

## A Role for Analytical Chemistry in Advancing our Understanding of the Occurrence, Fate, and Effects of Corexit Oil Dispersants

BEN PLACE

Oregon State University, Corvallis, Oregon

BRIAN ANDERSON

University of California, Davis, California

ABDOU MEKEBRI

California Department of Fish and Game,  
Rancho Cordova, California

EDWARD T. FURLONG

U.S. Geological Survey, Denver, Colorado

JAMES L. GRAY

U.S. Geological Survey, Denver, Colorado

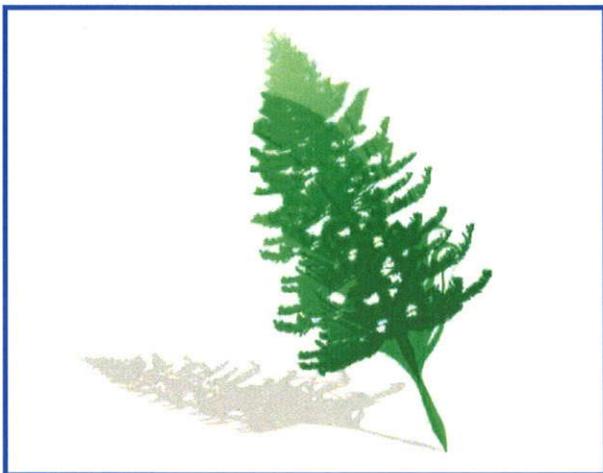
RON TJEERDEMA

University of California, Davis, California

JENNIFER FIELD\*

Oregon State University, Corvallis, Oregon

### Author's viewpoint



RHONDA SAUNDERS

On April 24, 2010, the sinking of the Deepwater Horizon oil rig resulted in the release of oil into the Gulf of Mexico. As of July 19, 2010, the federal government's Deepwater Horizon Incident Joint Information Center estimates the cumulative range of oil released is 3,067,000 to 5,258,000

\* E-mail: jennifer.field@oregonstate.edu.

barrels, with a relief well to be completed in early August. By comparison, the Exxon Valdez oil spill released a total of 260,000 barrels of crude oil into the environment. As of June 9, BP has used over 1 million gallons of Corexit oil dispersants to solubilize oil and help prevent the development of a surface oil slick (1).

Oil dispersants are mixtures containing solvents and surfactants that can exhibit toxicity toward aquatic life and may enhance the toxicity of components of weathered crude oil. Detailed knowledge of the composition of both Corexit formulations and other dispersants applied in the Gulf will facilitate comprehensive monitoring programs for determining the occurrence, fate, and biological effects of the dispersant chemicals. The lack of information on the potential impacts of oil dispersants has caught industry, federal, and state officials off guard. Until compositions of Corexit 9500 and 9527 were released by the U.S. Environmental Protection Agency online, the only information available consisted of Material Safety Data Sheets (MSDS), patent documentation, and a National Research Council report on oil dispersants (2). Several trade and common names are used for the components of the Corexits. For example, Tween 80 and Tween 85 are oligomeric mixtures.

### Composition of Corexit 9500 and 9527

Although compositions of Corexit products were reported in 1996 (3), selective and sensitive methods for the identification and determination of dispersant components in seawater–oil mixtures are not published. Furthermore, reaction byproducts may be present among the industrial-grade chemicals that may not be listed among the dispersant ingredients. Quantitative, selective, and sensitive methods need to be developed and widely disseminated to determine the short- and long-term fate and effects of dispersant components on oil-impacted ecosystems.

Separation and quantification methodology is being developed for the individual chemicals in each formulation. To this end, Corexits 9500 and 9527 and authentic standards of the ethoxylated components, including Tween 80, Tween 85, Span 80, and the bis(2-ethylhexyl)sulfosuccinate surfactant were infused into a tandem mass spectrometer. Using electrospray (ESI) mass spectrometry (MS) in negative-ion detection mode, a mass to charge ratio ( $m/z$ ) of 421 was obtained for both Corexit dispersants, which matches that obtained for an authentic standard of bis(2-ethylhexyl)sulfosuccinate (Figure 1). The  $m/z$  421 corresponds to the molecular ion while  $m/z$  81 corresponds to the sulfonate group. The diethylhexylsulfosuccinate surfactant is consistent with the "organic sulfonic acid salt" that is listed on the MSDS and reported by Singer et al. (3) Ammonium adducts of Tween 80 and Tween 85 oligomers were identified by ESI/MS in positive ion mode. Confirmation of whether other constituents are present in Tween 80, Tween 85, and Span 80 surfactants is part of an ongoing effort. Detailed analyses are underway to fully characterize the Corexit compositions and to fingerprint the complex oligomeric distribution of each of the ethoxylated surfactant classes. The ethoxylated surfac-

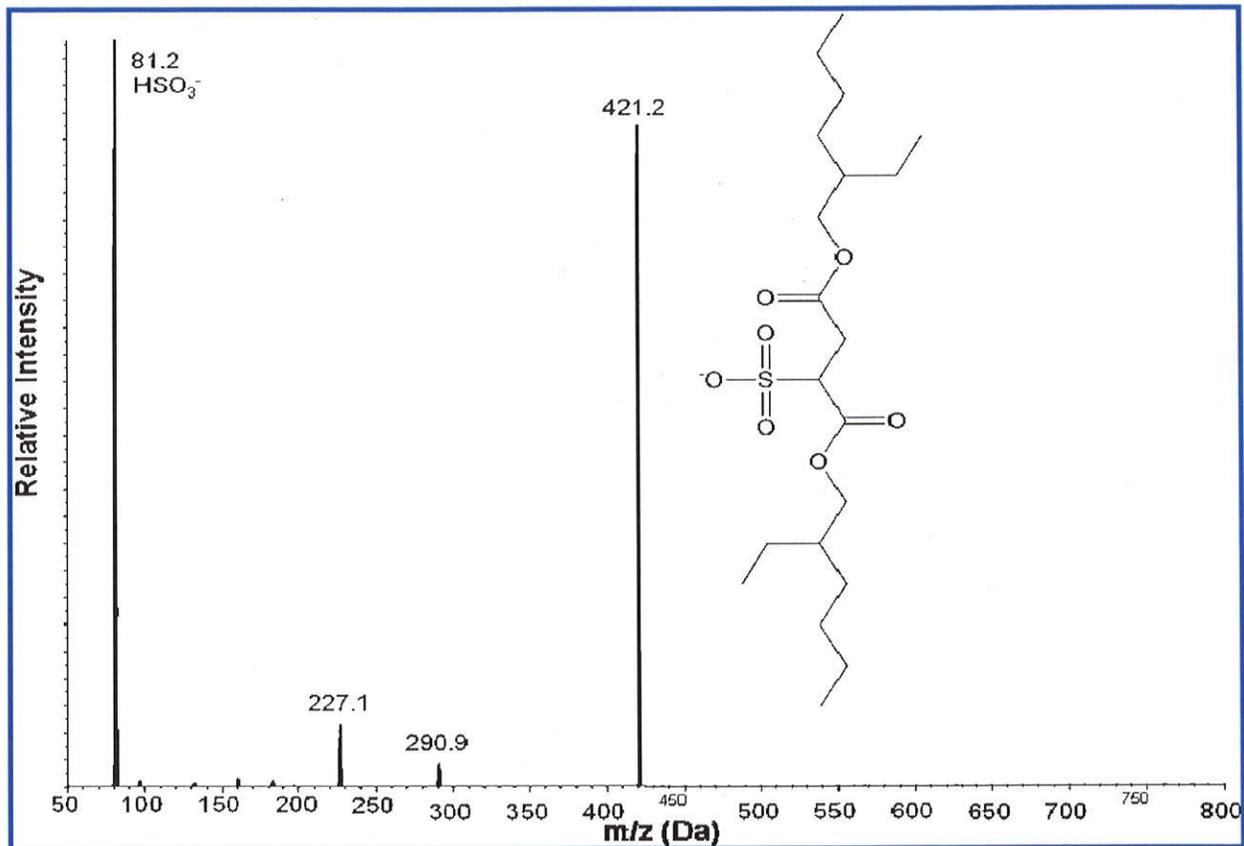


FIGURE 1. Electrospray mass spectrum of bis(2-ethylhexyl)sulfosuccinate surfactant in Corexit 9500 and 9527 oil dispersants.

tants and their respective ranges of oligomers will likely degrade at different rates in Gulf ecosystems, making the fingerprint of weathered dispersant mixtures even more complex.

Analysis by gas chromatography/mass spectrometry (GC/MS) using a National Institute of Standards and Technology library for spectral matching revealed several semivolatile chemicals not listed on the EPA Web site, including diethylhexyl maleate. It is not known if diethylhexyl maleate is an artifact of GC/MS analysis due to the decomposition of bis(2-ethylhexyl)sulfosuccinate surfactant in the injection port or if it is an actual component of the Corexit formulations. Further analyses are needed to confirm the identities of additional compounds detected in Corexit formulations and to fingerprint the petroleum distillate fraction, which is reported to be *n*-alkanes from nonane to hexadecane. Volatile chemicals in Corexit formulations, if not found in the spilled oil, may be useful as markers for the volatile dispersant fraction in air samples.

### Analytical Challenges and Quality Control

Analytical methods developed for the detection of the diethylhexylsulfosuccinate surfactant and other surfactants and their degradation products will need to perform well for a range of matrices. Methodology used to determine surfactant concentrations in aqueous and particulate phases needs to be robust and reliable over the range of expected salinities (from fresh water to ocean water), analyte concentrations, and states of emulsification. In the dispersed oil plume near the point of application, concentrations could be very high. In contrast, water and sediment samples collected far from the location of the spill may have much lower surfactant concentrations. In addition, because the dispersant was applied for the express purpose of emulsifying the oil, analysts attempting to measure concentrations of

individual dispersant components may need to address the emulsified state of the environmental samples collected. Incomplete separation of the emulsion (oil, dispersant chemicals, and seawater) prior to instrumental analysis may lead to variable measurements of the individual components.

Analytical methodologies ultimately may range from traditional approaches that require substantial pre-analysis sample isolation and cleanup to direct injection techniques. Regardless of the approach, internal standard calibration will be essential given the nature of the complex environmental samples and matrices that will be analyzed as part of monitoring campaigns. The current state-of-the-art for environmental analytical chemistry involves use of stable isotope-labeled internal standards. At the time of this writing, no authentic stable-isotope internal standards for the surfactants found in Corexit formulations are commercially available. Some researchers are using a custom-made, deuterated standard of the diethylhexylsulfosuccinate; however, it is in limited supply at this time. To the best of our knowledge, both deuterated and <sup>13</sup>C-labeled internal standards for the diethylhexylsulfosuccinate surfactants are currently under development by commercial vendors. In the absence of a commercial source of a high-purity internal standard, commercially available chemicals with similar properties (e.g., surrogates such as pyrene sulfonate) may be temporary solutions.

### Future Efforts

To the best of our knowledge, there are no published data on the occurrence of sulfosuccinates in environmental waters, sediment, or biota. The analysis of pre- and postspill samples will address the potential occurrence of the surfactants found in Corexit formulations due to sources other than the application of Corexit. A small number of laboratory studies indicate the potential biodegradability of the sulfosuccinate

under aerobic and anaerobic conditions (4) and biodegradation intermediates of similar toxicity to the parent surfactant may form (5). Evidence for the degradation of Corexit components under actual marine conditions is lacking. Information remains incomplete as to how the presence and fate of dispersant-derived surfactants affects oil toxicity and bioaccumulation in the short and long-term. Future research efforts should focus on surfactant sorption to sediments and particulate matter and on their environmental persistence. Degradation by both microbial activity (anaerobic and aerobic) and sunlight needs to be characterized, with a focus on identifying the possible formation of toxic products.

Because of the scale of the spill and its potential to affect a very large area for an undetermined length of time, there is an unprecedented need for consistency and comparability over decades between laboratories producing chemical data. An example of this scale of effort can be found in the U.S. Geological Survey's online National Water Quality Assessment or in the National Oceanic and Atmospheric Administration's online MusselWatch program. Both programs have developed decadal perspectives for assessing water quality. These programs were established in advance of any specific environmental contamination event. While not directly applicable to characterizing dispersant distributions in the Gulf, they provide archival samples germane to the assessment of prespill conditions and historical data describing background contamination from oil components. Moreover, they provide a template for the quality assurance and quality control necessary for scientists assessing the presence and distribution of dispersants and oil components now and in

the future. Given the increasing number of laboratories committed to monitoring the spill, unprecedented coordination among environmental chemists and toxicologists within government, academia, and industry will be needed to establish criteria for maximizing data quality and comparability. Mechanisms that permit objective comparison of results between laboratories over time, such as a consensus set of best practices and production and routine use of independent third party reference standards, are necessary because the scope and impact of the Deepwater Horizon incident transcends any one local, state, or federal agency.

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