2017 INTERNATIONAL OIL SPILL CONFERENCE

DISPERSANT PERFORMANCE: FINDING NEW RESULTS IN EXISTING DATA

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Abstract No. 092

Abstract: Chemical dispersants are used to mitigate oil spills in aquatic environments. Dispersants promote the breakdown of oil into smaller droplets that more readily diffuse into the water column. Federal agencies, industry, and academia have a long history of investigating dispersant performance at diverse scales and environmental conditions, including several recent publications. Several studies estimate dispersant performance as dispersion effectiveness (DE, measured as the percent of oil retained in the water column for a period of time after treatment), the concentration of oil in the dispersed in the water column, or the size of dispersed oil droplets. While many organizations have drawn qualitative conclusions from this body of work, a quantitative meta-analysis drawing together historic and recent research on the topic of dispersant effectiveness has not been conducted. This paper analyzed controlled studies measuring performance of dispersants across lab, tank, and large-scale studies. Although this paper examined only a subset of commonly tested oils, the findings strongly support that treatment with dispersants is correlated with increased effectiveness across several metrics, studies, and test methodologies. The conclusions provided by this analysis could be a critical tool for weighing the risks and benefits of using dispersants to respond to oil spills in aquatic environments.

INTRODUCTION

Dispersants are used to mitigate the potential effects of oil spills by promoting the break-down of a surface oil slick into small droplets dispersed into the water column (National Research Council 2005). During the April, 2010 *Deepwater Horizon* oil spill, dispersants were applied widely at both the surface and sub-surface source of the spill. Since 2010, there has been great interest and emerging studies on the toxicity and effectiveness of dispersants.

There is an opportunity to bring the results of recent studies together with the results of past studies in a quantitative way that bridges the limitations and strengths of an individual method, situation, or study. Bringing these studies together contributes to a broader understanding of the performance of dispersants and the overall uncertainty associated with a level of performance.

Meta-analysis is a quantitative tool widely used in ecology to synthesize results across studies and capture insights that cannot be inferred from a single study (see Osenberg et al. 1999). A key requirement of the meta-analysis approach is a no-treatment control to use as a baseline for comparing results. In light of recent studies raising concerns with the potential toxicity (e.g. Almeda et al. 2013) and ecological impacts (e.g. Kleindienst et al 2015) of dispersant use, the comparison of dispersant effectiveness to a no-treatment control is a critical element of weighing the risks and benefits of a given decision.

The purpose of this study is to analyze the effectiveness of dispersants for a subset of oils to identify operationally relevant trends, the influence of study design, and the overall effectiveness of dispersants compared to a no-treatment option. This study draws results from several experimental methods, locations, and approaches to identify these trends. Three primary

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metrics of dispersant performance are measured in this study: dispersion effectiveness, concentration of oil in the water column, and the size of oil droplets in the water column.

Dispersant Effectiveness (DE) describes the percent of an oil slick removed from the surface in terms of volume and may be estimated by re-collecting the oil that remains at the surface after experimental use of a dispersant (such as tank experiments at the Ohmsett facility, e.g. Belore et al. 2009) or other approaches. If the treatment of the oil with dispersants is effective (i.e., the volume of oil collected after application of the dispersant is less than the initial oil volume), DE is expected to increase.

The concentration of oil in the water column measures the oil dispersed into the water column once removed from the surface. If dispersant treatment is effective in a given situation, the concentration of oil in the water column is expected to increase commensurate with the decrease in surface oil volume.

The final metric also describes the oil dispersed in the water column, but rather than quantifying the amount of oil (as described by concentration), the characteristics of the droplets are described in terms of diameter or size. Generally, droplets less than 70 micrometer (µm) in size will stay suspended in the water column (Lunel 1995) and diffuse or biodegrade. If dispersant treatments are effective, the size of the droplets is expected to decrease and a greater proportion of the oil is expected to fall below this size threshold.

RESULTS AND DISCUSSION

Overall performance of dispersants

The initial analysis adapted traditional meta-analytical techniques to (refer to Methodology below) estimate dispersant effectiveness when other variables (e.g. turbulence, viscosity, etc.) are unknown. This analysis provided evidence that treatment with dispersants

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significantly increases DE, increasing DE by 49 % (95 % confidence interval: 43 to 56, two-sided t-test, df=52, $p<0.001$). An analysis of dispersed particle size found that dispersant treatment significantly decreased the size of dispersed oil droplets by 84 µm (95 % confidence interval: 36 to 132 µm reduction, two-tailed t-test, df=15, $p=0.002$). The concentration of submerged oil increased significantly (by 67 parts per million [ppm]) when treated with dispersants compared to the control (95 % confidence interval: 35 to 98, two-tailed t-test, df=12, $p<0.001$[1]). This analysis aggregated results from studies that used different testing facilities and techniques and does not account for these differences. These differences are accounted for in the ANCOVA analysis below.

These results provide evidence for the performance of dispersants that spans several studies for the selected oil types considered in this study. However, a follow-on analysis considering other types of oil is necessary to extrapolate these conclusions to broader situations where the characteristics of the oil and environment are unknown. DE increased with dispersant treatment, indicating that the dispersant treatment is generally successful in removing a portion of the oil from the water surface. Once dispersed below the surface, the size of the oil droplets partially determines whether the oil will remain distributed in the water column (Lunel 1995). The reduction in oil droplet size found across studies provides aggregate evidence that dispersants reduce the size of oil droplets once the oil is dispersed below the surface. This could prevent a proportion of the dispersed oil from re-surfacing, in addition to increasing the overall amount of oil in the water column.

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[1] Two outliers from a single study were excluded from this analysis. These outliers are shown on Figure 1.

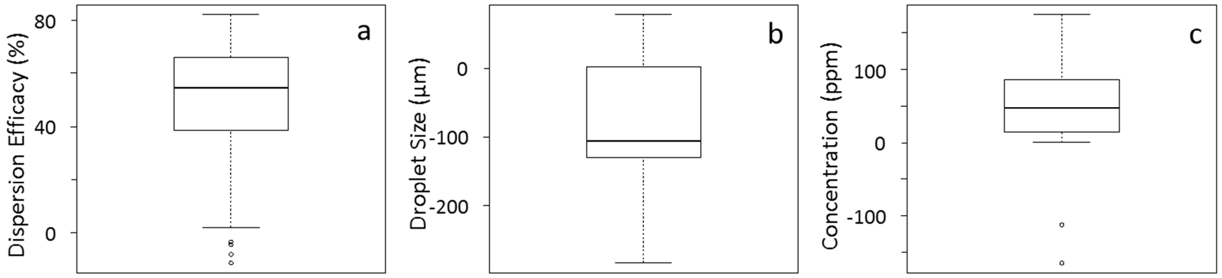

Figure 1: Boxplot of meta-analysis results across all studies and conditions for metrics of dispersant performance. The effect size of dispersant treatment compared to the control is shown for (a) dispersant effectiveness (%), (b) the size of oil droplets dispersed into the water column (µm), and (c) the change in concentration of oil in the water column (ppm). The solid line indicates the median of the data, the box indicates the 25-75 percentiles of the data, and the bars show the range of the data. Outliers are indicated as independent points on the plot.

Comparison of ANCOVA results across dispersant performance metrics

ANCOVA[2] was used to determine which experimental conditions (e.g. oil-to-water ratio, test type, study) and operational conditions (e.g. turbulence, oil type, viscosity, disperstant-to-oil ratio [DOR]) influenced dispersant performance. The η^2 for factors of the ANCOVA model was calculated (Ramanathan 2002) to determine the proportion of total variance in the data explained by a single variable in the model (Table 1) and is used here to determine which variables are most influential on each dispersant performance metric.

Table 1: η2 values for the ANCOVA models for three metrics of dispersant performance. η^2 describes the proportion of total variance in the underlying data that is explained by a given variable as a percent. Statistical significance was determined using α=0.05.

	DE (percent)	**Concentration (ppm)**	**Size (micrometer)**
Outcome metric	N/A	38%	N/A
DOR	38%	12%	30%
Oil-to-water ratio	3%	12%	Not Significant
Turbulence	3%	6%	9%
Viscosity	1%	3%	Not Significant
Oil type	10%	2%	8%
Test type	4%	6%	Not Significant
Study	18%	6%	Not Significant

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[2] Analysis of Covariance

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Variation due to oil characteristics

Viscosity was included in the analysis to explain some of the variation which might be due to oil type. Any variation due to the oil that is not explained by viscosity is captured by the "oil type" variable. "Oil type" represents the unexplained variation due to the oil that is not explained by this model, or viscosity. Viscosity, while statistically significant, did not explain substantial variation in the data across any outcome metric (Table 1). Oil type explained 10% of the variation in DE and 8 % of the variation in droplet size, but little of the variation in concentration change. The influence of oil type on DE suggests that there may be additional characteristics of oil, other than viscosity, that contribute to dispersant performance across scales. For instance, Fingas et al. (2003) suggested that specific chemical components of oil were effective chemical predictors of dispersability, and chemical characteristics might contribute to variability in oil not captured by this study.

Variation due to dispersant treatment and dosage

The operational factor of DOR (where DOR of 0 indicates that no dispersant was used) explained more variation in the data than any other factor for all outcome metrics. DOR alone accounted for 38 % of the variation in DE, 30 % of the variation in droplet size, and 12 % of the variation in oil concentration. DOR was a statistically and functionally significant predictor of dispersant performance for all dispersant performance outcomes (Table 2). DOR predicted an increase in DE of 46 % when dispersant was applied at a 1:20 DOR, an increase in subsurface oil concentration of 32 ppm, and a decrease in the mean oil droplet size of 52 µm.

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Variation due to testing conditions

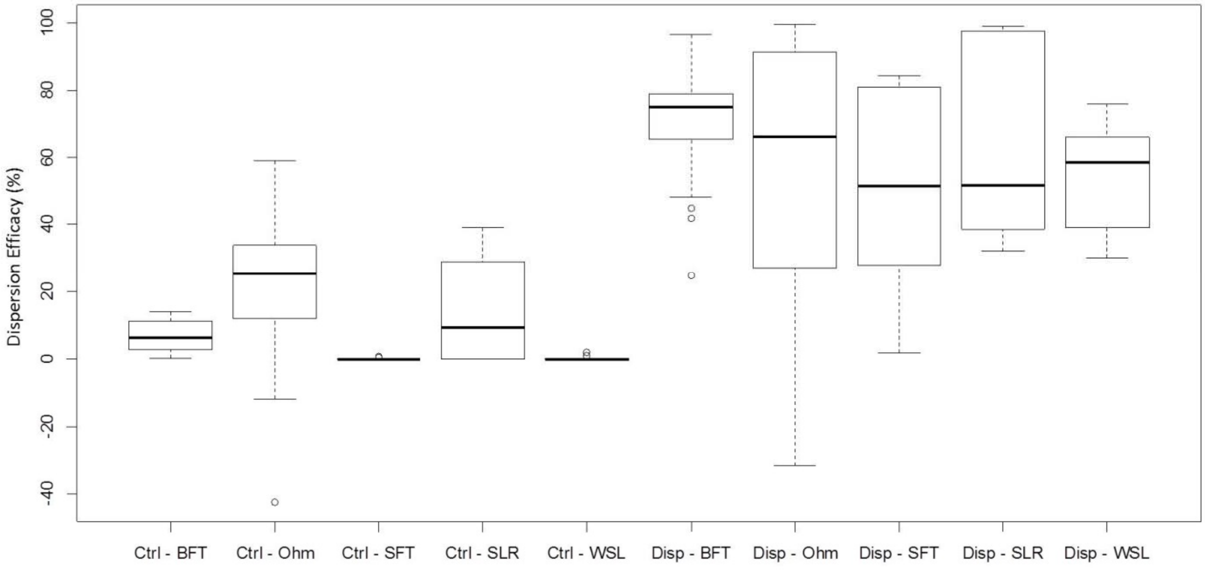

Figure 2: Measures of Dispersion Effectiveness varied significantly among tests (p<0.001, ANCOVA) and studies (p<0.001, ANCOVA). Some of the differences in test types may be due to methodology.

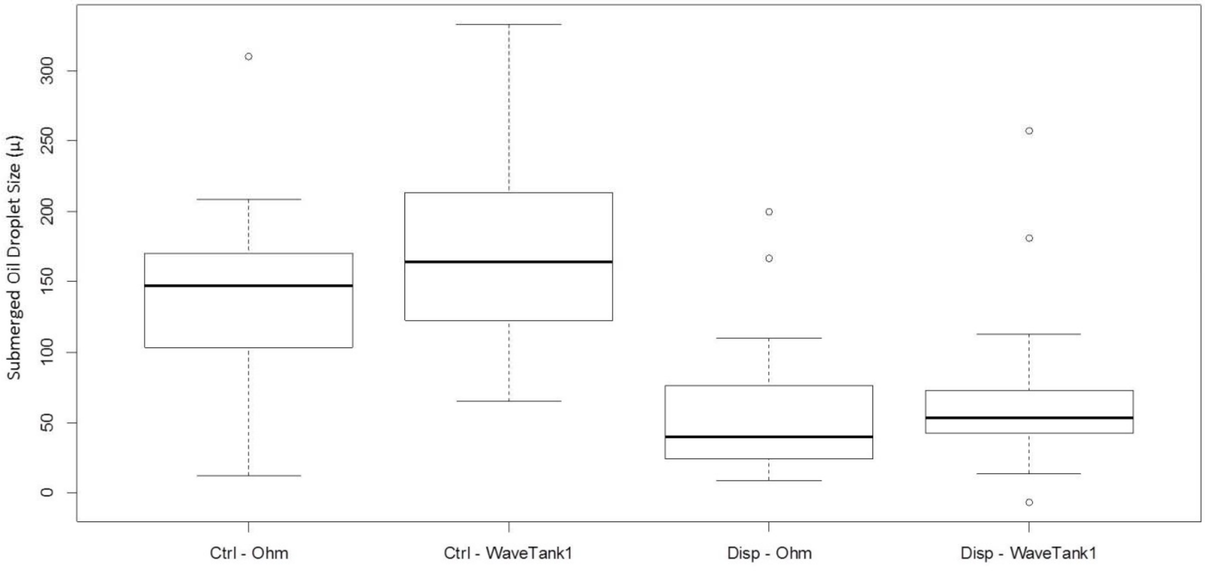

Figure 3: There were no significant differences among tests and studies for metrics of submerged oil droplet size.

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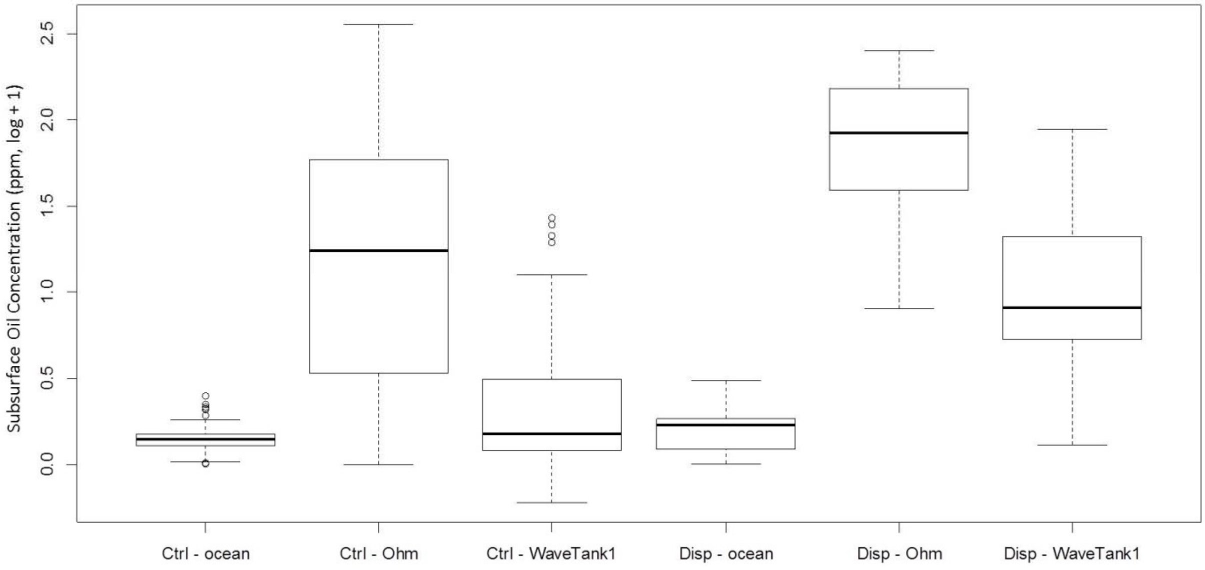

Figure 4: Measures of oil concentration in the water column varied significantly among tests (p<0.001, ANCOVA) and studies (p<0.001, ANCOVA).

The oil to water ratio and turbulence were explored to explain some of the variability among different testing methods. Variation not captured by these metrics is captured by the test type factor, which represents differences among tests not explained by the variables examined here. Overall, turbulence explained little of the variation in the DE and concentration, although the influence is statistically significant. Turbulence explained the most variation for oil droplet size, explaining 9 % of the total variance. The oil-to-water ratio explained as much variance in submerged oil concentration as DOR and was one of the most influential factors impacting oil concentration (12 %). Only 3 % of DE was explained by the oil-to-water ratio, and this variable was not a significant predictor of size metrics of performance outcomes.

While the exploratory factors of oil-to-water ratio and turbulence did explain some variation among studies, there is still variation among test types and studies that remains unexplained. For DE, turbulence and the oil-to-water ratio explained 6 % of the variation in the

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data, while unexplained variation due to test type and the specific study accounted for 18 % of the variation in the data. Some of the unexplained variation among tests for DE could be due to the different methodologies for calculating DE used among test facilities and individual studies. For concentration, turbulence and the oil-to-water ratio explained 17 % of the variation in the data, while unexplained variation due to test type and the specific study accounted for 12 % of the variation in the data. For oil droplet size, turbulence explained 9 % of the variation in the data, while test type and the specific study explained less than 1 % of the variation in the data. These results suggest that the experimental factors that were otherwise unaccounted for contribute variability to DE and concentration metrics remain unaccounted for, while particle size appears to have less variability due to the factors considered in this analysis. The oil-to-water ratio explained little of the inter-test and inter-study variability of DE and particle size, although the relationship was more substantial for oil concentration (discussed below).

Discussion of oil-to-water ratio

For metrics related to concentration of oil in the water column, the oil-to-water ratio was the most influential variable, second to the outcome measure selected (e.g. peak, average). The oil-to-water ratio explains 12 % of the variation in sub-surface oil concentration. As the oil-to-water ratio of the experiment increased (such as moving from a large scale testing facility with a small amount of oil relative to a massive volume of water to a laboratory scale flask experiment with a small amount of water) the concentration of dispersed oil measured in the water column also increased. The lower concentrations of oil within the water column under higher water volume conditions may be due to the increased dilution of dispersed oil droplets when water volume is not limited (suggested by Lee et al. 2011). However, the concentration of oil is usually used as a metric where an increase in oil concentration is linked to better dispersant performance.

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Therefore, a post-hoc analysis separating the dilution influence from the dispersant performance was performed.

A post-hoc regression was conducted to examine if dispersant effectiveness, as measured by the concentration of oil in the water column, changed depending on the oil-to-water ratio. This post-hoc regression analyzed the interaction of the oil-to-water ratio with a factor describing whether or not the oil had been treated with dispersants, in addition to the other general variables as described in the methods. This analysis found that there was a significant modifying effect between treatment and the oil-to-water ratio, with dispersant treatment expected to increase the influence of the oil-to-water ratio compared to the control. In operationally relevant terms, this translates to a 75 ppm increase in oil concentration when treated with dispersants (compared to the control) at the large Ohmsett facility compared to a laboratory test such as the Baffled Flask Test.

Parameter estimates and results of linear regression analysis

The magnitude of influence for each explanatory variable was estimated using linear regression, with significant parameter estimates shown on Table 4 with examples of operationally relevant estimates for key situations. Each parameter is estimated while controlling for all other variables included in the analysis, and estimates are not directly meaningful without considering the other conditions in a given situation. However, these estimates are very useful for making quantitative comparisons among different treatment options, such as deciding whether or not to treat a spill with dispersants.

It is important to consider parameter estimates in the context of the the range of conditions included in the analysis, and scales of operational significance (shown in gray on Table 2). The influence of DOR was functionally relevant for the outcomes of DE, oil droplet

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size, and concentration. The influence of oil- to-water ratio was functionally significant for metrics of DE, suggesting that differences between the laboratory tests (e.g. Baffled Flask Test) and large-scale tank tests (e.g. Ohmsett) are about 30 %. Turbulence did not have a functionally significant influence on concentration despite statistically significant results. However, the influence of turbulence on droplet size was operationally significant, suggesting a reduction in particle size of 32 µm for an increase in turbulence from a rolling wave to a breaking wave (as measured in tank by Lee et al. 2009). An increase in viscosity between Alaska North Slope (ANS) and a median Intermediate Fuel Oil (IFO) is predicted to lower DE by about 18 %.

Table 2: Summary of parameter estimates from linear regression models. Rows in gray show relevant examples of functional and operational implications of the parameter estimates. Note that the full model included estimates for differences among specific test types and studies, which are not shown on the table.

	DE (percent)			**Concentration (log of ppm)**			**Size (micrometer)**		
	Est.	St. Err.	p-value	Est.	St. Err.	p-value	Est.	St. Err.	p-value
DOR (ratio)	915	54	<0.001	19	4.9	<0.001	-1×10^3	190	<0.001
Difference from 0 to 1:20	46	Increase in DE when 1:20 dispersant treatment is applied.		32	Increase in oil concentration (ppm) when dispersants applied.		-52	Decrease in particle size (micrometer) when dispersants applied.	
Oil-to-water ratio (log)	-15.59	7.21	0.0315	7.35×10^5	2.97×10^5	0.0138	NS	NS	NS
Difference between Ohmsett and lab	-32	Decrease in DE expected when use lab-scale test.							
Turbulence (log m^2s^{-3})	NS	NS	NS	0.13	0.04	0.02	-14.03	4.02	<0.001
Difference between rolling and plunging wave (e.g. Lee et al. 2009)							-32.21	Decrease in particle size expected for a plunging wave.	
Viscosity (log cP)	-6.997	1.5	<0.001	NS	NS	NS	NS	NS	NS
Difference between ANS and median IFO	-19	Decrease in DE expected for more viscous IFO.							
adjusted R^2 for full model		0.759			0.843			0.449	

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CONCLUSIONS

This study presents meta-analysis as a powerful approach for drawing dispersant research together from diverse scales and conditions to draw quantitative results. While this study examined only a subset of commonly tested oils, the findings strongly support that treatment with dispersants is correlated with increased effectiveness across several metrics, studies and test methodologies. The ratio of oil-to-water in experiments as a proxy for scale may impact the results of key dispersant performance metrics and explain variability among test methodologies. Concentration and DE metrics were especially impacted by this factor, while oil droplet size was not highly impacted.

The confidence limits provided by this meta-analysis predict that dispersant treatment will impact outcome measures across several scales of tests, methodologies, and conditions. These confidence limits will help decision makers objectively predict the operational outcome of using dispersants during a response situation. The conclusions provided by this analysis and similar approaches may provide a critical tool for weighing the risks and benefits of using dispersants to respond to oil spills in marine environments.

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METHODOLOGY

Data sources and search methodology

Sources were identified using a google scholar search for studies with "dispersant" and "effectiveness" in the title in July 2015. Additional studies were identified and cross-validated against independently prepared literature syntheses and compilations such as Ufford et al (2014). The studies identified in this search were then evaluated with the following criteria for inclusion in the present study.

Criteria for inclusion in this study

- The study must evaluate one of the following oils: Alaska North Slope (ANS), Endicott, a South Louisiana Crude oil or similar (SLC, including Macondo and Dorado oils), or an intermediate fuel oil.
- The study must report the results of a control for the selected oils, which does not use dispersant and does experience exact conditions to the dispersant oil treatment.
- The study must evaluate the common dispersant, Corexit 9500, and identify which results apply to the specified dispersant.
- The study must include sufficient detail on the methodology to identify the water volume, oil volume, dispersant-to-oil ratio (DOR), and the general characteristics of the turbulence regime.
- The study must include original data (e.g. not present a re-analysis of existing or previously reported data). In cases where multiple studies present on the same underlying raw data, the study with the most detail was used.
- A table with the studies included in the analysis is attached at the end of this paper.

Methods of data extraction

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For studies that reported findings in tables, the data were transcribed directly. For studies that only showed data using figures or graphs, data were extracted using the online tool WebPlotDigitizer (Rohatgi 2016).

Some studies reported raw data (e.g. data per replicate), while others presented aggregate results. For studies presenting aggregated results with a standard deviation, lower 95% confidence interval, or standard error, the data were simulated[3] using the calculated standard deviation, presented mean, and sample size assuming an underlying normal distribution of experimental results. This technique was applied to data from four studies using the R statistical program (R Core Team 2013).

Description of data synthesis and estimation

This study synthesizes information from across several peer-reviewed sources to generate estimates of turbulence. Estimates of turbulence were either included directly in the study (e.g. Lee et al. 2009), estimated in independent empirical literature (e.g. Kaku et al. 2005), or calculated using estimated correlations to other measured variables (e.g. MacKenzie and Leggett 1993, Babanin et al. 2009). Table 3 presents the source and method for calculating turbulence for each test type.

Table 3: Methods of turbulence classification for each test type.

Test type	Method of turbulence calculation	Source(s)
Swirling Flask Test	Empirical metric	Kaku et al. 2005
Baffled Flask Test	Empirical metric	Kaku et al. 2005
Field	Estimated with historic data and correlations.	MacKenzie and Leggett 1993, weatherunderground
Ohmsett	Estimated from empirical data and correlations.	Babanin et al. 2009, Vernon et al. 2009
S.L. Ross Tank	Estimated from study data and correlations.	Babanin et al. 2009

Description of variables examined

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[3] http://archives.math.utk.edu/ICTCM/VOL18/C131/paper.pdf includes a description of this technique.

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Three broad groups of performance metrics for dispersant performance were examined in separate analyses: percentage metrics (such as Dispersant Effectiveness, DE), concentration metrics (such as oil content of the water column estimated as part per million [ppm]), and size metrics describing droplets dispersed in the water column (such as Volume Mean Diameter). Each of these broad performance metrics might capture a different measure despite reporting results in the same unit. For example, estimates of oil concentration in the water column can be reported as an average across a depth range or as peak values taken explicitly within an oil plume. The control variable outcome measure is a factor used to separate and analyze for the influence of these experimental differences in the analysis.

Variable selection

All explanatory variables were examined for cross-correlation using the Kendall's rank correlation in R. Explanatory variables that have high cross-correlations cannot be used effectively in multiple regression (Ramanathan 2002) as these variables may confound findings and inflate the variance of model estimates. For any pair-wise interaction greater than 0.35, a single explanatory variable was selected for the analysis. It is important to note that not all of the cross-correlations between explanatory variables are necessarily meaningful or represent a mechanistic link. Due to the nature of meta-analysis, some correlations might be due to experimental design, constraints, or random correlations across unrelated studies. There were strong interactions among oil volume, water volume, and viscosity; therefore the scaling factor of water volume was excluded from the analysis and the non-correlated oil-to-water ratio was selected instead.

Overarching meta-analysis methodology

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Traditional meta-analysis approaches (discussed by Osenberg et al. 1999) were not appropriate for data from many of the studies analyzed in this paper because many large scale dispersant tests do not include replicates. Therefore, results from each study were aggregated as a mean response for each unique oil type tested with dispersants, compared to a control for the same oil. This aggregated paired result was analyzed using the Student's t-test comparing the distribution to zero, or a negligible response. This aggregation gave equal weight to each study and oil type evaluated. While this approach ignores the influence of other crucial moderating factors (e.g. viscosity, turbulence, etc.), the meta-analysis approach offers useful parameter estimates and confidence intervals to use in situations where information is limited.

ANCOVA and regression analysis methodology

ANCOVA[4] and regression analyses were used to evaluate the influence of several moderating factors on dispersant performance and compare the importance of these moderating factors to treatment with dispersants. ANCOVA was used to evaluate main effects from variables of interest on outcome metrics of dispersant performance. Parameter estimates for continuous variables of interest were estimated using linear regression. All analyses were conducted in R (R Core Team 2013). The following variables were analyzed by the ANCOVA:

- Dispersant to oil ratio (DOR)
- Oil-to-water ratio
- Turbulence, log transformed ($m^2\ s^{-3}$)
- Viscosity, log transformed ($m^2\ s^{-3}$)
- Oil classification, as a factor. Oil classifications were summarized as shown in Table 4:

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[4] Analysis of Covariance

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Table 4: Classification of oil types analyzed

Original Oil Name	**Classification**
Alaska North Slope	ANS
Endicott	ENDI
IFO-120	IFO
IFO-180	IFO
IFO-380	IFO
Dorado	SLC
Macondo	SLC
South Louisiana Crude	SLC

- Test type, as a factor
- Study, as a factor
- Outcome measure was used only for concentration metrics, which measure a size-fraction of particles, peak concentrations, or mean concentrations.

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STUDIES SELECTED FOR ANALYSIS

Index	Author	Year	Title
4	Bejarano et al.	2013	Effectiveness and potential ecological effects of offshore surface dispersant use during the Deepwater Horizon oil spill: a retrospective analysis of monitoring data
10	Belore et al.	2005	Correlating wave tank dispersant effectiveness tests with at-sea trials
11	Belore et al.	2008	Dispersant Effectiveness Testing on Viscous, US Outer Continental Shelf Crude Oils and Water-in-Oil Emulsions at Ohmsett
12	Belore et al.	2009	Large-scale cold water dispersant effectiveness experiments with Alaskan crude oils and Corexit 9500 and 9527 dispersants
13	Belore et al.	2011	Wave Tank and Swirling Flask Dispersant Effectiveness Testing on Fresh Mississippi Canyon 252 Oil
32	Chandrasekar	2004	Dispersant effectiveness data for a suite of environmental conditions
33	Clark	2005	Assessing dispersant effectiveness for heavy fuel oils using small-scale laboratory tests
61	King et al.	2013	Interfacial film formation: Influence on oil spreading rates in lab basin tests and dispersant effectiveness testing in a wave tank
62	Lee et al.	2009	Wave tank studies on dispersant effectiveness as a function of energy dissipation rate and particle size distribution
88	Mullin et al.	2008	Cold water dispersant effectiveness experiments conducted at Ohmsett with Alaskan crude oils using Corexit 9500 and 9527 dispersants
89	Mullin	2004	Dispersant Effectiveness Experiments Conducted on Alaskan and Canadian Crude Oils in Very Cold Water
112	SL Ross and MAR	2003	Dispersant Effectiveness Testing on Alaskan Crude Oils in Cold Water
126	Stevens and Roberts	2003	Dispersant effectiveness on heavy fuel oil and crude oil in New Zealand
128	Sullivan et al.	1993	Evaluation of three oil spill laboratory dispersant effectiveness tests
130	Venosa and Holder	2011	Laboratory-Scale Testing of Dispersant Effectiveness of 20 Oils Using the Baffled Flask Test
78	Lunel	1995	Dispersant effectiveness at sea.
BSEE 685 ab	Trudel and SL Ross	2013	Comparison of Small-Scale Dispersant Testing Methods to Ohmsett: Effect of Dispersant Type and Oil Properties (https://www.bsee.gov/osrr-oil-spill-response-research/osrr-685ab)
BSEE 546 aa	SL Ross	2006	Chemical Dispersibility of U.S. Outer Continental Shelf Crude Oils in Non-Breaking Waves (https://www.bsee.gov/osrr-oil-spill-response-research/osrr-546aa)
BSEE 568 ab	SL Ross and MAR	2007	Corexit 9500 Dispersant Effectiveness Testing in Cold Water on Four Alaskan Crude Oils (https://www.bsee.gov/osrr-oil-spill-response-research/osrr-568ab)
BSEE 685ac	Belore and SL Ross	2014	Dispersant Effectivness Testing at Ohmsett Using Aircraft Application Dosages (https://www.bsee.gov/osrr-oil-spill-response-research/osrr-685ac)
BSEE 545aa	SL Ross	2006	Calm Seas Application of Dispersants, Final Report. September 2006, 51 pages. https://www.bsee.gov/sites/bsee.gov/files/osrr-oil-spill-response-research//545aa.pdf

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