Comparison of the Acute Toxicity of Corexit 9500 and Household Cleaning Products

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ABSTRACT

Surfactant formulations used in chemical dispersing agents are derived from the same functional components used in numerous household products such as dishwashing soaps and laundry detergents. During the *Deep Water Horizon* (DWH) oil spill response, a significant volume of chemical dispersant was deployed, causing members of the public and the media to question the role of chemical dispersant (Corexit 9500) usage in mitigating oil spill effects. Consequently, laboratory tests were conducted by regulatory agencies to further evaluate and substantiate the existing aquatic toxicity of Corexit dispersants. To help put dispersant toxicity in context, two independent accredited labs were commissioned to conduct parallel studies that compared the acute toxicity of Corexit 9500 to common household cleaning agents. The results indicate that the acute toxicity of Corexit 9500 to marine aquatic organism is either within the median range or less toxic than the household cleaning agents tested. The median LC50 value for Corexit 9500 exposures to *Americamysis bahia* was 42.5 mg/L (four products were less toxic and four products were more toxic); whereas, the median LC50 value for Corexit 9500 exposures to *Menidia beryllina* was 73.1 mg/L (one product was less toxic and seven products were more toxic).

Key Words: aquatic toxicity, Corexit 9500, household surfactant cleaners, relative acute toxicity.

INTRODUCTION

Although modifications to the chemical formulation of dispersant products have reduced toxicity to environmental resources as a result of more than 30 years of research, concerned citizens and organizations have been reluctant to accept use of dispersants as a countermeasure during large-scale response efforts to major oil spills such as the *Sea Empress* off the coast of Wales, and more recently, the *Deep Water Horizon* (DWH) spill in the Gulf of Mexico. Corexit 9500 was the primary dispersant used during the latter spill response effort, since it meets the rigid U.S. Environmental Protection Agency (USEPA) criteria established for the U>S> National Oil and Hazardous Substances Pollution Contingency Plan (NCP) listing, as well as subsequent testing conducted by USEPA laboratories to validate test results obtained during the listing process (USEPA NCP a,b). Since Corexit 9500 dispersants are composed of surfactant components similar to those used in common household products, the direct comparison of the aquatic toxicity of household cleaners and an oil-spill dispersant reported herein should be of interest to an informed public. Acute toxicity data are generally not published for household cleaning formulations as a whole, and in most cases the toxicity of a cleaning formulation is based on assessments of the known chemical ingredients and their individual toxicity characteristics as a percent of total composition and recommended dilutions for consumer use. These estimations are then compared to aquatic toxicity criteria to ensure relatively low toxicity thresholds are maintained (Swanson *et al*. 1995).

The acute toxicity of Corexit 9500 dispersant compared to commonly used household cleaner formulations has received little attention in the scientific literature. While dispersants are formulated for oil spill response applications, household cleaners contain many of the same chemical constituents designed for similar effects when applied to oily household materials in water. Each type of surfactant product (oil spill dispersant or household cleaner) is a mixture of chemicals comprising two principal components that act to disperse oil and grease: surfactants and solvents. A list of the principal ingredients of the nine products tested here is presented in Table 1. As noted in Table 1, the cleaning formulations and dispersant tested are composed of anionic, non-ionic, and/or amphoteric surfactants. Anionic surfactants (*e.g.*, sulfonic acid salts, alcohol sulfates, alkylbenzene sulfonates, phosphoric acid esters, and carboxylic acid salts) are good solubilizers and are slightly to moderately toxic. Nonionic surfactants (*e.g.*, polyoxyethylenated alkylphenols, alcohol ethoxylates, alkylphenol ethoxylates, and alkanolamides) tend to also be good solubilizers and relatively non-toxic; these compounds blend well with other surfactants, and are commonly used as co-surfactants in petroleum and environmental applications.

Surfactants have both hydrophilic (water miscible) and lipophilic (oil miscible) properties, which act to reduce surface tension at the oil-water interface allowing the oil to disperse into the water as tiny droplets (< 100 µm) and micelles with minimal mixing energy. A hydrophilic/lipophilic scale (HLB) numerically represents the balance of hydrophilic and hydrophobic properties and is used to represent basic functional categories (*e.g.*, antifoaming agents <5; water-in-oil emulsifiers < 10; oil-in-water emulsifiers < 15; high solubility in water >18) [Varadaraj *et al*. 2009; Hargreaves 2003]. The relative balance of these properties is similar for Corexit 9500 and the cleaning products tested (HLB ranges from10–16). Solvents are used to dissolve solid surfactants and reduce viscosity of the product, and are represented by three main groups of compounds (water, water miscible hydroxy compounds, and hydrocarbons)

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(Hargreaves 2003). Solvents and other additives augment the action of the surfactants in dispersants and household cleaning agents to break down oil, thus releasing the oil via smaller oil droplets into the receiving waters. For example, application of 1 part dispersant to 20–100 parts of oil transforms an oil slick into small droplets that become suspended in the water column enabling more rapid dilution and dispersion of the oil facilitated by the energetics of wind, wave, and current action (IMO/UNEP 2011). The smaller droplets of oil/dispersant mixtures also increase the relative surface area of the mixture exposed to natural microbial degradation. Household cleaners use a similar process, enhanced by agitation supplied by hand scrubbing, or with laundry machines and dishwashers. Once introduced into the waste stream, microbial action and/or municipal wastewater treatment systems foster biodegradation of the chemical components with subsequent mineralization to CO_2 and/or other basic chemicals.

This paper describes the comparative acute toxicity of eight household cleaners and Corexit 9500 dispersant based on results from aquatic toxicity tests conducted in parallel by two independent, accredited laboratories. Each laboratory was accredited through national programs, either the National Environmental Laboratory Accreditation Program (NELAP) and/or good laboratory practice (GLP) accreditation (USEPA a). Both accreditation programs ensure that rigorous test protocols are implemented with the highest degree of quality assurance and control measures as required by the USEPA National Contingency Plan. The consumer products and household cleaners (dish washing soaps, baby shampoo, laundry detergent, all-purpose cleaners), and Corexit 9500 were tested using the same test protocols and the same two representative species of standard bioassay test organisms. The results from acute toxicity tests of dispersants are conservative estimations of toxicity potential when released in the environment. These 48-h and 96-h static, relatively constant exposures underestimate the natural processes of dilution and biodegradation occurring under normal conditions. These dilutions and biodegradation processes rapidly reduce the exposure concentrations of dispersant and cleaning formulations that have been released into the environment to much lower concentrations within hours (Clark *et al*. 2001; George-Ares and Clark 1997; Lee *et al*. 2013). A hierarchical scale representing relative degrees of aquatic toxicity developed by the USEPA (USEPA b) is used for comparative purposes [‘practically non-toxic’ (PNT) = > 100 ppm; ‘slightly toxic’ (ST) = >10–100 ppm); ‘moderately toxic’ (MT) = >1–10 ppm; ‘highly toxic’ (HT) = < 1 ppm].

TEST METHODS

Experimental Design

The two laboratories, Environmental Enterprises USA (EE; Slidell, LA) and Stillmeadow Inc. Environmental Toxicology Laboratory (SM; Sugarland, TX), conducted the identical rounds of static bioassay tests following methods specified in U>S> federal guidelines of the NCP (revised Standard Dispersant Toxicity Test; FR/Vol.59, No. 178/47461-47464) and the USEPA [12]. Eight household products and two batches of Corexit 9500A were used in separate, parallel acute toxicity tests performed by each laboratory. An aquatic invertebrate species and a small estuarine fish were used as representative test organisms; percent survival was the biological endpoint for all tests. The standard USEPA toxicity testing for dispersants includes testing of dispersants alone, dispersants with a No. 2 fuel oil, and a No. 2 fuel oil by itself. For this study, only Corexit 9500 was tested.

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Test Organisms

The shrimp, *Americamysis (=Mysidopsis) bahia*, and the fish, *Menidia beryllina*, are standard test organisms and were used by both laboratories for conducting acute, static 48-h and 96-h tests, respectively. *M. beryllina* were 7-d old while *A. bahia* were 5-d old at test initiation. SM obtained *M. beryllina* from Aquatic BioSystems, Inc., whereas *A. bahia* were cultured at their laboratory. EE maintained cultured stocks of *M. beryllina and A. bahia,* and drew from pooled embryos to generate each lot of test organisms. The test organisms were acclimatized to test conditions prior to test initiation. *A. bahia* and *M. beryllina* were fed <24-h old Artemia nauplii once daily prior to and during testing. Sensitivity of test organisms to a known toxicant was determined by performing standard reference toxicant tests (USEPA 2002); potassium chloride was used by EE as the reference toxicant for *M. beryllina* and *A. bahia* tests, whereas sodium dodecyl sulfate (SDS) was used as the reference toxicant by SM.

Test Media

Product A is Dawn Ultra Concentrated Dishwashing Liquid™, Original Scent (www.pg.com/productsafety/ingredients);

Product B is Restore the Earth Dish Soap™;

Product C is Palmolive Ultra Concentrated Dish Liquid™, Original (http://www.colgate.com/app/Palmolive/US/EN/Product-Ingredients.cwsp);

Product D is Green Works Natural Dishwashing Liquid™, Original (http://www.greenworkscleaners.com/products/dishwashing-liquid/);

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Product E is Cascade Liquid Dishwashing Detergent™, Lemon (http://www.pg.com/productsafety/ingredients/household_care/dish_washing/cascade/Cascade_Dishwasher_Detergent_Ingredient_Disclosure.pdf);

Product F is Johnson's Baby Shampoo™ (http://www.johnsonsbaby.com/product/414);

Product G is Tide 2X Laundry Detergent, Original Scent™ (http://www.pgproductsafety.com/productsafety/);

Product H is Green Works All-Purpose Cleaner™, Original Scent (http://www.greenworkscleaners.com/products/all-purpose-cleaner/ingredients/). Corexit 9500® is manufactured by Nalco (http://www.nalcoesllc.com/nes/1602.htm).

Preparation of Stock Solutions

Ten separate tests series were prepared by each laboratory for the static acute tests with *M. beryllina* and *A. bahia*. EE conducted a series of range-finding experiments and then conducted definitive tests, while SM conducted only definitive tests with a broader range of test concentrations than the EE definitive tests. Each laboratory followed the same mixing protocol to prepare stock solutions for each of the surfactant products. For *M. beryllina* testing, each preparation was mixed for 5 minutes using a reciprocal shaker table with slight variation in stroke and frequency per minute (the EE shaker had longer strokes at less frequent intervals per minute than the SM table (3.8-cm horizontal stroke and 280 osc/min versus 2-cm and 315–333 osc/min). For *A. bahia* testing, each preparation was mixed for 5 seconds using a blender at speeds of 7300 to 8300 rpm (EE) or <10,000 rpm (SM; the precise rpm was not reported). Synthetic seawater prepared from MARINEMIX + Bio-Elements and Crystal Sea Marinemix

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Bioassay Laboratory Formula sea salts was used as the laboratory performance control solution and diluent. For each definitive test, three replicates of a laboratory performance control solution and a five-step series of product dilutions were prepared using appropriate aliquots of stock solution added to synthetic seawater. Observations of incomplete mixing were not noted. One liter of each test media was transferred to respective replicate test chambers (rectangular Pyrex dishes or glass jars).

Test Design

For the 96-h definitive acute static tests with *M. beryllina*, three replicates of five test concentrations and a laboratory control were prepared by SM and EE laboratories for each product (Table 2). Because of the viscous nature of product E, it was dispensed by weight. For the 48-h definitive acute static tests with *A. bahia,* three replicates of five test concentrations and a laboratory control treatment were prepared by each laboratory for each product (Table 2). Thirty 7-d old *M. beryllina larvae* or 5-d old *A. bahia* were exposed to respective test solution (10 organisms in each of three replicates containing 1 liter of test media).

Test Conditions

Water quality parameters were within ranges specified in the protocol for all treatments. Experimental conditions during definitive static 96-h tests for *M. beryllina* larvae were: 25±1°C temperature, 20 ppt salinity, pH 8.0, and a 16-h light and 8-h dark photoperiod in 1000-mL test solution. Experimental conditions for the static 48-h tests with *A. bahia* were: 25±1°C temperature, 20 ppt salinity, and a 16-h light and 8-h dark photoperiod in 1000-mL test solution with one replicate treatment. *Exception:* EE reported that temperature exceeded the required range by 0.2°C in the 48-h and 96-h tests with products F and H; however, these excursions were considered minor and deemed not to invalidate the test results.

Test Acceptability Criteria

The reproducibility of static acute tests between two laboratories using the same species/toxicant combination has been reported to generally fall within a narrow range. A 3.5-fold variation in results has been observed among laboratories using nominal concentrations (not chemically measured) and dilutions of nominal stock solutions for both different batches of freshwater and marine species (USEPA 1981). Because whole organisms were used in these tests, some variation in response is attributable to differences in parameters such as culture and acclimation conditions, stock populations, or minor water quality variations between the laboratories. However, control performance m*et* all criteria for an acceptable test in all laboratory experiments signifying that biological and water quality characteristics were not significantly different between the laboratories (≥ 90% survival and water quality control limits for each test). GLP requirements for acceptable and interpretable tests under USEPA guidelines were met (USEPA a). The reference acute toxicity test followed standard methods (USEPA 1997, 2002, 2010). Results from reference toxicant tests conducted by EE with potassium chloride indicated that fish and mysid test organisms were within control chart mean LC50 values (± 2 SD); results from tests conducted by SM with sodium dodecyl sulfate (SDS) were within acceptable limits.

Statistical Analyses

Mean lethal concentration (LC50) values were determined from the three replicate samples per treatment by statistical analysis of the survival data using ToxCalc software, version 5.0 (Tidepool Scientific). Definitive LC50 values were determined for tests representing a subset of household cleaners (Products A–H) and Corexit 9500 dispersant (batches A and B). A comparison of concentrations that produce lethality to 50 percent of the test population (LC50) was used to assess the relative magnitude of biological effects caused by various surfactant-containing products in marine receiving waters.

RESULTS

The LC50 results from the paired experiments conducted by the two laboratories with mysid shrimp and fish were within acceptable range of inter-laboratory variation (USEPA 1981). The results generated from both laboratories for acute exposures of the mysid, *A. bahia*, to Corexit 9500 were within a narrow range of toxicity (LC50 values that ranged from 40 to 45.3 mg/L; Table 3). The combined results from the laboratory experiments with the larval fish (*M. beryllina*) showed a broader range of toxicity indicating that the fish were generally equal to or less sensitive to Corexit 9500 than the mysid shrimp (LC50 concentrations ranged from 42.1 to 110 mg/L; Table 4). Laboratory-specific testing of each batch of Corexit 9500 did not produce statistically significant LC50 values. Data from two USEPA studies using the same test species are presented as additional reference data in Figure 1. USEPA data for Corexit 9500 exposures to mysids were within a narrow range (LC50 values ranged from 32.2 to 42.0 mg/L) while exposures to fish also exhibited a broader range (LC50 with values ranging from 25.2 to 130 mg/L) (Hemmer *et al*. 2010; USEPA NCP b). Nonetheless, the range of toxicity for Corexit 9500 exposures to mysid and fish by these and other laboratories would be characterized as ST to PNT as shown by all test results according to criteria for aquatic toxicity established by the USEPA (USEPA b on-line).

Results from experiments conducted with household cleansers and mysid shrimp, *A. bahia*, indicated that the laundry detergent had the greatest toxicity (Product G > Dish soap C > Dish soap A, B, D, E > Baby shampoo F > All-purpose cleaner H; Table 3). When the mysid test results from household product experiments were ranked by toxicity potential, all but two of the products would be classified into the ST category (LC50 values ranging from 10 to 100 mg/L); the exceptions, the baby shampoo and all-purpose cleaner, would be classified as PNT (LC50 > 100 mg/L). The same patterns were noted in results from the fish tests with *M. beryllina*, with the exception of increased toxicity potential for the laundry detergent (G), three of the dish soaps (A, B, and C), and baby shampoo (Table 4). The mysid test results from Lab A were consistently more sensitive, whereas the responses for fish tests were not consistently more or less sensitive between the two laboratories. Comparing the relative toxicity potential, the laundry detergent (G) and three of the dish soaps (A, B, and C) would be classified as MT to fish (LC50 concentrations ranging from 1 to 10 mg/L) whereas the remainder of the products would be classified as ST with the exception of the all-purpose cleaner, which would be classified as PNT (see Figure 1).

DISCUSSION

Surfactants are produced from a variety of raw materials including petrochemical (*e.g.*, crude oil and natural gas, including derivatives of ethylene, n-paraffins, and benzene) and/or oleochemical resources (derived from palm oil, tallow, and coconut oil), and in recent years there

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has been a trend to increase usage of oleochemically-derived surfactants considered to be a renewable resource (Knepper and Berna 2003). The relative proportions of the various chemical components in household cleaning formulations and environmental dispersants give each product its unique performance characteristics. In general, surfactant chemicals are the predominant ingredients in household cleaning products as well as dispersants, and are considered to be of relatively low acute toxicity (Swanson *et al*. 1995, Knepper and Berna 2003).

The range in toxicity of dispersant and detergent products stems from the relative balance of the solvent and surfactant chemicals as well as the proportion of non-ionic, anionic, and cationic chemicals used in the surfactant formulations. The ecotoxicity of surfactants to aquatic life has been summarized in other studies (Belanger *et al*. 2002, 2006; Kimerle 1989; Konnecker *et al*. 2011; Swisher 1987; Rosen *et al*. 2001; Staples *et al*. 1998). It is evident that the toxic mode of action of surfactant products results from the surface activity of the chemical components, which can cause disruptions of biological membranes (*e.g.*, skin or eye irritation) [Cserhati 1995; Knepper *et al*. 2003]. Hydrophobic moieties such as alkylated phenols may cause severe disturbances between apolar fatty acid chains, resulting in permeability and leakage (Cserhati 1995). Another typical reaction to surfactant exposure involves disruption of respiratory cells, often caused by electrolytic and/or osmotic imbalance (Singer *et al* 1996). A review of surfactant acute toxicity data reported in the literature indicated that LC50 values for anionic surfactant chemicals averaged 22.3 mg/L (ST) for invertebrate species (n=24) and 17.7 mg/L (ST) for fish species (n=18), whereas LC50 values for non-ionic surfactant chemicals averaged 146.5 mg/L (PNT) for invertebrate species (n=10) and 1054.8 mg/L (PNT) for fish species (n=16). The range of LC50 concentrations for amphoteric surfactants was 5.2 to 96.4

mg/L (ST). Although these data represent acute toxicity summaries from several resources (Swanson *et al*. 1995; European Chemicals Agency database, USEPA ECOTOX database, Pesticide Action Network database; Macek *et al*. 1977; Stache 1996; Steber *et al*. 1988; Steber and Wierich 1989), they should be interpreted with caution, as there is a wide distribution of compiled data points for each surfactant. A summary of LC50 values for solvents used in product formulations tested, excluding water, indicated that solvents are less toxic than the surfactants with an average LC50 value of 15503 mg/L (PNT) for fish (again, a large range in values was observed in the data reviewed).

The aquatic toxicity ranking system developed by the USEPA (USEPA b) provides a framework to evaluate the comparative toxicity of the products tested and is applied to test results as shown in Figure 1. As seen in Tables 2 and 3, results from the two laboratories are within a relatively narrow range for the household cleaners. Dawn, Palmolive, and Green Works dish soaps and Tide laundry detergent were more toxic to *M. beryllina* than to *A. bahia,* and would be classified as 'moderately toxic' to fish (MT) based on the LC50 concentrations reported and the USEPA ranking system). The remaining products fall into ST to PNT categories (Restore the Earth dish soap, Cascade dish detergent, Johnson's baby shampoo, and Green Works all-purpose cleaner). Based on the available information for the moderately toxic products, it appears that this group has a higher percent of anionic surfactants, which the literature suggests are more toxic than non-ionic surfactants.

The results of the laboratory tests reported herein indicate that the acute toxicity of Corexit 9500 would be classified as ST to *A. bahia* and ST to PNT to *M. beryllina*. Corexit exposure to *M. beryllina* showed the largest range of LC50 values between laboratory results;

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however, the most sensitive endpoints would be categorized as ST. Corexit 9500 was equal to or less toxic than most of the other commonly used household products tested. A review of published LC50 values for dispersant-only tests with Corexit 9500 is presented in Supporting Information (SI Table 1). For crustaceans exposed to Corexit 9500, LC50 concentrations ranged from 3.4 to 8103 mg/L with a mean value of 387.7 mg/L (PNT, N=35); for fish exposed to Corexit 9500, LC50 concentrations ranged from 2.61 to 1055 mg/L with a mean value of 181.3 mg/L (PNT), N=30). The mean LC50 concentrations for continuous exposures to crustaceans and fish were 338 and 111.1 mg/L (PNT), respectively; whereas the mean LC50 concentrations for spiked exposures to crustaceans and fish were 531.3 and 461.9 mg/L (PNT), respectively. Additionally, results from a similar side-by-side standard toxicity test conducted with several types of dispersants and household surfactant products conducted with rainbow trout, *Oncorhynchus mykiss*, support this trend (ExxonMobil 2008). For example, Palmolive dish soap was found to be 27 times more toxic than Corexit 9500 (the LC50 for the dispersant was 354 mg/L). In summary, the LC50 data from combined published sources indicates that Corexit 9500 toxicity ranges from ‘practically non-toxic’ (PNT) to ‘slightly toxic’ (ST) [Table S1-1 presents a summary of 67 toxicity test results from 23 studies].

Household cleaning products and Corexit 9500 dispersant are formulated to ensure safe use in home cleaning and environmental applications. Evaluation of environmental risk to marine resources due to the use of surfactant products must consider the volume entering marine receiving waters and ultimate fate of the chemical compounds. Surfactant chemicals are high production volume chemicals in the U>S>, Europe, and some countries in Asia, and have been an environmental concern since the early 1960s (Blasco *et al.* 2003). Of the total annual surfactant consumption in the U>S> (estimated to be 7.7 billion pounds), household detergents represent the largest fractional use category (~45%) [Zoller and Sosis 2009]. Surfactant chemicals discharged to waste streams and/or receiving waters are subjected to natural processes of microbial degradation. The more hydrophobic compounds, *i.e.*, with low water solubility's, from any formulation may be prone to bind with suspended particles or sediments (Knepper and Berna 2003). Bioaccumulation can also occur, but the constituent chemicals of Corexit 9500 have bioaccumulation factors in the range of 2.6 to 208, which are well below the regulatory bioconcentration factor threshold of 1000, or 500 per the Globally Harmonized System (United Nations 2013).

Aerobic biodegradation, as occurs in municipal wastewater treatment plants and receiving waters, results in alterations in the chemical structure of the molecules (leading to loss of surface-active properties and potentially reduced toxicity) [Knepper *et al*. 2003] and produces the ultimate breakdown products, CO_2 and H_2O. In-depth studies of the fate of high volume detergent ingredients have been conducted previously, particularly in Europe. One such study of five priority detergent ingredients (linear alkylbenzene sulfonates, alcohol ethoxylates, alcohol ethoxylated sulfate, alcohol sulfate, and soap) demonstrated a 99% removal by sewage treatment processes (Matthijs *et al*. 1999). Thus, most household cleaners are believed to be substantially degraded by microbial activity during aerobic wastewater treatment before being released to freshwater or marine receiving waters. However, some surfactant chemicals and biodegradation products entering coastal receiving waters as a result of household and industrial usage are not strictly regulated or routinely monitored in the U.S. at the present time and may retain recalcitrant properties. A recent study of a nearshore coastal environment of Alabama documented the presence of concentrations of surfactant chemicals derived from sources unrelated to oil dispersant usage (in this case, stormwater point and non-point discharges); authors indicated that although concentrations were below toxic thresholds, the presence of surfactant chemicals in nearshore waters reiterates the need for further study of the fate of surfactants in coastal marine environments (Hayworth and Clement 2012).

On the other hand, estimation of the ecotoxicity of Corexit 9500 deployment is accomplished by considering the known application rates, surfactant dispersive capabilities, ocean dilution processes, and biodegradation rates. Dispersants are deployed in order to alter the physical dynamics of petroleum hydrocarbons in water by increasing the rates at which oil constituents become both dissolved and dispersed in water, making the oil more available to petroleum-degrading microorganisms and natural dilution in the open ocean allows biodegradation to occur without oxygen or nutrient limits. The standard delivery rate for Corexit 9500 applied by air to surfaced oil is 5 gallon/acre [a nominal dispersant-to-oil ratio (DOR) of 1:20]; deployment from vessels typically occurs at a slightly higher dosage, a DOR of 1:15 to 1:20. After either deployment, there is an expected immediate dilution into the top 1 m of the water column, resulting in an initial environmental dispersant concentration of not more than 5 mg/L (Lewis and Aurand 1997). Further dilution into the top 10 m should occur within a few hours to days with wind, wave and current actions, thereby reducing dispersant concentrations to < 0.5 mg/L (Lee *et al*. 2013; Delvigne 1993; Prince and Butler 2013). Lateral and vertical dilution continues after the first few hours so that average concentrations should fall well below 0.5 mg/L over a 48-hr period after environmental deployment.

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Recently, researchers investigating the 2010 DWH oil spill in the Gulf of Mexico analyzed data collected on chemical constituents of Corexit dispersants. Dioctyl sulfosuccinate (DOSS; CAS# 577-11-7) and dipropylene glycol n-butyl ether (DPnB; CAS# 29911-28-2) concentrations were used as environmental tracers of dispersant fate in the marine waters (Hayworth and Clements 2013; Bejarano *et al*. 2013; Gray *et al*. 2014). Gray *et al*. (2014) analyzed water samples collected from the surface and subsurface waters near the well release site. Apart from a relatively high blank interference in the analytical method employed, an elevated concentration of DOSS (0.2 mg/L) was observed at only one location at the surface near the well site in samples collected contemporaneously with dispersant application, leading the authors to conclude that it was unlikely that DOSS concentrations exceeded the USEPA aquatic life benchmark during the period that dispersants were applied to the area (40 ppb; USEPA 2010). Kujawinski *et al*. (2010) determined that subsurface concentrations of DOSS at the well site during active dispersant deployment ranged from 7 to 12 ppb, similarly falling below the conservative USEPA benchmark which has a 1000-fold safety factor applied. Additionally, during another DWH investigation water samples were collected at depths of 1 and 10 m from background sites and under naturally and chemically dispersed oil slicks (collected generally 30 min after surface dispersant application and within 800 m). DPnB was used as a chemical marker for dispersant presence; no samples analyzed from these depths exceeded the USEPA chronic criterion (1000 ppb) for this constituent (Bejarano *et al*. 2013).

The biodegradation of Corexit 9500 in the presence and absence of oil was recently examined in laboratory microcosm studies that included testing conducted at the temperature regime relevant to the toxicity studies reported on herein (25°C) [Campo *et al*. 2013; McFarlin *et* *al*. 2014]. Results from these recent lab studies reported that 99% biodegradation of the most recalcitrant surfactant chemical in Corexit 9500-only exposures occurred within 8 d at 25°C using natural microbial cultures collected from the sea surface environment (dioctyl sodium sulfosuccinate was used as the most recalcitrant marker). Therefore, toxicity thresholds documented by the studies reported indicate that acute toxicity would not be expected to linger in surface marine waters after deployment of Corexit 9500 or discharge of household cleaning agents, although the fate of the latter class of chemicals warrants further study in coastal marine waters and sediments.

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Table 1. **Principal Surfactant & Solvent Chemicals in Dispersant and Household Cleanser Formulations.**

Product	Surfactant	CAS No.	Type	% Vol	Solvents &Other Cleaning Agents	CAS No.	% Vol
Product A Dawn Dish Soap	Sodium lauryl sulfate	151-21-3	An	10-30	Alcohol, Denatured	64-17-5	1-5
	Sodium laureth sulfate	9004-82-4	An	ND	2-Phenoxyethanol	122-99-6	ND
	Lauramine oxide	1643-20-5	Am	3-7	Water	7732-18-5	--
	Alkyl dimethyl amine oxide	70592-80-2	Am				
	Polypropylene glycol, PPG-26	31394-71-5	N	ND			
	PEG-8 Propylheptyl ether	166736-08-9	N	ND			
	PEI-14 PEG-10, PPG-7 copolymer	052501-07-2	N	ND			
Product B Restore the Earth Dish Soap	C9-11 Pareth-8 alcohol ethoxylate	68439-46-3	N	ND	Phenoxyethanol	122-99-6	ND
	Sodium laureth sulfate	9004-82-4	An	ND	Limonene	138-86-3	ND
	Sodium C14-16 olefin sulfonate	68439-57-6	An	ND	Water	7732-18-5	--
	Lauramine Oxide	1643-20-5	Am	ND			
Product C Palmolive Ultra Dish Soap	Ammonium alcohol ether sulfate	888888-04-2	An	10-30	Ethanol	64-17-5	5-10
	Lauramidopropylamine oxide	61792-31-2	Am	1-5	Water	7732-18-5	--
	Myristamidopropylamine	67806-	Am	1-5			

	oxide	10-4					
Product D Green Works Dish Soap	Sodium lauryl sulfate	151-21-3	An	7-15	Ethanol SDA-3C	64-17-5	0.5-1.5
	Alkyl polyglucoside	68515-73-1	N	3-7	Glycerin	56-81-5	1-5
	Lauramine oxide	1643-20-5	Am	1-5			
	Cocodimethylamine oxide	61788-90-7	Am				
Product E Cascade Liquid Dish Detergent	C13-15 Alkyl ethoxylate butoxylate	111905-53-4	N	ND	Hypochlorous acid, sodium salt	7681-52-9	1-5
	Trideceth-n	24938-91-8	N	ND	Glycerin	56-81-5	ND
	Dipropylene glycol	25265-71-8	N	ND	Sodium percarbonate	15630-89-4	15-40
					Sodium sulfate	156-89-4	10-70
					Water	7732-18-5	--
Product F Johnson's Baby Shampoo	Sodium lauryl sulfate	151-21-3	An	ND	Glycerin	56-81-5	ND
	Fatty alcohol sulfate, FAS	68955-19-1	An	ND	Water	7732-18-5	--
	Decyl glycoside	58846-77-8	N	ND			
	Cetyl hydroxyethylcellulose	80455-45-4	N	ND			
	PEG-80 sorbitan laurate	9005-64-5	N	ND			
Product G Tide 2X Laundry Detergent	Alcohols (C10-C16), ethoxylated, sulfated	68585-34-2; 68551-12-2	An	10-30	Ethanol	64-17-5	1-5
	Alcohols (C16-18),	68439-	N	1-5			

	ethoxylated	49-6					
	Alkyl (C10-C16) benzenesulfonic acid, sodium salt	68081-81-2	An	10-30			
	Benzene sulfonic acid, sodium salts with Ethanolamine	68910-32-7	An	10-30			
	Monoethanolamine	141-43-5	N	1-5			
	Sulfuric acid, mono-C10-16 alkyl esters, sodium salts	68585-47-7	An	10-30			
Product H Green Works All Purpose Cleaner	Alkyl polyglucoside	68515-73-1	N	1-5	Ethyl alcohol	64-17-5	1-5
					Water	7732-18-5	--
Corexit 9500	Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)*	577-11-7	An	10-30	1-(2-butoxy-1-methylethoxy)-2 propanol	29911-28-2	ND
	Sorbitan, mono-(9Z)-9 octadecenoate	1338-43-8	N		Petroleum distillates (C9-16)	64742-47-8	10-30
	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl derivs	9005-65-6	N		Water	7732-18-5	--
	Polyoxyethylene sorbitan trioleate	9005-70-3	N				

An = Anionic surfactant; Am = Amphoteric surfactant; N = Non-ionic surfactant; ND= no information

**Contains 2-Propanediol*

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Table 2. Nominal exposure concentration ranges (ppm) for each species and product tested by each laboratory.

Test Series	**Product A**	**Product B**	**Product C**	**Product D**	**Product E**	**Product F**	**Product G**	**Product H**	**Corexit Batch A**	**Corexit Batch B**
96-h *M. beryllina* (SM)	2-32	3-48	1-16	4.5-72	18.75-300	7.5-120	1-16	25-800	18.75-300	
96-h *M. beryllina* (EE)	1.3-20	2.5-40	0.6-10	4.5-72	10-160	2.5-40	0.6-10	138-2200	10-160	
48-h *A.bahia* (SM)	3-96	12.5-800	2.5-80	24.6-800	25-800	24.6-800	3.75-120	25-800	7.5-240	
48-h *A.bahia* EE	6-100	13-200	2-32	11-180	13-200	63-1000	3-48	90-2200	7-112	

Table 3. Mean LC50 results from Standard 48-h Testing Conducted with the Shrimp, *Americamysis bahia*, and Common Household Products**.**

Product ID	Product	Mean LC_{50} (95%CI) *(ppm)*	EPA Toxicity	Reference
A	Dawn Dish Soap	28.9 (25.8-32.3)	ST	Lab A (EE)
		35.1 (29.7-41.6)		Lab B (SM)
B	Restore the Earth Dish Soap	48.0 (43.1-55.4)	ST	Lab A (EE)
		91.2 (70.3-146.8)		Lab B (SM)
C	Palmolive Dish Soap	13.3 (11.9-14.8)	ST	Lab A (EE)
		20.7 (17.7-24.2)		Lab B (SM)
D	Green Works Dish Soap	32.9 (31.5-34.4)	ST	Lab A (EE)
		45.3 (39.6-52.0)		Lab B (SM)
E	Cascade Dish Detergent	35.4 (NC)	ST	Lab A (EE)
		67.7 (56.9-80.4)		Lab B (SM)
F	Johnson's Baby Shampoo	177 (NC)	PNT	Lab A (EE)
		413 (344.0-504.9)		Lab B (SM)
G	Tide Laundry Detergent	10.7 (9.5-12.1)	ST	Lab A (EE)
		12.4 (10.8-15.1)		Lab B (SM)
H	Green Works All Purpose Cleaner	328 (296-364)	PNT	Lab A (EE)
		387 (342.2-414.2)		Lab B (SM)
9500-A CRXV860132	Corexit Dispersant	40 (NC)	ST	Lab A (EE)
		44.8 (44.2-45.3)		Lab B (SM)
9500-B 20100619-CRXU087	Corexit Dispersant	40 (NC)	ST	Lab A (EE)
		45.3 (43.6-47.7)		Lab B (SM)

Notes: PNT = Practically Non Toxic; ST = Slightly Toxic; MT = Moderately Toxic; NC= Not Calculable

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Table 4. Mean LC50 Results from Standard 96-h Testing Conducted with the Fish, *Menidia beryllina*, and Common Household Products**.**

Product ID	Product	Mean LC_{50} (95%CI) *(ppm)*	EPA Toxicity	Reference
A	Dawn Dish Soap	8.9 (7.05-10.4)	MT	Lab A (EE)
		8.3 (0.0-13.4)		Lab B (SM)
B	Restore the Earth Dish Soap	26.9 (24.4-29.8)	ST	Lab A (EE)
		21.2 (19.9-22.5)		Lab B (SM)
C	Palmolive Dish Soap	7.1 (5.53-8.26)	MT	Lab A (EE)
		5.4 (2.5-6.5)		Lab B (SM)
D	Green Works Dish Soap	7.8 (6.8-9.0)	MT	Lab A (EE)
		9.9 (8.0-11.2)		Lab B (SM)
E	Cascade Dish Detergent	56.6 (42.7-65.7)	ST	Lab A (EE)
		55.6 (52.6-57.0)		Lab B (SM)
F	Johnson's Baby Shampoo	38.8 (28.2-53.3)	ST	Lab A (EE)
		42.0 (40.4-43.5)		Lab B (SM)
G	Tide Laundry Detergent	4.0 (3.15-4.58)	MT	Lab A (EE)
		11.8 (11.3-12.1)		Lab B (SM)
H	Green Works All Purpose Cleaner	386 (365-409)	PNT	Lab A (EE)
		591 (563.2-609.9)		Lab B (SM)
9500-A CRXV860132	Corexit Dispersant	42.1 (34.2-49.1)	ST	Lab A (EE)
		105 (87.0-112.0)		Lab B (SM)
9500-B 20100619-CRXU087	Corexit Dispersant	35.4 (12.6-40.6)	ST	Lab A (EE)
		110 (106.7-112.7)		Lab B (SM)

Notes: MT = Moderately Toxic; ST = Slightly Toxic; PNT = Practically Non Toxic

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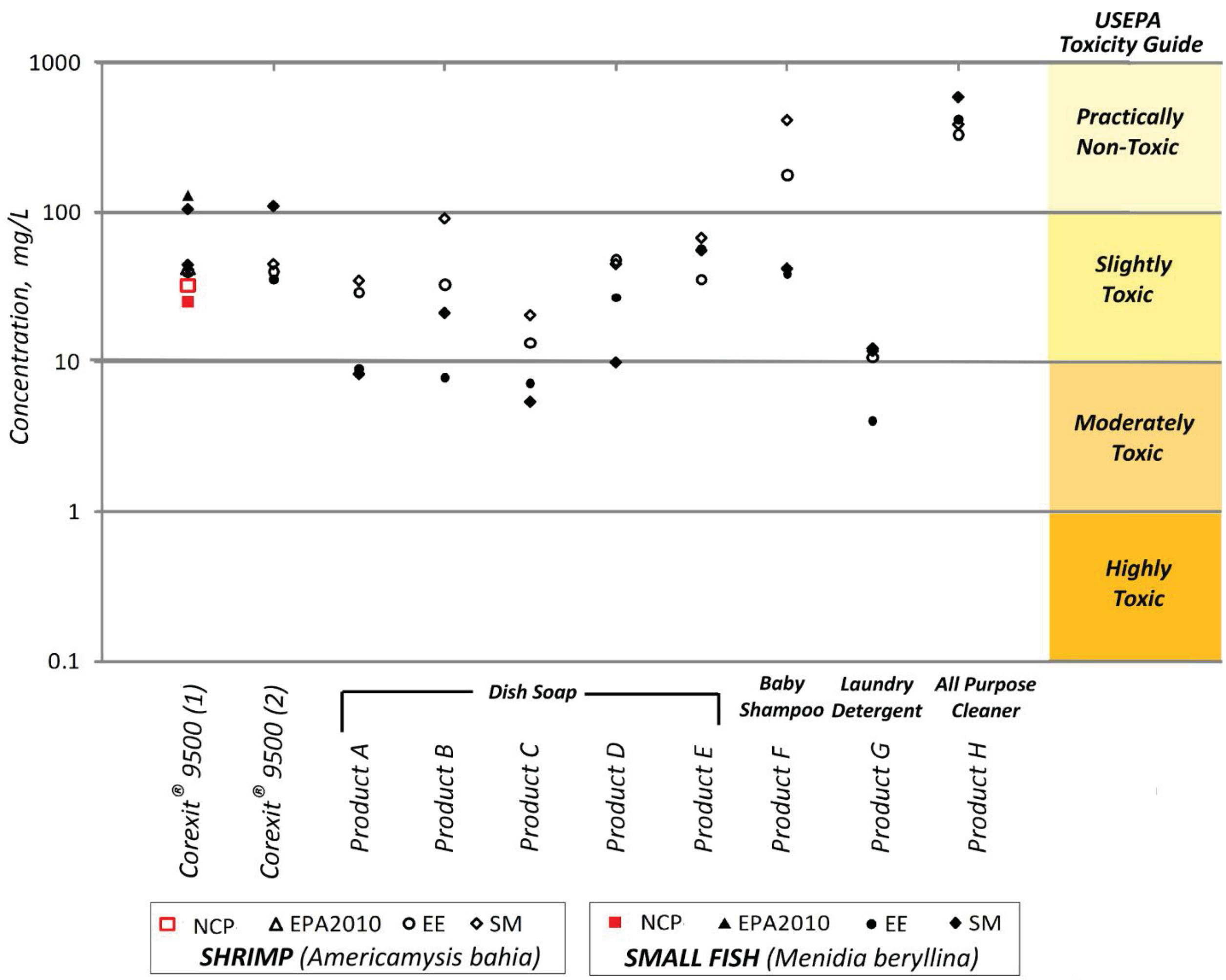

Figure 1. Results from Toxicity Tests with Common Household Products and Corexit® 9500 Conducted in Parallel by Two Independent Laboratories.

[USEPA and NCP test results added for reference (Hemmer *et al*. 2010; USEPA NCP b, respectively)]

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