

# **Oil Budget Calculator**

## **Deepwater Horizon**



### **TECHNICAL DOCUMENTATION**

**November 2010**

**A Report by:**

**The Federal Interagency Solutions Group,  
Oil Budget Calculator Science and Engineering Team**

9182
Exhibit No. _____
Worldwide Court Reporters, Inc.

# **Oil Budget Calculator**

## **Deepwater Horizon**



**TECHNICAL DOCUMENTATION**

**A Report to the National Incident Command**

**November 2010**



This document is the product of several individuals who were consulted on particular aspects of the Oil Budget Calculator, provided field data, suggested formulas, analysis methods, and/or reviewed the algorithms used in the calculator.

## LEADS:

Lehr, Bill	National Oceanic and Atmospheric Administration (NOAA)
Bristol, Sky	U.S. Geological Survey (USGS)
Possolo, Antonio	National Institute of Standards and Technology (NIST)

## MAJOR CONTRIBUTORS OR REVIEWERS: (See Appendix 9 for short biographies)

Expert	Affiliation	Major contribution
Allen, Alan	Spiltec	In-situ burning
Boufadel, Michel	Temple University	Review
Coolbaugh, Tom	ExxonMobil	Review
Daling, Per	SINTEF	Field data
Fingas, Merv	Environment Canada (retired)	Emulsion
French McCay, Debbie	Applied Science Associates (ASA)	Review
Goodman, Ron	Innovative Ventures Ltd.	Review
Jones, Robert	NOAA	Evaporation
Khelifa, Ali	Environment Canada	Dispersion
Lambert, Pat	Environment Canada	Review
Lee, Ken	Fisheries and Oceans Canada	Field data
Leifer, Ira	University of California Santa Barbara	Hydrates
Mearns, Alan	NOAA	Biodegradation
Overton, Ed	Louisiana State University	Dissolution
Payne, James	Payne Environmental Consultants	Review

Many others contributed directly or indirectly to the Calculator development but were not necessarily involved in the preparation of this document. Some are listed below:

<b>Expert</b>	<b>Affiliation</b>	<b>Major contribution</b>
Beegle-Krause, C.J.	NOAA	Subsurface oil
Farr, Jim	NOAA	Oil chemistry
Galt, Jerry	NOAA	Review
Hammond, Steve	U.S. Geological Survey	Interface
Lasheras, Juan	University of California San Diego	Natural dispersion
Mabile, Nere	BP	In-situ burning
Miller, Mark	NOAA	Initial summary
Svekovsky, Jan	Ocean Imaging	Remote sensing
Yapa, Pooji	Clarkson University	Subsurface oil

The Coastal Response Research Center (CRRC), a partnership between the National Oceanic and Atmospheric Administration and the University of New Hampshire, provided logistical support with document preparation and the peer-review process. Particular thanks to Nancy Kinner, Zachary Magdol and Kathy Mandsager.



## EXECUTIVE SUMMARY

---

An oil budget (ICS Form 209) is normally prepared as part of the Incident Action Plan for ordinary oil spills. The Deepwater Horizon spill was anything but ordinary, and a special tool had to be developed to construct a workable oil budget useful to the unified command in making its response decisions. This report describes that tool.

The National Incident Command (NIC) assembled several interagency expert scientific teams to estimate the volume of BP Deepwater Horizon oil that has been released from the well and the short-term fate of that oil. The expertise of government scientists serving on these teams was complemented by non-governmental and governmental specialists providing data, offering suggestions, and reviewing the calculations and conclusions.

The Flow Rate Technical Group (FRTG) and the Department of Energy (DOE) developed estimates of the flow rate and of the total volume of oil released. A second interagency team, led by the U. S. Geological Survey (USGS) from the Department of the Interior, and the National Oceanic and Atmospheric Administration (NOAA) and the National Institute of Standards and Technology (NIST) from the Department of Commerce, developed a tool called the Oil Budget Calculator to determine what happened to the oil.

The Oil Budget Calculator was designed to assist the Situation Unit of the Incident Command System (ICS). Therefore, its sole purpose was to inform and advise the response, and it should not be used to assess environmental damage or any other purpose.

The Calculator became operational on June 22, 2010 but continues to undergo modification and refinement, not only best to characterize what happened to the oil in this case, but also to assist in the response to future, similar spills. The numbers in this report may change as new information becomes available. The calculator assumed as an input the estimated 4.9 million barrels of oil discharged in total from the well from April 20 until July 14, 2010, provided by FRTG/DOE, and used both direct and indirect measurements and the best scientific estimates available to determine what has happened to the oil.

This report discusses the methods used to estimate the portions of that volume that were recovered directly from the well head, dispersed either chemically or naturally, evaporated or dissolved, burned or skimmed, and the portion left over (“other” oil) that may still be amenable to response actions. The latest results, by and large, are consistent with early results, produced by an early version of the Calculator and announced in a NOAA press release of



August 4, 2010: the early estimate of the percentage of “other” (or, “residual”) oil was 26%; the current version of the Calculator estimates it at 23%, and qualifies this estimate with the belief that, with high confidence, the true percentage should be between 11% (best-case scenario) and 30% (worst-case scenario).

The report also describes the methods used to qualify such estimates with uncertainty assessments. Processes such as direct capture and burning, that were directly measured on-scene, have the smallest uncertainty. Processes such as dispersion that have to be estimated based upon limited data, theoretical considerations and expert knowledge from past incidents, have the greatest uncertainty. The emphasis was on getting a conservative answer so as not to underestimate cleanup requirements. In terms of response, this translates into using conservative estimates for cleanup efficiency, particularly with regard to skimmer efficiency and dispersant success.

The Calculator does not track the final fate of the spilled oil. Instead it estimates oil that may be amenable to response decisions as opposed to oil that is not (e.g. dissolved or evaporated oil). No attempt was made to estimate the amount of dispersed oil that reached the sediments; nor was degradation rate of any of the oil components evaluated quantitatively. The focus was on estimating the fraction of the spilled oil that might still be amenable to response actions, so that informed decisions could be made.

The Oil Budget Calculator is believed to be sufficiently accurate to meet the needs of the Deepwater Horizon spill response. Thus, while it may have underestimated dispersed oil, it predicted sufficient amounts of subsurface oil as to encourage a large-scale water-sampling program. Suggestions are provided at the end of the report that would allow improved budgets in future large-scale incidents.



## TABLE OF CONTENTS

---

LEADS AND CONTRIBUTORS	i
EXECUTIVE SUMMARY	iii
LIST OF TABLES	vi
LIST OF FIGURES	vi
LIST OF ACRONYMS	vii
1. INTRODUCTION	1
2. PURPOSE OF OIL BUDGET CALCULATOR	3
3. PREVIOUS EXPERIENCE - IXTOC SPILL	8
4. LEAK RATE AND SUBSURFACE BEHAVIOR	10
5. DISSOLUTION	13
6. EVAPORATION	17
7. WEATHERING ESTIMATION BY EMULSIFICATION	20
8. NATURAL DISPERSION	21
9. CHEMICAL DISPERSION	24
10. BURNING	31
11. MECHANICAL RECOVERY	33
12. OTHER OIL	34
13. LONGER TERM PROCESSES	35
14. ASSESSMENT AND FUTURE PLANS	38
15. REFERENCES	41

## LIST OF TABLES

---

**Table 1:** Mass Balance for Ixtoc I. (*page 9*)

**Table 2:** USCG Surface Water Dispersant Study Sample Results. (*page 29*)

## LIST OF FIGURES

---

**Figure 1:** Schematic of Deepwater Horizon Oil Spill (*page 3*)

**Figure 2:** Ixtoc I Oil Spill (*page 8*)

**Figure 3:** Estimated flow rate for Deepwater Horizon Spill (DOE/FRTG) (*page 11*)

**Figure 4:** Droplet rise velocity (Yapa et. al, 2010) (*page 13*)

**Figure 5:** A typical ambient temperature and thermodynamic equilibrium curve for Methane (Chen and Yapa, 2004) (*page 14*)

**Figure 6:** Solubility per carbon number for hydrocarbon molecules, (Modified from McAuliffe, 1987 IOSC – proc. Pp 275 – 288) (*page 15*)

**Figure 7:** Histogram shows the C-10 to C-25 Alkanes of the whole Source Oil (Orange), a floating oil sample immediately adjacent to the source (red), and two floating oil samples at a relatively highly weathered oil further away from the source (green, purple). The highly weathered samples clearly show that virtually all the alkanes up to C-15 have been stripped from the original source oil. (*page 17*)

**Figure 8:** Cumulative dispersant use at the Deepwater Horizon Spill (*page 25*)

**Figure 9:** Multi-spectral images of the surface oil above leak (Ocean Imaging) (*page 26*)

**Figure 10:** Results from the MNS testing with Corexit 9500 at different dispersant dosages. Position 3 Light brown / reddish emulsion: Viscosity 7200 cP, water content 50%; Position 4: Dark Brown emulsion: Viscosity 1250 cP, water content 33 %. (*page 28*)

**Figure 11:** *In situ* burn history for Deepwater Horizon Spill (*page 32*)

**Figure 12:** Response estimates produced by the Oil Budget Calculator showing best case, expected, and worst case volumes of the seven different portions that the calculator tracks individually, of the cumulative volume of oil discharged through July 14, 2010. (*page 39*)

**Figure 13:** Response estimates expressed as percentages of the cumulative volume of oil discharged through July 14, 2010, in the best, expected, and worst cases. (*page 40*)



## LIST OF ACRONYMS

---

ASA	Applied Science Associates
AVIRIS	Airborne Visible Infrared Imaging Spectrometer
BOP	Blowout Preventer
DOE	Department of Energy
DOI	Department of the Interior
DOR	Dispersant to Oil Ratio
DWH	Deepwater Horizon
FRTG	Flow Rate Technical Group
ICS	Incident Command System
ITOPF	International Tanker Owners Pollution Federation Limited
LISST	Laser In Situ Scattering and Transmissometry
MNS	Mackay-Nadeau-Steelman Laboratory Test
NIC	National Incident Command
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NOAA/ERD	NOAA's Emergency Response Division
NRC	National Research Council
ORR	Oil Recovery Rate
PAH	Polycyclic Aromatic Hydrocarbon
RE	Recovery Efficiency
ROV	Remotely Operated Vehicle
SMART	Special Monitoring of Applied Response Technologies
TE	Throughput Efficiency
USCG	United States Coast Guard
USGPA	United States Gallon per Acre
USGS	United States Geological Survey
WHOI	Woods Hole Oceanographic Institute

# 1. INTRODUCTION

---

The Oil Budget Calculator grew out of a need to provide status of the spilled oil to the National Incident Command. Excel spreadsheets were first created to record volumes of skimmed oily water, of oil burned, and of dispersant applied. Later, the number of barrels that were directly captured was also recorded. However, there was no accounting for the fate of the remaining oil, and as the model became increasingly complex, the spreadsheets became difficult to interpret. Therefore, the U.S. Geological Survey (USGS), the U. S. Coast Guard, the National Oceanic and Atmospheric Administration (NOAA) and the National Institute of Standards and Technology (NIST) developed the Calculator, using data and supplementary expertise provided by non-government experts. The Calculator became operational, as a response tool, on June 22, 2010. However, it continues to undergo modification and refinement.

This document discusses the technical understanding that was captured in the model implemented in the Calculator — a simplified model that has evolved over time since it was first applied to produce results announced by NOAA on August 4, 2010 —, presents an assessment of the oil fate at the time of the well having been capped for good, and gives recommendations for future research. The aforementioned early results (published in a NOAA press release) included the estimate of 26% as the percentage of residual or “other” oil. The latest results presented in this report update this estimate to 23%, and assert that, with high confidence, the true percentage should be between 11% (best-case scenario) and 30% (worst-case scenario).

Because this matter has drawn the attention of scholars and other interested parties outside the oil spill science community, additional background material is included. However, in the end, this report is still only the technical documentation of a tool used for response, and it is neither a comprehensive review of the relevant technical literature, nor a research contribution intended for publication in a professional journal. Interested readers seeking more background on oil spill science are referred to Lehr (2001), NRC (2003), or Reed et al. (1999). Appendices describe the statistical approach used to qualify the Calculator’s estimates with uncertainty assessments, the Calculator itself, the raw data used in the Calculator, and supporting findings of laboratory and field studies.

It is important to remember that the Deepwater Horizon incident was an emergency, not an experiment. In spill emergencies, decision makers need immediate information that



sometimes requires estimates of unknown quantities without as much data as a scientific study normally would demand. Some of the processes governing the fate of the oil are poorly understood and knowledge about them mostly consists of the personal experience of skilled spill responders. In developing the Calculator, the team handled these poorly understood phenomena by constructing a simplified model that the participating experts could reach a consensus on, or by choosing compromise values (for rate or other constants, for example) if a consensus could not be reached.

The usefulness and accuracy of the Oil Budget Calculator needs to be assessed in light of its purpose, further discussed below. The answers that the Calculator provides to the response team only need to be accurate to the extent that they correctly inform cleanup decisions and do not lead to errors in response actions. Accuracy beyond that level, while desirable from a scientific viewpoint, is superfluous for the purpose for which the tool was designed. Hence, potentially large errors (e.g., in estimates of volumes of dispersed oil) likely would be inconsequential unless they would have led to misdirected response activities: we are not aware of instances of such misdirection in this case.

The reader is cautioned that the numerical values stated in this report are estimates based on the information available at the time that the estimates were produced, and are based on the simplified understanding that the time constraints of the response allowed: therefore, not only are they tentative, but most likely will change as new information becomes available. For this reason, the final mass balance calculation of the Deepwater Horizon Spill lies somewhere in the future, to be produced only after all the appropriate and necessary studies will have been completed.

## 2. PURPOSE AND BRIEF DESCRIPTION OF THE OIL BUDGET CALCULATOR

Once spilled into the marine environment and moved from the source, the oil interacts with the environment in a number of processes collectively called weathering. Figure 1 shows some short-term processes that acted on this spilled oil. These processes change both the composition and properties of the oil, and can result in the amount of oil in the water environment being continually reduced. Other longer-term processes such as biodegradation, photo-oxidation, and sedimentation may have an impact on the environment but are less amenable to response decisions.

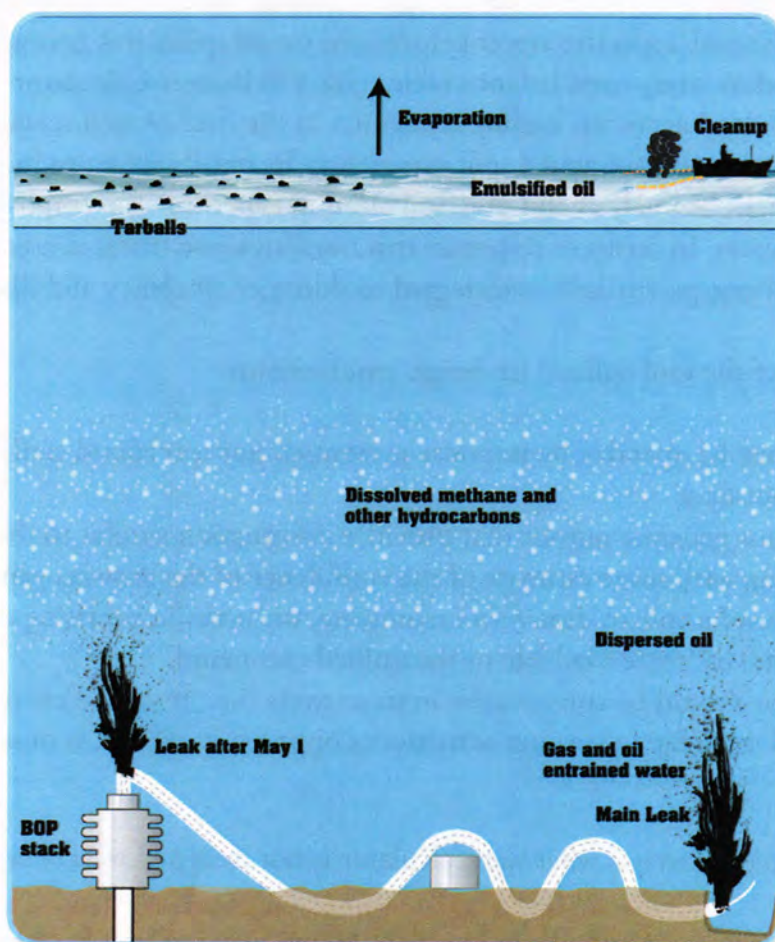


Figure 1: Schematic of Deepwater Horizon Oil Spill



The Oil Budget Calculator was designed to assist the Situation Unit of the Incident Command System (ICS). ICS was developed to provide federal, state, and local governments, as well as private and not-for-profit entities, with a consistent framework for the preparation for, response to, and recovery from any incident or event, regardless of the size, nature, duration, location, scope, or complexity. The ICS Form 209 provides the mass balance information that the unified command needs to assess the size of the threat and make informed response decisions. Preparing the mass balance tables for an ICS 209 form is usually a straightforward process. Vessel tanks are sounded, reports from the field estimate oil amount recovered or beached, and standard fate and behavior models, perhaps coupled with trained observer overflights, provide the remaining numbers for the tables. Such was not the case for the recent Deepwater Horizon Spill. Instead, the most sophisticated technology, involving expertise and apparatus never before used on oil spills, was necessary to construct even the most rudimentary mass balance table. The Oil Budget Calculator was a combined effort of several federal agencies, leading academics in the field of spill science, and practical response experts with years of actual spill experience. Its results are a product of field measurement, scientific analysis and practical cleanup expertise. The emphasis was on getting a conservative answer. In terms of response, this translates into using conservative estimates for cleanup efficiency, particularly with regard to skimmer efficiency and dispersant success.

The application of the tool defined its design requirements:

- Calculator must be operable by response personnel, not specialized staff, and use easily accessible input data.
- Calculator must generate output that provides information similar to the standard ICS 209 form along with some estimate of the confidence of the answers generated.
- Calculator must be able to deal with incomplete, uncertain, or missing data and still provide the best estimate available to the unified command.
- The Calculator should be conservative in its answers (i.e., it should err on overestimating oil that is still available to cleanup activities as opposed to oil that is outside of response capabilities).

It is important to understand what the Calculator is not designed to accomplish:

- The Calculator is not a spill research tool, although new research has been a product of its development. Simplifications were made to make it accessible to response personnel.
- The Calculator is not a damage assessment tool and is not applicable to determining environmental impact of the spilled oil. Other methods are required for this task.



- The Calculator does not track the final fate of the spilled oil. Instead it estimates oil that may be amenable to response decisions as opposed to oil that is not (e.g. dissolved or evaporated oil).

The logical structure of the algorithm that drives the Calculator is straightforward. Mass is conserved as processes act upon the spilled oil. The chronological order that is assumed for the unfolding of these processes is based on observations from other spills and our understanding of the corresponding science. Oil that comes from the well either is directly captured or not. The portion that is not captured there, in turn either is dispersed naturally or chemically in the jet zone at the leakage points, or rises to the surface. Some of the dispersed oil dissolves into the water column. Some of the oil that floats to the sea surface either dissolves on the way up or quickly evaporates. Oil that remains on the surface can be burned or skimmed. Some of the surface oil disperses naturally or chemically into the water column. After all these processes, there will be some oil left. A brief description of the governing equations (listed in full in Appendix 1) is given below.

(1) *Subtract off direct recovery from the total amount escaping from the reservoir.* While this oil does not enter the Gulf waters, it was important to record this amount for the Unified Command since logistical assignments depend upon it. If  $V_R(t)$  is the oil volume discharged on day  $t$  and  $V_{DT}(t)$  is the amount of oil directly recovered, then the effective discharge,  $V_{RE}(t)$ , is given by

$$V_{RE}(t) = V_R(t) - V_{DT}(t) \quad (1)$$

(2) *Determine the lower water column chemical dispersion amount.* The amount of oil that is dispersed as a result of the injection of dispersants is calculated. To guarantee that mass balance is maintained, this amount cannot exceed the effective discharge. Some of the oil that is dispersed as small droplets will have a portion of the hydrocarbons dissolve into the surrounding water. Subtracting this gives  $V_{DC}(t)$ , the net chemically dispersed oil:

$$V_{DC}(t) = (1 - k_7) \min(90k_2 V_{CB}(t), V_{RE}(t)) \quad (2)$$

Here,  $V_{CB}(t)$  is the volume of dispersing chemicals injected into the subsurface jet. The rate constants  $k_2$  and  $k_7$  are defined in Appendix 1 along with the other rate constants.



They are treated as random variables whose probability distributions describe our incomplete knowledge about their values, which is a consequence of our uncertainty about the exact attributes of the physical process the equations attempt to model.

(3) *Determine natural dispersion from the leaking jet.* From oil that is not chemically dispersed, compute the fraction that is naturally dispersed. Again, subtract oil that dissolves from the droplets.

$$V_{DN}(t) = (1 - k_7) \max(0, k_1(V_{RE}(t) - V_{DC}(t)/(1 - k_7))) \quad (3)$$

(4) *Calculate the dispersed oil near the bottom.* Add the amount that is chemically dispersed and naturally dispersed near the bottom. This oil is not available for evaporation, nor is the oil that dissolved near the bottom.

$$V_{DB}(t) = V_{DC}(t) + V_{DN}(t) \quad (4)$$

(5) *Compute skimmed oil as a fraction of oily water recovered.* Not all the liquid recovered by mechanical recovery,  $V_{OW}$ , is oil. The rate constant  $k_6$  specifies that fraction.  $V_{NW}(t) = k_6 V_{OW}(t)$  defines the net skimmed oil. Oil at all stages of weathering is skimmed. The model makes the assumption that the majority of the skimmed oil is 'older' oil. Hence, this oil is assumed to have already lost all oil that might evaporate.

(6) *Determine oil that evaporates or dissolves.* Compute oil that evaporates from surface oil during its first day on the surface or dissolves. Add evaporation from the second day on the surface plus oil that dissolves from dispersed oil. Let  $Z = V_{RE}(t) - V_{DB}(t)/(1 - k_7)$  be the oil that makes it to the surface on day  $t$ . The oil that rose to the surface on day  $t-1$  and is still left (neglecting natural surface dispersion and skimming) is  $W(t-1) = (1 - k_4)Z(t-1) - V_{BU}(t-1)$ . Since evaporation and dissolution are combined, dissolution from the bottom is added to  $V_E$ , the net evaporated or dissolved, where

$$V_E(t) = k_4 Z(t) + k_5 W(t-1) + \frac{k_7}{1 - k_7} V_{DB}(t) \quad (5)$$

Here  $V_{BU}$  is the volume of oil that is burned in-situ. The model uses reported values for daily volumes burned as one of its inputs. Since the burns involve oil that will have reached the

surface at any prior point in time, occasionally the total volume burned on a particular day may exceed the amount of oil surfacing on that day.

(7) *Determine natural surface dispersion.* Surface dispersion,  $V_{NS}$ , is a competitive process with emulsification and the potential for dispersion decreases as the oil weathers on the surface. Disperse the surface oil that is available for surface dispersion, after subtracting evaporation and burning:

$$V_{NS}(t) = k_8 \max(0, W(t)) \quad (6)$$

(8) *Determine chemically dispersed oil near the surface.* Compute volume of chemically dispersed oil from surfactants sprayed on the surface slicks,  $V_{DS}(t)$ . Check that it does not exceed oil volume on the surface, based upon  $V_S(t-1)$ , which is the total volume of surface oil remaining from the day before.

$$V_{DS}(t) = \min(20k_3V_{CS}(t), V_S(t-1)) \quad (7)$$

Here,  $V_{CS}(t)$  is the volume of dispersants used on day  $t$ . The remainder is then added to the “Other” oil category. For the purpose of the Calculator, this “Other” oil is treated as if it is all on the surface, when in fact some of it is not.

Appendix 1 lists all the equations used in the current version of the calculator, and explains how the uncertainty assessments for the estimates were produced. The corresponding results are described in Appendix 2, and are summarized in Figures 12 and 13.



### 3. PREVIOUS EXPERIENCE – THE IXTOC SPILL

---

The Deepwater Horizon incident is not the first large oil spill in the Gulf of Mexico. In June of 1979, the Ixtoc I exploratory well in the Bay of Campeche blew out, releasing oil for 290 days. It was the largest spill in history, at that time, totaling approximately 3.5 million barrels. The well was in much shallower water (165 ft) than the Deepwater Horizon.



**Figure 2: Ixtoc I Oil Spill**

In many ways, the present Deepwater Horizon spill and response is similar to Ixtoc incident. For example, in both cases the oil released at the well was saturated with gas and formed an emulsion on the surface. In terms of the response, various devices were employed at the Ixtoc and Deepwater Horizon but were unsuccessful at stopping the flow of oil from the well. Again in both situations, eventually a relief well was employed to stem the flow. As for countermeasures,

literature states mechanical recovery removed about 4-5% of the oil from the water surface during Ixtoc, which appears similar to the Deepwater Horizon incident. Large-scale dispersant operations were undertaken on oil on the water surface. In both events there was an impact on the fishing industry from the outright ban or local restrictions on fishing.

As much as the two incidents were similar, there are key differences. It is not the objective of this report to directly compare the two spills. However, as it relates to the subsequent discussion of the Oil Budget Calculator it is important to mention some pertinent detail.

Based on a limited literature review, the obvious difference is the depth of the oil release point where the Ixtoc I release point was approximately 165 ft (51m) below the water surface and the Deepwater Horizon release point was approximately 5000 ft. (1500m) below the water surface. Second, dispersants were used on the surface oil slick at the Ixtoc I but no subsurface application is noted (Jernelov and Linden, 1981). The loss to evaporation to the atmosphere of the Ixtoc I oil was reported as 50%. It is postulated that the circumstance of the Ixtoc I incident facilitated a larger mass of the oil reaching the water surface enabling greater overall mass loss to evaporation into the atmosphere in comparison to the conditions at the Deepwater Horizon incident.



There appears to be some differences in the physical and chemical properties of the two oils. Literature (Jernelov and Linden, 1981, Linton and Koons, 1983) noted the Ixtoc oil was a light type with an API gravity of 32, heavier than the Deepwater Horizon oil. Detailed chemical analysis of the Ixtoc I well head oil was not available in the literature reviewed preparing for the Oil Budget Calculator report. The literature did report that the Ixtoc I oil formed a “chocolate mousse” emulsion on the water surface within kilometers of the wellhead (Overton, 1981). Empirical evidence shows that the Ixtoc I and Deepwater Horizon Macondo oils differed; this will have some bearing on the mass balance determination of the oil spills.

Finally, literature on the Ixtoc I oil spill reported that the change in the chemical properties of the spill oil along with the heavy sediment load in the water column caused a good fraction of the oil to settle on the bottom of the Gulf of Mexico. News reports published in September 2010 indicated that this might also be true for this spill. However, ongoing sampling programs have not confirmed the claim of extensive oil being present on the bottom of the Gulf from Deepwater Horizon.

Jernelov and Linden (1981) constructed the following mass balance table for the Ixtoc I oil spill which has been included here for the convenience of the readers. It should be noted the table prepared by Jenelov and Linden reports values based on information available at the time. Readers are referred to the literature for further details on the assumptions used and contradictory opinions.

**Table 1: Mass Balance for Ixtoc 1**

	Percent	M Tons
<b>Burned at well site</b>	<b>1</b>	<b>5,000</b>
<b>Mechanically removed</b>	<b>5</b>	<b>23,000</b>
<b>Degraded biologically, photo, chemically</b>	<b>12</b>	<b>57,000</b>
<b>Landed on Mexican beaches</b>	<b>6</b>	<b>29,000</b>
<b>Landed on Texas beaches</b>	<b>&lt;1</b>	<b>4,000</b>
<b>Sank to bottom</b>	<b>25</b>	<b>120,000</b>
<b>TOTAL</b>	<b>100</b>	<b>476,000</b>



## 4. LEAK RATE AND SUBSURFACE OIL BEHAVIOR

Oil was initially leaking from two major sources several hundred meters apart. After severing the riser in early June, oil only leaked from the single location at the blowout preventer (BOP). The leak rate varied both in the short-term and in the longer-term. The latter was due mainly to the drop in reservoir pressure. Figure 3 shows the estimated flow rate, based upon studies done by various teams of experts employing a variety of methods. Details on the measurements of the Flow Rate Technical Group (FRTG) Plume Team using image correlation velocimetry are available in the Plume Calculation Team Report (2010). At the time of this document preparation (August and September 2010), the report by the joint effort of the FRTG and Department of Energy (DOE) was still in draft form. The source estimates by FRTG/DOE were considered to be accurate to within ten percent. This uncertainty level is adopted by the Calculator, with three release rates (FRTG/DOE estimate minus ten percent, FRTG/DOE estimate, and FRTG/DOE estimate plus ten percent).

The leak was a combination of gas and oil. In fact, a key parameter in estimating flow was the average ratio of these two. The actual value seemed to vary over the time period of the spill. Increasing gas increased the velocity of the plume but decreased the mass flow. Analysis of available short movies of the riser flow showed the existence of periods when the flow oscillates from pure gas to seemingly pure oil. The DOE/FRTG consensus generally accepted an average value of 44% oil percentage by volume for the exiting flow, based upon measurements of Woods Hole Oceanographic Institute (WHOI, 2010).

The Deepwater Horizon spill was unique not only for its size but also its location at a mile beneath the water surface. In general, when oil and gas are released from a deep-water location, they are expected to break into bubbles or droplets of various sizes. These sizes can vary widely. In field trials off Norway (Chen and Yapa, 2003), they were generally between 1 mm and 10 mm. Leifer (2010) has suggested, however, that the gas bubbles for the Deepwater Horizon spill were smaller than the North Sea experiments.

The larger droplets have a relatively stronger buoyancy force to friction force than the smaller droplets (this ratio increases with diameter) and therefore move faster towards the surface than smaller droplets. If the simple form of Stokes' law is assumed (not valid for larger droplets), droplet rise/fall velocity,  $v_{rise}$ , is a function of the water viscosity,  $\nu_w$ , relative density difference,  $\Delta\rho$ , and characteristic droplet size,  $d$ . The value of  $c_{stoke}$  varies, depending upon several factors. Figure 4 shows the rise velocity for this oil, according to Yapa et al. (2010).

$$v_{rise} = c_{stoke} \Delta\rho \frac{d^2}{\nu_w} \quad (8)$$



All the droplets are subject to cross currents that will move them laterally while moving upwards. For this reason the larger droplets and the smaller droplets may not come to the surface at the same location, but quite a distance apart. If there are droplets of very fine scale, it may take weeks or even months for them to come to the surface (Galt, 2010). Galt concluded that even for the large droplets, the rise time was several hours, an answer consistent with Yapa (2010) estimates. Galt also concluded that droplets in the 100 to 200 micron diameter range would take such a long time to surface from a depth of one mile that they were effectively dispersed. This is considerably larger than the common maximum diameter size limit for dispersed oil droplets of around 60-80 microns (Lehr, 2001; NRC 2005). Spaulding et al. (2000) estimated that the rise time for 200 micron droplets with specific gravity of 0.81, less dense than this oil, would have a rise time from this depth on the order of a week.

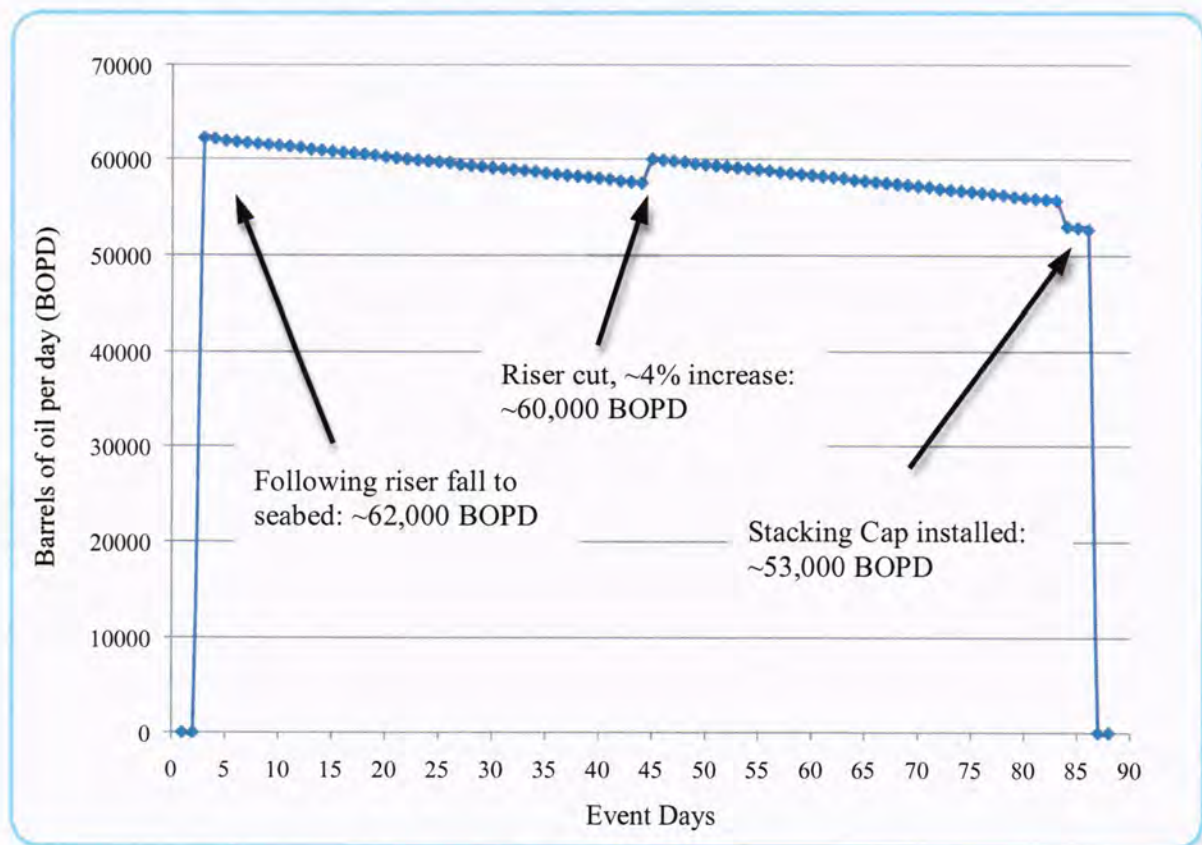


Figure 3: Estimated flow rate for Deepwater Horizon Spill (DOE/FRTG)

However, the large surface slicks showed that a good percentage of the released oil did make it to the surface. The remote sensing effort of the NASA ER/2 equipped with Airborne



Visible InfraRed Imaging Spectrometer (AVIRIS) surveyed about 30% of the core area of the surface spill on May 17, 2010. Extrapolating the examined area to the whole slick, Clark et al (2010) estimated that a minimum of floating oil of between 66,000 and 120,000 bbl. Limitations of the instruments do not allow measurement of very thick oil. The report suggested that if adjustments were made for this limitation, the surface oil could be as much as 500,000 bbl. According to the DOE-FRTG estimates, approximately 1.6 million bbl had been released from the well-head by that time. This suggests that somewhat less than a third of the oil had reached and remained on the surface if the report's hypothesis is correct. Since sub-surface recovery and dispersant applications were limited preceding this date, this estimate is not inconsistent with the later estimated values of remaining oil produced by the Oil Budget Calculator.

The plume also contained gas of many bubble sizes. For this incident, a large amount gas bubbles dissolved and may never have made it to the surface. Gas bubbles move faster than oil bubbles if they are the same size. Because of this, gases can separate from the main plume and start going in a slightly different direction (Chen and Yapa, 2004). Gases when released in deep-water, also have the potential to be converted into hydrates. Methane has a level of hydrate dissociation generally around 550 m of water depth as shown in Figure 5. This is not a fixed value. It depends on parameters like water temperature and gas type (Spaulding et al, 2000). Natural gas can get converted to hydrates at a much higher level. Therefore, gases can get converted into hydrates as they travel up. Hydrates are still buoyant with specific gravities of around 0.92 to 0.96. As hydrates travel towards the water surface they can get reconverted back into gas when they reach the lower pressure in the shallower regions (Leifer, 2010). Where the oil to gas ratio is sufficiently high, rather than an oily bubble, the aggregate is better described as a droplet with internal bubble. He concludes this effect could be very significant. For a primarily gas bubble (i.e., very low oil to gas ratio), in contrast, the effect of surface flow around the bubble pushing surface materials towards the downstream hemisphere could minimize any oil effect. This blowout occurred at far greater pressure than has been studied in the Deep Spill study (Johansen et al. 2000), or the lab (Masutani and Adams (2000), at depths where hydrate formation is far more rapid (Rehder et al. 2009). The oil budget calculator does not keep track of the gas bubbles, hydrates or dissolved gases.



## 5. DISSOLUTION

Unlike a typical spill, oil from the Deepwater Horizon spill entered the marine environment 5000 feet below the surface of the Gulf, and started weathering before it reached the air-water surface. Because of the nature of the material flowing from the riser, which was a miscible mixture of oil and natural gas, significant dispersion of the liquid oil occurred near the wellhead. Some of the oil droplets were so small, less than a 100 microns in diameter, that the turbulent diffusivity of the water was enough to overcome the oil's natural buoyancy, and caused the micro droplets to be dispersed at depth by ocean currents. Larger droplets floated to the surface, however the speed of the transit was determined by the size of the drops. Larger accumulations of droplets of oil rose fairly quickly while smaller droplets rose slowly and were dispersed further from the spill site by currents in the water column.

The important point about this movement of oil from the wellhead is that oil in tiny droplets is exposed to weathering processes both at depth as well as on its transit to the surface, and once on the surface, weathering continues. Another important point is that much of the oil moved through the marine environment as tiny drops, and these drops were continually exposed to uncontaminated Gulf water in their transit. This means that the dissolution of compounds from the tiny oil droplets was not controlled by equilibrium factors, and this resulted in an almost continuous molecular extraction from the oil droplets by the water column. The results of this continuous extraction are that even sparingly soluble compounds were extracted from the droplets and dissolution was a much more important factor in the weathering of Deepwater Horizon spilled oil than it is in more common surface oil spills.

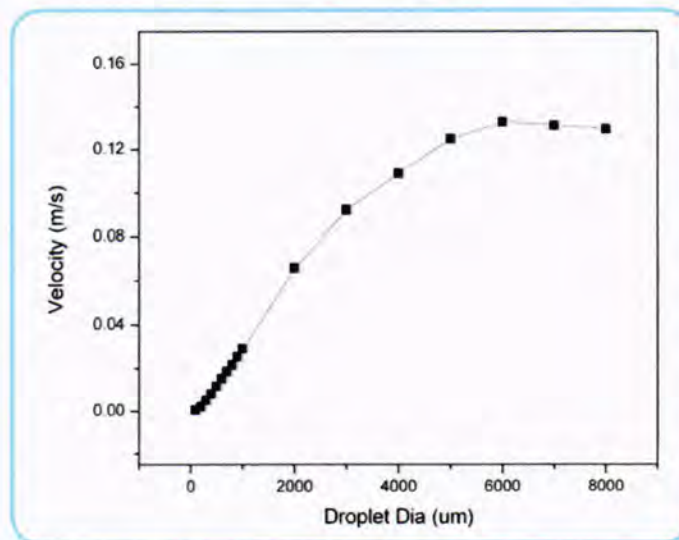


Figure 4: Droplet rise velocity (Yapa et al. 2010)



The proverb that oil and water do not mix is usually scientifically accurate when it relates to molecular dissolution of oil into the surrounding water from a surface spill. For the normal surface type spill, dissolution is less important for estimating the mass balance of the slick (NRC 2003). However, as described above, because of the nature and depth of the release, dissolution of oil into the water column was a significant weathering factor.

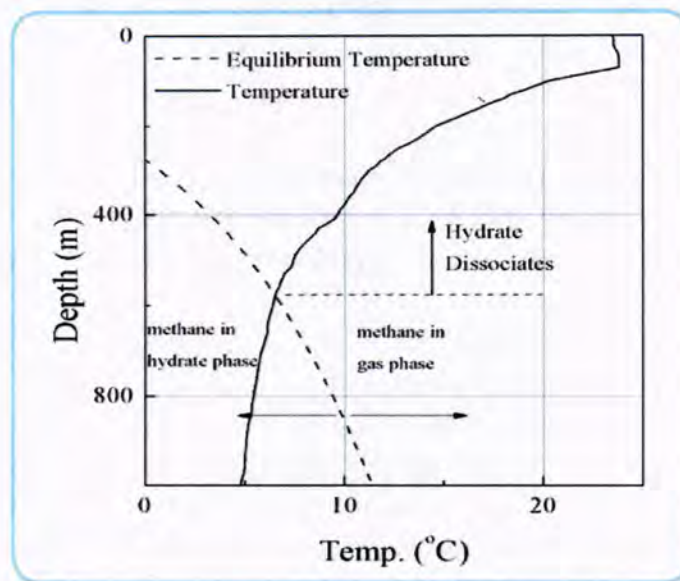


Figure 5: A typical ambient temperature and thermodynamic equilibrium curve for Methane (Chen and Yapa 2004)

The dissolution process is a very complex series of interactions between hydrocarbon molecules that are non-polar and surrounding water molecules that are polar. In general, polar molecules dissolve in polar solvents, seawater in this case, and non-polar molecules dissolve in non-polar solvents, the oil in this case. However, because of their molecular shapes, sizes, and chemical bonds, some non-polar compounds are slightly soluble in polar solvents. Such is the case when considering oil solubility in seawater. As a general rule, small mono-aromatic compounds, such as benzene and the alkyl benzenes, have significant seawater solubility compared to equivalently sized saturated compounds. This solubility extends to larger aromatic compounds, such as naphthalene and its alkyl homologues, and may also slightly extend to three-ringed aromatic compounds such as the phenanthrenes and the dibenzothiophenes. As a rule of thumb, saturate compounds are the least water soluble of the components of oil, probably because they have no significant interactions with solvent water molecules and do have significant interactions with similar non-polar compounds in the oil. The conclusions are consistent with experimental results obtained at SINTEF (Melbye et al. 1999) which showed that a component needs to have a water solubility of a



minimum 0.3 -1 mg/L in seawater (Figure 6) in order to have any significant potential to dissolve out from an oil droplet when rising to the surface. This means that n-alkanes up to maximum n-C8-9 may have a potential to dissolve but larger alkanes have very limited solubility potentials. However, the mono-aromatic benzene compounds (the BTEX's), C0-C3 Naphthalenes, and the C0-C1-alkylated 3-rings PAH can be stripped out of oil droplets because of their water solubilities. The bottom line is that when tiny droplets of oil transit the water column to the surface, many of the low molecular weight one, two and maybe three-ringed aromatic compounds can be dissolved into the water column. This dissolution can affect both the toxicity and physical properties of surface oil from deepwater releases.

Few models or studies exist for oil dissolution at spills, mostly in dated work and older generation spill models. Mackay and Shiu (1975) measured the aqueous solubility of fresh and weathered crude oil. Payne et al. (1984) reported that studies of Prudhoe Bay crude found that truly dissolved components were almost exclusively alkyl-substituted lower weight mono-aromatic hydrocarbons with very little n-alkane dissolution. The dissolution rate depends directly upon surface area, which was proportionally larger per volume spilled for this spill incident compared to a normal surface spill by factors of 100 to 1000. Mackay and Leinonen (1977) concluded that, for droplets less than 100 microns in diameter, dissolution

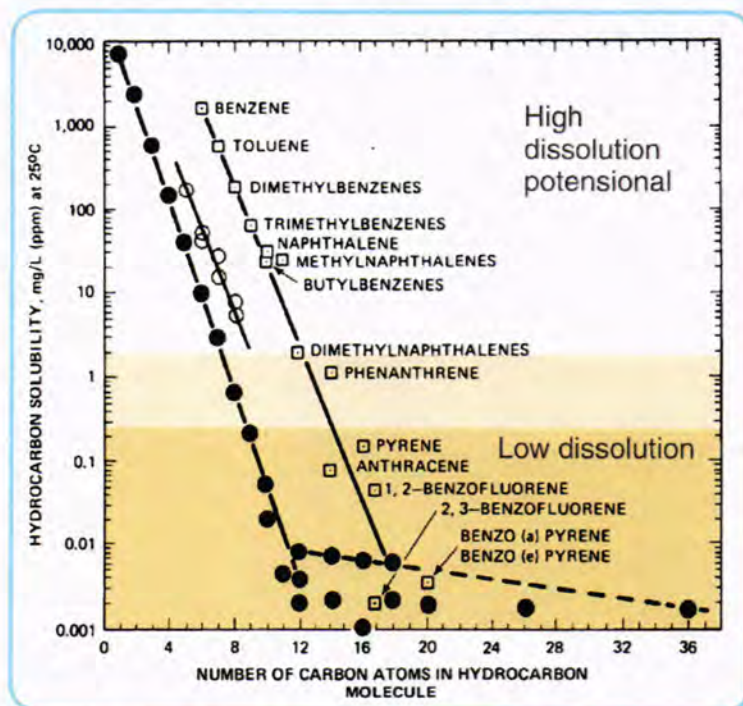


Figure 6: Solubility per carbon number for hydrocarbon molecules, (Modified from McAuliffe, 1987 IOSC - proc. Pp 275-288)

is very rapid for any component that will dissolve at all. Any remaining material in the droplet will consist of relatively insoluble saturate hydrocarbons, i.e. hydrocarbons with a carbon number greater than about 8, and larger multi-ringed aromatic PAHs. While the droplets that made it to the surface were larger than 100 microns, the extended time that it took for them to reach the surface suggests that dissolution of even marginally soluble compounds occurred.



It should be pointed out that initial chemical analysis of some samples collected below the Gulf's surface indicates that significant dissolution did occur. One and two ringed aromatic compounds, and some of the three ringed sulfur heterocyclic aromatic compounds, appear to have been dissolved during transit from the wellhead. These compounds have carbon numbers above 10, and there is some evidence that normal alkanes were also slightly affected by the long transit that occurred as oil drops moved through the water column.

Based upon the chemistry of the oil and the above discussions, it was estimated that any oil exposed to conditions that could lead to dissolution would lose between 5-10% of its volume this way. Since many of these same molecules would evaporate, this process was included in the evaporative losses estimate for any oil that made it to the surface. However, dissolution is subtracted from oil dispersed near the bottom that never reaches the air-water interface. These estimates may change as further studies underway at SINTEF and elsewhere provide additional information. At a minimum, it may be possible to separate dissolved fraction from evaporative fraction. If, on final review, we find that water samples with oil droplets were collected just below the water surface, then by using GC-MS, it is possible to look at the changes in ratios between the more semi-volatile aromatics (e.g. 2-3 rings PAH's and their alkyl homologues) versus the corresponding n-alkanes with same boiling Points (similar vapor pressure, but with far less solubility). In that way, it would be possible to say more specifically how much of the depletion of the components in the range of C10 -C17 is due to dissolution, and how much is due to evaporation. Such information would be useful for impact assessment but, for the purpose of response, would be of limited value. The Oil Budget Calculator groups dissolution and evaporation.

## 6. EVAPORATION

Laboratory and field studies of oil weathering under wide ranging conditions and for a wide range of crude oils demonstrate that surface slicks quickly lose volatile components to evaporation. As the more volatile compounds are lost, the rate of evaporation slows. Evaporation is often the most significant loss mechanism from surface slicks during the first week following a spill. Generally, after a week at sea, evaporation is no longer a significant loss mechanism for surface oil. For light crude oils, such as this oil, the great majority of the evaporative loss occurs within a couple days of its exposure to the air.

Empirical methods were used to estimate the evaporation rate during this spill. Samples of weathered oil collected from the sea surface were analyzed using GC/MS. Laboratory weathering of the source oil provided an independent assessment of evaporative behavior. Estimations of evaporation rates were not based on model predictions; rather models were used in analyzing data from field measurements.

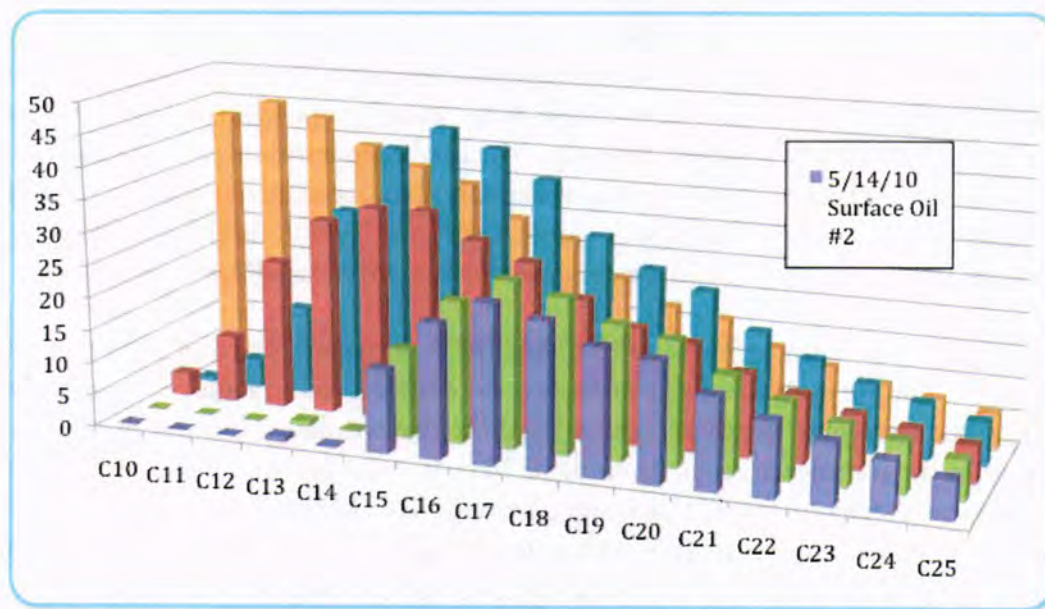


Figure 7: Histogram shows the C-10 to C-25 Alkanes of the whole Source Oil (Orange), a floating oil sample immediately adjacent to the source (red), and two floating oil samples at a relatively highly weathered oil further away from the source (green, purple). The highly weathered samples show that virtually all the alkanes below C-15 have been stripped from the original source oil. (Blue bar graph is sample from dispersant efficiency testing).



Evaporation changes not only the volume of a surface oil slick, but changes the chemical composition of the oil as well. Because smaller chemical compounds are preferentially lost during evaporation, it affects the relative abundance of individual chemical compounds within the oil. These changes can be observed by comparing the composition of unweathered oil to that which has weathered on the surface. Other loss processes, such as dissolution, can also change the composition of the oil. While dissolution is usually not a dominant loss mechanism for surface spills it might be significant for releases in deep water. Without the appropriate samples, it was not practical to try to resolve the relative importance of dissolution and evaporation, so these two losses are grouped. Oil that never reached the sea surface is not susceptible to evaporative loss, so the measured estimates of fraction evaporated only applies to the oil that surfaced.

Pseudo-component models (Payne et al. 1984; Kirstein et al. 1984) were used to process measured data. These models approximate the oil as an ideal mixture of a relatively small number of components, each component representing a range of individual chemical compounds with similar vapor pressures. Each component is characterized by a mole fraction and a vapor pressure. The rate, per unit area, at which a component evaporates from the surface slick is proportional to the wind speed, the mole fraction of that component within the oil (which varies with time), and the vapor pressure of that component (which varies with the temperature of the oil, assumed to be the same as the water temperature). The rate equations for the components are solved simultaneously. The total evaporation rate is set equal to the sum of the rates of the individual components. This method has been adapted for an oil-weathering model, ADIOS2™, developed by NOAA (Jones 1997), the Type A model developed by ASA (French et al., 1996) and the OWM model developed by SINTEF (Reed, Singaas et al. 2001).

NOAA's Emergency Response Division (NOAA/ERD) measured the composition of several oils (Figure 7). For the purpose of this discussion on evaporation, in Figure 7 we focus on the oil from the reservoir (Source oil, orange) and the two weathered oils (green and purple) collected from the sea surface on, or around, 16 May. It is not known how long the weathered samples were on the sea surface before being collected. GC/MS analysis was used to measure the relative abundance concentrations of chemical compounds that make up the oil. The weathered oil samples exhibited an expected depletion of the more volatile compounds. The pseudo-component evaporation model used in ADIOS2 (Jones 1997) was initialized with oil-composition data provided by BP in conjunction with oil-composition data measured by NOAA/ERD. The ratio of components measured in the more weathered oil samples was compared to those predicted by the model. The extent of evaporative loss was based on the correlation between the measured and modeled ratios. These two weathered oil samples exhibit an average mass loss of 36%. Since the age of these samples is not known, this provides a lower bound on the possible evaporative loss of the surface oil.



SINTEF analyzed three samples of floating oil collected on June 4<sup>th</sup> and 5<sup>th</sup> for fraction evaporated (Leirvik, Daling et al. 2010). They analyzed the samples by GC/MS and related the fraction evaporated to the depletion of alkanes in the C14 to C16 range. They correlated the degree of evaporation with the depletion of these peaks using past results. Their measured data indicated a mass loss to evaporation of 44%, 47%, and 50%. They estimate that the time at sea for these three samples was 1-2 days, 2-3 days, and 4-5 days, respectively.

Laboratory measurements performed by S.L. Ross Environmental Research Ltd. (S.L. Ross Environmental Research Ltd., 2010) on unweathered Deepwater Horizon oil were consistent with measurements of the above-mentioned surface oil samples. They artificially weathered a 2cm thick slick of Deepwater Horizon oil in a wind tunnel for 2 weeks. They measured that approximately 35% had evaporated after 2 days, and 45% after 2 weeks. Their measurements exhibit a cumulative evaporation, which is essentially a logarithmic function of time with the majority of the evaporation occurring in the first few days.

Camili et al. (Camili, Reddy et al. 2010) from Woods Hole Oceanographic Institute measured the composition of oil collected from the top 30 m of the water column. They made no attempt to quantify the fractional loss but did attribute the loss of the more volatile compounds to evaporation. Their measurements can be viewed as an additional observation suggesting substantial evaporative loss.

As mentioned above, dissolution also affects oil composition and so losses to dissolution must be considered as contributing to the measured values. Measurements reported here constitute lower bounds to the possible combined losses to evaporation and dissolution of oil that reached the surface. Loss fractions range from 36% to 50% and are self-consistent. The authors of this report believe that these data provide a close lower bound to the fraction of surface oil lost to the combination of evaporation and dissolution.

The oil budget calculator based the evaporation/dissolution estimates on the compositional change observed in samples of surface oil. It approximates the evaporation/dissolution process as occurring over 2 days; the majority of the loss occurring in the first day. To simplify data entry, requirements to enter variable wind speeds were eliminated. Cumulative evaporation is sensitive to oil composition and temperature but is relatively insensitive to wind speed. The original approximation was 37% lost during the first day (potentially as high as 44% and as low as 33%) with a second day loss of 4% (potentially as high as 6% and as low as 0%). Hence the range of total evaporation of the oil that surfaced was between 37% and 50%. Currently, there is no plan to revise these values.



## 7. WEATHERING ESTIMATION BY EMULSIFICATION

---

An alternative approach to calculating mass loss has been suggested by Fingas (2010) that uses the fact that the surfacing oil formed emulsions. One important factor to the formation of emulsions is that oils often must weather to a certain percentage before a certain type of emulsion occurs. This is because the asphaltenes and resins must be at a sufficient content to stabilize the oil and also the viscosity must be high enough to retain water droplets long enough for asphaltene/resins stabilization to take place.

Oils from similar oil fields have a tendency to form similar emulsions with similar weathering tendencies. Gulf oils that formed stable emulsions had weathering percentages of 37.7, 26.2, 16.4, 25.5, 22.6, 24, and 35.2%. These average 26.8%. If the Deepwater Horizon oil shows similar tendencies, the weathering that took place near the release of the Deepwater Horizon was about 16 to 38% with the likelihood that it was near 27%. However, experimental studies by SL Ross Ltd. (see pp. 3 in Appendix 8) and studies at SINTEF showed that an evaporative loss of at least 40-45 wt %, (representing a 200 - 250C+ residue) is needed for this crude oil to start form a significant and stable emulsion. Some additional evaporation would occur as the surface oil moved away from the area, transported by winds and surface currents. Observations of large amounts of emulsified oil indicate that such emulsified oil, at least, had already weathered sufficiently to emulsify.

## 8. NATURAL DISPERSION

---

While the oil released in this spill was buoyant, not all of the oil rose to the surface. Small droplets of oil stayed suspended in the water column just as small dust particles will stay suspended in the atmosphere due to the underlying fluid turbulence. Such droplets will eventually be assimilated through dissolution and biodegradation. They also may become attached to suspended sediment in the water.

Some limited data exists on dispersed oil from the results of RV Brook McCall Survey LISST (Laser In Situ Scattering and Transmissometry) measurements performed by the Bedford Institute of Oceanography (see Appendix 7). It lends support to the hypothesis that much of the oil released was dispersed into the water column. However, since the samples were subsurface, they may be preferentially sampling the droplet distribution with the larger droplets having risen to the surface. Payne's study reported plumes of oil droplets at depths greater than 2 km. away from the source with larger droplets on the top of the plume and smaller below. This would be consistent with a large amount of dispersion and weak buoyancy. One should be careful about over-interpretation of particle size distribution data that were collected for this specific purpose during the Gulf of Mexico oil spill emergency response operations. Under this emergency response effort, rapid, less than perfect actions had to be taken to support the requirement for immediate action to monitor the fate and transport of the oil.

The NOAA oil fate and behavior model, ADIOS2, uses the dispersion formulas developed by Delvigne and Sweeney (1988). These formulas estimate the distribution of droplets sizes based upon the dissipation energy rate  $\epsilon$ . For most surface spills, the turbulent energy comes from breaking waves. Li and Garret (1998) estimate that typical dissipation rates in breaking waves range from 0.1 to 10  $m^2/sec^3$ . Others have reported different values. For example, measurements in a wave tank gave values of 0.01 to 0.1  $m^2/sec^3$  at the surface (Wickley-Olsen et al., 2007). Field measurements showed lower values varying between about 0.1 and 1  $m^2/sec^3$  (Gemmrich and Farmer, 2004, Gemmrich, 2010). Additional information on the value of  $\epsilon$  can be found in Kaku et al. (2006).

ADIOS2 suggests that if this spill occurred at the surface under average conditions, only a few percent of the oil would disperse because the oil would emulsify. If emulsification is prevented, natural dispersion could be as much as 30%.

However, it is not breaking waves but the turbulence at the leak that formed these oil



droplets. In this case, a new method had to be developed to estimate dispersion rate. ADIOS2, following standard guidelines (NRC 2003), assumes that droplets must be smaller than 70 microns in diameter to be considered permanently dispersed. While appropriate for surface spills, it is probably too restrictive for spills happening a mile deep. The Calculator uses 100 microns as a cutoff. Based upon the earlier discussion of surfacing time, this was also too restrictive but was consistent with the conservative approach used to calculate oil fate.

Following DS,  $Q(\delta)$ , the entrained droplet mass density for droplets of diameter  $\delta$  is given by the equation

$$Q(\delta) = C\epsilon^{0.57}\delta^{0.7} \quad (9)$$

where  $C$  is a constant that depends upon the properties of the oil slick.

For a surface spill, ADIOS2 would expect that the dispersed oil would be

$$M_{disp(bw)} = \int_0^{70\mu} Q_{bw}(\delta)d(\delta) = C\epsilon_{bw}^{0.57} \frac{(70\mu)^{1.7}}{1.7} \quad (10)$$

where the  $bw$  subscript indicates that this applies to dispersion caused by breaking waves.

If we apply this method to the subsurface leaking pipe (subscript  $lp$ ) then the same equation would be

$$M_{disp(lp)} = \int_0^{100\mu} Q_{lp}(\delta)d(\delta) = C\epsilon_{lp}^{0.57} \frac{(100\mu)^{1.7}}{1.7} \quad (11)$$

and the ratio,  $R$ , between the two would be

$$R = \frac{M_{disp(lp)}}{M_{disp(bw)}} = 1.8 \left( \frac{\epsilon_{lp}}{\epsilon_{bw}} \right)^{0.57} \quad (12)$$

Thus the estimate of the increase in natural dispersion becomes a problem of estimating  $\epsilon_{lp}$  and  $\epsilon_{bw}$ . Lasheras (2010) has suggested that, to first approximation (Friche et al. 1972; Gibson, 1963), the maximum theoretical dissipation rate of turbulent kinetic energy can be estimated by

$$\epsilon_{lp} \approx U_{lp}^3 / D_{lp} \approx 7m^2 / sec^3 \quad (13)$$



where  $U_{ip}$  is the exit velocity of the flow jet and  $D_{ip}$  is the pipe diameter. He points out that experiments by Martinez –Bazan et al (1999) show that, for distances less than 15 pipe diameters from the orifice, the dissipation rate is much smaller, perhaps as little as  $0.02 \text{ m}^2 / \text{sec}^3$ . If we take a mid-range value from the Li and Garret suggested bounds for breaking wave dissipation rates compared to the theoretical maximum for  $\epsilon_{ip}$  we get virtually all of the oil naturally dispersing. This obviously does not match observation. If, instead, we use the experimental results of Martinez-Bazan et al., we get approximately 20% subsurface natural dispersion. This more conservative value was used by the Oil Budget Calculator with an assumed maximum of 30% and a minimum of 10%. The minimum value is considered to be the lowest credible estimate consistent with Camilli et al. (2010) and the maximum the largest estimate consistent with the AVIRIS and LISST results.

Lasheras also pointed out that the characteristic size  $D_{char}$  of droplets small enough not to be broken by the turbulent shear forces can be estimated by a simple function of the oil-water surface tension:

$$D_{char} = \frac{\left( \frac{1.5\sigma_{o-w}}{\rho_{oil}} \right)^{3/5}}{\epsilon^{2/5}} \approx 10mm \quad (14)$$

This matches the North Sea experiments discussed earlier. While the Oil Budget Calculator conservatively assumes that oil that is not dispersed near the bottom would come to the surface, this is not the case. For example, marine snow present in Gulf waters would scavenge some of the oil droplets on their journey to the surface. The extent of this affect for this spill is uncertain at this time.

Oil droplet size distribution is greatly affected by viscosity and surface tension. Since some of the lighter ends are lost through dissolution on the oil journey to the surface and since the surface oil emulsifies, the viscosity of the surface oil was quite high compared to the oil at the leaking riser. The seas were usually relatively calm, although there were periods of high winds. The original Budget Calculator assumption was that the surface oil would have negligible natural dispersion. This was consistent with the standard to conservatively estimate any reduction in surface oil through either natural or cleanup actions, although certain experts disagreed with this assumption. They pointed out that much of the initial surface oil was not on the surface after storm events. Also, the studies by SINTEF indicate that the weakly emulsified oil is dispersible with enough energy input. Therefore the Calculator was modified to include 5 % natural dispersion of surface oil, based upon ADIOS2 model results. Low value was no dispersion and high value was 10%. As in other dispersion estimations, there was not a uniform consensus by the experts on this revised estimate.



## 9. CHEMICAL DISPERSION

A typical commercial dispersant is a mixture of three types of chemicals; solvents, additives and surfactants. The surfactants are the active ingredient and contain both hydrophobic and hydrophilic groups. This allows them, when coating the oil surface, to reduce its surface tension by as much as a factor of 20 or more, reducing mean droplet size in droplet formation caused by turbulent shearing (Li and Garrett, 1998). Canevari et al. (1989) measured declines in oil-water interfacial tensions from 18 mN/m without dispersant to 0.1 mN/m with dispersant. More recently Khelifa and So (2009) used a spinning drop instrument to measure declines of oil-brine interfacial tension for three different oils. Declines from 18.3 mN/m without dispersant to  $6.5 \times 10^{-4}$  mN/m with Corexit 9500 at 1:20 dispersant to oil ratio (DOR) were measured. The same study showed that corresponding droplet size decreases from about 220 nm to 25 nm when the DOR increases from 1:500 to 1:10. (DOR is often expressed with the 1: omitted. Therefore, a DOR of 20 and a DOR of 1:20 refer to the same ratio).

Clayton et al. (1993) noted that successful dispersion of oil in actual dispersant applications only occurs if five requirements are met.

- (1) The dispersant must reach the oil surface
- (2) The dispersant must penetrate the oil surface
- (3) The surfactant must orient at the oil-water interface
- (4) The surface tension must be reduced
- (5) Sufficient mixing energy must be applied

A total of 43,884 barrels of dispersant were used at the DWH incident:

- 18,379 barrels of dispersant were used by sub-sea addition to the discharging oil and gas stream.
  - Initially this was at 12 gallons/minute, later reduced to 7 gallons per minute.
  - The EPA imposed maximum sub-sea use of 15,000 gallons/day (357 bbl/day), equivalent to 10.4 gallons/min
- 25,505 barrels of dispersant were applied to oil on the sea surface (see Figure 8).

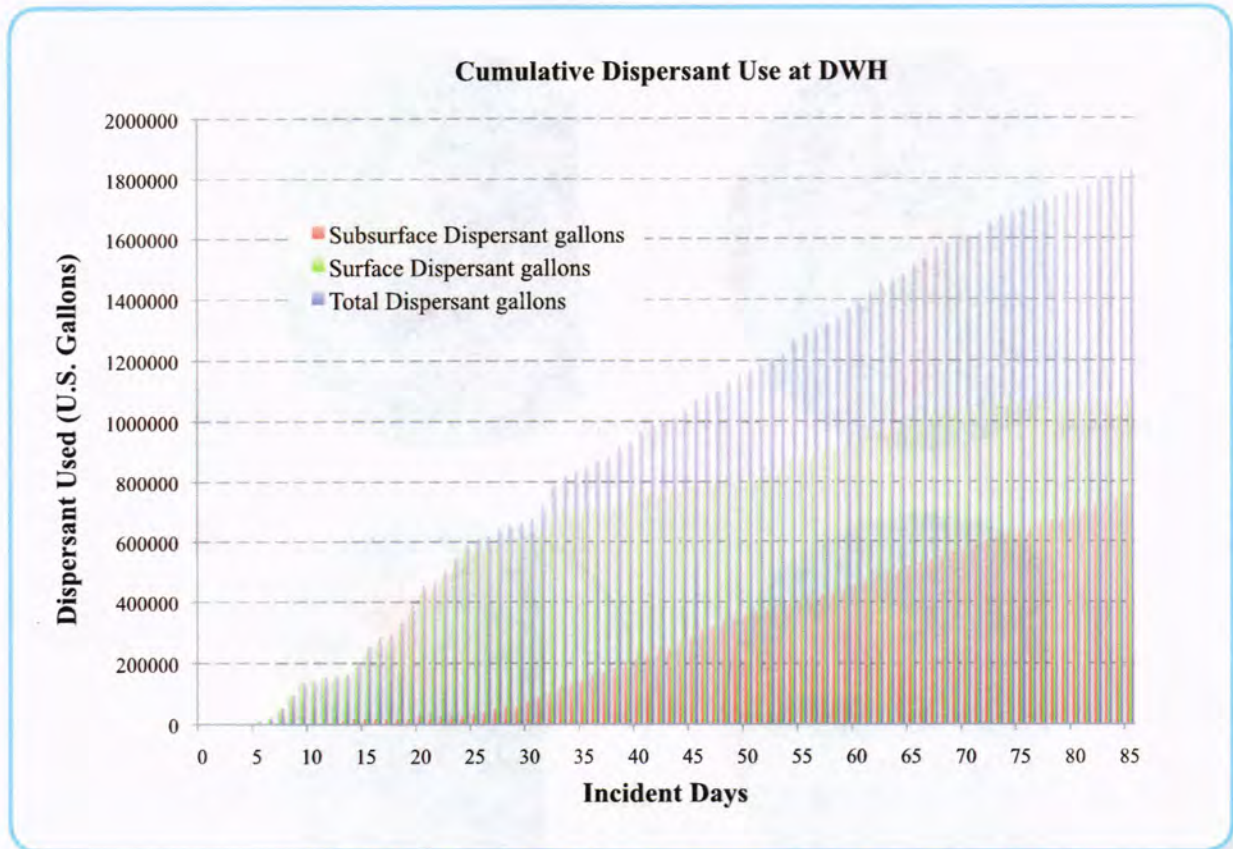
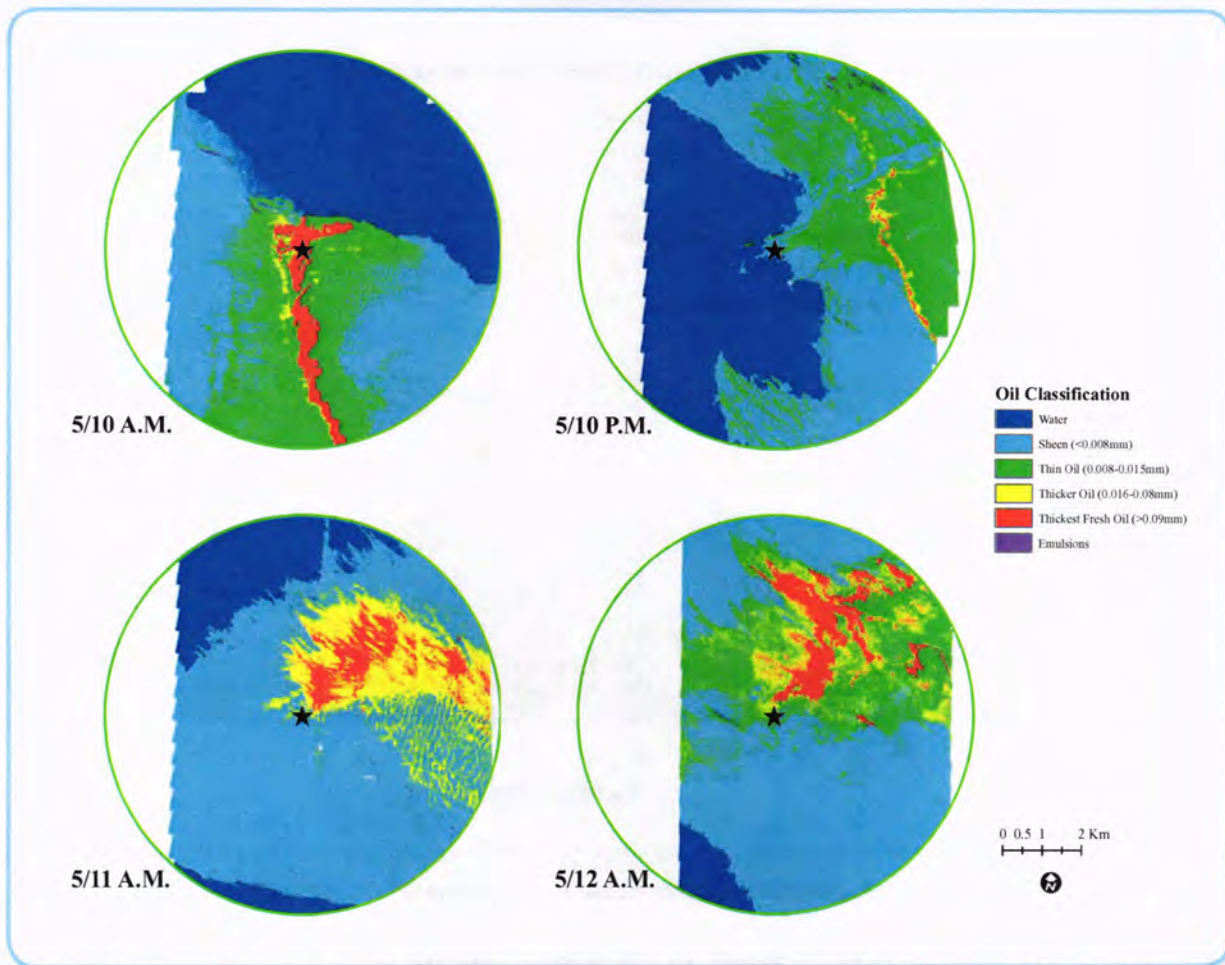


Figure 8: Cumulative dispersant use at the Deepwater Horizon Spill

Estimating effectiveness of these dispersant operations was the most difficult challenge in constructing the Budget Calculator, given the present state of oil response technology. As Lewis (2010) points out, the effectiveness of dispersant use at real oil spill incidents cannot be determined by measuring the dispersed-oil-in-water concentration in the water column with sufficient resolution in time or space to produce an accurate mass balance. Nor are there currently commercially available remote sensing techniques capable of measuring oil layer thickness with sufficient accuracy and with sufficient resolution to enable the volume of an oil slick to be determined at any point in time, or how the volume changes with time.

Some surface dispersant applications employed the SMART (2006) protocols. SMART (Special Monitoring of Applied Response Technologies) is a Federal cooperatively designed and regionally approved monitoring program for dispersant operations and *in situ* burning. However, SMART provides mostly qualitative, not quantitative, estimates of dispersant effectiveness. SMART teams could at best say that there was some dispersion caused by the dispersant applications.





**Figure 9: Multi-spectral images of the surface oil above leak (Ocean Imaging)**

Ocean Imaging, using a multi-spectral scanner to estimate slick coverage at the water surface directly over the spill site, observed the oil appearance both during dispersant operations and no dispersant operations. Figure 11 shows a time period from May 10 through May 12. The individual images represent relative thickness measurements of surface oil at specific times. The larger the red area, the more thick oil is present. Surface conditions were reasonably similar during this time period. Subsurface injection began at 0430 hrs on May 10 and continued with an average injection rate of 8 gallons per minute. If the dispersant was as highly effective as suggested by certain experts, then more than half of the released oil should have been chemically dispersed. The May 10<sup>th</sup> A.M. image may be too early to show these results and May 10<sup>th</sup> P.M. seems to show a drop in surface oil. However, May 11<sup>th</sup> and May 12<sup>th</sup> show similar surface expressions although the latter should be displaying more oil. Therefore, these observations provide inconclusive results.



The R/V Brooks McCall field study (Appendix 7) gave some droplet size distribution information but not with sufficient clarity to separate the amount of oil chemically dispersed from the amount of oil naturally dispersed. Analysis was ongoing at the time of preparation of this report and may yet provide useful guidance on this matter.

Given the limited nature of the field data, the best that could be done was to estimate effectiveness using the experience and knowledge of dispersant experts. Unfortunately, reaching consensus among the experts was not possible.

## **9A. CHEMICAL DISPERSION: SURFACE APPLICATION**

---

Surface application of dispersant for this spill was extensive. At over 25 thousand bbls, were it a spill by itself, it would be one of the larger spills in U.S. waters. Dispersants were normally applied by aircraft at a dosage of 5 gallons/acre (USGPA) (5000 liter/sq. km). The dosage (DOR) needed to disperse surface emulsions depends highly on the weathering degree (e.g., water content, viscosity) of the emulsion. In Figure 10, controlled laboratory testing shows (and is further discussed in Appendix 6, Figure 4.3) that for the low weathered dark brown (pos. 4) emulsions (i.e., the type of emulsions that the aerial applications was focused on), a very low “absolute” dosage of 1:250 is sufficient in order to disperse the dark emulsion effectively under high mixing energy (breaking waves). This means that an aerial application with typically 5 USGPA is sufficient dosage in order to disperse such dark-brown emulsion with thicknesses around 1 mm as long as the application is efficient and high mixing energy is available. SMART samples similarly show significant dispersed oil in the surrounding water after surface operations in 3 out of 19 samples (see Table 2). When the emulsion become more weathered (i.e. light brown-orange-reddish in color), with a typical water content of >50%, and a significantly higher viscosity, the emulsion was still dispersible under high mixing energy, but a more “traditional” dosage of 1:50 - 1:25 was needed in order to disperse the emulsion effectively using COREXIT 9500. It is probable that some sprayed dispersant missed the oil or was deposited on oil layers that are thinner (such as sheen) or much thicker (emulsified oil) than the nominal 0.1 mm thick oil layer that most dispersant spray systems are designed to treat. Also, the most heavily weathered state of the emulsified oil would impede dispersant success.



**Alternative View 1:** We believe the Oil Budget Calculator overestimates the effectiveness of chemical dispersants because:

- The WHOI survey and the Ocean Imaging pictures do not support it
- The surface oil was emulsified and there was insufficient mixing in the subsurface injection.

**Alternate View 2:** We believe that the Oil Budget Calculator underestimates the effectiveness of chemical dispersants because:

- Lab studies show that both the fresh and emulsified oil are dispersible
- There was sufficient energy both subsurface and at the surface to disperse the oil.

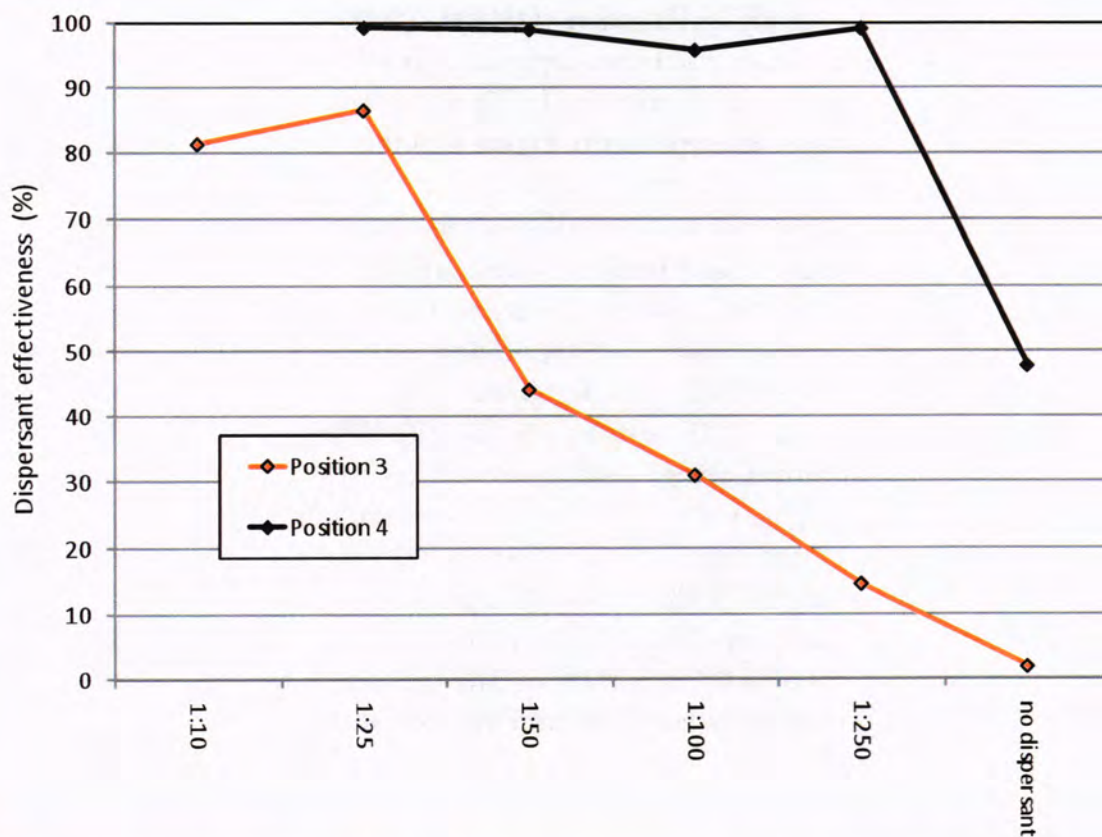


Figure 10: Results from the MNS testing with Corexit 9500 at different dispersant dosages. Position 3 Light brown / reddish emulsion: Viscosity 7200 cP, water content 50%; Position 4: Dark Brown emulsion: Viscosity 1250 cP, water content 33 %.



For the reasons stated in the subsurface dispersant application estimation, it was difficult to assess the efficacy of this effort, with a wide variation in the opinions of the experts. As in the case of subsea dispersant operations a compromise value is used in the new version of the Oil Budget Calculator in lieu of a consensus number. The expected DOR is 1:10 with a low value of 1:5 and a high value of 1:20

**Table 2: USCG Surface Water Dispersant Study Sample Results.**

<i>USCG ID#</i>	<i>Concentration (mg/ml)</i>
USCG-062	1.7
USCG-063	3.7
NSF-036-10-GB-064	4.1
NSF-036-10-GB-065	3.5
NSF-036-10-GB-067	3.2
NSF-036-10-GB-068	5.7
NSF-036-10-GB-070	1380
NSF-036-10-GB-071	1.7
NSF-036-10-GB-072	<MDL
NSF-036-10-GB-073	966000
NSF-036-10-GB-075	21
NSF-036-10-GB-076	98
NSF-036-10-GB-077	<MDL
NSF-036-10-GB-078	37
NSF-036-10-GB-079	1.2
NSF-036-10-GB-080	2.1
NSF-036-10-GB-082	7602
NSF-036-10-GB-083	53
NSF-036-10-GB-084	110
NSF-036-10-GB-085	66
NSF-036-10-GB-086	23300
NSF-036-10-GB-087	1180
NSF-036-10-GB-088	630
NSF-036-10-GB-089	31
NSF-036-10-GB-090	310
NSF-036-10-GB-091	20
NSF-036-10-GB-092	19



## 9B. CHEMICAL DISPERSION: SUBSURFACE APPLICATION

Measurement of subsurface operation was, at best, highly indirect. The most directly applicable was a published study by Camilli et al. (2010), who reported results from a subsurface hydrocarbon survey using an autonomous underwater vehicles and a ship-cabled sampler. Using BTEX results as an indicator of oil concentration, they concluded that an observed plume of oil at approximately 1100 m. depth represented about 6-7% of the oil leaking from the wellhead. The plume location was consistent with the expected location of subsurface dispersed oil based upon the Clarkson well blowout model (Latimer and Zheng, 2003).

Most of the experts believed that the conditions subsurface were good for dispersant operations. It is likely that all five of the conditions listed by Clayton et al (1993) were generally met. However, the addition of dispersant at 7 to 12 gallons / minute through a narrow diameter wand held by a ROV into the flow of escaping oil and gas would probably not have added dispersant to all of the oil; some oil would have escaped into the water column untreated with any dispersant. Without carrying out some experimentation, it is not possible to say what proportion of the escaping oil would and would not have been treated with dispersant. Also, using the estimated flow rate shown on Figure 3 and the data available on the daily rate of dispersant applications, the dosage of chemical dispersant (DOR) for subsurface application varies from 1:1200 to 1:92; 19% of the time (13 days) the DOR was less than 1:250, 34% of the time (23 days) it was between 1:150 and 1:250 and 43 % of the time (29 days) it was between 1:150 and 1:100. Yet, laboratory studies show that COREXIT 9500 is effective on this type of oil and there was more than sufficient turbulent energy.

The Oil Budget Calculator originally used a very conservative estimate for subsurface dispersant operations. The ITOPF Technical Information Paper for “The use of Chemical Dispersants to Treat Oil Spills” (<http://www.itopf.com>) recommends for planning purposes the use of 1 part dispersant for 20 parts oil as the dosage rate. They point out that spraying equipment is often preconfigured to achieve this. Some laboratory studies also support this number (Fingas et al. 1995; Khelifa and So, 2009).

Some experts were concerned that the entrained gas would reduce the effectiveness of the dispersant application by preventing contact between oil and surfactant. They also thought that the time of contact might be insufficient to achieve optimum effect. Their concerns are captured in the choice for minimum effectiveness. However, other experts believe that a 1:20 effectiveness ratio greatly underestimated that actual amount of oil dispersed. They point to successful applications in the North Sea, producing a larger ratio of dispersed oil to surfactant applied. Ratios as large as DOR 1:100 were suggested. One of the experts was concerned about hydrate interference with dispersant application.

Failing to achieve common agreement of the experts, the new calculator uses a compromise estimate of a DOR of 1:40 with a low estimate of 1:20 and high estimate of 1:90.



## 10. BURNING

---

Burning *in-situ* was extensively used during the Deepwater Horizon Spill. Environmental conditions, location of the incident and the nature of the oil made this possible. Oil was gathered into areas enclosed with special booms and set afire.

For ignition to occur with most oils, the oil film must generally be greater than 2 to 3 mm. Ignition will depend upon the water content of the oil, emulsions of 20 to 25 % or more typically being very difficult to ignite. Since free-floating oil slicks are typically on the order of a tenth of a mm or less, most oil spills need to be contained in special fire-resistant booms. High winds and waves (typically in excess of 1 m short-period, wind waves) may prevent burn operations because of the difficulty of preventing entrainment and splash over within the fire boom, and, because of the difficulty of achieving an initial ignition. Most relatively fresh crude oils (even emulsions of 15% to 20% water) may burn with a “thickness-reduction” or “regression” rate of approximately 0.05 mm/sec, slightly more than a tenth of an inch per minute (ASTM, 2003). This represents an oil elimination rate of approximately 0.07 gpm/sq.ft. Higher water contents of approximately 25% to 40%, though very difficult to ignite, may burn at rates of approximately 0.05 gpm/sq.ft. During the burning of oil or emulsions on water, part of the oil is turned into smoke. The actual percentage depends upon the size of the burn and other factors, but usually is in the range of only 5% to 15% of the original volume of oil burned. With typically less than 5 % of the original volume remaining as burn residue, the controlled elimination of spilled oil through combustion is recognized as a highly efficient response option. The burn rates used during the Deepwater Horizon incident range from 0.07 gpm/sq.ft (representing lightly emulsified oils) to 0.05 gpm/sq.ft for burns that may have involved more highly emulsified oils. These oil elimination rates are in line with ASTM standards, and most burns were carried out on emulsions with relatively low water content and along convergence lines where unstable emulsions and wind-herded films had accumulated as dark brown to black oil layers. Daily estimates of the volume of oil burned were recorded as minimum and maximum values reflecting these oil elimination rates. The results were calculated throughout the Deepwater Horizon incident using surface and aerial observations that included the size and duration of each burn. Nearly all burns involved 500-ft-long booms towed in a U-configuration, while attempting to maintain a “gap ratio” (i.e., swath-to-boom-length ratio) of ~ 0.3. A single fire boom could therefore hold 500 to 1000 bbl of oil in its apex, the downstream area only ~1/3 of the way toward the leading ends of the boom. A single burn could often eliminate its contents within an hour or less. Field crews concluded that some surface slicks must have been in the range of 2.5 mm to 5 mm to achieve some of the larger burns. This represents a very thick oil emulsion layer.



Figure 11 illustrates the minimum and maximum daily oil elimination rates based upon the burn rates described above. It should be noted that the percentage of burned oil reported by the Calculator applies to all the oil released by the well. If one computes burning share based only upon the volume of available surface oil, the fraction burned is much larger, representing a significant portion of the surface oil. The Oil Budget Calculator uses the range of reported burn values depicted in Figure 11 in its calculations. The uncertainty range for the amount of burned oil is small compared to the other processes discussed in this report.

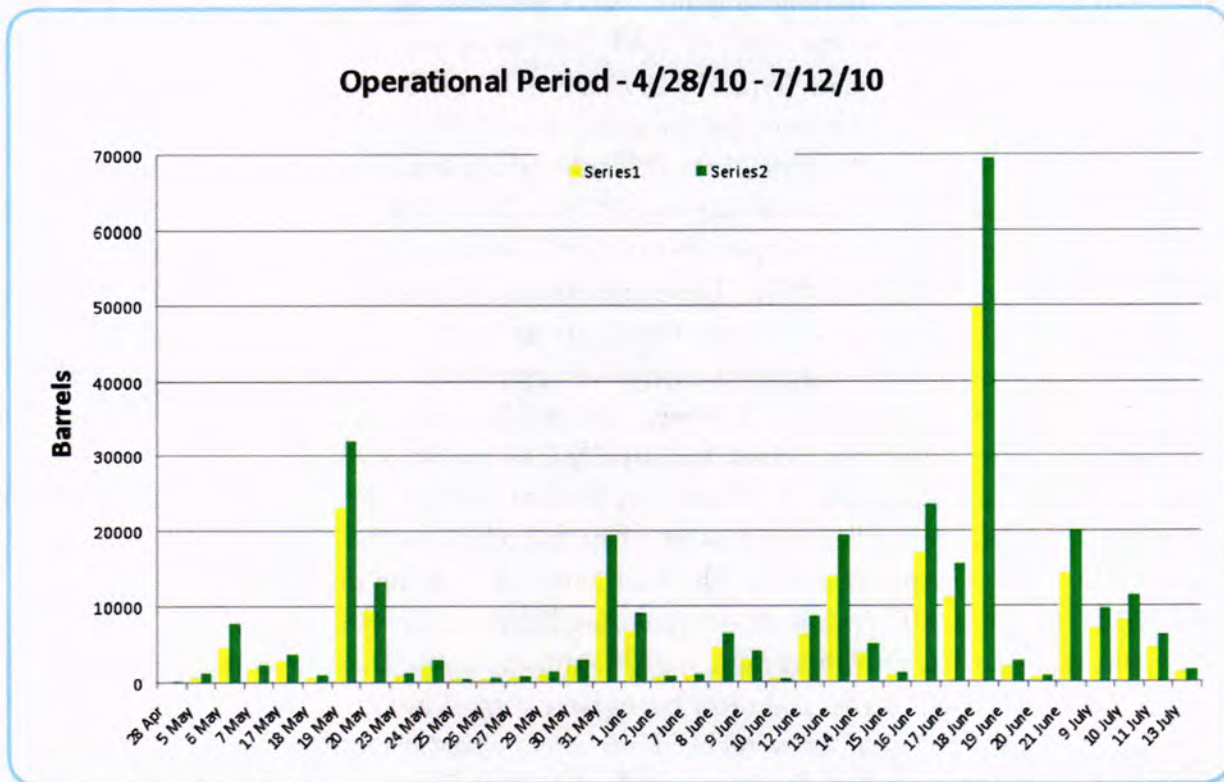


Figure 11: *In situ* burn history for Deepwater Horizon Spill



## 11. MECHANICAL RECOVERY

---

Skimmers were the most commonly used mechanical devices use to remove oil from the Gulf water surface. These skimmers varied greatly in size, application, and capacity, as well as in recovery efficiency and water pickup (Schulze, 1993; Schwartz, 1979). In the particular case of the Gulf oil spill the major issue was the amount of water recovered with the skimmed oil. Rather than estimate oil-water ratios, simple measurements of the barge oil would seem the rational way to determine this amount. However, to date, no such measurements are available. Therefore it was necessary to estimate skimmer performance based upon sea conditions, nature of the oil, and past experience.

A skimmer's performance is affected by a number of factors including the thickness of the oil being recovered, the extent of weathering and emulsification of the oil, the presence of debris, and weather conditions at the time of recovery operations. A skimmer's overall performance is usually determined by a combination of its recovery rate and the percentage of oil recovered. The maximum amount of oil that a skimmer could recover is called the 'Nameplate Recovery Rate' and is typically provided by the manufacturer of a skimmer (Fingas, 2010; Meyer et al, 2009). A similar definition is the 'Effective Daily Recovery Capacity', which is the amount that a skimmer could recover in daylight hours under ideal conditions. The recovery rate is the volume of oil recovered under specific conditions. It is measured as volume per unit of time and is usually given as a range. If a skimmer takes in a lot of water, it is detrimental to the overall efficiency of an oil spill recovery operation.

Skimmer performance is chiefly the product of three parameters. The Oil Recovery Rate (ORR) is the quantitative rate in volume per unit time, usually  $\text{m}^3/\text{hour}$  and is corrected for water recovery. The throughput efficiency (TE) is applicable only to advancing skimmers. The throughput efficiency is the percentage of oil presented to a skimmer versus that recovered, in percent. The recovery efficiency (RE) is the percent of oil recovered out of the total oil and water recovered. For the Gulf recovery effort, the RE is the most important factor. We know the total liquids recovered, but we do not know exactly how much oil was in this liquid and therefore must estimate the actual oil recovered. Past studies show that the average RE of the skimmers in wave conditions is 33%.

The measured water content of skimmed emulsions varied. An estimate of the actual recovered oil would be a product of the average RE times the oil content of the emulsion. The Calculator assumes that 20% of the skimmed liquid was oil, with a range between 10% and 40%. These are conservative estimates in line with the philosophy behind the Calculator. They are also considered temporary numbers, pending any measurement results.



## 12. OTHER OIL

---

The Oil Budget Calculator does not quantify the amount of oil volume that becomes tar balls, forms surface slicks, sinks due to sedimentation, remains in the surf zone or impacts the shore and is subsequently cleaned up. These are instead grouped together as 'other oil'.

The amount of oil listed as 'other' is quite large. Obviously, there are no longer large surface slicks in the Gulf of Mexico. So where is this oil? Some obviously did impact the coastline, particularly the Louisiana coastline. Cleanup operations recorded the volume of oil debris that was recovered during shoreline cleanup. However, no estimates were made of the percentage of oil in this debris so it is not possible to give a reliable estimate of this amount. Based upon past spills, the oil content of collected debris mass is only a few percent. Some of the oil may have aggregated with sediment in the water column and settled to the sea bottom. The Oil Budget Calculator does not estimate sedimentation.

Much of this oil probably formed tarballs or millimeter scale oil droplets since the conditions of this spill were conducive to such tarball/droplet formation (turbulent subsurface release, large use of dispersant on weak emulsions, etc). The larger tarballs are very persistent in the marine environment and can travel hundreds of miles, sometimes re-concentrating in convergence zones far from the original spill site. Some limited efforts were made to collect and quantify the larger tar ball mass density in the nearshore areas but the available data was insufficient to make a global estimate. The smaller oil droplets behave in some respects almost as dispersed oil and are similarly subject to biodegradation, dissolution, and sedimentation.



### 13. LONGER-TERM PROCESSES

---

While not tracked by the Oil Budget Calculator, there are other processes that work to break down the spilled oil. Two important ones for the Gulf of Mexico are photo-oxidation and biodegradation.

The combination of hydrocarbons with oxygen is called oxidation. The newly formed oxidized compounds may affect the oil slick by increasing dissolution, dispersion or emulsification. While trace metals in the oil may influence the oxidation process, ultraviolet light significantly increases oxidation. Virtually all of the molecules that evaporate from the slick undergo photochemical oxidation in hours or days. Also, beached oil will show the effects of exposure to sunlight. Even floating oil can show chemical changes due to this process. Overton (1981) exposed IXTOC I crude oil to sunlight and discovered the formation of tarry flakes, showing the involvement of photolysis. Observers at the *Mega Borg* spill in the Gulf of Mexico noticed the formation of crusts on floating tarmats and tar balls, with the hypothesis that this was due to photo-oxidation.

Hydrocarbons, including those found in oil slicks, are a food source for many microorganisms. The rate of such biodegradation depends upon the availability of nitrogen- and phosphorus-containing nutrients in the water, as well as the surface exposure of the oil to the organisms. Swannel and Daniel (1999) suggest that dispersant use on a slick may speed up biodegradation by promoting the growth of indigenous, hydrocarbon-degrading bacteria as well as increasing the surface area of the oil available for microbial colonization.

Bacteria capable of degrading various groups of petroleum hydrocarbons have been found in all oceans and in deep as well as shallow water. Research on biodegradation has occurred with many types of oils and fuels, at temperatures ranging from -1C (polar) to over 30 C (hot, tropical), and at natural oil seeps. Tools for documenting biodegradation rates include microbial taxonomy and abundance, nutrient uptake, oxygen utilization and mass loss.

The Deepwater Horizon blowout resulted in petroleum hydrocarbon contamination on sand beaches and marshes, at the sea surface, in the warm (30-35C) upper water column adjacent to dispersant operations, and in cold (4.5 to 5C) water at 1100 to 1300 m deep. Available results to date have been reported from surveys conducted in May and June, 2010, and focused on indicators of biodegradation in the contaminated deepwater layers (Camilli et al., 2010 and Hazen et al, 2010).



Camilli et al (2010) reported presence of sub-surface volatile hydrocarbons and also only slight reductions of oxygen at depth and suggested biodegradation rates were low potentially resulting in many months of hydrocarbon persistence. Hazen et al (2010) reported that the dispersed hydrocarbons in deep water originating from the Deepwater Horizon blowout source stimulated deep-sea indigenous  $\gamma$ -proteobacteria that are closely related to known petroleum-degraders. Hydrocarbon-degrading genes coincided with the concentration of various oil contaminants, namely alkanes. Changes in hydrocarbon composition with distance from the source and incubation experiments with environmental isolates demonstrated faster than expected hydrocarbon biodegradation rates at 5°C. The half-life degradation rates ranged from about 2 to 6 days, depending on the alkane. Based on these results, Hazen et al (2010) concluded that the potential exists for intrinsic bioremediation of the petroleum hydrocarbons in the deep-water column without substantial oxygen drawdown.

Other studies unrelated to this incident have reported a wide range of hydrocarbon degradation rates depending on all the variables indicated above. The Hazen et al (2010) rates are not inconsistent with those published by Venosa and Holder (2007) for cold water using dispersed Alaska North slope crude oil.

Past biodegradation research has focused on marine waters of moderate to warm temperatures, including oil-contaminated sediment interstitial waters of beaches and marshes as well as dispersed/dissolved hydrocarbons. Going back into history, Walker and Colwell (1977) measured the loss of mass South Louisiana crude oil during replicated in situ incubation field experiments in a North Carolina estuary at 30°C. The mean mass of 365 mg of oil was reduced to 235 mg in one week (35% reduction), 178.5 mg in 2 weeks (51.1 percent reduction), 11.2 mg in 3 weeks (97.0 per cent reduction) and 8.8 mg in 4 weeks (97.6 per cent), yielding a half life of about 2 weeks (14 days). Bacteria counts reached maximum in 3 weeks then started to decline. Presumably, the initial loss of mass was due to evaporation of more volatile components whereas the later stages were the result of biodegradation. These simple rate results fall somewhere between the predictions of Camilli et al (2010) and Hazen et al (2010).

Since the 1970's, there has been a considerable amount of field, mesocosm, and laboratory work done. The rates resulting from these studies also range widely depending on oil types, oil weathering, dispersion effectiveness, dispersant composition, nutrient loadings, and especially which target petroleum compounds or groups of compounds each research team analyzed. The National Research Council (NRC, 2005) reviewed much of the work done on biodegradation of dispersed oil concluding that most of the work has not been consistently



standardized sufficient to confidently extrapolate from the laboratory to the field. Further, there is a paucity of work on degradation of higher molecular weight polycyclic aromatic hydrocarbons, the most toxic compounds. Field studies in contaminated marshes and beach sediments, have demonstrated a wide range of biodegradation rates; oil biodegraded almost completely within a few weeks at some locations while it persisted for tens of years at other locations (Reddy et al., 2002; Short et al, 2004). Boufadel et al., (2010) noted low oxygen and nutrient concentration that might have prevented effective biodegradation of the Exxon Valdez oil spill. The study of Li and Boufadel (2010) highlighted that understanding beach hydraulics is a critical step in predicting the fate of oil within beaches. Therefore, we would expect this oil to undergo biodegradation at different rates in different compartments of the Gulf ecosystem



## 14. ASSESSMENT AND FUTURE PLANS

---

While pure scientific research can be done on oil spills, most oil spill science is applied science. Tools such as the Oil Budget Calculator are only useful if they provide information that will assist response decisions. Conversely, they need only be as accurate as the precision needed for these decisions. Improved accuracy beyond those levels may be important in the academic sense but not in the response area. Figures 12 and 13, below, show the output from the model, given the revisions described in this document. They vary somewhat from earlier calculations but probably not significantly according to the above criteria.

The estimates of the Calculator were admittedly rough for the reasons discussed in this report. However, the estimates were probably sufficient to meet the needs of the Response. Ultimately, of course, that judgment will be made by the NIC. The experience in developing the Calculator points to areas of needed future research and planning:

- (1) **Protocols for surface and subsurface sampling:** While oil samples were collected for impact assessment, few samples were properly collected and categorized for response. For example, samples often came from skimming barges, where oil in different states of degradation was blended together. Future response plans should specify methods for gathering proper representative samples.
- (2) **Dispersed oil droplet size:** A major improvement in estimating dispersant efficiency would be possible if practical operational tools and methods existed to characterize droplet size distribution of subsurface oil.
- (3) **Basic Models for Longer-term processes:** While longer-term processes such as biodegradation often happen outside the time frames of the response, understanding and being able to predict such longer-term changes may be useful in making response decisions.
- (4) **Estimation of collected shoreline oil:** For a complete mass balance, procedures should be implemented that estimate the fraction that is oil or oiled debris gathered from shoreline cleanup.
- (5) **Expanded modeling capabilities:** Many of the team members that assisted with the Oil Budget Calculator are also part of a working group of spill experts developing the specifications for the next generation of oil spill model. These specifications need to be translated into real code.
- (6) **Revised interface:** A better interface is necessary to more properly display the intrinsic uncertainty in the Calculator.



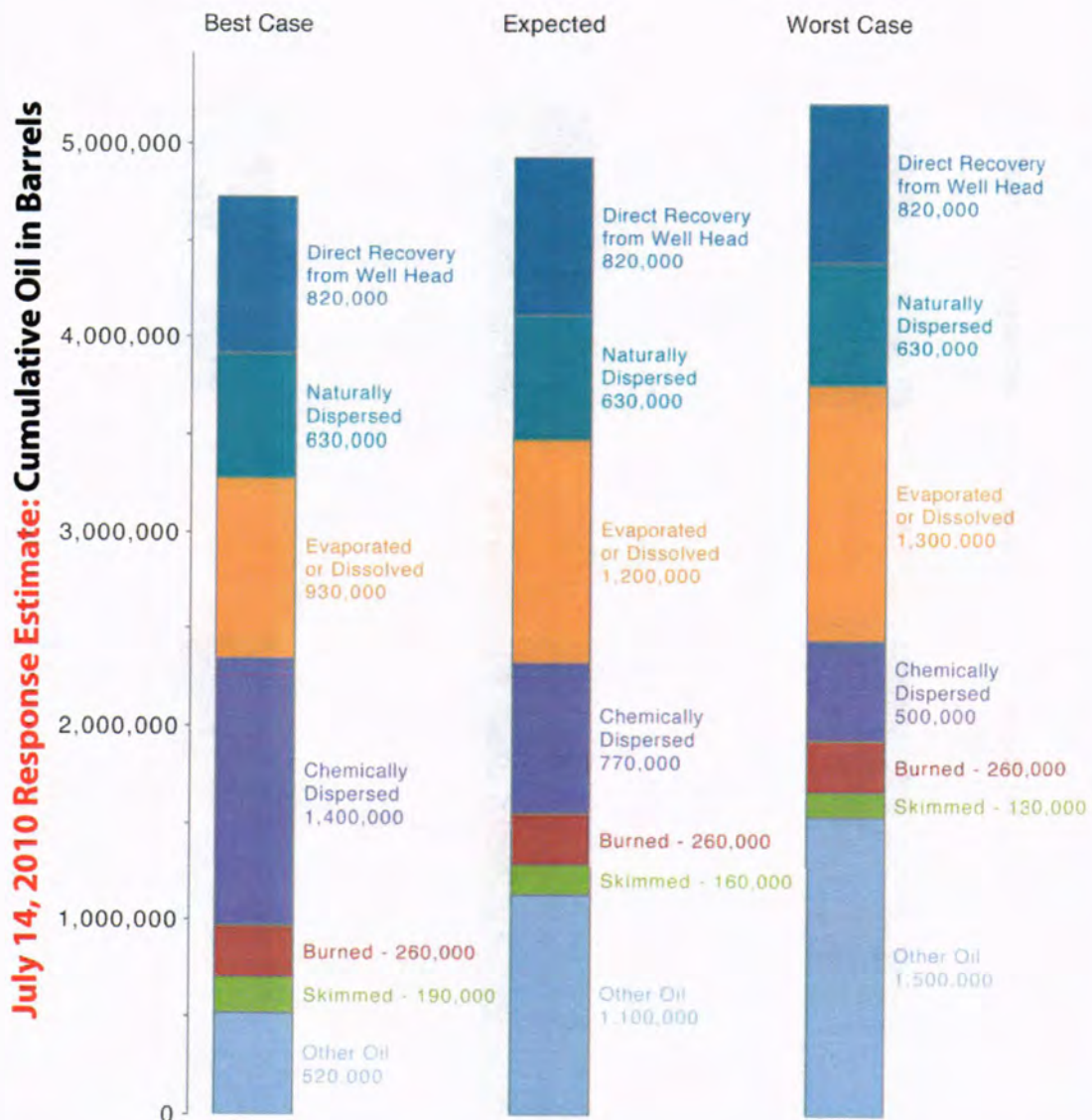


Figure 12: Response estimates produced by the Oil Budget Calculator showing best case, expected, and worst case volumes of the seven different portions that the calculator tracks individually, of the cumulative volume of oil discharged through July 14, 2010. These estimates served solely as a guide for the national response to the Deepwater Horizon MC252 Gulf Incident. The best and worst cases are defined in Appendix 1: they are the combinations of values of the seven variables depicted in each stack that correspond to the lower and upper endpoints of a 95% confidence interval for the volume of "Other Oil".



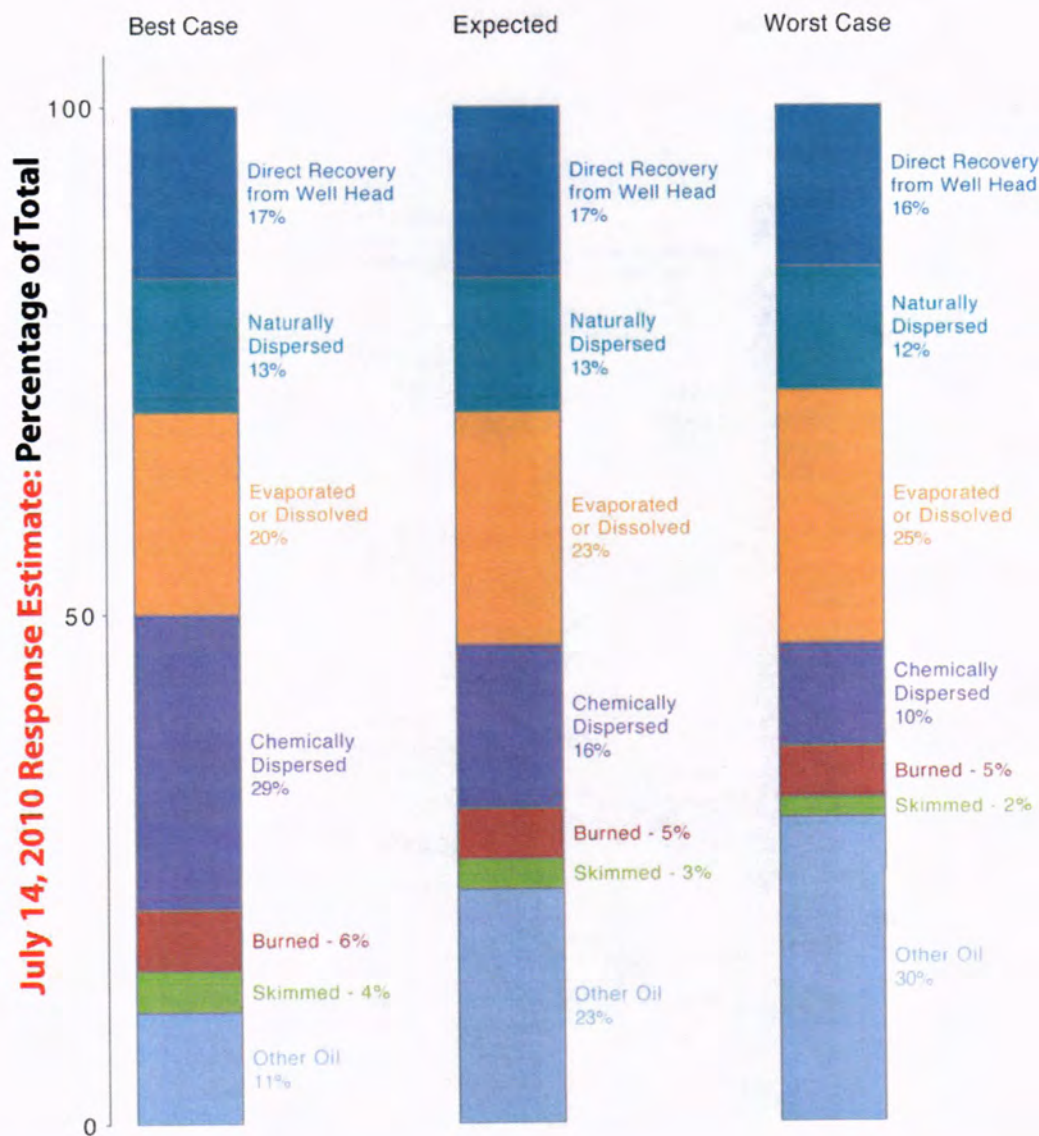


Figure 13: Response estimates expressed as percentages of the cumulative volume of oil discharged through July 14, 2010, in the best, expected, and worst cases. These estimates served solely as a guide for the national response to the Deepwater Horizon MC252 Gulf Incident.



## 15. REFERENCES

---

### 15A. WORKS CITED

---

- ASTM (2003) F 1788 – 97, Reapproved 2003, Standard Guide for In-Situ Burning of Oil Spills on Water: Environmental and Operational Considerations, 6 pp.
- Boufadel, M. C.; Sharifi, Y.; Van Aken, B.; Wrenn, B.A. and Lee, K. (2010) . “Nutrient and oxygen concentrations within the sediments of an Alaskan beach polluted with the Exxon Valdez oil spill”. Environmental Science and Technology, in press.
- Camilli, R.; Reddy, C.M.; et al. (2010). “Tracking Hydrocarbon Plume Transport and Biodegradation at Deepwater Horizon”. Scienceexpress, 19 Aug. 2010. 10.1126/science.1195223.
- Caneveri, G.P.; Bock, J; Robbins, M. (1989). “Improved Dispersant Based on Microemulsion Technology”. In: Proc. 1989 International Oil Spill Conf., American Petroleum Institute, Washington, DC. pp. 317-320
- Chen, F.H.; Yapa, P.D. (2003). “A Model for Simulating Deepwater Oil and Gas Blowouts - Part II : Comparison of Numerical Simulations with “Deepspill” Field Experiments”. *Journal of Hydraulic Research*, IAHR, August, 41(4), 353-365.
- Chen, F.H. and Yapa, P.D. (2004). “Modeling Gas Separation from a Bent Deepwater Oil and Gas Jet/Plume”. *Journal of Marine Systems*, Elsevier, the Netherlands, Vol 45 (3-4), 189-203.
- Clark, R.N.; Swayze, G.A.; Leifer, I.; et al. (2010). “A method for quantitative mapping of thick oil spills using imaging spectroscopy”. U.S. Geological Survey Open-File Report 2010–1167, p. 51.
- Clayton, J.; Payne, J.; Farlow, J; Sarwar, C. (1993). Oil Spill Dispersants, Mechanisms of Action and Laboratory Tests. CRC Press, Boca Raton, Fl., pp 113.
- Delvigne, G. A. L.; Sweeney, C.E. (1988). “Natural Dispersion of Oil”. Oil and Chemical Pollution Vol 4, Issue 4, pp 281-310.



Fingas, M.F., (2010). "Weather Effects on Oil Spill Countermeasures". Chapter 13 in Oil Spill Science and Technology, p. 339-426.

Fingas, M.F., D. Kyle and E. Tennyson, Dispersant Effectiveness: Studies into the causes of Effectiveness Variations, in The Use of Chemicals in Oil Spill Response, ASTM STP 1252, 1995, p.92-134.

French, D.; Reed, M.; Jayko, K.; et al. (1996). The CERCLA type A natural resource damage assessment model for coastal and marine environments (NRDAM/CME), Technical Documentation, Vol. I - V. Final Report, submitted to the Office of Environmental Policy and Compliance, U.S. Dept. of the Interior, Washington, DC, April, 1996; Available from National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161, PB96-501788.

Friehe, C. A.; Van Atta, C. W.; Gibson, C. H. (1972). "Jet turbulence: Dissipation rate measurements and correlations". In Turbulent Shear Flows, AGARD Conference Proceedings, vol. 93, p. 18-1.

Galt, J. (2010) personal communication to B. Lehr

Gemmrich, J., (2010). "Strong Turbulence in the Wave Crest Region". Journal of Physical Oceanography, Vol. 40, pp. 583-595.

Gemmrich, J.; Farmer, D.M., (2004). "Near-Surface Turbulence in the Presence of Breaking Waves". Journal of Physical Oceanography, Vol. 34, pp. 1067-1086.

Gibson, M. M. (1963). "Spectra of turbulence in a round jet". Journal of Fluid Mechanics, Vol 15, Issue 2, pp. 161-173.

Hazen, T.C.; Dubinsky, E.A.; DeSantis, T.Z.; et al. (2010). "Deep-sea Oil Plume Enriches Indigenous Oil-Degrading Bacteria". Scienceexpress, 24 Aug., 2010, 10.1126/science.1195223.

Jernelov, A.; Linden, O. (1981). Ixtoc I: A Case Study of the World's Largest Oil Spill. Ambio, Vol 10, No. 6, pp. 299-306.



- Johansen, O., et al. (2001), Deep Spill JIP Experimental Discharges of Gas and Oil at Helland Hansen, Parts I, II, and III – Technical Report, SINTEF Applied Chemistry, Norway.
- Jones, R. K. (1997). "A simplified pseudo-component oil evaporation model". In Proceedings of the 20th Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, Canada, Environment Canada. Pp.43-61.
- Kaku, V. J.; Boufadel, M.C.; Venosa, A.D. (2006). "Evaluation of mixing energy in laboratory flasks used for dispersant effectiveness testing". *Journal of Environmental Engineering*, ASCE 132(1): 93-101, 2006.
- Khelifa A.; So, L.L.C., (2009). "Effects of Chemical Dispersants on Oil Brine Interfacial Tension and Droplet Formation". In Proceedings of the Thirty-second Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, Environment Canada, Ottawa, Ontario, Vol. 1, pp. 383-396.
- Lasheras J. (2010) personal communication to B. Lehr
- Latimer, J.S.; Zheng, J. (2003). The sources, transport and fate of PAHs in the marine environment. In: Douben P.E.T. (Ed.). *PAHs: an ecotoxicological perspective*. John Wiley & sons Ltd., New York, USA. pp.10-22.
- Lehr, W (2001). "Review of the modeling procedures for oil spill weathering behavior, in Oil Spill Modelling and Processes". C.A. Brebbia (ed), WIT, Press, Southampton, U.K.
- 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.
- Leirvik, F.; Daling, P.; et al. (2010). "Assessment of dispersibility of DWH oil at different stages of weathering". SINTEF Marine Environmental Technology.
- Lewis, A. (2010) Estimated Effectiveness of Dispersant Use at the Deepwater Horizon Incident. Unpublished report, 31pp.



- Li, M.; Garret, C. (1998). "The relationship between oil droplet size and upper ocean turbulence". *Marine Pollution Bulletin*, Vol. 36, pp. 961-970.
- Li, H.; Boufadel, M.C. (2010). "Long-term persistence of oil from the Exxon Valdez spill in two-layer beaches". *NATURE geosciences*, Vol 3, pp. 96-99.
- Linton & Koons (1983). Oil Dispersant Field Evaluation IXTOC I Blowout, Bay of Campeche, Mexico. *Oil & Petrochemical Pollution*, Vol.1, No. 3. Graham & Trotman Ltd. Vol 1. pp 183-188
- MacKay, D.; Leinonen, P. (1975). "Mathematical model of the behavior of oil spills on water with natural and chemical dispersion". Report No EPS-3-EC-77-19, Environment Protection Service: Ottawa, Canada 84 pp.
- Mackay, D.; P. J. Leinonen. 1977. "Mathematical Model of the Behavior of Oil Spills On Water with Natural and Chemical Dispersion". Prepared for Fisheries and Environment Canada, Economic and Technical Review Report EPS-3-EC-77-19.
- Mackay D.; Shiu W. Y. (1975). "Determination of the solubility of hydrocarbons in aqueous sodium chloride solutions". *The Canadian Journal of Chemical Engineering*. Vol. 53, pp. 239-242.
- Martinez-Baz\_an, C.; Montanes, J.L.; Lasheras, J.C. (1999). "On the breakup of an air bubble injected into a fully developed turbulent flow. Part I: Breakup frequency". *Journal of Fluid Mechanics*, Vol. 401, pp. 157-182.
- Masutani, S., and E. E. Adams (2000), *Experimental study of multi-phase plumes with application to deep ocean oil spills*, 147 pp, Virginia.
- McAuliffe, C.D. (1987). "Organism exposure to volatile/soluble hydrocarbons from crude oil spills – a field and laboratory comparison". In *Proceedings of the 1987 Oil Spill conference (IOSC)*. American Petroleum Institute, Washington, DC. Pp 275-288.
- Melbye, A.G., Johansen, Ø., Resby, J.L.M., Moldestad, M.Ø., (1999). *Development of methodology for studying natural dispersion and emulsification of thin oil films*. SINTEF Report No. STF66 F99136. p. 32.



- Meyer P.; Schmidt, W.; Delgado, J.-E.; DeVitis, D.; et al. (2009). "Application of the American Society of Testing and Materials' (ASTM) New Skimmer Test Protocol". Arctic and Marine Oil Spill Program (AMOP) Technical Seminar Vol. 323.
- National Research Council (1989) Using Oil Spill Dispersants in the Sea, National Academy Press, Washington DC, 335 pp.
- National Research Council (2003), Oil in the Sea III: Inputs, Fates, and Effect, National Academies Press, Washington, D.C.
- National Research Council (2005). Oil Spill Dispersants: Efficacy and Effects. Washington, D.C.: National Academies Press. 377p. ISBN:030909562X
- Overton, E. (1981). "Chemical characterization and fate of the oil". In Hooper, C.H. (ed). pp. 75-84.
- Payne, J. R.; Kirstein, B.E.; et al. (1984). "Multivariate Analysis of Petroleum Weathering in the Marine Environment - sub Arctic". OCSEAP Final Reports. NOAA, U.S Department of Commerce, and U.S. Department of Interior, Mineral Management Service, Vol. 21.
- Plume Calculation Team, *Deepwater Horizon Release, Estimate of Rate by PIV*, Report to the FRTG, 215 pp. July, 2010.
- Reddy, C. M.; et al. (2002). "The West Falmouth oil spill after thirty years: The persistence of petroleum hydrocarbons in marsh sediments". *Environmental Science Technology*. Vol 36, 4754-4760.
- Reed, M., I. Singsaas, et al. (2001). "Modeling the water-accomodated fraction in OSCAR2000". In Proceedings of the 2001 International Oil Spill Conference (IOSC). Tampa, Florida.
- Reed, M.; Oistein, J.; Brandvik, P., et al (1999). "Oil Spill Modeling towards the Close of the 20<sup>th</sup> Century: Overview of the State of the Art". *Spill Science & Technology Bulletin*, Vol 5. Issue1. April 1999, pp 3-16.



- Rehder, G., et al. (2009), Controls on methane bubble dissolution inside and outside the hydrate stability field from open ocean field experiments and numerical modeling, *Mar. Chem.*, 114(1/2), 19-30.
- S.L. Ross Environmental Research Ltd. (2010). Spill Related Properties of MC 252 Crude Oil, Sample ENT-052210-178.
- Schulze, R., (1998). Oil Spill Response Performance Review of Skimmers, ASTM Manual Series, ASTM.
- Schwartz, S.H., (1979). "Performance Tests of Four Selected Oil Spill Skimmers". Arctic and Marine Oil Spill Program (AMOP) Technical Seminar. Vol 493.
- Short, J. W.; et al. (2004). "Estimate of oil persisting on the beaches of Prince William Sound 12 years after the Exxon Valdez oil spill". *Environmental Science Technology*, Vol. 38, pp. 19-25.
- Spaulding, M.; Bishnoi, P.; Anderson, E.; Isaji, T. (2000). "An Integrated Model for Prediction of Oil Transport from a Deep Water Blowout". Twenty-third Arctic Marine Oil Spill Program (AMOP) Technical Seminar , 611-635, Environment Canada, Ottawa.
- Swannel, R.P.J.; Daniel, F. (1999). "Effect of dispersants on oil biodegradation under simulated marine conditions". In Proceedings, 1999 International Oil Spill Conference (IOSC). American Petroleum Institute, Wash. DC.
- The IXTOC I Oil Spill: The Federal Response. NOAA Hazardous Materials Response Project, Boulder, Colorado. 202 pp.
- United States Coast Guard (USCG), National Oceanic and Atmospheric Administration (NOAA), United States Environmental Protection Agency (USEPA), Centers for Disease Control and Prevention (CDC), United States Minerals Management Service (USMMS), SMART - Special Monitoring of Applied Response Technologies, Report [http://response.restoration.noaa.gov/book\\_shelf/648\\_SMART.pdf](http://response.restoration.noaa.gov/book_shelf/648_SMART.pdf), 2006, 46 p.
- Venosa, A.D; Holder, E.L. (2007). "Biodegradability of dispersed crude oil at two different temperatures". *Marine Pollution Bulletin*. Vol. 54, 545 (May, 2007).



Walker, J.D.; Colwell, R.R. (1977). "Sampling device for monitoring biodegradation of oil and other pollutants in aquatic environments". *Environmental Science and Technology*, Vol. 11(1), pp. 93-95.

Wickley-Olsen E.; Boufadel, M.C.; King, T.; et al. (2007). "Evaluation of the energy dissipation rates in regular and breaking waves in a wave tank". In *Proceedings of the Arctic and Marine Oil Spill (AMOP)*, Edmonton Alberta, Canada, June 04-07, 2007.

Woods Hole Oceanographic Institute (2010). *Woods Hole Oceanographic Institute Report to DOE/FRTG*, July 2010.

Yapa, P. D., Dasanayaka, L. K., Bandara, U. C., and Nakata, K. (2010). "A Model to Simulate the Transport and Fate of Gas and Hydrates Released in Deepwater, *Journal of Hydraulic Research, IAHR*. (accepted for publication)

## 15B. ADDITIONAL KEY REFERENCES

---

Belore, R. (2003). "Large wave tank dispersant effectiveness testing in cold water". *International Oil Spill Conference; Prevention, Preparedness, Response and Restoration, Perspectives for a Cleaner Environment: April 6-11, 2003, Vancouver, British Columbia, Canada*, pp 381-385.

Belore, R.C.; Trudel, B.K.; Lee, K. (2005). "Correlating wave tank dispersant effectiveness tests with at-sea trials". *International Oil Spill Conference; Prevention, Preparedness, Response, and Restoration: May 15-19, 2005, Miami Beach Convention Center, Miami Beach, Florida*, pp 65-70.

Brandvik, P.; Daling, P.S.; Lewis, A.; Lunel, T. (1995). "Measurements of dispersed oil concentrations by *in-situ* UV fluorescence during the Norwegian experimental oil spill with Sture blend". In *Proceedings, Eighteenth Arctic Marine Oil Spill Program Technical Seminar, June 14-16, 1995, West Edmonton Mall Hotel, Edmonton, Alberta, Canada. Ottawa, Ont.: Environment Canada*. pp. 519-535.

Brutsaert, W. (1982). Evaporation into the Atmosphere: Theory, History, and Applications. Dordrecht, D. Reidel Publishing Company.



- Colcomb, K.; Salt, D.; Peddar, M.; Lewis, A. (2005). "Determination of the limiting oil viscosity for chemical dispersion at sea". *In* 2005 International Oil Spill Conference; Prevention, Preparedness, Response, and Restoration: May 15-19, 2005, Miami Beach Convention Center, Miami Beach, Florida. Washington, D.C.: American Petroleum Institute. pp. 53-58.
- Daling, P.S.; Brandvik, P.J.; Reed, M. (1998). "Dispersant experience in Norway: dispersant effectiveness, monitoring, and fate of dispersed oil". *In* Dispersant Application in Alaska: A Technical Update, Anchorage Hilton Hotel, Anchorage, Alaska, March 18 and 19, 1998. Cordova, Ak.: Prince William Sound Oil Spill Recovery Institute. pp. 111-146.
- Fiocco, R.J.; Daling, P.S.; DeMarco, G.; Lessard, R.R. (1999). "Advancing laboratory/field dispersant effectiveness testing". *In* Beyond 2000, Balancing Perspectives: Proceedings: 1999 International Oil Spill Conference: March 8-11, 1999, Seattle, Washington. Washington, D.C.: American Petroleum Institute. pp. 177-185.
- Lehr, W.; Jones, R.; Evans, M.; et al. (2002). "Revisions of the ADIOS Oil Spill Model", *Environmental Modeling & Software*, Vol 17, Issue 2, pp. 191-199.
- Lewis A.; Crosbie, A.; Davies, L.; Lunel, T. (1998). "Large scale field experiments into oil weathering at sea and aerial application of dispersants". *In* Proceedings: Twenty-First Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, June 10 to 12, 1998, West Edmonton Mall Hotel, Edmonton, Alberta, Canada. Ottawa, Ont.: Environment Canada. pp. 319-344.
- Lewis A.; Crosbie, A.; Davies, L.; Lunel, T. (1998b). "Dispersion of emulsified oil at sea". AEA Technology report. AEAT-3475. AEA Technology, National Environmental Technology Centre (NETCEN, Didcot, Oxfordshire, England.
- Li, Z., Lee, K., King, T., Boufadel, M. C., and Venosa, A. D. (2009a). "Evaluating Chemical Dispersant Efficacy in an Experimental Wave Tank: 2, Significant Factors Determining In Situ Oil Droplet Size Distribution." *Environmental Engineering Science*, 26(9), 1407-1418.



- Li, Z., Lee, K., King, T., Kepkay, P., Boufadel, M. C., and Venosa, A. D. (2009b). "Evaluating Chemical Dispersant Efficacy in an Experimental Wave Tank: 1, Dispersant Effectiveness as a Function of Energy Dissipation Rate." *Environmental Engineering Science*, 26(6), 1139-1148.
- Lunel, T.; Rusin, J.; Bailey, N.; Halliwell, C.; Davies, L. (1997). "The net environmental benefit of a successful dispersant operation at the *Sea Empress* incident". In Proceedings: 1997 International Oil Spill Conference: Improving Environmental Protection: Progress, Challenges, Responsibilities: April 7-10, 1997, Fort Lauderdale, Florida. Washington, D.C.: American Petroleum Institute. pp. 185-194.
- Lunel, T.; Lewis, A. (1999). "Optimization of oil spill dispersant use". In Beyond 2000, Balancing Perspectives: Proceedings: 1999 International Oil Spill Conference: March 8-11, 1999, Seattle, Washington. Washington, D.C.: American Petroleum Institute. pp. 187-193.
- Mackay, D.; Matsugu, R.M. (1973). "Evaporation rates of liquid hydrocarbon spills on land and water." *Canadian Journal of Chemical Engineering*, Vol. 51, pp. 434-439.



## APPENDICES

---

# Appendix 1

## A1 Uncertainty Assessment of Mass Balance Estimates

### A1.1 Introduction

We have developed and applied statistical methods to gauge the uncertainty associated with the estimates of the volumes of the principal fractions of the oil spilled from the Deepwater (Macondo) well that the Oil Budget Calculator tracks individually, in addition to the volume of oil that has been recovered via the Riser Insert Tube Tool (RITT) or via the Top Hat: (i) oil that has been naturally or chemically dispersed; (ii) oil that has evaporated or dissolved; (iii) oil in skimmed oily seawater; (iv) oil that has been burned; and (v) residual (or, other) oil that remains either on or below the sea surface, in other forms.

The uncertainty associated with the volume of each of these fractions includes contributions from the uncertainty of the eight rate constants in the mass balance equations that describe where the spilled oil will have gone.

Figure A1.1 on page A1.7 shows the result of the uncertainty analysis for the volume of residual oil, depicted as an uncertainty envelope, throughout the 86-day period from April 20 (explosion and fire on Deepwater Horizon platform) to July 14, 2010 (last day with discharge from the well). The lower bound of this envelope corresponds to a best-case scenario, and the upper bound to a worst-case scenario. Section A1.8 describes the methods used to characterize these scenarios quantitatively, and Appendix 2 shows the corresponding results.

### A1.2 Input and Output Quantities

The quantities that we are primarily interested in, and whose values we track, are referred to as *output quantities*; and the quantities that these depend on (which are measured directly or indirectly, or that we have other prior knowledge of), are referred to as *input quantities*.

For example, the volume  $V_{DC}(t)$  of oil that was dispersed on day  $t$  by underwater application of a volume  $V_{CB}(t)$  of a chemical dispersant can be modeled as  $V_{DC}(t) = (1 - k_7) \min(90k_2V_{CB}(t), V_R(t) - V_{DT}(t))$ , where  $V_R(t)$  denotes the volume of oil discharged from the well, of which  $V_{DT}(t)$  will have been recovered via RITT/TopHat, and  $k_2$  and  $k_7$  denotes *rate constants*.

In this example,  $V_{DC}(t)$  plays the role of output quantity, and  $V_{CB}(t)$ ,  $V_R(t)$ ,  $V_{DT}(t)$ ,  $k_2$ , and  $k_7$  play the role of input quantities. Of the latter, only  $V_{CB}(t)$  and  $V_{DT}(t)$  were measured directly;  $V_R(t)$  was estimated by other teams in the Flow Rate Technical Group equation A1.1 on page A1.2;  $k_2$  and  $k_7$  are the results of assessments supplied by subject-matter experts.

The *mass balance equations* A1.1 on page A1.2–A1.16 on page A1.2 express relations between all the relevant quantities, and involve what we have been calling input and output quantities, as well as other quantities that we call intermediate quantities because they are used in the calculations but are not of primary interest for the purposes of the Oil Budget Calculator.



$$V_{\text{RE}}(t) = V_{\text{R}}(t) - V_{\text{DT}}(t) \quad (\text{A1.1})$$

$$X(t) = 90V_{\text{CB}}(t) \quad (\text{A1.2})$$

$$V_{\text{DC}}(t) = (1 - k_7) \min \{k_2 X(t), V_{\text{RE}}(t)\} \quad (\text{A1.3})$$

$$Y(t) = V_{\text{RE}}(t) - \frac{V_{\text{DC}}(t)}{1 - k_7} \quad (\text{A1.4})$$

$$V_{\text{DN}}(t) = (1 - k_7) \max \{0, k_1 Y(t)\} \quad (\text{A1.5})$$

$$V_{\text{DB}}(t) = V_{\text{DC}}(t) + V_{\text{DN}}(t) \quad (\text{A1.6})$$

$$V_{\text{NW}}(t) = k_6 V_{\text{OW}}(t) \quad (\text{A1.7})$$

$$Z(t) = V_{\text{RE}}(t) - \frac{V_{\text{DB}}(t)}{1 - k_7} \quad (\text{A1.8})$$

$$W(t) = \max \{0, (1 - k_4)Z(t) - V_{\text{BU}}(t)\} \quad (\text{A1.9})$$

$$V_{\text{E}}(t) = k_4 Z(t) + k_5 W(t - 1) + \frac{k_7}{1 - k_7} V_{\text{DB}}(t) \quad (\text{A1.10})$$

$$V_{\text{NS}}(t) = \max \{0, k_8 W(t)\} \quad (\text{A1.11})$$

$$V_{\text{DS}}(t) = \min \{20k_3 V_{\text{CS}}(t), V_{\text{S}}(t - 1)\} \quad (\text{A1.12})$$

$$V_{\text{D}}(t) = V_{\text{DB}}(t) + V_{\text{DS}}(t) + V_{\text{NS}}(t) \quad (\text{A1.13})$$

$$V_{\text{SD}}(t) = V_{\text{RE}}(t) - (V_{\text{E}}(t) + V_{\text{NW}}(t) + V_{\text{BU}}(t) + V_{\text{D}}(t)) \quad (\text{A1.14})$$

$$V_{\text{S}}(t) = V_{\text{SD}}(1) + \cdots + V_{\text{SD}}(t) \quad (\text{A1.15})$$

$$V_{\text{C}}(t) = V_{\text{DS}}(t) + V_{\text{DC}}(t) \quad (\text{A1.16})$$

The input, intermediate, and output quantities are listed in Table A1.1 on page A1.4. Typically, all of these quantities vary from day to day, and this dependence will be indicated explicitly when necessary, as in  $V_R(t)$ , for the volume of oil discharged on day number  $t$  (day 1 being April 20, 2010).

All volumes are assumed to be expressed in barrels of oil (bbl), with 1 bbl = 42 U.S. (liquid) gallons  $\approx$  159 L. The policy of the National Institute of Standards and Technology (NIST) is to use the International System of Units (metric units) in all publications. In this document, however, the units used traditionally in the oil industry are also used.

All of the output quantities have cumulative counterparts, except  $V_S(t)$ , which, by definition, already includes contributions from oil released on day  $t$  as well as residues of oil that will have been released on prior days but have not yet been recovered, evaporated or dissolved, burned, or dispersed (which in practice means dispersion into droplets of less than 70  $\mu\text{m}$  to 100  $\mu\text{m}$  in diameter).  $V_{SD}(t)$  is the contribution to the residual oil originating from oil spilled on day number  $t$ , and  $V_S(t)$  is the corresponding cumulative sum (from day number 1 through day number  $t$ ), as defined in equation A1.15 on page A1.2.

### A1.3 Uncertainty

The *Guide to the expression of uncertainty in measurement* (GUM) [Joint Committee for Guides in Metrology, 2008a], and its companion *International vocabulary of metrology* (VIM) [Joint Committee for Guides in Metrology, 2008c], are international standards that codify the meaning of “uncertainty” in the context of measurement science, and provide the technical basis whereon it may be gauged quantitatively, and interpreted in practice.

The VIM defines *measurement uncertainty* as a “non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used.” *Measurand* is the “quantity intended to be measured.” In our case, the volumes of the different fractions of the spilled oil, aforementioned, that the Oil Budget Calculator tracks separately, all are measurands.

Here, and in many other studies, the measurands are not accessible for direct measurement, and the corresponding measured values, or estimates of their values, are obtained by applying *measurement functions* [Joint Committee for Guides in Metrology, 2008c, 2.49] to values of other quantities that are either measured directly, or themselves are functions of yet other quantities that will have been measured directly, or about which there exists some prior information. In our case, these measurement functions are the mass balance equations.

The uncertainty analysis we describe in Section A1.7 on page A1.11, serves to propagate the measurement uncertainty associated with the input quantities to the output quantities of interest. Since the methods used to model the uncertainty of the input quantities are probabilistic, and the methods used to propagate their uncertainties to the output quantities are statistical, the end-product of such analysis typically is an interval that, with some specified probability (typically 95 %) includes the true, albeit unknown value, of the output quantity.

For example, we will conclude that the volume of residual oil on day number 86 (July 14,



INPUT QUANTITIES	
$V_{BU}$	Oil volume burned
$V_{CB}$	Dispersant volume sprayed, subsurface
$V_{CS}$	Dispersant volume sprayed, surface
$V_{DT}$	Oil volume recovered via RITT/TopHat
$V_{OW}$	Oily water volume recovered
$V_R$	Oil volume discharged
INTERMEDIATE QUANTITIES	
$V_D$	Oil volume dispersed, total
$V_{DB}$	Oil volume dispersed, subsurface
$V_{DC}$	Oil volume dispersed chemically, subsurface
$V_{DS}$	Oil volume dispersed chemically, surface
$V_{RE}$	Oil volume effectively discharged
$V_{SD}$	Oil volume contributed to residual, daily
$W$	Auxiliary variable
$X$	Auxiliary variable
$Y$	Auxiliary variable
$Z$	Auxiliary variable
OUTPUT QUANTITIES	
$V_{DN}$	Oil volume dispersed naturally, subsurface
$V_{NS}$	Oil volume dispersed naturally, surface
$V_C$	Oil volume dispersed chemically
$V_E$	Oil volume evaporated or dissolved
$V_{NW}$	Oil volume skimmed
$V_S$	Oil volume residual (or, other oil)

Table A1.1: **Input, intermediate, and output quantities.**

2010), will have been between 0.53 and 1.5 million barrels (Mbbl) of oil, with 95% probability (Appendix 2). This means that one is prepared to bet at odds of 19:1 in favor of the true value of such volume indeed lying in this interval. Noting that 1 bbl = 42 U.S. (liquid) gallons  $\approx$  159 L, that interval may equivalently be stated as  $22 \times 10^6$  U.S. gallons to  $63 \times 10^6$  U.S. gallons, or as  $84 \times 10^6$  L to  $240 \times 10^6$  L.

All the quantities in play here are affected by uncertainty. In the example above, it is not only the rate constants  $k_2$  and  $k_7$  that have associated uncertainty reflecting the imperfect knowledge that experts have about their values. The values of  $V_{CB}(t)$ ,  $V_R(t)$ , and  $V_{DT}(t)$  all include some measurement error that we express as uncertainty about their true values.

However, the only quantities whose associated measurement uncertainty has been characterized are  $V_R(t)$  (oil volume discharged) and  $V_{BU}$  (oil volume burned), and the rate constants  $k_1, \dots, k_8$ . The subject-matter experts believe that these indeed are the major sources of uncertainty, and that the contributions made by measurement error affecting  $V_{DT}$ ,  $V_{CB}$ ,  $V_{CS}$ , and  $V_{OW}$  (all defined in Table A1.1 on page A1.4) are minor by comparison.

The mass balance equations that, among other outputs, produce an estimate of residual oil  $V_S$ , describe a simplified model for the partition of the oil among the several fractions that we track, shortly after release, and reflect a particular understanding of the physical and chemical processes that drive that partition.

Other models that could conceivably be entertained, or other choices that could be made about the values of the rate constants, which some oil spill experts might regard as equally reasonable, most likely would produce estimates for  $V_S$  different from those this model produces, even when applied to the same data. The corresponding dispersion of values of such alternative estimates would reflect model uncertainty. Although our uncertainty analysis does not reflect this, it is widely recognized that, in many studies, model uncertainty contributes substantially to the overall uncertainty.

#### A1.4 Approach

The uncertainties associated with the volume of oil discharged and with the rate constants in the mass balance equations are modeled probabilistically and then propagated to the output quantities using the Monte Carlo simulation method that, in one form or another, has been in use for many years in many different disciplines [Metropolis and Ulam, 1949], and that has been codified for use in measurement science in the form of an international standard [Joint Committee for Guides in Metrology, 2008b].

The probabilistic models used for this purpose serve to describe the imperfect or incomplete knowledge about the values of a quantity. For example, in Section A1.5 on page A1.7, we model the uncertainty about the volume discharged on day  $t$  as  $(1 + Q)V_R(t)$ , where  $Q$  denotes a Gaussian (or “normal”) random variable with mean 0 and standard deviation 0.05. This is one way of saying that, with high confidence (95 %), the actual volume is within 10 % ( $= 2 \times 0.05$ ) of the value estimated for the volume discharged. The same can be said in other ways, too: for example, by modeling  $Q$  as a random variable with a uniform (or rectangular) distribution



between  $-0.1$  and  $+0.1$ .

The same limitation applies to all the models we shall employ to model uncertainty with. Even though we believe that they are reasonable for the situations at hand, ultimately they all reflect arbitrary choices, because the science regulating these matters is not yet sufficiently developed to identify a single model as necessarily better or more adequate than all the others. In Section A1.9 on page A1.14 we will assess the sensitivity of our conclusions to this, and to other modeling assumptions.

As noted already in Section A1.3 on page A1.3, and except for  $V_R$ ,  $V_{BU}$ , and for the rate constants, the uncertainty associated with the input quantities ( $V_{DT}$ ,  $V_{CB}$ ,  $V_{CS}$ , and  $V_{OW}$ ) has not been quantified. We proceed on the assumption that the measurement uncertainty of these input quantities is negligible by comparison with the uncertainty components attributable to the imperfect knowledge of the “true” values of the volume discharged and of the rate constants. Also as noted towards the end of Section A1.3 on page A1.3, model uncertainty is not captured either, even though we cannot claim that it is negligible.

The Monte Carlo simulation method that we have used to propagate uncertainty from input to output quantities comprises two steps: first, the generation of multiple scenarios defined by combinations of conceivable values of all the input quantities; second, the summarization of the values of the output quantities corresponding to these scenarios. The results reported in Appendix 2 are based on 100 000 scenarios.

More precisely: for each scenario, we drew (or simulated) values from the probability distributions that model the uncertainty associated with the volume discharged, with the volume burned, and with the rate constants, and then used these simulated values in the calculations that produce time series of daily values of the output quantities. The values simulated for the rate constants vary from scenario to scenario, not from day to day.

Consider  $V_S(t)$ , the volume of residual oil on day  $t$ , for example. Its counterparts that correspond to  $m$  simulated scenarios are denoted  $V_{1,S}^*(t)$ ,  $\dots$ ,  $V_{m,S}^*(t)$ , and we refer to them as *replicates* of  $V_S(t)$ .

These  $m$  replicates may be summarized in a histogram, or by their average and standard deviation, or, as we do in Figure A1.1 on page A1.7, by means of an interval, ranging from  $V_{S,L}(t)$  to  $V_{S,U}(t)$ , that brackets a specified proportion of them, say 95 %, which we then regard as a 95 % confidence interval for the “true” value of  $V_S(t)$ , and interpret as explained in Section A1.3 on page A1.3. This is the so-called *percentile method* of constructing bootstrap confidence intervals [Efron and Tibshirani, 1993, §13.3].

The lower and upper envelopes depicted in Figure A1.1 on page A1.7 were obtained by joining with red lines the points corresponding to  $V_{S,L}(1)$ ,  $V_{S,L}(2)$ ,  $\dots$  (for the lower envelope), and to  $V_{S,U}(1)$ ,  $V_{S,U}(2)$ ,  $\dots$  (for the upper envelope).

In addition to these envelopes, we also compute the average of the simulated values of  $V_S(t)$ , over all  $m$  scenarios, for each day  $t$ . Owing to the non-linear way in which some of the participating quantities (rate constants or input variables) enter in the mass balance equations, and given that the probability distributions of some of the rate constants are markedly asymmetrical,

with one tail much longer than the other, those averages need not coincide with the values that one obtains by solving the mass balance equations using the expected values of the rate constants, and the measured or estimated (but otherwise undisturbed) values of the input quantities.

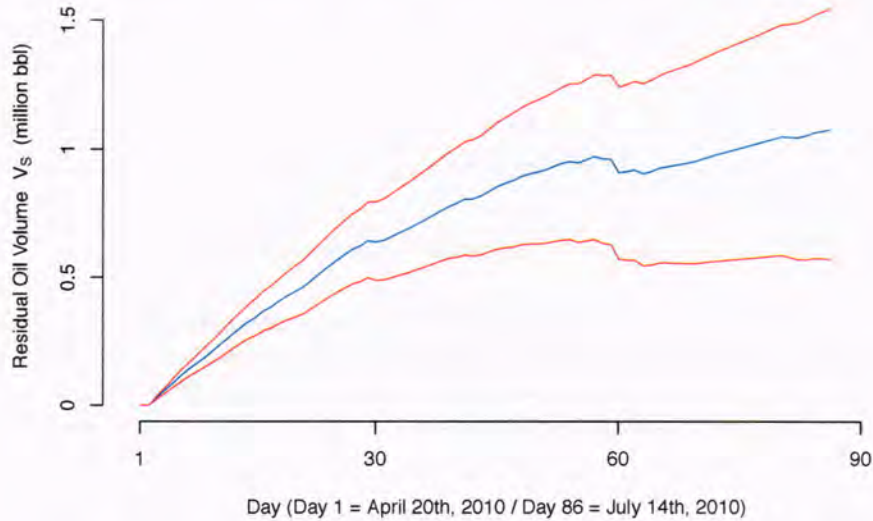


Figure A1.1: **Volume of residual oil ( $V_S$ ), and approximate 95 % confidence band.** The daily increments  $V_{SD}(1), \dots, V_{SD}(t)$  that  $V_S(t)$  is the cumulative sum of, occasionally are negative, which explains the behavior of the curves around day 61 (June 18, 2010), when a large volume of oil was burned on the surface, indeed far more than the residual increment for that day. Since there was no additional discharge after day 86 (July 14, 2010), the curves flatten beyond this date (not shown).

### A1.5 Volume Discharged $V_R$ and Volume Burned $V_{BU}$

The time series  $V_R(1), V_R(2), \dots$  of volume of oil discharged daily from the well, depicted in Figure A1.2 on page A1.8, is taken as an input to the mass balance calculations ( $V_R(t)$  denotes the volume discharged on day  $t$ , with day 1 being April 20th, 2010): in fact, these daily volumes reflect consensus estimates produced by the Flow Rate Technical Group (an explanation of how these estimates were derived will be published separately from this report).

The 10 % relative uncertainty that has been associated with the volume discharged is interpreted as follows: the simulated time series  $V_R^*(1), V_R^*(2), \dots$  of the daily discharge is modeled as the product

$$V_R^*(t) = (1 + Q)V_R(t), \text{ for } t = 1, 2, \dots, \quad (\text{A1.17})$$



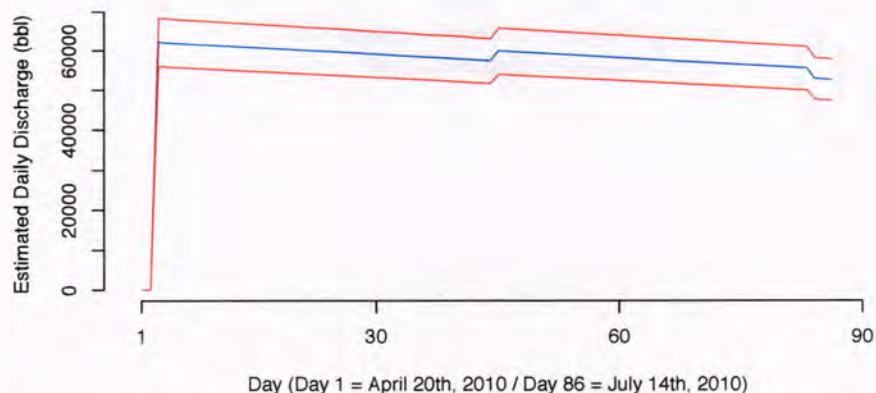


Figure A1.2: **Daily volume of oil discharged from the Deepwater (Macondo) well.** The best estimate is represented by the blue line, while the red envelope defines a range of  $\pm 10\%$  around the best estimate. Since there was no additional discharge after day 86 (July 14, 2010), the curves drop to zero beyond this date (not shown).

where  $V_R(t)$  denotes the nominal discharge on day  $t$ , and  $Q$  is a Gaussian random variable with mean 0 and standard deviation 0.05.

In these circumstances, and with high probability (95 %), the actual discharge should be within 10 % ( $= 2 \times 0.05$ ) of the nominal discharge; however, the model entertains a small chance (5 %) that it could deviate by more than  $\pm 10\%$  from nominal.

Whatever deviation from nominal is selected for one particular scenario, it is assumed to apply to all the days of that scenario. For example, if we were 3 % too low in one scenario (meaning that  $Q = -0.03$ ), then we would be 3 % too low in every day of that scenario; and if, in another scenario, we were 7 % too high ( $Q = 0.07$ ), then we would be 7 % too high in every day of this scenario.

Over a two and half-month period, about 400 controlled burns of oil on the surface were conducted, which eliminated about 5 % of the oil that was discharged from the well. For the several burns that typically occurred each day, estimates of the minimum and maximum volume burned were provided.

We model the uncertainty associated with the total volume burned on a particular day as uniformly distributed between the given minimum and maximum. The corresponding standard deviation equals the difference between the maximum and the minimum divided by  $\sqrt{12}$ . The relative standard deviation equals the standard deviation divided by the average of the minimum and the maximum.

For the purpose of generating stochastic scenarios, these daily relative standard deviations were summarized by their geometric average, which turned out equal to 9.65 %. Similarly to how we

treat the volume discharged, we have modeled the uncertainty associated with the daily volume of oil burned  $V_{\text{BU}}(t)$  as described in equation A1.18, where the  $\{B(t)\}$  denote independent Gaussian random variables with mean 0 and standard deviation 0.0965.

$$V_{\text{BU}}^*(t) = (1 + B(t))V_{\text{BU}}(t), \text{ for } t = 1, 2, \dots \quad (\text{A1.18})$$

Note that, differently from how we modeled the uncertainty of the volume discharged, here we perturb the estimates of the daily volumes of oil burned, independently from day to day.

### A1.6 Probability Models for Rate Constants

The mass balance equations listed above include *rate constants*  $k_1, \dots, k_8$ . Subject-matter experts have described their state of knowledge about the values of these constants by regarding them as outcomes of random variables, and by providing location and spread information about the corresponding probability distributions, listed in Table A1.2. This is a standard statistical device to express uncertainty assessments, and should not be interpreted as suggesting that these rate constants are intrinsically random, according to any of the common meanings of randomness.

RATE CONSTANT	DEFINITION	$\zeta_{0.025}$	$\mu$	$\zeta_{0.975}$
$k_1$	Natural dispersion (subsurface)	0.10	0.20	0.30
$k_2$	Chemical dispersion (subsurface)	2/9	4/9	1.00
$k_3$	Chemical dispersion (surface)	0.05	0.10	0.20
$k_4$	1st day evaporation	0.33	0.37	0.44
$k_5$	2nd day evaporation	0.00	0.04	0.06
$k_6$	Net oil fraction in skimmed oil	0.10	0.20	0.40
$k_7$	Dissolution of dispersed oil	0.05	0.075	0.10
$k_8$	Natural dispersion (surface)	0.00	0.05	0.10

Table A1.2: **Rate Constants.** Expected values ( $\mu$ ) and 2.5th ( $\zeta_{0.025}$ ) and 97.5th ( $\zeta_{0.975}$ ) percentiles of the probability distributions that model the associated uncertainties.

We have interpreted the information in Table A1.2 as follows: the probability is approximately 95 % that the true value of a rate constant lies in the interval from  $\zeta_{0.025}$  to  $\zeta_{0.975}$ , and has expected value  $\mu$ . In addition, we also assume that the possible values for the rate constants are non-negative, and also that they are no larger than 1, except possibly for  $k_2$  and  $k_3$ .

Once the probability model described below was fitted to the information in Table A1.2, these assumptions were satisfied (with probability just about equal to 1) for all but  $k_5$  and  $k_8$ . Indeed, as modeled, both  $k_5$  and  $k_8$  could be negative with probability about 2.5 %: for this reason, their distributions were truncated at 0.

For  $k_2$ ,  $k_3$ ,  $k_4$ , and  $k_6$ , it so happens that the distance from the expected value ( $\mu$ ) to the 97.5th percentile ( $\zeta_{0.975}$ ) is greater than or equal to the distance from the expected value ( $\mu$ ) to the



2.5th percentile ( $\zeta_{0.025}$ ): that is, their probability distributions have the right tail longer than the left tail (in other words, they are skewed to the right). For  $k_5$  the opposite happens, and its distribution is skewed to the left. The distributions for  $k_1$ ,  $k_7$ , and  $k_8$  are approximately symmetrical.

Many different probability models are available that describe right skewness, and a few can describe skewness either to the left or to the right, and still involve no more than three adjustable parameters, which is the number of pieces of information listed for each rate constant in Table A1.2 on page A1.9.

One of these, which includes the normal distribution as a special case, is the skew normal distribution described by Azzalini [1985], and implemented by Azzalini [2010] in package `sn` for the R environment for statistical programming and graphics [R Development Core Team, 2010].

Another model that we have considered, given that the rate constants have values essentially between 0 and 1, was the beta distribution. Since the skew normal distribution managed to reproduce the information available about the rate constants much more accurately than the beta distribution, we have used the skew normal distribution as a model for all of the rate constants.

The adjustable parameters of the skew normal distribution are the location  $\xi$ , the scale  $\omega$ , and a shape parameter  $\alpha$  that controls skewness. The values we selected for these parameters that reproduce the entries in Table A1.2 on page A1.9 are listed in Table A1.3 on page A1.11. We obtained them by taking the following steps (Figure A1.3 depicts the resulting probability densities):

- (a) If  $\zeta_{0.975}$  and  $\zeta_{0.025}$  denote the 97.5th and 2.5th percentiles of a skew normal distribution, the ratio  $(\zeta_{0.975} - \mu)/(\mu - \zeta_{0.025})$  (which depends neither on  $\mu$  nor on  $\omega$ ) is an effective proxy for the distribution's skewness. Since the shape parameter  $\alpha$  is a monotonically increasing function of the skewness of the skew normal distribution, we built an interpolating spline [Venables and Ripley, 2002]  $\psi$  such that  $\alpha \approx \psi((\zeta_{0.975} - \mu)/(\mu - \zeta_{0.025}))$  with negligibly small error for values of  $\alpha$  over a suitably wide range.
- (b) For each rate constant, first we estimated  $\alpha$  using the function  $\psi$  just described, by applying it to the values in Table A1.2, and then found values of  $\xi$  and  $\omega$  that minimize

$$(\zeta_{0.025} - F_{\xi, \omega, \alpha}^{-1}(0.025))^2 + (\zeta_{0.975} - F_{\xi, \omega, \alpha}^{-1}(0.975))^2 + \left(\mu - \xi + \omega \frac{\alpha\sqrt{2}}{\sqrt{\pi(1+\alpha^2)}}\right)^2,$$

where  $F_{\xi, \omega, \alpha}^{-1}$  denotes the inverse of the cumulative probability distribution function of the skew normal distribution with location  $\xi$ , scale  $\omega$ , and shape  $\alpha$ . The idea here is to choose values for the adjustable parameters that best reproduce the mean and percentiles given for each rate constant. The last term in the foregoing expression is determined by the fact that the expected value of a skew normal distribution with location  $\xi$ , scale  $\omega$ , and shape  $\alpha$ , is  $\xi + \omega\alpha\sqrt{2}/\sqrt{\pi(1+\alpha^2)}$ .

RATE CONSTANT	$\xi$	$\omega$	$\alpha$
$k_1$	0.200	0.0500	0.00
$k_2$	0.191	0.356	760
$k_3$	0.0470	0.0681	176
$k_4$	0.332	0.0483	8.44
$k_5$	0.0612	0.0272	-167
$k_6$	0.0940	0.136	176
$k_7$	0.075	0.0128	0.00
$k_8$	0.0500	0.0255	0.00

Table A1.3: **Parameters of Probability Distributions for Rate Constants.** Values of the location  $\xi$ , scale  $\omega$ , and shape  $\alpha$  of the skew normal distributions used to represent the information available about the values of the rate constants.

### A1.7 Uncertainty Analysis

The uncertainty analysis is based on statistics of multiple scenarios, generated by Monte Carlo simulation, as outlined in Section A1.4 on page A1.5. Each scenario is defined by a value of the random variable  $Q$  introduced in equation A1.17 on page A1.7, by values of the random variables  $\{B(t)\}$  in equation A1.18 on page A1.9, and by a set of values of the rate constants obtained by sampling the probability distributions fitted as described in Section A1.6 on page A1.9. The scenario proper consists of the time series of values of the output variables that correspond to the simulated values of  $Q$  and of the rate constants.

The fact that the same sampled value of each rate constant is used for every day of each scenario effectively induces statistical dependencies between the quantities that are functions of the rate constants. The uncertainty analysis does take these dependencies into account.

More precisely, we have taken the following steps:

- (a) We selected a value for  $m$ , the number of scenarios ( $m = 100\,000$  for the results in Appendix 2).
- (b) For  $i = 1, \dots, m$ :
  - (b1) We drew a sample of size one from the probability distribution of  $Q$ , and used it to generate a replicate of the time series of the values of oil volume discharged, by application of equation A1.17 on page A1.7.
  - (b2) We drew a sample of size one from the probability distribution of each of the random variables  $\{B(t)\}$ , and used them to generate a replicate of the time series of the values of oil volume burned, by application of equation A1.18 on page A1.9.
  - (b3) We drew a sample of size one from the probability distribution fitted to each rate constant.



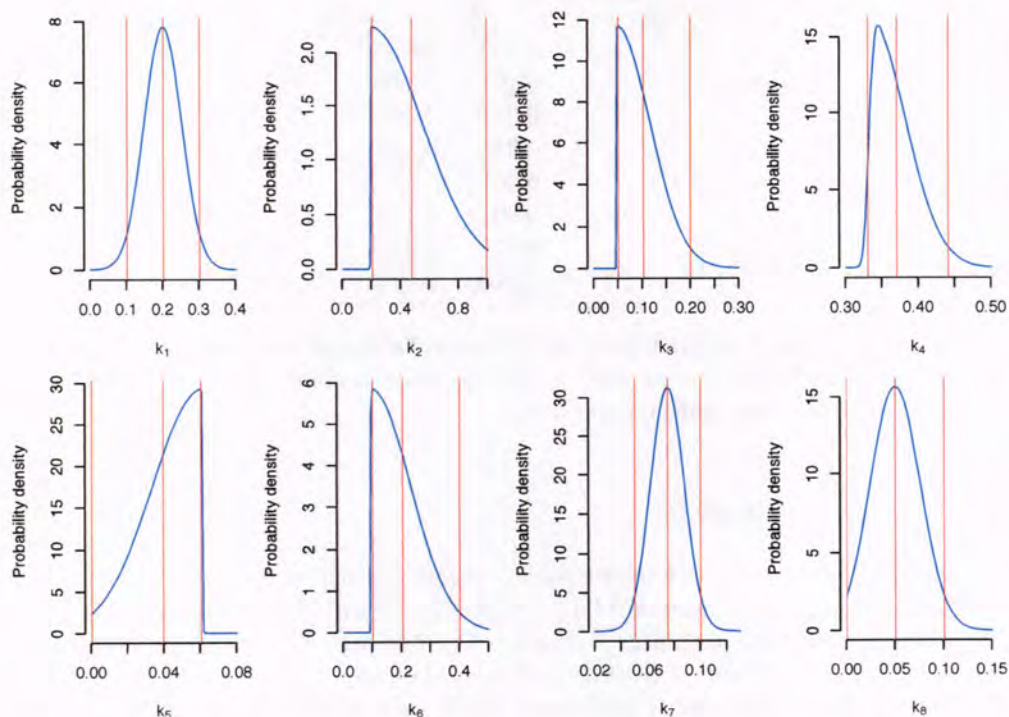


Figure A1.3: **Skew normal probability densities for the rate constants.** The vertical red lines mark the locations of the 2.5th percentile  $\zeta_{0.025}$ , the expected value  $\mu$ , and the 97.5th percentile  $\zeta_{0.975}$ , which reproduce the values specified by the subject-matter experts, listed in Table A1.2 on page A1.9.

- (b4) Using the time series obtained in step b1 on page A1.11, the values for the rate constants obtained in step b3 on page A1.11, and the values of the input quantities, we used the mass balance equations (equations A1.1 on page A1.2– A1.16 on page A1.2), to compute the time series of daily values of the output quantities, and of their cumulative sums (where applicable).
- (c) Step b on page A1.11 produced  $m$  simulated values of each output quantity on each day, whose 2.5th and 97.5th percentiles define the lower and upper 95 % probability envelopes for the value of the output quantity.

### A1.8 Best-Case and Worst-Case Scenarios

For any particular day  $t$ , the corresponding points on the lower and upper bounds (red envelope) for  $V_S(t)$ , depicted in Figure A1.1 on page A1.7 and whose ordinates are  $V_{S,L}$  and  $V_{S,U}(t)$ , bracket the true volume of residual oil on that day, with 95 % probability.

Given their fairly extreme nature, we take these endpoints to represent best-case and worst-case scenarios, even though there are scenarios that are better than that best, and worse than this worst because the interval from  $V_{S,L}(t)$  to  $V_{S,U}(t)$  encompasses only the middlemost 95 % of the  $m$  simulated replicates  $V_{1,S}^*(t), \dots, V_{m,S}^*(t)$  that will have been generated for  $V_S(t)$ .

This approximate, practical characterization of what the “best” and “worst” situations may be is motivated by the desire to focus the management of the crisis on scenarios that, although fairly extreme, still are “buffered” by non-negligible tail probabilities that lend them statistical credence, rather than on speculatively extreme cases.

Now, given  $V_{S,L}(t)$  for day  $t$ , we wish to find the combinations of values of all the other variables that correspond to this best-case scenario, and that also satisfy the mass balance equations. Similarly for  $V_{S,U}(t)$ , and for the worst-case scenario.

It is not immediately obvious what these combinations of values should be because  $V_{S,L}(t)$  does not necessarily correspond to the case where all the rate constants, and the variables  $Q$  and  $\{B(t)\}$ , simultaneously have their “best” values. This is so for two reasons: first, these variables are assumed to vary independently of one another from scenario to scenario (an assumption that is discussed and probed in Section A1.9 on page A1.14); second, such “best” values may yield a far more extreme, and practically irrelevant, value for the volume of residual oil, than what we have defined  $V_{S,L}(t)$  to be.

Since the volume of residual oil depends on the values of several other quantities, and does so in the complicated way that the mass balance equations describe precisely, we will write  $V_S(t) = h(V_R(t), \dots, V_{NW}(t))$  to denote this dependence summarily, omitting reference to  $Q$ , to the  $\{B(t)\}$ , and to the rate constants. The function  $h$  subsumes all the mathematical manipulations that these quantities undergo finally to produce  $V_S(t)$ .

Our goal is to find the most likely values of  $V_R(t), \dots, V_{NW}(t)$  that, once processed through  $h$ , yield  $V_{S,L}(t)$  as the volume of residual oil left on day number  $t$ , and that satisfy the mass balance equations. (Recall that  $V_{S,L}(t)$  denotes the 2.5th percentile of the set of  $m$  simulated values of the volume of residual oil, as defined in Step c on page A1.12.) And then to do similarly for  $V_{S,U}(t)$ , the 97.5th percentile.

Taken together, those most likely values will then define the best-case scenario. (And similarly the worst-case scenario.) Since this amounts to “inverting” the function  $h$ , our goal can be fairly described as *scenario inversion*. The problem, of course, is that  $h$  is not invertible in the strict sense of mathematics because there are many combinations of values of  $V_R(t), \dots, V_{NW}(t)$  that yield the same value of  $V_S(t)$ .

To perform a satisfactory scenario inversion that yields the best-case scenario, we start from the realization that such scenario will correspond to some combination of values of  $V_R(t), \dots, V_{NW}(t)$  that, once processed through  $h$ , produces a value for  $V_S(t)$  that is close to  $V_{S,L}(t)$ .



To find such combinations of values of the arguments of the function  $h$ , we selected a suitably small positive value  $\varepsilon$ , and searched through the set of simulated values of  $V_R(t), \dots, V_{NW}(t)$  for those that satisfy  $|h(V_{i,R}^*(t), \dots, V_{i,NW}^*(t)) - V_{S,L}(t)| < \varepsilon$ . Let  $\mathcal{S}_L$  denote the resulting subset of combinations of values of  $V_R(t), \dots, V_{NW}(t)$ .

Since  $\mathcal{S}_L$  comprises many such combinations, the problem remains of selecting one that is representative of the best-case scenario. We did this by finding, for each output variable of interest that the volume of residual oil is a function of, its average over those of its values that are present in  $\mathcal{S}_L$ .

We also verified that these averages indeed are representative of the values they subsume, by inspecting their locations in histograms of these values. This process was repeated, using a comparably defined set  $\mathcal{S}_U$  for the worst-case scenario. These best-case and worst-case scenarios for July 14, 2010 (day  $t = 86$ ) are characterized quantitatively, and depicted graphically, in Appendix 2.

## A1.9 Sensitivity Analysis

As described in Section A1.7 on page A1.11, the uncertainty analysis is based on simulated scenarios, and each of these scenarios is defined by a time series of simulated values of discharged oil, by a time series of volumes of burned oil, and by a set of simulated values of the rate constants.

These simulations are based on particular models (probability distributions) for all the participating quantities: although reasonable, other models could also reasonably be entertained. For example, we mentioned already, in Section A1.4 on page A1.5, that the variable  $Q$  that appears in equation A1.17 on page A1.7, and which we assumed had a particular Gaussian distribution, conceivably might also have been modeled as having a particular uniform distribution instead. The same applies to the variables  $\{B(t)\}$  relating to the volume of oil burned.

One assumption that we have made but that we have not yet discussed is that the random variables modeling the rate constants are stochastically independent. Although this represents an approximation suggested by the subject-matter experts, it is not only possible but indeed likely that some of them should be interrelated.

For example, it is reasonable to expect that the rates of evaporation,  $k_4$  and  $k_5$ , on the first and second days after discharge of a fresh batch of oil into the sea should vary together over time, because they may be driven by common factors. Similarly,  $k_2$  and  $k_3$ , the rate constants that describe the effectiveness of chemical dispersion under and on the sea surface, may be interrelated for similar reasons.

To ascertain the sensitivity of our results to our modeling assumptions, we have focused on the volumes of residual oil  $V_S$ , and performed an alternative uncertainty analysis assuming that the correlation coefficient between  $k_2$  and  $k_3$ , and between  $k_4$  and  $k_5$ , was  $\sqrt{0.5}$ , rather than 0. This assumption about the correlations means that the potential variability in  $k_2$  over time would “explain” about 50% of the corresponding variability in  $k_3$  (and similarly for  $k_4$  and  $k_5$ ).

To impose correlations between these two pairs of rate constants, we used a Gaussian copula [Nelsen, 2006, Possolo, 2010], which is a standard technique for this purpose. This creates a multivariate probability distribution with the correlations specified ( $\sqrt{0.5}$  between  $k_2$  and  $k_3$  and also between  $k_4$  and  $k_5$ , and 0 between all the other possible pairs), and such that the individual rate constants, when taken each one by itself, still has the same skew normal distribution that was fitted as described in Section A1.6 on page A1.9.

We have also studied the sensitivity of the results to the assumptions we made about the random variable  $Q$ , introduced in equation A1.17 on page A1.7, and about the random variables  $\{B(t)\}$  introduced in equation A1.18 on page A1.9. The former drives the variability between simulated scenarios, of the time series of volume of oil discharged from the well. The latter models the measurement uncertainty associated with the volume of oil that has been burned. Originally we assumed that  $Q$  has a Gaussian distribution with mean 0 and standard deviation 0.05. For the sensitivity analysis we have assumed instead that  $Q$  is uniformly distributed between  $-0.1$  and  $+0.1$ . Similarly for the  $\{B(t)\}$ .

The results of this sensitivity analysis, depicted in Figure A1.4 on page A1.16, show that the presence of such statistical dependence as we have entertained for selected pairs of rate constants, possibly in conjunction with a different model for  $Q$  and for the  $\{B(t)\}$ , widens the uncertainty envelope for the time series of values of  $V_S$ . However, it changes the upper bound hardly at all, and depresses the lower confidence envelope, thus suggesting that the assumptions we made originally are the more conservative ones among the alternatives we have considered.



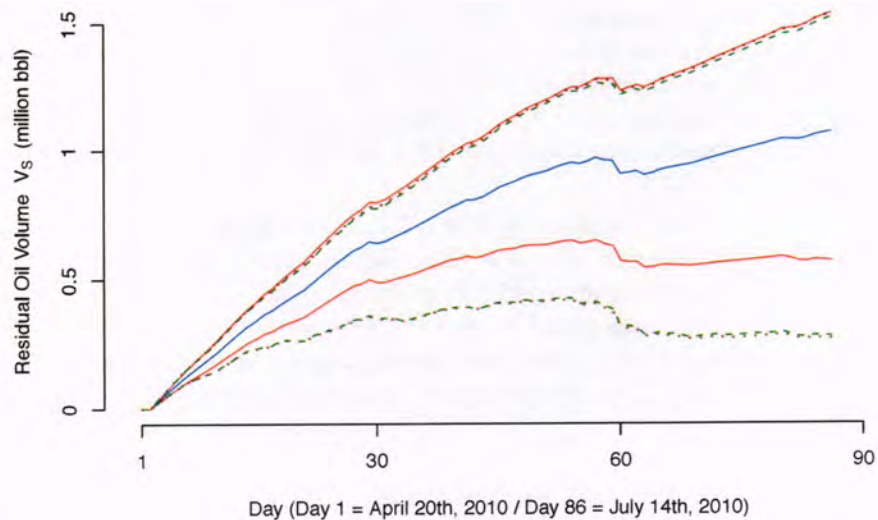


Figure A1.4: **Sensitivity Analysis.** Volume of residual oil ( $V_S$ ) and variants of the approximate 95 % confidence band, corresponding to assuming that  $k_2$  and  $k_3$ , as well as  $k_4$  and  $k_5$ , are correlated (dashed, green line), or that, in addition to this, the random variable  $Q$  and the random variables  $\{B(t)\}$ , introduced in equation A1.17 on page A1.7 and in equation A1.18 on page A1.9, respectively, are uniformly distributed, rather than Gaussian (dotted, brown line). These alternatives mostly reduce the lower confidence envelope, thus suggesting that the assumptions we made originally are the more conservative ones among the alternatives we have considered. Since there was no additional discharge after day 86 (July 14, 2010), the curves flatten beyond this date (not shown).

## References

- A. Azzalini. A class of distributions which includes the normal ones. *Scandinavian Journal of Statistics*, 12:171–178, 1985.
- A. Azzalini. *R package sn: The skew-normal and skew-t distributions (version 0.4-15)*. Università di Padova, Italia, 2010. URL <http://azzalini.stat.unipd.it/SN>.
- B. Efron and R. J. Tibshirani. *An Introduction to the Bootstrap*. Chapman & Hall, London, UK, 1993.
- Joint Committee for Guides in Metrology. *Evaluation of measurement data — Guide to the expression of uncertainty in measurement*. International Bureau of Weights and Measures (BIPM), Sèvres, France, September 2008a. URL <http://www.bipm.org/en/publications/guides/gum.html>. BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML, JCGM 100:2008, GUM 1995 with minor corrections.
- Joint Committee for Guides in Metrology. *Evaluation of measurement data — Supplement 1 to the “Guide to the expression of uncertainty in measurement” — Propagation of distributions using a Monte Carlo method*. International Bureau of Weights and Measures (BIPM), Sèvres, France, 2008b. URL <http://www.bipm.org/en/publications/guides/gum.html>. BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML, JCGM 101:2008.
- Joint Committee for Guides in Metrology. *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*. International Bureau of Weights and Measures (BIPM), Sèvres, France, 2008c. URL <http://www.bipm.org/en/publications/guides/vim.html>. BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML, JCGM 200:2008.
- N. Metropolis and S. Ulam. The Monte Carlo Method. *Journal of the American Statistical Association*, 44:335–341, September 1949.
- R. B. Nelsen. *An Introduction to Copulas*. Springer, New York, NY, 2nd edition, 2006. Corrected 2nd. printing, 2007.
- A. Possolo. Copulas for uncertainty analysis. *Metrologia*, 47:262–271, 2010.
- R Development Core Team. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria, 2010. URL <http://www.R-project.org>. ISBN 3-900051-07-0.
- W. N. Venables and B. D. Ripley. *Modern Applied Statistics with S*. Springer, New York, Fourth edition, 2002. URL <http://www.stats.ox.ac.uk/pub/MASS4>. ISBN 0-387-95457-0.



## Appendix 2

### A2 Oil Budget Calculator Web-based Tool

Section Authors: R. Sky Bristol<sup>1</sup>, David Mack<sup>2</sup>, Tim Kern<sup>3</sup>, Jeff Allen<sup>2</sup>

1. U.S. Geological Survey, Geospatial Information Office, Denver, Colorado

2. Arctic Slope Regional Corporation (contracted to USGS), Fort Collins, Colorado

3. U.S. Geological Survey, Fort Collins Science Center, Fort Collins, Colorado

#### Background

One of the most visible aspects of the Oil Budget Calculator is the technological application that was created as a response tool for personnel with National Incident Command (NIC). The first iteration of an oil budget calculator was built in a Microsoft Excel spreadsheet by U.S. Coast Guard (USCG) staff with the National Response Center. This tool captured simple daily variables from the response effort (e.g., amount of oil skimmed from the surface) and instantiated basic formulas for a best- and worst-case scenario based on calculations used in previous spill events. The USCG requested help from the Interagency Solutions Group established from NIC for help with the spreadsheet tool in terms of reporting and characterizing the results along with help from a science team in the underlying calculations and assumptions.

To address this need, the Interagency Solutions Group consulted a U.S. Geological Survey (USGS) computer science team on the tool itself and National Oceanic and Atmospheric Administration (NOAA) scientific support personnel to engage a team of oil fate and behavior scientists. After discussing the basic requirements for the final tool needed by NIC staff, in particular the need for ease of access without new software requirements, the USGS team opted for the creation of a Web-based application. This section of the report discusses the engineering of the Web-based system and its relationship to the scientific model developed by partners in NOAA and the National Institute of Standards and Technology.

#### Requirements for the Calculator

Initial requirements for the purpose and use of the calculator were received in phone conversation with NIC staff on June 17, 2010 (National Incident Command Personnel, 2010). Further requirements and requests for features in the application continued to evolve through the course of the project as NIC staff, scientific support personnel, and others began using reports from the tool in response activities. All technical requirements, features, and associated tasks for the tool were captured in an online project management system used by the USGS team as a way to document the evolution of the application and a record for any future activities.

A high-level discussion of requirements is summarized below:

- The tool needed to be easily accessible by NIC staff and NOAA scientific support personnel providing input to response activities, not requiring any additional desktop software or a major learning period.
- The tool needed to be secure so that only authorized personnel could access the system, and specific NIC staff needed the ability to specify who could perform specific functions in the system.
- Only certain personnel could be authorized to enter data into the Daily Values Database, and all data needed to be logged so that individual entries could be tracked to the user who entered them and when they were entered.
- Only certain personnel could be authorized to access daily and summary reports from the system, and those accesses needed to be logged.
- Only certain personnel involved with scientific support could be authorized to change the underlying calculations and assumptions used to calculate the oil budget.
- The tool needed to include the ability to view the daily and cumulative total figures and associated charts for any day in the incident.
- The tool needed to provide a print feature so that authorized report users could output a daily executive summary used by response and communications personnel.
- The tool needed a feature to output all daily values entered into the system in a spreadsheet table so that the figures could be shared and viewed independently.

In total, 98 separate features or improvements were captured and tracked in the project management application used for the work during the course of the engineering and development effort.

### **Scenarios**

The oil budget calculation needed to incorporate the concept of scenarios to include at least a theoretical best and worst case scenario in terms of the amount of oil being discharged and the relative effectiveness of response activities. A third scenario used mean values to provide a probable case, or at least a baseline set of numbers predicated on the best available knowledge of oil fate and behavior. The requirement to essentially bound the problem and effectiveness of the response played a critical role in the design of the application and reports.

During the period when the well was still discharging oil, the Oil Budget Calculator used a simplistic approach to calculating and presenting scenarios that used only the difference in flow rate estimates as the variable between scenarios. After continued examination of the tool with the statistical experts working on the oil budget model, the final iteration of the calculator (version 2.0) included a more rigorous presentation of the scientific uncertainty in the theoretical best- and worst-case scenarios. This version of the tool



incorporated the upper and lower bounds of uncertainty for the effectiveness of individual response activities in addition to the uncertainty bounds for the flow rate.

## **Components of the Calculator**

The tool consisted of the following basic elements:

- Daily Variables – daily variables entered by USCG staff with the NIC
- Global Variables – global flow rate values based on government estimates and formulas stored as variables to produce cumulative totals from the oil budget calculating model
- Modeling Application – technological application to pass daily variables to a scientific model that encapsulated assumptions and statistical calculations to produce daily oil budget figures
- Reporting Application – executive summary reporting component that presented daily oil budget numbers and charts

These components were brought together as a Web-based tool within a Java application framework called Grails (Grails Community, 2010) and several existing infrastructural elements already in place within the USGS network and able to be tuned toward the application. Front-end Web services were provided on an Apache Web server platform (Apache Project, 2010). Database elements were stored within a PostgreSQL (PostgreSQL, 2010) environment using Hibernate (JBoss Community, 2010) for data object and relational mapping and persistence. Authentication services were provided by a USGS framework founded on a technology called Java Open Single Sign-On (JOSSO Community, 2010). The Oil Budget Calculator model was written in the R scientific programming language (R Project, 2010) using a dedicated virtual machine set up as an “R Application Server.” All application components were configured to run on servers using the Red Hat (Red Hat, 2010) version of the Linux operating system.

## **Daily Variables**

A simple database table managed through the Web application housed variables of the response effort entered by NIC personnel. In some cases, the values were direct measurements, and in others the values were the results of established standard measurement protocols used by the USCG for incident response (National Incident Command Personnel, 2010).

- Oil Collected via RITT/Top Hat (barrels) – Values for the amount of oil recovered by the vessels Helix Producer, Discoverer Enterprise and the Q4000 and reported by British Petroleum.
- Oil Burned (barrels) – Total oil burned using standard rates from the American Society for Testing and Materials (American Society for Testing and Materials, 2006).
- Oily Water Collected (barrels) – Total of estimated measurements from multiple collection methods and contractors.

- Subsurface Dispersants Used (gallons) – Direct report from dispersant operations.
- Surface Dispersants Used (gallons) – Direct report from dispersant operations.

Later in the response effort, once inland recovery of oil reached a point where total numbers could be captured, a value of tons of oily debris was added to the daily variables database as a reporting value. This figure was not used in the oil budget calculation but was included in the reporting tool. Based on the requirement to have an output of daily variables in a spreadsheet format, a feature was added to export all daily values as an Excel spreadsheet file.

### **Global Variables**

The Oil Budget Calculator went through three distinct iterations based on the best government estimates of flow/discharge rate from the leaking well. All values were provided to the Oil Budget Calculator team from the Deepwater Horizon Flow Rate Technical Group and were refined over time as more and better information became available. The need to include multiple scenarios resulted in flow estimates of high, low, and mean being stored in the global variables portion of the database and used in the calculations.

The global variables data also contained several formulas stored as a simple formula language and used in the final calculations of cumulative totals on the output from the oil budget model. Global variables were considered the domain of the oil fate and behavior science team building the model and were only editable by application administrators.

### **Modeling Application**

The initial iteration of the Oil Budget Calculator employed a very simple model based directly on the individual calculations provided in an interim report. These formulas were stored in the application as global variables and acted directly on daily variables, triggered whenever daily variables were modified in any way. Initial reports from this method shared amongst the development and science teams prior to production release of the application indicated a need for an increased level of statistical sophistication in the model.

Following engagement of personnel from the National Institute of Standards and Technology (NIST), the oil budget calculations were refactored into a statistical model and codified using the R scientific programming language (R Project, 2010). The development team engineered an application server environment to house and run the R processing engine, receive values from the application maintaining daily variables, trigger the model to run calculations, and ingest calculated output variables from the model back into the final database.



### **Reporting Application**

The reporting toolset was built within the same Grails application framework (Grails Community, 2010). The executive summary report presented two to three scenarios over the course of the application. Initially, the application presented only a high flow scenario, based on the government's maximum discharge estimate, and a low flow scenario, based on the government's minimum discharge estimate. Personnel from NIC later requested the addition of a scenario based on mean discharge as a single value report that could be used in certain planning and communication processes. For each scenario, the reporting tool provided a table of the calculator output of daily and cumulative totals.

The report also included charting generated using the JFreeChart Java library (JFree.org, 2010). The Oil Budget pie chart provided a "response estimate" representation of the total amount of oil released over time for the actual government estimates of discharge as well as a higher flow and lower flow estimate from the  $\pm 10\%$  uncertainty factor, the relative amounts of oil recovered or dispersed by both natural and response methods, and the total remaining oil calculated by the oil budget model. A stylized stacked bar chart was used in place of the pie chart in earlier iterations of the tool.

The reporting application included a feature to select any day in the incident and view the full report for the day, showing cumulative totals at that point. The reports could be viewed online via a Web browser and exported in Adobe Acrobat (PDF) format. Charts could also be viewed individually as image files for incorporation into alternate presentations.

### **Evolution of the Oil Budget Calculator**

The Oil Budget Calculator online tool went through several distinct iterations recorded as versions of the tool throughout its lifecycle. The iterations of the tool used for the incident response activity were recorded as 1.x versions through the final version 1.3.1. This first generation of the tool was used for the public release of information about the Oil Budget Calculator (NOAA, 2010).

Based on input from the science team responsible for the final Oil Budget Calculator report to National Incident Command and a significant reworking of the scientific model, a second generation (version 2.0) of the tool was prepared. The major difference between the two generations of the tool was the calculation and characterization of scientific uncertainty for the variable elements in each of three scenarios. Version 1.x of the tool used only a variable discharge rate based on the  $\pm 10\%$  uncertainty in the official government estimates of discharge produced by the Deepwater Horizon MC252 Flow Rate Technical Group - 62,200 bbl on April 22, 2010 to 52,700 bbl on July 14, 2010 (Lehr and others, 2010) - to produce reports for three scenarios (official government estimates, high flow scenario, and low flow scenario). Version 2 of the tool used calculations of scientific uncertainty for individual elements of the report to produce

expected, best case, and worst case scenarios as discussed in Appendix 1 of the Oil Budget Calculator report.

Version 2 of the online tool was not used in the actual response effort. Rather it was prepared as the next generation of the tool and presented to National Incident Command as an improvement on the calculations based on increased information and knowledge about the Deepwater Horizon incident provided by the science team. It was meant to help inform future development of the response tool for other incidents.

The following sections present report elements from the two generations of the online tool captured for July 14, 2010 – the last day in the incident where reported values for skimming and burning oil were recorded.

### Oil Budget Calculator – Version 2.0

Table A2.1 comes directly from version 2.0 of the online tool using the calculations described in Appendix 1 of the report. The colors next to the individual calculated values correspond to colors in the charts that are part of the generated oil budget report. Two of the charts showing cumulative total oil and percentage of total are provided in the body of the report for the same day, July 14, shown in the table.

**Table A2.1. Oil Budget Calculator cumulative totals for the official estimated discharge rate and expected scenario (62,200 bbl on April 22, 2010 to 52,700 bbl on July 14, 2010) through July 14, 2010 (from version 2.0 of the Oil Budget Calculator)**

Calculated Values	Cumulative	July 14
<b>Discharged</b>	4,900,000	53,000
Recovered via RITT and Top Hat	820,000	13,000
Dispersed Naturally	640,000	5,200
Evaporated or Dissolved	1,200,000	9,500
<b>Available for Recovery</b>	2,300,000	25,000
Chemically Dispersed	770,000	13,000
Burned	260,000	1,100
Skimmed	160,000	5,200
<b>Other Oil</b>	1,100,000	6,000
<b>Recorded Values</b>		
Dispersant Used	43,695	327
Inland Recovery (Cumulative)	0 tons	

\* All unlabeled values in barrels; rounded to 2 significant digits



### Oil Budget Calculator – Version 1.x

Table A2.2 and figure A2.1 show the cumulative oil budget from the version of the online tool used in the response effort. The response tool used a numbered versioning scheme of 1.x, ending with 1.3.1. This version of the tool and the table and figure included here provide background documentation on the evolution of the tool. The previous section on version 2.0 represents a significant improvement in the Oil Budget Calculator based on the substance of this report.

**Table A2.2. Oil Budget Calculator cumulative totals for the official estimated discharge rate (62,200 bbl on April 22, 2010 to 52,700 bbl on July 14, 2010) through July 14, 2010 (from version 1.3.1 of the Oil Budget Calculator)**

Calculated Values		Cumulative	July 14
<b>Discharged</b>		4,928,100	52,700
Recovered via RITT and Top Hat		817,739	12,843
Dispersed Naturally		763,948	6,924
Evaporated or Dissolved		1,242,668	11,168
<b>Available for Recovery</b>		2,103,745	21,765
Chemically Dispersed		418,075	5,237
Burned		263,900	1,100
Skimmed		156,694	5,110
<b>Remaining</b>		1,265,075	10,318
<b>Recorded Values</b>			
Dispersant Used		43,695	327
Inland Recovery (Cumulative)		0 tons	

\* All unlabeled values in barrels.

Table A2.2 comes directly from the online tool. The colors next to the individual calculated values correspond to colors in the charts that were part of the generated oil budget report. Significant refinements occurred between the version of the tool used during the response the new version presented in the final report. Most notably for the table of values:

- The term “Remaining” was changed to “Other Oil” to help alleviate an impression that the other calculated values in the report might not remain in the environment at all.
- Numeric figures were rounded to two significant digits to better represent the level of scientific uncertainty inherent in the calculations.

Figure A2.1. Cumulative percentage of oil from the calculator for natural processes and response activities using the official estimated discharge rate (62,200 bbl on April 22, 2010 to 52,700 bbl on July 14, 2010) through July 14, 2010 (from version 1.3.1 of the Oil Budget Calculator)

### July 14, 2010 Response Estimate: Percentage of Total

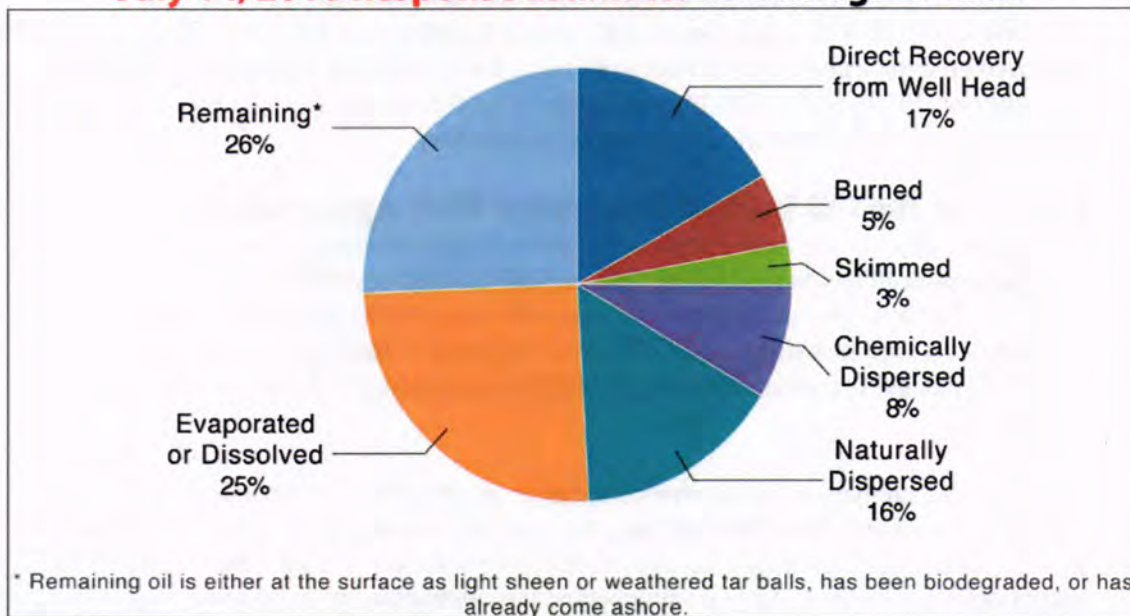


Figure A2.1 comes directly from the online tool. Significant refinements occurred between the charts included in the version of the tool used during the response and the new version presented in the final report. Most notably, the single pie chart that presented only one possible scenario at a time in three separate images was replaced with a bar chart that presented best case, expected, and worst case scenarios in one graphic to help show the scientific uncertainty inherent in the model. These charts are included in the body of the report.

### Application Security and Logging

Authentication for the application was provided using an existing framework in the USGS based on JOSSO technology (JOSSO Community, 2010) and a directory service of user accounts. Users were placed into one of three roles within the application:

- Report Readers – Access to view and print reports for any day in the incident
- Data Entry Personnel – Access to view and print reports and to enter and maintain daily variables
- Administrators – Each of the above rights plus access to enter and maintain global variables



All accesses to the online application were logged via the authentication system. Changes to daily and global variables were logged separately and available for viewing within the application. Printed reports, generated as a PDF download, were stamped with a user ID and date in the footnote of every page.

All versions of the Web application and R statistical model were tracked as they were deployed onto the technological framework using a versioning system called Subversion (Apache.org, 2010). Subversion logs and underlying Web site access logs are stored in a secure data storage framework and available as necessary.

### **Future of the Oil Budget Calculator Web Application**

The overall utility of the online application proved a valuable tool for the response and communication efforts as reported by NIC and NOAA staff involved directly in response activities. The first generation of the tool was still in use for the Deepwater Horizon incident at the time of writing, and USCG staff indicated a desire to continue discussions about either ongoing partnership with the USGS or technology transfer to a USCG facility.

Following the production of this report and major input by the oil fate and behavior science team, version 2.0 of the Oil Budget Calculator was prepared with modifications to the calculator model and major changes to the presentation of scientific uncertainty in the output reports. The scientific reasoning behind the calculations is discussed extensively in the report, and the new model is laid out within Appendix 2. The new model resulted in significant differences in the final cumulative totals and associated visualizations with a higher overall degree of confidence based on the extensive review of the model and input by the science team preparing the Oil Budget Calculator report.

The technological framework developed for the calculator, including the separation between data entry, model calculations, and reporting was created to be extensible and scalable to other incidents using variations on the model and to entirely different applications of similar concepts. Further discussions with NIC personnel will determine the eventual fate of the tool beyond the Deepwater Horizon incident.

### **References**

American Society for Testing and Materials. 2006. *ASTM D635 - 10 Standard Test Method for Rate of Burning and/or Extent and Time of Burning of Plastics in a Horizontal Position*. ASTM.

Apache Project. 2010. Retrieved August 20, 2010 from Apache Web Server Web Site: <http://httpd.apache.org/>

Apache.org. 2010. Retrieved August 20, 2010 from Apache Subversion: <http://subversion.apache.org/>

Grails Community. 2010. Retrieved August 20, 2010 from Grails Web Site:  
<http://www.grails.org/>

JBoss Community. 2010. Retrieved August 20, 2010 from Hibernate Web Site:  
<http://www.hibernate.org/>

JFree.org. 2010. *JFreeChart*. Retrieved August 22, 2010 from  
<http://www.jfree.org/jfreechart/>

JOSSO Community. 2010. Retrieved August 20, 2010 from JOSSO - Java Open Single Sign-On Project Home: <http://www.josso.org/>

Lehr, Bill and members of the Deepwater Horizon MC252 Gulf Incident Flow Rate Technical Group. July 31, 2010. Email correspondence to the Oil Budget Calculator engineering team with official government estimates for Deepwater Horizon MC252 discharge rate. (Official report from the Flow Rate Technical Group on the calculations and assumptions for discharge rates being prepared at time of writing.)

National Incident Command Personnel. 2010. Personal communication with National Incident Command staff on the requirements for the Deepwater Horizon Oil Budget Calculator; notes captured in USGS Jira project management system. (R. S. Bristol, Interviewer)

National Oceanic and Atmospheric Administration (NOAA). August 4, 2010. Federal Science Report Details Fate of Oil from BP Spill.  
[http://www.noaa.gov/stories2010/20100804\\_oil.html](http://www.noaa.gov/stories2010/20100804_oil.html)

PostgreSQL. 2010. Retrieved August 20, 2010 from PostgreSQL Web Site:  
<http://www.postgresql.org/>

R Project. 20-August). Retrieved August 20, 2010 from The R Project for Statistical Computing: <http://www.r-project.org/>

Red Hat. 2010. Retrieved August 20, 2010 from Red Hat Linux Web Site:  
<http://www.redhat.com/>

**Disclaimer:** Any use of trade, product, or form names is for descriptive purposes only and does not imply endorsement by the U.S. Government.



## Appendix 3

### A3 Data Input Used by Calculator

Date	Government Estimate of Discharge VRG bbls	Inland Recovery IR tons	Oil Burned VBU bbls	Oil Collected via RITT/TopHat VDT bbls	Oily Water Collected VOW bbls	Subsurface Dispersants VCBg gallons	Surface Dispersants VCSg gallons
04/20/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
04/21/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
04/22/2010	62200.00	0.00	0.00	0.00	0.00	0.00	1701.00
04/23/2010	62100.00	0.00	0.00	0.00	1630.00	0.00	0.00
04/24/2010	61900.00	0.00	0.00	0.00	155.00	0.00	0.00
04/25/2010	61800.00	0.00	0.00	0.00	0.00	0.00	9818.00
04/26/2010	61700.00	0.00	0.00	0.00	7832.00	0.00	14486.00
04/27/2010	61600.00	0.00	0.00	0.00	18557.00	0.00	27078.00
04/28/2010	61500.00	0.00	95.00	0.00	3306.00	0.00	42143.00
04/29/2010	61400.00	0.00	0.00	0.00	3245.00	0.00	40913.00
04/30/2010	61300.00	0.00	0.00	0.00	1427.00	2196.00	4900.00
05/01/2010	61200.00	0.00	0.00	0.00	992.00	0.00	11653.00
05/02/2010	61000.00	0.00	0.00	0.00	0.00	3399.00	0.00
05/03/2010	60900.00	0.00	0.00	0.00	0.00	5812.00	0.00
05/04/2010	60800.00	0.00	0.00	0.00	9996.00	7580.00	34273.00
05/05/2010	60700.00	0.00	880.00	0.00	0.00	0.00	49575.00
05/06/2010	60600.00	0.00	6155.00	0.00	21452.00	0.00	28770.00
05/07/2010	60500.00	0.00	2010.00	0.00	13788.00	0.00	7270.00
05/08/2010	60400.00	0.00	0.00	0.00	26189.00	0.00	41690.00
05/09/2010	60200.00	0.00	0.00	0.00	33865.00	0.00	55932.00
05/10/2010	60100.00	0.00	0.00	0.00	8957.00	9460.00	56220.00
05/11/2010	60000.00	0.00	0.00	0.00	0.00	2100.00	7940.00
05/12/2010	59900.00	0.00	0.00	0.00	0.00	0.00	39710.00
05/13/2010	59800.00	0.00	0.00	0.00	0.00	0.00	41620.00
05/14/2010	59700.00	0.00	0.00	0.00	0.00	0.00	44031.00
05/15/2010	59600.00	0.00	0.00	500.00	0.00	7222.00	14208.00
05/16/2010	59400.00	0.00	0.00	900.00	6987.00	6300.00	670.00
05/17/2010	59300.00	0.00	3175.00	1030.00	23873.00	7980.00	13213.00
05/18/2010	59200.00	0.00	785.00	1200.00	13903.00	3450.00	12386.00
05/19/2010	59100.00	0.00	27350.00	3000.00	11849.00	4879.00	3352.00
05/20/2010	59000.00	0.00	11150.00	2200.00	13600.00	14151.00	1.00
05/21/2010	58900.00	0.00	0.00	2175.00	13126.00	14400.00	29892.00
05/22/2010	58800.00	0.00	0.00	1361.00	12025.00	14130.00	52946.00
05/23/2010	58700.00	0.00	950.00	1120.00	14108.00	14738.00	18104.00
05/24/2010	58500.00	0.00	2450.00	0.00	4135.00	14494.00	630.00
05/25/2010	58400.00	0.00	350.00	6078.00	3943.00	12925.00	200.00
05/26/2010	58300.00	0.00	450.00	2596.00	7681.00	11529.00	7752.00
05/27/2010	58200.00	0.00	700.00	0.00	9936.00	14347.00	1029.00
05/28/2010	58100.00	0.00	0.00	0.00	10110.00	13670.00	18445.00
05/29/2010	58000.00	0.00	1200.00	0.00	27319.00	14588.00	2900.00
05/30/2010	57900.00	0.00	2550.00	0.00	10471.00	13073.00	17631.00
05/31/2010	57700.00	0.00	16550.00	0.00	11845.00	13936.00	11686.00
06/01/2010	57600.00	0.00	7900.00	0.00	11719.00	12201.00	0.00
06/02/2010	57500.00	0.00	700.00	0.00	18241.00	8073.00	3375.00

Date	Government Estimate of Discharge VRG bbls	Inland Recovery IR tons	Oil Burned VBU bbls	Oil Collected via RITT/TopHat VDT bbls	Oily Water Collected VOW bbls	Subsurface Dispersants VCBg gallons	Surface Dispersants VCSg gallons
06/03/2010	60000.00	0.00	0.00	0.00	4833.00	17753.00	6200.00
06/04/2010	59900.00	0.00	0.00	6087.00	8912.00	20655.00	13701.00
06/05/2010	59800.00	0.00	0.00	10496.00	8568.00	20306.00	125.00
06/06/2010	59700.00	0.00	0.00	11119.00	3123.00	13937.00	0.00
06/07/2010	59500.00	0.00	850.00	14842.00	11754.00	14732.00	10744.00
06/08/2010	59400.00	0.00	5450.00	15006.00	5350.00	13763.00	8324.00
06/09/2010	59300.00	0.00	3500.00	15816.00	12802.00	12112.00	2100.00
06/10/2010	59200.00	0.00	350.00	15402.00	9658.00	10163.00	5872.00
06/11/2010	59100.00	0.00	0.00	15554.00	18510.00	8447.00	14305.00
06/12/2010	59000.00	0.00	7550.00	15039.00	14459.00	4852.00	10356.00
06/13/2010	58900.00	0.00	16600.00	15208.00	12383.00	9916.00	36012.00
06/14/2010	58800.00	0.00	4300.00	15421.00	6083.00	9800.00	10741.00
06/15/2010	58600.00	0.00	1000.00	10448.00	11891.00	11726.00	2768.00
06/16/2010	58500.00	0.00	20150.00	18227.00	16995.00	8777.00	13593.00
06/17/2010	58400.00	0.00	13300.00	25295.00	9185.00	5763.00	12423.00
06/18/2010	58300.00	0.00	59550.00	24552.00	16436.00	9148.00	15711.00
06/19/2010	58200.00	0.00	2300.00	21041.00	12713.00	16911.00	8510.00
06/20/2010	58100.00	0.00	600.00	23291.00	11335.00	14070.00	19576.00
06/21/2010	58000.00	0.00	17050.00	25836.00	25583.00	14233.00	11217.00
06/22/2010	57800.00	0.00	0.00	27097.00	8828.00	9793.00	2008.00
06/23/2010	57700.00	0.00	0.00	16866.00	4660.00	9891.00	5099.00
06/24/2010	57600.00	0.00	0.00	23735.00	9875.00	12871.00	21088.00
06/25/2010	57500.00	0.00	0.00	24548.00	14530.00	12540.00	4633.00
06/26/2010	57400.00	0.00	0.00	22758.00	17462.00	12654.00	23022.00
06/27/2010	57300.00	0.00	0.00	24455.00	18641.00	11558.00	6626.00
06/28/2010	57200.00	0.00	0.00	23400.00	0.00	13174.00	0.00
06/29/2010	57100.00	0.00	0.00	25223.00	50.00	11560.00	324.00
06/30/2010	56900.00	0.00	0.00	23079.00	290.00	13609.00	0.00
07/01/2010	56800.00	0.00	0.00	25154.00	284.00	10558.00	17852.00
07/02/2010	56700.00	0.00	0.00	25291.00	74.00	11065.00	14210.00
07/03/2010	56600.00	0.00	0.00	25198.00	1966.00	11698.00	432.00
07/04/2010	56500.00	0.00	0.00	24960.00	854.00	10429.00	3079.00
07/05/2010	56400.00	0.00	0.00	24982.00	7417.00	11688.00	803.00
07/06/2010	56300.00	0.00	0.00	24761.00	218.00	11655.00	473.00
07/07/2010	56100.00	0.00	0.00	24578.00	156.00	11770.00	1245.00
07/08/2010	56000.00	0.00	0.00	24379.00	26.00	11512.00	0.00
07/09/2010	55900.00	0.00	8300.00	24792.00	12140.00	10748.00	0.00
07/10/2010	55800.00	0.00	9850.00	15199.00	25924.00	13210.00	0.00
07/11/2010	55700.00	0.00	5300.00	8235.00	18296.00	15420.00	0.00
07/12/2010	53000.00	0.00	0.00	8302.00	9397.00	14038.00	0.00
07/13/2010	52900.00	0.00	1400.00	17064.00	9998.00	13997.00	999.00
07/14/2010	52700.00	0.00	1100.00	12843.00	25551.00	13746.00	0.00
07/15/2010	0.00	0.00	350.00	9307.00	10793.00	8391.00	0.00
07/16/2010	0.00	0.00	1100.00	0.00	14135.00	0.00	0.00
07/17/2010	0.00	0.00	0.00	0.00	7601.00	0.00	0.00
07/18/2010	0.00	0.00	0.00	0.00	5122.00	0.00	0.00
07/19/2010	0.00	0.00	100.00	0.00	3113.00	0.00	200.00



Date	Government	Inland	Oil	Oil Collected	Oily Water	Subsurface	Surface
	Estimate of Discharge VRG bbls	Recovery IR tons	Burned VBU bbls	via RITT/TopHat VDT bbls	Collected VOW bbls	Dispersants VCBg gallons	Dispersants VCSg gallons
07/20/2010	0.00	0.00	0.00	0.00	930.00	0.00	0.00
07/21/2010	0.00	0.00	0.00	0.00	56.00	0.00	0.00
07/22/2010	0.00	0.00	0.00	0.00	142.00	0.00	0.00
07/23/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
07/24/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
07/25/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
07/26/2010	0.00	0.00	0.00	0.00	1.00	0.00	0.00
07/27/2010	0.00	0.00	0.00	0.00	226.00	0.00	0.00
07/28/2010	0.00	0.00	0.00	0.00	390.00	0.00	0.00
07/29/2010	0.00	0.00	0.00	0.00	264.00	0.00	0.00
07/30/2010	0.00	0.00	0.00	0.00	35.00	0.00	0.00
07/31/2010	0.00	0.00	0.00	0.00	79.00	0.00	0.00
08/01/2010	0.00	0.00	0.00	0.00	105.00	0.00	0.00
08/02/2010	0.00	0.00	0.00	0.00	51.00	0.00	0.00
08/03/2010	0.00	0.00	0.00	0.00	15.00	0.00	0.00
08/04/2010	0.00	0.00	0.00	0.00	11.00	0.00	0.00
08/05/2010	0.00	0.00	0.00	0.00	2.00	0.00	0.00
08/06/2010	0.00	0.00	0.00	0.00	98.00	0.00	0.00
08/07/2010	0.00	0.00	0.00	0.00	2.00	0.00	0.00
08/08/2010	0.00	0.00	0.00	0.00	179.00	0.00	0.00
08/09/2010	0.00	0.00	0.00	0.00	2.00	0.00	0.00
08/10/2010	0.00	41693.00	0.00	0.00	170.00	0.00	0.00
08/11/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/12/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/13/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/14/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/15/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/16/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/17/2010	0.00	4222.00	0.00	0.00	0.00	0.00	0.00
08/18/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/19/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/20/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/21/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/22/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/23/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/24/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/25/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/26/2010	0.00	2424.00	0.00	0.00	0.00	0.00	0.00
08/27/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/28/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/29/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/30/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
08/31/2010	0.00	2134.00	0.00	0.00	0.00	0.00	0.00
09/01/2010	0.00	126.00	0.00	0.00	0.00	0.00	0.00
09/02/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
09/03/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
09/04/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00

---

Date	Government	Inland	Oil	Oil Collected	Oily Water	Subsurface	Surface
	Estimate of	Recovery	Burned	via	Collected	Dispersants	Dispersants
	Discharge	IR	VBU	RITT/TopHat	VOW	VCBg	VCSg
	VRG			VDT		gallons	gallons
	bbls	tons	bbls	bbls	bbls		
09/05/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
09/06/2010	0.00	427.00	0.00	0.00	0.00	0.00	0.00
09/07/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
09/08/2010	0.00	429.00	0.00	0.00	0.00	0.00	0.00
09/09/2010	0.00	405.00	0.00	0.00	0.00	0.00	0.00
09/10/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
09/11/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
09/12/2010	0.00	562.00	0.00	0.00	0.00	0.00	0.00
09/13/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
09/14/2010	0.00	0.00	0.00	0.00	0.00	0.00	0.00
09/15/2010	0.00	493.00	0.00	0.00	0.00	0.00	0.00



## Appendix 4

### A4 ICS 209 Form (Oil Budget Component)

<b>1. Incident Name</b>	<b>2. Operational Period (Date / Time)</b> From:    To:                      Time of Report	<b>ICS 209-CG OIL/HAZMAT ATTACHMENT</b>	
<b>3. HAZMAT/Oil Spill Status (Estimated, in gallons)</b>			
Common Name(s):			
UN Number:	<input type="checkbox"/> Secured	<input type="checkbox"/> Unsecured	
CAS Number:	Remaining Potential (bbl):		
	Rate of Spillage (bbl/hr):		
	Adjustments To Previous Operational Period	Since Last Report	Total
Volume Spilled/Released			
<u>Mass Balance - HAZMAT/Oil Budget</u>			
Recovered HAZMAT/Oil			
Evaporation/Airborne			
Natural Dispersion			
Chemical Dispersion			
Burned			
Floating, Contained			
Floating, Uncontained			
Onshore			
Total HAZMAT/Oil accounted for:	N/A	N/A	
Comments:			
<b>4. HAZMAT/Oil Waste Management (Estimated, Since Last Report)</b>			
	Recovered	Disposed	Stored
HAZMAT/Oil (bbl)			
Oily Liquids (bbl)			
Liquids (bbl)			
Oily Solids (tons)			
Solids (tons)			
Comments:			
<b>5. HAZMAT/Oil Shoreline Impacts (Estimated in miles)</b>			
Degree of Impact	Affected	Cleaned	To Be Cleaned
Light			
Medium			
Heavy			
Total			
Comments:			

## Appendix 5

### A5 Oil Properties

Table A5.1: Macondo reservoir fluid composition, based upon Pencor data provided by BP.

Gas-Liquid Ratio 2.89 scf/stb		Vapor Gravity	0.807	(Air = 1.00)
		API Gravity	35.2	°API at 60 °F
		Water Content	0.02	(Water Free) weight %
Component (Symbol / Name)		Atmospheric Liquid (mole %)	Atmospheric Liquid (weight %)	
N <sub>2</sub>	Nitrogen	0.000	0.000	
CO <sub>2</sub>	Carbon Dioxide	0.000	0.000	
H <sub>2</sub> S	Hydrogen Sulfide	0.000	0.000	
C1	Methane	0.003	0.000	
C2	Ethane	0.148	0.021	
C3	Propane	0.456	0.097	
iC4	i-Butane	0.263	0.073	
nC4	n-Butane	0.958	0.268	
iC5	i-Pentane	0.943	0.327	
nC5	n-Pentane	1.536	0.533	
C6	Hexanes	3.977	1.648	
C7	Heptanes	8.318	3.747	
C8	Octanes	11.541	5.960	
C9	Nonanes	9.103	5.250	
C10	Decanes	7.837	5.048	
C11	Undecanes	5.965	4.215	
C12	Dodecanes	4.982	3.855	
C13	Tridecanes	4.754	4.000	
C14	Tetradecanes	4.254	3.886	
C15	Pentadecanes	3.563	3.528	
C16	Hexadecanes	3.455	3.688	
C17	Heptadecanes	2.755	3.139	
C18	Octadecanes	2.685	3.240	
C19	Nonadecanes	2.274	2.874	
C20	Eicosanes	1.963	2.594	



C21 Heneicosanes	1.599	2.237
C22 Docosanes	1.421	2.083
C23 Triacosanes	1.281	1.959
C24 Tetracosanes	1.149	1.827
C25 Pentacosanes	0.938	1.555
C26 Hexacosanes	0.850	1.467
C27 Heptacosanes	0.892	1.603
C28 Octacosanes	0.791	1.474
C29 Nonacosanes	0.704	1.361
C30 Triacontanes	0.642	1.283
C31 Hentriacontanes	0.607	1.255
C32 Dotriacontanes	0.543	1.159
C33 Tritriacontanes	0.470	1.035
C34 Tetratriacontanes	0.458	1.039
Pentatriacontane		
C35 s	0.379	0.885
C36 Hexatriacontanes	0.346	0.832
Heptatriacontane		
C37 s	0.333	0.823
C38 Octatriacontanes	0.316	0.802
C39 Nonatriacontanes	0.273	0.712
C40 Tetracontanes	0.268	0.717
C41 Hentetracontanes	0.195	0.534
C42 Dotetracontanes	0.217	0.610
C43 Tritetracontanes	0.194	0.557
Tetratetracontane		
C44 s	0.186	0.548
Pentatetracontan		
C45 es	0.169	0.508
Hexatetracontane		
C46 s	0.146	0.450
Heptatetracontan		
C47 es	0.160	0.503
Octactetracontane		
C48 s	0.135	0.434
Nonatetracontane		
C49 s	0.123	0.402
Pentacontanes		
C50+ Plus	2.482	11.355
Total	100.000	100.000
Calculated Mole Weight	208.03	
Measured Mole Weight	208.03	

Table A5.2: Analysis by Louisiana State University of fresh oil samples compared to reference oil.

<b>Source Oil, Pre-spill</b> <b>Sample Weight: 310 mg</b> <b>Final Extracted Volume: 30 mL</b>		<b>LSU ID#: Lab Ref Oil</b> <b>South Louisiana Crude</b> <b>Sample Weight: 500 mg</b> <b>Final Extracted Volume: 20 mL</b>	
<b>Alkane Analyte:</b>	<b>Concentration (ng/mg)</b>	<b>Alkane Analyte:</b>	<b>Concentration (ng/mg)</b>
nC-10 Decane	2600	nC-10 Decane	2600
nC-11 Undecane	2600	nC-11 Undecane	2700
nC-12 Dodecane	2600	nC-12 Dodecane	2600
nC-13 Tridecane	2500	nC-13 Tridecane	2600
nC-14 Tetradecane	2400	nC-14 Tetradecane	2300
nC-15 Pentadecane	2000	nC-15 Pentadecane	2200
nC-16 Hexadecane	1800	nC-16 Hexadecane	2000
nC-17 Heptadecane	1700	nC-17 Heptadecane	1900
Pristane	960	Pristane	970
nC-18 Octadecane	1500	nC-18 Octadecane	1700
Phytane	770	Phytane	910
nC-19 Nonadecane	1300	nC-19 Nonadecane	1500
nC-20 Eicosane	1300	nC-20 Eicosane	1400
nC-21 Heneicosane	1100	nC-21 Heneicosane	1300
nC-22 Docosane	1000	nC-22 Docosane	1200
nC-23 Tricosane	940	nC-23 Tricosane	1100
nC-24 Tetracosane	890	nC-24 Tetracosane	1000
nC-25 Pentacosane	600	nC-25 Pentacosane	620
nC-26 Hexacosane	510	nC-26 Hexacosane	510
nC-27 Heptacosane	350	nC-27 Heptacosane	360
nC-28 Octacosane	300	nC-28 Octacosane	310
nC-29 Nonacosane	250	nC-29 Nonacosane	260
nC-30 Triacontane	230	nC-30 Triacontane	230
nC-31 Hentriacontane	150	nC-31 Hentriacontane	190
nC-32 Dotriacontane	120	nC-32 Dotriacontane	150
nC-33 Tritriacontane	100	nC-33 Tritriacontane	110
nC-34 Tetratriacontane	90	nC-34 Tetratriacontane	110
nC-35 Pentatriacontane	92	nC-35 Pentatriacontane	110
<b>Total Alkanes</b>	<b>30752</b>	<b>Total Alkanes</b>	<b>32940</b>
<b>LSU ID#: 2010133-02</b> <b>Source Oil</b> <b>Sample Weight: 310 mg</b>		<b>LSU ID#: Lab Ref Oil</b> <b>South Louisiana Crude</b> <b>Sample Weight: 500 mg</b>	




Final Extracted Volume: 30 mL		Final Extracted Volume: 20 mL	
<b>Aromatic Analyte:</b>	<b>Concentration (ng/mg)</b>	<b>Aromatic Analyte:</b>	<b>Concentration (ng/mg)</b>
Naphthalene	750	Naphthalene	710
C1-Naphthalenes	1600	C1-Naphthalenes	1300
C2-Naphthalenes	2000	C2-Naphthalenes	1500
C3-Naphthalenes	1400	C3-Naphthalenes	1100
C4-Naphthalenes	690	C4-Naphthalenes	590
Fluorene	130	Fluorene	100
C1-Fluorenes	340	C1-Fluorenes	270
C2-Fluorenes	390	C2-Fluorenes	270
C3- Fluorenes	300	C3- Fluorenes	240
Dibenzothiophene	53	Dibenzothiophene	56
C1-Dibenzothiophenes	170	C1-Dibenzothiophenes	210
C2-Dibenzothiophenes	220	C2-Dibenzothiophenes	280
C3- Dibenzothiophenes	160	C3- Dibenzothiophenes	240
Phenanthrene	290	Phenanthrene	200
C1-Phenanthrenes	680	C1-Phenanthrenes	360
C2-Phenanthrenes	660	C2-Phenanthrenes	340
C3-Phenanthrenes	400	C3-Phenanthrenes	200
C4-Phenanthrenes	200	C4-Phenanthrenes	84
Anthracene	6.1	Anthracene	6.2
Fluoranthene	4.2	Fluoranthene	4.5
Pyrene	8.9	Pyrene	7.1
C1- Pyrenes	68	C1- Pyrenes	43
C2- Pyrenes	84	C2- Pyrenes	31
C3- Pyrenes	96	C3- Pyrenes	31
C4- Pyrenes	54	C4- Pyrenes	20
Naphthobenzothiophene	11	Naphthobenzothiophene	7.8
C-1		C-1	
Naphthobenzothiophenes	48	Naphthobenzothiophenes	30
C-2		C-2	
Naphthobenzothiophenes	37	Naphthobenzothiophenes	30
C-3		C-3	
Naphthobenzothiophenes	22	Naphthobenzothiophenes	25
Benzo (a) Anthracene	5.5	Benzo (a) Anthracene	5.4
Chrysene	36	Chrysene	14
C1- Chrysenes	100	C1- Chrysenes	28
C2- Chrysenes	100	C2- Chrysenes	27
C3- Chrysenes	54	C3- Chrysenes	18
C4- Chrysenes	19	C4- Chrysenes	5.6
Benzo (b) Fluoranthene	2.3	Benzo (b) Fluoranthene	1.7

---

Benzo (k) Fluoranthene	1.8	Benzo (k) Fluoranthene	1.5
Benzo (e) Pyrene	6.6	Benzo (e) Pyrene	2.9
Benzo (a) Pyrene	1.0	Benzo (a) Pyrene	1.0
Perylene	0.92	Perylene	0.89
Indeno (1,2,3 - cd) Pyrene	0.20	Indeno (1,2,3 - cd) Pyrene	0.22
Dibenzo (a,h) anthracene	1.3	Dibenzo (a,h) anthracene	0.92
Benzo (g,h,i) perylene	1.2	Benzo (g,h,i) perylene	1.1
<i>Total Aromatics</i>	<i>11203</i>	<i>Total Aromatics</i>	<i>8394</i>



## Appendix 6: SINTEF Report

 <b>SINTEF</b>  <b>SINTEF Materials and Chemistry</b>  P.O.Box: 4760 Sluppen Address: NO-7465 Trondheim, NORWAY Location: Bratterkaia 17C, 4. etg. Telephone: +47 4000 3730 Fax: +47 930 70730  Enterprise No.: NO 948 007 029 MVA		<h1>SINTEF REPORT</h1>	
		TITLE	
		Laboratory study of the dispersibility of DWH surface emulsions.	
		AUTHOR(S)	
		Frode Leirvik, Kjersti Almås and Per S. Daling	
		CLIENT(S)	
		BP	
REPORT NO.	CLASSIFICATION	CLIENTS REF.	
SINTEF A16134	Unrestricted	David Fritz	
CLASS. THIS PAGE	ISBN	PROJECT NO.	NO. OF PAGES/APPENDICES
Unrestricted	978-82-14-05008-0	801599	17
ELECTRONIC FILE CODE		PROJECT MANAGER (NAME, SIGN.)	CHECKED BY (NAME, SIGN.)
Report dispersibility testing DWH_final.docx		Per Daling	Ivar Singaas
FILE CODE	DATE	APPROVED BY (NAME, POSITION, SIGN.)	
	2010-07-13	Tore Aunaas, Research Director	
<b>ABSTRACT</b> A study using the MNS and IFP dispersibility tests has been performed at SINTEF on three emulsions from the DWH spill. <u>Difference in effectiveness of different dispersant products:</u> The products Corexit 9500, Corexit 9527 and OSR 52 were tested on two emulsions with different degrees of weathering (Viscosities of 2700 and 7200mPas). Corexit 9500 show good efficiency for both emulsions, Corexit 9527 showed reduced effectiveness for the heavily weathered emulsion, while OSR 52 showed reduced dispersibility for both tested emulsions <u>Dispersant dosage:</u> Tests were performed on two emulsions with a range of dispersant dosages. Results show that a relatively high dosage (DER = 1:25 or higher) was required to obtain good dispersant efficiency for the heavily weathered emulsion. For less weathered emulsions a lower dosage was sufficient.. -Aerial application of dispersants at a low dosage (5USGPA) can be recommended for moderately weathered emulsion (dark brown colour) -Boat application is recommended for highly weathered emulsions (light brown/orange). A high dosage should be used (25USGPA), and reapplication should be considered if necessary. <u>Mixing energy requirements:</u> Results from tests with different energy input were compared to assess the requirement for mixing energy on the sea surface to disperse the emulsions. Results show that as long as mixing energy is sufficiently high (i.e. breaking waves) even the most weathered sample showed good dispersibility (given sufficient dosage of dispersants). At low sea states artificial mixing energy may be a recommended option 0.5-1 hour after dispersant application. <u>Viscosity Limit for use of dispersants:</u> Testing indicate reduced dispersibility for emulsions with viscosity >9000 mPas, and poor dispersibility >25000mPas. These limits are valid for DER=1:25.			
KEYWORDS	ENGLISH	NORWEGIAN	
GROUP 1			
GROUP 2			
SELECTED BY AUTHOR			

## TABLE OF CONTENTS

<b>1</b>	<b>Background .....</b>	<b>3</b>
<b>2</b>	<b>Experiemental Setup.....</b>	<b>4</b>
2.1	The MNS Test .....	4
2.2	The IFP Test .....	5
<b>3</b>	<b>Sampling and Physical Characterisation of the Test Emulsions.....</b>	<b>6</b>
<b>4</b>	<b>Experimental Results.....</b>	<b>8</b>
4.1	Testing with Various Dispersants.....	8
4.2	Testing with Various Dispersant Emulsion Ratios (DER) .....	9
4.3	Testing with Different Energy Input .....	10
4.4	Chemical Dispersibility vs Viscosity .....	11
4.5	Visual Observations During Testing .....	13
<b>5</b>	<b>Conclusions and Operational Recommendations .....</b>	<b>15</b>
5.1	Testing with different dispersant products .....	15
5.2	Dispersant dosage requirement .....	15
5.3	Sea state dependency .....	16
5.4	Viscosity limit for use of dispersants .....	16
<b>6</b>	<b>References .....</b>	<b>17</b>



## 1 Background

A sampling campaign were conducted in the vicinity of the DWH release point cruise in the period June 2-5. Three samples were taken of weathered DWH-oil and the physical properties of the samples have been characterised. The sampled emulsions had a span in weathering time estimated to 1 to 5 days on the sea surface. The span in weathering gives the emulsions very different physical properties. Sampling and physical characterisation of the emulsions are described in the cruise report (Leirvik,*et.al.*2010).

As the physical properties change the dispersibility of the emulsions will change. From an operational point of view this would mean that different dispersant application strategies may be needed for emulsions at different stages of weathering.

A dispersibility study has been performed at SINTEF on the sampled emulsions. The following operational aspects have been studied:

- Dosage of dispersant at different stages of emulsion weathering.
- Effectiveness of three dispersant products at different stages of emulsion weathering
- Mixing energy required to efficiently disperse the DWH emulsions.
- Viscosity Limit for the dispersibility of DWH emulsions.

The IFP and MNS dispersibility tests are described in Chapter 2. Sampling positions and the physical properties of the emulsions are summarised in Chapter 3. Results from the dispersibility testing are given in Chapter 4. Conclusions and operational recommendations are given in Chapter 5.

## 2 Experimental Setup

There are several different tests for evaluating the effectiveness of chemical dispersants. Energy input will differ in different tests, and the obtained effectiveness will be representative for different wave energies. Most tests in this study is performed using the medium-to-high energy MNS test (representing breaking wave conditions). The MNS test is described in chapter 2.1. To assess the energy requirement for dispersing emulsions at different stages of weathering. Tests have also been performed with the low energy IFP test. The IFP test is described in chapter 2.2 .

### 2.1 The MNS Test

The MNS test (Mackay-Nadeau-Szeto, Mackay and Szeto, 1980) is estimated to correspond to a medium to high sea-state condition with breaking waves. The energy input in this system, applied by streaming air across the oil/water surface, produces a circular wave motion. The sample of the oily water is taken under dynamic conditions after a mixing period of 5 min. The test apparatus is shown in Figure 2.1.

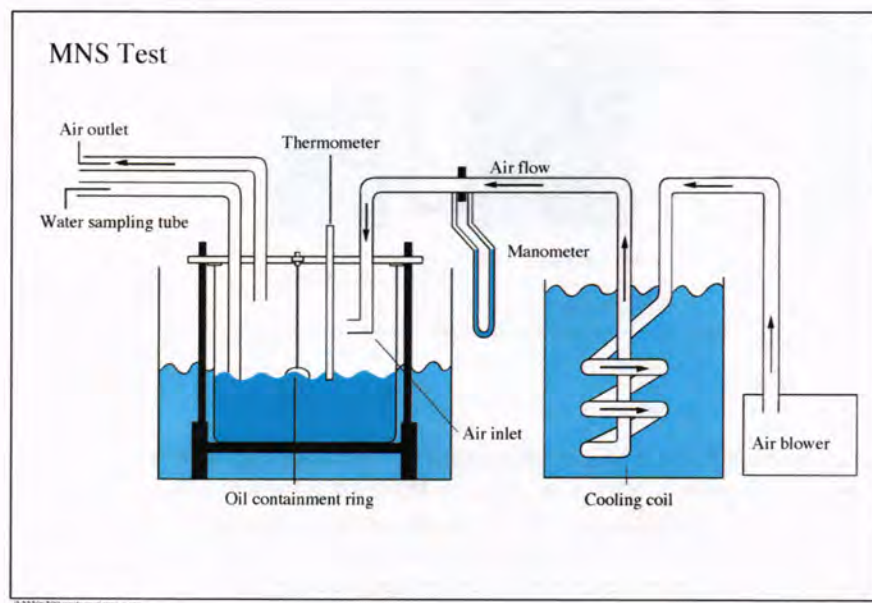


Figure 2.1 MNS test apparatus.

When the test results in the MNS test shows an effectiveness  $> 70 - 80\%$ , the emulsion is considered to be easily (good) dispersible. In the range down to  $5\%$  effectiveness, the emulsion is still dispersible, however, the dispersion process may need some more time. Effectiveness  $< 5\%$  means that the emulsions is poorly dispersible when using dispersant. These laboratory-derived dispersibility borders have been established based on correlations to field studies (Daling and Strøm, 1999).



## 2.2 The IFP Test

The IFP Test (Institut Francais du Petrole test, Bocard *et al*, 1984) is a low energy test estimated to represent low wave energies (2 - 5 m/s wind speed). A ring beating up and down in the test vessel at a given frequency, gives energy input to the seawater column. The water column is continuously diluted, which gives a more realistic approach to field conditions compared to other tests. The test apparatus is shown in Figure 2.2.

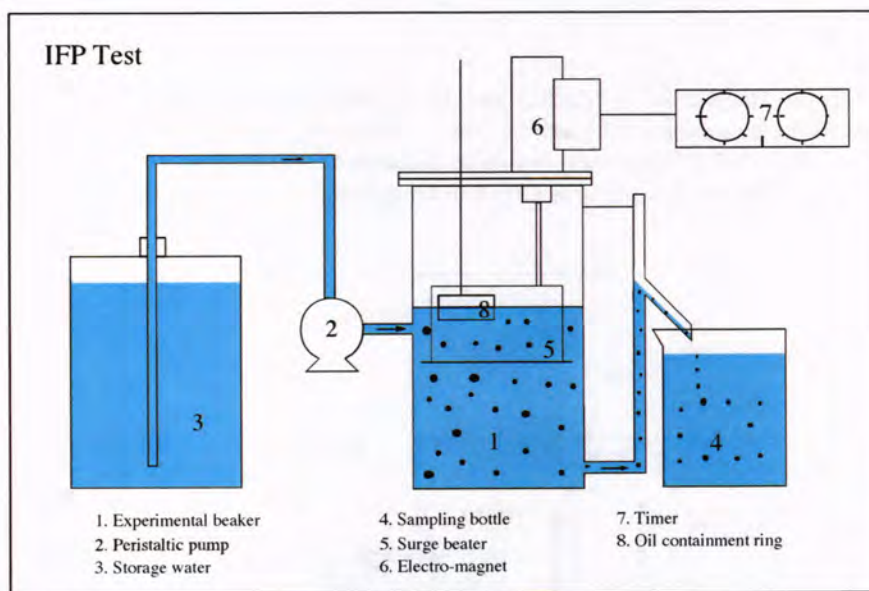


Figure 2.2 IFP test apparatus.

When the test results in the IFP test shows an effectiveness ~ 50%, the emulsion is considered to be easily (good) dispersible- even at low sea conditions. If the effectiveness is below 40 -50% effectiveness, the emulsion may still be dispersible. During a response operation under calm conditions in the field, additional mixing energy may be required. This extra turbulence can be supplied by e.g. propel-washing from vessels or by using high delivery FI-FI monitors 1-2 hours after a dispersant application in order to fulfil the dispersion process.

### 3 Sampling and Physical Characterisation of the Test Emulsions

The physico-chemical properties of the sampled emulsions were characterised both on site, and in analysis at SINTEF laboratories. The results from the measurements are summarised in Table 3.1. The sampling positions are shown in Figure 3.1, and the samples are described in brief below. Sampling and analysis is described in detail in the cruise report (Leirvik *et.al.*,2010).

Table 3.1 Summary of physical and chemical properties of the sampled emulsion

	Position 2	Position 3	Position 4
Evaporative loss (wt%)	47	50	44
Estimated time on sea surface (days)	1-1.5	4-5	2-3
Emulsion thickness (mm)	1.3	2.6-3.7	0.9-1.4
Water content (vol%)	67	50	33
Density (g/ml)	0.961	0.975	0.956
Viscosity (mPas)10 s <sup>-1</sup> at 32°C	2770	7230	1250
Viscosity (mPas)10 s <sup>-1</sup> at 27°C	3540	12500	2030
Viscosity (mPas)10 s <sup>-1</sup> at 25°C		17900	
Viscosity (mPas)10 s <sup>-1</sup> at 22°C		24700	
Viscosity (mPas)10 s <sup>-1</sup> at 20°C		32300	

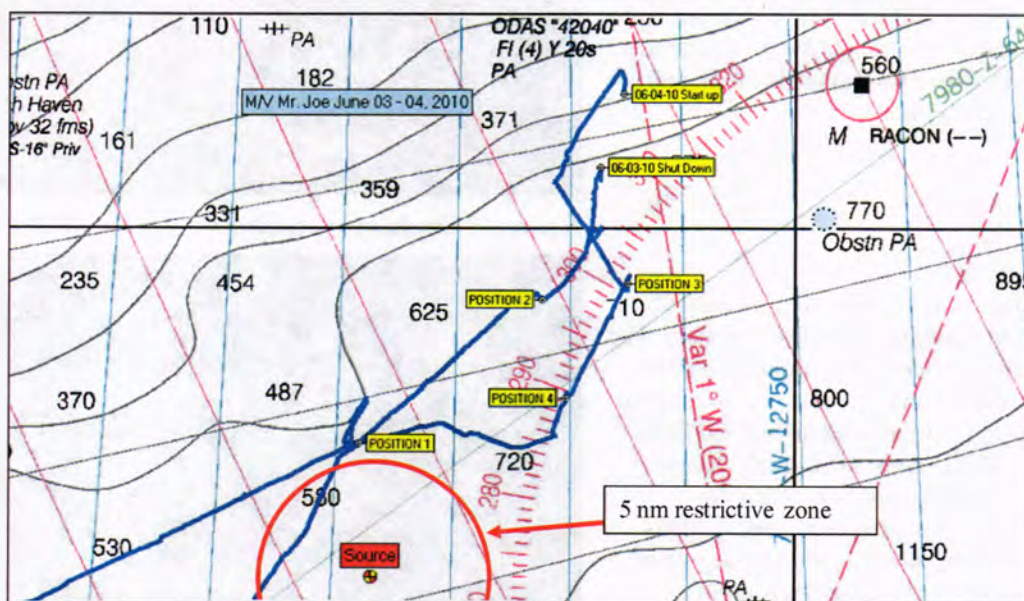


Figure 3.1 Sample positions compared to the DWH source



### Position 2

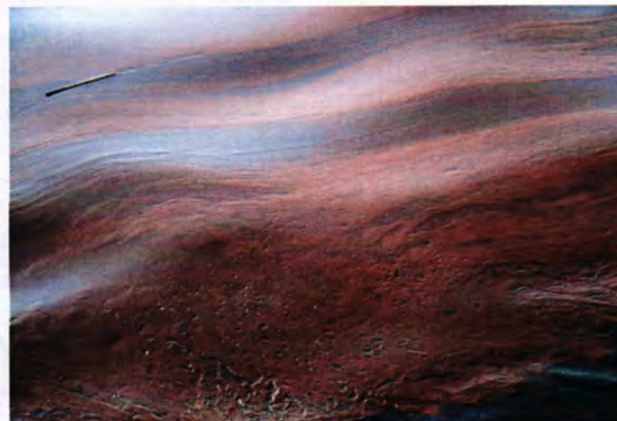
Samples were taken 12 nm miles NE (downwind) from the DWH source. The slick was only 100–200 m long and 2–10 m wide, and the oil was readily spreading on the sea surface. The emulsion was light brown in color, indicating significant emulsification.



*Figure 3.2 Emulsion in Position 2*

### Position 3

Samples were taken 17nm NE (downwind) from the DWH source. The slick was approximately 100 x 30 meters. The emulsion was light brown /orange /reddish in color and appeared more elastic and less prone to spreading on the sea surface, which indicates that this slick had been heavily weathered (evaporative loss, emulsification and photo-oxidation).



*Figure 3.3 Emulsion in Position 3*

### Position 4

Samples were taken 10 nm miles NE (downwind) from the DWH source. The sampled slick was approximately 50 x 30 meters, and was part of a continuous belt of slicks aligned downwind from the DWH source. The emulsion was dark brown, and darker than the emulsions in Positions 2 and 3. This dark color indicates a lower degree of weathering than the emulsion in Positions 2 and 3.



*Figure 3.4 Emulsion in Position 4*

## 4 Experimental Results

Laboratory tests have been performed to study different operational aspects. Comparative testing between different dispersant products is described in chapter 4.1. Results from testing with different dispersant dosages are shown in chapter 4.2. The requirement for energy is studied by testing with a low energy test representing sea states without breaking waves (IFP), and a Medium/high energy test (MNS) representing sea states with breaking waves. The results are shown in chapter 4.3. Viscosity limits for the dispersibility of DWH emulsions have been established by testing at increasing viscosities. This work is presented in Chapter 4.4.

### 4.1 Testing with Various Dispersants

Tests have been performed with different dispersant products for samples from position 2 and position 3. The three tested products were Corexit 9500, Corexit 9527 and OSR52. The comparative tests were performed with a **dispersant/emulsion-ratio (DER)** of 1:25.

Table 4.1 Results from the MNS test with different dispersant products. DER=1:25 in all tests.

	Position 3 (7200 mPas)	Position 2 (2770 mPas)
Corexit 9500	86	91
Corexit 9527	55	90
OSR 52	71	62
blank	2	44

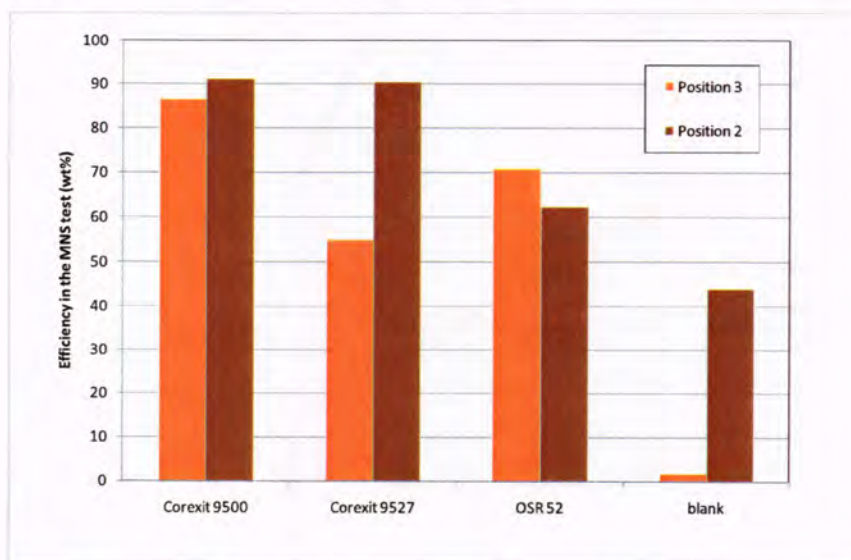


Figure 4.1 Results from the MNS test with different dispersant products. The dosage is 1:25 in all tests.

Reduced effectiveness in the MNS test is defined as <75% (Daling and Strøm,1999), while poor dispersibility is defined as <5%. The two Corexit products show good efficiency for the moderately weathered emulsion from position 2, while OSR 52 have a somehow reduced dispersibility. For the heavily weathered emulsion sampled in position 3, only Corexit 9500 show good dispersibility, while Corexit 9527 and OSR 52 showed reduced dispersibility.



#### 4.2 Testing with Various Dispersant Emulsion Ratios (DER)

Tests have been performed to study the dispersant effectiveness as a function of dispersant dosage. The tests have been done on the emulsions from position 3 and position 4. The medium/high energy MNS test has been used in the study. Results are shown in Table 4.2 and in Figure 4.2.

Table 4.2 Results from the MNS test with Corexit 9500 at different dispersant dosages

DER	%Effectiveness in the MNS test	
	Position 3 (7200 mPas)	Position 4 (1250mPas)
1:10	81	
1:25	86	99
1:50	44	99
1:100	31	96
1:250	15	99
no dispersant	2	48

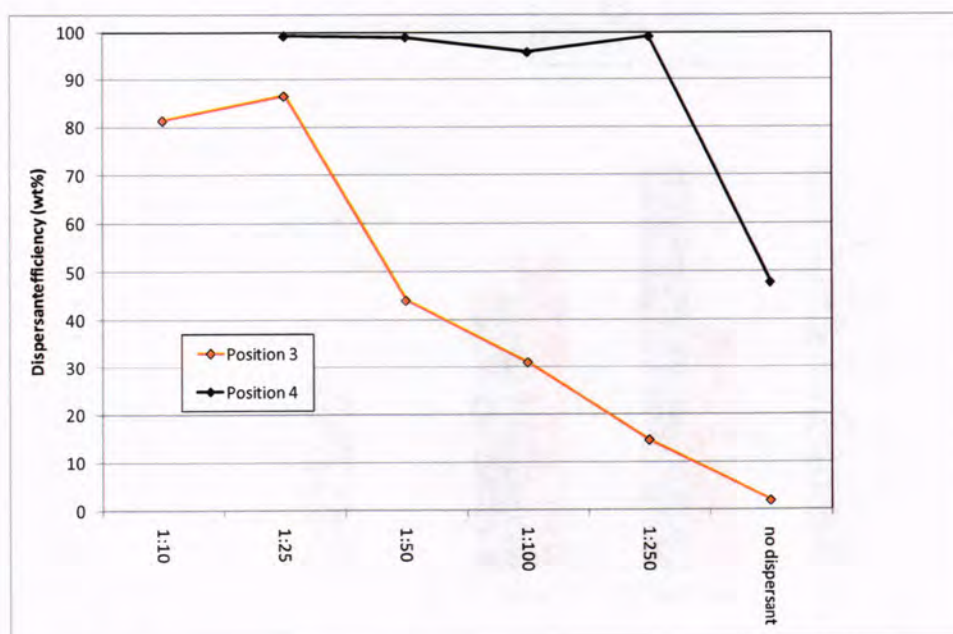


Figure 4.2 Results from the MNS testing with Corexit 9500 at different dispersant dosages.

Results show that at a dosage of 1:25 and higher, the dispersant efficiency is high for the highly weathered emulsion sampled in position 3. At lower dosages the efficiency will gradually decrease. Tests performed on the least weathered emulsion (position 4) show a good efficiency for all the tested dosages.

### 4.3 Testing with Different Energy Input

To study the effect of energy input on the dispersibility testing has been performed with both the MNS and IFP tests. The MNS is a high energy test representative to high sea states. The IFP test supply a relatively low energy input and is thought to be representative for low sea states without breaking waves. Results from testing with the two methods are shown in Table 4.3 and in Figure 4.3.

Table 4.3 Results from the MNS and IFP tests with samples from the different positions using Corexit 9500 and DER=25.

	Test effectiveness (wt%) w/ Corexit 9500 and DER=1:25	
	MNS	IFP
Position 4	99	46
Position 2	91	48
Position 3	86	34

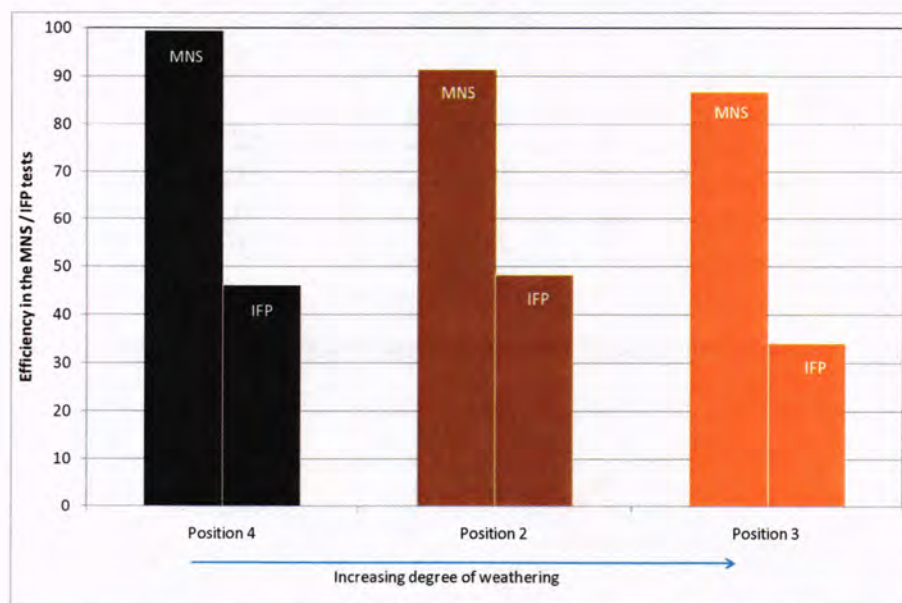


Figure 4.3 Results from the MNS and IFP tests with samples from the different positions using Corexit 9500 and DER=1:25.

Results show that with a dosage of 1:25 of Corexit 9500 all the samples show a relative good dispersibility for the MNS test. This is in accordance to the conclusions for the tests performed with the Field Effectiveness Test onboard Mr. Joe (Leirvik, *et.al.* 2010). For the low energy IFP samples from positions 2 and 4 show a slightly reduced dispersibility. The heavily weathered sample from position 3 show a significant reduction in dispersibility.



#### 4.4 Chemical Dispersibility vs Viscosity

In systematic weathering studies performed over the past 20 years at SINTEF (Daling and Strøm, 1999) an upper viscosity limit for an oil's dispersibility is determined. The viscosity limit is strongly related to the specific oil that is investigated. In this study with a limited amount of emulsions even the most weathered emulsion had a good dispersibility (at 32°C), a viscosity limit could not be established. Therefore additional testing was performed at lower temperatures to yield dispersibility data on higher viscosities. The results from all tests done with the MNS test is compared with the emulsion viscosities in Table 4.4.

Table 4.4 Results from the MNS test and the Viscosity of the emulsions. The table includes the additional tests performed at lower temperatures. Tests are performed with Corexit 9500 and DER=1:25.

Position	Temperature (°C)	Temperature (°F)	Viscosity at shear rate $10\text{s}^{-1}$ (mPas)	MNS dispersant efficiency (wt%)
4	32	90	1250	99
2	32	90	3700	91
3	32	90	7230	86
3	28	82	12500	66
3	25	77	17000	44
3	22	72	24700	16
3	20	68	32300	0

The dispersant effectiveness from the MNS test is plotted against the emulsion viscosity in Figure 4.4.

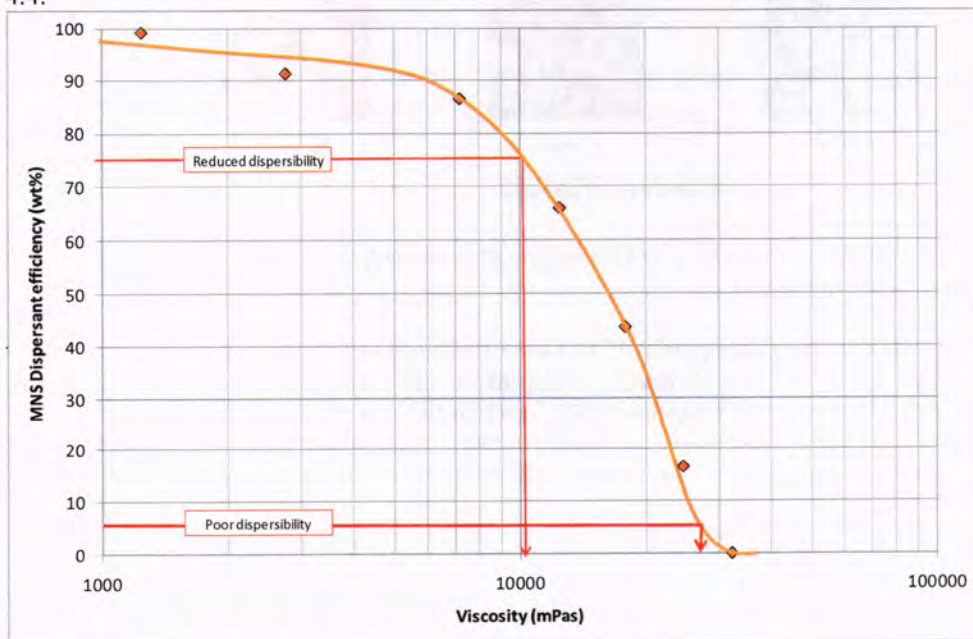


Figure 4.4 Dispersant efficiency in the MNS tests plotted against viscosity. Viscosity is reported at shear rate  $10\text{s}^{-1}$ .

As described in chapter 2.1, in the MNS test reduced dispersibility is defined as below 75%, while poor dispersibility is defined below 5%. Based on the curve drawn in Figure 4.4 reduced dispersibility will occur for viscosities above 10000mPas, while poor dispersibility can be expected for viscosities exceeding 25000 mPas. The drawn limits is based on studies using a dispersant/emulsion-ratio of 1:25.

The time it take for emulsions to reach the defined viscosity limits will depend on the wind speed and temperatures. The weatering time for the tested emulsions where estimated based on the evaporative loss of the samples in the cruise report (Leirvik,*et.al.*,2010). The estimated time on the sea surface for the emulsions is shown in Table 4.5.

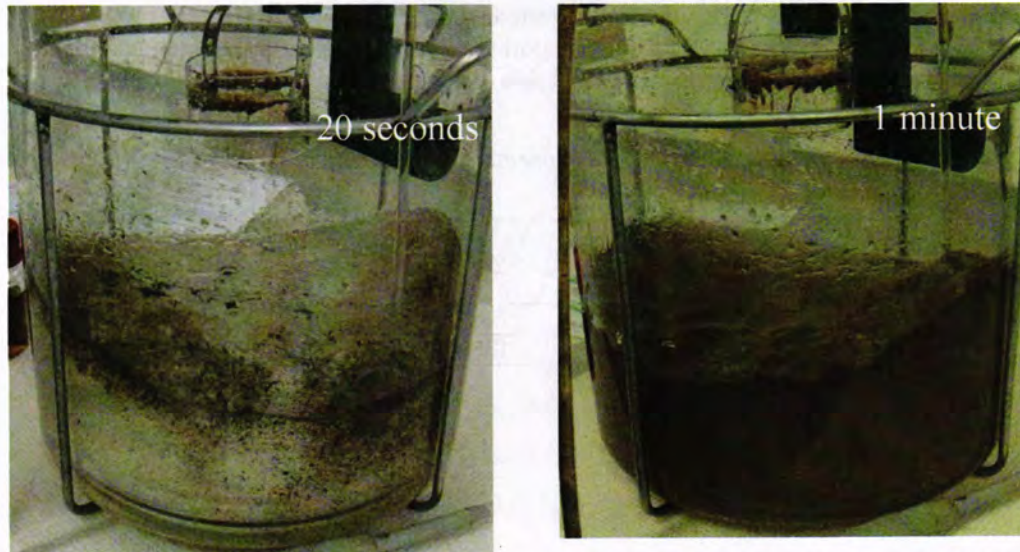
*Table 4.5 - Tentative time at sea based on evaporative loss and use of the SINTEF Oil Weathering Model.*

	Evaporative loss (wt%)	Viscosity (mPas)	Tentative time at sea
Position 2	47%	3700	2-3 days
Position 3	50%	7200	4-5 days
Position 4	44%	1250	1-2 days



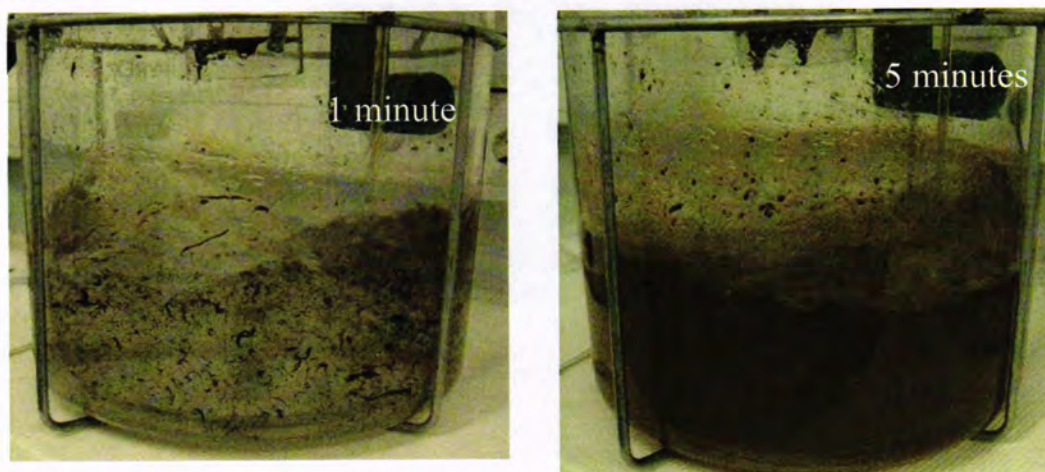
#### 4.5 Visual Observations During Testing

The moderately weathered emulsions sampled in position 2 and 4, generally dispersed well. For the emulsion from position 4 small droplets were formed within the first minute of the test as shown in *Figure 4.5*



*Figure 4.5 Gradual formation of small droplets with time in the MNS test. The image is from testing with Emulsion 4 and Corexit 9500 at DER=1:25*

In tests performed with the heavily weathered emulsion from position 3, the formation of small droplets was slower. After five minutes (the test duration) a significant amount of small droplets were formed, but strings of emulsion were still present in the water. This is demonstrated in *Figure 4.6*.



*Figure 4.6 Gradual formation of small droplets with time in the MNS test. The image is from testing with Emulsion 3 and Corexit 9500 at DER=1:25*



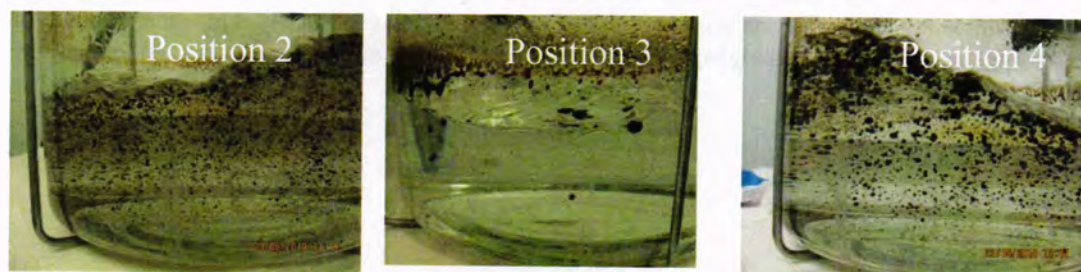
In the IFP test the same effects could be observed. For the less weathered emulsions (Position 2 and 4) small droplets were formed to make a cafe au lait coloured suspension. In the tests with the heavily weathered emulsion from position 3 the particles in suspension were non-spherical and larger in size. This is exemplified in Figure 4.7.



*Figure 4.7 Droplet formation in the IFP test with the emulsion from position 3. The test is performed with Corexit 9500 and DER=1:25.*

Even though not all dispersed particles are within the optimal particle size range, the dispersant will contribute to breaking up the viscous emulsion and significantly reduce the lifetime of oil on the sea surface.

Emulsions were also tested without addition of dispersants. Images from the tests are shown in Figure 4.8. The natural dispersion in the tests with emulsions from position 2 and 4 were relatively high. The emulsion from position 2 even formed quite small droplets. The emulsion from position 3 did not spread on the surface of the test vessel, and few droplets formed at all.



*Figure 4.8 Droplet formation in the MNS tests without addition of dispersant in the different positions.*



## 5 Conclusions and Operational Recommendations

### 5.1 Testing with different dispersant products

Tests have been performed with different dispersant products for one moderately weathered emulsion (position 2 / 2770mPas) and one heavily weathered emulsion (position 3 / 7250mPas). The three tested products were Corexit 9500, Corexit 9527 and OSR52. The comparative tests were performed with a DER of 1:25.

The two Corexit products show good effectiveness for the moderately weathered emulsion from position 2, while OSR 52 showed a somehow reduced dispersibility. For the heavily weathered emulsion sampled in position 3, only Corexit 9500 show good dispersibility, while Corexit 9527 and OSR 52 showed reduced dispersibility (<75% effectiveness in the MSN test).

### 5.2 Dispersant dosage requirement

A minimum DER is required to yield efficient dispersion of a slick. The required dosage usually increases as the oil weathers on the sea surface. As the physical properties of the emulsion change the thickness of the slick will also increase and the required dosage will increase accordingly. In dispersant application operations the dosage is often given in US Gallons Per Acre (USGPA). Dispersant/Emulsion-ratio at different dosages is given at differing slick thicknesses in Table 5.1.

Table 5.1 Dispersant/Emulsion-ratio at different dosage and slick thickness

USGPA	DER at varying Slick thickness		
	1 mm	2 mm	4mm
5	1:200	1:400	1:800
25	1:50	1:100	1:200
2x25	1:25	1:50	1:100

#### Low/Moderately weathered emulsions (dark brown appearance)

The results show good dispersibility in the MNS test for the least weathered emulsion (Position 4). The emulsion disperses even at DER as low as 1:250 in the MNS test. The slick sampled in position 4 had a thickness of ~1mm. To achieve a dispersant/emulsion-ratio of 1:250 for a slick of this thickness an application dosage of 5 USGPA is required (Table 5.1). This mean that the low dosage used in standard aerial application will be sufficient for emulsions at a such low degree of weathering.

#### Highly weathered emulsions (light brown/orange appearance)

The results show good dispersibility in the MNS test for the most weathered emulsion (Position 3) at DER of 1:25 and above. At ratios under 1:50 the efficiency in the MNS test were gradually decreasing. The highly weathered slick sampled in position 3 had a documented thickness of up to 4 mm. A dosage of 5 USGPA would correspond to a dispersant/emulsion-ratio of 1:800 for a slick with this thickness (Table 5.1). According to the test results, this is a too low dosage to disperse the emulsion. A dispersant/emulsion-ratio above 1:50 is recommended as the minimum dosage for heavily weathered emulsions such as the sample from position 3. According to Table 5.1 a minimum dosage of 25 USGPA is required to efficiently disperse heavily weathered emulsion similar to the tested emulsion from position 3.

The slick should be monitored after the dispersant treatment, and if emulsion is still on the surface a re-treatment of the slick should be considered in order to achieve sufficient dosage.

### **5.3 Sea state dependency**

Tests were conducted with the high energy MNS test and with the low energy IFP test. The MNS is thought to be representative for energy at high/medium sea states with presence of breaking waves (typically >5m/s). The IFP test is representative to calmer sea states with no breaking waves. The comparative tests were carried out on all the sampled emulsions and with a dispersant/emulsion-rate of 1:25. At this dosage all emulsions dispersed readily in the MNS test. The dispersibility was slightly reduced in the IFP test for the moderately weathered emulsions from position 2 and 4, while dispersibility was significantly reduced for the heavily weathered sample from position 3. This means that the emulsions are dispersible given sufficient wave energy. In calm sea conditions, introduction of additional mixing-energy/turbulence 0.5-1 hour after dispersant treatment, could be a rational operational strategy. Such mixing energy could be supplied to the treated slick e.g. by prop-washing or by spraying the slick with the vessels FI-FI system.

### **5.4 Viscosity limit for use of dispersants**

As an emulsion weather on the sea surface the physical properties will change, and the dispersibility will gradually decrease. The change in physical properties and thus the changes in dispersibility are highly dependent on the wind/wave conditions. In the systematic weathering studies performed in general at SINTEF, dispersant effectiveness is linked to the viscosity of the emulsion. The viscosity is predicted by use of the SINTEF Oil Weathering Model (Daling and Strøm, 1999) and a time window for effective use of dispersants can be estimated. The weathering properties of the DWH oil are not studied and predictions of the change in physical properties can not be done. A definite time window for use of dispersants can therefore not be established. In this study only the relationship between dispersibility and viscosity has been established.

The most weathered sample tested in this study had a viscosity of 7200 mPas after an estimated weathering time of 4-5 days on the sea surface under relative calm weather conditions. This emulsion still showed good dispersibility in the high energy MNS test at a dispersant/emulsion-ratio of 1:25. In lack of more viscous emulsions the emulsion from position 3 is tested at lower temperatures to gain higher viscosities. The tests indicate that at a dispersant/emulsion-ratio of 1:25 the dispersibility will be reduced at a viscosity of 10000 mPas. Poor dispersibility will occur as the emulsion reaches a viscosity of approximately 25000mPas.



## 6 References

- Bocard C. Castaing, C. G. and Gatillier, C. 1984: "Chemical oil dispersion in trials at sea and in laboratory tests". In: Oil Spill Dispersants, ASTM STP 840 (T.E. Allen ed.) Philadelphia, USA, pp 125- 142
- Daling, P.S., T. Strøm, 1999. Weathering of Oils at Sea: Model/Field Data Comparisons. Spill Science and Technology Bulletin, Vol. 5, no. 1, pp. 63-74, 1999
- Leirvik, F., Daling, P.S., Trudel, K., Parschal, B. 2010. "Cruise report – Assessment of dispersibility of DWH oil at different stages of weathering"
- Mackay, D. and Szeto, F. 1980. Effectiveness of oil spill dispersants - development of a laboratory method and results for selected commercial products. Institute of Environmental Studies, University of Toronto, Publ. no. EE-16.

## Appendix 7

### A7 “Bench Top” LISST Particle Size Analysis

**K. Lee, Z. Li and H. Niu – Centre for Offshore Oil, Gas and Energy Research,  
Fisheries and Oceans Canada**

The standard operational procedure (SOP) for LISST-100X particle size analysis used in the Gulf of Mexico oil spill monitoring program (i.e., Deepwater Horizon Spill) was developed for the measurement of particle-size distributions under two scenarios. The first was bench top measurement of small particles, and the second was continuous in-situ monitoring with the instrument deployed over the side of the vessel at specific depths.

Laboratory “*bench-top*” measurements with the LISST-100X instrument on board the vessel were specifically targeted at measuring *small particles* ( $d < 70 \mu\text{m}$ ) suspended in the water column. For this purpose, discrete samples were collected from both the surface (with bucket), and from different depths in the water column using CTD casts with a Niskin rosette sampler. On average, the total length of time between the recovery of sample and the bench-top LISST-100X analysis was more than half an hour including casting of rosette Niskin bottles, sub-sampling, and data acquisition by LISST-100X. Due to the buoyant nature of dispersed oil droplets in the water column, larger particles (Lunel, 1993; Lunel, 1995) would have risen at a speed that is beyond the limit of the time period for handling discrete seawater samples (Table 1).

TABLE 1 - Rise time of oil droplets

Diameter ( $\mu\text{m}$ )	Rise velocity (cm/min)	Time to rise 1 metre (min)
10	0.03	3330
20	0.132	760
30	0.294	340
40	0.522	190
50	0.84	120
70	1.62	62
80	2.10	48
100	3.30	30
150	7.20	14
200	13.20	8
300	29.40	3
400	52.2	2
500	81.6	1

The LISST-100X particle size analyzer (Type C) is an optical device that measures light intensity over a series of detector rings (numbered 1 through 32). After the acquisition of light intensity for the 32 discrete rings and eight other auxiliary parameters, the raw data are subsequently processed with the manufacturer provided inversion algorithm to automatically calculate volume concentrations (in  $\mu\text{l/l}$ ) for particle size bin number 1 through 32 (corresponding with the detector ring numbers), along with output of 10 other parameters including laser transmission sensor power, laser reference sensor in calibrated



units, pressure, temperature, computed optical transmission over path, and beam-attenuation, etc.

Under ideal conditions, the data acquired using the bench-top measurement SOP would have recorded discrete particle size volume concentrations over the first 20 size bins (bins 1-20 or 2.5 - 68.8  $\mu\text{m}$ ) only, and would have shown zero or close to zero readings for the large-sized bins (#21 – 32, or 68.8 to 500  $\mu\text{m}$ ). However, the recorded data do not always show the low readings expected. Instead, extremely high values over the last several bins were recorded. A number of conditions may exist that lead to high apparent values of large particles:

- (1) Variation of the seawater temperature of the samples collected from different depths in the water column and the ambient air temperature. The water temperatures vary widely from close to freezing ( $4^{\circ}\text{C}$ ) at maximum depths to very warm water at the surface ( $30^{\circ}\text{C}$ ). Stratification of the water inside the small chamber may cause laser beam reflection and a false signal of the presence of larger particles (Mikkelsen et al., 2008; Styles, 2006). Corrective action was taken in late June, 2010 to overcome the effect of temperature variation by introducing a full-path mixing chamber.
- (2) Slight miss-alignment of the LISST-100X (#1215 and #1174) that may impact the inner ring light intensity reading. This will subsequently propagate through inversion process to affect several numbers of upper-end particle size bins, but negligible impact on medium and small particle size data (communication with the manufacturer)
- (3) The presence of actual particles larger than the upper limit of our targeted small particles (68.6  $\mu\text{m}$ ). This is not unexpected, for a number of reasons such as the retention of larger oil droplets within the counting cell of the instrument due to (a) the relatively short time between sample recovery and analysis for the samples that were collected from the surface or near the surface (0-50m depth), (b) the potential presence oil droplets with a density close to the seawater because of the dissolution of light components, and (c) potential coalescence of small particles into larger ones. Furthermore, large particles other than oil (e.g., biogenic material) may also exist.

Considering the high uncertainties involved in the analysis of large particles, analysis of “bench top” data and interpretation should be focused on the small sized particles ( $d < 70 \mu\text{m}$ ) which have been recognized in the oil spill community as permanently dispersed oil droplets. We discourage over-interpretation of particle size distribution data that were collected for this specific purpose during the Gulf of Mexico oil spill emergency response operations. Under this emergency response effort, rapid, less than perfect actions had to be taken to support the requirement for immediate action to monitor the fate and transport of the oil following subsurface injection of dispersant.

Preliminary data analysis was performed with particle size bins 1 through 25, corresponding to particle size ranges of 2.5 to 157  $\mu\text{m}$  (Table 2). Figures 1 and 2 display discrete particle size distribution of the surface samples for all stations, and Figures 3 and 4 the peak total particle concentrations in sub-surface samples. The peaks that were used are defined as the maximum small particle concentration at depth for each station. These particle size distribution histograms clearly demonstrate the presence of a large amount of

very small particles ( $d < 10 \mu\text{m}$ ), suggesting the presence of chemically dispersed oil droplets (Li et al., 2008; Li et al., 2009; Lunel, 1993; Lunel, 1995). The strong signal of the chemically dispersed oil particles is also indicated by the observed multimodal distribution profiles rather than a mono-modal size distribution that is often generated by natural dispersion (Li et al., 2009).

Figures 5 to 8 summarize the fraction of small particles ( $d < 68.8 \mu\text{m}$ ) within the complete range of particle sizes ( $2.5 - 157 \mu\text{m}$ ). These data clearly indicate that the vast majority of volume fractions of the measured particles are in the small particles range. However, exceptions do exist for a number of stations where large fractions of particles appear to fall in the range above  $70 \mu\text{m}$  (e.g. the surface samples of stations 101-104 and subsurface samples of stations 101 and 102 of R/V Brooks McCall, surface samples of stations 60-80 and subsurface samples of stations 60-80 of R/V Ocean Veritas). This needs to be further investigated.

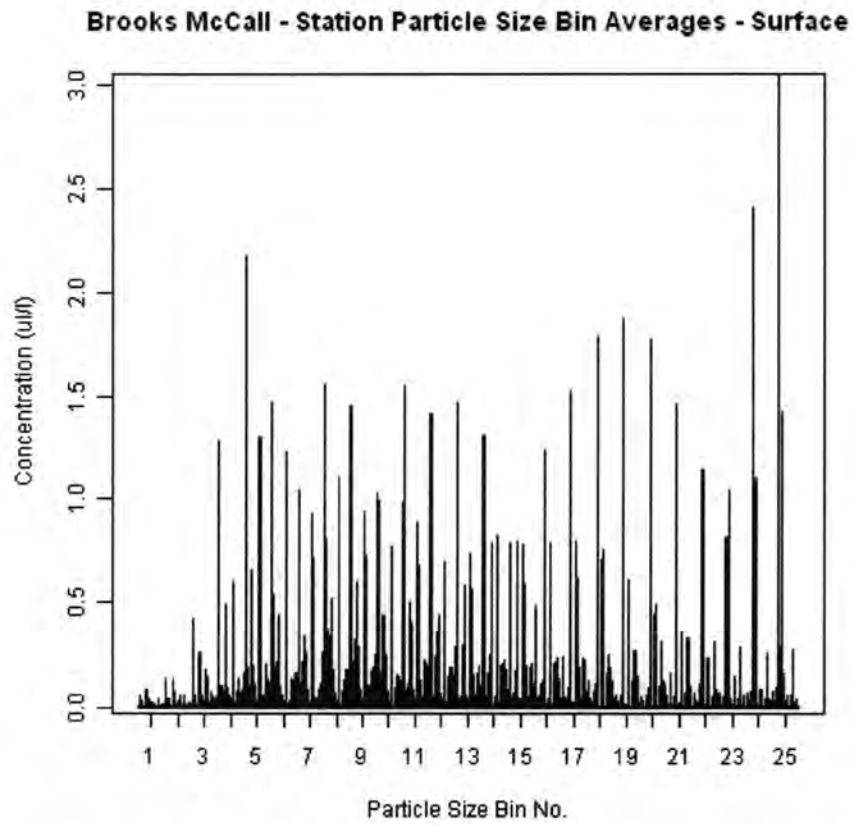
Figures 9-12 present the cumulative particle size distribution of all measured particles from all the surface stations and all the peak sub-surface stations. These graphs show that nearly 80-90% of the measured surface and subsurface particles are  $\leq 70 \mu\text{m}$  (bin 1 to 21), and the median diameters of the measured particles of both surface and subsurface particles are nearly 20 to  $30 \mu\text{m}$ . These size data are in good agreement with previous observations at sea (Lunel, 1993; Lunel, 1995).

Due to the restriction of time, more detailed data analysis and interpretation are certainly yet to be done. The association with field operational and oceanographic parameters needs to be further investigated. Nevertheless, the preliminary results and elementary data analysis suggest high effectiveness of chemical dispersants in oil dispersion from subsurface application. An estimation of the amount of oil dispersed based on the operational parameter, namely dispersant to oil ratio, in calculating the amount of chemically dispersed oil may not be the most accurate approach. A thorough inspection of all the field collected data, including discrete samples and continuous in-situ (over-the-side) vessel deployment data (to be addresses in future reports), and numerous other field sampling data should be synthesized and digested to provide a more scientifically sound estimation of dispersant effectiveness, the amount of oil naturally or chemically dispersed from the subsurface and surface dispersant application, and the oil mass balance on the whole. The possible impact of dispersant-containing oil in rising and after rising to the water-air interface should not be neglected. Effective chemical dispersion of oil after adding dispersant in calm sea proves still effective after prolonged standing time in static and flowing waters before increased wave energy becomes available (Lewis et al., 2010). Such a scenario may happen to the subsurface dispersant injection situation, in which an excellent mixture of oil and dispersant in situ at depth can facilitate continued dispersion of oil wherever turbulent mixing energy is encountered – regardless of whether it is at the surface or subsurface.



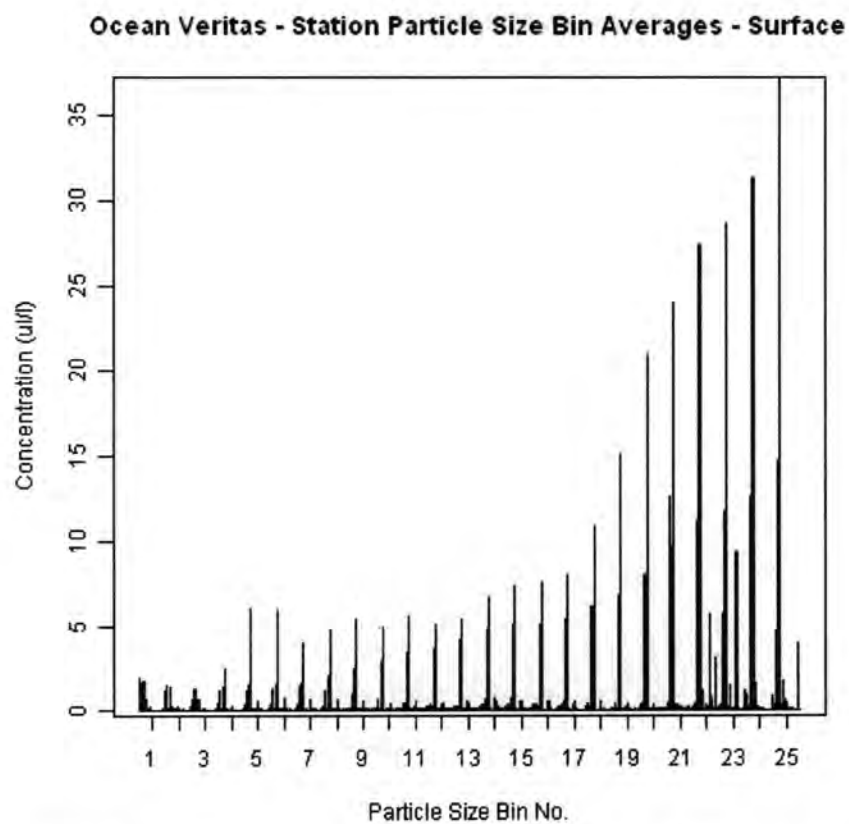
**Table 2: The lower, medium and upper limit of each size bin in microns for the LISST-100X particle counter**

Size bin #	Lower	Medium	Upper
1	2.50	2.72	2.95
2	2.95	3.20	3.48
3	3.48	3.78	4.11
4	4.11	4.46	4.85
5	4.85	5.27	5.72
6	5.72	6.21	6.75
7	6.75	7.33	7.97
8	7.97	8.65	9.40
9	9.40	10.2	11.1
10	11.1	12.1	13.1
11	13.1	14.2	15.4
12	15.4	16.8	18.2
13	18.2	19.8	21.5
14	21.5	23.4	25.4
15	25.4	27.6	30.0
16	30.0	32.5	35.4
17	35.4	38.4	41.7
18	41.7	45.3	49.2
19	49.2	53.5	58.1
20	58.1	63.1	68.6
21	68.6	74.5	80.9
22	80.9	87.9	95.5
23	95.5	104	113
24	113	122	133
25	133	144	157



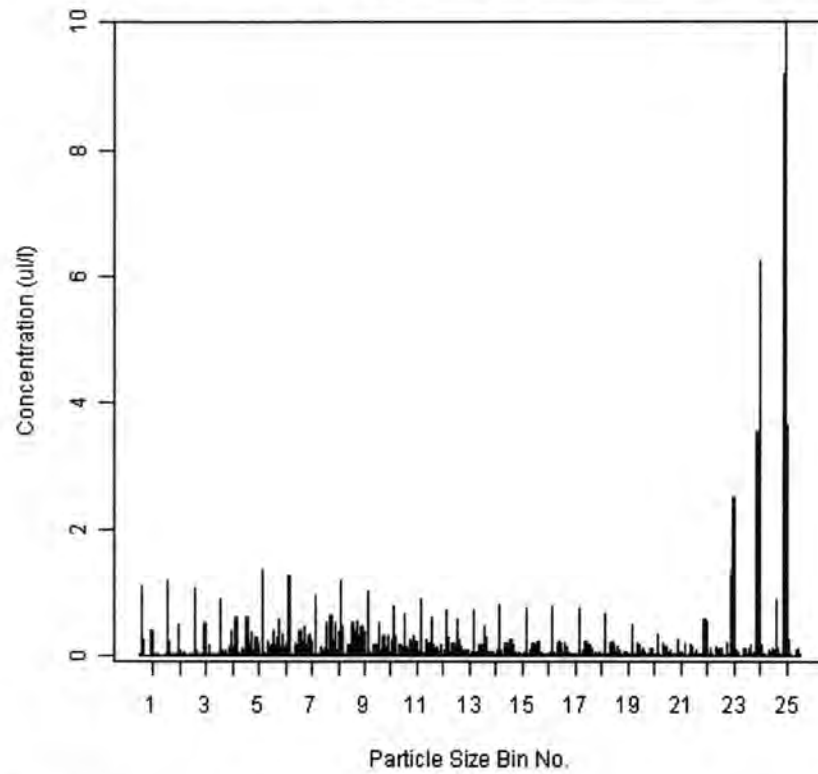
**Figure 1: Particle-size distributions (see Table 1 for size range of corresponding Bin No.) for the surface samples of all stations of the R/V Brooks McCall.**





**Figure 2: Particle-size distributions for the surface samples of all stations of the R/V Ocean Veritus.**

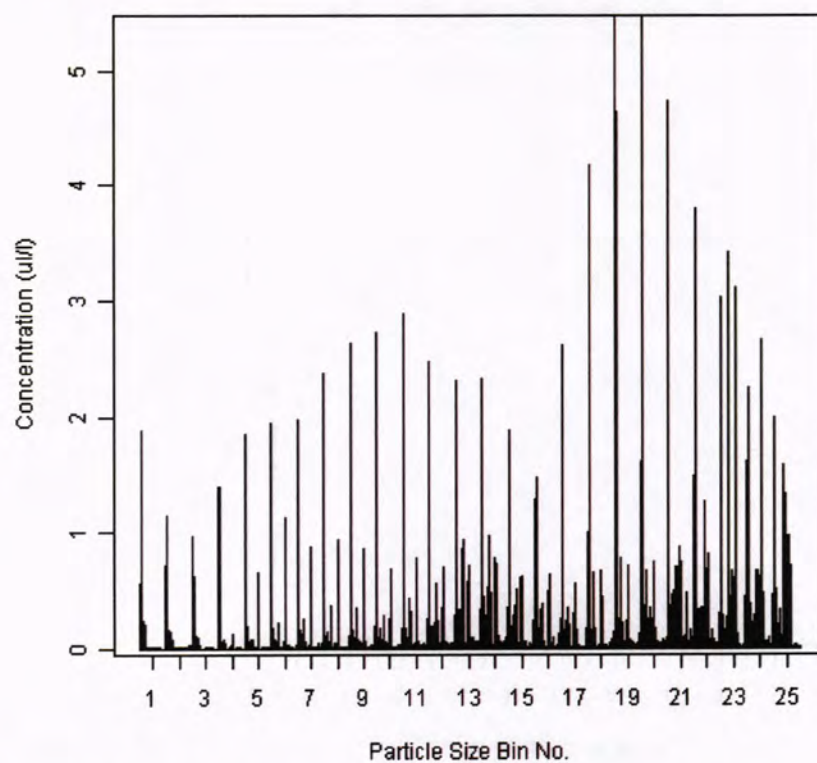
**Brooks McCall - Station Particle Size Bin Averages - Max at Depth**



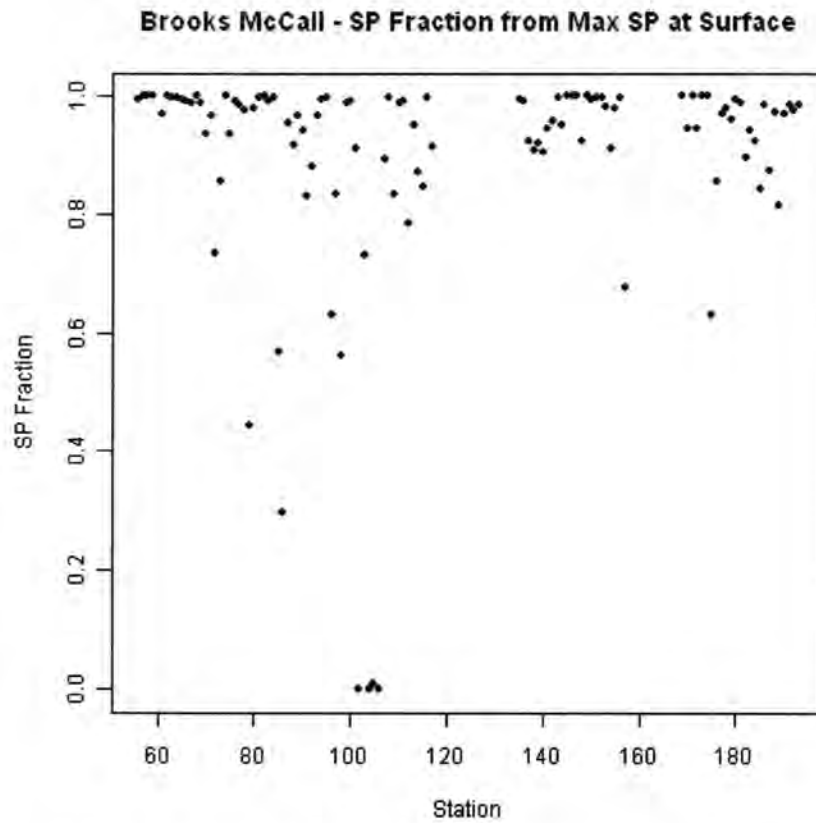
**Figure 3: Particle-size distributions for the peak total concentration in sub-surface samples of all stations of the R/V Brooks McCall.**



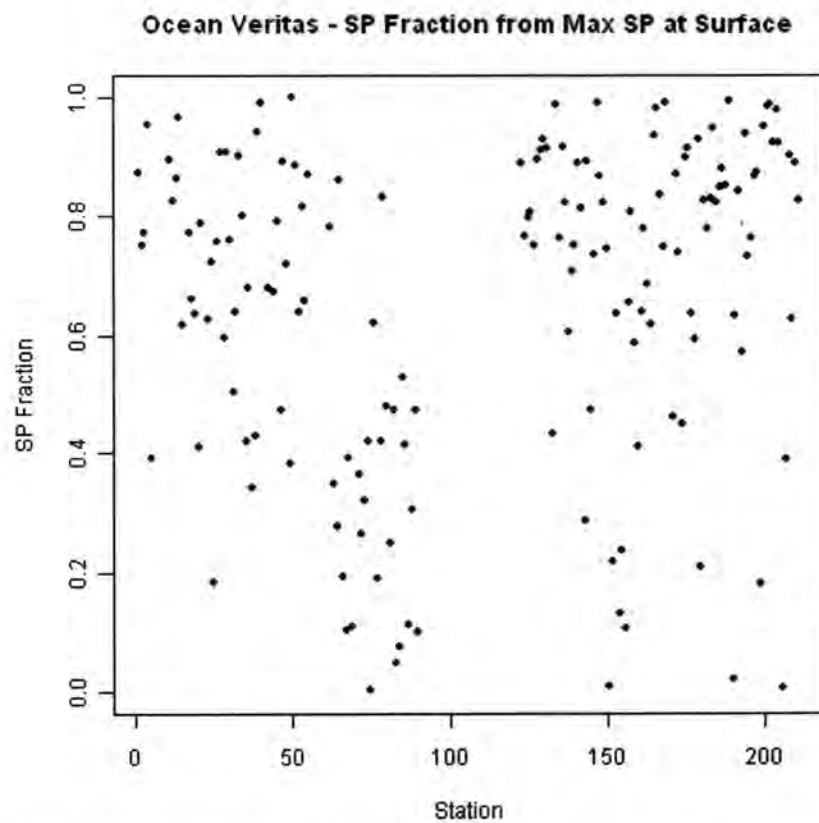
**Ocean Veritas - Station Particle Size Bin Averages - Max at Depth**



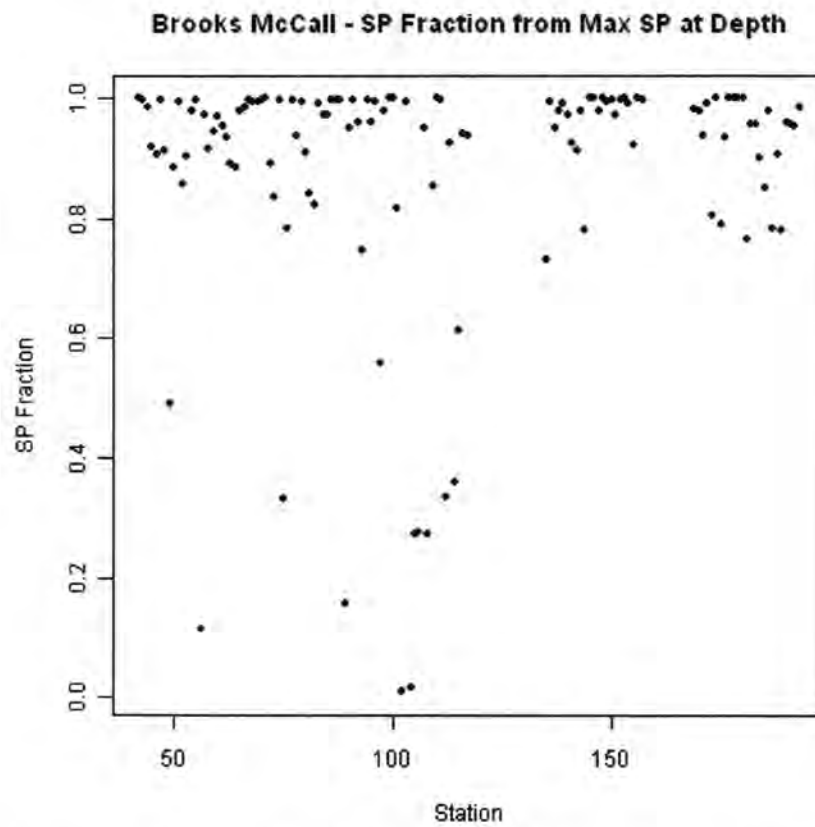
**Figure 2: Particle-size distributions for the peak sub-surface samples of all stations of the R/V Ocean Veritus.**





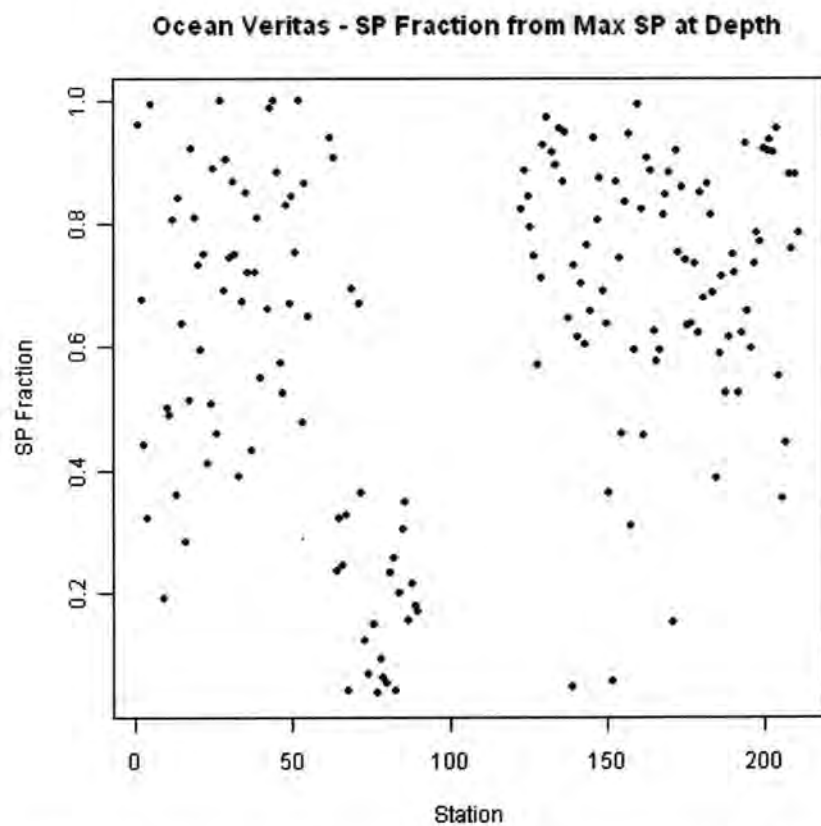


**Figure 6: Small particle ( $d < 68.6 \mu\text{m}$ ) fraction of the total measured particles ( $2.5 - 157 \mu\text{m}$ ) for the surface samples of all stations of the R/V Ocean Veritas.**

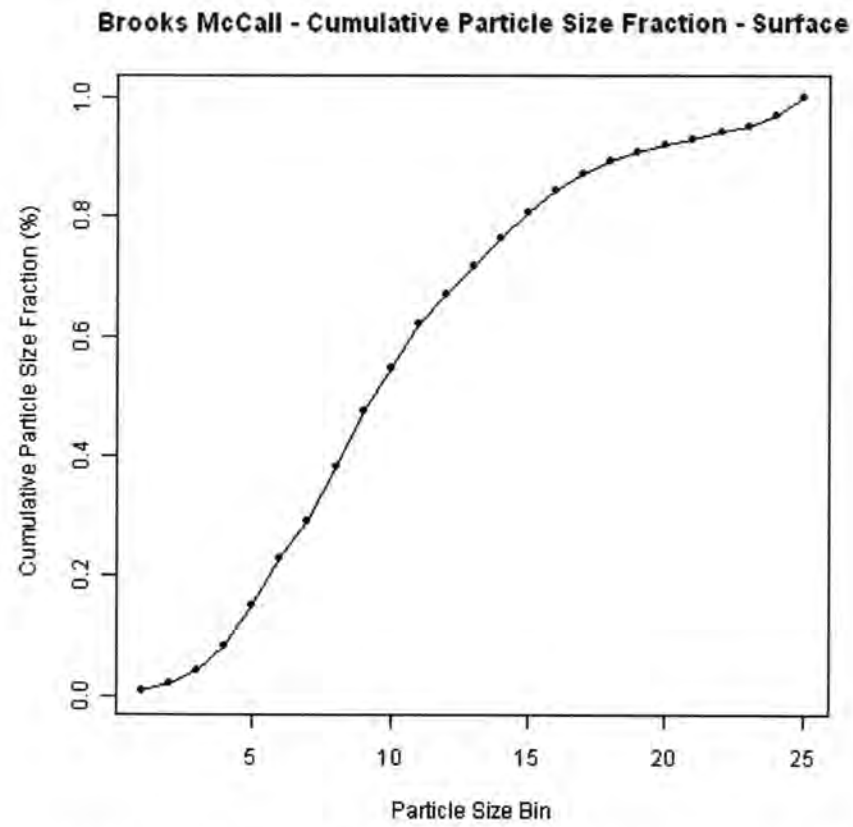


**Figure 7: Small particle ( $d < 68.6 \mu\text{m}$ ) fraction of the total measured particles ( $2.5 - 157 \mu\text{m}$ ) for the peak sub-surface samples of all stations of the R/V Brooks McCall.**



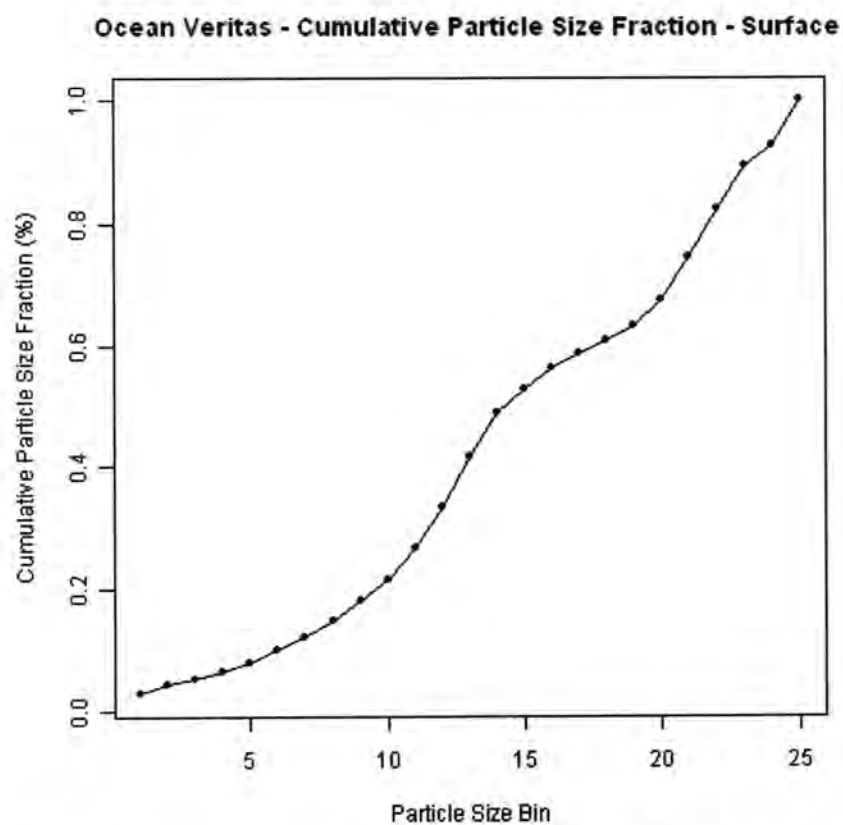


**Figure 4: Small particle ( $d < 68.6 \mu\text{m}$ ) fraction of the total measured particles ( $2.5 - 157 \mu\text{m}$ ) for the peak sub-surface samples of all stations of the R/V Ocean Veritas.**



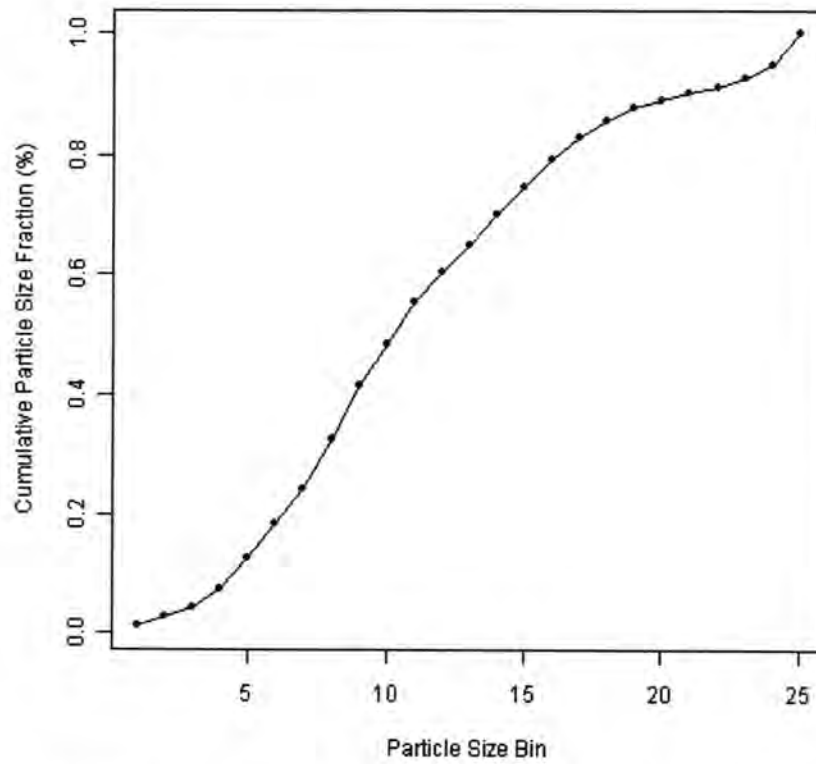
**Figure 5: Cumulative particle-size distribution for all the surface samples of all stations of the R/V Brooks McCall.**





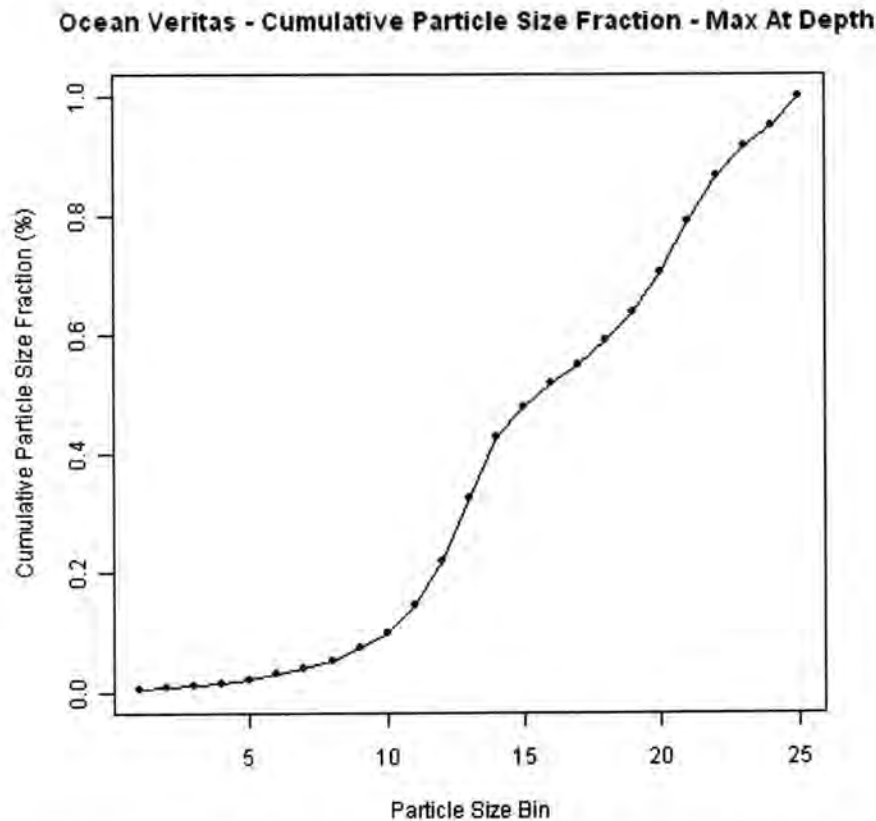
**Figure 10: Cumulative particle-size distribution for all the surface samples of all stations of the R/V Ocean Veritas.**

**Brooks McCall - Cumulative Particle Size Fraction - Max At Depth**



**Figure 11: Cumulative particle-size distribution for all the peak sub-surface samples of all stations of the R/V Brooks McCall.**





**Figure 6: Cumulative particle-size distribution all the peak sub-surface samples of all stations of the R/V Ocean Veritas.**

#### **References:**

- Lewis, A., K. Trudel, B., Belore, R.C. and Mullin, J.V., 2010. Large-scale dispersant leaching and effectiveness experiments with oils on calm water. *Marine Pollution Bulletin*, 60(2): 244-254.
- Li, Z., Lee, K., King, T., Boufadel, M.C. and Venosa, A.D., 2008. Oil droplet size distribution as a function of energy dissipation rate in an experimental wave tank 2008 International Oil Spill Conference. Americal Petroleum Institute, Washington D.C., Savannah, GA, pp. 621-626.
- Li, Z., Lee, K., King, T., Boufadel, M.C. and Venosa, A.D., 2009. Evaluating Chemical Dispersant Efficacy in an Experimental Wave Tank: 2, Significant Factors Determining In Situ Oil Droplet Size Distribution. *Environmental Engineering Science*, 26(9): 1407-1418.
- Lunel, T., 1993. Dispersion: Oil droplet size measurement at sea. In: *Proceedings of the Sixteenth Arctic and Marine Oil Spill Program (AMOP) Technical Seminar*, Calgary, Alberta, Canada. Environment Canada, Ottawa, Ontario, Canada. Pp. 1023-1056

- Lunel, T., 1995. Understanding the mechanism of dispersion through oil droplet size measurements at sea. In: P. Lane (Editor), *The Use of Chemicals in Oil Spill Response*, ASTM STP 1252. American Society for Testing and Materials, Philadelphia, PA, pp. 240-270.
- Mikkelsen, O.A. et al., 2008. The influence of schlieren on in situ optical measurements used for particle characterization. *Limnology and Oceanography-Methods*, 6: 133-143.
- Styles, R., 2006. Laboratory evaluation of the LISST in a stratified fluid. *Marine Geology*, 227(1-2): 151-162.



## Appendix 8

### **A8 Spill Related Properties of MC 252 Crude Oil Sample ENT-052210-178**

**For**

**BP**

**by**

**SL Ross Environmental Research Ltd.**

**July, 2010**

---

### **Table of Contents**

1. Introduction.....	1
2. Physical Property Tests: Methods and Results .....	1
2.1 Results.....	2
2.1.1 Evaporation .....	2
2.1.2 Density.....	6
2.1.3 Viscosity .....	6
2.1.4 Interfacial Tension.....	6
2.1.4 Pour Point.....	6
2.1.5 Flash Point.....	6
2.1.6 Emulsification Tendency and Stability .....	6
3. References.....	7
Appendix A. Oil Property Test Methodology and Relationship to Spill Behavior .....	8
A.1 Evaporation .....	9
A.2 Physical properties.....	9
A.2.1 Density .....	10
A.2.2 Viscosity .....	10
A.2.3 Interfacial Tension .....	10
A.2.4 Pour Point.....	11
A.2.5 Flash Point .....	11
A.2.6 Emulsification Tendency and Stability .....	11
Appendix B. Oil Property Analysis Results for MC 252 ENT-052210-178 Crude Oil .....	13

---

## 1. INTRODUCTION

When oil is spilled in the marine environment its physical and chemical properties will change over time through processes such as evaporation and emulsification. These changes will affect both the fate and behavior of the spill and the opportunities for using countermeasures effectively. For example, an oil may be relatively fluid and non-viscous when initially spilled, but may become viscous within a short time. It is important to know whether this will happen and how long it will take, defining the so-called Window of Opportunity for countermeasures.

The objective of this study was to conduct simulated oil spill weathering experiments on MC 252 ENT-052210-178 crude oil. The quantitative results of the tests (involving both fresh and weathered oil) can be used as input to most oil spill models that are used internationally to predict the fate and behavior of spills of specific oils.

## 2. PHYSICAL PROPERTY TESTS: METHODS AND RESULTS

The laboratory testing described here involved 2.7 L of the crude oil. The oil was subjected to the analyses outlined in Table 2-1. Test temperatures were chosen to cover the typical range of seasonal variation for the open water season in the target region. Temperature of 15°C and 35°C were chosen.

A discussion of the methodology of each of these tests is presented in Appendix A, along with an explanation of the effect that each oil property has on spill behavior.

The results of the weathering and analyses of the crude oil are presented separately in the following section. Complete test results can be found in Appendix B.

**Table 2-1** Test Procedures for Spill-Related Analysis of MC 252 ENT-052210-178 Crude Oil

<i>Property</i>	<i>Test Temperature(s)</i>	<i>Equipment</i>	<i>Procedure</i>
Evaporation	Ambient	Wind TunnelASTM Distillation Apparatus	ASTM D86
Density	15° and 35°	Anton Paar Densitometer	ASTM D4052
Viscosity	15° and 35°	Brookfield DV III+ Digital Rheometer c/w Cone and Plate	Brookfield M/98-211
Interfacial Tension	Room Temperature	CSC DuNouy Ring Tensiometer	ASTM D971
Pour Point	N/A	ASTM Test Jars and Thermometers	ASTM D97
Flash Point	N/A	Pensky-Martens Closed Cup Flash Tester	ASTM D93
Emulsification Tendency/Stability	15° and 35°	Rotating Flask Apparatus	(Mackay and Zagorski 1982; Hokstad and Daling 1993)



## 2.1 RESULTS

The results of the property analysis of MC 252 ENT-052210-178 are summarized in Table 2-2. The complete test results can be found in Appendix B. The two levels of evaporation noted in the table represent the amounts evaporated from a 2 cm-thick slick in the wind tunnel after two days and two weeks, respectively.

### 2.1.1 Evaporation

MC 252 ENT-052210-178 is a light crude with an API gravity of 37.2°. Approximately 35% of the oil evaporated after two days in the wind tunnel, and about 45% evaporated after two weeks of exposure.

Figure 2-1 is a predicted evaporation curve for a spill involving a 10-mm thick slick in a 5 knot wind at 25°C (77°F). Please note that the curve only applies at a water temperature of 25°C. If other temperatures (or slick thicknesses and wind speeds) are of interest, these curves can be generated using the equations in Appendix A and data in Appendix B<sup>1</sup>. Computerized oil spill models automatically do these calculations.

Figures 2-2, 2-3 and 2-4 show the effect of evaporation on the properties of oil viscosity, density and pour point.

---

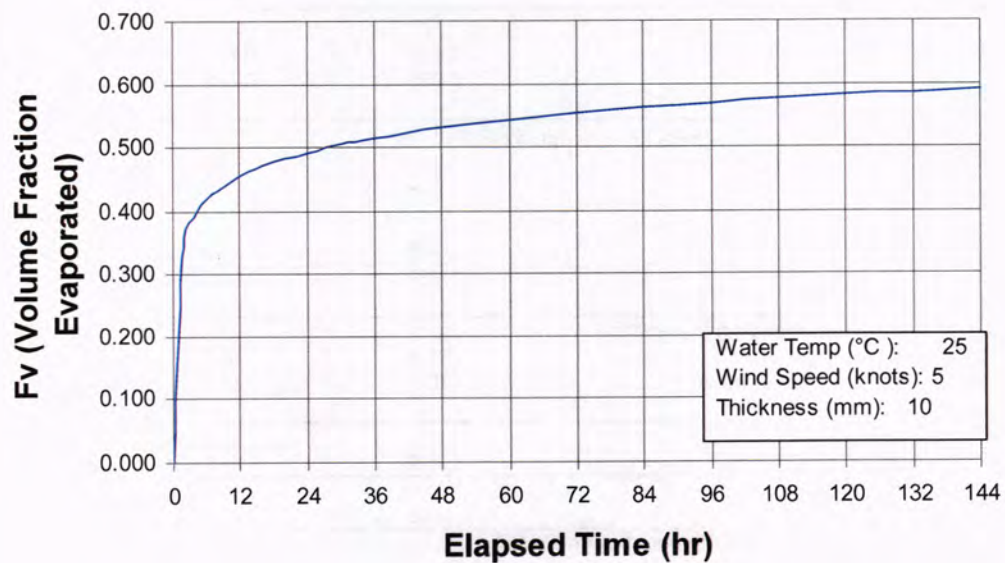
<sup>1</sup> The evaporation curve of the oil in the wind tunnel is shown in Appendix B, plotting the volume fraction of oil evaporated,  $F_v$ , on the y-axis versus evaporative exposure,  $\theta$ , on the x-axis, where  $\theta$  is the unit of time expressed in dimensionless form. Equations described in Appendix A and data in Table 2-2 of Appendix B can be used to convert this curve into a more usable form for estimating oil evaporation under various spill conditions of temperature, elapsed time and wind speed.

**Table 2-2 Spill-Related Properties of MC252 Crude Oil**

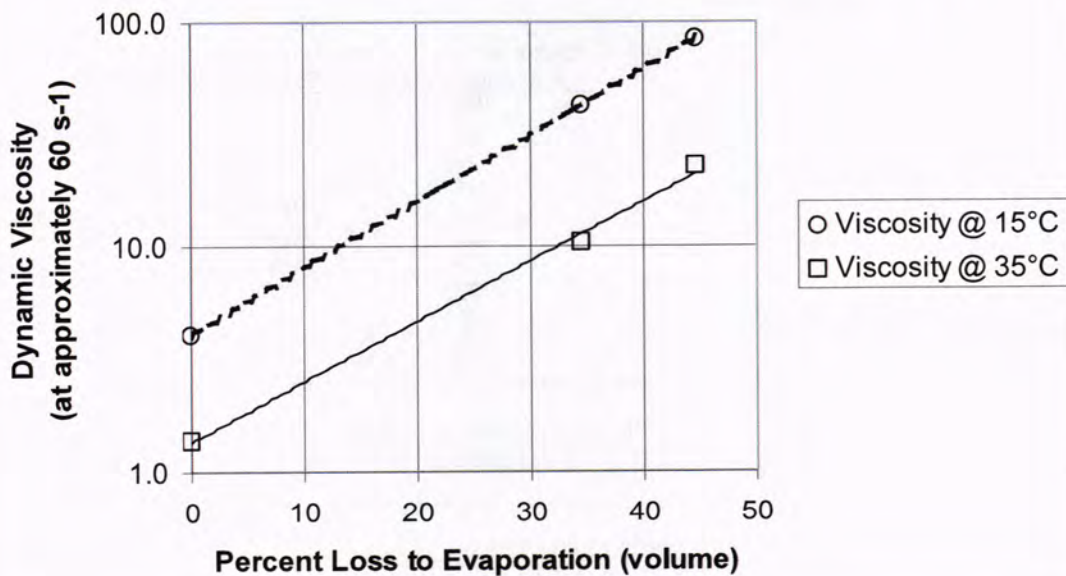
Spill-related properties			
BP MC252 ENT-052210-178		API ° = 37.2	
Evaporation (Volume %)	0	34.50	44.66
Density (g/cm <sup>3</sup> )			
15 °C	0.839	0.882	0.897
35 °C	0.825	0.868	0.883
Dynamic Viscosity (mPa.s)	at approx 460 s <sup>-1</sup>		
15 °C	4.1	43	85
35 °C	1.4	10	23
Kinematic Viscosity (mm <sup>2</sup> /s)			
15 °C	4.8	49	95
35 °C	1.7	12	26
Interfacial Tension (dyne/cm)			
Oil/ Air	23.5	26.8	30.1
Oil/ Seawater	23.3	22.6	22.5
Pour Point (°C)	<-9	6	6
Flash Point (°C)	<-8	54	100
Emulsion Formation-Tendency and Stability @	22.5 °C		
Tendency	Unlikely	Unlikely	Unlikely
Stability	Unstable	Unstable	Unstable
Water Content	0%	0%	0%
Emulsion Formation-Tendency and Stability @	34 °C		
Tendency	Unlikely	Unlikely	Unlikely
Stability	Unstable	Unstable	Unstable
Water Content	0%	0%	0%
ASTM Modified Distillation			
	Evaporation (% volume)	Liquid Temperature (°C)	Vapour Temperature (°C)
	IBP	84	39.8
	5	111.6	77.4
	10	124.4	91.7
	15	137	102.4
	20	151.2	115.8
	25	168.8	116
	30	188.2	126.4
	35	208	150
	40	227	129.7
	45	248	142.5
Weathering Model			
Fv =	$\frac{\ln[1 + (C_1/T_k)\theta \exp(C_2 - C_3/T_k)]}{(C_1/T_k)}$		
where:	Fv is volume fraction of oil evaporated		
	θ is evaporative exposure		
	Tk is environmental temperature (K)		
	C <sub>1</sub> =	5472	
	C <sub>2</sub> =	12.90	
	C <sub>3</sub> =	5739	

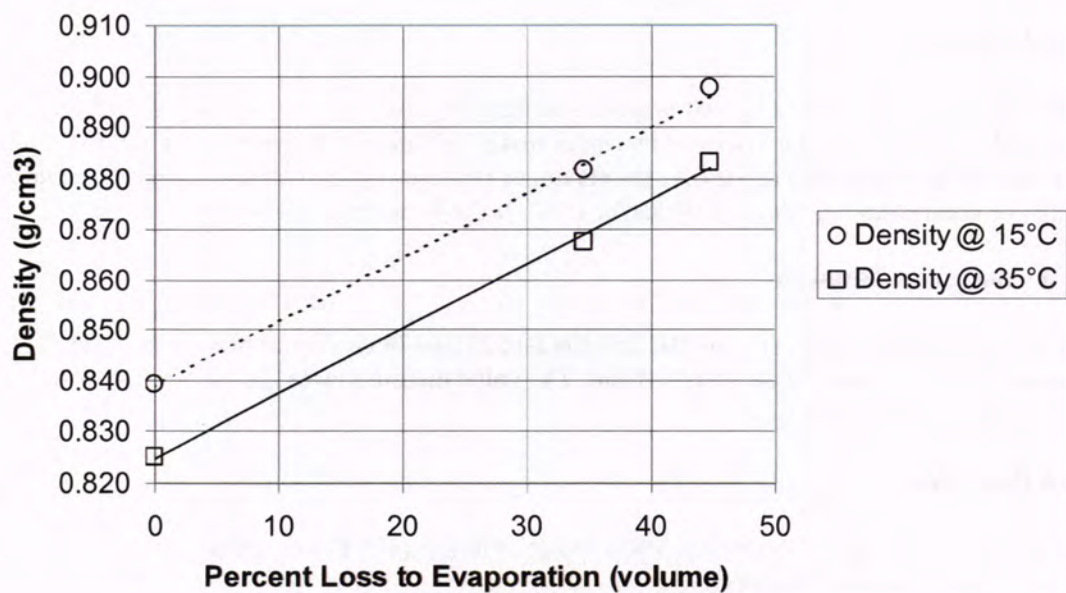
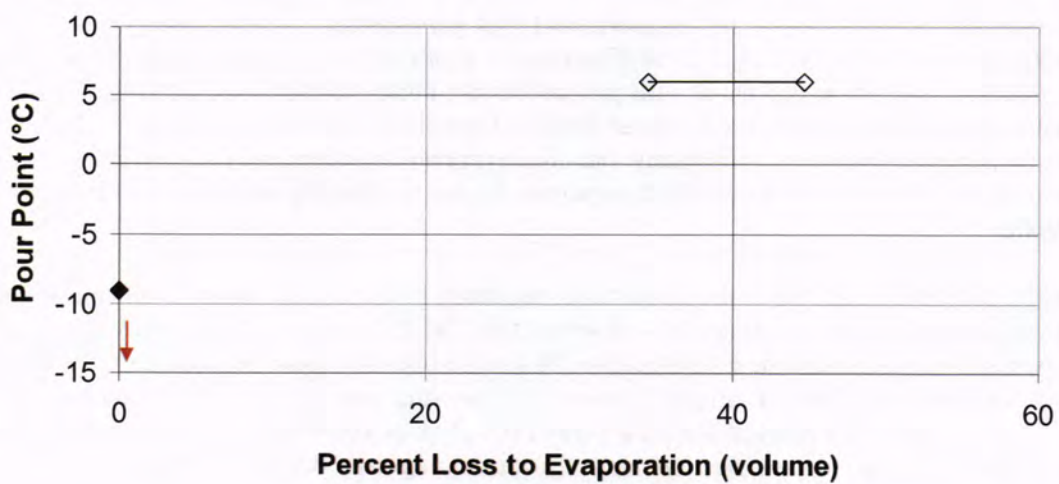


**Figure 2-1 Evaporation of MC252 Ent-052210-178**



**Figure 2-2 Effect of Evaporation on Oil Viscosity**



**Figure 2-3 Effect of Evaporation on Oil Density****Figure 2-4  
Effect of Evaporation on Pour Point**



### **2.1.2 Density**

MC 252 oil is a light crude oil, with a density of 0.839 g/cm<sup>3</sup> at 15 °C (API gravity of 37.2°).

### **2.1.3 Viscosity**

The oil has a very low viscosity that is typical of light oils. At 15 °C the viscosity of the fresh oil is about 4.1 cP (mPa.s). The viscosity increases to 42.9 cP after 35% evaporation and to 85.1 cP after 45% evaporation. The crude oil exhibits minor non-Newtonian behavior (slightly pseudo-plastic, or shear-thinning, characteristics) at 15°C. It is a Newtonian fluid at 35°C.

### **2.1.4 Interfacial Tension**

The oil/water interfacial tension of MC 252 ENT-052210-178 crude was measured using standard laboratory water with 35 ppt of salt. The value measured was 23.7 dynes/cm, which is in the range of most crude oils.

### **2.1.4 Pour Point**

MC 252 ENT-052210-178 crude has a pour point of less than -9 °C when fresh. This increases to 6 °C at 35 and 45 percent evaporation.

### **2.1.5 Flash Point**

MC 252 ENT-052210-178 has a low flash point (below -8 °C) when fresh. This rises after 45% evaporation to 100 °C.

### **2.1.6 Emulsification Tendency and Stability**

From the viewpoint of spill countermeasures and slick persistence, emulsification is a very negative process because strongly emulsified oils are highly viscous — they can have ten to 100 times the viscosity of the parent oil. It is general believed that oils that have relatively high concentrations of asphaltenes are the most likely to form stable water-in-oil emulsions. Some oil spills do not form emulsion immediately, but once evaporation occurs and the asphaltene concentration increases, the emulsification process begins and usually proceeds quickly thereafter.

The MC 252 ENT-052210-178 crude oil has no tendency to form stable water-in oil emulsions when mixed with seawater. At sea, it is observed that MC 252 crude does eventually form stable emulsions. The reason that the ENT-052210-178 sample does not could be due to several factors:

- The ENT-052210-178 sample evaporated in the wind tunnel for two weeks is equivalent to only about 10 hours at sea for a 1-mm thick slick or 100 hours for a 10-mm thick slick and the onset of emulsification may not occur until greater degrees of evaporative exposure that this are reached.
- The sample may have been exposed to an anti-foaming agent and/or methanol during it's collection from the damaged riser by the RITT and this exposure may inhibit emulsification.

- Exposure to sunlight (not a part of the SL Ross weathering protocol) can produce photo-oxidation products that promote emulsification.

Enough of the two-week weathered sample from the wind tunnel remains to place a thinner slick back into the wind tunnel and further expose it to the equivalent of one week at sea for a 1-mm slick. The emulsification of this sample will then be measured. As well, during the earlier alternative field-testing program, surface samples of the slick were collected and shipped to the SL Ross lab. Aliquots of these will be subjected to the laboratory emulsification test to determine their emulsification characteristics.

### 3. REFERENCES

- Fingas, M., B. Fieldhouse and J. Mullin. 1998. Studies of Water-in-Oil Emulsions: Stability and Oil Properties. *Proceedings of the 21<sup>st</sup> Arctic and Marine Oilspill Technical Seminar*. Environment Canada, Ottawa. pp 1-26
- Hokstad, J. and P. Daling. 1993. Methodology for Testing Water-in-Oil Emulsions and Demulsifiers. Description of Laboratory Procedures. In *Formation and Breaking of Water-in-Oil Emulsions: Workshop Proceedings* Marine Spill Response Corporation, Washington DC, MSRC Technical Report Series 93-108, pp 239-254
- Mackay, D., W. Stiver and P.A. Tebeau. 1983. Testing of crude oils and petroleum products for environmental purposes. In *Proceedings of the 1983 Oil Spill Conference*, American Petroleum Institute, Washington, D.C., pp 331-337.
- Zagorski, W. and D. Mackay. 1982. Water in oil emulsions: a stability hypothesis, in *Proceedings of the 5th Arctic and Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, ON, pp 61-74.

## **APPENDIX A. OIL PROPERTY TEST METHODOLOGY AND RELATIONSHIP TO SPILL BEHAVIOR**



## A.1 E VAPORATION

The oil was divided into three aliquots. Two aliquots were weathered in a wind tunnel: one for two days and one for two weeks. Depending on the conditions at a spill site, this is typically equivalent to a few hours and a few days at sea. In addition, the fresh oil was subjected to a modified ASTM distillation (ASTM D86-90, modified in that both liquid and vapor temperature are measured) in order to obtain two oil-specific constants for evaporation prediction purposes. Evaporation is correlated using Evaporative Exposure ( $\theta$ ), a dimensionless time unit calculated by:

$$\theta = kt/x$$

where:  $k$  = a mass transfer coefficient [m/s] (*determined experimentally in the laboratory wind tunnel or by an equation related to wind speed for spills at sea*)

$t$  = elapsed time [s]

$x$  = oil thickness [m]

The distillation information is used in conjunction with the wind tunnel data to predict evaporation rates for oil spills at sea.

## A.2 P PHYSICAL PROPERTIES

The oils were subjected to the analyses outlined in Table 1. Test temperatures are chosen to represent typical values for the region for those tests that are temperature-sensitive, such as density and viscosity.

**Table 1:** Test procedures for oil analysis

Property	Test Temperature(s)	Equipment	Procedure
Evaporation	Ambient	Wind Tunnel ASTM Distillation Apparatus	ASTM D86
Density	15 ° and 35 ° C	Anton Paar Densitometer	ASTM D4052
Viscosity	15 ° and 35 ° C	Brookfield DV III+ Digital Rheometer c/w Cone and Plate	Brookfield M/98-211
Interfacial Tension	Room Temperature	CSC DuNouy Ring Tensiometer	ASTM D971
Pour Point	N/A	ASTM Test Jars and Thermometers	ASTM D97
Flash Point	N/A	Pensky-Martens Closed Cup Flash Tester	ASTM D93
Emulsification Tendency/Stability	15 ° and 35 ° C	Rotating Flask Apparatus	(Mackay and Zagorski 1982; Hokstad and Daling 1993)

**A.2.1 Density**

Density, the mass per unit volume of the oil (or emulsion), determines how buoyant the oil is in water. The common unit of density is grams per millilitre or cubic centimetre (g/mL or g/cm<sup>3</sup>); the SI unit is kg/m<sup>3</sup>, which is numerically 1000 times the value in g/mL. The density of spilled crude oil increases with weathering and decreases with increasing temperature. Density affects the following spill processes:

- Sinking - if the density of the oil exceeds that of the water it will sink;
- Spreading - in the early stages of a spill, more dense oils spread faster;
- Natural dispersion - more dense oils stay dispersed more easily; and,
- Emulsification stability - dense oils form more stable emulsions.

**A.2.2 Viscosity**

Viscosity is a measure of the resistance of oil to flowing, once it is in motion. The common unit of dynamic viscosity is the centi-Poise (cP); the SI unit is the milli-Pascal second (mPas), which is numerically equivalent to the centi-Poise. The common unit of kinematic viscosity (calculated by multiplying the dynamic viscosity by the density) is the centi-Stoke (cSt) the SI unit is the square millimetre/second (mm<sup>2</sup>/s), which is numerically equivalent to the centi-Stoke. The viscosity of spilled crude oil increases as weathering progresses and decreases with increasing temperature. Viscosity is one of the most important properties from the perspective of spill behavior and affects the following processes:

- Spreading - viscous oils spread more slowly;
- Natural and chemical dispersion - highly viscous oils are difficult to disperse;
- Emulsification tendency and stability - viscous oils form more stable emulsions; and,
- Recovery and transfer operations - more viscous oils are generally harder to skim and more difficult to pump.

**A.2.3 Interfacial Tension**

Interfacial tension is a measure of the surface forces that exist between the interfaces of the oil and water, and the oil and air. The common unit of interfacial tension is the dyne/cm; the SI unit is the milli-Newton/metre (mN/m), which is numerically equivalent to the dyne/cm. Chemical dispersants work by reducing the oil/water interfacial tension to allow a given mixing energy (i.e., sea state) to produce smaller oil droplets. Emulsion breakers also work by lowering the oil/water interfacial tension; this weakens the continuous layer of oil surrounding the suspended water droplets and allows them to coalesce and drop out of the emulsion. Interfacial tensions (oil/air and oil/water) are fairly insensitive to temperature, but are affected by evaporation. Interfacial tension affects the following processes:

- Spreading - interfacial tensions determine how fast an oil will spread and whether the oil will form a sheen;
- Natural and chemical dispersion - oils with high interfacial tensions are more difficult to disperse naturally, chemical dispersant work by temporarily reducing the oil/water interfacial tension;
- Emulsification rates and stability; and,

- Mechanical recovery - oleophilic skimmers (e.g., rope-mop and belt skimmers) work best on oils with moderate to high interfacial tensions.

#### A.2.4 Pour Point

The pour point is the lowest temperature (to the nearest multiple of 3 °C) at which crude oil will still flow in a small test jar tipped on its side. Near, and below this temperature, the oil develops a yield stress and, in essence, gels. The pour point of an oil increases with weathering. Pour point affects the following processes:

- Spreading - oils at temperatures below their pour points will not spread on water;
- Viscosity - an oil's viscosity at low shear rates increases dramatically at temperatures below its pour point;
- Dispersion - an oil at a temperature below its pour point may be difficult to disperse; and,
- Recovery - crude oil below its pour point may not flow towards skimmers or down inclined surfaces in skimmers

#### A.2.5 Flash Point

The flash point of crude oil is the temperature at which the oil produces sufficient vapors to ignite when exposed to an open flame or other ignition source. Flash point increases with increasing evaporation. It is an important safety-related spill property.

#### A.2.6 Emulsification Tendency and Stability

The tendency of crude oil to form water-in-oil emulsions (or "mousse") and the stability of the emulsion formed are measured by two numbers: the Emulsification Tendency Index (Zagorski and Mackay 1982, Hokstad and Daling 1993) and the Emulsion Stability (adapted from Fingas *et al.* 1998). The Emulsification Tendency Index is a measure of the oil's propensity to form an emulsion, quantified by extrapolating back to time = 0 the fraction of the parent oil that remains (i.e., does not cream out) in the emulsion formed in a rotating flask apparatus over several hours. If a crude oil has an Emulsification Tendency Index between 0 and 0.25 it is unlikely to form an emulsion; if it has a Tendency Index between 0.25 and 0.75 it has a moderate tendency to form emulsions. A value of 0.75 to 1.0 indicates a high tendency to form emulsions. Recently the Emulsion Stability assessment has been changed to reflect the four categories suggested by Fingas *et al.* 1998. Emulsion types are selected based on water content, emulsion rheology and the visual appearance of the emulsion after 24 hours settling. The four categories, and their defining characteristics, are:

1. Unstable – looks like original oil; water contents after 24 hours of 1% to 23% averaging 5%; viscosity same as oil on average
2. Entrained Water – looks black, with large water droplets; water contents after 24 hours of 26% to 62% averaging 42%; emulsion viscosity 13 times greater than oil on average
3. Meso-stable – brown viscous liquid; water contents after 24 hours of 35% to 83% averaging 62%; emulsion viscosity 45 times greater than oil on average
4. Stable – the classic "mousse", a brown gel/solid; water contents after 24 hours of 65% to 93% averaging 80%; emulsion viscosity 1100 times greater than oil on average

Under the old emulsion stability assessment scheme, the stability was determined by the fraction of the original oil that remained in the emulsion after 24-hours settling (0 to 0.25 = unstable, 0.25 to 0.75 = fairly stable, 0.75 to 1 = very stable).



Both the Tendency Index and Stability generally increase with increased degree of evaporation. Colder temperatures generally increase both the Tendency Index and Stability (i.e., promote emulsification) unless the oil gels as the temperature drops below its pour point and it becomes too viscous to form an emulsion. Emulsion formation results in large increases in the spill's volume, enormous viscosity increases (which can reduce dispersant effectiveness), and increased water content (which can prevent ignition of the slicks and *in situ* burning).

**APPENDIX B. OIL PROPERTY ANALYSIS RESULTS FOR MC 252 ENT-  
052210-178 CRUDE OIL**

Oil Weathering								BP MC252 ENT-052210-178		Volume Weathered(ml)		970
								Volume for 2cm thick		969.50		
								Tray thickness (m)		0.02001031		
Tray Mass (g)		Tray 7	Tray 8	Average Air Temp								
		240.4	240.8	24.7 °C								
Date/Time	Mass of Oil + Tray		Mass of Oil		Fm		Oil	Fv		Fv vs. Theta Modeling		
	Tray 7	Tray 8	Tray 7	Tray 8	Tray 7	Tray 8	Density (g/cm³)	Tray 7	Tray 8	Evaporative Exposure (Corrected)	Model Evaporate (Fv)	
(g)	(g)	(g)	(g)									
07/06/2010 17:17	1032.7	1040.2	792.3	799.4	0.000	0.000	0.832	0.000	0.000	0.0	0.000	
07/06/2010 17:50	1001.2	1009.5	760.8	768.7	0.040	0.038	0.837	0.046	0.045	199.0	0.108	
07/06/2010 19:00	963.1	971.6	722.7	730.8	0.088	0.086	0.844	0.101	0.099	621.1	0.165	
07/06/2010 19:30	949.0	957.7	708.6	716.9	0.106	0.103	0.847	0.121	0.119	802.0	0.178	
07/06/2010 22:35	927.1	936.0	686.7	695.2	0.133	0.130	0.850	0.152	0.149	1917.5	0.224	
08/06/2010 10:30	833.6	839.6	593.2	598.8	0.251	0.251	0.868	0.282	0.282	6228.9	0.288	
08/06/2010 19:30	815.1	822.3	574.7	581.5	0.275	0.273	0.871	0.307	0.305	9485.1	0.311	
09/06/2010 10:22	795.8	800.7	555.4	559.9	0.299	0.300	0.874	0.333	0.334	14863.8	0.335	
09/06/2010 17:10	786.8	791.8	546.4	551.0	0.310	0.311	0.876	0.345	0.345	17324.0	0.343	
10/06/2010 10:13		776.3		535.5		0.330	0.879		0.366	23492.6	0.360	
11/06/2010 13:45		763.3		522.5		0.346	0.881		0.383	33454.1	0.379	
14/06/2010 13:16		742.2		501.4		0.373	0.885		0.410	59328.6	0.410	
16/06/2010 9:48		732.0		491.2		0.386	0.887		0.423	75440.6	0.423	
17/06/2010 11:15		728.4		487.6		0.390	0.887		0.428	84648.3	0.429	
21/06/2010 16:45		713.9		473.1		0.408	0.890		0.447	121370.6	0.449	

	2-day	2-week
Fm	0.310	0.408

	2-day	2-week
Fv	0.345	0.447



# Density BP MC252 ENT-052210-178

## Measurements

Mass Evaporated (Fm)	Density (g/cm <sup>3</sup> )	Temperature (°C)
0	0.838	16.6
0	0.823	37.8
0.31	0.880	17.3
0.31	0.866	37.4
0.41	0.896	17.1
0.41	0.881	38.2
0	0.832	24.69
0.31	0.875	24.69
0.41	0.891	24.69

slope 0.142  
intercept 0.832  
 $r^2$  0.999

## Density Constants for SL Ross Model

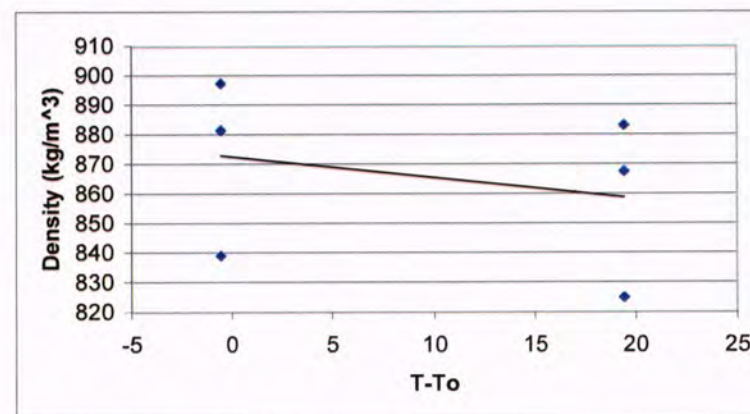
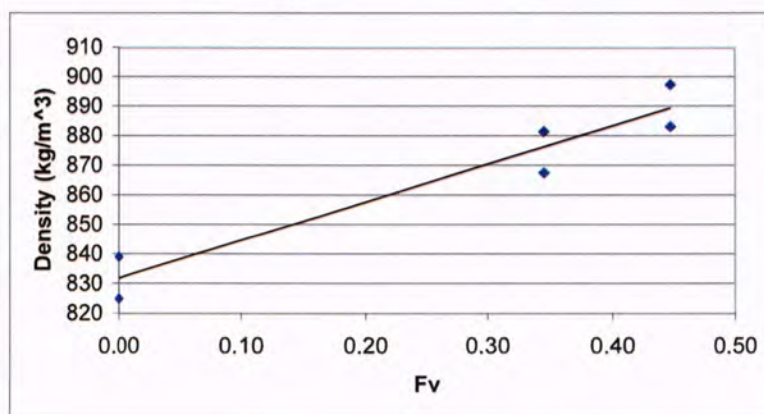
Density Constant 1 (slope, kg/m<sup>3</sup>) 128.770  
Density Constant 2 (kg/K.m<sup>3</sup>) 0.705

## Calculations

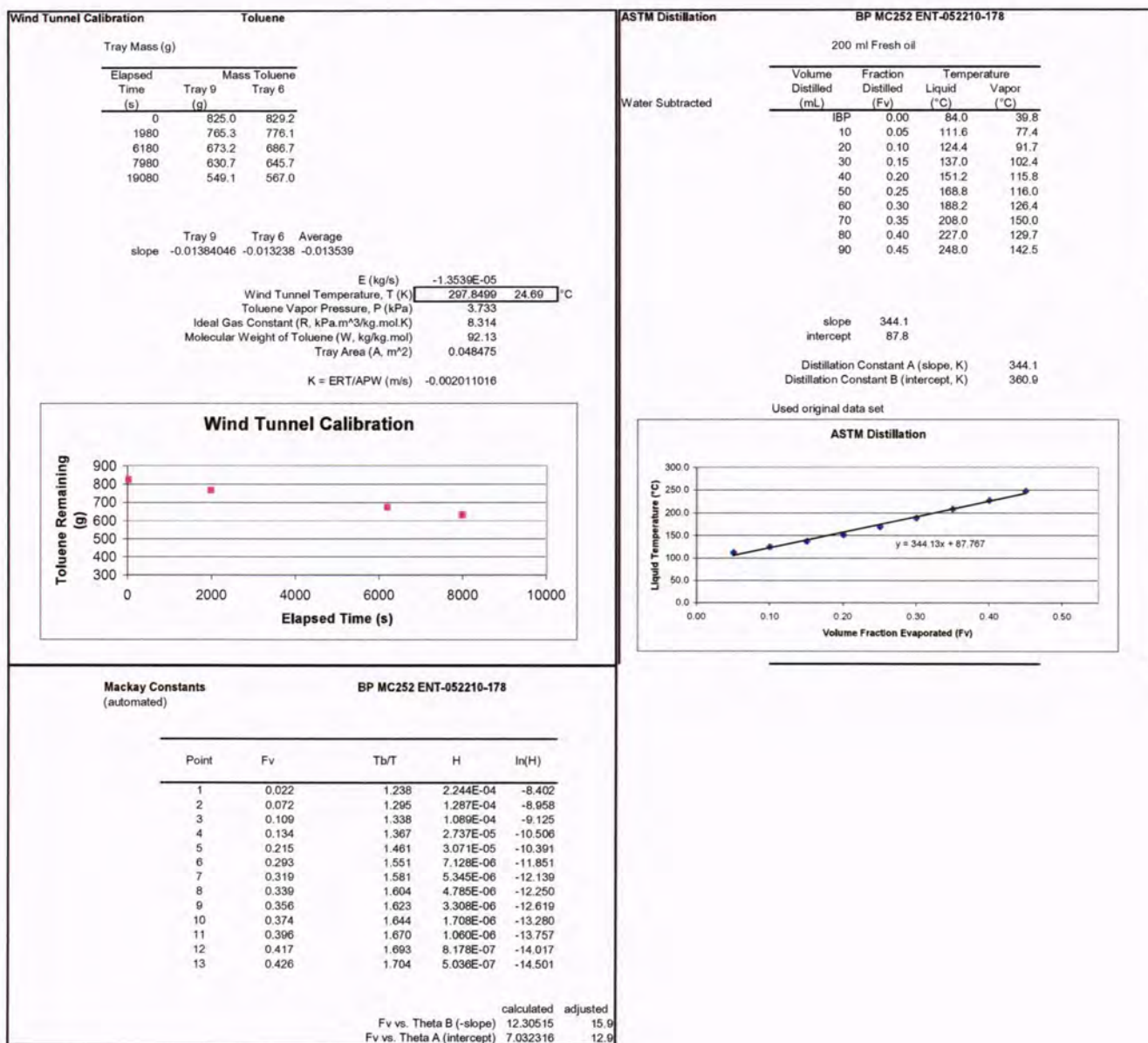
Temperature (°C)	Density (g/cm <sup>3</sup> )	Density (kg/m <sup>3</sup> )	Volume Evaporated (Fv)	T-To (K)
15	0.839	839	0	-0.56
15	0.882	882	0.345	-0.56
15	0.897	897	0.447	-0.56
35	0.825	825	0	19.44
35	0.868	868	0.345	19.44
35	0.883	883	0.447	19.44
15.5	0.897	897	0.000	

## API Gravity

Standard Density Temperature, To (K) 288.72  
Standard Density (kg/m<sup>3</sup>) 838.736  
API Gravity @ 15.5°C 37.21

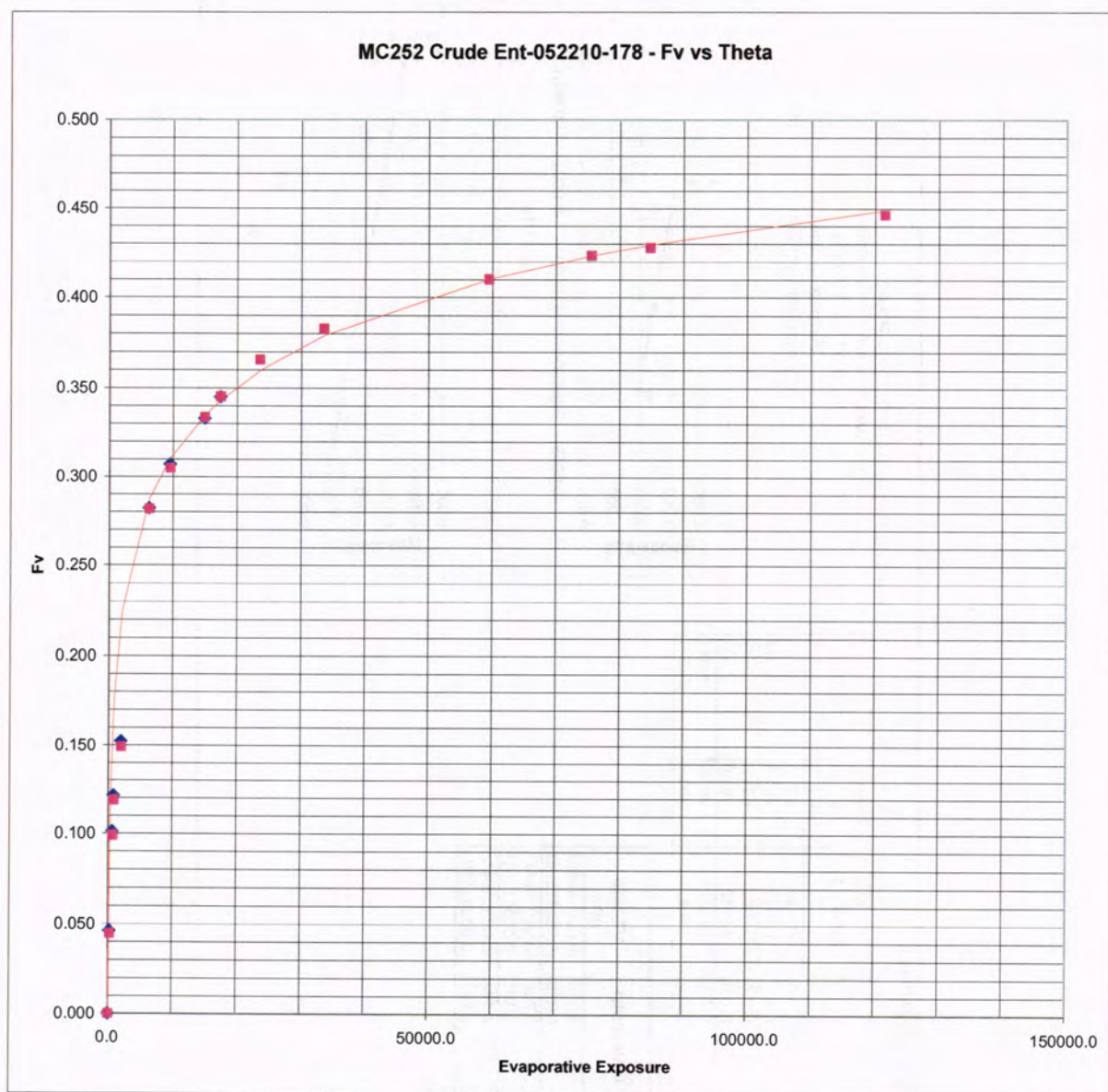












**Viscosity BP MC252 ENT-052210-178**

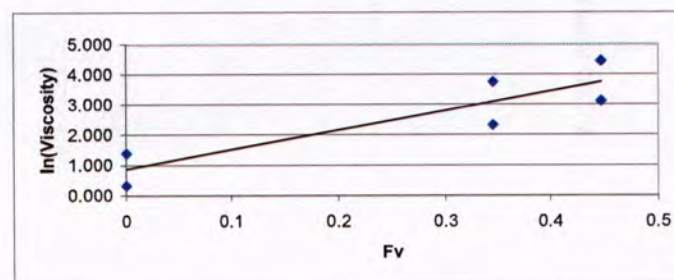
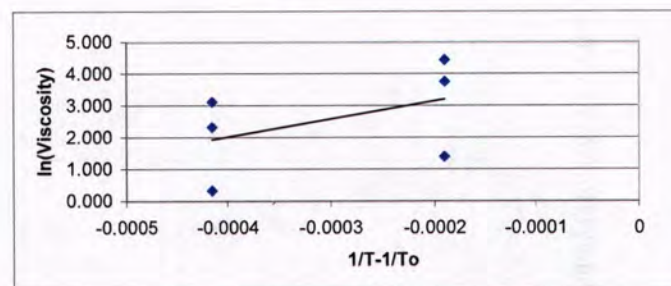
Mass Evaporated (Fm)	Viscosity (cP)	Temperature (°C)	rpm	Spindle #	Shear Rate (s <sup>-1</sup> )	ln(Viscosity)
0	4.1	15.0	120.0	CP-42	461.0	1.399
0	1.4	35.0	120.0	CP-42	461.0	0.329
0.31	42.9	15.0	120.0	CP-42	461.0	3.759
0.31	10.3	35.0	120.0	CP-42	461.0	2.332
0.41	85.1	15.0	120.0	CP-42	461.0	4.444
0.41	22.8	35.0	120.0	CP-42	461.0	3.127

Volume Evaporated (Fv)	Viscosity (cP)	Temperature (°C)	ln(Viscosity)	1/T-1/To (K <sup>-1</sup> )
0	4.1	15.0	1.399	-0.000190564
0	1.4	35.0	0.329	-0.000415685
0.34	42.9	15.0	3.759	-0.000190443
0.34	10.3	35.0	2.332	-0.000415685
0.45	85.1	15.0	4.444	-0.000190443
0.45	22.8	35.0	3.127	-0.000415685

Volume Evaporated (Fv)	Viscosity 1°C (cP)	Viscosity 15°C (cP)
0	4.1	1.4
0.34	42.9	10.3
0.45	85.1	22.8

**Viscosity Constants for SL Ross Model**

Standard Viscosity Temperature (K)	273.16
Standard Viscosity (cP)	9.03
Viscosity Constant 1	6.49
Viscosity Constant 2 (K <sup>-1</sup> )	5646.99





# Pour Point

BP MC252 ENT-052210-178

## Test Results

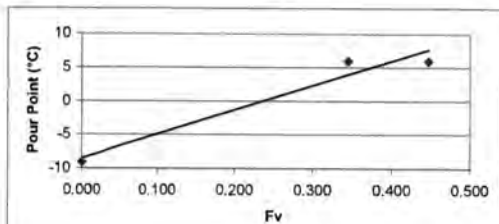
## Pour Point Constants for SLR Spill Model

Fv	Pour Point	
	Measured (°C)	Reported (°C)
0.000	<-10	-9
0.345	5	6
0.447	5	6

Initial Pour Point (K) 264.6211  
Pour Point Constant 0.136472

less than

slope 36.11327  
intercept -8.528878



# Interfacial Tension

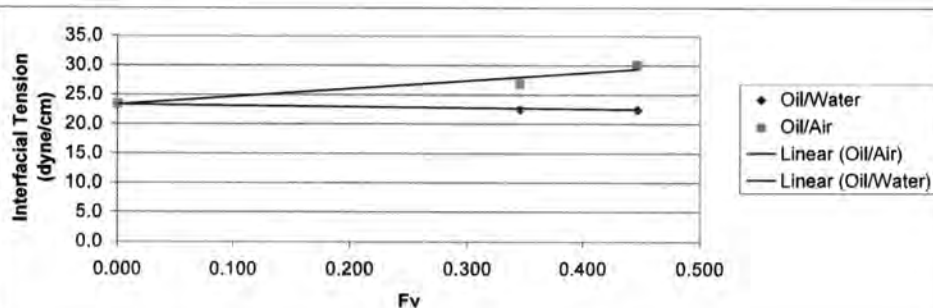
BP MC252 ENT-052210-178

Fv	Interfacial Tension		Dial Reading		Correction Factor (F)	
	Oil/Water (dyne/cm)	Oil/Air (dyne/cm)	Oil/Water (dyne/cm)	Oil/Air (dyne/cm)	Oil/Water	Oil/Air
0.000	23.3	23.5	23.7	26.4	0.985	0.893
0.345	22.6	26.8	22.4	30.0	1.007	0.896
0.447	22.5	30.1	22.1	33.4	1.019	0.900

slope -1.841 13.365  
intercept 23.273 23.300

## Interfacial Tension Constants for SL Ross Model

Oil/Water Interfacial Tension (dyne/cm) 23.273  
Oil/Water Interfacial Tension Constant -0.079  
Oil/Air Interfacial Tension (dyne/cm) 23.300  
Oil/Air Interfacial Tension Constant 0.574

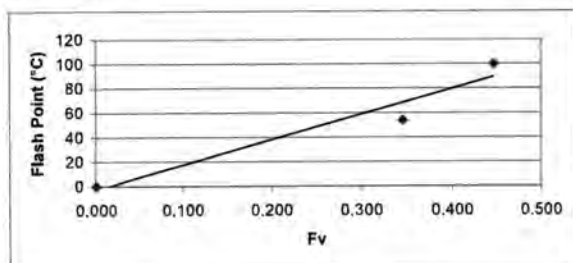


**Flash Point** BP MC252 ENT-052210-178**Test Results****Flash Point Constants for SLR Spill Model**

Fv	Flash Point (°C)
0.000	<-8
0.345	54
0.447	100

Initial Flash Point (K) 170.989  
Flash Point Constant 2.647

slope 452.664693  
intercept 170.989269

**SL Ross Model**  
**Modeling Constants****BP MC252 ENT-052210-178**

Standard Density	838.736 kg/m3
Standard Density Temperature	288.720 K
Density Constant 1	128.770 kg/m3
Density Constant 2	0.70499 kg/K.m3
Standard Viscosity	9.03203 cP
Standard Viscosity Temperature	273.160 K
Viscosity Constant 1	6.4856
Viscosity Constant 2	5646.99 K-1
Oil/Water Interfacial Tension	23.2729 dyne/cm
Air/Oil Interfacial Tension	23.3002 dyne/cm
Oil/Water Interfacial Tension Constant	-0.07910
Air/Oil Interfacial Tension Constant	0.57362
Initial Pour Point	264.621 K
Pour Point Constant	0.13647
ASTM Distillation Constant A (slope)	344.133 K
ASTM Distillation Constant B (intercept)	360.927 K
Emulsification Delay	9999999999
Initial Flash Point	170.989 K
Flash Point Constant	2.64733
Fv vs. Theta A	12.90000
Fv vs. Theta B	15.90000
B.Tg	5471.72
B.To	5738.73

# Emulsification Formation - Tendency and Stability

BP MC252 ENT-052210-178

## Emulsification Tendency and Stability - 23°C

<b>Test Results</b>		300ml H2C		22.5 °C									
		oil @		39.0 °C									
		mixing don		22.7 °C									
		settling dor		22.7 °C									
		Final 24 hr		22.7 °C									
		two replicates of each oil											
All measurements in mm	Fresh Oil				Weathered Two Days				Weathered Two Weeks				
	Emulsion	Free Oil	Emulsion	Free Oil	Emulsion	Free Oil	Emulsion	Free Oil	Emulsion	Free Oil	Emulsion	Free Oil	
Start	0	10	0	10	0	10	0	10	0	10	0	10	
After first hour mixing	10	0	10	0	11	0	11	0	10	0	10	0	
plus 10 minutes	0	9	0	9	10	0	0	9	0	9	10	0	
plus 20 minutes	0	9	0	9	0	9	0	9	0	9	0	9	
plus 30 minutes	0	9	0	9	0	9	0	9	0	9	0	9	
After second hour mixing	0	9	0	9	10	0	10	0	10	0	10	0	
plus 10 minutes	0	9	0	9	0	9	10	0	10	0	10	0	
plus 20 minutes	0	9	0	9	0	9	10	0	10	0	10	0	
plus 30 minutes	0	9	0	9	0	9	10	0	0	9	10	0	
After third hour mixing	0	8	0	9	10	0	10	0	10	0	10	0	
plus 10 minutes	0	9	0	9	10	0	10	0	0	9	0	9	
plus 20 minutes	0	9	0	9	0	9	0	9	0	9	0	9	
plus 30 minutes	0	9	0	9	0	9	0	9	0	9	0	9	
After fourth hour mixing	0	9	0	9	10	0	10	0	10	0	10	0	
plus 10 minutes	0	9	0	9	0	9	0	9	10	0	10	0	
plus 20 minutes	0	9	0	9	0	9	0	9	0	9	0	9	
plus 30 minutes	0	9	0	9	0	9	0	9	0	9	0	9	
Appearance	Brown solid	0		0		0		0		0		0	
	Brown viscous liquid	X		X		X		X		X		X	
	Black with large droplets	0		0		0		0		0		0	
	Looks like oil	X		X		X		X		X		X	
	plus 24 hour	0	9	0	9	0	9	0	9	0	9	0	9
<b>Conclusions:</b>		Fresh Oil		Weathered Two Days		Weathered Two Weeks							
Tendency		Unlikely		Unlikely		Unlikely							
Stability		Unstable		Unstable		Unstable							
Water Content (after 24 hr)		0%		0%		0%							



Emulsification Tendency and Stability - 35°C

<b>Test Results</b>		300ml H2C 34.0 °C oil @ 40.0 °C mixing don 36.0 °C settling dor 22.0 °C Final 24 hr 36.0 °C two replicates of each oil											
All measurements in mm		Fresh Oil				Weathered Two Days				Weathered Two Weeks			
		Emulsion	Free Oil	Emulsion	Free Oil	Emulsion	Free Oil	Emulsion	Free Oil	Emulsion	Free Oil	Emulsion	Free Oil
Start		0	0	0	10	0	10	0	10	0	10	0	10
After first hour mixing		0	9	0	9	0	9	0	9	0	9	0	9
plus 10 minutes		0	9	0	9	0	9	0	9	0	9	0	9
plus 20 minutes		0	9	0	9	0	9	0	9	0	9	0	9
plus 30 minutes		0	9	0	9	0	9	0	9	0	9	0	9
After second hour mixing		0	9	0	9	0	9	0	9	0	9	0	9
plus 10 minutes		0	9	0	9	0	9	0	9	0	9	0	9
plus 20 minutes		0	9	0	9	0	9	0	9	0	9	0	9
plus 30 minutes		0	9	0	9	0	9	0	9	0	9	0	9
After third hour mixing		0	9	0	9	0	9	0	9	0	9	0	9
plus 10 minutes		0	9	0	9	0	9	0	9	0	9	0	9
plus 20 minutes		0	9	0	9	0	9	0	9	0	9	0	9
plus 30 minutes		0	9	0	9	0	9	0	9	0	9	0	9
After fourth hour mixing		0	9	0	9	0	9	0	9	0	9	0	9
plus 10 minutes		0	9	0	9	0	9	0	9	0	9	0	9
plus 20 minutes		0	9	0	9	0	9	0	9	0	9	0	9
plus 30 minutes		0	9	0	9	0	9	0	9	0	9	0	9
Appearance	Brown solid	0		0		0		0		0		0	
	Brown viscous liquid	0		0		0		0		0		0	
	Black with large droplets	0		0		0		0		0		0	
	Looks like oil	X		X		X		X		X		X	
	plus 24 hour	0	9	0	9	0	9	0	9	0	9	0	9
note:		0											
Conclusions:		Fresh Oil				Weathered Two Days				Weathered Two Weeks			
Tendency		Unlikely				Unlikely				Unlikely			
Stability		Unstable				Unstable				Unstable			
Water Content (after 24 hr)		0%				0%				0%			

### Viscosity Measurements with Brookfield DV-III+ Rheometer

Nominal Test Temperature	15.0				35.0			
	Viscosity	RPM	Spindle	Shear Rate	Viscosity	RPM	Spindle	Shear Rate
Fresh	4.1	120.0	CP-42	461.0	1.4	120.0	CP-42	461.0
2 Day Weathered	42.9	120.0	CP-42	461.0	10.3	120.0	CP-42	461.0
2 Week Weathered	85.1	120.0	CP-42	461.0	22.8	120.0	CP-42	461.0

	Spindle	RPM	% Torque	Viscosity cP	Shear Rate	Temp °C	
Fresh	CP-42	15	0.3	2.6	57.6	14.9	
		30	0.8	3.4	115.0	14.9	
		45	1.5	3.7	173.0	14.9	
		60	1.8	3.8	230.0	14.9	
		90	2.8	4.0	346.0	14.9	
		120	3.8	4.1	461.0	14.9	<===
		180	5.8	4.1	691.0	14.9	
		250	8.1	4.2	960.0	14.9	
		15	6.8	58.0	57.6	14.9	
		30	12.3	52.5	17.4	14.9	
2 Day Weathered	CP-42	45	17.4	49.5	173.0	14.9	
		60	22.3	47.6	230.0	14.9	
		90	31.5	44.8	346.0	14.9	
		120	40.2	42.9	461.0	14.9	<===
		180	57.0	40.5	691.0	14.9	
		250	75.6	38.7	960.0	14.9	
	CP-42	15	15.1	128.9	57.6	15.1	
		30	26.9	114.8	115.0	15.1	
		45	37.1	105.5	173.0	15.0	
		60	46.3	98.8	230.0	15.0	
		90	63.7	90.6	346.0	15.0	
		120	79.8	85.1	461.0	15.0	<===
		180	-over-	-over-	691.0	15.1	
	CP-42	15	0.1	0.9	57.6	35.0	
		30	0.2	0.9	115.0	35.0	
		45	0.5	1.4	173.0	35.0	
		60	0.7	1.5	230.0	35.0	
		90	1.0	1.4	346.0	35.0	
		120	1.3	1.4	461.0	35.0	<===
		180	2.2	1.6	691.0	35.0	
		250	3.0	1.5	960.0	35.0	
2 Day Weathered	CP-42	15	1.2	10.2	57.6	35.0	
		30	2.4	10.2	115.0	35.0	
		45	3.7	10.5	173.0	35.0	
		60	4.9	10.5	230.0	35.0	
		90	7.3	10.4	346.0	35.0	
		120	9.7	10.3	461.0	35.0	<===
		180	14.4	10.2	691.0	35.0	
		250	19.9	10.2	960.0	35.0	
2 Week Weathered	CP-42	15	2.8	23.9	57.6	35.0	
		30	5.5	23.5	115.0	35.0	
		45	8.3	23.6	173.0	35.0	
		60	10.9	23.3	230.0	35.0	
		90	16.1	22.9	346.0	35.0	
		120	21.4	22.8	461.0	35.0	<===
		180	31.6	22.5	691.0	35.0	
		250	43.4	22.2	960.0	35.0	

---

## Appendix 9

### A9 Expert Resumes

**Mr. Alan A. Allen** has over 43 years experience as a technical advisor and field supervisor involving hundreds of oil spills around the world. He has developed specialized strategies and equipment for the prevention, surveillance and control of oil spills; and he has conducted many hundreds of oil spill training courses under arctic, temperate and tropical conditions. Mr. Allen is listed as a technical advisor for emergency response to oil spills in numerous emergency response plans worldwide. A few of the spills on which he has worked include the Santa Barbara blowout (1969), the Mizushima tank failure in Japan (1974), the *Ixtoc* blowout off Mexico (1979), the *Exxon Valdez* grounding (1989), the Gulf of Arabia war-related spills (1991), the *Sea Prince* grounding off South Korea (1995), the Deepwater Horizon blowout in the Gulf of Mexico (2010), and a number of pipeline spills onshore and in wetlands.

**Dr. Michel Boufadel** is Professor and Chair of the Department of Civil and Environmental Engineering at Temple University, Philadelphia, Pennsylvania, USA. He is a Professional Engineer (Environmental Engineering) in the Commonwealth of Pennsylvania (USA). He is also a Professional Hydrologist (hydrogeology) as accredited by the American Institute of Hydrology (USA). His area of expertise is Environmental Hydrology, where he develops methods to account for changes in the environment due to natural and anthropogenic stressors. He has been the lead researcher on various projects funded by the Oil Spill Research program within the United States Environmental Protection Agency (USEPA). He is currently investigating the lingering of the Exxon Valdez oil (1989) in the beaches of Prince William Sound, where he and his team conducted field studies on various beaches and are exploring remediation technologies for dealing with the 20-year old spill. Dr. Boufadel is author of numerous articles in publications such as *NATURE*, geoscience, Environmental Science and Technology, the Journal of Environmental Engineering, Environmental Geology, Journal of the American Water Resources Association, Journal of Contaminant Hydrology, and Journal of Stochastic Environmental Research and Risk Assessment. The work of Dr. Boufadel has been reported in various media outlets such as the New York Times, the Washington Post, and the BBC World News and numerous international media outlets.



---

**Mr. Sky Bristol** leads a computer and information science research and development effort with the U.S. Geological Survey (USGS), pursuing a concept called the Integrated Information Environment. Before coming to the USGS in 2004, Sky held various positions with the U.S. Fish and Wildlife Service (USFWS) as a biologist in the Environmental Contaminants Program and an engineer and developer with the Information Resource Management Program. Sky was educated as a wildlife biologist and criminologist at the University of New Mexico, learning computer and information science as a secondary vocation in the course of creating program in these areas for the USFWS and USGS.

**Dr. Thomas S. Coolbaugh** is a Distinguished Scientific Associate with ExxonMobil Research & Engineering. Dr. Coolbaugh has extensive experience in a variety of research settings as a research scientist and research leader and currently leads ExxonMobil's downstream oil spill response technology group. Dr. Coolbaugh earned a B.A., magna cum laude in Chemistry from Amherst College, and a Ph.D. in Chemistry from the California Institute of Technology with Prof. Robert Grubbs, 2005 Nobel laureate in Chemistry. He also earned an M.S. in Management of Technology from Polytechnic University (New York).

**Mr. Per Daling** is a Senior Research Scientist at Marine Environmental Technology Dept. at SINTEF. He has 30 years of experience within the field of oil pollution, and has been project manager and scientist responsible for many research programs involving weathering and behaviour of oil at sea, field and laboratory testing of oil spill dispersants and countermeasure techniques and oil spill planning. Mr. Daling has authored or co-authored 40 refereed publications, and more than 150 non-refereed publications, papers and invited presentations. He has a MSc in Organic Analytical Chemistry from Institute of Chemistry, University of Trondheim.

**Dr. Merv Fingas** was Chief of the Emergencies Science Division of Environment Canada for over 30 years and is currently working privately in Western Canada. His specialities include; spill dynamics and behaviour, spill treating agent studies, remote sensing and detection, and in-situ burning. He has over 750 papers and publications in the field. Dr. Fingas has been an editor of the Journal of Hazardous Materials for 6 years. He has served on two committees on the National Academy of Sciences of the United States on oil spills including the recent 'Oil in the Sea'. He is chairman of several

---

ASTM and inter-governmental committees on spill matters. Dr. Fingas has a PhD in environmental physics from McGill University, three masters degrees; chemistry, business and mathematics, all from University of Ottawa.

**Dr. Deborah French-McCay** is a Principal at Applied Science Associates (ASA, Narragansett, RI, USA), where she specializes in quantitative assessments and modeling of oil and chemical releases: transport and fates, exposure, bioaccumulation of pollutants by biota, toxicity, and effects on populations and aquatic ecosystems. Dr. French McCay was principal investigator in the development of NRDA models, established in the US Federal regulations for simplified assessments under CERCLA and the Oil Pollution Act. She has been principal investigator and primary author of more than one hundred technical reports and papers, and is an internationally recognized expert in oil spill fate and effects modeling. Dr. French-McCay received her bachelor's degree in Zoology from Rutgers in 1974 and her Ph.D. in Biological Oceanography from the University of Rhode Island in 1984

**Dr. Ron Goodman** attended the University of Saskatchewan and graduated with a Bachelor of Arts in Science with specialization in physics. He undertook graduate studies at McMaster University in Hamilton and obtained a PhD. in nuclear physics in 1964. Innovative Ventures Ltd. (IVL) was started by Dr. Goodman in 1971 to consult on Arctic Environmental issues. Joining Imperial Oil in 1978, he developed the only industry-based oil-spill research program in Canada. He served as the manager of surveillance and tracking for the Exxon Valdez response during 1989. Dr. Goodman retired from Imperial Oil in 2000, and reactivated Innovative Ventures Ltd. IVL has been involved in the JESSICA spill in the Galapagos Islands and the rail spill at Wabamun, Alberta Canada. He has been in the oil-spill technology business for thirty-five years, specializing in remote sensing, arctic oil-spill response and oil-spill models. Dr. Goodman has served on a number of national and international committees including IMO/MEPC and ASTM. He has published over 200 papers.

**Dr. Ali Khelifa** is Head of the Spill Modelling Laboratory at the Emergencies Science and Technology Section of Environment Canada. He received his Master in 1992 and PhD in 1998 in Environmental Hydraulics from Laval University in Québec in Canada. Dr. Khelifa has conducted extensive research on transport and fate of pollutants spilled in the environment using computer and laboratory modelling for the last 20 years. The last nine years of his

---

research were devoted to developing quantitative understanding of the fate of physically and chemically dispersed oils in the aquatic environment. He has authored over a hundred of scientific papers and technical reports and his extensive contribution related to oil dispersion and oil-sediment interaction is internationally recognized.

**Dr. Robert Jones** is a Chemist in NOAA's Office of Response and Restoration, Emergency Response Division. He is extensively involved in the development of computer models used to predict the fate and transport of chemicals in the environment and is a member of the spill response team.

Dr. Jones received his B.S. in Chemistry from Xavier University, and his Ph.D. in Physical Chemistry from Indiana University. After graduation he worked as a research associate at the National Institute of Standards and Technology in Washington D.C. Prior to joining NOAA in 1988, Dr. Jones was an assistant professor in the chemistry department at Western Washington University.

**Mr. Patrick Lambert** is a chemist with twenty years experience in the environmental field of chemical and oil spill research and development, and twenty-three years of laboratory experience in both the private and public sectors. He is Head of Field Work and Response, Emergencies Science and Technology Section, Environment Canada. He has been part of the science team in numerous oil spill projects such as the Newfoundland Offshore Burn Experiment and has extensive operational experience with contaminated sites, environmental emergency response, contaminated site and counter-terrorism related.

**Dr. Kenneth Lee** is a senior research scientist and Director of the Centre for Offshore Oil and Gas Environmental Research, Fisheries and Oceans Canada. The centre is responsible for the coordination of a national strategic program in environmental and oceanographic research relating to oil and gas activities. Dr. Lee is the recipient of Fisheries and Oceans Canada's Prix d'Excellence (Science) for his research contributions on environmental issues associated with offshore oil and gas activities; and the Government of Canada's Federal Partners on Technology Transfer (FPTT) Leadership Award for the development of oil spill countermeasures. He currently serves as a Committee Member of NATO's Science for Peace and Security Program.

**Dr. Ira Leifer** has a Ph.D. in bubble-mediated air-sea interaction from the



---

Georgia Institute of Technology, Earth and Atmospheric Sciences Department. Over the last decade, he has been a leader in research related to natural seepage, including numerical bubble modeling, video observations of bubbles including oily bubbles, multibeam sonar bubble plume observations, remote sensing of atmospheric methane and of oil slicks by imaging spectroscopy, weathering of oil slicks from natural seepage, and in situ measurements of light n-alkanes in the air and water. Research sites have spanned the Gulf of Mexico, to Santa Barbara Channel, to Norwegian and Russian Arctic waters, from submarines to research vessels, to airplanes.

**Dr. William (Bill) J. Lehr** is Senior Scientist at the Office of Response and Restoration of the National Oceanic and Atmospheric Administration (NOAA). He was previously Spill Response Group Leader for the same organization. Dr. Lehr has also served as an adjunct professor for the World Maritime University and oil spill consultant for UNESCO. Dr. Lehr is a world-recognized expert in the field of hazardous chemical spill modeling and remote sensing of oil spills. He has served as guest editor for the journal, *Spill Science and Technology* and the *Journal of Hazardous Materials* and as Co-Chair of the International Oil Weathering Committee. NOAA and the United States Coast Guard have awarded him several medals for his spill response efforts at major spill incidents of national or international significance. He has numerous publications in the field. Dr. Lehr holds a Ph.D. in Physics from Washington State University.

**Dr. Alan Mearns** is Senior Staff Scientist, Ecology, with NOAA's Emergency Response Division (ERD), Office of Response and Restoration. Dr. Mearns holds a PhD in Fisheries from the University of Washington, and Master of Science and Bachelor of Science degrees from California State University at Long Beach. He is past leader of the Biology Division of the Southern California Coastal Water Research Project and served as Ecologist for the NOAA Puget Sound MESA Program. He has provided support to the US Coast Guard and the NOAA Scientific Support Coordinators (SSC's) on numerous oil spills throughout the US and internationally. He supports numerous oil spill science training programs, is a member of several technical advisory committees in Alaska and has recently started a third decade of annual shoreline monitoring in Prince William Sound. He has received various awards from California State University and NOAA.

---

**Dr. Edward B. Overton** is Professor Emeritus in the Department of Environmental Sciences, School of Coast and the Environment at LSU. He received his B.S.(1965) and Ph.D.(1970) degrees from the University of Alabama, Tuscaloosa. His research interests include understanding the fates and distributions of hydrocarbons following an oil spill, the environmental chemistry of hazardous chemicals, and the detection of environmental pollutants at the site of sample collection. Dr. Overton held the Clairborne Chair in Environmental Toxicology and Air Quality prior to his retirement, and was honored as an LSU Distinguished Faculty in 2008, and was the 1996 Louisiana Technologist of the Year.

**Dr. James Payne** has been involved in oil-spill research for over 36 years, including work at the Woods Hole Oceanographic Institution, the University of California Bodega Marine Laboratory, Science Applications International Corporation, and the last 12 years as President of Payne Environmental Consultants, Incorporated. He has conducted oil fate and behavior research and studies on oil-spill dispersants since 1979, and he has served on four National Academy of Sciences/National Research Council Committees dealing with petroleum in the marine environment. Most recently he served on the NRC Committee on Understanding Oil Spill Dispersants.

**Dr. Antonio Possolo** is a statistician and Chief of the Statistical Engineering Division at the National Institute of Standards and Technology (NIST, U.S. Dept. of Commerce). He has been a statistician at General Electric and at Boeing, and has taught at the University of Washington in Seattle and at Princeton University. His areas of specialty include statistical modeling of spatio-temporal data and uncertainty analysis. Dr. Possolo holds a Ph.D in Statistics from Yale University.

## Appendix 10

### A10 Reviewer Comments and Replies

Sixteen reviewers (see Table 1) with diverse background were selected by the Coastal Response Research Center to review all or part of the report. Fourteen responded within the allotted time frame. We would like to thank all the reviewers for their efforts under conditions that required expeditious action on their part. While the list of names is provided in this Appendix, individual comments were provided to the team anonymously. One should not, for example, identify Reviewer 1 with the first name in Table 1. Page numbers refer to the unedited draft report and may not correspond to those in the final report.

First	Last	Affiliation
Eric	Adams	Massachusetts Institute of Technology (MIT) Dept. of Mechanical Engineering
Kathryn	Burns	Austrailian Institute of Marine Sciences, Organic Geochemist, Water Quality Team
Robert	Chen	University of Massachusetts Boston, Environmental Earth and Oceans Sciences
Kurt	Hansen	U.S. Coast Guard, Research & Development Center
Terry	Hazen	Lawrence Berkeley National Laboratory - Ecology Dept.
Wolfgang	Konkel	ExxonMobil
Buzz	Martin	Texas General Land Office - Oil Spill Prevention & Response
Joseph	Mullin	Bureau of Ocean Energy Management, Regulation & Enforcement (BOEMRE)
Michael	O'Brien	Internation Tanker Owners Pollution Federation Ltd. (ITOPF)
Rob	Swift	University of New Hampshire, Mechanical Engineering/Ocean Engineering
Terry	Wade	Texas A & M
Xiaomong	Wang	Florida State University, Dept. of Mathematics
Tom	Weber	Center for Coastal & Ocean Mapping
Steven	Werely	Purdue University



---

Reviewers' comments are in italics and replies are in plain text.

## **Reviewer 1:**

*This section focuses on estimating the amount of oil recovered by surface skimmers. The total amount of oil and water mixture held in tanks on the skimmers is measurable, but the percent that is actually oil, referred to as the recovery efficiency (RE), is needed to calculate the amount of oil collected. The report states that a RE of 33% was used based on "prior studies" (no reference). To assess whether this is a reasonable value, the types of skimmers employed would have to be taken into account. Oliophilic mechanisms such as disk and drum skimmers can have RE's of 90% or better (see, for example, Schulze, 1998). Suction or weir skimmers, on the other hand, typically have RE values of a few percent unless the slick is unnaturally thick and the surface is without waves. Thus assuming an average RE for the skimming fleet should be based on the distribution of skimmer types (as well, of course, sea state and slick thickness).*

*It should also be pointed out that determining the water content in recovered oil and water mixtures is a standard laboratory analysis done at the OHMSETT oil spill test facility. It would seem that their protocol could be adapted to either on-board determination of RE or representative samples could be transported to a shore laboratory for RE analysis.*

Skimmers were the most commonly-used mechanical devices used to remove oil from the Gulf water surface. These skimmers varied greatly in size, application, and capacity, as well as in recovery efficiency and water pickup. (Schulze, 1998; Schwartz, 1979). In the particular case of the Gulf oil spill the major issue is the amount of water recovered. A skimmer's performance is affected by a number of factors including the thickness of the oil being recovered, the extent of weathering and emulsification of the oil, the presence of debris, and weather conditions at the time of recovery operations. A skimmer's overall performance is usually determined by a combination of its recovery rate and the percentage of oil recovered. The maximum amount of oil that a skimmer could recover is called the 'Nameplate Recovery Rate' and is typically provided by the manufacturer of a skimmer (Fingas, 2010; Meyer et al, 2009). A similar definition is the 'Effective Daily Recovery Capacity', which is the amount that a skimmer could recover in daylight hours under ideal conditions. The recovery rate is the volume of oil recovered under specific conditions. It is measured as volume per unit of time, e.g., m<sup>3</sup>/h, and is usually given as a range. If a skimmer takes in a lot of water, it is detrimental to the overall efficiency of an oil spill recovery operation. The

---

summary results of performance testing on various types of skimmers are given in Table 1 (Schulze, 1998;Fingas, 2010).

Table 2 shows the three most important values of skimmer performance, ORR, TE, and RE. This is a sample table showing a fraction of the skimmers tests reported in the reference (Fingas, 2010). The Oil Recovery Rate(ORR) is the quantitative rate in volume per unit time, usually m<sup>3</sup>/hour and is corrected for water recovery. The throughput efficiency (TE) is applicable only to advancing skimmers. The throughput efficiency is the percentage of oil presented to a skimmer versus that recovered, in percent. The recovery efficiency (RE) is the percent of oil recovered out of the total oil and water recovered. For the Gulf recovery effort, the RE is the most important factor. We know the total liquids recovered, but we do not know exactly how much oil was in this liquid and therefore must estimate the actual oil recovered. Table 2 shows that the average RE of the skimmers in wave conditions is 33%.

The emulsion recovered typically contained 30- 60% water (Appendix 6). Using 40% as an average water fraction, the typical amount of oil in the recovered mixture is 0.6 X 0.33 or 0.20 (20%). The amount of liquid recovered was 735,000 barrels and thus the amount of oil recovered was about 20% of this or 147,000 barrels.

- 1 Schulze, R., *Oil Spill Response Performance Review of Skimmers*, ASTM Manual Series, ASTM, 1998
- 2 Schwartz, S.H., Performance Tests of Four Selected Oil Spill Skimmers, *AMOP*, 493, 1979
- 3 Fingas, M.F., Weather Effects on Oil Spill Countermeasures, Chapter 13 in *Oil Spill Science and Technology*, p. 339-426,2010
- 4 Meyer P., W. Schmidt, J.-E. Delgado, D. DeVitis, S. Potter, E. Haugstad and M. Crickard, Application of the American Society of Testing and Materials' (ASTM) New Skimmer Test Protocol, *AMOP*, 323, 2009
- 5 SINTEF, Laboratory study of the dispersibility of DWH surface emulsion, 2010

**Table 1 Performance of Typical Skimmers**

Recovery Rate (m <sup>3</sup> /hr) for given oil type*				Percent
Skimmer Type	Light Crude	Heavy Crude	Bunker C	Oil**
Oleophilic Skimmers				
small disc	0.2 to 2			80 to 95
large disc	10 to 20	10 to 50		80 to 95
brush	0.5 to 20	0.5 to 2	0.5 to 2	80 to 95
large drum	10 to 30			80 to 95
small drum	0.5 to 5			80 to 95
large belt	1 to 20	3 to 20	3 to 10	75 to 95
inverted belt	10 to 30			85 to 95
rope	2 to 20	2 to 10		
Weir Skimmers				
small weir	0.5 to 5	2 to 20		20 to 80
large weir	30 to 100	5 to 10	3 to 5	50 to 90
advancing weir	5 to 30	5 to 25		30 to 70
Elevating Skimmers				
paddle conveyer	1 to 10	1 to 20	1 to 5	10 to 40
Submersion Skimmers				
large	1 to 80	1 to 20		70 to 95
Suction Skimmers				
small	0.3 to 2			3 to 10
large trawl unit	2 to 40			20 to 90
large vacuum unit	3 to 20	3 to 10		10 to 80
Vortex/Centrifugal Skimmers				
centrifugal unit	0.2 to 10			2 to 20

\* Recovery rate depends very much on the thickness of the oil, type of oil, sea state, and many other factors

\*\* This is the percentage of oil in the recovered product or recovery rate. The higher the value, the less the amount of water and thus the better the skimmers' performance



**Table 2 Skimmer Performance (Sample cases)\***

Skimmer	Year	Oil	Oil Viscosity	Slick Thick.	#of	Speed	Wave height	Wave	ORR	TE	RE
	of Test	Type	mPa. S	mm	Tests	m/s	m	Conditions	m <sup>3</sup> /h	%	%
<b>Harbour/small skimmers</b>											
Skimming Barrier	1977		200	120	3	0.25	calm		58.2		56
Skimming Barrier	1977		200	120	5	0.25	0.3	harbour chop	47.4		34.5
Skimming Barrier	1977		200	120	4	0.5	0.3	regular	71.7		48.9
Sirene Skimming Barrier	1979		545	3	1	0.75	calm		15.8	11	26
Sirene Skimming Barrier	1979		545	3.2	1	0.38	0.6	harbour chop	18.6	99	31
Sirene Skimming Barrier	1979		545	3.2	1	0.38	0.5	regular	16.4	99	27
Lori Brush Skimmer	1979	med. oil	600	ns	1	1.5	calm		0.96		78
Lori Brush Skimmer	1979	med. oil	600	ns	1	0.75	0.16	regular	0.35		81
Disc skim. - flat -CCG tests	1993	lt. crude	5 to 50	10	1	0	0.4	regular			65
Disc skim. - flat -CCG tests	1993	lt. crude	5 to 50	10	1	0	0.8	harbour chop			48
Disc skim. - flat -CCG tests	1993	lt. crude	5 to 50	25	1	0	calm				96
Disc skim. -T-disk -CCG tests	1993	lt. crude	5 to 50	10	1	0	0.4	regular			46
Disc skim. -T-disk -CCG tests	1993	lt. crude	5 to 50	10	1	0	0.8	harbour chop			24
Paddle skimmer	1977	heav. oil	1900	26	1	0	calm		9.4	91	84
Paddle skimmer	1977	heav. oil	1900	26	1	0	0.2	regular	4.8	70	18
Rope Mop towed single	1978	med. oil	793	5	1	1.3	0.6	harbour chop	5.7		49
Rope Mop towed single	1978	med. oil	793	5	1	1.5	0.6	harbour chop	5		46
Oil Mop ZRV	1976	lt. crude	65	4 ave	1	1.25	calm		7	36	23
Oil Mop ZRV	1976	lt. crude	65	4 ave	1	1.5	0.6	harbour chop	4.8	21	10
Marco Belt skimmer	1976	heav. oil	837	8 to 11	6	0.5	calm		11.5	85	57
Marco Belt skimmer	1976	heav. oil	837	8 to 11	4	1.5	calm	harbour chop	20.6	62	76
DIP 2001	1973	Alberta crude	8	.7 ave	1	1.3	calm		2.7	88	30
DIP 2001	1975	Arab crude	24	0.5	1	1	calm		0.9	77	94
DIP 2001	1975	Arab crude	24	1	1	0.5	0.4	natural	0.9	81	95
Stationary skim. - Manta Ray	1975	DOP	79	20	6		calm		20.1		27
Stationary skim. - Manta Ray	1975	DOP	79	20	1		0.6	harbour chop	15.2		22

Stationary skim. - Skim pak	1980	medium	200	7	3	calm			2.5	8
Stationary skim. - Skim pak	1980	medium	200	7	1	0.26	regular	2		7
Destroil weir skimmer	1979	heavy	810	5	5	calm			16.2	69
Destroil weir skimmer	1979	heavy	810	5	2	0.47	harbour chop	11.5		59
GT-185	1988	Bunker c	11700		1	0.4	regular	15		50
GT-185	1988	Terra Nova	100-600		1	calm			30	100
Walosep	1988	Bunker c	>100k		1	calm			38	2
Walosep	1988	Bunker c	>100k		1	0.4	regular	10		2
Veegarm towed weir	1980			1	1	0.25	calm		11	100
Veegarm towed weir	1980				1	0.25	1.9	regular	10	40
Veegarm towed weir	1980	light	9	2	1	0.25	0.19	harbour chop	5	60
Averages (taken from whole Table)					476	mixed wave conditions			15	58
										44
										under test conditions
										under typical wave conditions
* See reference 3 for the full table										33

## Reviewer 2:

*Page 11, paragraph 2: This paragraph is not based on data and only media reports from some dramatized news conferences. I would not include this speculation.*

Paragraph is modified to note that extensive DHS oil on the bottom has not been confirmed in the ongoing sampling programs.

*Page 39, paragraph 1:*

*The factors affecting biodegradation rates are as follows:*

- 1.Type of oil*
- 2. limiting nutrients, P, N, O, and in the ocean Fe*
- 3. Concentration of the oil*

---

4. how weathered the oil is

5. oil droplet size

6. adaption of microbial community to long-term episodic events like natural seeps.

The purpose of the report is to describe the oil budget calculator, not provide an in-depth study of long-term weathering processes. Therefore, we feel it would be inappropriate to expand on the admittedly brief discussion of biodegradation.

### **Reviewer 3:**

*P 7, line 2 remove: if slightly dull*

*P 8, Item 4, Line 2-3: replace bottom with lower water column*

*P 9, Line 3-4, rephrase: Hence, this oil is assumed to have already lost all oil that might evaporate.*

*P 10, Para 3, Line 4: Formed an emulsion when surfacing.... on*

*P 11, Para 1 Line 6, formed emulsion on the water surface within Km's of wellhead. This needs to be consistent.*

*P11, Para 1, last line: this sentence is unclear*

Revisions made for the above.

*P 11, Para 2, Line 3: Basing anything here on News Reports would seem to be a dramatic flaw. The news reports were abysmally incorrect with respect to all aspects of the science of the DWH spill.*

Paragraph is modified to note that the claim of extensive DWH oil on the bottom has not been confirmed in the ongoing sampling programs.

*P 12, Para 2, Line 6: Can "44% oil percentage" be replaced with a unitless GOR (Gas Oil Ratio) for accuracy and understanding here and throughout the document? (e.g. P14, para 1, Line13)*

We have kept the units of the cited report for consistency.

*P 14, Para 1, Line 13: Should high not be low?*

*P 14, Para 2, Line 9: Replace globs with accumulations of droplets or particles*

Section text revised



---

*P 15, Para 2, Line 1: Replace old saying with proverb.*  
*P 15, Para 2, Line 3: Replace unimportant with less important*  
*P 17, Para 2, Line 5: Is this naturally or chemically dispersed oil?*  
*P 19, Para3, Last line: to the wind speed and temperature*  
*P 20, Para 2 , Line 4: from the sea*

*P 22, Figure 8 and all additional similar figures: Please make a table, these are indecipherable*

Figure 8 and similar figures have been removed

*P 22, Para 4, Line 5: I am not familiar with cubic seconds. My utilization of horizontal and vertical spreading rates have been as m<sup>2</sup>/sec. Check here and following*

The unit of m<sup>2</sup>/sec<sup>3</sup> relates to the energy dissipation rate and not to spreading. It is equivalent to energy per unit mass per unit time.

*P 27, Last line: remove =*  
*P 28, Para 1, Line 4: Less oil, not more oil*  
*P 28, Figure 12, Move under 9a Header.*  
*P 29, Section 9a, Location of tables and figures is awkward and needs to be revised.*

Revisions made

*P 30, Table 2 Concentration as what units, also please provide detail regarding these samples, e.g. depth sampled, time after dispersants applied, measured how, etc. If this is a scattershot of nonspecific sampling, please say so.*

New table 2 Heading inserted

*P 31, Last line: for*  
*P 36, Para 2, Line 2: to*  
*P 36, Para 3, Line 8: What evidence is there that oil settled to bottom in offshore areas?*

The text was revised to say some of the oil has combined with sediment in the water column and settled to the bottom in the nearshore or, perhaps, offshore areas.

*P 39, Does this paper not deserve conclusions? We've spent 39 pages getting to this point, provide the DWH Mass Balance.*

## Reviewer 4:

*Generating a modeling tool such as the Oil Budget Calculator is no simple task, not least because there is a paucity of information – both theoretical and empirical - on which to base it. The need for better information on which to base the model is apparent throughout much of the document, with a few exceptions (e.g., section 6 on Evaporation). Still, assembling the Calculator seems to have been a worthwhile exercise for two reasons: 1) it provides a framework for assembling actionable data; 2) it highlights areas where the information gaps are the largest (e.g., direct observations of subsea dispersant effectiveness). I would encourage the further development of this tool both through efforts to better model the processes (e.g., chemical and natural subsurface dispersion) and by adding more capability to the model. If the latter could be done in such a way that the model could adaptively tune itself to new scenarios using field data (see comment 4. below), it could become very powerful.*

*There are several technical issues which should be addressed. These are listed below. In addition, the writing of this document should be tightened up considerably. There are better editors than myself for doing this, so I won't provide an exhaustive list of corrections, but will say that there are many ambiguous comments or phrases (e.g., a "good" fraction; "very" rapid;) and several unnecessary comments and colloquialisms (e.g., filling out an ICS209 is "slightly dull"; "the old saying that oil and water do not mix..."). Physical interpretations and definitions for the rate constants do not belong in an appendix – this makes following the body of the text too onerous. The figures that take the form of Figure 8 are totally non-intuitive – this information should be provided in a much clearer way. Clearly, this document is in draft form – a thorough polishing and reworking is warranted.*

Corrections to the language have been implemented. Unfortunately, multiple authors and strict publication deadlines prohibit extensive wordsmithing or style uniformity. Figure 8 and similar figures have been removed.

1. *The amount of subsurface dispersed oil is assumed to be high (seemingly, greater than 25% of the oil based on the combination of rate constants), although the data presented here do not seem to either support or refute that assessment. If the goal is to bring a conservative*

---

*assessment (from the perspective of not underestimating the response resources required, such as skimmers, burners, surface dispersant, amount of subsurface chemical dispersant – the “lesser of two evils” - to be used, etc.) to the Unified Command, as was stated, than I would have to conclude that the analysis of the dispersed oil at the bottom was incorrect (too high). I recognize that there have been many observations of subsurface oil, and would not be surprised to learn that enough oil made it into the subsurface to have a large and long term impact (in fact, I would be more surprised to learn the opposite). But given that 4.9 million barrels were released, even this finding would not suggest that a large fraction of the oil was dispersed into the subsurface. That is, it is conceivable that even 5% of 4.9 million barrels of oil could have a large, long term impact (clearly, better methods for empirically determining the amount of subsurface oil are needed). Specific comments along the lines of this theme follow.*

*I do not see how the LISST data support the hypothesis that “much” of the oil released was dispersed into the water column, as stated on page 22, or that they “suggest the high effectiveness of the chemical dispersants...from subsurface application” as stated in appendix 6. Assuming that equations (13) and (14) are correct (and they need to be better supported than a personal communication with Lasheras), it does seem reasonable to expect that the only way to generate these small droplets is through the use of chemical dispersant (otherwise, it would seem that the smallest characteristic size of a droplet would be about 1 mm). However, the LISST measurements only provide estimates of these very small droplets – they don’t appear to say anything about the relative quantity of the small droplets compared to larger droplets. Based on these measurements, it appears just as likely that the application of subsea dispersant was ineffective, and that only a small fraction of chemically dispersed bubbles was created, some of which eventually had the eventual fate of being sampled. From the perspective of figuring out how much surface oil can be responded to, it would seem more conservative (and just as likely based on these measurements) to say that only a small amount of oil was dispersed and that the chemical dispersant was ineffective.*

Equation 13 is supported by the two preceding references to peer reviewed publications. Equation 14 has been proposed by Hinze (1955). It gives an estimate of the characteristic droplet size in a dispersion process based on the assumption that the dynamic pressure forces due to turbulent fluctuations control droplet formation due to breakup. It is provided in this report for background only (it is not used in the Calculator). The natural dispersion model itself is a variation of the Delvigne model, commonly used to estimate natural dispersion.

The LISST data found oil droplets in the locations consistent with dispersed



---

oil and subsurface current patterns. The lack of such droplets would be a strong indicator of little dispersion. Therefore, the Report states that these findings lend support to the hypothesis of significant dispersion, while citing other findings that do not support this hypothesis. As noted in the report, the experts were unable to reach a consensus on the amount of dispersion and a compromise value was used for the Calculator. This is obviously an area that requires further research.

Hinze, J.O., (1955). Fundamentals of the hydrodynamic mechanism of splitting in dispersion processes. *AIChE Journal*, Vol. 8 (4), 289-295.

Due to the limitations of available technologies in droplet size measurement (for example, current available LISST can only go as deep as 300 m, LOPC has detection limit of  $> 100$   $\mu\text{m}$  and resolution of  $10^6$  counts/ $\text{m}^3$ ), the present LISST method has been used to monitor small particles generated in the water column by retrieving water column samples using Niskin bottles and surface bucket sampler. It is unfortunately that the current method did not measure the full spectrum of droplet size distributions in subsurface, and in particular, there were large uncertainties and measurement gaps for large particles. However, it is not true to say that “they don’t appear to say anything about the relative quantity of the small droplets compared to larger droplets”. As a matter of fact, the data presented in Figures A7-5~8 are the fractions of small particles ( $d < 68.8\mu\text{m}$ ) to the total particles in an expanded range between 2.5 and 157  $\mu\text{m}$ . Similarly, Figures A7-9~12 present cumulative particle size fractions between 2.5 and 157  $\mu\text{m}$ , too. These data all indicate that the vast majority of the measured particles are within the defined small particle frame (i.e.,  $d < 68.8\mu\text{m}$ ), and therefore support our conclusion that dispersion of oil was effective at subsurface. However, we do emphasize there are tremendous amount of unknowns in terms of efficacy evaluation of the subsurface dispersant injection, and the knowledge gaps in this regard must be bridged in the forthcoming research activities now that the importance of this issue has come into light.

*Are Payne’s reports of oil droplets at depths greater than 2 km (page 22) supported by any other measurements (e.g., CDOM fluorometer, hydrocarbon fluorometer, DO, etc.)? What is the mechanism by which the oil droplets sank through the water column into a stable deeper plume? Most importantly, how can these type of observations be translated into the stated assessment that there was a “large amount of dispersion”? That is, why couldn’t Payne have been observing the result of a small amount of dispersion? If Payne had a way to extrapolate a few observations to a general behavior, it should be clearly stated here. Otherwise, the conservative approach (from the perspective of figuring out how much surface oil can be responded to) would be to assume that Payne’s observations support a small amount of dispersion.*

---

The report of dispersed oil droplets between 1000 and 1200 m was based on: 1) visual (video and digital photographic) observations of droplets (0.5–3 mm) in the water column and impinging on a down-ward facing grid mounted on the ROV; 2) video and digital recording of said droplets with white (tungsten) and “black light” illumination; 3) CDOM fluorometry; 4) DO anomalies or “sags” in the water-column within that depth range; and 5) GC/MS measurements of PAH in dissolved (filtered) seawater samples and SHC plus PAH associated with particulate-phase components (trapped on 0.7  $\mu$ m glass fiber filters) from finite water samples collected at these depths. In addition, the dispersed droplet concentrations were high enough to be observed by sonar (670 kHz) on the ROV, and we photographed droplets of different sizes (between 100 and 500 micrometers) at different depths using the Holographic Camera provided by Cabell Davis of WHOI.

These plumes were observed consistently within this depth range on two cruises on the M/V Jack Fitz in the May-June time-frame out to 4 km from the well head, and other vessels observed similar DO anomalies and fluorometer signals elsewhere at distances up to 18 km from the well head during that period. These other vessels did not have the ROV and video/digital photography to document the droplet sizes, but the chemistry data on whole water samples collected between 1000 and 1300 m yielded similar PAH and SHC patterns documenting the presence of dissolved components and whole oil droplets. More recently (in August and September 2010), PAH components associated with finite oil droplets in this depth range have been measured by UV/fluorescence using AquaTracka fluorometers and confirmed by GC/MS well beyond 200 km from the well head. Measurements above and below these depths do not show the oil signal. In more recent cruises, the Aqua Tracks signals also corresponded with DO anomalies at the same depth.

With regard to the mechanism of how these droplets reached this depth, it is important to stress that we are not implying that they were dispersed at the surface and somehow «sank» or were entrained to 1000 m. Rather, we believe that the physically (and chemically) dispersed oil released from the well head at depth broke up to yield finite droplets that advected away from the well as they slowly rose toward the surface, and that those droplets removed from the rapidly rising gas plume and within a particular size range became entrained within a density or stratification layer at this depth. Particle size measurements clearly indicated that the larger droplets were still slowly rising (between 1300 and 1000 m), and that smaller droplets were left behind over time. This entrainment of smaller oil droplets in the 0.2 – 3 mm size range follows the expected behavior described by Socolofsky and Adams (2002, 2003), where oil is detrained (along with seawater) from the plume as it ascends through a density-stratified ocean and passes a level of neutral buoyancy. Such detrainment events are clearly evident in laboratory mea-

---

surements of gas and water plumes and in field experiments of oil and gas mixtures released at depth (Masutani and Adams 2000; Adams and Socolofsky 2005), and evidence for such detrained oil droplets was observed in subsurface plumes between 1300 and 1000 m from numerous vessels and over 4-5 months.

Masutani, S., and E. Adams. 2000. Experimental study of multiphase plumes with application to deep ocean oil spills. Final report to U.S. Dept of Interior, Minerals Management Service. Contract No. 1435-01-98-CT-30946. <http://www.mms.gov/tarprojects/377.htm>.

Socolofsky, S. and E. Adams. 2002. Multiphase plumes in uniform and stratified crossflow. *J. Hydr. Res.*, 40: 661-672.

Socolofsky, S. and E. Adams. 2003. Liquid volume fluxes in stratified multiphase plumes. *J. Hydr. Engrg.* 129: 906-914.

Adams, E.E. and S. A. Socolofsky. 2005. Review of Deep Oil Spill Modeling Activity Supported by the Deep Spill JIP and Offshore Operator's Committee. Final Report.

*It seems odd, and not very conservative, to assume that 1 gallon of dispersant generates 20 gallons of dispersed oil at the surface and 90 gallons of dispersed oil subsurface. Multiplying these values by  $k_3$  and  $k_2$  respectively, it appears that 1 gallon of dispersant would generate 2 gallons of dispersed surface oil, or 40 gallons of dispersed subsurface oil if deployed at depth. This disparity should be clearly addressed.*

The expected subsurface DOR is 40 and the expected surface DOR is 10. The reason for the disparity is explained in sections 9a and 9b. In many respects, the subsurface operations were ideal dispersant applications. The oil was fresh and in direct contact with the dispersant. There was significant turbulent energy. This was not always the case for the surface operations.

*The report states on page 30 that the best (most) direct evidence collected during the spill suggested that 6-7% of the oil – in a plume where models expected the subsurface plume to be – was dispersed near the bottom (apparently negating the remote sensing estimate on page 13). Presumably this was both chemically and naturally dispersed. So why not use 6-7% rather than the approximately 5 times this amount suggested by the rate constants?*

The Camilli study concluded that 6-7% of the BTEX leaking from the well was required to support the plume that they found. This defines a lower bound to the dispersed oil, not an upper bound since one cannot presume



---

that they detected all of the subsurface oil. The Camilli study is not in contradiction to the AVIRIS findings since the latter looked at the cumulative amount of oil that both made it to the surface and did not evaporate. Also, it must be noted that the remote sensing estimate has a high degree of uncertainty.

*Even if the chemical dispersant was effective, just because a droplet is small doesn't necessarily mean it takes a long time to get to the surface. If the volume fraction of the droplets is high enough, there can be a net transport upward that is faster than the individual rise speed of the droplets. If bubbles are added to the mix – and they apparently constitute 56% of the mix as stated on page 12 of this report – the upward net transport can be even greater (this type of group behavior can be demonstrated in the extreme by going to a bar and ordering a pint of Guinness and watching the individually buoyant bubbles flow downward). A conservative assessment of the amount of surfacing oil should either explain why this net transport isn't happening, or conversely it should take it into account.*

The reviewer is correct. In the dynamic zone above the riser (the first tens of meters or more, depending on the intensity of jet), the vertical transport of small droplets is mostly controlled by the jet flow and its bouncy, and later on by the flow induced by the movement of large oil droplets and gas bubbles rising to surface. Above this dynamic zone there is abundant evidence that gas bubbles will separate from the plume of oil-gas mixture (explained in Section 3) and the small droplets will continue to rise to the surface according to their terminal rising velocity controlled by their size and effective density. In deep waters, the last process is dominant (because of the long distance the droplets have to travel to reach the sea surface), while in relatively shallow water (water depth of few tens of meters or possibly hundred meters) the first process (induced upward transport) becomes dominant and cannot be neglected in accessing oil movement to the sea surface. The depth at the DWH oil spill is 1.5 km, which is large enough to assume that oil droplets will travel the major part of this depth according to their terminal rising velocity as explained above and shown from previous well blowout incidents, field experiences and modeling (Johansen, 2000, 2003; Johansen et al., 2001, 2010; Chen and Yapa, 2007; Yapa and Chen, 2004)."

- Chen F., and Yapa, P.D., (2004). Estimating the Oil Droplet Size Distributions in Deepwater Oil Spills. *Journal of Hydraulic Engineering*, 133(2), pp. 197-207.
- Johansen, O., (2003). Development and verification of deep-water blowout models. *Marine Pollution Bulletin*. 47, pp. 360–368.
- Johansen, O., (2000). DeepBlow - a Lagrangian Plume Model for Deep Water Blowouts. *Spill Science & Technology Bulletin*, 6 (2), pp. 103-111.

- 
- Johansen, O., Rye, H., and Durgut I., (2010). Generalized integral plume model for simulation of marine discharges. In AMOP proceedings, Environment Canada, Ottawa, 1, pp. 863-878.
- Johansen, O., H. Rye, A.G. Melbye, H.V. Jensen, B. Serigstad, T. Knutsen (2001). Deep Spill Jip Experimental Discharges of Gas and Oil at Helland Hansen, Technical Report STF66 F01082, 159p.
- Yapa, P.D., and Chen F., (2004). Behavior of Oil and Gas from Deepwater Blowouts. Journal of Hydraulic Engineering, 130(6), pp. 540-553

*The report (p13) assumes that gas associated with the plume dissolved before reaching the surface. Without evidence to the contrary, I find it hard to believe that the surface flow around the bubble would push enough oil on a bubble surface to the downstream hemisphere so that the gas transfer rate out of the bubble or methane-seawater contact was not appreciably changed. Although the oil budget does not keep track of gas, adsorption of oil onto gas bubbles is a mechanism by which the oil can surface more quickly and by which smaller droplets can reach the surface. Therefore, it is not sufficient (or conservative, from the calculator perspective) to simply neglect the gas, especially when it is estimated to be more than 50% of the discharge volume (page 12).*

Although the mechanism suggested by the reviewer is perhaps possible and worthy of further study, it does not reflect existing understanding of subsurface well blowouts, as discussed in the references cited. As stated on page 8, the Calculator is not a research tool.

*The model inherently appears to assume that the oil that is skimmed, naturally dispersed, or evaporated at the surface is negligible compared to the oil that is burned (see calculation of W). This may have been accurate for DWH (I couldn't say), but it doesn't seem to be appropriate to assume that this will always be correct.*

This is not correct. The model does not neglect skimmed, naturally dispersed or evaporated oils. These are important in the oil budget calculations. Skimmed oil is counted as shown in equation A1.7), naturally dispersed in equation A1.11, and evaporated oil is counted by the terms  $k_4 Z(t) + k_5 W(t-1)$  in equation A1.10. The note "(neglecting natural surface dispersion and skimming)" mentioned in the report applies to calculation of evaporation from the previous day and still available on day t, as mentioned in the report "The oil that rose to the surface on day t-1 and is still left". This "old" oil is estimated by the intermediate variable W.

*The report states that some 18,000 barrels of subsea dispersant were used, and multiplying this by  $(1-k_7)*90*k_2$  (from equation 2) gives 700,000 barrels of chemically dispersed oil in the subsurface. Figures 1 and 2 in Appendix 2 (example outputs from day 86, the last day dispersant was used, I believe)*



---

*gives an answer of only about 400,000 barrels. Why is this different? Note that  $90 \cdot k_2 V_{cb}$  should always have been smaller than the government estimate of the discharge even when 12 gallons/minute of subsurface dispersant was being used.*

Figures 1 and 2 in Appendix 2 refer to the earlier version of the Oil Budget Calculator (version 1.3) while the formulas listed in the Report are those for the present version (2.0). See Appendix 2, Figure 3 for the equivalent tables using the new formulas.

2. *One of the stated goals is to provide the UC with actionable data even when there is missing or incomplete data. I'm wondering what happens when the estimate of the discharge is either not available or has a very high level of uncertainty. If stated too low, this would presumably result in a response (dispersant, skimmers, etc.) that was too low, if state too high, this would result in too much dispersant deployed and inefficiency (too many skimmers floating around). If either of these scenarios occur, I don't see any built-in mechanism (e.g., feedback) that allows the calculator to adjust, which could render the calculator ineffective. Given the uncertainty surrounding the flow rate for a significant portion of the DWH spill timeframe, this seems likely to occur. I would suggest that future work include exploration of feedback mechanisms. One that readily comes to mind is tracking the daily amount of oil estimated to be reaching the surface, which is  $V_{RE} - V_{DC}/(1-k_r) - V_{DN}/(1-k_r)$ , and comparing it with the daily amount of oil skimmed and burned (normalized by effort). One could imagine a scenario in which such a tracking mechanism is used to tune the basic model inputs (e.g. the leak discharge rate), which in turn gives the response the indirect ability to tune decisions for which the result is difficult to monitor (e.g., amount of subsurface dispersant). Place holders for new feedback mechanisms (advances in technologies to assess surfaced or subsurface oil amounts or characteristics) could also be added.*

Mass balance was used by another group to estimate flow rate during DWH. Certainly having a corrective feedback mechanism in future model applications would be useful.

3. *Considering that  $V_{DC}$  cannot be greater than  $V_{RE}$  by definition, the "max" in equation (3) does not seem to be necessary.*

True, but it does not affect the calculations. Equation was written this way for consistency .



- 
4. *It seems misleading to state that a similarity between DWH and Ixtoc is that relief wells were used to stem the flow in both cases. Didn't DWH utilize a cap to almost completely stem the flow? In any case, what is the relevance of the method of stemming the flow to the assessment of oil fate and transport before the flow is stemmed?*

The use of relief wells is mentioned because in both cases this was the final method to assure no future leakage and because it was believed during both responses that this was possibly the ultimate method to stop the flow. For IXTOC, this proved to be the case. As noted by the Reviewer, DWH was successfully capped at the top.

5. *In describing the difference between DWH and Ixtoc, it is stated that Ixtoc I oil formed a "chocolate mousse." Wasn't this also observed in DWH? I recall seeing something that could be described as a "mousse", at any rate.*

Both oils emulsified although the Deepwater Horizon spill formed a less stable emulsion and took longer to emulsify.

6. *On page 11, there is a statement suggesting that "current news reports" provide evidence that a scientific hypothesis (that a "good" fraction of the oil is settling to the bottom) is true. Given the inaccuracies often associated with press reports, and the lack of peer review associated with news media report, I would suggest that the report only state that such a hypothesis exists but has not yet been evaluated, and that references to the news media be deleted. Further, what is a "good" fraction? These kind of ambiguous statements found throughout the document.*

Sentence discussing bottom oil is modified to note that these reports have not been confirmed

7. *What is a "glob" of oil (page 14)?*

Corrected

*I don't see how the 5-10% dissolution rate is supported. It would seem to me that in order to assess this, you would need to know a) the oil composition; b) the dissolution rates as a function of droplet size (not solubility – presumably the Gulf of Mexico is still under-saturated; c) the droplet size distribution. I don't see that any of this is sufficiently known to estimate a dissolution rate. The text makes the case that some oil will dissolve, but does not go further. This should be addressed; if it is a guess, than this should be clearly stated*

---

Dissolution was only considered as a separate process for dispersed subsurface oil (less than 100 micron droplet size). As stated in the Report, the dissolution rate depends directly upon surface area, which was proportionally larger per volume spilled for this spill incident compared to a normal surface spill by factors of 100 to 1000. Mackay and Leinonen (1977) concluded that, for droplets less than 100 microns in diameter, dissolution is very rapid for any component that will dissolve at all. Using the known composition of the oil, we arrived at the 5-10% number.

## Reviewer 5:

*This document needs a more straightforward description of what the major processes are that need to be considered. Once the simple formula is provided then they can describe their more sophisticated formulas for deriving the estimate. Here is a simplified example of how they should proceed. The fate of oil in the marine environment has been of concern for many years and the major processes determining its fate are known in relative terms. A budget can be constructed which would contain these parameters:*

*Total oil discharged = TD  
Oil Recovered before entering the ocean = REC  
Oil Dissolved/Dispersed = DD  
Oil on sediments/shore = SED  
Oil on the ocean surface = SURF  
Oil evaporated = EV  
Oil Biodegraded = BD  
Oil Burned = BUR  
Oil Skimmed = SK*

*Then the following equation can be used:*

$$TD = REC + DD + SED + SURF + EV + BD + BUR + SK$$

*The National Incident Command (NIC) is most interested in the surface oil (SURF) as that is where they can attempt to burn skim or disperse the oil or set up booms to keep the oil from sensitive ecosystems. The equation is therefore solved to estimate this term:*

$$SURF = TD - (REC + DD + SED + EV + BD + BUR + SK)$$

*Since the spill occurred offshore where the suspended sediment load is small sedimentation near the spill site is not likely to be a major term in this budget*

---

*for this spill. This term for the offshore areas was assumed to be comparatively small. The NIC was trying to keep the oil of the shore. Once on the shore it is difficult to estimate the amount of oil stranded and how much of that oil is recovered. This oil budget calculator does not attempt to estimate this process, but includes this oil with the surface oil. The equation for the calculator is therefore:*

$$SURF + SED = \text{Other Oil} = TD - (REC + DD + EV + BD + BUR + SK)$$

*The budget then uses the physical properties of the oil, estimated rates and developed a model to calculate and estimate the above parameters. Modelers and other experts will need to comment on how well they were able to estimate these parameters. Based on my review of the parameters that the oil budget calculator used it has captured the most important aspects. While SED can be assumed small it does not mean it is not important especially for selected near shore areas and perhaps some off shore areas.*

Spilled oil undergoes a number of processes. Dispersion and evaporation are just two examples. Collectively they are called weathering. The circumstances surrounding the Deepwater Horizon incident resulted in interdependence of these processes. To address this the approach taken was to follow a logic structure beginning at the wellhead and the released oil. Unfortunately, interdependencies of the weathering/cleanup processes made the simple approach proposed by the Reviewer not possible. For example, evaporation depends upon surface oil but surface oil depends upon the amount of oil that disperses subsurface. The formulas chosen by the development team were as simple as we believed possible while still retaining these basic dependencies. However, a descriptive narrative has been added to the section before the formal equations are presented.

*My conclusion is that they have oil budget calculator used it has captured the most important aspects of the fate of the oil.*

The Oil Budget Calculator is designed to capture short-term oil behavior as it affects response. Environmental Impact Assessment studies are needed to track the ultimate fate of the oil.

#### *Specific sections Comments*

##### *Dissolution and Evaporation:*

*I discuss these sections together as it make since for the calculator to talk about these processes together. The discussion in these sections is very good. They explains how the unique aspects of this spill led to enhanced*



---

*dissolution even of sparingly soluble components. Based on the paucity of studies they have done a good job of estimating dissolution process. And since the same components of the oil are more water soluble and more volatile it makes sense to combine as a process called "weathering" as it is difficult to establish which was the dominant process. Separating the two processes is also of limited value for the NIC. Some editorial comments:*

*Page 17 Figure 6. The open and filled circles are not labeled.*

We are reluctant to modify a figure produced by someone outside the development group. The original figure appeared in the proceedings of the 1987 Oil Spill Conference.

*Page 17 ...lose between 5-10% of its volume. Is this also 10 % of the mass since mass is used in the calculator.*

The Calculator uses volume in its calculations and output. However, oil density changes little so that mass and volume percentages are quite similar.

Page 18 "The Oil Budget Calculator groups these terms" change "terms" to "dissolution and evaporation".

*Page 19 Figure caption change to ...alkanes below C-14 have been removed...*

Change implemented

**Residual Oil** (in my letter) or **Other Oil** (in draft document) plus **Program Structure & Interface** (Appendix 2 Oil Budget Calculator-Web-based Tool)).

*In the equations I provided above the Other Oil is equivalent to my term SURF + SED. This is the most important parameter for the NIC. This is the oil that they have to attempt to mitigate (skim, disperse, burn) or contain (booms) and the proportions that they were unable to keep from the shore. In short it is the number they wanted calculated. The final test of this Oil Budget Calculator is was it of value to the NIC to make management decisions. It would be good to include in this report a statement by the NIC that this Oil Budget Calculator was useful or that they think it would be helpful in the event of future spills. They are the ultimate primary users. It is also important to attempt to improve these estimates as the results contradict some of the original unrealistic predictions.*

We agree that the ultimate judge of the usefulness of the Calculator was/is the unified command. The development team was encouraged by the support given to its development by the NIC who are reviewing future plans for the tool.

---

### Other Comments:

*Figures 8, 9, 13, 15 and 16 appear to be taken from appendix 2 figure 4. It would be better to just use that figure in the main text and delete the other figures as they are hard to understand until you see figure 4 Appendix 3.*

Figure 8 and other related figures have been removed.

*Appendix 2 Figure 1 and 3 (which are actually tables unless the colors have some significance) appear to be the same except rounding. One should be eliminated or the reason to have both explained.*

### Specific Comments:

*Page 7 A copy of ICS 209 should be available as an appendix.*

A copy of the ICS 209 form has been added as an Appendix

*Page 8 The model uses not assumes. This whole page should use the same terminology found in Figure 1 Appendix 2. For example "(1) Subtract off direct recovery from total amount escaping from the reservoir", just say recovered. This section is extremely hard to follow and should be edited by a non-technical person.*

A challenge in a document of this type is to reconcile precise technical terminology with more common descriptions. 'Direct recovery' is used to distinguish this oil from other oil recovered by, for example, skimming operations. We have simplified the equation expressions, added an introductory narrative to them and added a table of acronyms to the final version to assist the reader.

*Page 12 Par 3 add surface after water.*

*Page 14 ...converted to hydrates at a much higher level... do you mean shallower depth or deeper depth?*

Shallower depth

*Page 22 (representing a 200 -250C+ residue) is this a boiling point? Need to explain.*

50degC+ residue is that the residue has lost all components with boiling point below 250degC

*Page 25 Par 1. change "disappeared during" to was not on the surface after*

---

*Page 27 last line half=of ?*

*Page 32 Par 2. 2 to 3 mm thick.... Oil with emulsions...delete typically. ...mm or less thick.*

*Page 35 Simple measurement of barge oil!!! This should be made a requirement!!*

We agree when practical.

*Page 39 (5) this is self advertisement and should be deleted. What is real code? Is there fake code!!*

We disagree with this conclusion. A weakness of oil spill science in the past was translating new ideas into practical tools.

*Page 39 (6) Jargon. Explain what the "Interface" you are talking about is. Consider deleting this as it seems to serve no purpose.*

One of the key challenges for the team was to provide to the unified command output that is simple to understand yet captures the uncertainty in the estimates. We believe this is a topic that requires more research.

### **Conclusion**

*My conclusion is that this model appears to provide a valid estimation of the source and fate of the oil from the DWH incident. It generally agrees with what has been found by previous oil spill research and currently available research on this specific incident.*

Unfortunately, the ultimate fate of the oil is more complicated than can be calculated by this tool. Environmental impact assessment is ongoing and will provide a more complete picture than the Oil Budget Calculator.

## **Reviewer 6:**

### *The OBC as an NRDA tool?*

*The introduction in particular and the paper overall set the scene well and describe the operational needs that led to the creation of the OBC, the limitations that this development faced, and the authors' overall (and reasonable) conclusion that the OBC outputs "only need to be accurate to the extent that they correctly inform cleanup decisions and do not lead to errors in response actions." (p. 5) Explicit warnings are also made that the OBC tool is not appropriate for damage assessment. While there is no protection against misuse, perhaps the*



---

*paper could describe more explicitly just why the OBC is not appropriate as an NRDA tool.*

The Oil Budget Calculator is unsuitable for NRDA because it does not track the final fate and environmental impact of the spilled oil. This is explicitly stated on page 3 of the report.

#### The problem with DOR

*The model is a nest of part-weathering, part-response/fate equations describing processes that are partly simultaneous, partly consecutive. For example, while subsurface dissolution is nicely modelled as occurring after subsurface dispersion (i.e. consecutive processes), chemical dispersion, skimming and in-situ burning on the sea surface are all allowed to happen at the same time (simultaneous processes).*

*One key problem we have with the model is that a great part of the results (in fact, all the consecutive elements, such as evaporation, dispersion and dissolution) are based on the theoretical volume of oil that can be dispersed by a given quantity of dispersant (i.e. DOR = dispersant-to-oil ratios). These are the  $90V_{CB}$  and  $20 V_{CS}$  elements of the equations. The issue is that outputs are measured solely in terms of inputs, albeit with the correction factors  $k_2$  and  $k_3$  (which must capture not only the 'encounter rate' of the dispersant application, but also all other technical and environmental factors that may influence the dispersant application). The Appendix (in particular) explains that outputs are measured on the basis of inputs, but we do not believe that this makes it acceptable.*

*In the real world, DORs are meant as a planning guideline, an indication as to the quantity of dispersant that should be made available (i.e. what should be put in), not the end result (i.e. what comes out). Further, they refer to the dispersibility of surface slicks of a certain thickness (0.1mm according to the ITOPF Technical Paper quoted).*

*The matter is made worse by the fact that the DOR figures come up so many times in the same equation/ model. For example, if the model equations are solved simultaneously for total evaporation/ dissolution (not even dispersion!), the  $90V_{CB}$  component comes up numerous times in relation to:*

- Day t evaporation of non-chemically dispersed at bottom oil (that just rose)*
- Day t evaporation of non-naturally dispersed at bottom oil (that just rose)*
- Day t evaporation of non-chemically dispersed at bottom oil from the previous day(s)*
- Day t evaporation of non-naturally dispersed at bottom oil from the previous day(s)*
- Day t dissolution of chemically dispersed at bottom oil*

- *Day t dissolution of naturally dispersed at bottom oil*

The use of DOR to define effectiveness was based upon industry familiarity with this approach. Similar results would have been produced if the development team had used fraction dispersed as a function of dispersant applied to available oil with an upper limit on the fraction allowed. What is really needed is solid research to empirically determine effectiveness.

#### Multiple expert coefficients.

*Although the model makes logical sense when analysed part by part, when the equations are solved simultaneously there are numerous places where the educated guesses of experts are multiplied by a series of other such educated guesses. For example, the 2<sup>nd</sup> day surface evaporation (with coefficient  $k_5$ ) is a function of the first day evaporation (with coefficient  $k_4$ ) which is a function of sub-surface natural dispersion (with coefficient  $k_1$ ) which is a function of sub-surface chemical dispersion (with coefficient  $k_2$ ) which is a function of theoretical sub-surface chemical dispersibility (i.e. DOR = 90). In other words, that part of the overall evaporation function which looks like:*

$$k_5 W(t-1)$$

*really takes the following form when solved for "W" which includes "Z" which includes "Y" which includes "X":*

$$+k_5[(1-k_4)[(1-k_1)[V_{RE}(t)-k_2 90V_{CB}(t-1)]]-V_{BU}(t)]$$

*As can be seen, if the equation is solved, the results include such elements as:  $k_5 * k_4 * k_1 * k_2 * 90 * V_{CB}$  which is the multiplication of 5 guesses by the observed number of drums of dispersant applied. It is very, very hard to accept this as a meaningful result.*

*Naturally, the paper includes a number of various variance histograms for each of the main fate/ recovery alternatives, and the Appendix includes a long and detailed statistical model based on repeated computer simulations (i.e. the Monte Carlo analysis). These do not, however, in our opinion, get over the fact that there are very few variables in the overall set of theoretical equations which are actually populated by real measurements, observations, or even observation-based estimates.*

*While an argument could be made that having an inaccurate result, even if far from reality, may be more useful than having no result at all when faced with emergency-phase decision making, it cannot be stressed enough that it is not appropriate to use the results in post-spill evaluations of impact or response actions.*

The Reviewer is correct in assessing that these numbers chiefly rest upon the experienced judgment of the dispersant experts consulted for this project. However, using expert judgment when hard data is not available is often employed in many fields.



We agree that there are many alternative ways of re-writing the equations that describe the simplified model that we have adopted for the fate of the oil. Some of these may appear counter-intuitive. The formulation we have settled on represents our particular way of viewing the chronology, chemical reactions, and phase changes affecting the spilled oil, which is based on our own, varied experience with oil spills into the ocean. One of our colleagues, who has no expertise in this specific area, and merely as an exercise, did use our description of these processes to formulate an alternative set of equations, independently of our formulation. This alternative had shortcomings that were obvious to those with expertise in the subject. However, it produced estimates for the different volumes that we track that were within the uncertainty range of the estimates that the equations we did use had produced. This suggests that the simplified model we have adopted is fairly robust to varied interpretations, and that rather different sets of equations that may be used to represent our understanding may end-up bringing about no more than relatively minor changes to the bottom line.

Regarding the comment on the 2<sup>nd</sup> day surface evaporation, this is evaluated by the following expression after development and assuming that  $V_{DC} = (1-k_7) k_2 90V_{CB}$  and  $V_{DN} = (1-k_7) k_1 [V_{RE} - V_{DC} / (1-k_7)]$ :

$$k_5 (1-k_4) (1-k_1) [V_{RE} - k_2 90V_{CB}] - k_5 V_{BU}$$

This expression includes terms that are function of one rate constant such as  $k_5 V_{RE}$  and  $k_5 V_{BU}$ , terms that are function of two rate constants such as  $k_5 k_1 V_{RE}$  and  $k_5 k_4 V_{RE}$ , terms that are function of three rate constants such as  $k_5 k_4 k_1 V_{RE}$  and  $k_5 k_2 90 V_{RE}$ , and terms that are function of four and five rate constants such as the one mentioned in the reviewer comment. Of course, the terms that include less rate constants have more influence on the end results than the one multiplied with four and five rate constants, given that all the rate constants are less than or equal to 1. The other terms were kept in the equations of the Calculator for logical consistency and for transparency of the method used.

The uncertainty analysis certainly was done assuming that the rate constants were like realized values of independent random variables, whose probability distributions expressed the knowledge that the subject-matter experts had about their values. This assumption, of statistical independence, clearly is questionable for at least some of them. For this reason, Appendix 1 describes a study of the sensitivity of the conclusions to this assumption, by considering the effects that substantial dependence between several of them would bring about. As it turned out, this lowered the lower endpoint of the confidence interval for the volume of residual oil (or, "other oil"), but hardly changed the upper endpoint, meaning that the assumption of independence



---

actually was conservative, at least for the variables considered in the sensitivity study.

#### Re-coalescence

*The model has no explicit mechanism by which some part of the initially-dispersed (sub-surface or surface) oil re-coalesces and rises to join the surface oil. One could, of course, say that the oil that disperses in the model is, by definition, only that which is permanently dispersed. We do not believe that this is a particularly neat solution, given the important discussion in the spill world on the fact that naturally-dispersed oil tends to be less permanently dispersed than chemically-dispersed oil.*

Near the riser, it is possible for dispersed oil droplets to collide and form larger droplets due to the abundance of oil droplets and sufficient mixing energy. However, due to the relatively low concentration of oil away from the source, the collision frequency of droplets is very small when one moves away from the riser. Thus, the conditions there are not favorable for coalescence. Any coalescence would compete with shear forces breaking up the larger droplets. There may be an intermediate area where coalescence dominates. The impact of coalescence near the riser might affect the overall effectiveness of dispersant but would be included in the wide uncertainty range selected for oil dispersion.

#### Dissolution from chemically- vs. naturally-dispersed oil

*Related to the point just above, it would be expected that the (mean) droplet size for chemically- and naturally-dispersed oil would differ. This would surely have an important impact on the sub-surface dissolution potential (i.e.  $k_d$ ), even disregarding the question of effect of droplet size on dispersion stability (as discussed above). In other words,  $k_d$  might be best split into two separate coefficients (e.g.  $k_{dC}$  and  $k_{dN}$ ).*

Mean droplet size would be considerably smaller for chemically dispersed oil. Mean droplet size for natural dispersion would be expected to be much larger than our cutoff value of 100 micron diameter. However, some droplets would be 100 microns or smaller. These are the ones considered naturally dispersed. Mackay and Leinonen (1977) concluded that, for droplets less than 100 microns in diameter, dissolution is very rapid for any component that will dissolve at all.

#### Emulsion & Emulsion effects for surface dispersant effectiveness

*There is no explicit modelling of emulsion formation in spite of the fact that this was an important process in this incident. Likewise, there is no discussion of the effect of emulsification on surface dispersant effectiveness. This is a key factor, considering the practical experience that shows that emulsions, if dispersible at all, require greater quantities of dispersant than non-emulsified (surface) slicks.*

Emulsification is not a process that directly contributes to mass balance in the way that, for example, does evaporation. The observation that the oil did emulsify is reflected in the burn estimates and in the effectiveness of surface dispersion. Both were reduced to account for the characteristic behavior change of oil that has emulsified. Certain experts thought that the reduction was insufficient, a judgment summarized by Alternate View 1.

#### Weather & response activity

*We find no explicit variables to account for variations in the weather and how these might have affected the response success, for example surface dispersion operations.*

Several of the report authors have developed much more complex oil fate and behavior models than the Oil Budget Calculator. However, these models required more detailed input than the design specifications allowed for the Calculator. Sea state, in particular, affects surface processes but, for this spill, varied both temporally and spatially. Also, the subsurface release and extended duration of the leak were not compatible with the standard fate and behavior model used by NOAA and USCG for routine spills. Recommendation 5 suggests expanding existing modeling capabilities so that perhaps this difficulty will not arise in future incidents.

#### Equations

*While we find no mathematical fault in the equations, there are places where slightly different forms would leave the equations more easily interpretable.*

*For example:*

<i>Equation number</i>	<i>As presented</i>	<i>More easily followed form</i>
<i>A1.4</i>	$Y(t) = V_{RE}(t) - \frac{V_{DC}(t)}{(1 - k_7)}$	$= V_{RE}(t) - k_2 90 V_{CB}(t)$ <p>or</p> $= V_{RE}(t) - k_2 X(t)$
	<i>Interpretation: Oil volume available to natural dispersion (and subsequent rising to the surface for that part that does not disperse), once chemical dispersion at the well head has run its course.</i>	



A1.8	$Z(t) = V_{RE}(t) - \frac{V_{DE}(t)}{(1 - k_7)}$	$= (1 - k_1)(V_{RE}(t) - k_2 90 V_{CB}(t))$ or $= (1 - k_1)Y(t)$
	<i>Interpretation: Oil that rises to the surface after chemical and natural dispersion has run its course.</i>	
Part of A1.10	$\frac{k_7 V_{DE}(t)}{(1 - k_7)}$	$+ k_7 k_2 X + k_7 k_1 Y$
	<i>Interpretation: That part of the subsurface chemically-dispersed and naturally dispersed oil that dissolves into the water column</i>	

While the proposed forms to represent the three equations appear to be simpler than what is proposed in Appendix 1, these simplifications do not respect logical consistency in the formulation and the solution of the problem. The “min” and “max” functions were introduced in equations A1.3, A1.5, A1.9, A1.11, and A1.12 to ensure that the oil volume is conserved and no non-realistic results are generated in the Calculator.

### Conclusions

*The equations on which the OBC is based offer an interesting theoretical study of many of the fate and weathering processes relevant for a sub-sea blowout incident such as the DWH. There are some elements which could be added to the model such as explicit weather (e.g. wind, waves), emulsification, re-coalescence of dispersed oil, or refined such as droplet-size-based dissolution.*

*As a practical tool, however, the OBC suffers the same shortcomings of most mass-balance efforts: lack of real-world observations. In this case, lack of actual observations of dispersion effectiveness in particular render the overall result practically meaningless. The only true observations in the model appear to have been the volume of oil/water mix collected by skimming operations (traditionally a very suspect measure of actual oil volume collected), the volume of oil dispersant used (probably reasonably well counted but utterly meaningless in terms of estimating actually-dispersed oil), and the number and approximate size of in situ burns (a very rough value for a very rare activity).*

*One could argue that having the OBC result, although an inaccurate number, was better than having no number. The truth is, however, that the overall result could have been no better or no worse without it. In fact, the response operations were guided primarily by 1) the visible presence of oil, whether it was escaping from the wellhead, on the surface in the form of slicks that could be burned, skimmed, or dispersed, 2) the availability of resources, and 3) non-*



---

*technical concerns (such as the maximum daily-dosage of subsurface dispersant application).*

The Oil Budget Calculator was only one tool among many that the unified command used to make response decisions. As with any tool, it has its strengths and limitations. The skill of the decision maker is to utilize all the tools available in an appropriate manner to optimize the response. Based upon the request by the NIC for this tool, and its continued usage during the spill, we must conclude that they found some value in it.

## **Reviewer 7:**

General;

*I thought the report was informative and as precise as was possible under the constraints of the available data. Errors and uncertainties were identified. I was specifically asked to review Oil properties, Dissolution and long-term processes. I think each section was adequately presented under the terms of reference.*

*I suggest you provide a list of acronyms for all the various agencies, etc. "in situ" or "in situ" is not consistently presented in the report*

A list of acronyms will be included.

*I have the following specific suggestions to the text.*

*P12 p 2. L 6. "an average"...*

*P13 p1 L4 "considerably larger"*

*Fig 3. Define bopd in the figure caption.*

*Fig. 7 The blue series is not described. Presumably it is a surface oil sample taken near the source. Thus the title should be amended to read "..., floating oil samples immediately adjacent to the source (red,blue)....."*

The blue series is not a sample collected at the surface, but came from a sample from dispersant efficiency testing.

*P. 20 p2. L10 "data provided (to, by???) BP"*

Provided by BP. Correction will be made in the text.

*Fig. 8 should be moved up 2 paragraphs to appear under its description.*

---

*P27 under Fig 11. L3 delete "when" L 7. delete "—"*

*P27 under Fig 11. I could not see a conclusion from this paragraph. The issue of dispersant efficacy is left hanging. A statement that says there is no conclusion possible from the satellite data would be useful.*

Sentence added

However, May 11th and May 12th show similar surface expressions although the latter should be displaying more oil. Therefore, these observations provide inconclusive results.

*P 29-30. Delete reference to Fig 13 here as the same sentence appears on P 13 just above the figure.*

*P31 last L "from"*

*P38 p1 L8 What is the basis for concluding hydrocarbon degradation in the water column occurs without oxygen drawdown? This needs to be expanded to clarify and justify this statement.*

Hydrocarbon degradation doesn't occur without oxygen utilization. There was draw down, as discussed in the JAG 2 report. The fact that the DO2 drawdown was not as high as expected is most likely do to mixing as described in Appendix 2 of the JAG 2 report.

*References:*

*P. 12 Yapa 2010 should be et.al.*

*P 19 Kirsten et al 1984 is not in the list*

*There are several citations in this section where multiple citations are not properly presented*

*Eg: P. 20 (Payne, Kirsten et al., 1984) should be (Payne et al, 1984; Kirsten et al., 1984)*

*There are 3 such citations on Page 20. Other sections of the report do it properly.*

*References in the list but not cited in text or figures*

*These should be cited, deleted or added as "additional useful references" or some such.*

*Belore, R. (2003). "Large wave tank dispersant effectiveness testing in cold water". International Oil Spill Conference; Prevention, Preparedness, Response and Restoration, Perspectives for a Cleaner Environment: April 6-11, 2003, Vancouver, British Columbia, Canada, pp 381-385.*

- 
- Belore, R.C.; Trudel, B.K.; Lee, K. (2005). "Correlating wave tank dispersant effectiveness tests with at-sea trials". *International Oil Spill Conference; Prevention, Preparedness, Response, and Restoration: May 15-19, 2005, Miami Beach Convention Center, Miami Beach, Florida*, pp 65-70.
- Brandvik, P.; Daling, P.S.; Lewis, A.; Lunel, T. (1995). "Measurements of dispersed oil concentrations by in-situ UV fluorescence during the Norwegian experimental oil spill with Sture blend". In *Proceedings, Eighteenth Arctic Marine Oil Spill Program Technical Seminar, June 14-16, 1995, West Edmonton Mall Hotel, Edmonton, Alberta, Canada. Ottawa, Ont.: Environment Canada*. pp. 519-535.
- Brutsaert, W. (1982). *Evaporation into the Atmosphere: Theory, History, and Applications*. Dordrecht, D. Reidel Publishing Company.
- Colcomb, K.; Salt, D.; Peddar, M.; Lewis, A. (2005). "Determination of the limiting oil viscosity for chemical dispersion at sea". In *2005 International Oil Spill Conference; Prevention, Preparedness, Response, and Restoration: May 15-19, 2005, Miami Beach Convention Center, Miami Beach, Florida. Washington, D.C.: American Petroleum Institute*. pp. 53-58.
- Daling, P.S.; Brandvik, P.J.; Reed, M. (1998). "Dispersant experience in Norway: dispersant effectiveness, monitoring, and fate of dispersed oil". In *Dispersant Application in Alaska: A Technical Update, Anchorage Hilton Hotel, Anchorage, Alaska, March 18 and 19, 1998. Cordova, Ak.: Prince William Sound Oil Spill Recovery Institute*. pp. 111-146.
- Fiocco, R.J.; Daling, P.S.; DeMarco, G.; Lessard, R.R. (1999). "Advancing laboratory/field dispersant effectiveness testing". In *Beyond 2000, Balancing Perspectives: Proceedings: 1999 International Oil Spill Conference: March 8-11, 1999, Seattle, Washington. Washington, D.C.: American Petroleum Institute*. pp. 177-185.
- Lehr, W.; Jones, R.; Evans, M.; et al. (2002). "Revisions of the ADIOS Oil Spill Model", *Environmental Modeling & Software*, Vol 17, Issue 2, pp. 191-199.
- Lewis A.; Crosbie, A.; Davies, L.; Lunel, T. (1998b). "Dispersion of emulsified oil at sea". AEA Technology report. AEAT-3475. AEA Technology, National Environmental Technology Centre (NETCEN, Didcot, Oxfordshire, England.
- Lewis A.; Crosbie, A.; Davies, L.; Lunel, T. (1998). "Large scale field experiments into oil weathering at sea and aerial application of dispersants". In *Proceedings: Twenty-First Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, June 10 to 12, 1998, West Edmonton Mall Hotel, Edmonton, Alberta, Canada. Ottawa, Ont.: Environment Canada*. pp. 319-344.
- Lunel, T.; Rusin, J.; Bailey, N.; Halliwell, C.; Davies, L. (1997). "The net environmental benefit of a successful dispersant operation at the Sea Empress incident". In *Proceedings: 1997 International Oil Spill Conference: Improving Environmental Protection: Progress, Challenges, Responsibilities: April 7-10, 1997, Fort Lauderdale, Florida. Washington, D.C.: American Petroleum Institute*. pp. 185-194.
-



---

Lunel, T.; Lewis, A. (1999). "Optimization of oil spill dispersant use". In *Beyond 2000, Balancing Perspectives: Proceedings: 1999 International Oil Spill Conference: --- 44--- March 8-11, 1999, Seattle, Washington*. Washington, D.C.: American Petroleum Institute. pp. 187-193.

Mackay, D.; Matsugu, R.M. (1973). "Evaporation rates of liquid hydrocarbon spills on land and water." *Canadian Journal of Chemical Engineering*, Vol. 51, pp. 434- 439.

National Research Council (1989) *Using Oil Spill Dispersants in the Sea*, National Academy Press, Washington DC, 335 pp.

## Reviewer 8:

*General comment. In the report use laboratory not lab.*

*Page 6, Top Paragraph, Third sentence – "Other longer-term processes" Name the processes are the authors referring to.*

Sentence revised

Other longer-term processes such as biodegradation, photo-oxidation, and sedimentation may have an impact on the environment but are less amenable to response decisions

*Page 7, Top paragraph, second sentence. Suggest changing "...usually a simple, if slightly dull, process" to "... usually a straightforward process." Do not minimize the task of correctly filling out Form ICS 209.*

*Page 8, (2) Determine the bottom chemical dispersion amount. The equation uses a term  $90k_2$ . Why was 90 used? I reviewed Appendix 1. I see that  $k_2$  is the constant for subsurface chemical dispersion Table A1.2. on pp. A1.9. Why was 90 added to the constant?*

All the rate constants are defined in such a manner that they vary between 0 and 1. In the model, the DOR for subsurface dispersants has a maximum possible of 90. Therefore, the 90 appears as a scaling factor.

*Page 10. The Ixtoc Spill. First paragraph, last sentence refers to depth of the well "about 50 m". Last paragraph, First sentence has depth as "approximately 165 feet (51 m). Be consistent.*

*Comment for Section 3.0 Ixtoc spill - I suggest when comparing Ixtoc to DWH add the fact that that distance to shore was a factor in differences.*

---

*Comment for Section 3.0 Ixtoc spill – I suggest mentioning that dispersant application was more closely targeted for DWH than Ixtoc. During Ixtoc, dispersants were applied very close to shore, in the surf zone, and at the entrances to tidal creeks and other waterways.*

*Page 13, Top paragraph, Start of Third sentence. Is something missing at the start? The sentence starts out with “estimated”  
Or does the sentence start out with the citation (Lehr , 2001....)? Not clear to the reviewer.*

*Page 27. Last paragraph. The multi-spectral scanner measures the thickness and distribution of the oil slick in coastal and offshore waters in real-time. I suggest the explanation of the 4-picture sequence be explained in better detail.*

*Explanation expanded*

*Found a number of references in Section 15 not in the report.*

*Belore (3002)  
Belore et al (2005)  
Brandvick et al (1995)  
Brutsaert (1982)  
Colcomb (2005)  
Daling (1998)  
Fiocco (1999)  
Lehr (2002)  
Lewis (1998b)  
Lewis (1998)  
Lunel (1997)  
Lunel (1999)  
Mackay (1973)  
Mackay (1975)  
NRC (1989)  
The IXTOC I Oil Spill*

*Appendix 1 – Reference Section. No reference for W.N. Venables (2002) in the appendix.*

*The reference to Venables & Ripley (2002) is made on page A1.10 (Appendix 1), and the reference itself is specified on page A1.17.*

---

## Reviewer 9:

*Overall: There were problems in following the calculations as the descriptions were in the front and the equations in the appendix. It is not clear if the equations had any background or references. Did the authors develop them independently or was there a background or previous papers on each? I also had difficulties following the Appendixes due to lack of consistent numbering.*

A challenge in constructing a report of this nature is the diversity of the audience. We anticipate readers who will gravitate to the intricate mathematics of Appendix 1 while others will wish to see only the descriptive explanation of the model. As an imperfect compromise, the authors have chosen to provide the basic equations with a descriptive narrative at the beginning of the report, leaving the more complex mathematics to the Appendix. The equations themselves were constructed specifically for the calculator, based upon mass balance preservation and the spill experiences of the development team. Previous algorithms were used or modified for specific processes and are referenced in the main text.

*Consider putting in Resumes for the other contributors so that when they are referenced through "Personal Communication", readers know their background to add credibility. (especially Yappa and Galt)*

There are important differences between the major report contributors, who have all read the report and determined that it was acceptable for external review and the other contributors who may have not read the report in its entirety. We have chosen to acknowledge the latter's help but do not believe it would be appropriate to put them in an Appendix of major contributor resumes.

*Check all figures and move so that they are placed conveniently. (For example, Figure 7 is on page 19 but referenced on page 20 and figure 8 should be placed before Section 7 On page 21.*

*Individual Comments.*

*1) Table of Contents: appendix names not consistent with titles in Appendix themselves.*

*2) page 8, report goes right into equations without enough explanation. Try adding a couple of sentences at top of page 8 after straightforward: Something like "There are eight general categories for identifying the mass balance and..."*

Additional introductory material is added, including a narrative explanation



---

of the equations

*3) page 8-9, any specific references to these equations? If not, consider stating "These equations are based on...". Also consider putting a copy of Table A1.1 near beginning of report.*

See the new narrative.

*4) page 22, the range of volume figures used throughout is confusing. Consider placing the left-hand line under the rectangle and labeling the individual dotted/shaded areas. It is not clear what these are showing unless somehow they are combined at the end to show range.*

Figure 8 and similar figures in the report have been deleted.

*5) page 23, again are equations from NRC 2003 or ADIOS2?*

Equations are adapted from the Delvigne-Sweeney dispersion model (Delvigne and Sweeney, 1988)

*6) move figure 12 to page 29.*

*7) page 39. Why are results given in Appendix?*

Model results will be added to Section 14.

*8) Appendix 1 is confusing due to multiple page numbers.*

This has been improved pursuant to the reviewer's observation.

*9) Need a better link from main section of report to Appendix 1. Note that there are 16 equations with limited explanations.*

Appendix 1 provides the mathematical underpinning of the model. The purpose of the main section is to provide the science behind it. Section 2 provides an explanation of the important equations that control the processes. Deleted in this explanation, are auxiliary equations that sum results for graphing.

*10) Table A1.2 – Not completely clear if and how rate constants are related to estimates given in main section.*

Toward the end of each section is a discussion of the range of values that can be expected for that process. For example, the section on natural dispersion defines 20 % as the expected fraction of oil that will naturally disperse with a

---

range between 10% and 30%. This translates into an expected value for  $k_1$  of 0.2 with a range between 0.1 and 0.3.

*11) Appendix 3, consider wrapping text in title cells so that all number can fit on single page for easier reading.*

*12) Appendix 4, need better explanation of how samples were collected and analyzed. Just a brief paragraph that provides more than the Figure titles.*

*13) Appendix 6, need to state in first paragraph that "this Appendix does not provide information on the in-situ monitoring.*

*14) Consider describing test apparatus/process. For example, is the water sample poured through a column that the LISST monitors?*

*15) Consider adding more information about sampling depths, etc.*

*16) Appendix 7 – Label and reference all tables and figures in Appendix B. Had much difficulty in correlating with explanations.*

Appendices 4 through 7 reproduce already published reports reprinted here with the owners' permission to provide completeness to the report. We cannot modify them.

## **Reviewer 10:**

*Overall, this is a well-written document, with a clear objective of advising response options rather than being a comprehensive scientific study. The document references the literature of spill science well, and appropriate experts have contributed to various aspects of the report. It appears that the calculator was useful to inform response options over the summer. Below are several detailed comments:*

*The Executive Summary summarized the report well for the most part. Extra emphasis on the differences between a deep water spill such as this one and much more common surface spills should be made to overcome misconceptions that most managers will hold having only experienced shallow waters spills.*

**Introductory paragraph added to the Executive Summary**

*An estimate of the oil budget should be included in the Executive Summary. Maybe even just the pie chart (Figure 2 in the web-based tool section)*

While there is much to be said for including the results in the executive summary, it was also recognized that this could lead to some readers

---

proceeding no further. The development team believes that it is essential to understand the purpose and limitations of the calculator before considering its results. As a compromise, the results are now included in Section 14 of the report where the Calculator itself is assessed.

*Degradation rate of the oil components should be evaluated quantitatively if possible. Over the timescales relevant to the response, degradation rates are seen to be significant. Degraded oil should be a fate in Figure 2 pie chart.*

The development team believes that this would lead the use of the Calculator away from response toward damage assessment, something that it is ill-suited to assist.

*The changing composition of the oil should be part of the analysis. While this may seem to be too much detail for response, some fractions of oil are more toxic (will have bigger impacts) than others, so response options should consider the composition (e.g. toxicity) of the remaining oil in addition to just the total amount.*

A good point but it exceeds the purpose of the Oil Budget Calculator since it is only about the oil budget. We have tried to stay as close as possible to the standard ICS 209 output categories. See new Appendix that includes that part of the ICS 209 form that deals with the oil budget.

*The pie chart seems to be a good instantaneous visual for making decisions. If uncertainty could be built into the graphic, that would be very effective.*

I think this is a point where you would find universal agreement among the Calculator developers. The challenge has been to provide that uncertainty explanation and yet keep the output graphic clear and understandable. We are still working on it. See recommendation number 6 at the end of Section 14.

*My biggest criticism of the report is the handling of dissolution vs. evaporation of the oil. The discussion in Section 5 is good. It is most likely that dissolution of lower molecular weight hydrocarbons will occur at a much higher proportion for a deep water spill compared with a shallow water spill, especially as oil was dispersed. The processes of evaporation and dissolution, while similar, are not identical, and should not be treated as such in the sense that they will affect the composition of remaining oil differently. Of larger concern is that the composition of oil will be altered in sub-surface oil as well as surface samples, so the sampling protocols and expected compositions of oil would be different than for a shallow water spill. The ultimate fate of dissolved oil will not be considered with this model, and in some senses, dissolved oil is the most toxic as it is readily bioavailable. I would suggest the*



---

*dissolved quantities be separated from the evaporated quantities. Evaporative losses require no response as atmospheric processes act on wholly different spatial and temporal scales. The dissolved "losses" means that there is a significant amount of oil still in the ocean that needs consideration if not some hydrophobic recovery option.*

Your points are well taken here and the group had considerable discussion about the merits of separating the two processes into two categories. Certainly, any environmental impact assessment calculation would be required to do that. However, this is strictly a response tool, and from the responder's point of view, there is no further cleanup applicable to evaporated or dissolved oil. Plus, we did not believe we had sufficient sample data to distinguish between the two overlapping processes. Therefore, we reluctantly kept them together. As more data become available, we may wish to revisit this decision.

*The Longer Term Processes section was indeed needed in this report, even though it does not affect short-term response efforts. This section describes the processes of photodegradation and biodegradation. The literature review and discussion were good. A simple table illustrating the quantitative removal of various components of oil would be useful in communicating the fact that photo- and biodegradation are important processes that can remove (or at least change composition) of a significant amount of oil in the environment. Conditions (mainly temperature and depth) need to be included. This understanding of longer term impacts should affect decisions that are made in the short term, in that the ultimate fate and impact of the oil must be weighed against costs of response.*

We included the section on longer-term processes to provide background to those who are new to spill science. We are wary of expanding this section because there are others preparing much more complete and detailed analysis on these phenomena that should be the true reference sources on the subject.

*In the assessment and future plans section, #2 states that practical operational tools are needed to characterize droplet size. Has the LISST-100 (Sequoia) particle size analyzer been considered? It measures particle size in 32 size class bins from 1-55 um by laser, Mie scattering. An Optical Plankton Counter (e.g. Brooke Ocean Technologies) uses laser shadow graphs to measure particles from 100 um to over 1.5 mm. If these instruments cannot be used, it would be useful to know why not. If they were not tested, maybe they could be mentioned in the future plans section.*

As noted in Appendix 7, the LISST-100X was used for particle size analysis

---

on the R/V Brooks McCall and the R/V Ocean Veritas. The accompanying documentation outlined the limitations of using the LISST in the bench-top mode for the provision of data for the calculation of total dispersed oil for calculation of mass balance. However, the mission was to verify if the chemical oil dispersants were effective by quantifying the formation of smaller oil droplets and to identify the presence of the subsurface oil plume. This was conducted successfully. However, in the bench top mode utilized, explained in Appendix 7, the team could not trust the data in the larger size class bins. At the time of the spill, Sequoia had discontinued the manufacture of of a LISST for deepwater deployment (>300m for the LISST-100X) due to the lack of sales (and apparent problems with leaks). A LISST DEEP (depth range of 2500-6000m) is now in production as direct result of demand generated by the Gulf of Mexico spill that will resolve some of the limitations of using the LISST in bench top mode.

A Laser Optical Plankton Counter (LOPC), developed by Dr. Alex Herman at Department of Bedford Institute of Oceanography, Fisheries and Oceans Canada, measures particles >100um. NOAA is currently deploying a LOPC with a *Moving Vessel Profiler* (MVP™) in the Gulf of Mexico. A new prototype for the monitoring of plankton in ballast water with a lower size limit of > 20 um is being evaluated. For the sampling work in the Gulf of Mexico, the sampling team chose to use the LISST-100X as chemically dispersed oil typically results in an increase in oil particles in the <10um size range. It is important to note that both the LISST and LOPC cannot distinguish oil droplets from other particles.

Regarding future plans, there is a need to evaluate the various other in situ instruments that may be capable of measuring of oil droplet size. Years ago, Dr. Jim Bonner at Texas A&M evaluated field instruments including the LISST for real time in-situ crude oil concentration measurements but not oil droplet size distributions.

For work in the Gulf of Mexico, the sampling team chose to use the LISST-100X as chemically dispersed oil typically results in an increase in oil particles in the <10um size range. It is important to note that both the LISST and LOPC cannot distinguish oil droplets from other particles.

*Figures 4&5 of the Web-based tool section were informative in that the estimates were fairly close from worst case to best case so that the inherent uncertainty was not very large. I would agree with the report that some visual representation of the uncertainty in the calculator would help decision makers dramatically.*

We agree.

---

## Reviewer 11:

*The report contains a lot of good information, and the approach to the budget calculations is sound. However, the draft could be improved in several ways. Firstly, it is somewhat uneven in its coverage (e.g., stronger coverage of surface processes such as evaporation and surface dispersibility than on corresponding sub-surface processes). Secondly, it would benefit the reader to include results of at least the base case budget, obtained using the calculator, in the main text and the Executive Summary, instead of just the appendix. Most importantly, I wonder if the motivation for the report should be expanded. The stated objective was for "response advice only and...not... any other purpose." This may be literally true but it seems very limited. Everyone understands that there was at least some oil in each of the "pieces of the pie", and there was a tacit assumption that it was worth responding to any oil that was amenable to clean-up. (A lot of effort was put into skimming surface oil even though it only amounted to 3% of the total release.) Do we really need a budget calculator for this purpose? Given the enormity of the spill, its environmental consequences, the fact that the opportunity for most clean-up procedures has passed, the threat of future spills, and our uncertainty regarding much of the science, a far more important motivation would be to better understand the underlying processes affecting the oil's fate. And this calculator makes a good place to start. More specific comments (many minor) are provided below by section.*

The Oil Budget Calculator was developed to meet response needs only and the group would strongly counsel against using it for any other purpose. The report was written to document for the external scientific community the inner workings of the Calculator and provide recommendation for future research.

*Page 8 (and elsewhere). In several places the report refers to dispersed oil "at" the bottom. "Near" the bottom would be more descriptive.*

*Page 8. In calculating the chemically dispersed "bottom" oil (eq 2), the factor 90 is not explained. Nor is the factor 20 in eq 7 in the subsequent discussion of chemically dispersed surface oil. (I assume these relate to the respective DORs?)*

Your assumption is correct. The two values relate to the respective maximum DOR and are used in the equations as scaling factors so that the rate constants will have a maximum range of 0-1.

*Page 9. Since chemically dispersed surface oil is time dependent (efficiency*



---

*decreases with weathering, like evaporation), was consideration given to introducing time dependent (day 1, day 2,...) values for  $k_3$  as is done for evaporation ( $k_4$  and  $k_5$ )?*

This was considered. However, surface dispersant operations were applied to oil slicks at various states of weathering. Therefore, it would have been logistically impossible to assign a t-value to the sprayed surface oil.

*Page 11, paragraph 2 mentions "Current news reports..." and Page 12, paragraph 1 mentions "At the time of this document preparation...". Better to include the date (or at least month) since the information may not be current when it is read.*

*Page 13, paragraph 2. The Clark et al (2010) study estimates a minimum amount of surface oil on May 17 as 66,000 to 120,000 bbl, but implies the value could have been as high as 500,000 bbl (a little less than 1/3 of the oil spilled at that point) which is the value used in the calculator. This fraction (~1/3) seems quite high, especially since, subsequent to May 17, sub-surface recovery and dispersant use would dramatically reduce the oil reaching the surface, and ongoing evaporation and natural surface dispersion would reduce the equilibrium fraction of oil on the surface.*

The NASA/AVIRIS system was measuring cumulative oil remaining on the surface by mid-May. Through April and early May, burning, direct capture, and subsurface dispersant usage were limited, leaving more surface oil. Some of this early oil, probably emulsified, would still be on the surface during the NASA ER/2 flights. However, we agree that this would be at the high end of our estimates.

*Pages 13 (bottom) and 14 (top) discuss the gas portion of the release and mention that a large portion of the gas dissolved and hence may never have made it to the surface. Is there observational evidence (or modeling) that suggests that ANY significant fraction of the gas made it to the surface? The paragraph mentions the potential for hydrate formation. Clearly hydrates were formed within the confining spaces of some of the earlier containment vessels, but was there evidence of their formation in the free plume? (If so, please indicate.) Since the principle components of natural gas (methane, ethane and propane) have different hydrate stability zones, it would be helpful to know the composition of the natural gas. Concentrations are given in Appendix 4, but I gather this is just for the oil. Steve Masutani from U. Hawaii performed some nice experiments demonstrating the effect that an oil film has in inhibiting hydrate formation on a gas bubble (Masutani and Adams, 2000).*

---

See revised text. Leifer (2010) modeled plume behavior based on observations presented in Camilli et al. (2010) and concluded that the gas phase of the plume dissolved in the mid-water column and deeper and was transported by oil plume processes to the thermocline. Only gas components dissolved in oil reached the sea surface to exsolve and evaporate. As a result, atmospheric measurements (Leifer et al., 2010, in progress) do not show enhancement in atmospheric methane (except associated with flaring). In contrast, hexane and large organic compounds were enhanced. Tow sled video data (Asper, unpublished, 2010), showed extensive plumes of orange-white material uncommon to the deep sea (i.e., not marine snow), which was interpreted as oily hydrate flakes in the depth where others have reported enhanced CDOM (a fluorometric indicator of oil, albeit with very poor sensitivity).

Leifer, I., et al. (2010 in progress), Air quality implications of the Great Macondo Oil Spill.

*Page 14, last paragraph. It is mentioned that the tiny oil droplets were continually exposed to uncontaminated Gulf waters and hence their dissolution was not controlled by equilibrium factors. It seems likely that much of the sub-surface oil was contained in thick (hundreds of meters in the horizontal and at least tens of meters in the vertical) intrusions with fluxes of thousands of cubic meters per second. So even without exposure to ambient GoM water, dissolution would not likely have been constrained by equilibrium build-up.*

Point noted. The development team is cautious about reaching extensive conclusions on dissolved hydrocarbons while studies are ongoing.

*Page 15 (Fig 4 on droplet rise velocity). It would be helpful to give the density of the oil that was assumed, and to expand the graph to the physically more interesting lower diameter range.*

The graph was meant to illustrate the fact that the rise velocity for even larger droplets was small enough that the transit time to the surface was long. See the discussion and reference by Spaulding. The fresh oil density was 0.85 gm/cm<sup>3</sup> (API 35).

*Page 15 (and elsewhere). Much of the most useful information in the report has been provided by the experts, and cited as personal communication (Yapa on this page; also Galt, Lasheras elsewhere) or unpublished reports (Lewis). Can additional information be provided when there is no formal reference?*

Common in spill response is research that is used before it is formally documented. The Oil Budget Calculator is one example. We hope that these

---

experts will formally publish their findings but are reluctant to release their private communications beyond what is necessary in the report. In all cases we have tried to cite published references to supplement their unpublished comments.

*Page 17, paragraph 2. It was estimated that any oil exposed to conditions that could lead to dissolution would lose 5-10% of its volume... Presumably this explains the mean value of 0.075 for  $k_r$ ? (It would help reinforce the readers' understanding if this was mentioned.) Can the authors relate Fig 6 showing the dissolution potential vs C-number to the oil composition in Appendix 4 to show the reader where the 5-10% comes from?*

A dissolution potential of 5-10 % is a rough estimate based on earlier experiences from dissolution studies of various oils (referred to Melbye et al 1999 in the report) and with the present available chemistry of the DWH crude oil. Unfortunately, the detailed chemistry of the BTEX'es are not specified in the appendix 4 data. (which will be a significant contribution to the dissolution potential). That is why we ended up in this relatively wide span of 5-10 %. It is therefore difficult to directly relate the dissolution from the chemistry data in appendix 4 to Fig. 6.

More specific estimate of the dissolution potential will be calculated when the more detailed data of the crude oil chemistry are available.

*Page 22 (Figure 8, and others like it). The range of volumes (mean and with uncertainty) relative to the total spill (4.9 Mbbl) is clear, but what does the placement of the colored bar mean? Is there a horizontal bar chart envisioned that aims to add all of these up? (I know there is a pie chart in Appendix 2.)*

Figure 8 and similar figures have been removed

*Pages 21 (bottom) and 22 (top). The discussion of emulsification is useful but brief. Where do the percentages (16 to 38) come from?*

Most crude oils and petroleum products require weathering (evaporation) before they will form emulsions (NAS, 2000) This weathering is necessary to increase the viscosity and the asphaltene/resin content to the point where the next water-in-oil type is possible. Oils from similar oil fields have a tendency to form similar emulsions with similar weathering tendencies. It should also be noted that there are some exceptions to this as well. Table 2 shows the emulsification tendencies of Gulf of Mexico oils (Fingas, 2009). Table 2 shows that oils that formed stable emulsions had weathering percentages of 37.7, 26.2, 16.4, 25.5, 22.6, 24, and 35.2%. These averaged 26.8%.



- 1 NAS, *Oil in the Sea III, Inputs, Fates and Effects*, National Research Council, National Academies Press, Washington, D.C., 2002
- 2 Fingas, M. and B. Fieldhouse, *Studies on Crude Oil and Petroleum Product Emulsions: Water Resolution and Rheology*, *Colloids Surf. A*, 67, 2009

**Table 2 Stable Emulsions from Gulf Oils**

Oil	Weathering to form emulsions		Density (@15C)	Viscosity	Saturates	Aromatics	Resins	Asphaltenes	Stability	Complex	Water
	evap.	Visual Stability								Modulus (mPa)	Content (%w/w)
Garden Banks 426	37.7	Stable	0.8993	136	56	32	10	3	588	8.00E+04	64.7
Mississippi Canyon 72	26.2	Stable	0.9095	195	52	34	11	3	1128	2.20E+05	74.4
Mississippi Canyon 807	16.4	Stable	0.9375	491	39	41	13	7	111	5.45E+04	67.5
Mississippi Canyon 807	25.5	Stable	0.9582	3454	31	43	18	8	46	1.60E+05	65.4
Neptune Spar (Viosca Knoll 826)	22.6	Stable	0.8986	187	61	29	8	2	4947	9.25E+05	62.5
Viosca Knoll 826	24	Stable	0.9067	325	59	29	8	3	1046	3.40E+05	64.1
Viosca Knoll 990	35.2	Stable	0.8905	91	62	28	8	2	1075	9.8E+04	63.9
average of weathering of Louisiana crudes to yield Stable emulsions	26.8										

*Were there no direct measurements of emulsification in oil samples from the DWH spill?*

Only very limited emulsion analysis was available at the time of the Calculator construction. It indicated a weak and easily broken emulsion.

*How has percent emulsification been used in the budget? Was it used? (Since emulsified oil was skimmed and presumably could no longer be evaporated, does it matter to the budget calculator what its percentage was?) Where does the analysis from Appendix 7 enter the discussion?*

The observed tendency of the oil to emulsify was used in reducing the effectiveness for burning and surface dispersion.

*Page 22, Section 8, paragraph 2. Is there a reference for "Payne reports plumes of oil droplets..."?*

See reply to the Fourth Reviewer of a similar question.

*Page 23, paragraph 2 mentions that using 100 microns as an upper bound diameter for dispersible droplets is conservative (presumably in view of the fact that somewhat larger droplets are also slow to rise). It should be mentioned that this is conservative in that it may overestimate the amount of oil reaching the surface, but is NON conservative in estimating the oil retained sub-surface. Aren't both fractions important?*

---

By overestimating surface oil, and hence oil that potentially could be subject to further recovery, we meet the Calculator definition of conservative. It may not be conservative in regard to environmental impact.

*Page 23, eq 12. Is the ratio reversed? As written  $R$  appears to be the dispersed mass due to leaking pipe divided by dispersed mass due to breaking waves*

Corrected expression inserted

*Page 24, top. There is a huge (2.5 order of magnitude) difference in the predicted "theoretical" dissipation rate (Eq 13) of  $7 \text{ m}^3/\text{s}^3$  and the Martinez-Bazen et al. (1999) value of  $0.02 \text{ m}^3/\text{s}^3$  (rate =  $0.003 U_o^3/D_o$ ). The latter rate is based on actual measurements, but the measurements are for a pure water jet near the orifice, while the dissipation rate in a real oil/gas leak would be higher due to the turbulence introduced by the bubbles and droplets. Thus the real dissipation rate is likely to be in between as the authors state. (It would help to give the exit velocity and pipe diameter so that the reader could verify these computed dissipation rates.) Compounding the uncertainty in dissipation rates are the differences between a sub-surface oil plume and a surface oil slick. A sub-surface oil plume is reasonably steady and uniform (in an Eulerian framework), whereas surface wave conditions are quite patchy over space and time scales of tens of meters and hours. On the other hand, surface oil has a time window of a few days during which it is dispersible, while an oil parcel traveling through a plume has a window of only a few tens of seconds, since dissipation rate drops off rapidly with distance. (The dissipation rate is proportional to the plume velocity (which decreases) cubed divided by the plume diameter (which increases).) In view of the above, quantitative calculation of the rates of subsurface and surface natural dispersion are quite uncertain. Also, could the authors provide more explanation as to where the 10 to 30% figures come from?*

Your observations are correct and illustrate the challenges faced in estimating subsurface dispersion, both natural and chemical. One of the unsettled points among the experts, for example, was whether there was sufficient mixing time between the surfactant and the oil for effective dispersion. Following the rule to be conservative, the lower dissipation rate of Martinez-Bazen is used, minimizing natural dispersion and increasing oil on the surface. The minimum natural dispersion value is considered to be the lowest credible estimate consistent with Camilli et al. (2010) and the maximum the largest estimate consistent with the AVIRIS and LISST results.

Information on exit velocity and pipe dimensions can be found in the FRTG report, Deepwater Horizon Release, Estimate by PIV, 215 pp. (2010),

---

available on the USGS Deepwater Horizon website.

*Page 31, second paragraph. It would be helpful to have more information about how the dispersants were added sub-surface. For example, how close to the plume was the narrow diameter wand held by a ROV? The high plume velocity would have introduced an entrainment (radially inward towards the plume) velocity of about 10% of the local plume centerline velocity, and this entrainment velocity should have carried dispersant into the plume if it were released anywhere near the plume edge.*

The team did not have access to videos of dispersant injection, only data on the volume of dispersant used.

*Page 31, bottom. There appears to be little consensus among the report authors as to the effectiveness of sub-surface dispersant use, making this a prime topic for further research. My feeling is that it was probably quite effective. In addition to the arguments presented by "Alternative View 2" on page 29, we know that vertical profiles of fluorescence (indicating oil), typically showed a major intrusion a few hundred meters above the seafloor, with much smaller intrusions similarly spaced above the first intrusion. (See figure from one of the R/V Brooks McCall surveys below.) I believe that the intrusions contain oil that is detrained (along with seawater) from the plume as it ascends through a density-stratified ocean and passes a level of neutral buoyancy. Such detrainment events are clearly evident in laboratory measurements of gas and water plumes (Socolofsky and Adams, 2002, 2003). Oil droplets would follow the seawater into the intrusion only if they were small, with insignificant rise velocity, as if chemically dispersed. (A small amount of dissolved oil could also be included in the intrusions.)*

Many of our experts would agree with your conclusions. Unfortunately, others, including another reviewer, disagree. All would agree that there is little consensus on the subject and further research is required.

*Appendix 1 (Uncertainty). I did not have time to do this section justice, but it appears to be solid. I do question if the  $k$ -values in Table A1.2 should be called "rate" constants. Rate constants usually have dimensions of reciprocal time, whereas the values of  $k$  are dimensionless.*

We have used the expression "rate constant" by force of analogy with chemical kinetics, and agree with the reviewer that this may not have been the most accurate characterization for these constants: alternatives that came to mind, including "efficiency constants" and "yield factors", also suggest analogies that could be deemed deficient. Since we believe that the risk of misinterpretation is minor, we have chosen to retain this expression.



---

*Appendix 2 (Oil budget calculator). The appendix should have a number (2) and its title should match that listed in the TOC. (Appendix 5 also needs a number.) These are small points, but “Figures” 1 and 3 are actually tables. It would also be nice to make the figure and table numbering consistent with the rest of the report, e.g., Figure A2.1, etc. Similar comments apply to other appendices.*

*Appendix 5 (SINTEF dispersibility study). The MNS tests were conducted for 5 minutes; for how long were the IFP tests conducted? Was there any thought given to similar studies with sub-surface oil like that in the plume (unweathered but subjected to relatively high energy for short periods of time)?*

*Appendix 6 (LISST measurements). Paragraph 1 of page 1 refers to both bench top LISST measurements (of collected samples brought onboard) and continuous in-situ measurements with the instrument deployed at specific depths. The text only describes the former. Were the in-situ measurements not useful? It seems they would have avoided some of the issues described on pages 2 and 3 concerning the finite handling times and corresponding loss of large droplets. I gather that the droplet size distributions (both discrete and cumulative) are number distributions, but it is not clear. For example, the captions for Figures 5-8 indicate that the figures plot the FRACTIONS of the total measured particles that are small, while the text that refers to these figures (third paragraph of page 3) suggests that the vast majority of VOLUME fractions ...are ...small. Assuming the plotted distributions are by number, it would help to also include cumulative mass (or volume) distributions so the reader could determine the droplet diameters below which a give portion of the dispersed oil was contained. The text mentions (last paragraph of page 3) that the median diameters are nearly 20-30 microns; however my reading of Figures 9-12 suggest that these ranges are closer to 9 to 16%. Figures 4, 5, 8, 9 and 12 are mis-numbered. It would also help if figure numbers were consistent with the whole oil budget calculator report instead of (or in addition to) starting over with each new appendix. (This comment refers to several appendices.)*

The in situ measurements are very useful. The data analysis is currently ongoing and cannot be included here due to the deadline of this report.

All the LISST data presented in this appendix are based on volume concentration and are expressed in  $\mu\text{l/l}$ . This is stated on the first page of this Appendix.

Figures 4,5,8,9 and 12 were mislabelled. Their corrections are suggested in this response (see 2 above).

---

Note the x-axis of Figures A7-9~12 (Cumulative particle-size distribution is expressed as bin number, see Table 2 of this appendix for corresponding lower, medium, and upper size of each bin. For example, bin # 9 has medium size of 10.2um, and bin # 16 has medium size of 32.5 um.

*Appendix 7 (Ross oil properties report). Table 2-2 gives MC252 oil properties at temperatures of 15 and 35 °C. What was the temperature of the oil as it emerged from the pipe? Much of the oil resided/resides in intrusions a few hundred meters above the seabed where the temperature is ~5 °C. It would help to know oil properties (especially density) at these temperatures. Can the authors suggest a reasonable way to extrapolate from the data at 15 and 35 °C? It is too bad that the emulsification tests were conducted with a 2 cm thick oil which is mentioned in the text as a possible reason the oil in the lab did not emulsify, while the oil in the field did. It makes sense to repeat the tests with a 1 mm thick sample as suggested. Has this been done already? Also why would a 20 mm thick sample weathered for two weeks (336 hr) correspond to a 1 mm field sample exposed for 10 hrs? Wouldn't it be  $336/20 = 17$  hrs?*

Appendices 5 through 8 reproduce already published reports reprinted here with the owners' permission to provide completeness to the report. We cannot modify them. However, the author of Appendix 6 has offered the following reply. The IFT test is a dilution test conducted over a test period of 1 hour. Both the medium/high energy MNS method and low-energy IFP method are both standard laboratory methods designed to test the relative effectiveness of dispersant applied on surface oil/emulsions. In order to simulate and study the effectiveness of dispersant injection into a sub-surface oil plume, special designed laboratory test systems have to be constructed.

*Appendix 8 (Expert resumes). Michel Boufadel is not represented.*

He is now included

### **References**

- Masutani, S., and E. Adams. 2000. *Experimental study of multiphase plumes with application to deep ocean oil spills. Final report to U.S. Dept of Interior, Minerals Management Service. Contract No. 1435-01-98-CT-30946.*  
<http://www.mms.gov/tarprojects/377.htm>.
- Socolofsky, S. and E. Adams. 2002. *Multiphase plumes in uniform and stratified crossflow. J. Hydr. Res., 40: 661-672.*
- Socolofsky, S. and E. Adams. 2003. *Liquid volume fluxes in stratified multiphase plumes. J. Hydr. Engrg. 129: 906-914.*

---

## Reviewer 12:

*Overall, a very good document. I have only minor suggestions to offer.*

*Page: 3, Executive Summary*

*I really like the line "It is important to remember that the Deepwater Horizon incident was an emergency, not an experiment" from your introduction on page 5. You should consider incorporating it somewhere in your Executive Summary.*

We also thought it was an important point but concluded that it would require too much additional explanatory material if it was added to the Executive Summary.

*Page: 20, 1<sup>st</sup> paragraph*

*Since you mention the temperature of the oil here, it might be helpful to state the relationship between the oil's temperature and water temperature if it has not been previously stated.*

Oil temperature is assumed to be the same as the water temperature. Report is revised to clarify this point.

*Page: 21, 2<sup>nd</sup> full paragraph*

*In the sentence beginning with "The stronger color ...", replace the word "stronger" with "darker".*

*Page: 22*

*Figure 8 (and the other, similar figures) is a confusing graphic. I understand what the writer is trying to do, but this is unconventional to the point that it may cause confusion for some readers. It contains too many elements that are not important: height of the box and position of the shaded portion within the box.*

Figure 8 and similar figures have been removed.

*In Section 8, 2<sup>nd</sup> paragraph*

*The acronym LISST should be defined (Laser In-Situ Scattering and Transmissometry) at first use.*

*Page: 23*

*First paragraph*

*I can't tell if the sentence beginning with "ADIOS2 suggests that ..." is part of the previous paragraph or if it's supposed to be the start of a new paragraph.*



---

*Second paragraph,*

*For the sentence beginning with "Also, ADIOS2, following ..." delete the word "Also" so that the sentence reads "ADIOS2, following standard guidelines ...".*

*Page: 25, 2<sup>nd</sup> paragraph*

*In the sentence beginning with "As before, the stronger color ...", replace the word "stronger" with "darker".*

*Page: 26*

*There's something wrong with the color assignments for the bars in this graph. There's some strange optical effect that makes it difficult to view.*

*Adjusted.*

*Page: 27*

*Second paragraph, second sentence*

*Add the phrase "and regionally approved" so that it reads "... is a Federal cooperatively designed and regionally approved ...".*

*Figure 11*

*What is the blue rectangle that overlaps the 5/10 A.M. circular image? Also, the legend for this figure is not legible.*

*Figure replaced*

*Last paragraph*

*There's a typo in the sentence that begins with "If the dispersant ..." after the word "half" there's an "=" sign that shouldn't be there.*

*Page: 28*

*Second paragraph*

*The sentence that reads "Analysis was undergoing at the time ..." should read "Analysis was ongoing at the time ...".*

*Third paragraph*

*The sentence that reads "Given this limited nature ..." should read "Given the limited nature ...".*

## **Reviewer 13:**

*The document is longer than I expected with 156 pages and the content goes well beyond my own expertise.*

---

*The document addresses an urgent and difficult problem of estimating oil budget in the gulf due to the Deepwater Horizon Spill. Moreover, the authors tried to simplify the process so that the output (Calculator) can be used by non-specialized staff. The various kind of simplification leads to huge uncertainties. The authors have done a very good job in addressing many of these uncertainties. However, I'm not fully convinced that all these uncertainties are properly quantified (this is due partly to the limited time and the length of the document). There are also a few other minor issues:*

- 1. Low resolution of some of the mathematical symbols and equations;*
- 2. A few misconception (typo) such as the relationship between the kinematic viscosity and dynamic viscosity in A.2.2.*

## **Reviewer 14:**

*General thoughts on each section:*

- 1. Introduction: no comments*
- 2. Purpose and brief description: seems well thought through. The formulae seem to be well constructed and shouldn't lead to absurdities like more oil evaporating than leaving the well head. However, it seems that something like this should have appeared in the literature already from previous disasters yet there are no citations in this section.*
- 3. Previous experience Ixtoc: Good discussion of most relevant previous case.*
- 4. Leak Rate and Subsurface Oil Behavior: good discussion, no criticisms.*
- 5. Dissolution: well referenced but out of my area of expertise*
- 6. Evaporation: "To simplify data entry, requirements to enter variable wind speeds were eliminated. Cumulative evaporation is sensitive to oil composition and temperature but is relatively insensitive to wind speed." This statement should be supported, preferably with a citation to the literature. Evaporation rates depend strongly on temperature and also on the relative saturation of the air with the compound evaporating (for example, relative humidity in the case of water evaporating). It may be that keeping track of wind speed is prohibitively complicated and the model needs to be simplified but that argument is not well made.*

While the evaporation rate is sensitive to wind speed, cumulative evaporation depends upon the mole fractions of the hydrocarbons that make up the oil. If high wind on day 1 cause large amounts of evaporation, there will be less volatile hydrocarbons the next day, slowing evaporation rate. Calm winds on the first day lowers evaporation, making more of the volatile factions able to evaporate later. The cumulative fraction remains much the same after a

---

few days in both cases, although second order effects such as evaporation reducing oil available for dispersion exist, but are not included in the calculator.

7. Weathering Estimation by Emulsification: no comment
8. Natural Dispersion: good discussion, good references to the appropriate literature
9. Chemical Dispersion: there seems to be quite a diversity of opinion on the effectiveness of dispersants. In keeping with the nature of this report, a judgment needed to be made to estimate the amount of oil remaining in the sea. However, it is clear that more scientific research needs to be conducted into the use of dispersants, both on the surface and sub-surface.
10. Burning: good discussion
11. Mechanical Recovery: good discussion
12. Other Oil: this seems to be another area of considerable uncertainty.
13. Longer Term Processes: another area for future research.
14. Assessment and Future Plans: it is clear that we should learn from this terrible disaster. I hope that the recommendations (some of which I echo in my review) of this panel for future research are heard and acted upon so that we can more effectively respond to future accidents.

Itemized list of spelling and grammar errors

Page 9, the following sentence fragment does not make sense: "Disperse the surface oil that is available for surface dispersion, after subtracting evaporation and burning,..."

Page 11, "chocolate mouse" should be "chocolate mousse" unless the quoted source also made this mistake.

Page 12, "The DOE/FRTG consensus generally accepted a average value of 44% oil percentage by ..." 'a' should be 'an'.

Page 13, "This is considerable larger than the common maximum...", should be 'considerably'.

Page 13, Figure 3 has text on it saying "62 bopd" and the like. These labels should say "62 kbopd".

Page 20, "the two weathered oils (green and purple) collected from th sea surface on or around 16 May." The word 'the' is misspelled.

Page 22, "Payne reports plumes of oil droplets at depth over 2 km." awkward sentence.

Page 27, "...then more than half =of the released oil..." misplaced '='.





# Oil Budget Calculator

Deepwater Horizon

Layout and design by Jason D. McIntosh - [www.5dcreative.com](http://www.5dcreative.com)