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Physical Transport and Chemical Behavior of Dispersed Oil

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1. Overview of dispersant transport and chemical behavior of dispersed oil

1.1 Overview of topic as it related to dispersant use during DWH

During response operations, scientific information is provided to decision makers, such as the Federal On-Scene Coordinator (FOSC), state and federal trustees, and the public. The decision to use chemical dispersants during a response is made among all these parties, and during the Deepwater Horizon (DWH) oil spill the dispersant discussion included both surface and subsurface application of chemical dispersants. This paper is intended to provide perspective on research needs considered pre- and post-DWH oil spill related to response modeling and data collection needs for decision support of dispersant application and its potential effects. Given time constraints for implementing models and sampling strategies for response, requirements for data and types of questions to be addressed may be significantly different than requirements for research or damage assessment activities. At the time of this writing, just over a year after the successful response operations to cap the well, many studies are still in progress, and data are still being collected and evaluated to assess dispersant effectiveness and possible impacts. More information and research results will become available over the next months to years. Thus these research needs, as summarized for this workshop, should be evaluated again at a later time.

Transport of chemically dispersed oil at the surface is downward, into the mixed layer, where we have a conceptual model that wind and wave induced mixing move the dispersant and any dispersed oil vertically into the water column, and, in general, droplets less than 70-100 μm in diameter do not resurface. Concentration variations are primarily related to surface initial conditions, e.g. oil ($x, y, \text{thickness}, t$), chemical dispersant ($x, y, \text{concentration}, t$), wind (x, y, z, t), and waves (x, y, t). In the subsurface, particularly the deep ocean, vertical mixing is very low, so, inert chemicals put into the water column travel along the density surface with little mixing. The Deepwater Horizon MC 252 well, and much of the U.S. deepwater development, is located along the Louisiana-Texas continental slope. The circulation along the continental slope is complex. These dynamics affect bottom water movement and, thus advection of dissolved constituents and tiny oil droplets (with rise velocities on the order of weeks to months). In the surface mixed layer, droplets less than 100 μm are viewed as too small to rise against the turbulent mixing. In the deep ocean, the turbulence is much less (Ledwell and Hickey, 1995, Ledwell and Bratkovich, 1995, and Ledwell, Watson and Law, 1993).

During the Deepwater Horizon oil spill, dispersants were also injected into the oil plume at the release point into the water column, first from the broken riser and then from the cut riser at 1,500 *m*. During an oil spill response, we do not have near-real-time information on mixing energy, target or actual dispersant-oil-ratios (DOR), the duration of oil-dispersant interactions, dispersant efficiency, oil droplet size distributions, or identification of physically- vs. chemically-dispersed oil available for decision makers. However, analyses and data to date do indicate that much of the transition from the multiphase gas-oil plume to separate oil and gas bubble phases occurred between 1000 - 1300 *m* (Socolofsky *et al.* (2011), see also Yapa *et al.* (2001)). This layer is the subject of continuing reporting from the Joint Analysis Group (JAG, 2010a, b, c), including a summary report to be completed by the end of 2011.

The separation of oil droplets and gas bubbles from the multiphase flow from the well was accompanied by almost complete dissolution of lower molecular-weight-aliphatics (through heptane, McAuliffe, 1987) and lower-molecular-weight aromatics (alkylated benzenes) (Reddy *et al.*, 2011), with more limited dissolution of two- and three-ring aromatics (alkylated naphthalenes, phenanthrenes/anthracenes, and dibenzothiophenes). Camilli *et al.*, (2010) tracked this subsurface plume at depth for over 35 *km*, and literally thousands of water-column samples collected during numerous Response- and NRDA-cruises have provided measurements of BTEX and PAH distributions throughout the water column. Figures 1 and 2 show dispersant indicators (2-butoxyethanol, glycol ethers, and bis-(2-ethylhexyl) fumerate) and selected BTEX and PAH constituents from the public Operational Science Advisory Team (OSAT) and GeoPlatform.gov data sources. Dissolution kinetics rapidly increase as the oil droplet surface-area-to-volume-ratio increases (i.e., as the droplet sizes get smaller). The intention of the subsurface dispersant application was to transition oil mass from larger to smaller droplet sizes. Presumably, if the subsurface injection of dispersants was effective, dissolution kinetics would have been enhanced, but research is needed to develop methods to be able to evaluate effectiveness on a response time-scale.

2. Surface Chemically Dispersed Oil

2.1 Overview of what was known about topic prior to DWH

Research needs related to decision support for the potential application of chemical dispersants have been discussed previously to the DWH oil spill, and many of these remain relevant today. A comprehensive review of oil-dispersant interactions and fate was completed by the National Academy of Sciences/National Research Council (2005), and since then there have been dozens of studies undertaken under the Dispersant Working Group coordinated by the Coastal Response Research Center (CRRC) and sponsored by the CRRC and a number of other agencies and companies (for a detailed listing of previous research recommendations, projects, and sponsors see: CRRC 2006; 2009; and http://www.crrc.unh.edu/dwg/topic_1.html).

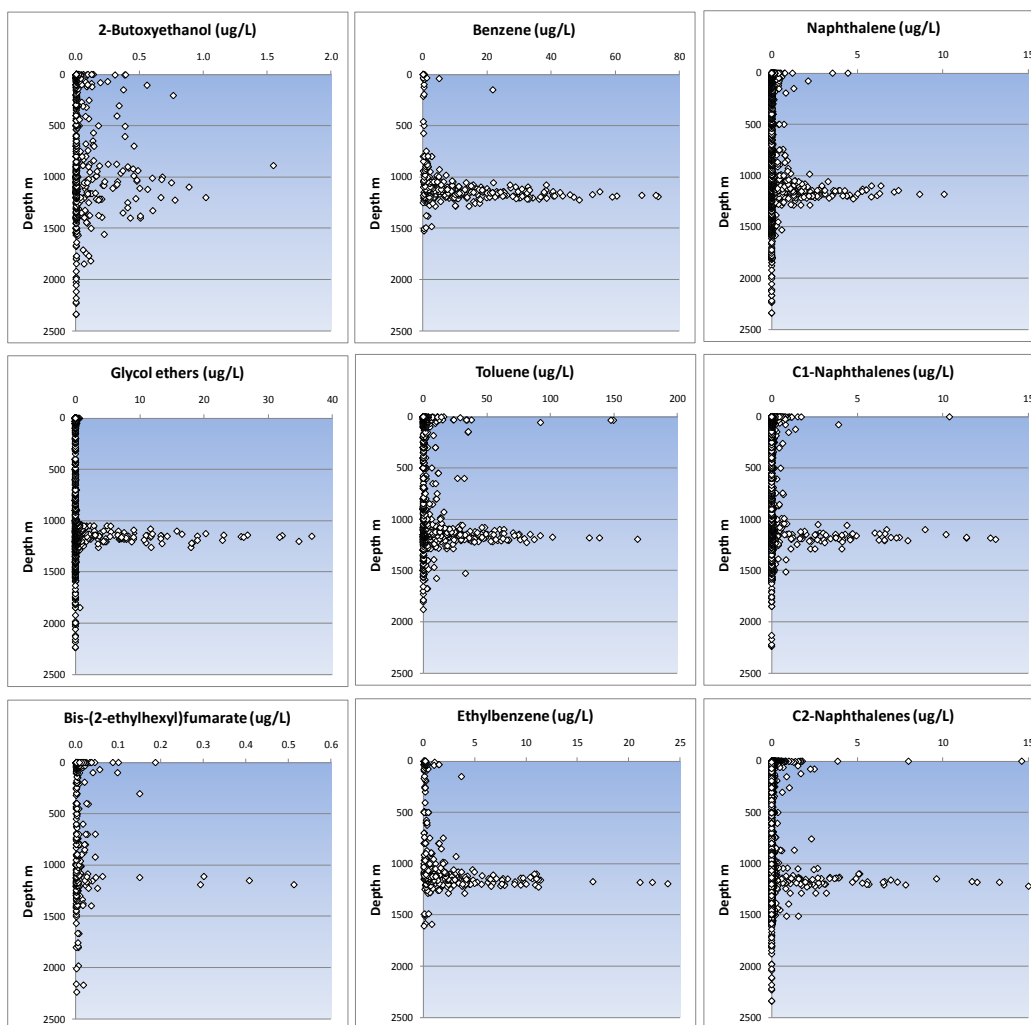


Figure 1. Depth distribution of dispersant indicators (2-butoxyethanol, glycol ethers, and bis-(2-ethylhexyl) fumarate) and selected BTEX and PAH constituents measured in seawater collected throughout the Gulf of Mexico between 11 May and 15 December 2010. [Data source: public Operational Science Advisory Team (OSAT) and GeoPlatform.gov data.]

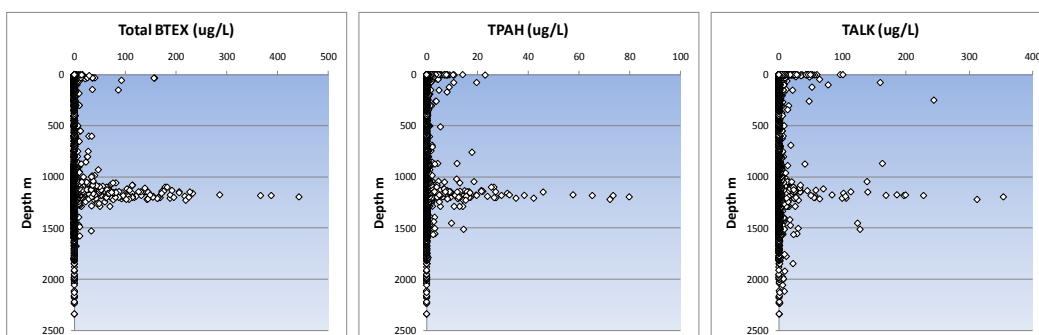


Figure 2. Depth distribution of total BTEX, total PAH (TPAH) and total alkanes (TALK) measured in seawater collected throughout the Gulf of Mexico between 11 May and 15 December 2010. [Data source: public Operational Science Advisory Team (OSAT) and GeoPlatform.gov data.]

During any oil spill response, controlling the source of the oil has a higher priority than research. Access to areas very near the DWH well for sampling was restricted due to response operations. Thus, we have significantly more information about deepwater well blowouts than we did before the DWH oil spill, but research will be needed to develop sampling strategies for areas near the blowout that do not interfere with response activities and that provide more near-real-time information. Innovative research in both technology for direct observations and other chemical and transport proxies that can be used to estimate the droplet size distribution or its properties or derivative (e.g. mass distribution) could improve our ability to operationally forecast more details during a response. As of this writing, however, (1) not all the droplet size data at depth have been characterized, (2) there are operational problems with some of the measurement approaches during the spill (described further below in Section 3.2.1), and (3) these types of measurement need to be more synoptic in order to support response decision activities as compared to longer-term analysis. In addition, the nature of the blowout release(s) likely changed during response activities (e.g. the cutting of the riser between June 1st – 3rd, 2010), which complicates understanding the measurements.

As a result, the observational data from the DWH have yet to be fully leveraged toward answering some or all of these proposed research needs. For example, in the area of dispersed-oil/suspended particulate material (SPM) interactions:

- We have limited data available on SPM concentrations (number density or particle sizes) in the water column at depth close to the wellhead (mid water column or just above the sediments) for subsurface dispersant injection.
- Near-real-time measurements of the oil droplets and SPM for decision support evaluation would have been important near the site of the dispersant injection (at depth), and yet these types of measurements were impossible due to the response activities as noted earlier. The closest most of the scientifically-based ROV platforms could get to the wellhead at depth during response operations was 1-2 *km*, although Reddy *et al.* (2011), were able to mount an isobaric gas-tight sampler on the *Millennium 42* ROV during the response to obtain gas and oil samples immediately above the wellhead on 21 June 2010.
- Post spill sediment core analyses near the wellhead (<2-4 *km*) have shown DWH oil in the upper sediment layers (0-3 *cm*) suggesting oil/SPM interactions, flocculation, and sedimentation, but not all the available sediment cores have been analyzed as of this writing, so our understanding of oil/SPM agglomerate deposition may expand as more information becomes available. In addition, some of the sediment samples also contain drilling mud (possibly related to the Top Kill operations), and drilling mud-oil interactions would also contribute to the sediment load near the wellhead.

Other topics are addressed throughout the rest of this paper. Some topics are addressed in more detail than others, depending on the extent of our pre-DWH knowledge base). Unfortunately, the NRC (2005) report did not address transport issues in any detail.

2.2 Factors influencing:

2.2.1 Chemically dispersed oil droplet size distribution

Droplet size distributions from premixed dispersant/oil mixtures were reviewed in the NRC (2005) report, and since then additional work on surface treated- and untreated-oil has been completed in wave-tank and laboratory studies by Li *et al.*, (2007), Lee *et al.*, (2009), Khelifa *et al.*, (2008), Reed *et al.*, (2009), and Katz (2009). Katz has completed the most in-depth investigation of the mechanism of dispersed oil droplet shearing and droplet fractionation. Droplet size distribution is discussed in more detail in Section 3.2.1.

2.2.2 Sedimentation, mucus adherence, and other physical scavenging

The most recent, extensive, and thorough laboratory investigations of chemically and physically dispersed oil/suspended particulate matter (SPM) interactions were completed by Khelifa *et al.* (2008). A number of additional research needs are discussed in that report and in CRRC Workshop documents, but as noted earlier in Section 2.1, not all the new information from the DWH oil spill is available at this time.

Oil droplets (ranging from 20-200 μm) were observed by photo microscopy to accumulate in mucus agglomerates collected by bucket casts 5-70 km from the wellhead (J.R. Payne, personal observations), and these generally exhibited near neutrally buoyant behavior residing just below the air-water interface. One possibility is that these were from extra-cellular exudation products from bacterial activity, but we do not yet know if this can be addressed from the available samples. Likewise, we do not yet know if we can discern whether or not these mixtures had been previously treated with dispersants.

Another mechanism for getting oil to the bottom includes ingestion of oil droplets by copepods and excretion of basically unaltered oil within fecal pellets (NRC 2003). While much of this material can be re-worked as these fecal pellets settle through the water column, some fraction of this oil is also subject to sedimentation. Methods are needed to assess the relative contribution of this mechanism versus others as it relates to oil deposition on the bottom.

2.2.3 Dissolution

Lower molecular weight aromatics (benzene, toluene, ethylbenzene, xylene(s) – BTEX), and other alkylated benzenes along with lower-molecular-weight polycyclic aromatic hydrocarbons (PAH) have finite solubilities in seawater, and can dissolve to an appreciable extent during an oil spill (NRC 2003, 2005). For the PAHs, the solubility decreases with increased alkylation, such that truly dissolved PAH distributions often do not resemble the fingerprint pattern in the starting oil. Likewise, lower molecular weight aliphatics (methane through heptane) can truly dissolve to varying degrees (decreasing as the molecular weight increases). These processes have been reviewed in detail in several National Research Council reports (2003, 2005), and more recently by Faksness (2007). Successful addition of

dispersants will reduce the oil droplet size, and this will significantly increase the oil surface area-to-volume ratio, which will increase the kinetics or rate of the dissolution process.

In the case of the Deepwater Horizon oil spill, the release was at depth so the oil droplets resulting from both physical and chemical dispersion rose in and, for the largest droplets, through the water column. During this contact with the ambient seawater, significant levels of BTEX and PAH dissolved and were measured in hundreds of filtered water samples taken at depth (Figures 1 and 2). Similar behavior was observed during the IXTOC I blowout in the Bay of Campeche, GOM in 1979 (Boehm and Fiest, 1982; Payne *et al.*, 1979a, b). The airborne measurements by Ryerson *et al.* (2011) support these conclusions for the Deepwater Horizon well blowout. The influence of subsurface dispersant injection on this process is considered further in Section 3.3.3.

2.2.4 Droplet Re-coalescence

A comprehensive review of the tendency of dispersed oil droplets to resurface has been prepared by Fingas (2005), and re-coalescence of dispersant-treated oil in OHMSETT Wave Tank studies has been reported by Payne (2006). In the OHMSETT test tank, some resurfacing was observed after 12-24 *hrs* when the wave generator was turned off and turbulence was allowed to dissipate from the system. In those instances, however, re-coalescence primarily occurred after turbulence was reduced or stopped, and it was affected by the lack of advective removal of the dispersed oil in the test tank. In the open ocean, there is unlimited dilution available, and even modest turbulence from surface cooling is enough to introduce sufficient turbulence to maintain small ($< 70\text{-}100\ \mu\text{m}$) droplets in suspension in the surface mixed layer. The DWH deep submerged plume (1000-1300 *m*) data show no evidence to suggest that any re-coalescence of dispersed oil occurred in the water column as the plume moved away from the wellhead. We expect this to be true from normal advective-diffusive behavior and our understanding of tracer movement within the deep ocean (Ledwell and Hickey, 1995, Ledwell and Bratkovich, 1995, and Ledwell, Watson, and Law, 1993).

2.3 Weathering of dispersed oil

Chemically dispersed oil droplets are subject to the same weathering phenomena (evaporation, dissolution, and microbial degradation) as physically dispersed oil droplets, except the rates would be expected to be higher after successful dispersant application due to the higher surface-area-to-volume ratio of the smaller droplets. Reports indicate that when dispersant-treated oil surfaces the slicks formed are thinner compared to untreated oil. If this is indeed the case, then evaporative weathering would be expected to be faster from such slicks. To the extent that dispersant treatment and enhanced dispersion throughout the water column reduces droplet re-coalescence and surfacing, dispersed droplets would likely not form stable water-in-oil emulsions (mousse) to the extent that non-treated slicks do. Water-in-oil emulsification only occurred with DWH oil after considerable surface weathering (Belore *et al.*, 2011, Leirvik *et al.*, 2010a, 2010b, and Daling *et al.*, 2011) and

convergence of oil in Langmuir cells with near-surface wave turbulence. Thus, if dispersed oil remains at depth and diffuses in three dimensions, less oil will be available at the surface for the emulsification process. To the extent that any subsurface chemically dispersed oil eventually does reach the surface, however, it is likely that once the surfactant components have leached out, the oil will be subject to the same convergence cells, photochemistry, and surface turbulence as non-treated oil only with the considerations of having lost more lighter oil components due to higher dissolution. Under these conditions, subsurface chemically-dispersed oil would likely form an emulsion (if this oil surfaces) just as readily as non-treated subsurface released oil.

2.4 Photolytic factors and rates

We are not aware of information that advances our knowledge about the rates and effects of photolysis on chemically-dispersed oil droplets, but presumably the chemically dispersed droplets are subject to the same photo-oxidation reactions as non-dispersed oil if they are near the water surface (\sim upper 5 m) where UV light penetration is sufficient to catalyze photochemical reactions (Payne and Phillips, 1985, NRC 2003; Maki *et al.*, 2001). In this case, non-chemically-dispersed surface oil would probably be subject to increased rates of photolysis compared to chemically-dispersed oil at greater depths.

Numerous toxicity studies have been completed to assess photo-enhanced toxicity (also reviewed in NRC 2005), and it is well established that selected PAH absorbed into transparent organisms (eggs and larval fish) can impart 10-1000 fold increases in toxicity when exposed to UV light (Barron, 2000; Barron and Ka'ahue 2001; Barron *et al.*, 2002). Similar photo-enhanced toxicity was noted in herring eggs with the same PAH loadings (with either naturally or chemically dispersed oil), but to the extent that dispersants decrease oil droplet size and enhance dissolution, this could increase the potential uptake/partitioning through cell membranes into lipophilic eggs and larvae. Such transport could lead to enhanced phototoxic effects in near-surface transparent organisms where dispersants were used.

2.5 Transport in the Mixed Layer

2.5.1 Slick to droplet continuum

The conceptual model of surface chemically applied dispersant is that the mixing energy from waves (above a minimal energy) in combination with the chemical dispersant leads to smaller droplets. These droplets then move down into the mixed layer through Langmuir Circulation (LC). In shallow areas, $z < 40$ m, with steady winds, the resulting LC can reach the bottom (e.g. Gargett *et al.*, 2004).

2.5.2 Langmuir Circulation

In 1999, NOAA and BOEMRE (then MMS) jointly sponsored a workshop on Langmuir circulation (LC) and oil spills, in order to bring experts from both fields together. The results of the workshop were published in a special issue of Spill Science and Technology (volume 6, issues 3-4) in 2000. The workshop recommendations (Simecek-Beatty and Lehr (2000)) focused on LC modeling needs

for response based on information that could be obtained during a response, such as mixed layer depth, wind, and waves. Mixed layer depth is a proxy for the depth of penetration of the largest LC, while wind and waves provide the forcing, and so could be used as a proxy for LC intensity. This is more a bulk mixed layer approach. The special issue also included a detailed bibliography (Simecek-Beatty and Overstreet (2000)).

LC is found at all scales within the ocean mixed layer. Colbo and Li (1999) did a very nice study on particle dispersion in LC, showing that particles tended to move within individual Langmuir cells, with the smallest cells persisting over a much smaller time period than the larger cells. By comparing buoyant and neutrally buoyant particles within LC, they showed that buoyant particles do not disperse (spread) as much in the cross-wind direction as neutrally buoyant particles.

Thorpe (2004) noted in a review of LC noted that LC simulations using Large Eddy Simulation (LES) methods was a great step forward in terms of understanding mixed layer dynamics. LES models of the mixed layer could be used to develop more detailed statistics for oil droplet dispersion within LC, and thus may be able to give statistical information on hydrocarbon concentrations that could be used in oil spill models. We expect this to result in details of small volumes of higher hydrocarbon concentrations than the overall concentration estimates from bulk methods. Transitioning this type of work into decision support materials or models is also a significant effort to undertake.

2.6 R&D Recommendations

2.6.1 Overview of NRC and/or CRRC R&D recommendations prior to DWH

UNH CRRC (2009). “Research & Develop Priorities: Oil Spill Workshop, March 16-19th, 2009.

Chemical Dispersion

“The research will require meso-scale and, full-scale field trials that include tracking and monitoring techniques. Other guidelines include investigating cold water environments, and multiple oil (including heavy) and dispersant types. Potential impediments to research are public perception and politics, the difficulty of control, the limited scope, and the expensive field trials.”

2.6.2 Post DWH oil spill

See sections 3.6.2 and 3.6.3.

2.6.3 R&D needed to resolve outstanding questions relative to topic

Below is a summary of the research needs from the 2005 UNH CRRC dispersant workshop (with a current status estimate by the authors in parentheses):

- Literature synthesis on physical and chemical properties of oils that determine the overall effectiveness of dispersant application (largely completed);

- Refining existing datasets to correlate physical and chemical properties of different types of oil with dispersability (ongoing);
- Update SMART monitoring protocols;
- Workshop on requirements for integrating oil toxicity and biological data with oil fate and transport models;
- Improved models to predict dispersant effectiveness and oil fate;
- Understanding the interactions of chemically dispersed oil droplets with suspended particulate matter (largely completed) and how these processes affect the rate of oil biodegradation and ultimate fate of dispersed oil (ongoing);
- Assessment of the degree, rate, and consequences of surfactant leaching from surface slicks and chemically dispersed oil droplets;
- Reconciliation of the differences between the empirical evaporation approach and traditional pseudo-component approach;
- Improve, verify, and validate oil-spill trajectory and fate models;
- Monitoring dispersed oil concentrations at spills of opportunity; and
- Integration of fate and toxicity models with population models to predict short- and long-term effects of dispersant application.

3. Subsurface Chemical Dispersant Application as Applied During the Deepwater Horizon Oil Spill

3.1 Overview of what was known about topic prior to DWH

The authors are not aware of any published evidence that subsurface dispersant application was considered for deepwater well blowouts or other response scenarios before the DWH oil spill, though at the workshop, industry indicated consideration as early as 2000. The BP Thunder Horse deepwater well riser break, which was a dry run for response considerations for the DWH oil spill, is discussed in Beegle-Krause and Lynch (2004). Modeling and response considerations for deepwater well blowouts previously focused on the timing and location of the surface oil expression.

3.1.1 Conceptual model

For subsurface dispersant application, our conceptual model is that by injecting chemical dispersants into the blowout multiphase plume, the inherent mixing from the blowout would lead to oil-dispersant contact and creation of more smaller oil droplets (*i.e.* transition a portion of the mass from larger to smaller droplet sizes). The fluid emerging from the wellhead is not a mixture of oil and gas separately but multiphase flow, which means that the oil and gas emerge as a single phase. Unfortunately, while overflight data support the notion that the freshest surface oil slick decreased in size when subsurface dispersant application was on-going, tracing the oil droplets creating the surface oil back to the riser with and without dispersant injection was not possible in real time for response decision makers. Ryerson *et al.* (2011) used aircraft measurements of promptly evaporating hydrocarbons to evaluate the area of freshest oil with a measureable atmospheric hydrocarbon signal.

The blowout scenario likely changed (e.g. droplet size distribution) with the various response options, particularly when the riser was cut. This is evidenced by the change in the isopycnal expression of the subsurface plume over time (Socolofsky *et*

al., 2011 and JAG final report to be published). Kujawinski *et al.* (2011) found the evidence of dispersants within the depth range of the subsurface plume, but not enough information on the exact isopycnal location of the Dioctyl Sulfosuccinate Sodium Salt (DOSS) was provided to determine the detailed relationship between the DOSS and the CDOM fluorescence. For example, did the DOSS occur at the same density level as the peak CDOM fluorescence or throughout the layer? Elsewhere, the correlation of subsurface dispersant components and dissolved/particulate-phase oil was observed (e.g., Figures 1 and 2), and this is discussed further in Section 3.3. In addition, it would be interesting to compare the mechanical frictional effects of the broken riser leaks to create smaller droplets (e.g. picture your thumb over the flow from a garden hose) to the efficacy of the subsurface chemical dispersant application. There is potential that mechanical dispersion could be utilized to replace subsurface chemical dispersant usage.

3.2 Factors influencing:

3.2.1 Droplet size distribution

Droplet size measurements were completed as part of the DWH response effort to inform Command and Control of dispersant effectiveness (Li *et al.*, 2011) and as a component of several NRDA-cruises completed in the spring, summer, and fall of 2010. Unfortunately, very few of the Laser *In Situ* Scattering and Transmissometry (LISST) instruments used at the time of these studies were capable of reaching the depths necessary to monitor droplet sizes *in situ*. Therefore, most measurements were completed on water samples collected at depth (with Go Flo or Niskin bottles) and then returned to the surface for analyses on the ship(s). SINTEF is currently undertaking new research on oil droplet size and size distribution using tower basins.

With this approach, oil-droplet coalescence can occur inside the water sampling bottles during the 1-3 *hr* period between sample collection at depth, retrieval of the sampling equipment, and analysis of the water sample on the ship. Oil sheens were frequently observed on the upper surface of the standing water in Go Flo bottles on the *Jack Fitz* NRDA cruises, and special care had to be taken during water filtration using the Portable Large Volume Water Sampling System (PLVWSS – Payne *et al.* 1999) to ensure that the surface meniscus (containing such oil sheens) was processed as part of the sample. This was not possible with LISST measurements because there is no way to get the surface-separated oil in the sampling bottles back into suspension as finite droplets, and there is no guarantee that the droplet size distribution would be the same as it was at depth. Also, as the water samples warm up in the flow-through chambers or cuvetts used with the LISST instrumentation, degassing can cause air bubbles to form. Both of these issues (recoalescence in the sampling bottles and air bubbles) need to be considered when accessing the accuracy of droplet size measurements for response decision support.

To avoid these issues, additional instrumentation including an *in situ* Holographic Camera and towed video-cameras designed to measure droplets, suspended sediments, and plankton (owned by Cabell Davis, WHOI) were deployed on a

number of cruises, but data from these systems are not yet available at the time of this writing. Likewise, a Deep-LISST capable of reaching the bottom at 1500 *m* was deployed on several NRDA cruises, but those data are also not available at this time.

3.2.2 Sedimentation

As indicated in section 2.2.2, laboratory studies have demonstrated that chemically dispersed oil droplets can interact with suspended particulate material (SPM) in the water column to yield oil/SPM aggregates that have densities high enough to cause enhanced sedimentation. During the DWH oil spill, settling chambers were deployed to measure flux of oil-laden SPM to the bottom, but at the time of this writing the results from those studies are not yet available. Furthermore, specific studies to differentiate oil droplets created from subsurface dispersant injection have not been put forward.

The OSAT summary report on subsurface oil and dispersant detection (OSAT 2010) identified DWH oil in seven sediment samples within 3 *km* of the wellhead, but the samples were composites of the upper 3-plus *cm* of the sediment, so background PAH contributed to the signal and could have masked and underestimated the DWH contribution to the surface layer. In addition, the primary focus of the OSAT report was on actionable levels above aquatic life benchmarks for PAH (with oil concentrations > 2000-5000 *ppm*) for making response decisions. The OSAT authors were quick to point out that these indicators do not represent injuries to natural resources under NRDA, which may occur at lower concentrations, and in other studies, DWH-sourced oil has been measured in sediment and surface floc samples at distances out to 4 *km*. Preliminary reports on hydrocarbon fingerprinting of publicly available data (Scott Stout, verbal communication) indicated DWH oil in the surface sediment (0-1 *cm* and 1-3 *cm*) and DWH oil in surfacial floc samples, so it is believed that oil/SPM interactions and sedimentation has occurred. Our expectation is that this type of information during response would be useful for decision makers. We expect that ongoing studies will provide additional data to possibly ascertain if these interactions occurred with dispersant-treated oil, but for future response we need to have a better understanding of the formation mechanisms.

3.2.3 Dissolution and evidence of dispersant effectiveness at depth

Dissolved components (methane through pentane, plus BTEX) were reported by Camilli *et al.*, (2010) and Reddy *et al.* (2011), and dispersant components plus BTEX and PAH were measured in thousands of water samples collected as part of the Response and NRDA efforts (Figures 1 and 2). Three dispersant indicators (2-butoxyethanol, generic glycol ethers, and bis-(2-ethylhexyl) fumerate) and numerous oil components are observed to be co-located between ~750 and 1500 *m* (Figure 1). While all three dispersant components were readily observed (and all are water soluble), we have more data for the glycol ethers, so additional discussions regarding dissolution behavior presented below will focus on them.

The BTEX components are known to be primarily in the dissolved phase (Reddy *et al.*, 2011), but the higher-molecular weight PAHs have variable water solubilities, and n-alkanes (C₉-C₄₀) are known to exist only in the oil phase (finite oil droplets) or very fine colloidal fractions. Thus, from the data in Figures 1 and 2, it is clear that the subsurface oil plume contained both truly dissolved components and finite oil droplets. From the available data at this time, further analysis is needed to know if we can definitively determine whether or not the dispersants shifted the droplet size distribution toward smaller droplets. At this time, analysis of available deep oil droplet data has not yielded any dispersant components associated with the oil, but there are data from many samples remaining to be examined. Preliminary analyses from Fisheries and Oceans Canada (Ken Lee, personal communication) indicates a transition of Volatile Organic Compounds (VOCs) between the surface and deep subsurface layer that correlates with subsurface dispersant application.

Before considering that point further, however, it is first necessary to discuss the fate of the detrained oil droplets as the smallest (presumably colloidal sizes up to possibly up to several hundred μm) are advected horizontally while the larger (*mm* plus) sized droplets rise much more rapidly (hours) up through the water column.

During the NRDA water sampling activities on three *Jack Fitz* cruises (May-June 2010), the first *American Diver* cruise (August 2010), four *HOS Davis* cruises (August – December 2010), and the first two *HOS Sweet Water* cruises (March/April and July/August 2011), water column samples were processed with the Portable Large Volume Water Sampling System (PLVWSS) developed by Payne *et al.* (1999) to allow examination of separate dissolved- and particulate/oil-phases. Data from five discrete depths are available for most samples, but only data from 1 *m*, 600 *m*, and 1430 *m* collected 2.2 *km* from the wellhead are presented here (Figure 3) due to space limitations. Each depth is represented by four histogram plots vertically arranged to show PAH components above the corresponding alkane (or aliphatic – ALK) components in each sample. The dissolved-phase samples (passed through a 0.7 μm glass-fiber filter at the time of collection) are shown in the left-hand column, and the particulate/oil-phase samples (retained on the filters) are shown in the right-hand column. The red line in each PAH plot is the profile of the DWH source oil normalized to the C-2 phenanthrene (C-2P) in each plot. The red line in each ALK plot is the relative distribution of the alkanes plus pristane and phytane, but they are not normalized to any specific component in the sample.

The data very clearly illustrate the enrichment of parent and alkylated naphthalenes, fluorenes, and phenanthrenes in the aqueous phase (compared to the starting oil) with concomitant depletion of these same components in the particulate/oil phase trapped on the respective filter obtained with each sample (compare PAH profiles in the left- and right-hand columns). Likewise, the insoluble n-alkanes and isoprenoids are almost exclusively found in the particulate/oil phase trapped on the filters (right-hand column).

Figure 3. Paired dissolved (left side) and filtered particulate/oil-phase (right side) PAH and alkane (ALK) profiles from water depths of 1m, 600m, and 1,430 m collected 2.2 km (1.3 mi) to the NW (bearing 330 degrees) from the wellhead on 28 June 2010. The red PAH line is fresh DWH oil normalized to C2-phenanthrene showing enhanced dissolution of lower-molecular-weight PAH in the dissolved phase (left-hand column) and depletion of these same constituents in the particulate/oil-phase (right-hand column). Higher-molecular-weight aliphatics (alkane – ALK) are only observed in the particulate/oil-phase (see text). [Data source: Publicly available data from GeoPlatform.gov.].

Correlations of glycol ethers with specific components (BTEX and PAH) as a function of the depth range of the collected samples (Figures 4 and 5) also can be used to better define the plume dynamics. In Figure 4 for all water depths, good correlations are observed between the glycol ethers and the more water soluble constituents (BTEX through C2-naphthalenes), but the correlations break down for the lower soluble fluorene, phenanthrene and dibenzothiophene suggesting separation of the dissolved components from the finite oil droplets as they rise through the water column. In Figure 5 for water depths only between 750 *m* and 1500 *m*, the correlations are more significant for all of the constituents.

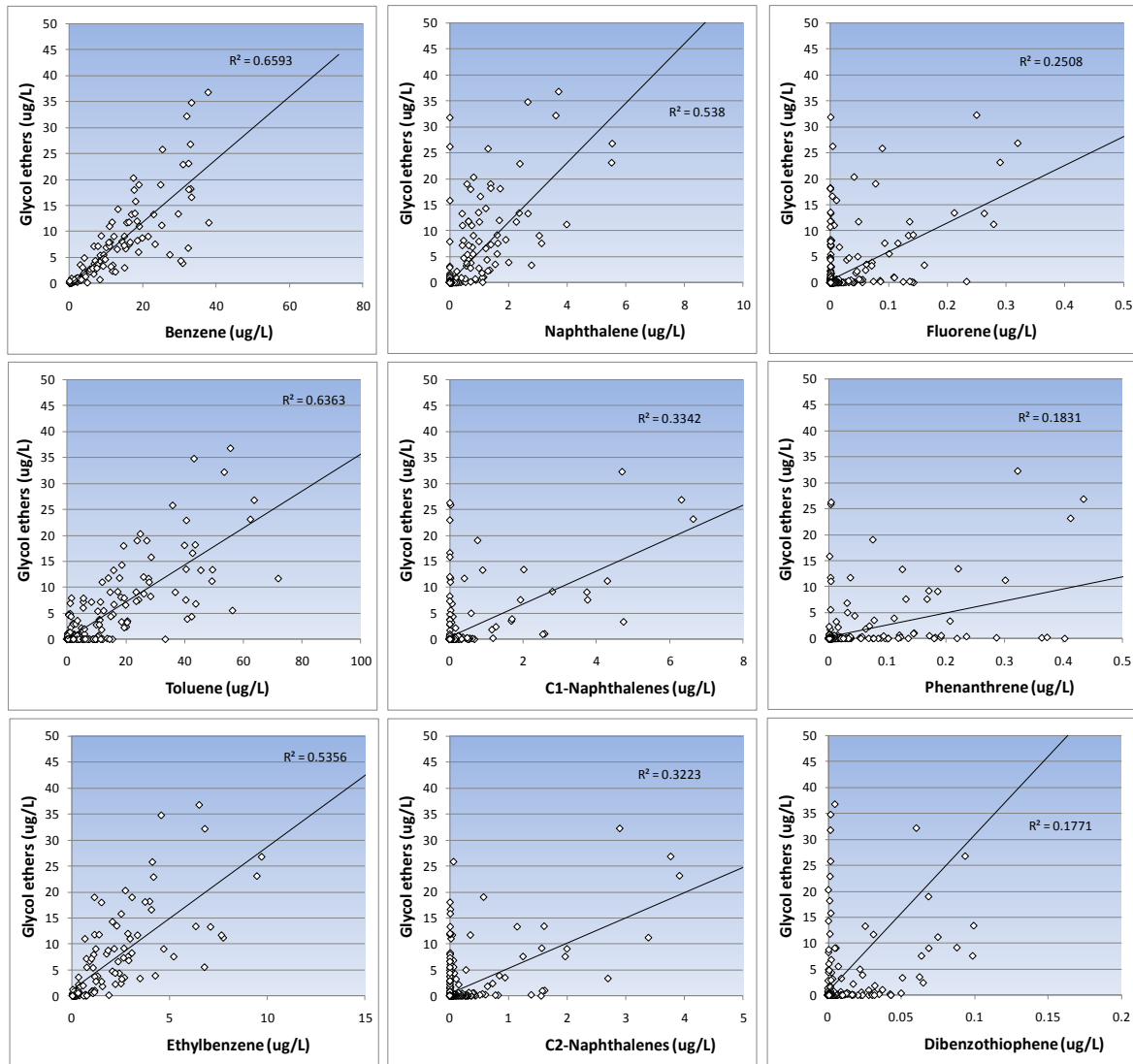


Figure 4. Glycol ethers vs. individual BTEX and PAH constituents in water samples from all depths collected throughout the Gulf of Mexico between 11 May and 15 December 2010. [Data Source: publicly available data from GeoPlatform.gov].

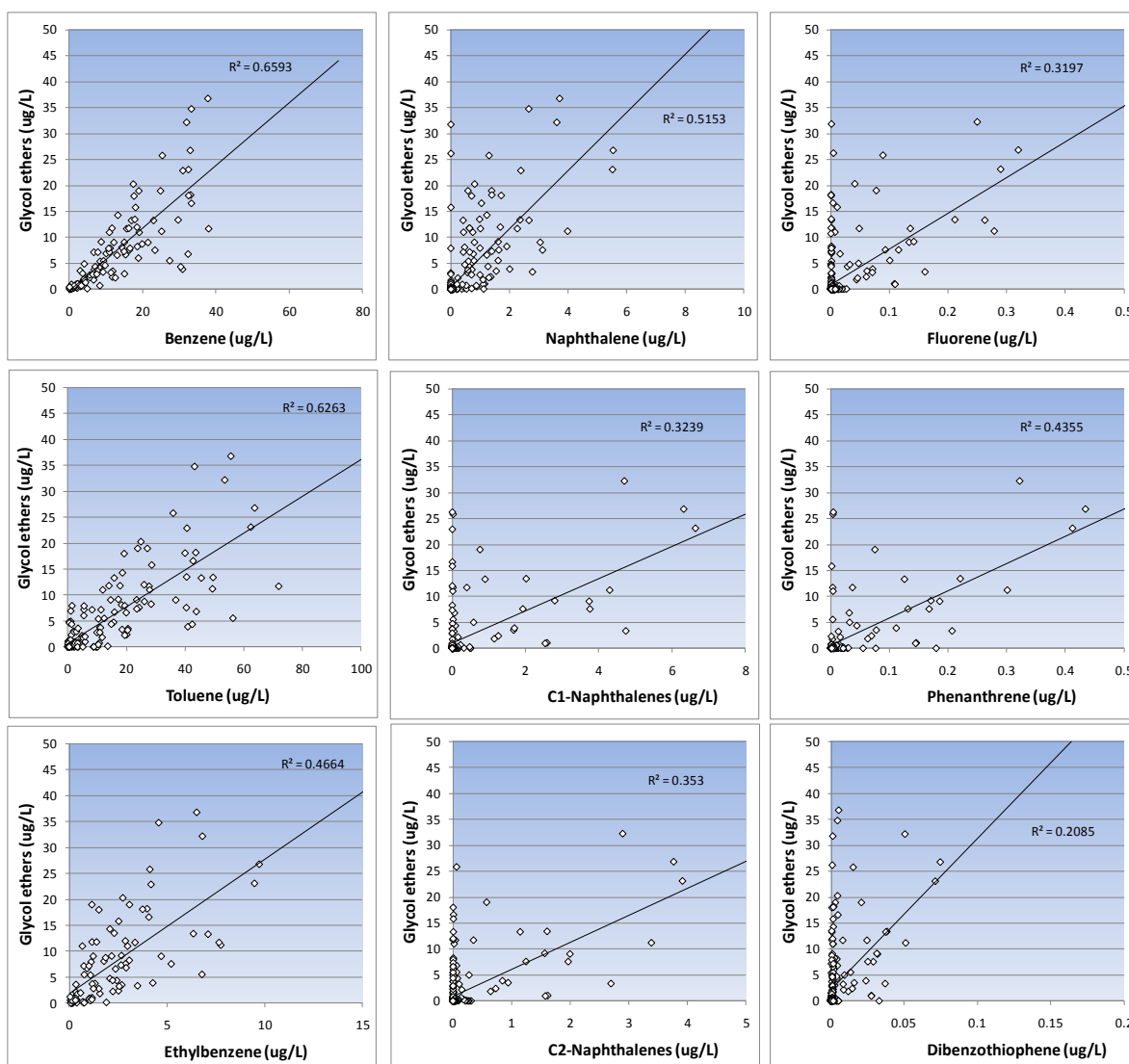


Figure 5. Glycol ethers vs. individual BTEX and PAH constituents in water samples between depths of 750 and 1500 m collected throughout the Gulf of Mexico between 11 May and 15 December 2010. [Data Source: publicly available data from GeoPlatform.gov.].

3.2.4 Re-coalescence

As part of response, USCG SMART water sampling protocols were employed during the DWH surface dispersant applications (Levine *et al.* 2011), but no data to date have been presented to assess droplet re-coalescence and resurfacing. When dispersants were applied by air, the observation vessels were required to stand-by at considerable distance from the target area for safety, and when they approached the dispersant-treated slick, the logistics were challenging to ensure that the SMART teams were exactly within areas of surface dispersant application. It may have been advisable to deploy drifters and/or smoke markers in the target areas before dispersant applications by air as described in the California Dispersed Oil

Monitoring Plan (Payne *et al.*, 2007a,b; 2008a,b; French McCay *et al.*, 2007; 2008a, b), but that approach is more suited to oil-spill-of-opportunity research rather than operational sorties in response to a spill of the magnitude of the DWH.

3.3 Biodegradation of dispersed oil

At the time of this writing, further analysis is needed to determine if biodegradation of subsurface chemically-dispersed oil is the same as the smallest oil droplets created by the subsurface blowout dynamics. Studies of microbial degradation of dissolved oil are ongoing and being published, for example: Hazen *et al.*, 2010, and Reddy *et al.*, 2011. Other weathering considerations were presented in Section 2.3. The DWH subsurface layer transitioned from dissolved oil and gas and the smallest oil droplets into a dissolved oxygen depression (or “anomaly”), that research indicates to be from microbial degradation of the oil at depth. This dissolved oxygen (DO) anomaly has been discussed extensively by the JAG (JAG 2010a, b, c), with the final JAG report expected to be published at the end of 2011.

3.4 Transport in the Deep Ocean

Consideration for the subsurface transport of chemical dispersant and any resulting chemically dispersed oil are very different from the surface. At the surface, application is at the air-water interface, where the oil resides at the interface, wind and waves supply the mixing energy, and dispersed oil and chemical dispersant mix downward into the surface mixed layer. In the subsurface, mixing is greatly reduced compared to the surface, so persistent chemical tracers can be found for long periods of time. For example, the work of Ledwell and Hickey, 1995, Ledwell and Bratkovich, 1995, and Ledwell, Watson and Law, 1993 using sulfur hexafluoride has shown that an inert tracer can injected into the subsurface ocean can be found again over a course of years. Transport in the horizontal is along constant density surfaces (“isopycnals”), which are roughly the same as depth levels, but not exactly. The upcoming final JAG report and Beegle-Krause *et al.* (2011) show and discuss the key isopycnals for the DWH MC 252 oil spill.

Kujawinski *et al.* (2011) collected and published data on deep water samples that contained very low concentrations of DOSS from the chemical dispersant (see also Figures 1 and 2). Kujawinski *et al.* (2011) provided information on the long-term horizontal transport of the DOSS, but, as noted in the paper, not on the efficacy of the subsurface dispersant application. Further water mass and other analyses could potentially complement chemical analyses in understanding the effectiveness of subsurface dispersant application.

3.5 Dispersed oil transport

Due to isopycnal transport in the deep ocean, water-soluble dispersant components would be expected to follow the isopycnal where they entered the larger scale environment. Smaller chemically-dispersed oil droplets would be expected to travel similarly to any dissolved species in the deep water column, although larger (> 100 µm) droplets might slowly rise over time.

3.6 R&D Recommendations

3.6.1 Overview of NRC and/or CRRC R&D recommendations prior to DWH (Are these still relevant post-DWH?)

The NRC and UNH CRRC have not previously considered research needs for potential subsurface dispersant application.

3.6.2 Overview of R&D recommendations post DWH oil spill

With new response measures come new R&D recommendations to help us better understand the effectiveness and potential effects of using these new measures in the field. Below some examples:

- Could a frictional/mechanical oil droplet dispersion method be more effective at creating smaller droplets than the subsurface application of chemical dispersant?
- How effective is application of subsurface dispersant in creating more small droplets? What specific dispersant injection methods (and/or orientations relative to the plume) are necessary to accomplish various degrees of effectiveness? Does dispersant use affect dissolution as oil particles rise to the surface or change the gas bubble size distribution? How long does the surfactant stay with the dispersed oil droplets?
- Can subsurface injection of chemical dispersant reliably reduce the amount of oil reaching the surface? If so, what are the most effective injection methods? Can dispersant formulations be optimized for subsurface use?
- How would we better measure subsurface chemical dispersant effectiveness during the next event?
- How do these processes affect biodegradation kinetics, composition of sedimented oil, and the ultimate fate of dispersed oil?
- Can SMART Protocol improvements be developed to allow better tracking of dispersed oil at depth? For example, can holographic cameras be utilized as a standard component of the Protocol to measure *in situ* droplet sizes at depth?

4. Overall Summary of Response Decision Support Research Needs for Chemical Dispersant Applications

Below in section 4.1 is a summary of post-DWH research needs related to chemical dispersant decision support discussed within this paper. A separate addendum is also available that lists a summary of research needs discussed by the Fate and Transport working group at the CRRC Workshop. Many of these are significant efforts to undertake, so research needs and results will have to be reevaluated again at a later date. See section 2.6.3 for the pre-DWH outstanding dispersant decision support research needs summary.

4.1 Overall Summary of Post-DWH Research Needs for Response Decision Support

- Can mechanical methods be developed to increase the oil mass within the subsurface layer that are more (or at least as) effective as chemical dispersants?

- The effectiveness of mechanical dispersion (friction from riser kinks and brakes and post-riser-cut) should be evaluated so as to compare with the effectiveness of subsurface chemical dispersant application.
- We need to transition our understanding of surface dispersant application and effectiveness to the specific case of a deepwater well blowout. Topics/data needs include:
 - Evaluation of our understanding of the mechanism of dispersed oil droplet shearing and droplet fractionation under subsurface conditions.
 - Evaluation of emulsion stability for surface oils previously weathered by dissolution (e.g. surface oil slicks created from droplets rising from a deepwater well blowout) with and without the application of subsurface chemical dispersants.
- What methods and protocols could be used to determine effectiveness of subsurface chemical dispersant application for decision support? Topics/data needs include:
 - Measurements to support detailed water mass analysis of oceanographic and oil spill related chemical parameters.
 - Measurements of mixing energy, target or actual dispersant-oil-ratios (DOR), the duration of oil-dispersant interactions.
 - Measurements of dispersant components within oil droplets (as isolated from the dissolved phase by the Portable Large Volume Water Sampling System (Payne *et al.*, 1999).
 - Measurements of droplet size distribution and temporal variance.
 - Near-real-time measurement systems that can work near a deepwater blowout well without interfering with response activities or near-real-time proxies that can be measured outside the response exclusion zone.
 - Quantitative near-real-time evaluation of the footprint (x,y,t) , mass(t) and chemical composition (x,y,t) of the freshest surfacing oil.
- What is the role of physical scavenging (oil/SPM interactions) in chemical dispersant application and effectiveness (surface and subsurface)? Topics/data needs include:
 - Spatial and temporal (x,y,z,t) background, natural variance, and near-real-time SPM concentrations (number density or particle sizes) in the water column.
 - Near-real-time measurement systems that can work near a deepwater blowout well without interfering with response activities or near-real-time proxies that can be measured outside the response exclusion zone.
 - Protocols for decision support evaluation of mucus agglomerates for chemical signatures of dispersants or byproducts of biological interaction with dispersant components or dispersed oil droplets.
 - Protocols for decision support sediment core analyses near the wellhead ($<2-4\text{ km}$) in the upper sediment layers ($0-1\text{ cm}$) for evidence of dispersant effects, e.g. oil/SPM interactions, flocculation,

- and sedimentation, fecal pellets containing dispersant products, and other response related chemical constituents (e.g. drilling mud).
- Detailed analysis of SPM interactions with oil droplets.
- How these processes affect biodegradation kinetics, composition of sedimented oil, and the ultimate fate of dispersed oil.
- How can SMART Protocol improvements be implemented to provide:
 - Better positioning of the SMART team into the surface chemically dispersed oil for sampling.
 - Measurements to estimate droplet re-coalescence and resurfacing.
 - Tracking and sampling of dispersed oil at depth.
 - Aerial documentation of the surface manifestation of oil that can be quantitatively compared with the subsurface dispersant application.
- Are the effects of photolysis the same on chemically- and physically-dispersed oil droplets?
- Prepare post DWH guidance documents for:
 - Decision makers on effects of chemically dispersed oil.
 - The scientific community on oil-related sampling equipment, standard analyses, and fingerprinting.

5. Relationship of R&D recommendations & Arctic dispersant use

The risks of potential well blowouts are real in any oil development. The arctic and Gulf of Mexico scenarios for oil spills are very different.

5.1 Surface oil

Ice conditions are a key consideration to surface dispersant application to oil in the Arctic. The DWH oil spill is an example of very high volumes of dispersant applied in an effort to improve the outcome from the oil spill in very deep water.

Consideration in detail of the potential for a well blowout in the Arctic and application of dispersant should be done carefully, as lessons learned from the DWH oil spill may not all apply to the Arctic.

5.2 Subsurface oil

Oil development within the Arctic is expected to be at much shallower depth than the deepwater development that included the DWH. These shallower depths may point to blowout events behaving more like the IXTOC I exploratory well blowout than the DWH. The ability to potentially manipulate the subsurface release or apply subsurface dispersants exists, but needs further consideration relative to the Arctic ecosystem.

6. Summary

The needs of response are higher than the needs for research – this is an important trade-off to recognize when evaluating previous observational programs under the DWH and considering future research needs. The DWH oil spill resulted in an unprecedented oil spill data set that can be used to improve our response capability

should another deepwater well blowout occur. Nevertheless, there are still areas where research could advance our understanding and predictive ability regarding deepwater well blowouts.

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