluxes from the plume to the water column and to the atmosphere (e.g. *Solomon et al.*, 2009a; *Leifer et al.*, 2006; *Mau et al.*, 2007; *Grant and Whiticar*, 2002).

KEY BROADER IMPACTS

This study will provide a thorough overview of the vertical distribution of the oil flux out of the benthic plume. The formation of gas hydrate in the water column in the vicinity of the spill site could provide a golden opportunity to empirically determine the hydrocarbon fractionation factors between the lighter and heavier hydrocarbons into the hydrate structure (I or II forms). Because the water column concentrations will be determined, measurements of the hydrate concentrations will allow hydrates water column formation rates to be determined.

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Science Question: What is the oil loss to the water column from mixing and detrainment?

OIL CONTRIBUTION to OCEAN DISSOLVED ORGANIC MATTER CYCLE

Team Leader: Chris Osburn, North Carolina State University, N.C.

OBJECTIVE

Estimate rates of oil released from the Macondo Well that is partitioned into the marine dissolved organic matter (DOM) C cycle by measuring the ultraviolet fluorescence (UVF). Spatial surveys of UVF (in-water and shipboard) will determine 3D distributions of oil released from the Macondo Well, dispersed throughout the Gulf of Mexico water column, and migrating into the ocean's carbon (C) cycle.

HYPOTHESES

- Hypothesis 1: Oil released from the Macondo Well will enter the ocean C cycle via the marine DOM pool.
- Hypothesis 2: The ultraviolet fluorescence (UVF) of oil is similar to, but distinct from the background natural UVF of dissolved organic material (DOM) and these signals can be separated in an array of Excitation Emission Matrix Spectroscopy (EEMS) using a statistical model.

METHOD BACKGROUND and SUMMARY

Oil emulsification, dissolution, and dispersion cause its partitioning into the aqueous phase (see the adjacent figure), thus creating a mechanism by which oil release from the subsurface into the ocean's water column can enter the ocean's C cycle (Kepkay et al. 2008). The oil enters the C cycle via the DOM pool of organic compounds, many that are consumed by marine bacteria and metabolized to CO₂ (and possibly to methane, CH₄). Both DOM and oil absorb light and fluoresce, so UVF,



especially excitation-emission matrix spectroscopy (EEMS), is a rapid way to simultaneously measure the oil and DOM in seawater (*Kepkay et al.* 2002; *Boyd and Osburn* 2004; *Budgen et al.* 2008). However, in the presence of DOM will mask oil UVF, so EEMS must be processed statistically (using parallel factor analysis, PARAFAC) to separate these discrete signals (*Liu et al.* 2009; *Boyd et al.* 2010). In water UVF measurements alone cannot do this successfully, requiring substantial validation and calibration of UVF signals shipboard on a spectrofluorometer. EEMS/UVF can then be used to trace oil movement (e.g., *Stedmon et al.* 2010). At the sea surface, it will then be important to incorporate the effects of sunlight degradation on DOM and oil (e.g., *Osburn et al.* 2009).

DETAILED METHODOLOGY

- A Wetlabs fluorometer will be deployed to measure real time UVF at discrete channels set with the ROV operator. The excitation-emission matrix spectral (EEMS) fluorescence of DOM in seawater and of extracted oil will be measured shipboard on a spectrofluorometer from 220 to 500 nm excitation (at 5 nm increments) and from 350 to 650 nm (at 2 nm increments) (*Liu et al.* 2009).
- EEMS will be modeled by PARAFAC to decompose the DOM and oil UVF spectral signals (*Christensen and Tomasi* 2007; *Boyd et al.* 2010).
- PARAFAC-EEMS models will be used to calibrate and validate the UVF measurements collected by the in-water fluorometer to determine concentrations of oil and DOM in the water column.

KEY BROADER IMPACTS

Study data will contribute to assessing the total fate of the Deep Water Horizon spill and its impact on the C cycle of the Gulf of Mexico. Coupled with an overview of the oil distribution in the water column, the oil dispersion and microbial and photochemical transformation rates based on UVF signals will be developed as integrated into hydrodynamic and circulation models (e.g., *Stedmon et al.* 2010).

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Science Question: What is the spatial variation in source oil relative to natural seep oil?

OIL SOURCE TRACKING

Team Leader: Richard Coffin: Marine Biogeochemistry Section, Naval Research Laboratory, Washington, DC 20375

OBJECTIVE

Determine spatial variation in water column natural seep oil and surface sediment relative to the Horizon spill. Analyses will use C6 to C20 alkanes and polyaromatic hydrocarbons (PAHs) to trace sources.

HYPOTHESIS

Hypothesis 1: Oil near the Macondo Well site, primarily originates from the well with a spatial distribution and flux determined by a combination of dispersion, hydrate flake detrainment, and interaction with marine snow and currents.

METHOD BACKGROUND and SUMMARY

Stable isotope analysis is well developed to trace carbon sources in bulk material and specific compounds (Coffin et al. 1989; 1990; 1997; 2001; 2008; Kelley et al. 1997). Analysis of a mixture of individual compound speciation and stable carbon isotope ratio has been shown to provide strong capability to trace petroleum sources; nalkanes in the fuel, analyzed for variation in the stable carbon isotope ratio, have been shown to have a wide range in the data (see the adjacent figure). This study applies



stable carbon isotope analysis and oil compound speciation for a thorough statistical analysis of spatial variation in the oil source (*Boyd et al.*, 2006). Samples will be taken through the water column and surface sediments to account for the contribution of different sources. These data can be coupled with the analysis of the total petroleum hydrocarbon concentrations to determine source responsibility.

DETAILED METHODOLOGY

- Four liter water samples will be collected from CTD casts, in dark glass bottles baked at 450°C, preserved with addition of sodium hydroxide, and stored in a refrigerator until returned to the laboratory.
- Shallow sediment samples are obtained with a sediment grab, with caution to subsample surface sediments. Samples are stored in a refrigerator until processing.
- PAHs and alkanes are extracted from the water column and sediment samples for analysis of speciation and carbon isotope analysis using previously published methods (*Pohlman et al.* 2002; *Trust et al.* 1998).
- Laboratory instrumentation included for the compound speciation and δ^{13} C analysis will be a custom-configured GC-Combustion-Isotope Ratio MS (GC-C-IRMS). The current configuration consists of a Helwlett Packard 6890 GC with a 5973 quadrapole MS outfitted with a 250 µm ID 30 m Supelco SPB-05 capillary column. A post column 4-way valve (Valco) allows a 20:80 split between the quadrapole MS and the IRMS, respectively. IRMS flow is routed through a Finnigan GC combustion interface, which is, in turn interfaced to a Finnigan MAT Delta S IRMS. Injections are run splitless to minimize potential isotope fractionation in the inlet.
- Compound specific isotope analysis will be coupled with multivariate statistics to determine if multiple sources exist (*Boyd et al.* 2006).

KEY BROADER IMPACTS

Data from this study will be used to confirm the oil contribution from the Horizon spill relative to natural seepage. If multiple sources are observed, the range in $\delta^{13}C$ and variation in compound speciation between the Horizon spill and natural seepage can be used to estimate the percent contribution to the total concentration. A thorough analysis of the spatial impact of the spill, in terms of total petroleum hydrocarbon concentrations, and coupled with $\delta^{13}C$ will estimate the total spill volume.

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Science Question: How does the coinciding methane flow influence the transport of oil?

ELEVATED SEDIMENT METHANE FLUX

Team Leader: Richard Coffin: Marine Biogeochemistry Section, Naval Research Laboratory, Washington DC. 20375

OBJECTIVE

Evaluate increased transport of methane to the water column from the Macondo Well on the oil transport and ocean oxygen cycling as well as tracing the methane as a proxy for oil transport. This study will focus on the water column as the methane end point with analysis of dissolved methane concentrations through vertical profiles. Data obtained will be coupled with bubble flux surveys for a total overview of elevated methane fluxes.

HYPOTHESES

- Hypothesis 1: Methane serves as a proxy for estimating the petroleum flow out of the Macondo Well.
- Hypothesis 2: Elevated gas fluxes, associated with the Macondo Well oil flow, influence the oil transport and fate through the water column.
- Hypothesis 3: Increased gas flux to the water column elevates the water column hypoxic and anoxic conditions.

METHOD BACKGROUND and SUMMARY

There is a complicated interaction of gas and oil flux from the sediment that needs to be addressed to understand the fate of the oil and the methane influence on the ecosystem (see adjacent figure). Oil coating the methane bubbles at the source, *i.e.* on the ocean floor, can physically control the fate of the oil during transport as a function of the bubble size and thickness of oil coating the bubble (Labeled A in the figure).



Methane advection associated with the

spill flow needs to be assessed as a tracer for estimating the spill volume (Labeled B in Fig. 1). In addition the methane can be a significant contribution to the ocean carbon cycling and the associated oxygen demand (Labeled C in the figure). Stable carbon isotope analysis of microbial

nucleic acids suggests that the sediment gas flux is a significant contribution (30% to 50%) to bacterioplankton carbon cycling in the Gulf of Mexico water column (*Kelley et al.* 1998). Other studies support this observation, for example, there are regions in the Gulf of Mexico where methane advection dominates the shallow sediment carbon cycling and suggests a flux to the water column (*Coffin et al.*, 2008). Radiocarbon isotope analysis of the bacterial biomarkers shows a ¹⁴C depleted biomass signature suggesting deep sediment methane has potential to be a strong contribution to the bacterioplankton carbon cycling (*Cherrier et al.* 1999; *Grabowski et al.*, 2004).

DETAILED METHODOLOGY

- Sample locations will be coupled with methane sensor data taken from ROV time and CTD casts.
- Using an insulated pressure vessel, the ROV will collect plume samples for shipboard and later analysis for hydrates, water, oil, and gas from each water-column depth zone.
- 30 ml water samples will be taken with a gas tight syringe and transferred to sealed 60 ml serum bottles that are purged with nitrogen gas and evacuated. Samples are fixed with 0.5% mercuric chloride.
- The dissolved methane concentration is determined by the head space equilibration technique. For this analysis, methane was stripped from water samples in a 60-ml syringe with N₂ and injected into a Shimadzu min-2 gas chromatograph (GC) equipped with a Hayesep Q packed column (Alltech).
- $CH_4 \delta^{13}C$ will be measured using a Trace GC interfaced via a GC-C III combustion unit to the IRMS. Samples were cryogenically concentrated according to the method of *Plummer et al.* (2005).
- Potential oxygen demand will be estimated on samples through the water column in BOD bottles incubated for 48 hours at ambient temperatures (*Coffin et al.*, 1993).

KEY BROADER IMPACTS

This study will: 1) address the control of methane on the oil transport through the water column; 2) evaluate using the methane gas flux as a proxy for tracing the petroleum transport; and 3) provide an estimate of the methane impact on coastal Gulf of Mexico water column anoxia and hypoxia. Data obtained during this survey will set plans for future ecosystem evaluation in terms of the oil turnover and anoxic conditions.

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Science Question: How much oil sediments back to the ocean floor?

OIL PARTICLE ABSORPTION and SEDIMENTATION

Team Leader: Richard Coffin, Marine Biogeochemistry Section, Naval Research Laboratory, Washington DC. 20375.

OBJECTIVE

Estimate oil sedimentation rates from the Macondo well for naturally and anthropogenically dispersed oil across the water column to the sediment–water interface. Spatial sediment trap surveys will determine oil downward vertical transport to the ocean floor from absorption on clay and natural ocean detritus (marine snow).

HYPOTHESES

- Hypothesis 1: Oil sedimentation rates are directly related to water-column particle loading, hydrate flake formation, and correlate with seabed sediment deposition through the intermediary of current transport.
- Hypothesis 2: With increasing distance, the chemical composition of sedimented oil will more closely relate to oil component fractionation higher in the water column.

METHOD BACKGROUND and SUMMARY

Organic contaminant transport on oceanic particulate material in the water column is well documented in previous studies (*Pohlman et al.* 2001) and plays an important role in the fate and potentially in the mass balance of oil released from a subsea spill.

The sedimentation occurs through: 1) particle absorption to surface ocean particles; 2) absorption to clay particles that are transported with the oil; and 3) formation of tar balls comprised of consolidated heavier molecules from the oil plume. For natural systems, all three factors control oil sedimentation.



DETAILED METHODOLOGY

- Site selection of locations for the sediment traps will be established on the initial surveys of the spill migration. Traps will be set at locations downstream of the spill source.
- Ocean floor moored and surface traps will be set through the water column. Trap funnels will have 0.25 m² mouths.
- The sediment trap depths will be chosen based on an overview of the ROV total petroleum hydrocarbon concentration (TPH) data obtained during the initial survey stages.
- Traps will be set for time periods of days to weeks depending on observed particle loading.
- Trap samples traps will be analyzed for TPH and levels of high molecular weight to low molecular weight polyaromatic hydrocarbons (*Coffin et al. 2004*) to evaluate light oil dissolution and tar ball formation and general sediment stable carbon isotope analysis to assess the sediment carbon source(s) (*Coffin et al. 2007; 2008*).
- Sediment trap data will be compared to the particle loading from samples taken in the water column.

KEY BROADER IMPACTS

Data will contribute to assessing the total fate of the Horizon spill. Coupled with an overview of the oil distribution in the water column, the oil transport rates can be developed as well as natural biotic and abiotic oil degradation to estimate residence times.

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Science Question: Are non methane and low molecular weight alkanes are a proxy for high molecular weight dissolved oil components?

DETERMINATION of the DISTRIBUTION of DISSOLVED HYDROCARBONS

Team Leader: R. Timothy Short, Marine Technology Program, SRI International, St. Petersburg, FL 33701

OBJECTIVE

Determine spatial variation of dissolved gases, light hydrocarbons, and volatile organics in water column near the Deepwater Horizon oil spill using in situ membrane introduction mass spectrometry.

HYPOTHESES

- Hypothesis 1: Gas fractionation within the plume due to bubble processes leads to spatially distinct aqueous n-alkane plumes.
- Hypothesis 2: Aqueous higher molecular weight n-alkanes exhibit a spatial distribution that correlates with dissolved PAH and other high molecular weight oil components, unlike lighter n-alkanes, such as methane.

METHOD BACKGROUND and SUMMARY

SRI International in St. Petersburg, Florida has developed and proven the use of underwater mass spectrometer (UMS) systems [1-6] for the **quantification** of multiple dissolved gases, dissolved hydrocarbons and volatile organic compounds (VOCs) in subsurface plumes. The mass spectrometer is a versatile analyzer with capabilities that far exceed traditional in-situ underwater chemical sensing techniques. SRI has experience in deploying these systems at MC118 near the spill site and thus is well qualified to study the extent of subsurface hydrocarbon plumes resulting from the Deepwater Horizon spill.

DETAILED METHODOLOGY

- The SRI underwater mass spectrometer will be deployed from a profiling winch to determine the vertical distribution of dissolved gases, light hydrocarbons and VOCs in the water column at various locations near the spill site. CTD data will be taken to enable quantification of the measurements.
- Data are gridded in 3D space for analysis in terms of fluxes.

KEY BROADER IMPACTS

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Science Question: How are oil droplets and globules distributed through the water column?

OIL DROPLET and GLOBULE MAPPING with MULTIBEAM SONAR

Team Leader: Eric Maillard, Reson Inc., US, Goleta, CA, Reson GmbH, DE

OBJECTIVE

Use water-column multibeam data to quantify oil droplet and globule spatial distribution in the near surface water column where observations shows significant suspended oil, as well as at other depths in the water column. Sonar returns will be calibrated based on in situ video observations.

HYPOTHESIS

Hypothesis 1: Oil globules are dispersed within the mixed layer, with a depth distribution related to mixing processes - wind and wave development – in the case of natural dispersion and suspension processes.

METHOD BACKGROUND and SUMMARY

Sonar data has been used to quantify bubble flux based on sonar return (*Hornafius et al.*, 1999) and more recently, multibeam sonar has been used to observe suspended oil globules in near surface waters in the Gulf of Mexico during the current Macondo Spill Incident.



Fig. 1. SeaBat 7125 (Reson) data from Coal Oil Point seep field, collected June 2010 of rising seep bubble plumes. Currents were strong and cause significant plume diversion

DETAILED METHODOLOGY

- Multibeam sonar data using a SeaBat 7125 in the upper water column (to 200 m depth at 200 kHz), covering the entire mixed layer will be collected during along-current shipboard transects. Full water column observations will be with a combination of a SeaBat 7111.
- Sonar return values are multi-pass, 3D gridded [*Smith and Wessel*, 1990] by first averaging all normalized σ within each grid cell at a coarse resolution. Empty grid cells were filled by a harmonic interpolation algorithm. Data is analyzed in a series of depth windows.

KEY BROADER IMPACTS

Use of multibeam sonar to map oil suspensions in the water column presents a powerful tool not only for monitoring and response, but also to related the behavior and fate of oil suspension to oceanographic process.

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Science Question: What is the oil volatilization from surface slicks?

QUANTIFYING SPILL HYDROCARBON FLUXES to the ATMOSPHERE

Team Leader: Ian MacDonald, Dept. of Oceanography, Florida State University, FL.

OBJECTIVE

To collect oil slick samples of known age at known positions and meteorological data to allow evaluation of oil weathering due to evaporation, dispersion, and dissolution for the Macondo oil spill for comparison with standard oil spill weathering and advection models and with satellite and airborne observations and data.

HYPOTHESES

- Hypothesis 1: Most of the volatile loss from the seabed flow is due to (solubility-driven) dissolution, rather than vapor pressure evaporation. Thus, slick evaporative losses are both lower and chemically distinct from those due to weathering over time for the same oil if spilled at the sea surface.
- Hypothesis 2: Oil advection by winds and currents in a massive oil spill is unique from a conventional oil spill due to wide-scale alteration of the ocean-atmosphere boundary by the extensive oil slick.
- Hypothesis 3: Thickness categories of floating oil layers can be distinguished by comparing satellite SAR with visible wavelength data (e.g. MERIS, MODIS).

METHOD BACKGROUND and SUMMARY

Oil released from the wellhead will result in a reasonably well-characterized hydrocarbon plume rising towards the surface. During transit, the plume is predicted to include separation of a substantial midwater component with extended residence time at depth [*Zheng et al.*, 2003]. The buoyant phase; however, will be expected to rise fairly rapidly to the surface. This trajectory can be predicted accurately using a random walk model (SLIKTRAK) conditioned on water column current direction and speed (from on-scene ADCP readings) (*MacDonald et al.*, 2002). It has been shown that freshly surfaced oil from Gulf seep oil at half-kilometer depths alters rapidly (minutes to hours) by the loss of lighter components through evaporation and dispersion (*MacDonald et al.*, 2002; *NOAA*, 2009).

On the surface, the oil forms a large, semi-continuous layer that can be reliably distinguished in synthetic aperture radar data (*Garcia-Pineda et al.* 2009) will be thickest near the oil slick origin and will be thinner as the oil spreads and is weathered. Remote sensing time-series will be obtained from available ENVISAT and ALOS SAR platforms. Slick areas will be segmented with use of a Texture Classifying Neural Network Algorithm (*Garcia-Pineda* et al. 2009).

Sampling time-series will include positioning the ship near the freshly surfaced oil based on SLIKTRAK predictions and/or aerial observations. When the surfacing position for the oil is located, the ship will maintain contact with the oil as it drifts away from the source by deploying small, low profile markers. A time-series of surface oil samples will be collected to examine the short-term alteration of Macondo oil under ambient surface conditions. Freshly surfaced oil samples will be compared with oil samples from a range of depths spanning the water column, including near surface waters, to identify chemical partitioning during water column transit.

DETAILED METHODOLOGY

- Oil slick samples will be collected using standard oil sample collections kits into cleaned glass containers and stored cold. Slick age is determined by tagging oil with hollow glass microspheres (*Leifer et al.*, 2006), and GPS position noted for each sample. Contemporaneous wind profile and meteorological data will be collected.
- Samples will be analyzed by GERG analytic laboratory.
- Numerical oil advection models will model oil slick advection (as in *Leifer et al.*, 2006) with wind and meteorological data for model input.
- ADIOS2 will be used to model weathering for comparison with data.
- Satellite data will be analyzed for the studies' duration to identify context of oil age from wind and current advection.

KEY BROADER IMPACTS

Improved modeling of oil spill volatilization and advection rates, particularly for the unique conditions where there is large-scale alteration of the ocean-atmosphere boundary condition by the oil. This will develop better understanding of the partitioning of different oil components between the sea surface, atmosphere, and near surface waters.

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Science Question: What is the surface and near surface tar ball flux? What fraction of the tar balls comes from natural seepage? What is the tar ball formation time-scale?

ASSESSMENT of SPILL SOURCED

TAR BALL FORMATION

Team Leader: Rick Coffin, **Team Leader:** Richard Coffin, Marine Biogeochemistry Section, Naval Research Laboratory, Washington DC. 20375

Key Collaborators: Tom Lorenson and Bob Rosenbauer, USGS, Menlo Park, CA, pending internal review

OBJECTIVE

This study focus on the formation of tar balls sourced from the spill. Evaluation will include confirmation of source oil in the formation, observation of the transport, and estimates of the amount of oil that is transported back to the ocean floor in this format.

HYPOTHESES

- Hypothesis 1: The types and rates of crude oil weathering and degradation differ between oil on the sea surface and oil in the water column.
- Hypothesis 2: In the absence of photo-oxidation, subsurface degradation will follow a different pathway from surface oil with different intermediate compounds.
- Hypothesis 3: Sub-surface degradation of oil may exacerbate oxygen demand in an already oxygen limited environment.

METHOD BACKGROUND and SUMMARY

Following any spill, crude oil undergoes a multitude of physical and chemical weathering processes including evaporation, dissolution, photo-oxidation, and biodegradation. The degradation pathway of spilled oil/tar is of interest scientifically as well as environmentally. Aerobic, and to a lesser extent anaerobic, degradation of petroleum has been well studied and follows specific patterns. Evaporation and dissolution of the more volatile, low molecular weight components generally occur in the initial hours and days of the spill. There then follows a general hierarchy for rates of biodegradation: saturated alkanes are more quickly degraded by microorganisms than aromatic compounds; alkanes and smaller-sized aromatics are degraded before branched alkanes, multi-ring and substituted aromatics, and cyclic compounds. One unique attribute of this spill is that the oil is discharging from a depth of more than 5000' below the sea-surface and about 40 mi from the Louisiana coast into "blue water". The possible impacts of crude oil and chemical dispersants in the open waters of the Gulf of Mexico remain

largely unknown. Oil droplets, dispersant, and dissolved natural gas will be distributed vertically in the water column according to rise rates determined by droplet size and density and ambient water density. Because the droplet size has been reduced by as much as ten-fold at the source by addition of dispersants, much of the oil will rise very slowly and may be trapped indefinitely in deep water. Large plumes of submerged oil are now being mapped in the deep waters of the Gulf of Mexico. Similarly, most, if not all, of the natural gas will dissolve before reaching the surface. These submerged contaminants will be transported by deep currents and may impact a large region of the Gulf of Mexico, including the shelf waters that are highly productive and diverse. Breakdown of the hydrocarbons will consume oxygen, raising concerns about ecological harm far below the sea surface.

The long-term impact of the Deepwater Horizon Oil Spill on the Northern Gulf of Mexico and other Gulf coastal systems will depend on how the oil and oil degradation products are incorporated and cycled among the various components of the coastal system.

DETAILED METHODOLOGY

- Systematic examination of water and oil along a continuum of sampling sites from the point source to the edge of the spill and tar by-products in adjacent coastal sediment and shorelines;
- An analysis of the original well-head oil as a control in determining its fingerprint and levels of degradation/weathering;
- Sampling along radial transits through the oil plume from the surface above the well head to the edge of the plume to document the types and levels of degradation;
- Sample and analyze the concentration and state of degradation of oil in submerged plumes;
- Assess the petrochemical component and its state of degradation in various environmental habitats;

KEY BROADER IMPACTS

Study results will aid in assessing long-term effects on benthic organisms in the inner and outer continental shelves likely will be affected by oil contamination. Oil has the potential to persist in the environment long after a spill has been stopped. Assessments of long-term impacts on fish and wildlife across all trophic levels will remain critical interdisciplinary research components. Because many of these oil transformations will occur initially in the mid-water column as opposed to the surface and nearshore, transport processes will play an important role in the environmental fate of the oil and dispersants.

Recent literature related to this study

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Science Question: What is the total loss of volatiles due to dissolution?

QUANTIFYING SPILL HYDROCARBON FLUX to the ATMOSPHERE

Team Leader: Donald R. Blake, Department of Chemistry, University of California, Irvine, CA.

OBJECTIVE

Air samples will be collected to assess the volatile organic compound fluxes into and the spatial distribution in the atmosphere. Data will be compared with oil slick compositional changes to understand the slick volatilization process.

HYPOTHESES

- Hypothesis 1: Due to the depth of the spill, volatile components in the atmosphere are shifted towards higher molecular weight, less soluble components compared to a conventional oil spill.
- Hypothesis 2: Photo-degradation of older, drifting surface oils causes distinct atmospheric composition over slick portions with freshly surfaced versus older oils, while oil component photolysis leads to smog precursors.
- Hypothesis 3: Winds advect significant quantities of volatile oil components over land.

METHOD BACKGROUND and SUMMARY

Air samples will be collected and analyzed. Preliminary gulf sampling suggests significant higher carbon number alkanes and aromatics present (Fig. 1) while the lower carbon oil components are missing, suggesting significant volatile dissolution in the water column.



Fig. 1. Methylcyclohexane concentrations (ppt) from shipboard measurements in the Gulf of Mexico, June 2010. Exceptionally high total hydrocarbon loads (non methane) more than 2 ppm were observed.

Our research group has flown on every NASA sub-orbital airborne photochemistry mission since 1988. This includes sampling on the NASA Electra aircraft in Alaska in 1988 studying marsh emissions and biomass burning (Blake et al., 1992); sampling in Canada in 1990 studying the Arctic Boundary Layer, (Blake et al., 1994); studying the ozone hole in the northern hemisphere during AASE2 in 1993 (Anderson et al., 1993); obtaining baseline data for pollutant outflow from Asia during PEM-West A (Blake et al., 1995); determining biomass burning emissions from South America and Africa (Blake et al., 1996); comparison of Asian emission during high outflow conditions (Blake et al., 1997); estimating methyl bromide's atmospheric lifetime by using south central Pacific airborne data (Colman et al., 1998); studying south central Pacific gas profiles (Blake et al., 1999); estimating chlorine chemistry in the southern ocean (Wingenter et al., 1999); estimating aircraft emission in the North America/Europe flight corridor (Simpson et al., 2000); distribution of a variety of volatile organic gases in the southern hemisphere (Blake et al., 2001); exploring cirrus activated removal of perchloro-ethene in the upper troposphere (Simpson et al., 2003); pollutant transport from Asia change between 1994 to 2001 (Blake et al., 2003); satellite validation (Emmons et al., 2007); constraining emissions from biomass burning of methylchloroform, (Simpson et al., 2007); studying continental outflow from the US (Kim et al., 2008); and studying gas emissions of oil sands in Canada (Simpson et al., 2010). We participated in the NSF funded NOMHICE intercomparison during which more than 30 of the world's most capable volatile organic compound analysis groups participated (Apel et al., 1999; 2003).

In all NOMHICE studies UCI was ranked at the top for all international groups involved in VOC analysis. Our analytical technique is always evolving but is not that different from the apparatus used for NOMHICE and we are still on the calibration scale used during NOMHICE.

DETAILED METHODOLOGY

- Air samples are collected into evacuated 2-liter stainless steel canisters, with guidance from in situ GC measurements of total hydrocarbons.
- The air sample is preconcentrated in a stainless steel loop filled with glass beads and submerged in liquid nitrogen. The sample is then heated to about 80°C, injected, and split into five different column/detector combinations using UHP helium as the carrier gas.
- The different column/detector combinations allow the identification and quantification of different classes of compounds. However many gases are measured by more than one column/detector combination so that intercomparison between different columns can be carried out as part of the quality control process. Every peak is checked and the baseline is manually adjusted if the integration performed automatically by the software is not correct.
- The first column detector combination was a DB-1 column output to a flame ionization detector (FID) for the identification and quantification (in our experimental conditions) of hydrocarbons with a number of carbon atoms ranging from C₃ to C₁₀. Other compounds of interest quantified with this specific set up are oxygenated molecules.
- The second was a DB-5 column connected in series to a RESTEK 1701 column and output to an electron capture detector (ECD) for the identification and quantification (in our experimental conditions) of halocarbons and alkyl nitrates.
- The third combination was a RESTEK 1701 column output to an ECD, which allows for the identification and quantification (in our experimental conditions) of halocarbons and alkyl nitrates.
- The fourth combination was a PLOT column connected in series to a DB-1 column and output to an FID for the identification of hydrocarbons.
- The final combination was a DB-5ms column output to a quadrapole mass spectrometer detector (MSD). The MSD was set to operate in selected ion monitoring (SIM) mode with one ion chosen to quantify each compound in order to achieve the maximum selectivity and to avoid potential interferences. This combination allows for the identification and quantification (in our experimental conditions) of selected hydrocarbons, halocarbons, alkyl nitrates, and sulfur compounds.

KEY BROADER IMPACTS

Data analysis will provide important field validation of oil slick volatilization models within oil slick evolution models. Furthermore, a thorough, at sea atmospheric pollution inventory will provide important data to better understand the atmospheric impact of a large oil spill, and the unique implications of a deep-sea oil spill where dissolution is important,

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- Apel, E.C., J.G. Calvert, T.M. Gilpin, F. Fehsenfeld, W.A. Lonneman, "Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Task 4, Ambient air J. Geophys Res 108, D9, 4300, 10.1029/2002JD002936, 2003.
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- Blake, D.R.; T.W., Smith, T-Y. Chen, W.J., Whipple, F.S. Rowland, "Effects of biomass burning on summertime nonmethane hydrocarbon concentrations in the Canadian wetlands" *J. Geophys Res [Atmospheres]*, 99(D1), 1699-719, **1994**.
- Blake, D.R., T-Y. Chen, T.W. Smith, C.J-L. Wang, O.W. Wingenter, N.J. Blake, F.S. Rowland, "Three-dimensional distribution of nonmethane hydrocarbons and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A)" J. Geophys Res [Atmospheres], 101(D1), 1763-78, 1996.
- Blake, N.J., D.R. Blake, B.C. Sive, T-Y. Chen, F.S. Rowland, J.E. Collins, G.W. Sachse, B.E. Anderson, "Biomass burning emissions and vertical distribution of atmospheric methyl halides and other reduced carbon gases in the South Atlantic region" *J. Geophys Res [Atmospheres]*, 101(D19), 24151-24164, **1996.**
- Blake, N.J., D.R. Blake; T-Y. Chen, J.E. Collins, G.W. Sachse, B.E. Anderson, F.S. Rowland, "Distribution and seasonality of selected hydrocarbons and halocarbons over the western Pacific basin during PEM-West A and PEM-West B" J. Geophys Res, [Atmospheres], 102(D23), 28315-28331, 1997.
- Blake, N. J., D. R. Blake, O. W. Wingenter, B. C. Sive, L. M. McKenzie, J. P. Lopez, I. J. Simpson, H. E. Fuelberg, G. W. Sachse, B. E. Anderson, G. L. Gregory, M. Carroll, G. M. Albercook, F. S. Rowland, "Influence of southern hemispheric biomass burning on midtropospheric distributions of nonmethane hydrocarbons and selected halocarbons over the remote South Pacific" *J. Geophys. Res., [Atmospheres]*, 104(D13), 16213-16232, 1999.
- Blake, N.J., D.R. Blake, I.J. Simpson, J.P. Lopez, N.A.C. Johnston, A. L. Swanson, A. S. Katzenstein, S. Meinardi, B.C. Sive, J.J. Colman, E. Atlas, F. Flocke, S.A. Vay, M.A. Avery, F.S. Rowland, "Large-scale latitudinal and vertical distributions of NMHCs and selected halocarbons in the troposphere over the Pacific Ocean during the March-April 1999 Pacific Exploratory Mission (PEM-tropics B)" *J Geophys Res, Atm*, 106(D23), 32627-32644, 2001.
- Blake, N. J., D. R. Blake, I. J. Simpson, S. Meinardi, A. L. Swanson, J. P. Lopez, A. S. Katzenstein, B. Barletta, T. Shirai, E. Atlas, G. W. Sachse, M. A. Avery, S. A. Vay, H. E.

Fuelberg, C. M. Kiley, K. Kita, F. S. Rowland, "NMHCs and halocarbons in Asian continental outflow during the transport and chemical evolution over the Pacific (TRACE-P) field campaign: comparison with PEM-West B" *J. Geophys Res.*, *[Atmospheres]*, 108(D20), GTE27/1-GTE27/24, 16 plates, **2003.**

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- Emmons, L. K., G. G. Foster, D. P. Edwards, J. C. Gille, G. Sachse, D. Blake, S. Wofsy, C. Gerbig, D. Matross, and P. Nedelec, "Measurements of Pollution in the Troposphere (MOPITT) Validation Exercises during Summer 2004 Field Campaigns over North America" *Journal of Geophysical Research*, *112*(D12) D12S02, 2007.
- Kim, S. Y., R. Talbot, H. Mao, D. Blake, S. Vay, and H.E. Fuelberg, "Continental Outflow from the US to the Upper Troposphere over the North Atlantic during the NASA INTEX-NA Airborne Campaign" *Atmospheric Chemistry and Physics 8* (7) 1989-2005, 2008.
- Simpson, I. J., B. C. Sive, D. R. Blake, N. J. Blake, T.-Y. Chen, J. P. Lopez, B. E. Anderson, G. W. Sachse, S. A. Vay, H. E. Fuelberg, Y. Kondo, A. M. Thompson, F. S. Rowland, "Nonmethane hydrocarbon measurements in the North Atlantic Flight Corridor during the Subsonic Assessment Ozone and Nitrogen Oxide Experiment" J. Geophys Res [Atmospheres], 105(D3), 3785-3793, 2000.
- Simpson, I.J., O.W. Wingenter, D.J. Westberg, H.E. Fuelberg, C. M. Kiley, J.H. Crawford, S. Meinardi, D.R. Blake, F.S. Rowland, "Airborne measurements of cirrus-activated C2Cl4 depletion in the upper troposphere with evidence against Cl reactions" *Geophysical Research Letters*, 30(20), ASC3/1-ASC3/5, 2003.
- Simpson, I. J., N. J. Blake, D. R. Blake, S. Meinardi, M.P.S. Andersen, and F. S. Rowland. "Strong Evidence for Negligible Methyl Chloroform (CH₃CCl₃) Emissions from Biomass Burning" *Geophysical Research Letters*, 34, (10) L10805, 2007.
- Simpson, I. J., S. Meinardi, B. Barletta, N. Blake, G.S. Diskin, H.E. Fuelberg, K. Gorham, L.G. Huey, F.S. Rowland, S.A. Vay, A.J. Weinheimer, M. Yang, and D.R. Blake.
 "Characterization of trace gases measured over Alberta oil sands mining operations: 75 speciated C₂-C₁₀ volatile organic compounds (VOCs), CO₂, CO, CH₄, NO, NO_y, O₃ and SO₂", Submitted.
- Wingenter, O.W., D.R. Blake, N.J. Blake, B.C. Sive, F.S. Rowland, E. Atlas, F. Flocke, "Tropospheric hydroxyl and atomic chlorine concentrations, and mixing timescales determined from hydrocarbon and halocarbon measurements made over the Southern Ocean" J. Geophys Res [Atmospheres], 104(D17), 21819-21828, 1999.

Science Question: What are the processes needed to balance the mass between the different compartments?

NUMERICAL MODELING the FATE of OIL and GAS HYDROCARBONS in the OCEAN ENVIRONMENT

Team Leader: Poojitha Yapa, Clarkson University, IN.

OBJECTIVE

To run the Clarkson Deepwater Oil and Gas (CDOG) blowout model to aid in data interpretation.

HYPOTHESIS

Hypothesis 1: Numerical modeling in tandem with detailed water column data will allow investigation of the underlying physical processes.

METHOD BACKGROUND and SUMMARY

CDOG simulates the behavior of oil and gas accidentally released from deep water. This is a three-dimensional model. In deepwater, the ultra-high pressure and cold temperature causes phase changes in gasses. These effects combined with deepwater currents in some regions presents extraordinary challenges to modeling jets/plumes from deepwater oil and gas blowouts. CDOG model incorporated the phase changes of gas, associated changes in thermodynamics and its impact on the hydrodynamics of the jet/plume. Hydrate formation, hydrate decomposition, gas dissolution, non-ideal behavior of the gas, and the jet/plume hydrodynamics and thermodynamics. CDOG can take 3-D currents, salinity, water temperature (hence water density) that varies both spatially and temporally. CDOG model has been used to numerically simulate the large scale and unique field experiments "Deep Spill."

DETAILED METHODOLOGY

- Relevant initial conditions are chosen, current fields are applied and model simulations are run.
- Model simulations are compared with data and underlying processes are examined to better understand the driving mechanisms.

KEY BROADER IMPACTS

Data analysis will provide important field validation and allow for improvements of CDOG.

- Yapa, P. D. and Chen F.H., (2004). "Behavior of Oil and Gas from Deepwater Blowouts," *Journal of Hydraulic Engineering*, ASCE, 540-553
- Zheng, L., Yapa, P. D., and Chen, F.H. (2003). "A Model for Simulating Deepwater Oil and Gas Blowouts - Part I: Theory and Model Formulation," *Journal of Hydraulic Research, IAHR*, 41(4), 339-351
- Chen, F.H. and Yapa, P.D. (2003). "A Model for Simulating Deepwater Oil and Gas Blowouts -Part II: Comparison of Numerical Simulations with "Deep Spill" Field Experiments," *Journal of Hydraulic Research, IAHR*, 41(4), 353-365
- Yapa, P. D., Xie, H. (2002). "Modeling Underwater Oil/Gas Jets and Plumes: Comparison with Field Data," *Journal of Hydraulic Engineering*, ASCE, 855-860

SENIOR RESEARCH TEAM RESUMES



Rick Coffin

Ira Leifer

Bruce Luyendyk



Poojitha Yapa

Eric Maillard

Ian MacDonald

Chris Osburn



Don Blake



Vernon Asper



Arne Diercks





Evan Solomon

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EDUCATION:	B.S. in Chemistry, University of California Los Angeles, 1978 M.S. in Chemistry, University of California Irvine, 1980
	Ph.D. in Chemistry, University of California Irvine, 1984
PROFESSIONAL:	Chair of Chemistry Department, 2007-2010
	Professor of Chemistry, University of California Irvine, 1998- present
	Research Chemist, University of California Irvine, 1994-1998
	Associate Research Chemist, University of California Irvine, 1991-
1994	Research Specialist, University of California Irvine, 1985-1991
	Postdoctoral Research Associate, University of California Irvine,
1984-1985	Research Assistant, University of California Irvine, 1978-1984
	U.S. Navy, 1971-1974

AWARDS:

Lauds and Laurels, University of California, Irvine,	2009
AGU Fellow,	2009
AAAS Fellow,	2008
NASA Group Achievement Award,	1993, 1998, 2000, 2006,
2008	
Outstanding Professor Alpha Phi Society,	2000, 2002, 2005
ACS Chuck Bennett Service through Chemistry	2004
Excellence in Undergraduate Research	2001
UCI Chemistry Department Outstanding Teaching Award,	1979
Bank of America Chemistry Award,	1975

Selected Publications (of 366)

- "Methane: Inter-hemispheric Concentration Gradient and Atmospheric Residence Time", *Proceedings of the National Academy of Sciences*, **1982**, *79*, 1366-1370
 E. Mayer, D. R. Blake, S. Tyler, Y. Makide, D. C. Montague and F. S. Rowland
- "Global Atmospheric Concentrations and Source Strength of Ethane", *Nature*, 1986, 321, 231-233
 D. R. Blake and F. S. Rowland
- 3. "Continuing World-wide Increase in Tropospheric Methane, 1978 to 1987", *Science*, March 1988, *239*, 1129-1131, D. R. Blake and F. S. Rowland
- 4. "Urban Leakage of Liquefied Petroleum Gas and Its Impact on Mexico City Air Quality", *Science* **1995**, *269*, 953-956., D. R. Blake and F.S. Rowland
- "Extensive Regional Atmospheric Hydrocarbon Pollution in the Southwestern United States" Proceedings of the National Academy of Sciences, 100, 2003 11975-11979.
 A. S. Katzenstein, L. A. Doezema, I. J. Simpson, D. R. Blake, and F. Sherwood Rowland

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EDUCATION:

- NSF funded Postdoctoral Fellow (Mar. 1986 Dec. 1987) Gordon College, Wenham, MA. Supervisor: Dr. Richard T. Wright.
- Ph.D., Oceanography (Sep. 1982 June 1986), University of Delaware. Supervisor: Dr. Jonathan H. Sharp.
- M.S., Microbiology (Sep. 1978 May 1980), University of New Hampshire. Supervisor: Dr. Galen E. Jones.
- B.A., Microbiology (Sep. 1973 June 1977), University of New Hampshire.

PROFESSIONAL EXPERIENCE: (Last 10 Years)

- Section Head Code 6114, Marine Biogeochemistry. Naval Research Laboratory, Washington DC, September 2003 to present.
- Senior Research Microbiologist, Naval Research Laboratory, Washington DC, June 1996 to September 2003.
- Adjunct Faculty Member, University of Hawaii Manoa, Hawaii Institute for Energy, Honolulu Hawaii. September 2003 to present.

RELATED CURRENT ACTIVITY (2010):

- 2009, Beaufort Sea, Alaska Shelf. Chief Scientist. International geochemical exploration of methane hydrates and climate change.
- Co-organizing research in Hyderabad India for 2012 in the Bay of Bengal.
- Planning expedition in the Kara Sea with US, Russian and Netherlands researchers, summer 2011.
- Planning geochemical evaluation of ChevronTexaco JIP hydrate drill site in the Gulf of Mexico for March 2011.
- Planning fall 2011 hydrate exploration off the mid Chilean Margin.
- Planning future methane hydrate exploration on the Hikurangi Margin, New Zealand.

FIVE RELATIVE PUBLICATIONS: (110 total)

- **Coffin, R.** and J. Greinert. 2009. Review: Developing Long Term International Collaboration on Methane Hydrate Research and Monitoring in the Arctic Region International workshop at Royal NIOZ, The Netherlands EOS 90:240.
- Pecher, I. A., S.A. Henrys, W.T. Wood, G. Crutchley, A.R. Gorman, **R. Coffin**, N. Kukowski, J. Greinert, and K. Faure (Submitted). Focused Fluid Expulsion on the Hikurangi Margin, New Zealand Evidence from Possible Local Upwarping of the Base of Gas Hydrate Stability. Marine Geology
- Coffin, R. B., L. Hamdan, R. Plummer, J. Smith, J. Gardner, W. T. Wood. 2008. Analysis of Methane and Sulfate Flux in Methane Charged Sediments from the Mississippi Canyon, Gulf of Mexico. Marine and Petroleum Geology doi:10.1016/j.marpetgeo.2008.01.014
- **Coffin, R.B.**, Pohlman, J.W., Grabowski, K.S., Knies, D.L., Plummer, R.E., Magee, R.W., Boyd, T.J. 2008. Radiocarbon and stable carbon isotope analysis to confirm petroleum natural attenuation in the vadose zone. Environmental Forensics 9:75-84
- **Coffin, R B.** J. W. Pohlman, J. Gardner, R. Downer, W. Wood, L. Hamdan, S. Walker, R. Plummer J. Gettrust and, J. Diaz 2007. Methane Hydrate Exploration on the Mid Chilean Coast: A Geochemical and Geophysical Survey. Am. Chem. Soc., Div. Pet. Chem. Doi:10.1016/j. petrol.2006.01.013

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Education

1995:	Ph.D. Geological Oceanography, The University of Southern Mississippi.
1990:	Diploma (M.S.), Geology / Paleontology, Univ. Hamburg, Hamburg, Germany.
1986:	Vordiplom (B.S.), Geology, Zoology, Chemistry, Physics, University of
	Hamburg, Hamburg, Germany.

Professional Experience

2007 -	Present	AUV Manager at the University of Southern Mississippi. In charge of AUV
		operations of the National Institute of Undersea Science and Technology
		(NIUST) in Oxford, MS.
0000	0007	

- 2000 2007 Director Radar Programs. Established funding sources, managed operations and contracts of HF Radar and general oceanographic contracts at Ocean Technologies, LLC.
- 1999 2001 Lecturer Department of Marine Science, The University of Southern Mississippi (USM). Taught classes in Introductory Oceanography and Classical Geodesy.
- Senior Geologist Geological Oceanographer in the Slidell Area Office of Neptune Sciences, Inc. Responsible for geological and environmental sections in numerous environmental reports, supervising drafters and technical personal. Completed a geological study for the Army Corps of Engineers Jacksonville District Office. Managed software development team for a commercial software package. Involved in the company's proposal writing efforts.
- 1995 1997 Adj. Assistant Professor, Department of Geology, The University of Southern Mississippi. Taught courses in general and historical geology.
- 1995 1996 Postdoctoral Scientist, Institute for Marine Sciences, University of Southern Mississippi. Taught Introductory Oceanography classes. General work in the Institute for Marine Sciences, performing administrative tasks as well as research in particle dynamics.

Offshore Experience (details 2009-present)

Date	Days	Research Vessel	Registry	Location
May 2009	8	NASA M/V Liberty Star	U.S.A.	Bahamas
June 2009	5	R/V Tommy Munro	U.S.A.	Gulf of Mexico
June 2009	5	R/V Pelican	U.S.A.	Gulf of Mexico
August 2009	12	NOAA Henry Bigelow	U.S.A.	N Atlantic
October 2009	18	NOAA Nancy Foster	U.S.A.	Gulf of Mexico
March 2010	3	R/V Tom McIllwain	U.S.A.	Gulf of Mexico
May 2010	16	R/V Pelican	U.S.A.	Gulf of Mexico
TOTAL	345	14 ships	7 countries	11 locations

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Professional Preparation

1964 M.Sc.	Hebrew University, Jerusalem, Geology and Chemistry
1970 Ph.D.	Harvard University, Geochemistry
1970-1971	Research Associate, Harvard University, Geochemistry and Geology
Appointments	
2006-present	Distinguished Professor, Scripps Institution of Oceanography
1982-2006	Professor, Scripps Institution of Oceanography
	recessor, semps mentation of occurrently

1977-1982 Associate Professor, Scripps Institution of Oceanography

Closely Related Publications

- Kastner, M., Becker, K., Davis, E.E., Fisher, A.T., Jannasch, H.W., Solomon, E.A., and Wheat, C.G. (2006). New insights into the hydrogeology of the ocean crust through longterm monitoring. *Oceanography*, 19, 30-41.
- Kastner, M., Claypool, G., and Robertson, G., (2008). Geochemical constraints on the origin of pore Fluid gas hydrate distribution at Atwater Valley and Keathley Canyon, Northern Gulf of Mexico. Special Edition on Scientific Results of 2005 Chevron JIP Drilling for Methane Hydrates Objectives in the Gulf of Mexico, Ruppel, C., Boswell, R., and Jones, E. Edts., Marine and Petroleum Geology, 25, 860-872. doi:10.1016/j.marpetgeo.2008.01.022.
- Newman, K.R., Cormier, M-H., Weissel, J.K., Driscoll, N.W., Kastner, M., Solomon, E.A., Robertson, G. Hill, J.C., Singh, H. Camilli, R., and Eustice, R., (2008). Active methane venting observed at giant seafloor pockmarks along the U.S. mid-Atlantic shelf break. *Earth Planet. Sci. Letters*, 267: 341-352.
- Solomon, E.A., Kastner, M., Jannasch, H., Weinstein, Y., and Robertson, G., (2008). Dynamic fluid flow and chemical fluxes associated with a seafloor gas hydrate deposit on the northern Gulf of Mexico slope. *Earth Planet. Sci. Letters*, -270:95-105,doi:101016/j.epsl.2008.03.024.
- Solomon, E.A., Kastner, M., and MacDonald, I.R., (2009). Considerable methane fluxes to the atmosphere from hydrocarbon plumes in the Gulf of Mexico, *Nature Geoscience*, *doi:10.1038/NGEO574*.

Other significant related publications

- Carson, B., Kastner, M., Bartlett, D., Jaeger, J., Jannasch, H, and Weinstein, Y. (2003). Implications of carbon flux from the Cascadia accretionary prism: results from long-term measurements at ODP Site 892B. Mar. Geol. 19, 159-180.
- Jannasch, H.W., Wheat, C.G., Plant, J. Kastner, M., and Stakes, D., (2004). Continuous chemical monitoring with osmotically pumped water samplers: OsmoSamplers design and applications. *Limnol. Oceanogr.: Methods V. 2, 102-113.*
- Kastner, M., Solomon, E., Wei, W., Chan, L.H., and Saether, O.M. (2006). Chemical and isotopic compositions of pore fluids and sediments from across the Middle America Trench, offshore Costa Rica., Morris, J., Villinger, H., and Klaus, A. (Eds), Proceed. of ODP, Scientific Results Volume 205, 1-21.
- Kastner, M., Spivack, A.J., Torres, M., Solomon, E., Borole, D.V., Robertson, G.A., and Das, H.C., (2008).Gas hydrates in three Indian Ocean regions, a comparative study of occurrence and subsurface Hydrology. *Proceed.* 6th Interntl. Conf. on Gas Hydrates (ICGH 2008), Vancouver, BC, Canada,1-6.

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a. Professional Preparation

Marine Seeps, Bubbles, Marine Petroleum	Current
Bubble Theory and Analysis	1998 – 1999
Bubble Visualization	1996 - 1998
Atmospheric Sciences	Ph.D., 1995
Aeronomy	M. S., 1989
Physics, Astronomy	B. Sc., 1984
	Marine Seeps, Bubbles, Marine Petroleum Bubble Theory and Analysis Bubble Visualization Atmospheric Sciences Aeronomy Physics, Astronomy

Assoc. Researcher 2, Marine Sciences Institute, Univ. of Calif., Santa Barbara	2008-Current
Assoc. Researcher 1, Marine Sciences Institute, Univ. of Calif., Santa Barbara	2005-2008
Assist. Researcher 3, Marine Sciences Institute, Univ. of Calif., Santa Barbara	2003-2005
Assist. Researcher 1, Marine Sciences Institute, Univ. of Calif., Santa Barbara	2001-2003
Postdoc, Chemical Engineering Science, Univ. of Calif., Santa Barbara	2000-2001

c. i. Relevant Publications (6 of 58 Peer Reviewed)

- Leifer, I., 2010. Characteristics and scaling of bubble plumes from marine hydrocarbon seepage in the Coal Oil Point seep field. *J Geophys Res*, In Press, *doi:10.1029/2009JC005844*.
- Leifer, I., H. Jeuthe, S.H. Gjøsund, V. Johansen, 2009. Engineered and natural marine seep, bubbledriven buoyancy flows. *Journal of Physical Oceanography*, **52**, 2769-2778.
- Bradley, E.S., I. Leifer, M. Moritsch, D.A. Roberts. 2009. Atmospheric long-term monitoring of temporal trends in seep field emissions. *Atmos Environ*, *Submitted*.
- Leifer, I., M. Kamerling, B.P. Luyendyk, and D. Wilson, 2010. Geologic control of natural marine methane seep emissions, Coal Oil Point seep field, California. *Geo-Marine Letters*, 30(3-4), 331-338, doi:10.1007/s00367-010-0188-9.
- Leifer, I., B. Luyendyk, J. Boles, J.F. Clark, 2006. Natural marine seepage blowout: Contribution to atmospheric methane. *Glob Biogeochem Cyc*, **20(3)**, doi:10.1029/2005GB002668.

c. ii. Additional 5 Publications

- Solomon, E., M. Kastner, I. MacDonald, I. Leifer, 2009. Considerable methane fluxes to the atmosphere from hydrocarbon seeps in the Gulf of Mexico. *Nature GeoScience* **2**, 561-565.
- Leifer, I., D.J. Tang, 2007. The acoustic signature of marine seep bubbles, *J Am Soc of Acoust Exp Lett* 121(1), EL35-EL40, *doi:10.1121/1.2401227*.
- Vazquez, A., I. Leifer, and R.M. Sanchez, 2009. Analysis of bubble growth phases based on the related dynamic forces. *Chem. Eng. Sci.*, 65(13) 4046-4054.
- Leifer, I., B.P. Luyendyk, and K. Broderick, 2006. Tracking an oil slick from multiple natural sources, Coal Oil Point, California, *Mar Petr Geol.* 23(5), 621-630.

Shakhova, N., I. Semiletov, I. Leifer, P. Rekant, A. Salyuk, and D. Kosmach, 2010. Geochemical and geophysical evidence of methane release over the East Siberian Arctic Shelf. *J. Geophys. Res.*, *In Press.* doi:10.1029/2009JC005602

Bruce P. Luyendyk Professor Above Scale

Professor Above Scale Department of Earth Science University of California Santa Barbara

PLACE OF BIRTH: Freeport, New York NATIONALITY: U.S.A.

EDUCATION:	<u>Degree</u>	Institution	Year	Scientific Field
	B.S.	San Diego State College (Univ.)	1965	Geology (Geophysics)
	Ph.D.	Scripps Inst. of Oceanography	1969	Oceanography (Marine Geophysics)
POSITIONS: 2005 – present 1981 - present	Assoc Profes Califo	viate Dean, Mathematical, Life, and ssor, Department of Geological (Ea prnia, Santa Barbara.	l Physica arth) Scie	l Sciences, UCSB nces, University of
1997 - 2003 1988 - 1997 1973 - 1975	Chair, Direct Assist	, Department of Geological (Earth) tor, Institute for Crustal Studies, Ut tant Professor, Department of Geol	Sciences CSB ogical Sc	s, UCSB viences, University of
1970 - 1973	Assistant Scientist, Department of Geology and Geophysics, Woods Hole Oceanographic Institution.			
1969 - 1970	Postdoctoral Fellow, Department of Geology and Geophysics, Woods Hole Oceanographic Institution.			
1969	Postg	raduate Research Geologist, Scripp	s Institut	ion of Oceanography.
HONORS HIGHLIG	GHTS:			
1975	Fellow	w of the Geological Society of Ame	erica	_
1980	Co-Recipient, Newcomb Cleveland Prize of AAAS			
1983	Distinguished Alumni Award, Dept. of Geological Sciences, San Diego State University			
1990	Antar	ctic Service Medal, U. S. National	Science 1	Foundation, and
	Departm	ent of the Navy	_	
2002	Fellow	w of the American Geophysical Un	ion	
RECENT PROFES	SIONAL SEF	RVICE HIGHLIGHTS:	ttee for tl	a Inst of
1))/	Geophys	sics and Planetary Physics		ic mst. of
1998 - 2000	memb	per Coordinating Board Southern C	alifornia	Integrated GPS
2001 - 2006	U.S. N	(SUGN) Minerals Management Service, Qua	ality Revi	iew Board, offshore
2003 - 2008	Santa M Symp	aria Basin project osium Organizer; 10 th Internationa	l Sympos	sium on Antarctic
2006 – present	ANDRILL (ANtarctic DRILLing) Science Committee (member)			

Eric P. Maillard

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Summary

Over 15 years of R&D experience in the field of underwater acoustics for military and commercial applications.

Academic Degrees

Ph.D. in EE Haute Alsace University (UHA), Mulhouse, France, February 1993.D.E.A. in EE Equivalent to M.Sc., UHA, Mulhouse, France, June 1989.M.S.T. in EE, UHA, Mulhouse, France, June 1988.First Year of M.S.T. in EE Equivalent to B.Sc., UHA, Mulhouse, France, June 1987.

Professional Experience

1/2000 to present: RESON, Inc

4/2006 to present: **Product Lifecycle Manager, Core Technology**

• Identify Intellectual Properties, Organize scientific activities, Define technology strategy for RESON group, Manage new technology research projects, Design signal processing architecture for RESON sonars, Support R&D projects

3/2005 to 3/2006: Firmware Manager

• Lead the effort of sonar firmware development, Define and validate digital processing application on FPGAs, Work with scientists to define optimum solutions, Mentor junior engineers, Participate on the design of new sonar concepts, Participate in the time planning of the firmware team, Interface with the hardware and software teams

12/2002 to 2/2005: Senior Scientist

• Design an auto-mode (cruise control) process for multibeam echosounder, Lead the effort of diver detection system development. The system was selected as underwater harbor protection to protect cruise ships during the 2004 Greek Olympics, Designed post-processing of new imagery information for multibeam sonar, Participated in the effort in the specification of a military 3 frequencies forward-looking sonar and dedicated mine-warfare processes, Designed and validated various terrain navigation processes for underwater vehicle using sonar.

1/2000 to 11/2002: Lead Scientist

• Design signal and image processing systems for bathymetry and imagery data including a calibration software for Multibeam Echosounder, Digital Terrain Model generation, mosaicing, pipeline detection and tracking, terrain reference based navigation, texture analysis, man-made object detection.

Ian R. MacDonald

Geochemical and Environmental Research Group

Texas A&M University 727 Graham Road College Station, Texas 77845

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EDUCA TION: Ph.D. in Oceanography, Texas A&M University, 1990 M.S. in Fisheries Science, Texas A&M University, 1983 B.A. in Environmental Studies, The Friends World College, 1976

EMPLOYMENT HISTORY:

1992-CurrentAssociate Research Scientist, Geochemical and Environmental Research Group 1992-1995Assistant Research Scientist, College of Geosciences, Texas A&M University

PUBLICATIONS RELEVANT TO PROPOSED RESEARCH

- MacDonald, I.R., D.B. Buthman, W.W. Sager, M.B. Peccini, N.L. Guinasso, Jr. Pulsed flow of oil from a mud volcano. *Geology* (in review).
- Sassen, R., I.R. MacDonald, N.L. Guinasso Jr., S. Joye, A.G. Requejo, S.T. Sweet, J. Alcala-Herrera, D.A. DeFritas, and D.R. Schink. 1998. Bacterial methane oxidation in sea-floor gas hydrate: significance to life in extreme environments. *Geology*. 26 (9). 851-854.
- MacDonald, I.R., J.F. Reilly Jr., S.E. Best, R. Venkataramaiah R. Sassen, J. Amos, N.L. Guinasso Jr. A Remote- Sensing Inventory of Perennial Oil Seeps and Chemosynthetic Communities in the Northern Gulf of Mexico. In D. Schumacher and M.A. Abrams, Eds. Hydrocarbon migration and ts near-surface expression: *AAPG Memoir* 66 p 27-37 (1996).
- MacDonald, I R, N L Guinasso Jr, J M Brooks, R Sassen S. Lee, K.T. Scott. Gas hydrates that breach the sea-floor and interact with the water column on the continental slope of the Gulf of Mexico. *Geology* 22:699-702 (1994).
- MacDonald, I.R., J.F. Reilly, N.L. Guinasso, Jr., J.M. Brooks, R.S. Carney, W.A. Bryant, T.J. Bright; Chemosynthetic mussels at a brine-filled pockmark in the northern Gulf of Mexico. *Science* 248: 1096-1099 (1990)
- Kastner, M., **I.R. MacDonald**, A. Paytan, and S. Sweet. 1999. Isotopic and molecular composition of shallow gas hydrates from Gulf of Mexico hydrocarbon seeps. *EOS Supplement*. 80 (49). OS242.
- MacDonald, I.R., W.W. Sager, N.L. Guinasso, and E. Powell. 1999. Evidence of long-term fluctuation in fluid expulsion at hydrocarbon seeps. *EOS Supplement*. 80 (49). OS242.
 Sager, W.W., C.S. Lee, I.R. Macdonald, and W.W. Schroeder. 1999. High-frequency near-bottom acoustic reflection signatures of hydrocarbon seeps on the northern Gulf of Mexico continental slope. *Geo Marine Letters*. 18 (4). 267-276.
- MacDonald, I.R. Habitat forming processes at Gulf of Mexico hydrocarbon seeps. *Cahiers de Biologie Marine*, 39: 337-340 (1998).
- Reilly II, J.F., I.R. MacDonald, E.K. Biegert, J.M. Brooks. Geologic controls on the distribution of chemosynthetic communities if the Gulf of Mexico. In D. Schumacher and M.A. Abrams, Eds. Hydrocarbon migration and its near-surface expression: *AAPG Memoir* 66 p 38-61 (1996).

MacDonald, I.R., N.L. Guinasso, Jr., S.G. Ackleson, J.F. Amos, R. Duckworth, R. Sassen, and J.M. Brooks. Natural oil slicks in the Gulf of Mexico visible from space. *Journal of Geophysical Research*. C9 98:16351-16364 (1993).

PARTICIPATION IN JOHNSON SEA-LINK CRUISES

Chief Scientist - July 1998 (14 days) – Sponsored by MMS R/V Edwin Link – Submarine Johnson Sea-Link II Co-Chief Scientist – July 1997 (24 days) – Sponsored by MMS R/V Edwin Link – Submarine Johnson Sea-Link II

Chief Scientist - July-August 1995 (11 days) - Sponsored by NOAA NURP

Deep Spill 2 Technical Science Plan

Christopher L. Osburn

Dept. of Marine Earth and Atmospheric Science North Carolina State University, chris osburn@ncsu.edu, Tel. (919) 515-0382

Professional Preparation

1991, B.S., Public Affairs, Indiana University
1995, B.A., Geological Sciences, Indiana University
2000, Ph.D., Environmental Science, Lehigh University
2000 – 2003, National Research Council Postdoctoral Fellow, US Naval Research Laboratory

Appointments

2008—present	Assistant Professor, Dept. of Marine, Earth, and Atmospheric Sciences, North
	Carolina State University, Raleigh, NC
2003 - 2008	Research Chemist, US Naval Research Laboratory, Washington, DC

Five Relevant Publications:

Boyd, T.J., Barnham, B.P., Hall, G.J., and <u>Osburn, C.L.</u> (2010) Variation in ultrafiltered and LMW organic matter fluorescence properties under simulated estuarine mixing transects. I – Mixing alone. *Journal of Geophysical Research Biogeosciences*, in press.

- 1. Stedmon, C.A., <u>Osburn, C.L.</u>, and Kragh, T. (2010) Tracing water mass mixing in the Baltic-North Sea transition zone using the optical properties of coloured dissolved organic matter. *Estuarine*, *Coastal*, and Shelf Science, 87: 156-162.
- Montgomery, M. T., Boyd, T. J., <u>Osburn, C. L.</u>, and Smith, D. C. (2010) PAH mineralization and bacterial organotolerance in surface sediments of the Charleston Harbor estuary. *Biodegradation* DOI 10.1007/s10532-009-9298-3.<u>Osburn, C.L.</u>, Retamal, L., and Vincent, W.F. (2009)
- 3. Photoreactivity of chromophoric dissolved organic matter transported by the Mackenzie River to the Beaufort Sea. *Marine Chemistry*. doi:10.1016/j.marchem.2009.05.003.
- Osburn, C.L., O'Sullivan, D.W., and Boyd, T.J. (2009) Increases in the longwave photobleaching of chromophoric dissolved organic matter in coastal waters. *Limnology and Oceanography*. 54: 145-159.

Five Other Significant Publications:

- Osburn, C. L. and St-Jean, G. (2007) The use of wet chemical oxidation with high-amplification isotope ratio mass spectrometry to measure stable isotope values of dissolved organic carbon in seawater. *Limnology and Oceanography: Methods*, 5:296–308.
- Vallieres, C., Retamal, L., Ramlal, P., <u>Osburn, C.L.</u>, and Vincent, W.F. (2008) Bacterial production and microbial food web structure in a large arctic river and the coastal Arctic Ocean. *Journal of Marine Systems*, 74: 756-773.
- Retamal, L., Vincent, W.F., Martineau, C., and <u>Osburn, C.L</u>. (2007) Comparison of the optical properties of dissolved organic matter in two river-influenced coastal regions of the Canadian Arctic. *Estuarine, Coastal and Shelf Science.*, doi:10.1016/j.ecss.2006.10.022.
- Tzortziou, M., <u>Osburn, C.L.</u> and P. J. Neale. (2007) Photobleaching of dissolved organic material from a tidal marsh-estuarine system of the Chesapeake Bay. *Photochemistry and Photobiology*. 83: 782-792.
- Boyd, T. J. and <u>Osburn, C. L.</u> (2004). Changes in CDOM fluorescence from allochthonous and autochthonous sources during tidal mixing and bacterial degradation in two coastal estuaries, *Marine Chemistry*, 89:189-210.

Robert Timothy Short

Address:	SRI International 140 Seventh Avenue South, COT 100 St. Petersburg, Florida 33701-5016	phone: (727) 553-3990 FAX: (727) 553-3529 email: timothy.short@sri.com
Education:	1987, Ph.D. Physics, University of Tenness 1979, B.S. Physics, Florida State University	see y

Professional Experience (Recent):

Program Manager, Chemical Sensors Group (2007-) Engineering Systems Division, SRI International

Sensor Development Engineer (1997-2007) Center for Ocean Technology, University of South Florida

Research Scientist, (1991-97) Analytical Chemistry Division, Oak Ridge National Laboratory

Research Interests: Mass spectrometry, Marine sensors, Power Sources, Microsystems technology

Professional Societies: American Society for Mass Spectrometry, IEEE Oceanic Engineering Society, American Chemical Society.

Five Relevant Publications:

R. T. Short, D. P. Fries, M. L. Kerr, C. E. Lembke, S. K. Toler, P. G. Wenner and R. H. Byrne, "Underwater Mass Spectrometers for *In-situ* Chemical Analysis of the Hydrosphere" J. Am. Soc. Mass Spectrom. 12 (2001) 676-682.

R. T. Short, S. K. Toler, G. P. G. Kibelka, D. T. Rueda Roa, R. J. Bell and R. H. Byrne, "Detection and quantification of chemical plumes using a portable underwater membrane introduction mass spectrometer", Trends in Anal. Chem. 25 (2006) 637-646.

R. J. Bell, R. T. Short, F. H. W. van Amerom and R. H. Byrne, "Calibration of a deep-water in situ membrane introduction mass spectrometer with respect to hydrostatic pressure", Env. Sci. & Technol. 41 (2007) 8123-8128.

F. H. W. van Amerom, A. Chaudhary, M. Cardenas, J. Bumgarner and R. T. Short, "Microfabrication of cylindrical ion trap mass spectrometer arrays for handheld chemical analyzers", Chem. Eng. Comm. 195 (2008) 98-114.

A. Chaudhary, F. H. W. van Amerom and R. T. Short, "Development of microfabricated cylindrical ion trap mass spectrometer arrays", IEEE Journal of MEMS 18 (2009) 442-448.

Evan A. Solomon

School of Oceanography University of Washington Seattle, WA 98195-5351 Tel: (206) 221-6745 email: esolomn@uw.edu

Professional Preparation

2001 B.Sc.	University of Nevada, Reno, Geology
2007 Ph.D.	Scripps Institution of Oceanography, UC-San Diego
2007-2008	Postdoctoral Researcher, Scripps Institution of Oceanography
2008-2009	NRC/NETL Postdoctoral Research Fellow, Scripps Institution of Oceanography

Appointments

2000	w.		DC	TT 1 1/2	CTT7 1 '
ninu n	recent	Accidtant	Proteccor	nivercity	of Washington
2002-0	rosoni	Assistant	110103501.	Oniversity	or washington
0.1			2		<i>(</i>)

Closely Related Publications

- Solomon, E.A., Kastner, M., MacDonald, I.R., Leifer, I., Considerable methane fluxes to the atmosphere from hydrocarbon seeps in the Gulf of Mexico. *Nature Geoscience*, 2(8), 561-565 (2009).
- Solomon, E.A., Kastner, M., Jannasch, H., Weinstein, Y., Robertson, G., Dynamic fluid flow and chemical fluxes associated with a seafloor gas hydrate deposit on the northern Gulf of Mexico slope. *Earth and Planet. Sci. Lett.*, 270(1-2), 95-105 (2008).
- Newman, K.R., Cormier, M-H., Weissel, J.K., Driscoll, N.W., Kastner, M., Solomon, E.A., Robertson, G., Hill, J.C., Singh, H., Camilli, R., Eustice, R., Active methane venting observed at giant seafloor pockmarks along the U.S. mid-Atlantic shelf break. *Earth and Planet. Sci. Lett.*, 267, 341-352 (2008).
- Solomon, E.A., Kastner, M., Wheat, G., Jannasch, H.W., Robertson, G., Davis, E.E., Morris, J.D, Longterm hydrogeochemical records in the oceanic basement and forearc prism at the Costa Rica subduction zone. *Earth and Planet. Sci. Lett.*, 282 (1-4), 240-251 (2009).
- Riedinger, N., Brunner, B., Formolo, M.J., Solomon, E.A., Strasser, M., Oxidative sulfur cycling in the deep biosphere of the Nankai Trough, Japan. *Geology in press*, paper #G31085.
- Solomon, E.A., Spivack, A.J., Kastner, M., Torres, M., Borole, D.V., Robertson, G., Das, H.C., Hydrogeochemical and structural controls on heterogeneous gas hydrate distribution in the K-G basin offshore SE India. *Proceedings of the Sixth International Conference on Gas Hydrates*, Vancouver, B.C., paper 5509, available at <u>https://circle.ubc.ca/handle/2429/1022</u> (2008).

Related Recent Meeting Abstracts

- Solomon, E.A., Spivack, A., Kastner, M., Torres, M., 2010, Biogeochemical cycling and methane generation in gas hydrate-bearing sediments offshore SE India, Gordon Research Conference on Gas Hydrates, June 2010.
- Solomon, E.A., Kastner, M., Leifer, I., Ethane and propane emissions to the ocean and atmosphere from 550-1200 m seeps in the Gulf of Mexico. *EOS Trans. AGU*, 90(52), Fall Meet. Suppl., Abstract OS31A-1182 (2009b).

Douglas S. Wilson

University of California, Santa Barbara Dept. Earth Science & Marine Science Inst. Santa Barbara, CA 93106 Phone: (805) 893-8033, Fax: 893-2314 E-mail: dwilson@geol.ucsb.edu

Education:

B.S., Geophysics, Stanford University, 1978. M.S., Geophysics, Stanford University, 1979. Ph.D., Geophysics, Stanford University, 1985.

Professional Experience:

Research Geophysicist, University of California, Santa Barbara, 2010-present. Associate Research Geophysicist, University of California, Santa Barbara, 1993-2010. Assistant Research Geophysicist, University of California, Santa Barbara, 1988-1993. Research Associate, National Research Council/USGS, 1985-1987. Research Associate, Hawaii Institute of Geophysics, 1979-1981.

Selected publications:

- Wilson, D. S. Confirmation of the astronomical calibration of the magnetic polarity time scale from rates of sea-floor spreading, *Nature*, *364*, 788-790, 1993.
- Wilson, D. S. and R. N. Hey, History of rift propagation and magnetization intensity for the Cocos-Nazca spreading center, *J. Geophys. Res.*, *100*, 10,041-10,056, 1995.
- Wilson, D. S., Fastest known spreading on the Miocene Cocos-Pacific plate boundary, *Geophys. Res. Lett.*, 23, 3003-3006, 1996.
- Krijgsman, W., F.J. Hilgen, I. Raffi, F.J. Sierro, and D.S. Wilson, Chronology, causes and progression of the Messinian salinity crisis, *Nature*, 400, 652-655, 1999.
- Wilson, D.S., P.A. McCrory, and R.G. Stanley, Implications of volcanism in coastal California for the Neogene deformation history of western North America, *Tectonics*, 24(3), TC3008, doi:10.1029/2003TC001621, 2005.
- Wilson, D.S., D.A.H. Teagle, J.C. Alt, N.R. Banerjee, S. Umino, S. Miyashita, and 45 others, Drilling to gabbro in intact ocean crust, *Science*, *312*, 1016–1020, 2006.

Recent Seagoing experience:

- 1999 R/V M. Ewing, Guatemala Basin (Chief Scientist for ODP site survey)
- 2002 D/V JOIDES Resolution, Guatemala Basin (Co-chief Scientist for ODP Leg 206)
- 2004 RVIB N.B. Palmer, Ross Sea (Co-chief Scientist)
- 2005 D/V JOIDES Resolution, Guatemala Basin (IODP Expeditions 309 & 312)

POOJITHA D. YAPA

Box 5710 - Department of Civil and Environmental Engineering Clarkson University, Potsdam, New York, 13699-5710 Phone: 315 268-7980, FAX: 315 268-7985 e-mail: pdy@clarkson.edu

PRESENT POSITION

Professor

EDUCATION

Ph.D. (Civil and Environmental Engineering), Clarkson University, Potsdam, NY, 1983
M. Eng. (Hydraulic Engineering), Asian Institute of Technology, Bangkok, Thailand, 1979
B.Sc. Eng. (Honors) (Civil Engineering), University of Moratuwa, Sri Lanka, 1976

HONORS

- Erskine Fellowship, Department of Civil Engineering, University of Canterbury, Christchurch, New Zealand, 2007
- Gledden Senior Visiting Fellowship, Centre for Water Research, The University of Western Australia, Nedlands, Perth, Australia, 1999-2000
- Invited Research Fellow, Department of Civil Engineering, Science University of Tokyo, Japan, Sept. 1992 Aug. 1993
- Visiting Researcher, Environmental Assessment Dept., National Institute for Resources and Environment, Tsukuba, Japan, June Aug. 1992

JOURNAL EDITORIAL WORK

Associate Editor of ASCE Journal of Hydraulic Engineering : 2001 – 2006 Associate Editor of Journal of Hydro-Environment of Research – International Association of Hydraulics Research (IAHR)/ Elsevier : 2006 – present

TASK COMMITTEES

- Member, Task Committee on Best Practices in Oil Spill Modeling, CRRC/NOAA, 2009-2010
- Chair, Environmental Hydraulics Committee, ASCE, 1996
- Chair, Task Committee on Modeling of Oil Spills, ASCE, 1990-1993

MAIN RESEARCH AREA

Modeling of deep water oil and gas jets/plumes, Modeling of oil spills PUBLICATIONS AND PRESENTATIONS

Peer reviewed papers (65); Non peer reviewed conference papers (25); Technical reports (54); Invited presentations (47 in 8 countries)

Congressman Markey Letter to BP, June 10 2010

HENRY A. WAXMAN, CALIFORNIA

JOHN D. DINGELL. MICHIGAN CHAIRMAN EMERITUS EDWARD J. MARKEY, MASSACHUSETTS RICK BOUCHER, VIRGNIA RIKAK PALLONE, J.K., NEW JERSEY BART GORDON, TENNESSEE BOBBY L. RUSH, ILLINOIS BUBBY L. HUSH, ILLINÕIS ANNA G. ESHDO, CALIFORNIA BAHI STUPAK, MICHIGAN ELIOT L ENGEL NEW YÖRK IAAHI STUPAK, MICHIGAN BHIOT LI BIGELINEW YORK GENE GALEN, TZXAS DI MA BLEEL, NEW YORK GENE GALEN, TZXAS DI MA BLEEL, DI MANADO MICHIGAN, MICHIGAN MICHIGAN, MICHIGAN AND CANADA STANDAR AND CANADA STANDAR AND CANADA STANDAR AND SCH. MICHIGAN CHARLES A. GONZALLZ, TZXAS AND TXAS SCH. MICHIGAN CHARLES A. TXXAS AND TXAS SCH. MICHIGAN CHARLES AND TXAS SCH. MICHIGAN CHARL VIRGIN ISLANDS DONNA CKRISTENSPN, VIRGIN ISLANDS KATHY GASTOR, FUGRIDA JOHN SARBANES, MARYLAND CHRISTOPHER MURPHY, CONNECTICUT ZACHARY T. SPACE, DNIO JERRY MURPHENEY, CALIFORNIA BETTY SUTTOR, DHIO BRUCE BRAIEY, JOWA ME FER WEECH, VERMONT

ONE HUNDRED ELEVENTH CONGRESS.

Congress of the United States House of Representatives

COMMITTEE ON ENERGY AND COMMERCE 2125 RAYBURN HOUSE OFFICE BUILDING WASHINGTON, DC 20515-6115

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June 10, 2010

JOE BARTON, 1EXAS

AUNIVICA REVISER RAVIN MARKING MEMBER DEPUTY RAVING MEMBER RALPH MI HALL, TEXAS INDEPUTY RAVING MEMBER RALPH MI HALL, TEXAS ULF STGANES, CHARGE DEWINTERD, KENTUCKY JOEN SI MANUS, KANTON BUE WILLING SI MANUS, AUTONIA SULF WILLING SI MANUS, NORTH CAROLINA JOEN SULMAN, ORLAHOMA TIM MURPHY, PENNSYU ANIA MICHAEL SURGESS, TOXAS MARKAB BLACKOURN. TUNNESSEE PHIL GINGREY, LOUISIAA SITEVE SULMES, LOUISIAA SITEVE SULMES, LOUISIAA PARKER GRIFFITH, ALABAMA ROBERTE, LATTA, OHIO

Mr. Lamar McKay President and CEO, BP America, Inc. 501 Westlake Park Boulevard Houston, Texas, 70779

Dear Mr. McKay:

BP is now reportedly collecting 15,000 barrels of oil per day through a cap placed on the top of the blowout preventer at the Deepwater Horizon/ Macondo well accident site. However, as is evident from the live video feeds being shot on the ocean floor, substantial quantities of oil continue to escape from around the sides of the cap and from vents on the cap.

While conservative estimates indicate that the lower bound of the flow rate before the riser was severed was between 12,000 and 19,000 barrels per day, questions remain about the upper bound of the flow rate estimate. Some members of the Flow Rate Technical Group have said that the maximum flow could be much higher.

As one example, Dr. Steve Wereley of Purdue University, who is on the Flow Rate Technical Group, has said that the size of the spill could be more than 40,000 barrels of oil per day.

I and other members of Congress have now received high-definition footage of the spill site, and understand that scientists on the flow rate team have also received this footage. This footage includes the important time period between when the riser was cut and removed and when the current cap system was installed.

While this footage has helped these independent scientists to better estimate the size of this spill, they will provide only an approximation. To get the most accurate flow-rate possible, direct measurements are needed.

During discussions my staff have held with Dr. Ira Leifer of the Marine Sciences Institute at the University of California-Santa Barbara, who is on the Flow Rate Technical Group, it has come to my attention that there is an upcoming potential opportunity to reach such an accurate assessment. BP has indicated that there is a plan to place a larger containment cap on the well in the next couple of weeks to capture more of the oil gushing from the site.

During the switching of the cap, an experiment could be conducted to better measure the size of the flow. The experiment would consist of injecting fluorescent dye into the oil stream, which would allow scientists to better estimate how fast the gusher is moving and thus the total quantities of oil, gas, and other materials leaving the well. The scientific methods for this activity are well-developed and have been published in peer-reviewed scientific journals.

Scientists could be at the well site within one week with their equipment, provided the proper budget. The measurement would take only a couple hours. Monitoring equipment could be left at the well site to provide an ongoing assessment of the spill, and would be safely installed away from BP's operations at the well.

I want to emphasize that any efforts to measure the flow rate should not interfere with or delay any efforts to eliminate or limit the flow of oil. However, based on BP's plans as reported in the media, removal of the cap and placement of an additional cap may not take place for 2-3 weeks which should provide ample time to prepare for the flow rate measurements being proposed.

This measurement could help inform the ongoing effort to end the spill, which is the number one priority. There are concerns that, without the best information on the size and force of this gusher, that the effectiveness of the new containment cap and relief wells could be compromised. By knowing the true size of the spill, the robust response efforts currently being coordinated by the Obama administration can also be aided.

My understanding is that BP has not yet responded to Dr. Leifer's request to make direct flow measurement. Therefore, I encourage you to immediately engage with Dr. Leifer and other members of the Flow Rate Technical Group to explore the opportunity this new strategy presents. I request that you provide whatever budget and ROV access is needed to allow these scientists to deploy their measurement activities and allow them full and safe access to the spill site at the sea floor to conduct this measurement. As you know, BP will be fined for every barrel of oil spilled during this disaster. The residents of the Gulf of Mexico and all Americans deserve a true understanding of the size of what is already the worst environmental disaster in U.S. history.

Sincerely,

Mer

Edward J. Markey Chairman Energy and Environment Subcommittee Energy and Commerce Committee

CC:

Admiral Thad Allen, USCG Honorable Henry Waxman, Chairman Honorable Joe Barton, Ranking Member Honorable Fred Upton, Ranking Member