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Photochemical fate of solvent constituents of Corexit oil dispersants

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ABSTRACT

In 2010, an estimated 1.87 million gallons (7079 cubic meters) of chemical dispersants were applied to open ocean waters in the Gulf of Mexico as part of the response to the Deepwater Horizon blowout. This unprecedented volume of dispersant application highlighted the importance of dispersant chemical formulations, raising questions of dispersant fate and transport in the open ocean and spurring research into formulation improvements. The research presented here elucidates the contribution of photolytic processes to the degradation of two solvent constituents of these dispersant mixtures: propylene glycol (PG) and 2-butoxyethanol (2-BE). A series of photodegradation experiments were conducted to determine the contribution of direct photolysis and indirect photolysis via hydroxyl radical ($HO^•$) to compound degradation. Experiments were performed using both deep UV light sources (low pressure (LP) and medium pressure (MP) mercury vapor ultraviolet (UV) lamps) and a solar simulator. Sample matrices included ultrapure water, nitrate amended water, hydrogen peroxide (H_2O_2) spiked water, Gulf of Mexico seawater, and a surface water from Boulder, CO. Experiments included determination of the molar absorption coefficients (ε) and the $HO^•$ reaction rate constants ($k_{HO^•}$) of the individual compounds. Data illustrated that significant direct photolysis of either PG or 2-BE from sunlight is unlikely. The $k_{HO^•}$ for PG and 2-BE were determined to be $6.15 \times 10^8\ M^{-1}\ s^{-1}$ and $1.15 \times 10^9\ M^{-1}\ s^{-1}$, respectively. Solar simulation and UV experiments indicate that in natural systems, neither PG nor 2-BE is expected to undergo significant, rapid degradation due to direct or indirect photolysis. PG and 2-BE are effectively degraded through indirect photolysis in the presence of high $HO^•$ concentrations, suggesting UV/H_2O_2 is a feasible possibility for the treatment of waters containing PG and 2-BE.

1. Introduction

In 2010, an estimated 1.87 million gallons (7079 cubic meters) of the chemical dispersants Corexit 9500 and 9527 were applied to open ocean waters in Gulf of Mexico as part of the response to the Deepwater Horizon blowout (Kujawinski et al., 2011; Hayworth and Clement, 2012). This unprecedented volume of dispersant application highlighted the importance of dispersant chemical formulations, raising questions of dispersant fate and transport in the open ocean and spurring research into formulation improvements. Prior to the Deepwater Horizon blowout, the chemical compositions of most chemical dispersants were proprietary information. In 2010,

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List of abbreviations

AOP	advanced oxidation process
Ct	concentration-time
DOC	dissolved organic carbon
DOSS	dioctyl sodium sulfosuccinate
DPnB	dipropylene glycol monobutyl ether
ε	molar absorption coefficient
FID	flame ionization detector
GC	gas chromatograph
HO	hydroxyl radical
$[\mathrm{HO}^\bullet]_{ss}$	hydroxyl radical steady state concentration
H_2O_2	hydrogen peroxide
$k_{\mathrm{HO}^\bullet}$	hydroxyl radical reaction rate constant
k'_{obs}	observed first order degradation rate
k'_d	first order direct photolysis rate
LP	low pressure
MDL	minimum detection limit
MP	medium pressure
NO_3^-	nitrate
NO_2^-	nitrite
NREL	National Renewable Energy Laboratory
pCBA	para-chlorobenzoic acid
PG	propylene glycol
PQL	practical quantitation limit
$R_{\mathrm{HO}^\bullet}$	formation rate (hydroxyl radical)
R_{trans}	transmittance ratio
RSD	relative standard deviation
SMARTS	Simple Model of the Atmospheric Radiative Transfer of Sunshine
UV	ultraviolet
2-BE	2-butoxyethanol

the compositions of the Corexit dispersants were released to the US Environmental Protection Agency (EPA); the constituents and their functions within the formulations are listed in Table 1. Chemical dispersants are comprised of two main constituent groups: surfactants and solvents. In Corexit 9500 and 9527, propylene glycol (PG) and 2-butoxyethanol (2-BE) are main solvent components of the mixtures, along with dipropylene glycol monobutyl ether (DPnB) and other petroleum distillates (EPA, 2010). Solvents are key constituents of any dispersant formulation. Solvents aid in delivery of the active surfactant ingredients in dispersant mixtures, and also allow these surfactants to penetrate the oil films and get to the water–oil interface where micelles can be formed, increasing bioavailability and biodegradation of the oil.

One aspect contributing to the overall effectiveness of a dispersant mixture is the operational effectiveness. Operational effectiveness monitors how efficiently the dispersant is applied and penetrates the oil film. Of the total volume of Corexit applied in response to the Deepwater Horizon Blowout, 1.1 million gallons (4164 cubic meters) (59%) were applied at the surface and in direct contact with sunlight during the application process (Hayworth and Clement, 2012). If any of the Corexit constituents were degraded due to this solar exposure, the operational efficiency of Corexit would be reduced. Despite this potential impact, the photochemical fates of the chemical constituents of Corexit 9500 and 9527 remain relatively unexplored.

Table 1 – Chemical constituents of Corexit 9500 and 9527.

CAS registry number	Chemical name	Short name	Function
57-55-6	Propylene glycol	PG	Solvent
111-76-2[a]	2-Butoxyethanol	2-BE	Solvent
577-11-7	Dioctyl sodium sulfosuccinate	DOSS	Surfactant
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate	Span 80	Surfactant
9005-65-6	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivatives	Tween 80	Surfactant
9005-70-3	Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1, 2-ethanediyl) derivatives	Tween 85	Surfactant
29911-28-2	Dipropylene Glycol Monobutyl Ether	DPnB	Solvent
64742-47-8	Petroleum distillates		Solvent

[a] Not a component of Corexit 9500.

The research presented here elucidates the contribution of photolytic processes to the degradation of solvent constituents of these dispersant mixtures to aid in optimizing the operational effectiveness with respect to application and understanding their environmental fate. Specifically, the compounds PG and 2-BE were examined. If solvents such as PG and 2-BE were rapidly photodegraded upon surface application, dispersant mixtures that are applied may not work as designed, resulting in reduced response efficiency, increased lag time for biodegradation of oil, and increased cost. Small changes made to solvent concentration based on spill location and solar flux may prevent such unnecessary over-application.

Propylene glycol and 2-BE are also used for many other industrial applications other than oil dispersal, and thus have potential to be present in many natural waters. Propylene glycol is a compound commonly used as a functional fluid for its solvency properties and its widespread use provides ample opportunity for unintentional release to natural waters. The largest industrial use of concern is the use of PG in aircraft deicing fluids. About 4000 L of deicing fluid are required to service a typical large jet (Castro et al., 2001) and it is estimated that deicing fluid usage is 41,940 cubic meters per season, only accounting for the 20 largest airports (Corsi et al., 2001). 2-Butoxyethanol is commonly used in the manufacture of industrial and commercial household products. Some examples of the manufacturing uses of 2-BE include lacquers, cleaning products, paints, paint thinners, textiles, and dry-cleaning compounds (ATSDR, 1998). This prevalence of use provides ample opportunity for 2-butoxyethanol to be introduced to natural waters. Potential pathways for 2-BE release into the environment include waste streams from manufacturing facilities, return water from industrial operations, and leachate