

Estimation of Airborne Vapor Concentrations of Oil Dispersants COREXIT™ EC9527A and EC9500A, Volatile Components Associated with the *Deepwater Horizon* Oil Spill Response and Clean-up Operations

Mark R. Stenzel^{1,*}, Susan F. Arnold², Gurumurthy Ramachandran³, Richard K. Kwok^{4,5}, Lawrence S. Engel^{5,6}, Dale P. Sandler⁴ and Patricia A. Stewart⁷

¹Exposure Assessment Applications, LLC, 6045 N. 27th St., Arlington, VA 22207, USA; ²Division of Environmental Health Sciences, University of Minnesota School of Public Health, 420 Delaware St. SE, Minneapolis, MN 55455, USA; ³Department of Environmental Health and Engineering, Bloomberg School of Public Health, Johns Hopkins University, 615 N. Wolfe St., Baltimore, MD 21205, USA; ⁴Epidemiology Branch, National Institute of Environmental Health Sciences, 111 T.W. Alexander Drive, MD A3-05, PO Box 12233, Research Triangle Park, NC 27709, USA; ⁵Office of the Director, National Institute of Environmental Health Sciences, 9000 Rockville Pike, Bethesda, MD 20892, USA; ⁶Department of Epidemiology, University of North Carolina at Chapel Hill, 35 Dauer Drive, Chapel Hill, NC 27599, USA; ⁷Stewart Exposure Assessments, LLC, 6045 N. 27th St., Arlington, VA 22207, USA

*Author to whom correspondence should be addressed. Tel: +01 703 303-7585; e-mail: Mark_StenzelEAApps@hotmail.com

Submitted 20 October 2020; revised 1 July 2021; editorial decision 1 July 2021; revised version accepted 12 July 2021.

Abstract

The *Deepwater Horizon* (DWH) drilling unit explosion above the Macondo oil well on 20 April 2010 caused the release of approximately 4.9 million barrels (779 million L) of oil into the Gulf of Mexico. As part of a larger spill response and clean-up effort, approximately 1.84 million gallons (6.81 million L) of chemical dispersants COREXIT™ EC9500A and COREXIT™ EC9527A were applied to the resultant oil slicks through spraying on the water surface by plane and by vessel and through injection at the release source near the seabed. The Gulf STUDY is investigating the health effects of workers involved in the oil spill response and clean-up after the DWH explosion, and estimates of possible exposure to chemical dispersants were needed. Exposures were estimated to the volatile components of COREXIT™ EC9500A [petroleum distillates, hydrotreated light, and propylene glycol (PG)] and of COREXIT™ EC9527A [2-butoxyethanol (2-BE) and PG] using two of AIHA IHMOD2.0® mathematical modeling tools along with the dispersants' chemical and physical properties. Monte

Carlo simulations were used to reflect uncertainty in input parameters with both the two-box, constant emission model and the near and mid field plume model for indoor and outdoor activities, respectively. Possible exposure scenarios considered various evaporation rates, sizes of the dispersant pool, wind speeds, and ventilation rates. For the two-box model, mean near field exposure estimates to 2-BE ranged from 0.9 to 5.7 ppm, while mean far field estimated exposures ranged from 0.3 to 3.5 ppm. Estimates of mean near field plume model exposures ranged from 0.01 to 3.7 ppm at 2.5 ft from the source, and <0.01 to 0.3 ppm at 10 ft from the source. Estimated exposures to PG were approximately 10% of the calculated 2-BE exposures and exposures to petroleum distillates about 40% higher than the 2-BE estimates. Results indicate that compared with current occupational exposure guidelines, overexposure to petroleum distillates and PG probably did not occur in our study, but under some conditions, for short periods, exposure to 2-BE may have exceeded the limits for peak exposures. These estimates were developed for use in job-exposure matrices to estimate exposures of workers having contact with dispersant vapors for the GuLF STUDY.

Keywords: *Deepwater Horizon*; dispersants; mathematical exposure modeling; oil spill

Introduction

The *Deepwater Horizon* (DWH) drilling unit explosion above the Macondo oil well on 20 April 2010 caused the release of approximately 4.9 million barrels (779 million L) of oil into the Gulf of Mexico (Lehr *et al.*, 2010). As part of a larger oil spill response and clean-up (OSRC) effort, chemical dispersants were applied to the resultant oil slicks through spraying on the water surface by plane and by vessel and also through injection at the release source near the seabed. Dispersants were used to break up the oil in or on the water by reducing the interfacial tension between crude oil and water, resulting in small droplets that are thought to be more easily dispersed by natural processes such as evaporation, dispersion, emulsification, dissolution, photo-oxidation, sedimentation, and biodegradation. A total of 1.84 million gal (6.81 million L) of COREXIT™ EC9527A (9527A) and COREXIT™ EC9500A (9500A) was used, either sprayed by plane [214 669 gal (812 611 L) of 9527A, and 761 568 gal (2 882 848 L) of 9500A] and by vessel [96 277 gal (364 448 L) of 9500A] or injected below the water surface [771 272 gal (2 919 582 L) of 9500A]. Workers were potentially exposed to dispersant aerosol when spraying dispersant or by being in the general area where the dispersants were being sprayed. Workers also may have had exposure to dispersant vapor from handling dispersant-related equipment or being in an area where dispersant had been sprayed.

The unprecedented amount of dispersants used (NOAA On scene coordinator report: *Deepwater Horizon* oil spill, 2011) raised concerns about the potential health hazards associated with their use. The GuLF Long-Term Follow Up Study (GuLF STUDY), conducted by the National Institute of Environmental Health Sciences, is investigating possible adverse health effects among workers involved in the DWH OSRC. A recent investigation from that study

found that participants' accounts of coughing, wheezing, shortness of breath, tightness in the chest, and burning in the nose, throat, or lungs were associated with their reported dispersant-related tasks (McGowan *et al.*, 2017).

The goals of this paper are to: (i) develop dispersant vapor estimates for a number of scenarios, including some that may not be applicable to OSRC work, but may provide insights into expected concentrations that could be encountered in other scenarios associated with dispersant use; (ii) develop dispersant-related exposure estimates for the Gulf Study. All estimates were developed using varying model input parameters to address uncertainty in the knowledge of specific exposure scenarios. An accompanying paper addresses possible dispersant aerosol exposures (Arnold *et al.*, 2021).

An overview of the entire exposure assessment for the study is presented by Stewart, Gorman Ng *et al.* (2021). The strategy for developing exposure groups for the Gulf Study is described in Stenzel *et al.* (2021). Inhalation exposures of workers performing other spill-related activities to six oil-related substances (Groth, Banerjee *et al.*, 2021, Groth, Huynh, *et al.*, 2021; Huynh *et al.*, 2021a,b,c; Ramachandran *et al.*, 2021) and exposures to other substances [i.e. PM_{2.5} (Pratt *et al.*, 2021), dispersant aerosol (Arnold *et al.*, 2021), and oil mist (Stewart, Gorman Ng *et al.*, 2021)] are presented elsewhere. Estimation of dermal exposures has also been described (Gorman Ng *et al.*, 2019; Stewart, Groth *et al.*, 2021).

Background

Dispersant application

COREXIT™ EC9527A contains 2-butoxyethanol (2-BE) (30.0–60.0%, w/w), a proprietary organic

sulfonic acid salt (10.0–30.0%, w/w), and propylene glycol (PG) (1.0–5.0%, w/w) (COREXIT9527A, 2019). COREXIT™ EC9500A contains petroleum distillates, hydrotreated light (10.0–30.0%, w/w), PG (1.0–5.0%, w/w), and a proprietary organic sulfonic acid salt (10.0–30.0%, w/w) (COREXIT9500A, 2019). Application of both dispersants was done neat (i.e. undiluted).

Aerial spraying was done by dedicated aerial dispersant planes deployed out of the Stennis Space Center Airport in Mississippi and the Houma-Terrebonne Airport in Louisiana. Dispersant was delivered to the airports by the dispersant supplier and off-loaded to field storage tanks. In some cases, the dispersant was delivered in totes. The airports had staging locations where the planes were refueled and the dispersant loaded. Portable pumps were used to transfer the dispersant from the storage tanks to the tanks on the spray aircraft. A total of 412 documented aerial dispersant application sorties were flown to spray dispersant to the oil slicks on the water surface between 22 April and 19 July 2010 for 16 days (9527A) and 57 days (9500A). Each sortie took about 1.5 h of flying time (take off to landing). The pumping capacity was ~ 300 gal min^{-1} (1136 l min^{-1}). The quickest turnaround time (landing, refill dispersant tanks, refueling, and takeoff) was reported to be 15 min but that was done by a highly trained Air Force ground crew. A more typical turnaround time was likely on the order of 30 min. The planes with the largest tanks (5000 gal) had a spraying time about 16 min. 98% of dispersant volume was applied more than 10 nautical miles (nmi, 18 km; 11 mi) offshore (NOAA On scene coordinator report: *Deepwater Horizon oil spill*, 2011). It was common for a specific aircraft to fly multiple sorties per day, with the highest reported number for a specific plane in 1 day being 6. For the Gulf Study we divided the study period (22 April–30 June 2011) into seven time periods (TPs) to allow step changes in exposure. Spraying of 9527A was done only in TP1a (22 April–14 May 2010), whereas 9500A was sprayed by plane in TP1a and TP1b (15 May–15 July 2010).

Aerial spraying was not allowed within 5 nmi (9.3 km) of the Macondo oil wellhead. Within that area, large vessels equipped with spray booms sprayed the dispersant onto the water surface. We found no information on loading of dispersant onto the spray vessels, but based on how dispersant was supplied to the injection vessel (see below), presumably dispersant was delivered to the spray vessel by supply vessels, either in portable tanks (totes) or transferred from tanks on the supply vessels to tanks located on the spray vessels. A total of 118 vessel surface applications of dispersant 9500A were reported between 15 May and 13 July 2010 (TP1b) on 41 days. In reviewing the payload of each application and the

capacity of vessels dispersant application tanks, however, there may actually have been 126 applications (NOAA On scene coordinator report: *Deepwater Horizon oil spill*, 2011).

One vessel [*Skandi Neptune (Skandi)*] conducted subsea injection of dispersant 9500A. Dispersant was transferred to the *Skandi* from land via an Offshore Supply Vessel (OSV) either by portable tank or by transfer lines from the OSV storage tanks to the storage tanks to the *Skandi*. For the injection, dispersant was transferred from the *Skandi* storage tanks via a dispersant pumping system connected to a subsea manifold. A wand on the end of a hose connected to the manifold was positioned into the leaking oil stream to break up the oil as it was being released at the point in the broken pipe about 5000 ft (1.5 km) below the water surface. Six days of intermittent testing of the injection operation started 30 April 2010 (TP1a), but after May 15 injection was done almost continuously (24 h d^{-1}) until 15 July 2010 (TP1b).

Workers on land were potentially exposed to dispersant vapor from filling dispersant field storage tanks, from connecting and disconnecting dispersant transfer lines from the storage tanks to the airplane tanks or vessel storage tanks and from actual pumping of the liquid dispersant to these tanks. Exposure during transfer and pumping of dispersant also may have occurred between vessel storage tanks and the spray booms on the vessels applying the dispersant to the water surface, between the storage tanks on the OSV to those on the *Skandi*, and between the *Skandi* storage tanks to the subsea pumping system. Exposures also may have occurred during maintenance and decontamination of this dispersant-containing equipment and in contact with leaky equipment and clean-up of spills (NOAA On scene coordinator report: *Deepwater Horizon oil spill*, 2011). Workers on research vessels (RVs) may have been exposed to dispersants when they were collecting water and oil samples for research purposes. Finally, workers may have been exposed while being on a vessel located in a pool of dispersant.

Quantitative measurements

Almost 1300 air monitoring measurements were collected on 2-BE or PG, two of the volatile dispersant components. Vapors associated with a third volatile component, petroleum distillates, hydrotreated light (composition similar to kerosene), found in 9500A, contributed to total hydrocarbon (THC) concentrations, and so cannot be differentiated from the THC contribution from the crude oil as reported elsewhere (Huynh *et al.*, 2021a,b,c; Ramachandran *et al.*, 2021). No dispersant aerosol measurements were collected.

The only measurements relevant to spraying or injecting dispersant or the handling of dispersant associated with these activities are described below. The other 2-BE and PG measurements are reported and discussed in [Supplementary Materials](#) (available at *Annals of Work Exposures and Health* online), Quantitative Measurement Data, and [Supplementary Table S1](#) (available at *Annals of Work Exposures and Health* online). The 2-BE measurements were collected in a TP or location where 9527A was not used and the description associated with the PG measurements provided no indication that the activity being monitored was associated with the application of dispersant.

The Responsible Party of the spill, as designated by the US government, collected three personal and two area samples of PG relevant to the work described here. PG is a component of both 9500A and 9527A. The dispersant type was not identified, although it was likely 9500A, because the sampling date was after the use of 9527A had been discontinued. The two area samples (0.22 and 0.07 ppm) were taken while filling airport dispersant storage tanks that were vented to the atmosphere. The duration of the samples was about 2 h. Two 15-min personal samples were collected while transferring dispersant from storage tanks to the airplanes' dispersant tanks and one 40-min personal sample was collected while cleaning up spilled dispersant around storage tanks. All three measurements were censored (limit of detection (LOD) = 0.64 ppm for the 15-min sample and 0.24 ppm for the 40-min sample).

Methods

As there were no 2-BE and few PG personal samples relevant to dispersant activities, exposures were modeled based on conditions that may have been encountered by the workers involved with handling the neat dispersant.

The AIHA IHMOD_{2.0}[®] software ([Drolet, 2018](#)) was selected because it includes a suite of 11 modeling programs that develop estimates of descriptive statistics of air concentrations relevant to occupational exposure assessments (see [Supplementary Fig. S1](#), available at *Annals of Work Exposures and Health* online). Additionally, the software includes Monte Carlo capabilities to reflect uncertainty in model input parameters ([Keil et al., 2009](#)). We were interested in the exposure of workers performing a task where the exposure source was in their immediate breathing zone (direct exposure), as well as further away (indirect exposure). For tasks performed indoors or in other protected areas, the two-box, constant emission model ([Nicas, 2009](#)) was deemed to be the most appropriate. The inner box (near field)

corresponds to the area around the source where work is being performed within approximately an arm's length or ~30 inches (0.76 m) of the worker. The outer box (far field) refers to exposure encountered in the remaining volume of the room, with a rather low rate of air exchange between the two boxes. For exposure scenarios that occurred out of doors, the near and mid field plume models were selected as the best predictors of exposures at various distances from the emission source.

Both models consider evaporation rate (in this paper, the terms evaporation rate and emission rate are used interchangeably) of the chemicals, wind speed, and the size of the dispersant surface area or 'pool' [as referenced in AIHA IHMOD2.0[®] ([Drolet, 2018](#))] releasing the dispersant volatiles. For the two-box model, various room sizes, air changes per hour (ACH) in the room, random air velocities, and configurations of the near fields were incorporated, in addition to the emission rates (see section 'Two-box model'). For the plume model, emission rates, distances of the worker relative to the dispersant surface area and advective air speeds (described in the section 'Plume model') were used.

Evaporation rates were calculated from the Hummel equation software provided in the IHMOD2.0[®] support file ([Hummel et al., 1996](#)) (see [Supplementary Material](#), available at *Annals of Work Exposures and Health* online, Mathematical Modeling, emission or evaporation rate, and [Supplementary Fig. S2](#), available at *Annals of Work Exposures and Health* online). The software considers the overall system pressure (typically 1 atmosphere); wind speed, surface temperature; surface area of the pool; length of the pool along the air flow, and the molecular weight and vapor pressure of the component of interest. The Hummel equation was originally derived for pure materials, while the dispersants in this work are mixtures. In mixtures, such as dispersants, that contain surfactants, the vapor pressure of the mixture components will closely approach the vapor pressure of the pure component of the mixture (J. I. Siepmann, personal communication). Therefore, in calculating evaporation rate, we used the vapor pressure of the pure volatile component (2-BE = 0.00115 atm, PG = 0.00017 atm), rather than the vapor pressure expected in the mixture (see [Groth, Huynh et al., 2021, Supplementary Material, section 2](#), available at *Annals of Work Exposures and Health* online). This assumption means that the vapor pressure of the pure component will result in maximum evaporation rates and will yield maximum reported estimates for each exposure scenario. Vapor pressures at 25°C, which is the temperature of the liquid dispersant, rather than of the air, were used in the calculation.

Because there was likely a wide range of possible conditions (i.e. for wind speed and pool size) related to the dispersant vapors in our study, evaporation rates were calculated at 7 wind speeds, ranging from 6.25 to 894.1 cm s⁻¹ (0.14–20 mph) and 11 pool sizes, ranging from 25.8 to 33 445.1 cm² (4–1944 in²). For the worst-case analysis where a vessel was located in a pool of dispersant on the water surface, areas of the pool ranged from 9 to 21 m² (900–4900 ft²). A square-shaped pool was selected for all scenarios for simplification. Evaporation rates for 2-BE in dispersant 9527A were calculated for 77 combinations of wind speed and pool size (Table 1). The worst-case vessel pool calculations added 21 additional combinations. For example, a low wind speed of 44.7 cm s⁻¹ (1 mph) and a small square pool of 232.26 cm² (36 in²) [15.24 cm (6 in) on a side] resulted in an evaporation rate of 44.0 mg min⁻¹. For both the two-box and the plume models, the evaporation rates in Table 1 were used as the models' input parameters for emission rate (*G*). With limited information, it is much easier to estimate possible ranges of conditions than to identify detailed input parameters associated with a specific exposure scenario.

Typically, modeling is conducted for a concise set of conditions, but because detailed information regarding the dispersant conditions was not available, we used Monte Carlo methods to reflect uncertainty in the two-box and plume models. Ranges of wind speed were grouped into three categories of low, medium, and high, and source sizes were grouped into five categories i.e. small, medium, large, very large, and vapor pool scenarios (Table 1).

Two-box model

Nicas (2009) provides a technical discussion of the model's application but uses slightly different terminology than that used by Drolet (2018) (see Supplementary Table S2, available at *Annals of Work Exposures and Health* online). We use here the Nicas terminology. The two-box model accounts for the spatial variability of exposure intensity in a working area, such as a room, by dividing the room conceptually into two boxes (Supplementary Fig. S3, available at *Annals of Work Exposures and Health* online). One box contains the emission source (termed the near field). Its dimensions are sized to approximate the breathing zone of the worker located near the source i.e. an arm's length or ~30 inches (0.76 m) of the worker. The remainder of the room is the far field, i.e. the second box. The two-box model assumes the air within each box is perfectly mixed, with limited air flow rate (β) between boxes. The

β parameter is a function of the free surface area of the near field box and the random air speed. Free surface area refers to the surface area of the near field box where the flow of air is not obstructed or not occluded (occluded means that the box, for example, was on a surface such as a table and therefore the bottom of the box was not available for air exchange). Random air speed is the non-directional speed of the molecules moving between the two boxes.

For tasks that may have been performed indoors or in protected areas and where the surface area of the dispersant was limited (because the entire surface area of the pool must fit inside the near field box), such as the connection of a transfer line, near field and far field exposure estimates were developed using the two-box model. We assumed constant emission, that is, sufficient liquid was available for evaporation to have occurred over the entire duration of the task.

Monte Carlo simulations were conducted varying emission rates (*G*) (from Table 1) and ventilation rates (*Q*, derived from ACH), with low ventilation rates being 1–3 ACH and medium, 3–6 ACH. A uniform distribution was used for both evaporation rates and ventilation rates. Random air speed (*S*) was expressed with a triangular distribution, varying from 2 to 6 m min⁻¹ and a mode of 4 (Baldwin and Maynard, 1998). The near field was configured as a rectangular box with the bottom occluded with a width, length, and height of 0.76, 0.76, and 1 m (2.5 by 2.5 by 3.3 ft), respectively. The far field box (less the volume of the near field box) considered two room sizes, small (3 × 3 × 3 m³, 955 ft³) and large (5 × 5 × 5 m³, 4415 ft³). See Supplementary Material (available at *Annals of Work Exposures and Health* online) for additional discussion of the model's application, including an illustration of a Monte Carlo simulation for a specific scenario (Supplementary Fig. S3, available at *Annals of Work Exposures and Health* online).

Plume model

The theory supporting application of the plume model is discussed by Armstrong (2009) and his terminology is used here (Drolet's (2018) corresponding terminology is in Supplementary Table S2 (available at *Annals of Work Exposures and Health* online). The plume model can be used to estimate exposures under outside conditions with wind using a near and mid field plume model (Supplementary Fig. S4, available at *Annals of Work Exposures and Health* online). The plume model assumes the exchange of air between the near field and the mid field is much greater than assumed by the two-box model, resulting in a much more uniform

Table 1. Evaporation rates (G) of 2-BE related to various wind speeds and source surface area sizes.

Surface area	inch ^a	cm ^a	cm ²	Wind speed										
				Low			Medium			High				
				0.14	0.5	1	3	5	10	20				
			Wind speed (mph)	0.14	0.5	1	3	5	10	20				
			Wind speed (cm s ⁻¹)	6.25	22.40	44.70	134.10	223.50	447.00	894.10				
			Wind speed (m min ⁻¹)	3.75	13.44	26.82	80.46	134.10	268.20	536.46				
2-BE evaporation rate (mg min⁻¹)														
Small	2	5.08	25.81	3.17	5.99	8.47	14.70	18.90	26.80	37.90				
	4	10.16	103.23	8.96	17.00	24.00	41.50	53.60	75.70	107.00				
	6	15.24	232.26	16.50	31.10	44.00	76.20	98.40	139.00	197.00				
Medium	8	20.32	412.90	25.30	48.00	67.70	117.00	151.00	214.00	303.00				
	10	25.44	647.19	35.50	67.20	94.90	164.00	212.00	300.00	424.00				
	12	30.48	929.03	46.50	88.10	124.00	216.00	278.00	394.00	557.00				
Large	18	45.72	2090.32	85.50	162.00	229.00	396.00	511.00	723.00	1020.00				
	24	60.96	3716.12	132.00	249.00	352.00	610.00	787.00	1110.00	1570.00				
Very large	36	91.44	8361.27	242.00	458.00	647.00	1120.00	1450.00	2050.00	2890.00				
	48	121.92	14 864.49	372.00	705.00	996.00	1720.00	2230.00	3150.00	4450.00				
	72	182.88	33 445.09	684.00	1290.00	1830.00	3170.00	4090.00	5780.00	8180.00				
Vessel pool scenarios	360	914.40	836 127.36	7650.00	14 500.00	20 500.00	35 400.00	45 700.00	64 700.00	91 500.00				
	600	1524.00	2 322 576.00	16 500.00	31 100.00	44 000.00	76 200.00	98 400.00	139 000.00	197 000.00				
	840	2133.60	4 552 248.96	27 300.00	51 600.00	72 900.00	126 000.00	163 000.00	230 000.00	326 000.00				

^aLength of the pool along the airflow.

concentration gradient with increasing distance from the source. In this model, a Gaussian function is used to describe the concentration gradient in the plume emitted from a contaminant source resulting from turbulent diffusion and mixing. Plume model equations have slightly different forms depending on the distance from the source. The near field equation is used for distances from 0.1 to 3 m and the mid field equation for distances from 3 to 100 m. The plume model uses evaporation rates derived from the Hummel equation that considers liquid pool size and wind speed for the model emission rate (G) input. The model also considers the advective air speed (U , the speed of a directional wind moving over the length of the pool), which affects the diameter of the plume (the slower the wind, the wider the plume, because it has time to disperse) and the speed at which the vapors in the plume are carried away from the source.

Monte Carlo simulations varied emission rates that were dependent on the exposure scenario's range in wind speed and surface area of the liquid pool. We assumed a uniform distribution for both the G and U . [Table 1](#) presents G s associated with various ranges in wind speed [$<27 \text{ m min}^{-1}$ ($<1 \text{ mph}$), $80\text{--}135 \text{ m min}^{-1}$ ($3\text{--}5 \text{ mph}$), and $268\text{--}537 \text{ m min}^{-1}$ ($10\text{--}20 \text{ mph}$)] and size of the liquid pool [small ($25.8\text{--}232.3 \text{ cm}^2$), medium ($412.9\text{--}929.0 \text{ cm}^2$), large ($2090.3\text{--}3716.1 \text{ cm}^2$), and very large ($8361\text{--}33\,445 \text{ cm}^2$)]. We evaluated distances of 0.3, 0.8, 1.5, 3, 6, 9, and 15 m ($\sim 1, 2.5, 5, 10, 20, 30,$ and 50 ft) to encompass a subset of likely distances that workers could have been positioned relative to the source. Assuming that the pool remains the same size for the duration of the task, the air concentration that a worker would have encountered at a specific position should be constant. With the plume model, the reported concentrations represent estimated exposures downwind from the source.

Finally, although we do not have any information that indicated that dispersant could form a pool on the water surface, we evaluated a worst-case scenario where a vessel could be located in pool sizes ranging from $840\,000$ to $4\,600\,000 \text{ cm}^2$ ($900\text{--}4900 \text{ ft}^2$). Considering that the dispersants are completely soluble in water, the spray application would have resulted in a dispersant film that was 0.005 mm (0.0002 in) thick. Considering wave action, it is very unlikely that a pool have existed more than a few seconds.

Estimates

Average 2-BE concentrations are reported for tasks with durations of 5, 10, and 15 min for both the near field and far field boxes. Durations for the plume model were

not relevant for estimation of air concentrations because an increase in duration does not affect the plume concentration, since buildup of concentrations would not have occurred due to the lack of air mixing between the two fields. The activity-related 2-BE vapor exposure statistics developed from both models were the arithmetic means (AMs), geometric means (GMs), geometric standard deviations (GSDs), 95th percentiles (%iles), and 90% confidence intervals (CIs). For the GuLF STUDY, we report the range of the possible means and mean GSDs across the various cases. For the two-box model a total of 72 cases were investigated, each using 10 000 iterations, reflecting the various combinations of source size, ACH, room size, and wind speed using the near field rectangular configurations described above. An additional 16 cases were run using a semi-hemisphere near field configuration with a 0.76 m radius to determine the impact of the near field configurations (analysis not shown), but it was found that the shape of the near field had little impact of the results of the analysis.

For the plume model, a total 30 cases were run (15 near field and 15 mid field), each using 10 000 iterations, corresponding to the 5 pools sizes and 3 wind speeds reported in [Table 1](#).

Equivalent PG and petroleum distillates exposures can be estimated from the 2-BE modeling results by comparing the evaporation rates of PG and petroleum distillates to the 2-BE evaporation rate. Thus, under the same conditions, PG and the petroleum distillates exposures are a factor only of the molecular weight and vapor pressure, i.e. 0.106 and 1.43 times, respectively, of the reported 2-BE level. To illustrate the use of these factors, from the Quantitative Measurements section above, we consider the two PG area samples collected (0.22 and 0.07 ppm) while filling the vented airport dispersant storage tanks. If the storage tank had been filled with 9527A, i.e. containing 2-BE, the expected 2-BE concentration for the same area samples would have been approximately $0.22/0.106 = 2.08 \text{ ppm}$ and $0.07/0.106 = 0.66 \text{ ppm}$, respectively.

Results

The complete set of 2-BE and PG concentration results using the two-box model and the plume model, i.e. the mean (as calculated from the Monte Carlo simulations) AMs, GMs, GSDs, 95th %iles, and the 90% CI are provided in [Supplementary Tables S4–S7](#) (available at [Annals of Work Exposures and Health](#) online). The petroleum distillates estimates are not shown because they cannot be differentiated from the THC concentrations related to the crude oil.

Estimates for OSRC workers

Two-box model

Possible mean estimates of workers' exposures to 2-BE in the near field ranged from approximately 966 to 5730 ppb as a 15-min average concentration (Table 2; Supplementary Table S4, available at *Annals of Work Exposures and Health* online) depending on the workplace conditions. The 15-min average AMs in the remainder of the room (far field) ranged from 219 to 3480 ppb, with most concentrations below 1000 ppb. The condition of low wind speed, medium surface area, low ACH, and small room size produced the highest estimated concentration for both near and far field. Values for PG are in Supplementary Table S5 (available at *Annals of Work Exposures and Health* online).

Plume model

Table 3 and Supplementary Table S6a and b (available at *Annals of Work Exposures and Health* online) present a summary of predicted exposures under conditions that workers would have likely encountered out of doors. The column at the distance of 0.767 m corresponds to the near field/mid field boundary in the two-box model. The near field mean 2-BE concentrations with small or medium surface area ranged from 12.4 to 261 ppb, considerably lower than those observed from the two-box model near field estimates of 966–5730 ppb. In contrast to the two-box model, the highest concentration (20 300 ppb) from the plume model was associated with low wind speed, approximately 0.3 m from a very large surface area. For the mid field at 3.0 m, predicted

mean concentrations were ~1.00 to 300 ppb across all evaluated size pools, wind speeds and mid field distances, with the highest concentrations under the same conditions as those of the near field. Values for PG are in Supplementary Table S7a and b (available at *Annals of Work Exposures and Health* online). Tables S6b and S7b (available at *Annals of Work Exposures and Health* online) present the hypothetical worst-case scenario present above where a vessel is located in a large pool of dispersant.

Estimates for Gulf Study participants

The workplace conditions for all three tasks for which we have study participant information were likely conducted out of doors near the source of the dispersant vapor. Table 4 identifies the task or activity, the TP, the location (within ~10 nmi (18 km) of the wellhead or >10 nmi [because 9527A (for 2-BE) was only used outside of the 10 nmi area] and the estimated AM concentration (ppb) and GSD for both 2-BE and PG. The model applied and the expected conditions identify where the work was likely performed (indoors or out of doors), which determines the two-box or plume model, the distance of the worker's breathing zone from the dispersant vapor source, the source of the vapor, such as pumps or tanks, the surface area size, and the wind speed. For example, for 'Maintained/worked on pumps/tanks that held dispersant', the tanks were assumed to be located outside. Even if the work had been conducted inside a tank, OSHA confined space entry regulations require that tanks have adequate forced air ventilation (typically

Table 2. Two-box model, 2-BE estimated AM concentrations for near field and far field.

Wind speed ^a	Surface area ^b	ACH ^c	Room size ^d	2-BE TWA AM (ppb)			2-BE TWA AM (ppb)		
				Near field ^d			Far field ^d		
				5 min	10 min	15 min	5 min	10 min	15 min
Low	Small	Low	Small	1160	1560	1880	437	819	1137
Low	Small	Low	Large	839	939	1010	98.1	188	264
Low	Medium	Low	Small	3520	4710	5730	1320	2480	3480
Low	Medium	Low	Large	2580	2890	3090	301	578	805
Low	Small	Medium	Small	1130	1450	1710	405	717	967
Low	Small	Medium	Large	822	907	966	90.1	162	219
Low	Medium	Medium	Small	3520	4530	5170	1260	2240	2930
Low	Medium	Medium	Large	2530	2790	2940	278	500	667

ppb, parts per billion; TWA, time-weighted average.

^aLow wind ranged from 3.75 to 26.8 m min⁻¹.

^bSmall surface areas ranged from 25.8 to 232.3 cm² and medium surface areas ranged from 412.9 to 929.0 cm².

^cLow ACH ranged from 1 to 3, medium ranged from 3 to 6 ACH.

^dThe near field small room size was 0.76, 0.76, and 1 m (2.5 by 2.5 by 3.3 ft). The far field small room size was 3 × 3 × 3 m (27 m³) and the far field large room size was 5 × 5 × 5 m (125 m³).

Table 3. Plume model, estimated 2-BE AM concentrations for near and mid field.

		Distance from source						
		Near field				Mid field		
Meters		0.303	0.767	1.521	3.00	5.91	8.82	15.60
Feet		0.99	2.52	4.99	9.84	19.40	28.90	51.20
Wind speed ^a	Surface area ^b	2-BE AM concentration (ppb)						
Low	Small	469	85.0	24.1	6.91	0.88	0.42	0.15
Medium	Small	128	23.2	6.58	1.89	0.23	0.11	0.04
High	Small	68.6	12.4	3.53	1.01	0.13	0.06	0.02
Low	Medium	1440	261	74.1	21.2	2.62	1.27	0.45
Medium	Medium	427	77.3	21.9	6.28	0.79	0.38	0.14
High	Medium	226	40.9	11.6	3.32	0.42	0.20	0.07
Low	Large	4260	771	219	62.7	7.62	3.69	1.31
Medium	Large	1280	232	65.7	18.8	2.34	1.13	0.40
High	Large	671	121	34.5	9.88	1.24	0.60	0.21
Low	Very large	20 300	3670	1040	299	37.2	18.0	6.42
Medium	Very large	5740	1040	295	84.6	10.5	5.08	1.81
High	Very large	3070	555	158	45.2	5.60	2.71	0.97

For abbreviations, see [Table 2](#).

^aLow wind ranged from 3.75 to 26.8 m min⁻¹, medium wind speed varied from 80.5 to 134.1 m min⁻¹, and high wind ranged from 268.2 to 536.5 m min⁻¹. For any wind speed value, the same value was used for the advective wind speed.

^bSmall surface areas ranged from 25.8 to 232.3 cm², medium surface areas ranged from 412.9 to 929.0 cm², large surface areas ranged from 2090.3 to 3716.1 cm², and very large surface areas ranged from 8361 to 33 445 cm².

20 ACH) in the immediate area of the worker, so that the ventilation was more like (low) outside wind speeds than those inside. Tanks have a relatively large surface area that could be contaminated with dispersant and maybe even have some pooled dispersant on the bottom. In TP1a, the tank could have contained either 9527A or 9500A if it was not located near the wellhead or 9500A only if it was near the wellhead. In [Table 3](#), at low wind and large surface area, the estimated 2-BE AM is 771 ppb at 0.77 m (2.5 ft) and 219 ppb at 1.52 m (5 ft). As we assumed that the individuals' activities placed the workers between 0.77 and 1.52 m, we assigned the average of the two values of 495 ppb 2-BE. The corresponding concentrations for PG were 81.8 and 23.2 ppb, respectively, averaging 52.5 ppb.

For most tasks, the surface area was estimated to be small or medium, except for tasks on the RVs, where the equipment used to monitor the oil plume was contaminated with dispersant from being in the water. The wind was generally considered to be low [0.14–1 mph (0.23–1.61 kph) to medium (3–5 mph, 4.8–8 kph) except in situations on the open water [i.e. for a moving RV 10–20 mph (16–32 kph)]. Time period also was considered because the dispersant containing the 2-BE (9527A) was only applied in TP1a, whereas PG was a component of both dispersants, and therefore was relevant to TP1a and TP1b.

We estimated dispersant concentrations from the unlikely scenario of there being a dispersant pool on the water surface. These conditions could be considered worst-case situations and depended on the location of the application. The first situation would have occurred in open waters if the aerial application had been conducted in TP1a and a vessel had entered a recently sprayed location 30 min after the spraying occurred (the earliest allowable amount of time as designated by the Responsible Party) ([Table 4](#)). If such a circumstance could have occurred and a film of dispersant could have remained on the water, workers on the vessel could have encountered 2-BE and PG vapors. In TP1b only 9500A was used and so only PG exposure was possible. Virtually all aerial applications occurred more than 10 nmi (18 km) from shore, where larger vessels were used, so the occupants' breathing zone was estimated to be at least 3 m (9 ft) above the water surface. Under these conditions, the 2-BE highest exposure estimates would have occurred at low winds with vessel pool surface areas of 30–70 square feet, i.e. 11.7 ppm (note units of ppm) and a corresponding PG concentration of 1.24 ppm. At approximately a 9 m height (88 ft) (for a larger marine vessel), the 2-BE concentration would be 0.71 ppm or a PG concentration 0.075 ppm (see [Supplementary Tables S6b and S7b](#), available at *Annals of Work Exposures and Health* online).

Table 4. Estimated exposures for work performed during OSRC.

Task/activity	Conditions	Time period	Can see the wellhead? ^a	2-BE AM (ppb) (GSD)	PG AM (ppb) (GSD)
Maintained/worked on pumps/tanks that held dispersant	Plume model: out of doors Distance: 0.77–1.52 m Source: pumps Surface area: small Wind speed: medium	TP1a	Yes	NA	2.46–0.70 ppb Ave = 1.58 ppb (1.465)
Maintained/worked on pumps/tanks that held dispersant	Plume model: out of doors Distance: 0.77–1.52 m Source: pumps Surface area: small Wind speed: medium	TP1a	No	23.19–6.58 ppb Ave = 14.9 (1.465)	2.46–0.70 ppb Ave = 1.58 ppb (1.465)
Maintained/worked on pumps/tanks that held dispersant	Plume model: out of doors Distance: 0.77–1.52 m Source: tanks Surface area: large Wind speed: low	TP1a	Yes	NA	81.8–23.2 ppb Ave = 52.5 ppb (2.190)
Maintained/worked on pumps/tanks that held dispersant	Plume model: out of doors Distance: 0.77–1.52 m Source: tanks Surface area: large Wind speed: low	TP1a	No	771–219 ppb Ave= 495 ppb (2.190)	81.8–23.2 ppb Ave = 52.5 ppb (2.190)
Maintained/worked on pumps/tanks that held dispersant	Plume model: out of doors Distance: 0.77–1.52 m Source: pumps Surface area: small Wind speed: medium	TP1b	Yes or No	NA	2.46–0.70 ppb Ave = 1.58 ppb (1.465)
Maintained/worked on pumps/tanks that held dispersant	Plume model: out of doors Distance: 0.77–1.52 m Source: tanks Surface area: large Wind speed: low	TP1b	Yes or No	NA	81.8–23.2 ppb Ave = 52.5 ppb (2.190)
Handled/pumped dispersant	Plume model: out of doors Distance: 0.77 m Source: handled/pumped Surface area: medium Wind speed: medium	TP1a	Yes	NA	8.19 ppb (1.324)
Handled/pumped dispersant	Plume model: out of doors Distance: 0.77 m Source: handled/pumped Surface area: medium Wind speed: medium	TP1a	No	77.3 (1.324)	8.19 ppb (1.324)
Handled/pumped dispersant	Plume model: out of doors Distance: 0.77 m Source: handled/pumped Surface area: medium Wind speed: medium	TP1b	Yes or No	NA	8.19 ppb (1.324)
Connect/disconnected hoses/lines used to transfer dispersant	Plume model: out of doors Distance: 0.77 m Source: connect/disconnects Surface area: small Wind speed: low	TP1a	Yes	NA	9.01 ppb (2.305)

Table 4. Continued

Task/activity	Conditions	Time period	Can see the wellhead? ^a	2-BE AM (ppb) (GSD)	PG AM (ppb) (GSD)
Connect/disconnected hoses/lines used to transfer dispersant	Plume model: out of doors Distance: 0.77 m Source: connect/disconnect Surface area: small Wind speed: low	TP1a	No	85.0 ppb (2.305)	9.01 ppb (2.305)
Connect/disconnected hoses/lines used to transfer dispersant	Plume model: out of doors Distance: 0.77 m Source: connect/disconnects Surface area: small Wind speed: low	TP1b	Yes or No	NA	9.01 ppb (2.305)
Worked on RV (Assumed moving)	Plume model: out of doors Distance: 3.0–5.91 m Source: water surface and equipment Surface area: very large Wind speed: high	TP1a	Yes	NA	4.79–0.59 ppb Ave = 2.69 ppb (1.465)
Worked on RV (Assumed moving)	Plume model: out of doors Distance: 3.0–5.91 m Source: water surface and equipment Surface area: very large Wind speed: high	TP1a	No	45.2–5.60 ppb Ave = 25.4 ppb (1.465)	4.79–0.59 ppb Ave = 2.69 ppb (1.465)
Worked on RV (Assumed moving)	Plume model: out of doors Distance: 3.0–5.91 m Source: water surface and equipment Surface area: very large Wind speed: high	TP1b	Yes or No	NA	4.79–0.59 ppb Ave = 2.69ppb (1.465)
Aerial application—dispersant pool (See SM ST6b for 2-BE and SM ST7b for PG)	Plume model: out of doors Distance: 3.0 m Source: vessel located in surface pool of dispersant Surface area: vessel pool Wind speed: low	TP1a	No	11 700 ppb (2.274)	1240 ppb (2.274)
Aerial application—dispersant pool (See SM ST7b for PG)	Plume model: out of doors Distance: 3.0 m Source: vessel located in surface pool of dispersant Surface area: vessel pool Wind speed: low	TP1b	No	NA	1240 ppb (2.274)
Vessel application—dispersant pool (See SM ST7b for PG)	Plume model: out of doors Distance: 10 and 30 m Source: vessel spraying dispersant source/hotzone Surface area: vessel pool Wind speed: low	TP1a and TP1b	Yes	NA	62.3–8.1 ppb Ave = 35.2 ppb (2.296)

^aIndicates location, i.e. yes = ≤10 nmi of the wellhead and therefore 2-BE was not possible because 9527A was not used there. No = >10 nmi where 9527A use occurred. RV, Research Vessel; SM, Supplemental materials; ST, Supplemental table located in the supplemental materials.

Another worst-case scenario is for the workers on vessels present in the wellhead area when dispersant was being sprayed onto the water surface by a vessel near the wellhead (Table 4). In this scenario, only 9500A dispersant was used, so only PG was evaluated. This area was restricted to large rigs, or marine or RVs, with deck heights of approximately 30 m (98 ft) (rigs) to 10 m (32 ft) (marine or RVs). We again assumed low wind and a pool size corresponding to the vessel pool sizes included in Table 1. For these workers, the predicted PG concentrations were 62 ppb at ~10 m) and 8 ppb at ~30 m if the vessel was 50 m downwind from where the dispersant was sprayed (Table 4).

Discussion

In this paper, we have modeled exposures to vapors from the volatile components of two dispersants to describe possible mean exposure levels of the workers performing dispersant-related tasks generating vapors under various workplace conditions and to inform the exposure assessment of the GuLF STUDY. Each of the modeling results generally relates to a single task performed over a short (e.g. <15 min) period of time, although activities such as tank cleaning may have taken a longer time. Based on the information available to us, we felt that it was likely that all activities related to handling dispersant in the Gulf Study were conducted outside where the plume model is appropriate. We also modeled using the two-box model so that our exposure assessment would be complete if additional information related to inside activities becomes available to future investigators or if future oil spills are characterized by indoor dispersant activities. Also, by presenting results using both models, we could determine the impact of selecting one model over the other.

In general, the two-box model exposure estimates were much higher than those from the plume model because air is exchanged between the boxes, meaning that some dispersant vapor returns from the far field box to the near field box, adding to the near field concentration. In contrast, for outdoor activities where the plume model was used, the estimates were generally much lower due to the much higher air flow rate (or wind speed) outdoors that moved the vapor away from the source. Thus, with the two-box model, the near field 15-min mean concentrations ranged from 966 to 5730 ppb 2-BE, whereas with the plume model the corresponding concentrations ranged from 85 to 261 ppb. The two-box model far field estimates represent the average exposures in the room outside of the near field without specifying a specific distance from the source and ranged

from 219 to 3480 ppb 2-BE depending on the room conditions. In contrast, the plume model requires the input of distance from the source; at a mid field distance of 3 m (~10 ft) from the source, the plume model concentrations ranged from 1 to 300 ppb 2-BE, with only the concentrations associated with a very large surface area (8361–33 445 cm²) generally being above 100 ppb 2-BE. Concentrations were even lower at greater distances.

The Hummel equation finds that wind speed had a major effect on the model estimates, primarily through its effect on the evaporation rate. With a small, 25.8 cm² pool and a low wind speed of 3.75–26.82 m min⁻¹, evaporation rates ranged between 3.17 and 8.47 mg min⁻¹. Surface area also was important to the evaporation rate. A small pool of 25.8 cm² (2 in²) versus a small pool of 103.2 cm² (4 in²) under a wind speed of 3.75 m min⁻¹ resulted in an evaporation rate change from 3.17 to 8.96 mg min⁻¹.

For the two-box model, holding ACH and room size constant, the mean exposure concentrations increased with increasing size of dispersant surface area (in addition to affecting the evaporation rate as described above). For example, when ACH was low and room size large, the 15-min near field mean increased from 1010 (small area) to 3090 ppb (medium), and the far field 15-min mean increased from 264 to 805 ppb, respectively. Room size was also important. Holding surface area and ACH constant (e.g. surface area = medium and ACH = low), the near field 15-min decreased from 5730 ppb in a small room to 3090 ppb in a large room. The corresponding far field 15-min mean decreased from 3480 to 805 ppb. Wind speed was not varied in this model because the model applied to conditions indoors or in protected areas and ACH appeared under our conditions to have a minimal impact on the 15-min mean. For a specific set of conditions, the mean concentrations also increased as exposure duration increased because the air flow rate in the room was likely insufficient to reduce the vapor concentration faster than the vapor was being generated.

The highest mean 2-BE concentrations (3520, 4710, and 5730 ppb) were observed near field in a small room (3 × 3 × 3 m = 27 m³) with a medium dispersant surface area (412.9–929.0 cm²), low wind (26.8 m min⁻¹), and low ACH (<3) for 5, 10, and 15 min, respectively. The corresponding far field mean 2-BE concentrations were 1320, 2480, and 3480 ppb, respectively. Examples of (two-box) tasks in the near field are cleaning a contaminated surface area inside an airplane or cleaning the inside of a tank that was not ventilated. Far field exposure could relate to the ambient concentration in the plane just described further from the source or

monitoring outside a tank while work was being done inside the tank.

The major variable to affect the plume model appeared to be wind speed, which also affected, as described above, the evaporation rate of the dispersant. Plume concentrations decreased with increasing wind speed. For example, with a medium surface area at a distance of 0.767 m from the source, the mean 2-BE concentrations were 261, 77.3, and 40.9 ppb at wind speeds of low, medium, and high, respectively. Surface area was also important. At constant wind speed (e.g. medium) at 0.767 m from the source, the 2-BE mean concentrations increased from 23.2 to 1040 ppb as the surface area increased from small to very large [8361–33 445 cm² (9–36 ft²)]. Small surface areas [25.8–232.0 cm² (0.03–0.25 ft²)] represent, for example, connects and disconnects of pipes and transfer lines, whereas medium areas [413–929 cm² (0.44–1.0 ft²)] represent surface areas for tank transfers, such as those that occurred between the OSVs and the *Skandi*. Tasks such as cleaning equipment or small spills likely had a surface area of medium to large. Large [2090–3716 cm² (2.25–4.00 ft²)] surface areas also could represent collecting samples from the water surface after dispersant had been applied but before all of the dispersant had been absorbed by the water and oil, and very large [8361–33 445 cm² (9–36 ft²)] areas could be dispersant-contaminated containers being cleaned and in the wellhead areas where vessel spraying was being done.

The highest observed 2-BE concentrations were observed with low wind speeds and very high surface areas. In this scenario, for a worker performing a task at arm's length [~2.5 ft. (0.767 m)], the mean concentration was predicted to be 3670 ppb, while at 5 ft (~2 m) from the surface area, the concentration was calculated to be 1040 ppb, such as during the collection of a water sample. For distances greater than 0.767 m from the source, the only modeled scenario where the 2-BE mean concentration exceeded 1000 ppb was where the surface area was very large and the wind low, and even in this case the concentration exceeded 1000 ppb only at distances less than 5 ft from the source.

Although specific information on the duration and frequency of relevant activities was not available, most of the activities evaluated here were likely of short duration. Thus, a comparison of the predicted levels to the current full-shift occupational exposure limits may be inappropriate. (If tasks or activities were performed multiple times per day, the frequency of these tasks, of course, needs to be considered in a daily average.) As a point of reference, established occupational full-shift exposure limits (OELs) for 2-BE vapor

are 50 ppm (OSHA's Permissible Exposure Limit) (OSHA, 2019), 20 ppm (ACGIH's Threshold Limit Value (TLV[®]) (American Conference of Governmental Industrial Hygienists (ACGIH), OSHA, 2019), and 5 ppm (NIOSH's Recommended Exposure Limit for up to 10 h d⁻¹) (OSHA, 2019). The ACGIH provides general guidelines referred to as excursion criteria for situations where exposures are short term, i.e. 'excursions in worker exposure levels may exceed three times the TLV[®]-TWA for no more than 30 min during a workday, and under no circumstance should they exceed five times the TLV[®]-TWA, provided that the TLV[®]-8-hr TWA is not exceeded' (ACGIH, 2019). Applying these excursion criteria to the most conservative 2-BE exposure limit (NIOSH's 5 ppm limit for up to 10 h), exposure should not exceed 15 ppm for more than 30 min per day, with a peak exposure of 25 ppm never to be exceeded. The appropriate metric to assess compliance with exposure limits is the 95th %tile. [Supplementary Table S4](#) (available at *Annals of Work Exposures and Health* online) reports the two-box model's possible %iles for various exposure scenarios that could be encountered during an oil spill. The near field 15-min 95th %iles ranged from 1.69 to 9.27 ppm 2-BE, the latter being associated with a low wind speed, medium surface area, low ACH, and small room. With the plume model ([Supplementary Table S6](#), available at *Annals of Work Exposures and Health* online), the 2-BE 95th %ile concentrations at 2.5 ft (0.767 m), ranged from 0.023 to 10.12 ppm for low wind speed and a very large surface area, such as could be associated with a worker inside a tank cleaning a wall. Thus, although the exposure levels were slightly lower than current excursion recommendations, the levels suggest exposures exceeding the thresholds could have occurred under certain conditions.

The only recommended OEL for PG was established by American Industrial Hygiene Association (AIHA) Workplace Environmental Exposure Levels (WEELs[®]) (American Industrial Hygiene Association, 2004) as 10 ppm for an 8-h TWA. Applying ACGIH's definition of excursions, the corresponding excursion levels for PG are 30 ppm for 30 min, never to exceed 50 ppm. The near field mean two-box model 95th %iles estimated for a 15-min mean exposure to PG in ranges of 0.018–2.25 ppm. The plume model estimates at 0.767 m (near field) ranged from 0.002 to 1.07 ppm ([Supplementary Tables S5 and S7](#), available at *Annals of Work Exposures and Health* online). Thus, it is not likely that PG exposures would have exceeded the excursion criteria under conditions described here. The purpose of this paper is to report estimated concentration levels rather than to assess compliance with occupational exposure limits.

One limitation of the task-related modeling is that the conditions under which the tasks were performed, including the location and the duration, were not observed by us, nor were the specific workplace conditions available to us. Rather, the conditions were characterized from available (and somewhat general) documentation and our extensive experience and so represent possible, not actual exposure estimates. We cannot be certain of the size of the sources in our scenarios or how diligent workers were in cleaning up spills. The dispersants do not have objectionable odors, so that workers may not have felt an urgency to avoid breathing in the vapors or clean up spills promptly. In this case, the surface areas may have been larger or the duration longer than we anticipated, resulting in an underestimation of exposure. In addition, the generalizability of the three personal measurements cited above to other workplaces also is not known. If the samples had been taken under idealized conditions, real exposures could have been higher than recorded. Based on the two PG areas samples collected by the RP, field storage tanks were vented to the atmosphere. We do not have any information on whether the dispersant tanks on the aircraft were vented or how close personnel were to tank vents. If the vents were a significant contributor to exposure compared with the activities and tasks performed, actual exposures may have been higher than those estimated with this modeling effort. On the other hand, as long as the tanks were vented outside under typical wind conditions on the Gulf [average hourly wind speed was approximately 10 mph (16 kph)] the plume model indicates that exposures would drop off very quickly with distance from the source. Severe conditions (i.e. at 0.1 m from the source at low wind and a very large surface area) resulted in the highest 2-BE AM concentration of 20.3 ppm (Table 3), but this is not likely to be a situation encountered by the study participants. At 0.767 m (~2.5 ft), the concentration dropped to 3.67 ppm and at 3 m (~10 ft), the estimated AM was calculated to be only 0.30 ppm. Note that for this severe scenario, concentrations are reported in ppm rather than ppb.

Another limitation is that the dispersant was not the only source of the 2-BE, PG, and petroleum distillates. All may have been contained in other mixtures such as decontamination solvents, which were used extensively. Thus, the modeled estimates developed may be on the low side of actual exposure levels. The contribution from those other sources, however, is likely to be small because the other sources likely had lower concentrations of volatiles and did not contain the surfactants that caused the components to reach a vapor pressure near that of the pure component. This composition would

have resulted in much lower evaporation rates than those observed with the neat dispersant. Second, all the modeling was conducted at 25°C (77°F). Temperature affects vapor pressure (evaporation rate) and the vapor pressure of most chemicals roughly doubles for every 10°C increase in the temperature of the liquid producing the vapor. The actual vapor pressure of the 2-BE and PG likely varied by less than a factor of two between when the dispersant was first sprayed in late April and when spraying ended in mid-July. Finally, we assumed from unpublished research that the vapor pressure of the components of a surfactant approached the vapor pressure of the pure component. If this is not the case, the results presented will have overestimated the actual exposures encountered in these activities.

A strength of this work is that the recognized models used here are credible and have been in use for over 20 years. Although there were few quantitative measurements available for us to validate our results, the models have been used in other situations where their performance has been compared with quantitative measurements. Arnold *et al.* (2017a, b) provide evaluations of model performance for the near field model for ten exposure scenarios involving a range of particulate and chemical contaminants. Contaminant concentrations ranged from low (<10% of the OEL) to high (>100% of the OEL). Those authors evaluated bias using the fractional (or normalized to make it dimensionless) bias equation. Fractional bias associated with the near field model estimates for the scenario with low exposure was 1.75, whereas the fractional bias for the scenarios with high exposures ranged from -1.28 to 0.91 (0 is considered as having no bias). Categorically, modeled exposure estimates agreed with measured estimates for 9/10 exposure scenarios. Though limited in size, these results suggest that levels may be overestimated at low exposures, but at high exposures bias is fairly low. The predicted values are also consistent with estimates that are derived from exposure assessment guidelines found in Stenzel (2015).

Another strength is that the models allowed a range in input parameters that provided the flexibility to populate the potential activities associated with dispersant handling across a range of conditions. Almost 100 scenarios involving liquid transfers were evaluated here to inform exposure levels possibly encountered by OSRC workers. Exposures from being in a sprayed area were also assessed, although this scenario was not very likely. Additionally, we performed Monte Carlo simulations that allowed for uncertainty in the input parameters for each scenario modeled, which is particularly important when the precise parameters are not known. These simulations also allowed for an estimation of variability, as evidenced in the GSDs.

These estimates were developed for the GuLF STUDY, an epidemiologic study investigating the potential adverse health effects arising from the OSRC work after the DWH disaster. Activities associated with OSRC work were predominately performed out of doors where there was likely some wind, so that the plume method was deemed to be the most applicable to the activities evaluated. Unfortunately, we combined maintained/worked on a pump with maintained/worked on a tank in our study questionnaire, so that we cannot distinguish which participants were doing each of those tasks. This lack of differentiation could result in overestimating exposure of the workers who performed the former and underestimating the exposures of those who performed the latter. Considering all the limitations described, there is not an obvious bias in one direction or the other that would suggest a substantial over or underestimation of exposures, but applying these exposure estimates to risk assessments is not advised.

Conclusions

The quantity of dispersant used in the DWH response and clean-up effort was unprecedented, but there were few quantitative measurements related to handling of dispersant-containing equipment. The use of publicly available and widely accepted exposure assessment models provided a mechanism to approximate exposure levels when handling this equipment. Modeled vapor exposure estimates for handling equipment containing the PG-containing dispersants (COREXIT™ EC9500A and COREXIT™ EC9527A) suggested low exposures compared with occupational guidelines. Vapor concentrations for the 2-BE-containing dispersant (COREXIT™ EC9527A) could potentially have resulted in short duration (peak) overexposures. These results can be used in job-exposure matrices to categorize the exposures of participants in the GuLF STUDY.

Supplementary Data

Supplementary data are available at *Annals of Work Exposures and Health* online.

Funding

This study was funded by the NIH Common Fund and the Intramural Research Program of the NIH, National Institute of Environmental Health Sciences (ZO1 ES 102945).

Acknowledgements

We thank Wendy McDowell and Caitlin Roush of McDowell Safety and Health Services, LLC for their assistance in compiling the study information.

Conflict of interest

The authors declare no conflict of interest relating to the material presented in this article. Its contents, including any opinions and/or conclusions expressed, are solely those of the authors.

Data availability

The data underlying this article will be shared on reasonable request, consistent with protections for the privacy of study participants and existing multiparty agreements. Requests should be made following instructions on the study website <https://gulfstudy.nih.gov>.

References

- American Conference of Governmental Industrial Hygienists. (2019) *Threshold limit values for chemical substances and physical agents & biological exposure indices*. Cincinnati, OH: ACGIH®.
- American Industrial Hygiene Association (AIHA). (2004) *Workplace Environmental Exposure Levels (WEELs®)*, propylene glycol (CAS No. 57-55-6). Available at <https://www.tera.org/OARS/WEELs.pdf>. Accessed 21 July 2021.
- Armstrong TW. (2009) Air dispersion plume models. In Simmons CE, Keil CB, Anthony TR, editors. *Mathematical models for estimating occupational exposures to chemicals*. Fairfax, VA: AIHA Press.
- Arnold SF, Shao Y, Ramachandran G. (2017a) Evaluation of the well mixed room and near-field far-field models in occupational settings. *J Occup Environ Hyg*; 14: 694–702.
- Arnold SF, Shao Y, Ramachandran G. (2017b). Evaluating well-mixed room and near-field-far-field model performance under highly controlled conditions. *J Occup Environ Hyg*; 14: 427–37.
- Baldwin PE, Maynard AD. (1998) A survey of wind speeds in indoor workplaces. *Ann Occup Hyg*; 42: 303–13.
- COREXIT™ EC9500A. (2019) Sugar Land, TX: COREXIT™ Environmental Solutions LLC. Available at <https://www.corexit.com/wp-content/uploads/2019/09/COREXIT%E2%84%A2-EC9500A-GHS-SDS-USA.pdf>. Accessed 31 August 2020.
- COREXIT™ EC9527A. (2019) Sugar Land, TX: COREXIT™ Environmental Solutions LLC. Available at <https://www.corexit.com/wp-content/uploads/2019/09/COREXIT%E2%84%A2-EC9527A-GHS-SDS-USA.pdf>. Accessed 31 August 2020.
- Drolet DT and Armstrong T. (2018) IHMOD 2.0© (MS Excel®) workbook of deterministic and Monte Carlo Simulation mathematical models to estimate airborne concentrations of chemicals. AIHA, EASC. © 2019 American Industrial Hygiene Association. All rights reserved. Available at <http://bit.ly/eascaiha>. Accessed 19 July 2021.
- Gorman Ng M, Cherrie JW, Sleuwenhoek A *et al.* (2021) GuLF DREAM: a model to estimate dermal exposure among oil spill response and clean-up workers. *Ann Work Expo Health*; 66: i218–i233.

- Groth CP, Banerjee S, Ramachandran G *et al.* (2021) Methods for the analysis of 26 million VOC area measurements during the *Deepwater Horizon* oil spill clean-up. *Ann Work Expo Health*; **66**: i140–i155.
- Groth CP, Huynh TB, Banerjee S *et al.* (2021) Linear relationships between total hydrocarbons and benzene, toluene, ethylbenzene, xylene, and *n*-hexane during the *Deepwater Horizon* response and clean-up. *Ann Work Expo Health*; **66**: i71–i88.
- Hummel AA, Braun KO, Fehrenbacher MC. (1996) Evaporation of a liquid in a flowing airstream. *Am Ind Hyg Assoc J*; **57**: 519–25.
- Huynh TB, Groth CP, Ramachandran G *et al.* (2021a) Estimates of occupational inhalation exposures to six oil-related compounds on the four rig vessels responding to the *Deepwater Horizon* oil spill. *Ann Work Expo Health*; **66**: i89–i110.
- Huynh TB, Groth CP, Ramachandran G *et al.* (2021b) Estimates of inhalation exposures to oil-related components on the supporting vessels during the *Deepwater Horizon* oil spill. *Ann Work Expo Health*; **66**: i111–i123.
- Huynh TB, Groth CP, Ramachandran G *et al.* (2021c) Estimates of inhalation exposures among land workers during the *Deepwater Horizon* oil spill clean-up operations. *Ann Work Expo Health*; **66**: i124–i139.
- Keil CB, Simmons CE, Anthony TR. (2009) *Mathematical models for estimating occupational exposure to chemicals*. 2nd edn. Fairfax, VA: AIHA.
- Lehr B, Bristol S, Possolo A. (2010) Oil Budget Calculator [WWW Document]. Available at https://www.restorethegulf.gov/sites/default/files/documents/pdf/OilBudgetCalc_Full_HQ-Print_111110.pdf. Accessed 6 January 2020.
- McGowan CJ, Kwok RK, Engel LS *et al.* (2017) Respiratory, dermal, and eye irritation symptoms associated with Corexit™ EC9527A/EC9500A following the *Deepwater Horizon* oil spill: findings from the GuLF STUDY. *Environ Health Perspect*; **125**: 097015.
- National Oceanic and Atmospheric Administration (NOAA) [Internet]. (2011) On scene coordinator report *Deepwater Horizon* oil spill. Submitted to the National Response Team, September 2011. NOAA. Available at <https://repository.library.noaa.gov/view/noaa/283>. Accessed 14 September 2020.
- Nicas M. (2009) The near field/far field (two-box) model with a constant contamination emission rate. In Keil CB, Anthony TR, editors. *Mathematical models for estimating occupational exposures to chemicals*. Fairfax, VA: AIHA Press.
- OSHA. (2019) Permissible Exposure Limits, OSHA annotated Table Z-1, 2-butoxyethanol (CAS 11-76-2). OSHA PEL, NIOSH REL, ACGIH 2019 TLV, 2019. Available at <https://www.osha.gov/dsg/annotated-pels/tablez-1.html>. Accessed 21 July 2021.
- Pratt GC, Stenzel MR, Kwok RK *et al.* (2021) Modeled air pollution from *in situ* burning and flaring of oil and gas released following the *Deepwater Horizon* disaster. *Ann Work Expo Health*; **66**: i172–i187.
- Ramachandran G, Groth CP, Huynh TB *et al.* (2021) Using real-time area VOC measurements to estimate total hydrocarbons exposures to workers involved in the *Deepwater Horizon* oil spill. *Ann Work Expo Health*; **66**: i156–i171.
- Stenzel M. (2015) Rules and guidelines to facilitate professional judgment. In Jahn S, Bullock WH, Ignacio JS, editors. *A strategy for assessing and managing occupational exposures*. 4th edn. Fairfax, VA: AIHA.
- Stenzel MR, Groth CP, Huynh TB *et al.* (2021) Exposure group development in support of the NIEHS GuLF STUDY. *Ann Work Expo Health*; **66**: i23–i55.
- Stenzel MR, Arnold SF, Ramachandran G *et al.* (2021) Estimation of airborne concentrations of oil dispersants COREXIT™ EC9527A and EC9500A, volatile components associated with the *Deepwater Horizon* oil spill response and clean-up operations. *Ann Work Expo Health*; **66**: i202–i217.
- Stewart PA, Gorman Ng M, Cherrie JW *et al.* (2021) Estimation of Dermal Exposure to Oil spill Response and Clean-up Workers after the *Deepwater Horizon* Disaster. *Ann Work Expo Health*; **66**: i234–i246.
- Stewart P, Groth CP, Huynh TB *et al.* (2021) Assessing Exposures from the *Deepwater Horizon* Oil Spill Response and Clean-up. *Ann Work Expo Health*; **66**: i3–i22.