Dispersant Science

Alaska Department of Environmental Conservation
Division of Spill Prevention and Response

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Overview

- The Scientific Method
- Test Facility & Field Test Descriptions
- Functional Norms
- Dispersant Testing & Effectiveness
- Crude Oil Toxicity
- Transferability to Operational Setting
- Mitigating Consequences Through Policy

Understanding Key Oil Properties

- Specific Density (SD) Describes if Substances Float on Water
  - Values >1 sink
  - Values <1 float
    - ANS Crude: SD= 0.88-0.93
- Pour points describe temperatures at which liquids become semi-solid
  - ANS Crude: PP= $^{-}8$ °C
- High viscosity reduces dispersability. Temperature affects oil viscosity
  - V= 29-34cP at 0C & 14-16cP at 15°C
- Natural vs. Chemically Enhanced Dispersion
- Sedimentation and adherence can alter buoyancy
  - Turbid coastal waters typically have increased turbidity, sedimentation, and risk

How We Know What We Know

- Academic Research
- US Testing Primarily at OHMSETT (Leonardo, NJ)
- USCG's Research & Development Center (New London, CT)
- Field Tests in Norway, Canada, France, Netherlands, the UK, and US
- Operational Case Studies from Major Spills
- Scientific Method
  - Pros: Controlled, Measured, Accurate, Repeatable, Conducive to Hypothesis Testing and Precise Experimentation, Peer Reviewed by SMEs, Published, Criticized, Refined, and Produces Results/Recommendations
  - Cons: Scale is Often Limited, Precise Environmental Replication is Often Limited, Describe Results Within Specific Parameters, Results Only Describe Measured Endpoints, Waste Management, Cost

OHMSETT Testing

BSEE
Bureau of Safety and Environmental Enforcement

interspill AMSTERDAM 2015

Comparative Testing of Corexit EC9500A, Finasol OSR52, Accell Clean DWD, and ZI 400 at Ohmsett in a Simulated Arctic Environment

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Abstract

The Bureau of Safety and Environmental Enforcement (BSEE) recently conducted independent dispersant effectiveness testing. Several products were tested under simulated arctic conditions at Ohmsett. The test program was conducted to better understand the effectiveness of various dispersants under the test conditions and compare the products. The results will assist BSEE and its federal partners in their decision making in regards to the various dispersants being considered by the oil spill response organizations (OSROs) for use on the U.S. Outer Continental Shelf.

Four dispersants were selected from the Environmental Protection Agency's (EPA) National Contingency Plan (NCP) Product Schedule and were tested on an Alaskan crude oil. They include Corexit® EC9500A, Finasol® OSR 52, Accell® Clean DWD, and ZI 400. To capture operational effectiveness issues, the dispersants were applied to a surface slick using Ohmsett's spray bar, which simulated a system similar to a boat spraying system.

Data collected included dispersant effectiveness (DE) based on the volume of the surface slick which remained after the test as compared to the volume dispersed into the water column and particle size distribution of the oil droplets dispersed at 1 meter and 2 meters below the water surface. Particle size distribution was captured using two LISST-100x instruments from Sequoia Scientific. The instruments allowed researchers to quantify the

Test Conditions

- 610' L x 60' W x 10' D
  - 2.6 million gallon test tank
  - Filled with saltwater (26.7 ppt)
- Source oil: Blended Cook Inlet and ANS Crude
- 5 treatments, 3 replicates each
  - (Corexit 9500, Finasol, Accell, ZI 400, Control)
- Air temp: 23°F – 48°F
  - Avg: 34°F
- Surface water temp: 26°F - 32°F
- Surface application via spray bar
- 20 minute tests
- Breaking wave every 4-6 waves

Comparative Dispersant Test Results

Dispersant Type	Median Droplet Size (uM)*	Mean % Effectiveness	% Improvement Over Control	Comments
Corexit	83.85	72.7	46	No foam or freezing, minimal resurfacing
Finasol	95.28	72.2	45	Greater viscosity, needs 5% more pressure to spray, minimal resurfacing
Accell	138.37	51.3	25.7	Droplets remain shallower than others
ZI 400	382.98	45.7	-0.8	Major surface foaming and oil resurfacing. Product froze in nozzles
Control	457.26	49.8	---	

*Droplet ≤70 µM remain dispersed. Larger droplets resurface.

Functional Norms

DISPERSANTS: COMPARISON OF LABORATORY TESTS AND FIELD TRIALS WITH PRACTICAL EXPERIENCE AT SPILLS

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ABSTRACT: *Laboratory tests can demonstrate the effectiveness of dispersants relatively easily but it is far more difficult to assess effectiveness in field conditions. In many oil spills, timely application of dispersants is the best approach. It is therefore necessary to study their use in field trials and actual incidents to see what lessons can be learned about the amounts used relative to the amount of oil spilled, types of oil on which dispersants are relatively effective, methods of application, the period after release into the sea during which dispersants remain effective, and the influence of sea conditions and temperatures.*

This paper discusses these questions, reviewing published data on the performance of dispersants in field trials and in actual oil spills in which staff of the International Tanker Owners Pollution Federation Ltd. have been involved in recent years. Recommendations are made regarding further work in the laboratory and field that appears necessary to determine the conditions under which dispersants are likely to be most effective.

Natural dispersion is an important process leading to the dissipation of oil spills from the sea surface. It can sometimes be enhanced by reducing the interfacial tension between oil and water through the application of dispersants. However, despite the fact that dispersants have been in use for some 20 years, the question of how much natural dispersion can be increased by the use of dispersants remains a matter of debate. While the chemical dispersion of oil can be readily demonstrated in simple laboratory tests, a number of practical trials at sea and experiences gained at actual spills have indicated that the conditions required for optimal use of dispersants have still not been clearly defined.

This paper considers the role of laboratory and field experiments in gaining a clearer understanding of the factors influencing dispersant effectiveness and reviews the performance of dispersants at a number of spills. While the toxicological aspects of dispersant use are also important, they are beyond the scope of this paper.

Laboratory testing of dispersants

Laboratory testing serves two main purposes: first, to evaluate the relative effectiveness of different dispersants under standard test conditions and, second, to investigate how efficiency varies with such factors as the increase in oil viscosity brought about by weathering processes and the effects of dilution, sea temperature, and salinity. Some tests are based on visual observation of the amount of oil dispersed. Some tests also include an assessment of the stability of the dispersion with time or with progressive dilution.

During the past 20 years more than 20 different performance tests have been developed, which vary according to such factors as relative volumes of oil and seawater, method of applying dispersant, method of mixing, and method of assessing effectiveness.[18] Direct comparison of these tests is difficult since much of the published data does not identify the dispersants evaluated or provide information on their composition due to confidentiality. Although some tests attempt to simulate real sea conditions and practical application techniques, the results are rarely compared with field data. However, it is useful to consider briefly the differences in test conditions and how these may affect the results.

Relative volumes of oil and water. The volume of seawater in which oil and dispersant are mixed is a critical factor in determining dispersant effectiveness. For example, a dispersant formulation with strongly hydrophilic surfactants may appear to be highly effective in a laboratory test that uses small volumes of seawater. However, if the same dispersant is tested in a relatively large volume of water, the initial dispersion may prove to be unstable due to the dissolution of the surfactant. Although the capacity for dilution in the sea is high, this is not reflected in many laboratory tests.

Method of applying dispersant. Method of dispersant application is an important factor in the test procedure since a prerequisite for good dispersion is that the dispersant is distributed uniformly throughout the oil so that surfactants can migrate to the oil-water interface, thereby reducing the interfacial tension and promoting droplet formation. The best dispersions are achieved when the oil and dispersant are mixed together prior to being introduced into water. Although such premixing is sometimes adopted to achieve reproducible results, it cannot be considered realistic in relation to practical applications at sea. Tests that require the chemical to be applied dropwise to oil floating on water also indicate the ability of the material to penetrate the oil layer and migrate to the oil-water interface.

Method of mixing. Methods of introducing mixing energy into the oil-dispersant-water system fall into two main categories: bulk mixing of the three and mixing concentrated at the oil-water interface. Examples of the former usually involve shaking or rotating the test container or circulating the mixture through a pump; for the latter, simple wave-making devices are employed. The advantage of concentrating the mixing energy at the oil-water interface is that it simulates the natural mixing conditions in the sea more closely and ensures that dilution is gradual. Such methods may be particularly appropriate for the evaluation of dispersants for aerial application.

Highlights

- Authors summarized 54 *field tests* to establish operational norms
- Most hydrocarbon stay in upper <10m
- Oil concentrations quickly decline below 2m
- [TPH] averages 10mg/L in upper 10m in 1st hr
  - Measured range equals 1-150 mg/L
  - Typically dilutes to around 1mg/L within 5 hrs
- 3-5 ringed PAHs are more abundant in CEWAF than WAF
  - PAHs exist within any plume, but dispersants change their location (i.e. water column vs. surface)
- High viscosity fuels, like HFOs, disperse poorly
- Field tests range from 1:1 to 1:67, but show optimal DOR at 1:20
- Lab tests support 1:20 dispersant/oil ratios
- 90% of slick lies within 10% of slick area
  - Intra-slick thickness may vary by 5 orders of magnitude, so maintaining appropriate DOR can be challenging
- Aerial platforms can improve application accuracy

Oil Toxicity

SETAC PRESS

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TOXICITY OF DISPERSED WEATHERED CRUDE OIL TO EARLY LIFE STAGES OF ATLANTIC HERRING (*CLUPEA HARENGUS*)

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Abstract—Reports of the chronic toxicity of dispersed crude oil to early life stages of fish perpetuate uncertainty about dispersant use. However, realistic exposures to dispersed oil in the water column are thought to be much briefer than exposures associated with chronic toxicity testing. To address this issue, the toxicity of dispersed weathered oil to early life stages of Atlantic herring (*Clupea harengus*) was tested for short exposure durations, ranging from 1 to 144 h. Toxicity was a function of concentration and duration of exposure, as well as of the life stage exposed. Medium South American crude oil dispersed with Corexit 9500 caused blue sac disease in embryos, but not in free-swimming embryos. The age of embryos was negatively correlated with their sensitivity to oil; those freshly fertilized were most sensitive. Sensitivity increased after hatch, with free-swimming embryos showing signs of narcosis. Gametes were also tested; dispersed oil dramatically impaired fertilization success. For exposures of less than 24 h, gametes and free-swimming embryos were the most sensitive life stages. For those of more than 24 h, young embryos (<1 d old) were most sensitive. The results are presented as statistical models that could assist decisions about dispersant use in the vicinity of fish spawning habitats. Environ. Toxicol. Chem. 2010;29:1160–1167. © 2010 SETAC

Keywords—Fish embryos Dispersed oil toxicity Exposure time Predictive model

INTRODUCTION

To minimize the damage caused by oil spills, responders may chemically disperse spilled oil into the underlying water before it contacts shorelines and wildlife. Quantifying this strategy's net environmental impact requires analyses of its subsurface aquatic effects. Currently, spill responders lack much of the toxicological data upon which these analyses depend.

After a spill, waves and currents mechanically mix a small fraction of oil below the surface, introducing a water-accommodated fraction (WAF) of oil into the water column. Adding chemical dispersant to slicks enables a larger quantity of oil, the chemically enhanced water accommodated fraction (CEWAF), to mix with water. Toxic constituents of oil, such as three- to five-ringed polynuclear aromatic hydrocarbons (PAH) [1], are more abundant and bioavailable in CEWAF (i.e., dispersed oil) than in WAF (nondispersed oil). Accordingly, CEWAF can be 100- to 1,000-fold more toxic than WAF [2]. Early life stages of sensitivity of the early life stages is well documented (e.g., [6]), and experience with the *Valdez* spill corroborated lab-scale results on an ecological scale. The subsequent collapse of Prince William Sound's herring fishery underscored the interdependency of early life stages, adult populations, and fisheries.

Despite the number of publications on dispersed oil and early life stages of fish [7], most deal with chronic toxicity (i.e., 10–20-d exposures). However, dispersion efficacy tests suggest that appreciable concentrations of waterborne hydrocarbons persist only 1 to 48 h postdispersion, and almost certainly not several days [8]. Lessard and DeMarco [9] reported that in the first hour following a ''typical'' dispersion application, the waterborne hydrocarbon concentration ranges from 40 to 60 mg/L in the upper 10 m of water, but dilutes to 1 mg/L within 5 h. Traditional toxicity tests based on 10- to 20-d exposure regimes may therefore be unrealistic and overly

Representative Herring Data

- Gametes & free swimming larvae are most sensitive life stages
  - Gamete viability (EC50 for fertilization rate) dramatically reduced at 0.32% (v/v) for 1hr exposure
- Embryo sensitivity greatest during 1st 24hrs post-fertilization
  - Chorion hardening confers partial resistance after fertilization
- [Exposure] 4x more important to free swimming embryo mortality than exposure duration (through 10dpf) up to 3% (v/v)
- BSD couldn't be induced 11dpf at 3% (v/v)
- Dispersant exposure, alone, not different from control water (NAS Report, 2005)

Data Applicability

SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 33, No. 4, pp. 732–742, 2014

Critical Review

ISSUES AND CHALLENGES WITH OIL TOXICITY DATA AND IMPLICATIONS FOR THEIR USE IN DECISION MAKING: A QUANTITATIVE REVIEW

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(*Submitted 14 October 2013; Accepted 12 December 2013*)

Abstract: Aquatic toxicity considerations are part of the net environmental benefit analysis and approval decision process on the use of dispersants in the event of an offshore oil spill. Substantial information is available on the acute toxicity of physically and chemically dispersed oil to a diverse subset of aquatic species generated under controlled laboratory conditions. However, most information has been generated following standard laboratory practices, which do not realistically represent oil spill conditions in the field. The goal of the present quantitative review is to evaluate the use of standard toxicity testing data to help inform decisions regarding dispersant use, recognizing some key issues with current practices, specifically, reporting toxicity metrics (nominal vs measured), exposure duration (standard durations vs short-term exposures), and exposure concentrations (constant vs spiked). Analytical chemistry data also were used to demonstrate the role of oil loading on acute toxicity and the influence of dispersants on chemical partitioning. The analyses presented here strongly suggest that decisions should be made, at a minimum, based on measured aqueous exposure concentrations and, ideally, using data from short-term exposure durations under spiked exposure concentrations. Available data sets are used to demonstrate how species sensitivity distribution curves can provide useful insights to the decision-making process on dispersant use. Finally, recommendations are provided, including the adoption of oil spill–appropriate toxicity testing practices. *Environ Toxicol Chem* 2014;33:732–742. © 2014 SETAC

Keywords: Chemical dispersants   Oil spill   Species sensitivity distribution curves   Aquatic toxicity

INTRODUCTION

The debate on the use of dispersants in oil spill response, revived after the Deepwater Horizon oil spill in the Gulf of Mexico in 2010, has been a recurring issue since at least 1970. Dispersants are considered in spill response because their application may mitigate the environmental impacts of oil by moving it from the water surface to the top few meters of the water column, promoting dilution and enhancing oil biodegradation. This not only reduces the likelihood of oil exposures to marine wildlife with long life spans (seabirds, marine mammals, and turtles) but also reduces the amount of oil that might reach shoreline habitats, which would recover relatively slowly, compared with the water column community, from oil impacts and cleanup activities [1,2].

As with all response techniques, the decision to use dispersants should be carefully considered, while taking into

toxicity considerations are an integral part of net environmental benefit analysis (NEBA) and the dispersant approval decision process. The outcome of the NEBA process shows that, under most circumstances, the rates of mixing and dilution in open waters that are ≥3 nm offshore or ≥10 m in depth are sufficient to minimize the potential toxic effects of dispersed oil on marine communities [1,2]. At these depths and distances from shore, the short-term and decreasing risks to aquatic organisms (particularly entrained fauna and flora) from chemically dispersed oil are usually much less than the risks to wildlife, shallow water marine life, and shoreline communities if oil slicks persist on the water surface. These analyses have been used to support the establishment of preapproved areas for dispersant use for offshore oil spills in a number of countries, including the United States, United Kingdom, France, and Australia (e.g., Addassi et al. [3]).

However, data on the toxicity of chemically dispersed oil are

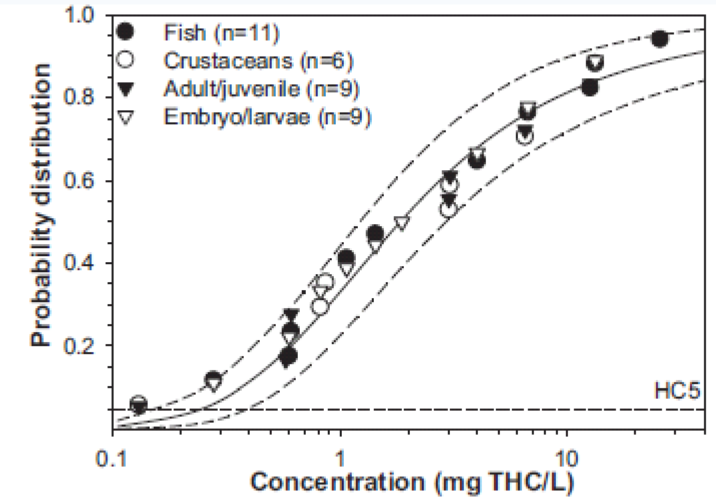

Figure 7. Species sensitivity distributions (SSD) of chemically enhanced water accommodated fraction (CEWAF) and water accommodated fraction (WAF) toxicity data (96 h median lethal concentration [LC50] and median effective concentration [EC50] data; measured total hydrocarbon content [THC] concentrations) from constant exposures comparing taxonomic groups (circles) and life stages (triangles). The curved lines represent the mean estimated SSD (solid) and its 95% confidence interval (dashed), and the horizontal line represents the 5th percentile of the probability curve (HC5; dashed).

Findings

- Toxicity begins with exposure, which isn't automatic
- Constant exposure lethality much greater than spiked / attenuated treatments (WAF LC50=7x lower; CEWAF=5-27x lower)
  - Decisions from spiked/attenuated treatments are more more ecologically relevant
- Species Sensitivity Distributions (SSDs) reveal inter-species variation

Generalizations

- The Dose Makes the Poison
- Life stage at exposure often more important than exposure concentration when predicting effects
- Exposure Duration is Much Less Important Than Concentration or Life Stage when Exposed
- SIMAP Model Predicts Weathered Crude (for 10h) is 4x Less Toxic

Note:

- Maximum [TPH] during DWH reached 2 mg/L at 1m depth approx 30 minutes after surface dispersion
- Subsea concentrations ranged from 0.03-0.07mg TPH/L near source

Persistence Depends on:
Dispersability Depends on:

- Mixing energy (wave action/sea state)
- Temperature
- Chemical composition
- Weathering state
- Water flow rate
- Wind Speed
- Adsorption/Sequestration in soil/water/sediment/vegetation/biota
- Salinity
- Emulsification state
- Application rate (dosage)
- Means of application
- Maintaining appropriate dispersant : oil ratios

Wise Policy Utilizes Scientific Knowledge to Reduce Risks

Science:

- Dispersed oil typically sinks ≤30’
- Gametes, embryos, & newly hatched fish are most vulnerable
- Critical habitat has disproportional importance
- Crude oil is highly toxic to many species
- Weathering and environmental variables affect dispersability. Oil changes constantly
- Effectiveness reduced with time
- Precise application becomes challenging in high winds
- Refined product dissipates rapidly, complicating dispersant efficacy

Policy:

- Policy calls for use in waters ≥60’ deep
- Policy avoids freshwater and nearshore application to protect many species. Diffusion, depth, and seasonality protect others
- Preauthorization area begins 24nm offshore. Avoidance areas identified
- Spotter planes locate bait balls, rafting birds, marine mammals, haul-outs. Daylight application only
- Pilot tests precede full scale use every operational period, and SMART Tier III monitoring characterizes success
- Preauthorization only valid prior to 96hrs post-spill
- High winds favor natural dispersion. Dispersants discouraged in winds >27mph
- Preauthorization only applies toward crude oil spills

References and Questions

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