

Monitoring Effects of Aerial Dispersant Application during the MC252 Deepwater Horizon Incident

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ABSTRACT

The MC252 Deepwater Horizon (DWH) incident released large volumes of oil which threatened marine wildlife and sensitive coastal habitats. Response strategies to reduce the impact of the oil included mechanical removal, controlled burning, and use of dispersants. Dispersants were applied by aerial spray from low-flying aircraft, by boat spray on the water surface for volatile organic compound (VOC) control and for effectiveness testing, and by subsurface injection into oil released at the wellhead. Monitoring of dispersant effectiveness and potential environmental impact following aerial and vessel application was conducted by the *M/V International Peace*. Visual observations, fluorometry tows and water quality measurements were made before and after surface dispersant application.

Water samples were collected for analytical characterization and toxicity testing at 1 and 10 meter depths below the slick prior to and following dispersant application to evaluate the distribution of the dispersed oil through the water column, and at reference and background locations. Fluorometry measurements provided a field measurement of total aromatic hydrocarbon fluorescence as the vessel traversed the slick during the effectiveness monitoring and sampling program. Chemical analyses and toxicity testing of the water samples with fish, invertebrates, and algae were performed to determine the concentration of oil components and dispersant in the water column and their potential environmental impact. Results of chemical analyses during the DWH response indicate that total polycyclic aromatic hydrocarbons (tPAH) and total petroleum hydrocarbon (TPH) measurements were greater below the slick after dispersant application. Hydrocarbon concentrations at 10 meter depths were consistently lower than those measured at 1 meter in both pre- and post-dispersant application samples. The dispersant indicator dipropylene glycol n-butyl ether (DPnB) concentrations in the samples showed a general trend that the more dispersant indicator was present, the more oil was measured in the same sample. No significant toxicity to fish or shrimp were observed in the

field-collected samples, while algae test results were inconsistent, but did not show a correlation between toxicity and dispersant application.

BACKGROUND

During the MC252 Deepwater Horizon Spill of National Significance, a combination of skimming, booming, controlled burning, dispersant use, and shoreline cleanup techniques were used to reduce the overall impact of released oil on the environment. Corexit dispersant was applied by aerial dispersant spraying by low-flying aircraft, water surface spraying from vessels, and subsea injection at the wellhead. Dispersants were used on oil slicks at the water surface to chemically enhance oil dissolution through formation of small droplets that spread laterally and to depth in the water column. Extensive field monitoring was conducted during and after dispersant use in May to July 2010 to monitor its operational effectiveness and environmental impact.

Analyses of dispersant effectiveness at the water surface from aerial and vessel spraying activities were conducted using the *Special Monitoring of Applied Response Technologies* (SMART) protocols developed by the U.S. Coast Guard (USCG), National Oceanic and Atmospheric Administration (NOAA), US Environmental Protection Agency (EPA), Centers for Disease Control and Prevention (CDC), and the Minerals Management Service (MMS) (2006). The SMART protocols provide guidance for rapidly collecting real-time data and providing operational feedback for decision-making by the Unified Command. The monitoring procedures range from Tier I which involves visual observations by trained observers to Tier III, which includes on-water collection of field data on the transport and behavior of dispersed oil in the water column.

DATA COLLECTION ACTIVITIES

Fluorometry measurements, field water quality data, and water samples for chemical analysis and toxicity testing were collected before and after dispersant application around and underneath oil slicks to evaluate dispersant efficacy and measure the distribution and characterize the behavior of untreated and chemically dispersed oil in the water column following treatment of the slick. Background and reference samples were also collected outside of the slick's influence at locations proximate to the slick (background) and remote from oil spill influence (reference). Fluorometry measurements were used as an operational field tool to evaluate dispersant effectiveness by measuring polycyclic aromatic hydrocarbon (PAH) fluorescence as the sampling vessel traversed the slick. Geo-referenced data on vessel path and sample locations were collected, along with conductivity, temperature, pH, and dissolved oxygen measurements.

Water samples for chemical analysis and toxicity testing were collected at depths of 1 meter (3.3 ft) and 10 meters (32.8 ft) below the water surface both before and after dispersant application. Following collection, the water samples were analyzed for benzene, toluene, ethylbenzene, and xylenes (BTEX); saturated hydrocarbons; polycyclic aromatic hydrocarbons (PAHs); petroleum biomarkers (steranes, triterpanes), and the dispersant indicator dipropylene glycol n-butyl ether (DPnB). Toxicity studies were conducted on undiluted samples using the estuarine inland silversides fish (*Menidia beryllina*), planktonic mysid shrimp (*Mysidopsis bahia*,

also scientifically known as *Neomysis americana*), and marine diatom (*Skeletonema costatum*) following standard test procedures (Fucik et al. 1994; USEPA 2002, 2007).

RESULTS

Based on chemical analysis of the field samples collected during the DWH response, the Macondo MC252 oil collected from the sea surface was depleted in the more soluble and readily biodegraded components as a result of dissolution and weathering (Brown et al. 2010, Gong et al. 2010). Field observations and fluorometry measurements correlated well with the chemical analyses, and provided an early indication of oil dispersion. BTEX levels were below method detection limits in all samples collected from the surface oil slicks. Total polycyclic aromatic hydrocarbons (tPAH) and TPH measurements followed similar trends in both pre- and post-dispersant application samples. As illustrated in Figure 1 using results from evaluation of a single slick on June 17, 2010 following vessel spraying, the dispersant was effective at increasing oil dispersion in the water column, with the highest concentrations seen at 1 meter depths, and significantly lower concentrations measured at 10 meters. Two sets of post-dispersant application samples at each depth were taken on this day to evaluate changes in below slick concentrations with time.

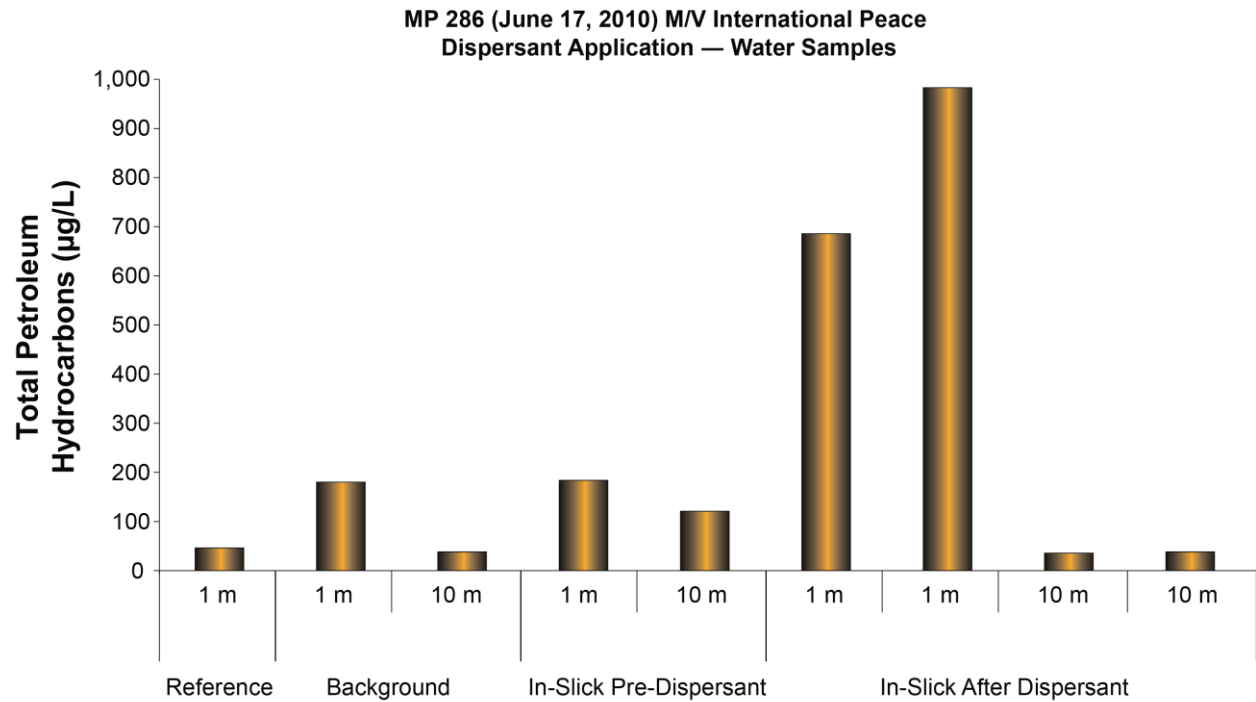


Figure 1. Total Petroleum Hydrocarbon (TPH) Analysis for Samples Collected on June 17, 2010 during the Deepwater Horizon Response

The results for the samples collected on June 17th are consistent with those determined throughout the response (Figure 2). Pre-dispersant application water samples showed consistent or slightly higher tPAH and TPH concentrations than background samples, demonstrating that natural dispersion of the surface oil was occurring. Hydrocarbon concentrations were highest around and below the slick after dispersant addition, illustrating the enhanced dispersion of the oil in the upper 1 meter of the water column. Concentrations at 10 meter depths were significantly lower in all samples compared to results seen at 1 meter, and were consistent with background levels.

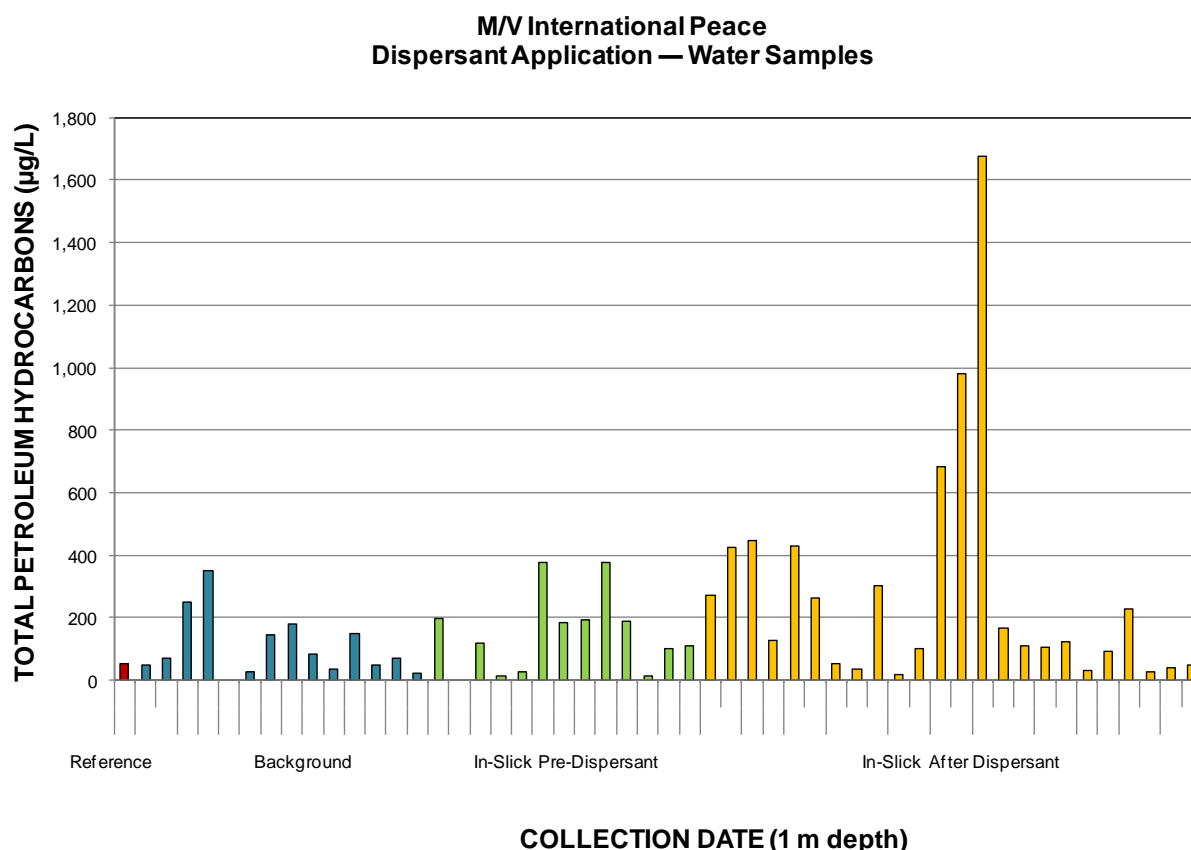


Figure 2. Total Petroleum Hydrocarbon (TPH) Results for Samples Collected at 1 Meter Depth during the Deepwater Horizon Response

One of the constituents of the Corexit dispersant, dipropylene glycol n-butyl ether (DPnB), can be readily detected using the same gas chromatography/mass spectrometry (GC/MS) procedure (EPA Method 8270M) conducted to determine PAH content of the samples. Analytical data for the dispersant indicator in the surface water samples collected prior to and following dispersant application showed a correlation between the concentration of DPnB in the water sample and measured tPAH and TPH levels (Mudge et al. 2011).

Toxicity testing with the estuarine silversides fish and mysid shrimp showed no significant effects in any sample collected prior to or following dispersant application (Table 1). Chronic test results with the marine diatom were less conclusive, with scattered effects on mean cell growth seen in a number of samples including those collected from reference and background locations. No correlation between toxicity and dispersant application was seen in the marine diatom studies, or with the other test species, demonstrating that the dispersed oil was not toxic to these representative marine organisms. These field results are consistent with the predicted toxicity of oil and Corexit dispersant (George-Ares and Clark 2000; Fuller and Bonner 2001; Wetzel and vanFleet 2001; Couillard et al. 2005).

Species	Study Endpoint ^a	# of Studies Conducted with Each Sample Type				Total # of Studies Conducted	# with Statistically Significant Effect ^b
		Reference	Background	Pre-Dispersant	Post-Dispersant		
Inland silversides fish (<i>Menidia beryllina</i>)	Survival (A, W)	16	35	31	40	122	0
Mysid shrimp (<i>Mysidopsis bahia</i>)	Survival (A, W)	4	5	7	6	22	0
	Survival, Growth (C, W)	8	23 ⁺	20	26 ⁺	77	3
Pink Shrimp (<i>Farfantepenaeus duorarum</i>)	Survival (C, W)	2	5	2	8	17	0
Marine diatom (<i>Skeletonema costatum</i>)	Cell Growth (C, W)	12 ⁺	28 ⁺	27 ⁺	30 ⁺	97	41

Notes:

^a Endpoint: A – Acute, C- Chronic, W- Water, LC/EC – lethal/effect concentration, NOEC – No observed effect concentration (chronic study endpoint)

^b Effect: LC/EC50 <100% sample, NOEC of 100% sample significantly different than control

+ Studies with statistically significant effects

Table 1. Results of Toxicity Tests for Samples Collected During Aerial Dispersant Monitoring during the Deepwater Horizon Response

CONCLUSIONS

The chemical and toxicity data collected as part of the SMART monitoring program to evaluate aerial and boat spray effectiveness of Corexit dispersant during the DWH Spill of National Significance demonstrated that dispersion of the surface oil was occurring naturally, and that dispersion was enhanced following Corexit application. The data demonstrate that oil dispersion is observable at 1 meter below and around the slick, and that concentrations drop below detectable levels by 10 meters below the surface. Toxicity testing results for representative aquatic organisms showed no observable effect related to dispersed oil exposure.

REFERENCES

Brown, J.S., D. Beckmann, L. Bruce and S. Mudge. 2010. PAH depletion ratios document the rapid weathering and attenuation of PAHs in oil samples collected after the Deepwater Horizon incident. Presented at SETAC North America 31st Annual Meeting, Portland, OR.

Couillard, C.M., K. Lee, B. Legare, and T. King. 2005. Effect of dispersant on the composition of the water-accommodated fraction of crude oil and its toxicity to larval marine fish. *Environm. Toxicol. Chem.* 24(6): 1496-1504.

Fucik, Kenneth W., Kelly A. Carr, and Brian J. Balcom. 1994. Dispersed oil toxicity tests with biological species indigenous to the Gulf of Mexico. Jupiter (FL): United States Department of the Interior Minerals Management Service, Gulf of Mexico Outer Continental Shelf (OCS) Region. OCS Study No. 94-0021.

Fuller, C. and J.S. Bonner. 2001. Comparative toxicity of oil, dispersant, and dispersed oil to Texas marine species. *Proceedings International Oil Spill Conference*, Tampa, FL. pp. 1243-1248.

George-Ares, A. and J.R. Clark. 2000. Aquatic toxicity of two Corexit dispersants. *Chemosphere.* 40: 897-906.

Gong, C., A.V. Milkov, D. Grass, M. Sullivan, T. Searcy, L. Dzou, and P. Depret. 2010. The significant impact of weathering on MC252 oil chemistry and its fingerprinting of samples collected from May to September 2010. Presented at SETAC North America 31st Annual Meeting, Portland, OR.

Mudge, S.M., M.T. BenKinney, J.S. Brown, and D. Beckmann. 2011. Tracking the dispersant applied during the MC252 Deepwater Horizon Incident. To be presented at IOSC Meeting, Portland, OR.

United States Coast Guard, National Oceanic and Atmospheric Administration, United States Environmental Protection Agency, Centers for Disease Control and Prevention, and United States Department of the Interior Minerals Management Service. 2006. Special Monitoring of Applied Response Technologies. Version 8/2006. 43 pp.
http://response.restoration.noaa.gov/book_shelf/648_SMART.pdf.

United States Environmental Protection Agency (USEPA). 2002. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms, Fifth Edition. Washington (DC): EPA-821-R-02-012.

United States Environmental Protection Agency (USEPA). 2007. Final NPDES General Permit for new and existing sources and new discharges in the offshore subcategory of the oil and gas extraction category for the western portion of the outer continental shelf of the Gulf of Mexico. GMG290000.

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Wetzel, D.L. and E.S. vanFleet. 2001. Cooperative studies on the toxicity of dispersants and dispersed oil to marine organisms: A 3-year Florida study. International Oil Spill Conference, Tampa, FL. pp. 1237-1241.