

Effectiveness and potential ecological effects of offshore surface dispersant use during the Deepwater Horizon oil spill: a retrospective analysis of monitoring data

Adriana C. Bejarano · Edwin Levine ·
Alan J. Mearns

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Abstract The Special Monitoring of Applied Response Technologies (SMART) program was used during the Deepwater Horizon oil spill as a strategy to monitor the effectiveness of sea surface dispersant use. Although SMART was implemented during aerial and vessel dispersant applications, this analysis centers on the effort of a special dispersant missions onboard the *M/V International Peace*, which evaluated the effectiveness of surface dispersant applications by vessel only. Water samples ($n=120$) were collected from background sites, and under naturally and chemically dispersed oil slicks, and were analyzed for polycyclic aromatic hydrocarbons (TPAHs), total petroleum hydrocarbons (TPH), and a chemical marker of Corexit® (dipropylene glycol *n*-butyl ether,

DPnB). Water chemistry results were analyzed relative to SMART field assessments of dispersant effectiveness (“not effective,” “effective,” and “very effective”), based on in situ fluorometry. Chemistry data were also used to indirectly determine if the use of dispersants increased the risk of acute effects to water column biota, by comparison to toxicity benchmarks. TPAH and TPH concentrations in background, and naturally and chemically dispersed samples were extremely variable, and differences were not statistically detected across sample types. Ratios of TPAH and TPH between chemically and naturally dispersed samples provided a quantitative measure of dispersant effectiveness over natural oil dispersion alone, and were in reasonable agreement with SMART field assessments of dispersant effectiveness. Samples from “effective” and “very effective” dispersant applications had ratios of TPAH and TPH up to 35 and 64, respectively. In two samples from an “effective” dispersant application, TPHs and TPAHs exceeded acute benchmarks (0.81 mg/L and 8 µg/L, respectively), while none exceeded DPnB’s chronic value (1,000 µg/L). Although the primary goal of the SMART program is to provide near real-time effectiveness data to the response, and not to address concerns regarding acute biological effects, the analyses presented here demonstrate that SMART can generate information of value to a larger scientific audience. A series of recommendations for future SMART planning are also provided.

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A. C. Bejarano (✉)
Research Planning, Inc,
1121 Park Street,
Columbia, SC 29201, USA
e-mail: abejarano@researchplanning.com

E. Levine
National Oceanic and Atmospheric Administration,
1 South St,
New York, NY, 10004, USA

A. J. Mearns
National Oceanic and Atmospheric Administration,
7600 Sand Point Way NE,
Seattle, WA 98115, USA

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Introduction

The use of chemical dispersants to mitigate the threat of offshore oil spills is a response option preauthorized under conditions specified in the US National Oil and Hazardous Substances Pollution Contingency Plan, often referred to as the NCP (40 CFR Part 300, Section 300.910; USEPA 1994). During the Deepwater Horizon (DWH) oil spill, and in accordance with the NCP, the Region VI Regional Response Team (RRT) had the authority to preauthorize the use of dispersants via aircraft or vessels in waters offshore of Louisiana (3 nm offshore or water depths >10 m; RRT 6 2001). The implementation of the use of dispersants during the DWH response ultimately resided with the Federal On Scene Coordinator (FOSC). The FOSC deemed necessary the use of dispersant to primarily protect workers from exposure to volatile organic compounds near the wellhead, and secondarily to reduce the amount of impacts from surface oil on shoreline habitats. As a result, both Corexit® 9500A and Corexit® 9527A were used at the water surface, resulting in the application of ~25,505 barrels (bbl) of dispersants on approximately 790 km² over 87-days (Lehr et al. 2010).

During the DWH incident, the use of dispersants at the water surface faced great challenges including decreased dispersant effectiveness¹ with increased oil emulsion thickness, time at sea, viscosity and oil evaporation loss by weight (Leirvik et al.² unpublished). Hundreds of samples from oil slicks off Louisiana and Texas were substantially weathered (>80 % total TPAH depletion of oil by hopane; Brown et al. 2011). These more heavily weathered and viscous oils with high water content required dispersant to oil ratios (DOR) as low as 1:25 for an evaporative oil loss by weight, an indirect measure of dispersant effectiveness, greater than 40 % (Leirvik et al. unpublished). As a comparison, the standard aerial application of dispersants recommended for moderately weathered emulsions (1 mm slick thickness) is at a DOR of 1:200, equivalent to 5 gallons of dispersants per acre, with lower DORs (1:120) for dispersant applications from vessels (Leirvik et al. unpublished).

¹ Defined as the amount of oil that is dispersed into the water column relative to the amount that remains on the surface

² During the DWH oil spill, several investigations were undertaken by SINTEF, Norway, on the dispersability of the oil. Some of these reports are not available in the public domain.

Several dispersant monitoring strategies were in place during the DWH to assess the effectiveness of surface dispersant operations (RRT 6 2001). One such program was the Special Monitoring of Applied Response Technologies (SMART) program (USCG et al. 2006) conducted by trained personnel from the US Coast Guards with contractor support. The implementation of the SMART program is a condition required by the RRT during offshore use of dispersants (RRT 6 2001). The SMART program allows for rapid collection of quantitative and qualitative data on the effectiveness of dispersant applications, and it relays real-time scientifically based information to the Unified Command, facilitating operational decisions on the use of dispersants. Information generated through the implementation of the SMART program can help the Unified Command determine when the use of dispersants does not provide an additional benefit from that obtained through natural oil dispersion, and when dispersant use is no longer effective in removing oil from the water surface and into the surrounding media (air and water column). During the DWH, all three tiers of the SMART program were implemented: Tier I—visual observation, Tier II—in situ fluorometry monitoring at 1 m depth, and Tier III—in situ fluorometry monitoring at 1 and 10 m depths with collection of water samples for chemical analyses. Fluorometry monitoring of dispersed oil concentrations in the water column provides a semi-quantitative measure of dispersant effectiveness by comparing changes in fluorescence (emitted by aromatic hydrocarbon molecules) relative to natural background fluorescence (Henry et al. 1999). Although the definition of an effective dispersant application is spill-specific, “effective” dispersant applications are typically detected when fluorometry readings are five times above background at least 1 m below the surface.

The SMART program has evolved over the last decade and has provided high value information to spill responders. Gugg et al. (1999) described the usefulness of fluorometry and visual observations during two spills in 1998 in the Gulf of Mexico: the rupture of the High Island Pipeline releasing 2,500 bbl of sweet crude oil and a hole in the tank of the *T/S Red Seagull* releasing 600 bbl of medium Arabian crude. Both these spills were treated with Corexit® products, and oil dispersability was characterized by SMART field assessment teams as “effective,” as in situ fluorometry post-dispersant application was well above background levels. Similarly, the

rupture of the Poseidon Pipeline 65 miles off Houma, Louisiana, in 2000 released approximately 2,000 bbl of oil into the Gulf of Mexico forming an oil slick that was treated with Corexit® 9527 (Stoermer et al. 2001). The day of the incident SMART-Tier II teams reported 75 % dispersion of the oil slick treated with the dispersant, while a day later reduced oil dispersability and dispersant effectiveness (Stoermer et al. 2001) triggered the end of dispersant use. More recently, implementation of the SMART-Tier I and II program during the Montara wellhead blowout off the Western Australian showed that given the lack of optimal hydrodynamic conditions and calm weather, dispersant use was effective (fluorescence >5 times above background) only when mechanical mixing energy was introduced via vessel transects (Tan 2011).

The usefulness of in situ fluorometry monitoring of chemically dispersed oil is greatly amplified by chemical analysis of field collected samples (Henry et al. 1999). Chemical analysis of water samples collected before and after dispersant use can quantitatively verify field observations regarding dispersant effectiveness. Water sampling can also be useful in assessing potential risks to water column biota from exposure to oil constituents after dispersant use via laboratory and in situ toxicity testing, or by comparisons of oil constituents to thresholds of concern.

Data collected as part of the SMART-Tier III program during the DWH oil spill were intended to provide information and guidance to the oil spill response community, and to generate information for operational decisions, but not to test scientific hypotheses or to address any concerns regarding injuries to water column biota. However, the results of water chemistry analyses from water samples collected by the SMART-Tier III program during the spill provided an opportunity for a retrospective analysis of: (1) field assessments of dispersant effectiveness, based on in situ fluorometry, relative to changes in oil constituent concentrations before and after dispersant use, and (2) the potential risk of acute effects to water column biota from exposures to oil constituents and a chemical marker of the dispersant Corexit® by comparison to toxicity benchmarks. Conclusions emerging from the analyses presented here can help inform future planning for use of SMART protocols and dispersant applications.

Materials and methods

Sample collection

When first developed, the SMART monitoring program was envisioned for situations of limited geographic scope and duration, and not for a long-term operational response of the magnitude of the DWH oil spill. During the response, aerial spraying of dispersants from planes applied the bulk of the dispersants over oil slicks within a prescribed area of the Gulf of Mexico [see Electronic supplementary material (ESM)]. These dispersant applications were monitored by SMART field assessment teams who were ready to collect fluorometry data and water samples for chemical analysis from areas where dispersant were applied. Because of the large scale of the prescribed zone for offshore dispersant use, it was difficult for the SMART teams to monitor and sample every dispersant application. Consequently, a special research mission that went beyond regulatory requirements was created to assist in a more thorough field assessment of dispersant effectiveness. As a result, a mission onboard the *M/V International Peace*, a vessel equipped with a dispersant spray system and SMART-Tier III capabilities, was undertaken to target specific oil slicks and to evaluate the effectiveness of surface vessel dispersant applications (BenKinney et al. 2011a; BP 2010). These oil slicks had the same physical characteristics of oil slicks targeted for aerial surface dispersant application. As part of the mission onboard the *M/V International Peace*, SMART-Tier III field teams collected in situ fluorometry data, while consultants collected unfiltered water samples for chemical analyses. Both, fluorometry data and water samples were collected at 1 and 10 m depths from background sites (no oil slicks observed at the water surface), and under oil slicks before and shortly after (generally 30 min) surface vessel dispersant applications (see ESM); hereafter termed naturally and chemically dispersed samples. Background, and naturally and chemically dispersed samples were generally collected from the same area (average radius of 800 m) during the same surface dispersant application event. Chemical analyses were performed on these unfiltered water samples to quantify total polycyclic aromatic hydrocarbons (TPAH; sum of 43 PAHs including alkyl homologues), total petroleum hydrocarbons (TPH; sum of C9-C40), and dipropylene glycol n-butyl ether (DPnB; CAS# 29911-28-2), a chemical marker of

Corexit® (BenKinney et al. 2011a; BP 2010). TPAH is the fractions of the oil that causes acute and chronic toxicity via narcosis, while the TPH fraction is generally less bioavailable and is considerably less acutely toxic than TPAHs. Chemical analyses followed standard procedures: modified EPA method 8270 for TPAHs and DPnB, and modified EPA Method 8015C for TPHs. In a few cases, SMART field assessment teams also collected information on the size and concentration of oil droplets in the water column via laser in situ scattering and transmissometry (LISST-100X, 100X, Sequoia Scientific Inc. Seattle, WA). All sampling protocols and analyses were carefully implemented for field conditions following multiagency requirements established during the DWH oil spill. Data collection as part of this special mission was intended to support the Unified Command with scientific information to help inform surface dispersant application decisions.

Oil dispersant effectiveness

Dispersant effectiveness was assessed by field teams following standard SMART guidance documents (USCG et al. 2006). Using in situ fluorometry, SMART field assessment teams categorized dispersant effectiveness after each vessel dispersant application as “not effective” (fluorometric readings indistinguishable from background), “effective” (fluorometric readings 1.5–3 times above background) or “very effective” (fluorometric readings >3 times above background).

Water samples taken by consultants for chemical analysis were matched to the geo-referenced position of SMART field assessment teams, and comparisons were made between SMART teams’ assessment of dispersant effectiveness based on in situ fluorometry, and measured TPAH and TPH concentrations in samples from the same water body. At each site and by depth, TPAH or TPH ratios between chemically (post-dispersant application) and naturally dispersed concentrations (pre-dispersant application) were calculated to provide a quantitative measure of dispersant effectiveness over natural oil dispersion alone.

Characterization of effects from oil constituents

Analytical results for TPHs and TPAHs were used to determine if chemical dispersion of oil slicks from surface dispersant applications during the DWH oil

spill increased the risk of acute effects to water column biota from both, oil and dispersant constituents, by means of comparisons to toxicity benchmarks.

For the purpose of this analysis, an acute TPH benchmark was developed using acute toxicity data from studies reporting TPH concentrations following exposure of aquatic organisms to oil chemically dispersed with Corexit® products (mostly Corexit® 9500). A literature review was conducted, and only data from studies that met the following criteria were included in the estimation of this benchmark: reported dispersant to oil ratio (DOR) 1:10 or 1:20, and TPH reported as C7-C30, C8-C42, or C10-C36. Given data limitations, distinctions were not made among source oils, oil-weathering stages, and between tests using freshwater and seawater species, or life stages. Data included mostly mortality (median lethal concentration, LC50), as well as a few data points from sub-lethal (median effective concentration, EC50) endpoints (e.g., fertilization success, blue sac disease, CYP1A induction) (Aurand et al. 2009; Aurand and Coelho 2005; Clark et al. 2001; Fuller et al. 2004; Greer et al. 2012; Gulec et al. 1997; Hemmer et al. 2011; Lin et al. 2009; McIntosh et al. 2010; Mitchell and Holdway 2000; NCP 2012; Pace et al. 1995; Perkins et al. 2003, 2005; Pollino and Holdway 2002; Ramachandran et al. 2004; Rhoton et al. 2001; M. Singer et al. 1998; Singer et al. 2001; Wetzel and Van Fleet 2001; Wu et al. 1998). Efforts were made to identify laboratory exposure durations realistic of field conditions (a few hours), but since 96-h exposures had a larger number of species tested than shorter exposures (i.e., 24 h), these data were used to construct a TPH Species Sensitivity Distribution (SSD; Posthuma et al. 2002). The 96-h SSD was generated by plotting the geometric mean of effects concentration by species in order of decreasing sensitivity. Under the assumption of a log-normal distribution, the SSD was re-sampled 2,000 times to derive the fifth percentile hazard concentration (HC₅) and its associated 95 % confidence interval (95 % CI; Bejarano and Farr 2013; Posthuma et al. 2002). The HC₅ value corresponds to the chemical concentration that is assumed to be protective of 95 % of the species tested. For the purpose of this analysis, the lower bound confidence interval of the HC₅ was used as a conservative TPH benchmark.

Potential acute effects from exposures to a co-existent mixture of 43 PAHs (assuming PAH additive toxicity via narcosis) were characterized using

the Equilibrium Partitioning Benchmark Toxic Unit approach (USEPA 2003; hereafter TPAH-EBTU_{FAV, 43}). This approach was developed by establishing a causally link between PAH-specific concentrations and toxicological effects to several aquatic species (USEPA 2003), and it facilitates comparisons across samples under a protective scheme. Using this approach, samples with TPAH-EBTU_{FAV, 43} values greater than one may have had TPAH mixture concentrations unacceptable for the protection of aquatic organisms. For the purpose of this analysis, the lowest TPAH concentration at which TPAH-EBTU_{FAV, 43} >1 was used as the TPAH benchmark.

Characterization of effects from a dispersant constituent

During the DWH oil spill, DPnB was used as a chemical marker for the presence of Corexit®. In response to the spill, the USEPA established an aquatic life chronic benchmark for DPnB equivalent to 1,000 µg/L (OSAT 2010) as the screening level above which dispersant applications were restricted. Although an attempt was made to refine this benchmark, little acute toxicity data exist for this chemical, and therefore the USEPA chronic value was used as a benchmark in the analyses presented here.

Small particle distribution

The detection and quantification of oil droplets in the water column (0–12 m depths), as well as their size and concentration, were performed by SMART field assessment teams via laser in situ scattering and transmissometry (LISST) following the standard methodology used during subsea dispersant applications (JAG 2011,³ unpublished, Li et al. 2011).

Oil droplet size distribution and concentration is another indicator of dispersant effectiveness as the chemical dispersion of the oil emulsion facilitates the formation of oil droplets (typically <70 µm in diameter) that easily disperse into the water column by wave action. LISST data from background, and naturally and chemically dispersed sites were collected on four

different occasions. Because of limited LISST sampling during surface dispersant applications, LISST data shown here are the maximum small particle (<70 µm in diameter) concentration by depth for the combined observations by water type (background, naturally and chemically dispersed).

Results

The SMART-Tier III special mission onboard the *M/V International Peace* collected 120 water samples from 18 locations between May 17 and July 13, 2010. At each site, between one and three samples were collected at 1 and 10 m depths from each treatment type: background, naturally (pre-dispersant application) and chemically (post-dispersant application) dispersed oil. The total number of 1 and 10 m depth samples analyzed for TPAH, TPH and DPnB were 70 and 50, respectively.

Oil dispersant effectiveness

TPAH and TPH concentrations in water samples were variable (range, <0.01–77.33 µg TPAH/L, <0.01–5.1 mg TPH/L), and statistically significant differences ($p>0.05$; Kruskal–Wallis non-parametric ANOVA test) were not found across background samples, and naturally and chemically dispersed oil samples. However, samples collected at 1 m depth had an increasing trend in TPAH and TPH concentrations from the “not effective” (mean, 0.94 µg TPAH/L, 0.06 mg TPH/L) to the “very effective” (mean, 10.47 µg TPAH/L, 0.96 mg TPH/L) categories (based on in situ fluorometry; Fig. 1). No such trend was observed in samples collected at 10 m depth. Except for background and “not effective” samples, TPAH concentrations at 1 m depth were statistically significantly higher ($p<0.05$; Kruskal–Wallis non-parametric ANOVA test) than those from 10 m depths, even in naturally dispersed areas (median 1 m vs. 10 m, naturally dispersed 2.71 vs. 0.19 µg TPAH/L; “effective” 3.73 vs. 0.13 µg TPAH/L; “very effective” 8.18 vs. 0.29 µg TPAH/L).

Ratios of chemically-to-naturally dispersed TPAHs and TPHs were calculated to provide a quantitative measure of dispersant effectiveness over natural oil dispersion alone. Ratios >1 indicate increased concentration of oil constituents in the water column beneath the oil slick after dispersant applications. Ratios of

³ The Joint Analysis Group (JAG; <http://www.ncddc.noaa.gov/activities/healthy-oceans/jag/>) was a multiagency working group created during the DWH oil spill to analyze data and information generated through the response by several ongoing surface and sub-surface sampling efforts.

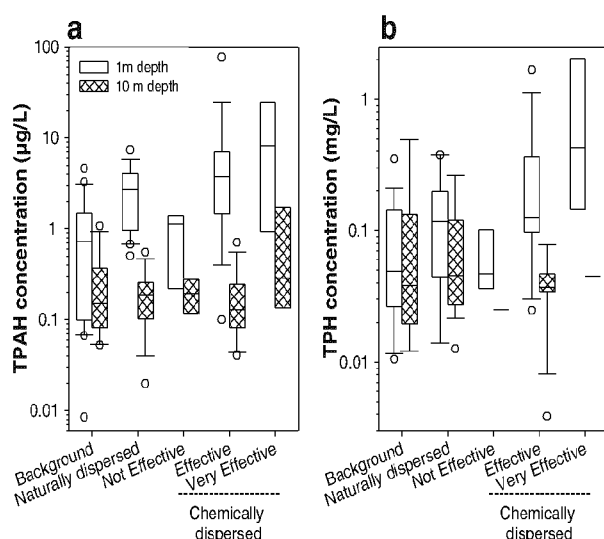


Fig. 1 Box-plots of TPAH (a) and TPH (b) concentrations in samples collected from background areas, and before and after surface dispersant applications, and by the SMART program's characterization of dispersant effectiveness, based on in situ fluorometry. The length of the box represents the distance between the 25th and the 75th percentiles, while the whiskers represent the 5th and 95th percentiles. The horizontal line in the box represents the median, while the open circles indicate potential outliers

chemically-to-naturally dispersed TPAHs and TPHs showed a reasonable agreement with SMART field teams' fluorometry-based assessments of dispersant effectiveness, particularly at 1 m depth (Fig. 2). At 1 m depth, TPAH and TPH ratios were >1 in 56 and 68 %, respectively, of the dispersant operations categorized by SMART field assessment teams as "effective" and "very effective." In these "effective" and "very effective" operations, TPAH ratios ranged from 1.2 to 35 (median 6), and TPH ratios ranged from 1.2 to 64 (median 5). In "not effective" dispersant operations, TPAH and TPH ratios were ≤ 1 in 100 and 86 %, respectively, and all but one of these TPH ratios were <1 . At 10 m depth, TPAH and TPH ratios were >1 in 61 and 43 %, respectively, in "effective" and "very effective" dispersant operations. In these dispersant operations, TPAH ratios ranged from 1.1 to 12 (median 1.3), while TPH ratios ranged from 1.1 to 3 (median 2). Similarly, in "not effective" dispersant operations TPAH and TPH ratios were ≤ 1 in 75 and 100 %, respectively, and all but one of the TPAH ratios were <1 . Greater ratios at 1 m than at 10 m depth are consistent with a greater dilution of oil constituents from the treated oil slick, while concentrations of TPAH and TPH at 10 m may have resulted from natural dispersion.

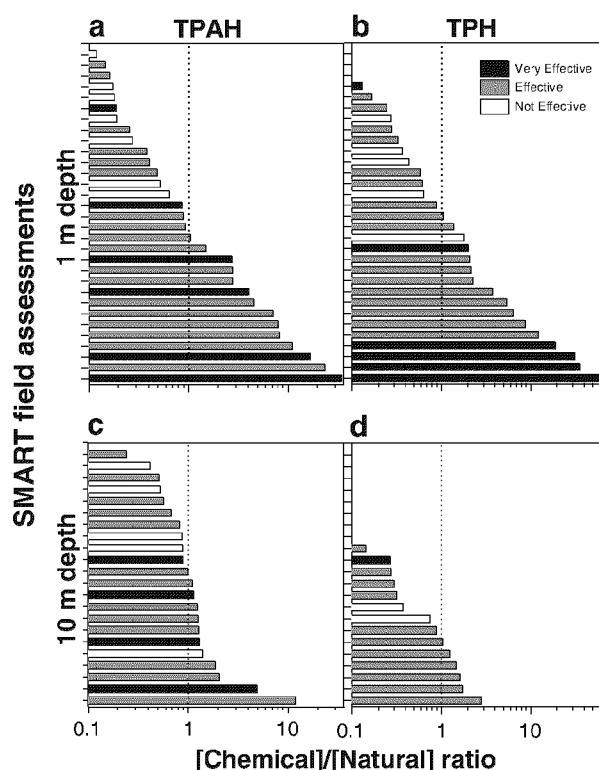


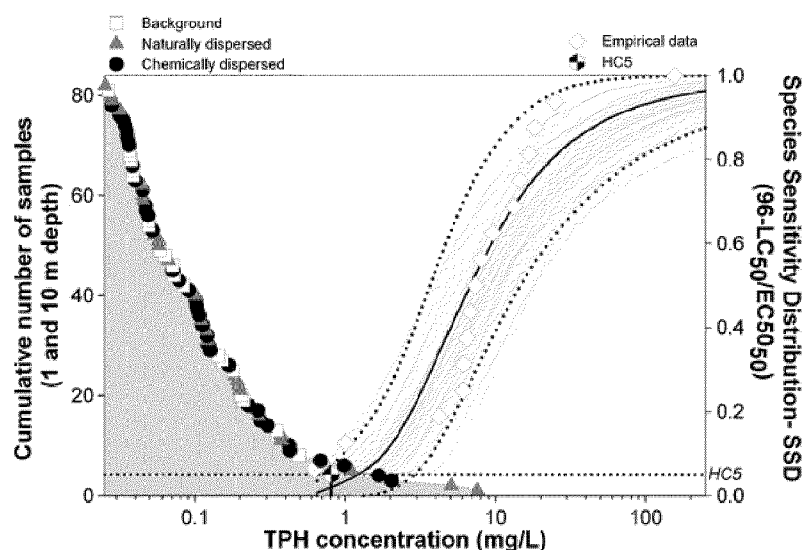
Fig. 2 Ratios of chemically-to-naturally dispersed TPAH (a, c) and TPH (b, d) concentrations by depth in samples collected in the same general area before and after dispersant applications. Bar colors represent SMART field assessment teams' characterization of dispersant effectiveness, based on in situ fluorometry, while the dotted lines show a ratio equal to one

Characterization of effects from oil constituents

The 96-h Species Sensitivity Distribution (SSD) curve generated via re-sampling of the empirical data yielded a TPH fifth percentile hazard concentration (HC_5) and associated 95 % confidence interval (95 % CI) of 1.68 mg/L (0.81–3.36 mg/L; Fig. 3). This concentration is assumed to be protective of 95 % of the species tested. For the purpose of this analysis, the lower 95%CI value (0.81 mg/L) was used as a conservative acute TPH benchmark. The large majority of field water samples (94 %) were below this benchmark, with the exception of three samples collected before and three samples collected after dispersant applications; all but one of these six samples were collected at the water surface.

Five samples collected at 1 m depth after dispersant application had $TPAH-EBTU_{FAV,43} > 1$, suggesting that in these samples TPAH concentrations may have been unacceptable for the protection of aquatic organisms.

Fig. 3 TPH concentrations in samples collected by SMART field teams from background (*squares*), and naturally (*gray triangles*) and chemically (*black circle*) dispersed samples relative to the Species Sensitivity Distribution (SSD) curve derived using empirical toxicity data (*white diamonds*). The SSD includes the mean (*solid line*) and 95 % CI (*dotted lines*; left lower 95 % CI) values derived by re-sampling (*light gray lines*) the empirical data 2,000 times. The *semi-filled dot* represents the lower 95 % CI of the HC₅ (0.81 mg/L)



In all these cases, 74–83 % of the overall TPAH-EBTU_{FAV,43} was attributed to the high molecular weight PAHs C1-C4 Chrysenes, C2-C4 Phenanthrenes/Anthracenes, and C2-C3 Fluoranthenes/Pyrenes. In these samples, the presence of high molecular weight PAHs, combined with detection of linear alkane analytes with low solubility and recalcitrant characteristic (i.e., phytane, pristane), suggested the presence of particulate oil droplets. TPAH-EBTU_{FAV,43} >1 were not found in samples collected at 10 m depth. TPAH concentrations in samples exceeding TPAH-EBTU_{FAV,43} >1 were above 8 µg/L. Thus, this value was used in this analysis as the TPAH benchmark.

A concurrent comparison of TPH and TPAH concentrations across all water samples relative to their acute benchmarks (Fig. 4) showed that these values were exceeded in two samples collected at the water surface from “effective” surface dispersant applications. Only one sample at 10 m depth from a naturally dispersed site exceeded the TPH, but not the TPAH benchmark.

Characterization of effects from a dispersant constituent

None of the samples analyzed here exceeded the USEPA chronic value (1,000 µg/L) for DPnB, and in only one sample at 1 m depth the concentration exceeded 100 µg/L (Fig. 5). At 1 m depth in samples collected after surface dispersant applications, there was a positive correlation between DPnB and both, TPAH

($r^2_{\text{adj}}=0.63$; $p=0.0001$) and TPH ($r^2_{\text{adj}}=0.48$; $p=0.0017$) concentrations. Given these trends, it is not surprising that only samples with high DPnB concentrations, from “effective” and “very effective” dispersant applications based on in situ fluorimetry, exceeded acute TPAH and TPH benchmarks. Interestingly, trace amounts of DPnB (<3 µg/L) were found in samples from 1 m and 10 m depths from some background and naturally dispersed areas, presumably from previous dispersant application operations.

Small particle distribution

Limited data were collected by the SMART program for analysis of small particle concentration (<70 µm diameter), though a few observations were taken from background, and naturally and chemically dispersed areas. With a few exceptions, maximum small particle concentration in samples collected in background waters was between 0.2 and 0.6 µl/L and relatively constant throughout the water column (water surface to 12 m depth; Fig. 6). Particle concentration among samples collected before dispersant applications was generally lower in deeper waters (≥ 6 m; 0.2–0.6 µl/L), but higher at the surface (<6 m depth; 0.4–0.9 µl/L). By contrast, particle concentrations after dispersant applications were generally between 0.6 and 0.9 µl/L at water depths ≤10 m. Samples from naturally and chemically dispersed sites had particle concentrations relatively higher at the water surface (<2 m depth). The clear shift in the distribution of

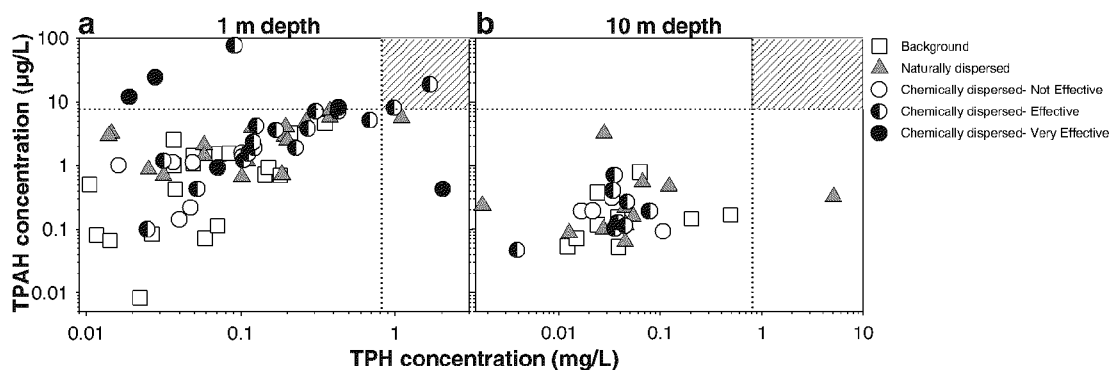


Fig. 4 Comparison of measured TPAH (a) and TPH (b) concentrations relative to their benchmarks (8 µg/L and 0.81 mg/L, respectively; dotted lines). The shaded area indicates exceedances of both benchmarks. Symbols represent samples from background (white squares), naturally dispersed (gray

triangles) and chemically dispersed (circles) areas by SMART field assessment teams' characterization of dispersant effectiveness—"not effective" (white circle), "effective" (partially filled circle), "very effective" (black circle)

small particles across category types is also evident in the sample distribution of all LISST data. While most (90 %) background observations had small particle concentrations in the 0.15–0.45 µm range, small particle concentrations, particularly in chemically dispersed samples (60 %), were ≥ 0.45 µm, indicating a higher concentration of oil droplets.

Discussion

Oil dispersant effectiveness

In this analysis, ratios of chemically-to-naturally dispersed TPAHs and TPHs were up to 35 and 64, respectively, in samples collected at 1 m. This increase in the

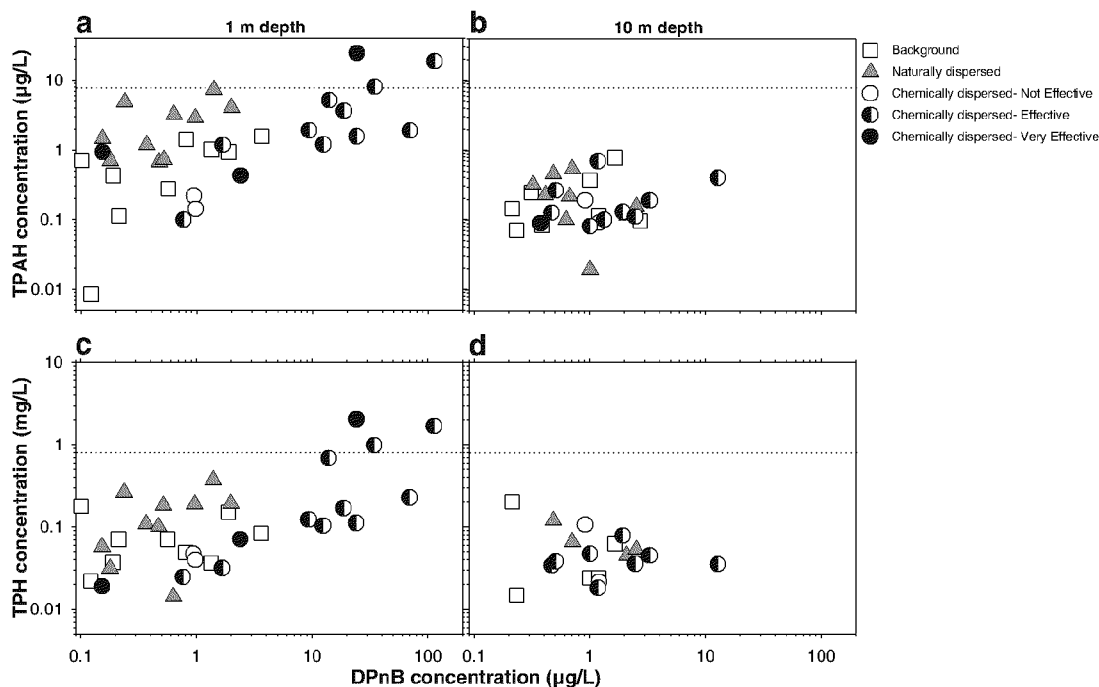


Fig. 5 Comparison of TPAH (a, b) and TPH (c, d) concentrations relative to the concentration of a chemical marker of Corexit® (dipropylene glycol *n*-butyl ether, DPnB). Dotted lines represent TPAH and TPH benchmarks (8 µg/L and 0.81 mg/L, respectively). Symbols represent samples from background

(white squares), naturally dispersed (gray triangles) and chemically dispersed areas by SMART field assessment teams' characterization of dispersant effectiveness—"not effective" (white circle), "effective" (partially filled circle), "very effective" (black circle)

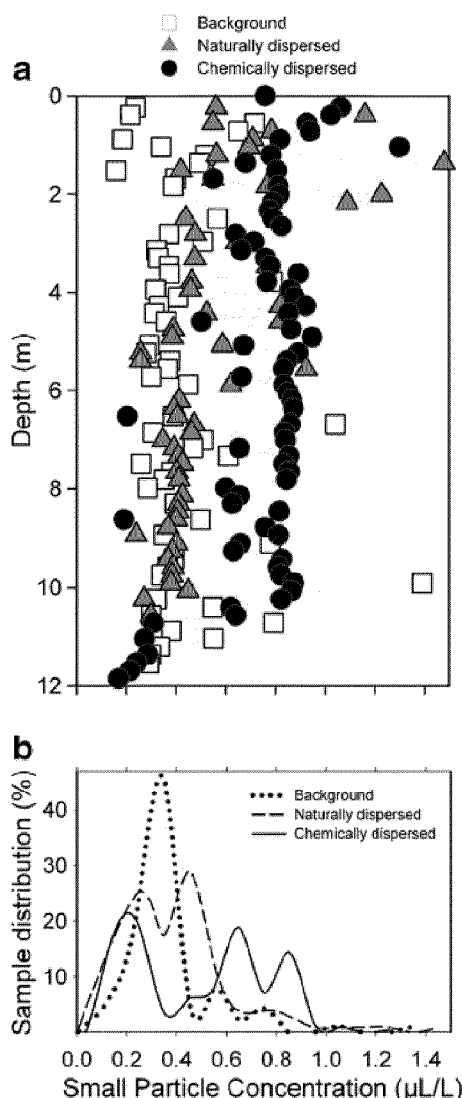


Fig. 6 Maximum concentration of small particles (<70 μm diameter) among four different observations (a). Symbols represent LISST data for background (squares), and naturally (gray triangles) and chemically (black circle) dispersed samples. The bottom panel (b) represents the sample distribution for all observation by sample type

concentration of oil constituents in the upper portion of the water column is similar to those observed during other oil spills or field oil trials where oil slicks were treated with dispersants. During the *Sea Empress* oil spill off the coast of Wales, total hydrocarbon concentrations (THC) in the top 1 m of the water column were in the 3–10 mg/L range prior to dispersant application, and relatively low (<0.5 mg/L) at 4 m depth (Lunel et al. 1997). Minutes after dispersant application, oil transfer from surface waters to waters 4 m deep increased 2- to 12-fold, with THC levels in the 1–6 mg/L

range. Controlled field trials have also reported a 2- to 20-fold oil increase, relative to naturally dispersed levels, at water depths <5 m shortly after dispersant use (Daling et al. 1998; Lewis 1998; Lunel and Davies 1996; Lunel et al. 1996). From these studies, it is clear that the use of dispersants remobilized oil from the sea surface and increased its dispersion/partitioning into the water column, potentially increasing the likelihood of impacts on water column organisms, but reducing impacts on shoreline habitats and surface dwelling organisms. It is important to clarify that potential increased risk of acute effects to water column organisms is the result of increased bulk oil and oil residues in the water column, and greater oil bioavailability, but not to an increase in the inherent toxicity of the oil per se, with the use of dispersants.

In this retrospective analysis, there was a greater variability of TPAH concentrations at 1 m depth compared to that of samples from 10 m. At 1 m depth there was also an increasing trend in TPAH and TPH concentrations from “not effective” to “very effective” dispersant operations. This trend is not surprising since by definition, effectiveness refers to the amount of oil that dispersed into the water column. In the case of “very effective” dispersant operations, water chemistry quantitatively confirmed the dispersant effectiveness observed via fluorometry. Despite the fact that samples were collected from background areas where surface oil slicks were not visually observed, some of these samples had comparable TPAH and TPH concentrations to samples collected under untreated oil slick, which is not surprising given the spatial scale of the spill and the volume of oil released.

One of the contributions of this retrospective analysis is that it allowed a comparison of field assessment of dispersant effectiveness, based on in situ fluorometry, with chemical analysis of samples collected from the same water bodies. Although there was an overall reasonable agreement between field assessments of dispersant effectiveness and increased TPH and TPAH concentrations in water samples collected after dispersant applications, there were a few cases where field assessments of effectiveness were not consistent with chemistry results. That is, fluorometry indicated “effective” dispersant applications, but water chemistry did not reveal ratios of chemically-to-naturally dispersed concentrations greater than one. Several contributing factors, including a potential delay in the collection of water samples relative to the time when fluorometry

data were taken, or a rapid dilution under the water surface, may have contributed to these findings. As stated elsewhere (Henry et al. 1999), fluorometric measurements can be influenced by natural (salts, suspended sediments, and microscopic flora and fauna) and abiotic (oil weathering, oil droplet size) variables leading to less accurate measurements of background conditions and dispersant effectiveness. Thus, the collection of water chemistry samples in tandem with in situ fluorometry provides added scientific value to oil spill monitoring efforts over assessments based on fluorometry alone (SMART-Tier II). Overall, the analyses presented here indicated that the use of dispersants was still warranted despite the weathered nature of the targeted oil slicks.

Characterization of effects from Oil constituents

The analyses presented here regarding potential increased risks of acute effects to water column biota from TPH and TPAH immediately following surface dispersant applications were based purely on desktop calculations. There are several limitations in deriving a consensus value for TPHs, including inconsistencies across studies in the preparation of exposure media, and differences in analytical methods and target analytes (e.g., C10-C36) (Singer et al. 2001). In this analysis, efforts were made to reduce the uncertainty of TPH benchmark estimates by filtering the available toxicity information, but we acknowledge that future refinements are needed to derive a more defensible benchmark. Based on the available information, the estimated 96-h HC₅ for TPHs was 1.68 mg/L (95 % CI, 0.81–3.36 mg/L). Under field conditions, water mixing by currents and wind reduce the concentration of the chemically dispersed oil constituents over time, thereby limiting acute exposures to aquatic organisms from a few minutes to hours. Therefore, comparisons to empirical data derived from rapidly declining exposures (Aurand and Coelho 2005) are more realistic of field conditions, than comparisons versus toxicity data from static exposure conditions. TPH values for short exposure durations (<24 h) were only available for one species (*Clupea harengus*; early life stages; McIntosh et al. 2010), which fell within the 70th percentile of the 96-h SSD. Assuming a similar curve shape for the 96-h SSD, estimates based on this species suggest a 1-h TPH HC₅ of 38.72 mg/L (95 % CI, 17.96–81.17 mg/L). Under these more realistic exposure conditions, none of the samples collected after surface

dispersant applications would have exceeded the 1-h benchmark value. However, empirical toxicity data and testing is especially lacking for many species, including early life stages, which are likely more sensitive to the acute effects of dispersed oil. Therefore, these assessments are tentative until short-exposure data on more sensitive species and life stages can be incorporated into TPH SSDs.

Because little information has been published on the toxicity of individual analytes present in TPH mixtures this analysis used a sum of TPHs as an indicator of risk. More appropriate approaches have been developed for TPAHs (Di Toro et al. 2007; USEPA 2003). Data on the acute toxicity of TPAH have been generated over decades on these lower molecular weight analytes which are not only water soluble components of oil but also the oil constituents with the highest acute toxicity potential; therefore, TPAHs may be better predictors of oil toxicity than TPHs. One important advantage of the TPAH-EBTU approach (USEPA 2003) used here is that it accounts for the relative contribution of each individual PAH to the overall toxicity of the mixture, thus accounting for different stages of oil weathering. The TPAH-EBTU approach was developed under the assumption of narcosis as the primary mode of PAH toxicity, which is largely based on chemical-specific aqueous solubility (Di Toro et al. 2007; USEPA 2003). Under this assumption, filtered water samples would have provided a better measure of the toxicity of water following chemical dispersion of oil. Filtration would have removed oil droplets leaving the truly dissolved analytes in the sample and leading to much lower TPAH concentrations than those measured in unfiltered samples. Here, five unfiltered water samples collected at 1 m depth, which represent worst case exposure concentrations, exceeded the TPAH-EBTU_{FAV,43} >1. However, it is important to remember that the TPAH-EBTU was developed using acute toxicity data generated under exposures conditions longer (days) than those expected during an oil spill (minutes to hours). Nevertheless, while the TPAH-EBTU is a sound and conservative approach, it has not been widely used in the oil spill field to characterize potential risks of acute effects to water column biota. However, the TPAH-EBTU approach can be used in conjunction with standard toxicity testing, or used as an alternative when toxicity testing is prohibitive, or when there is limited access to toxicity testing facilities. While analytical chemistry results from unfiltered

water samples, which likely contained oil droplets (worst case), were used in these analyses, there was little indication of increased risk of acute effects from oil constituents immediately after surface dispersant applications.

In this analysis, TPAH concentrations (sum of 43 individual PAHs) in unfiltered water samples ranged from <0.01 to 77 µg/L, and most (96 %) had concentrations <10 µg/L. To date, there is little comparable published data in the peer review literature on the concentration of PAHs in surface water samples collected during the DWH oil spill. Diercks et al. (2010) reported a TPAH concentration of 85 µg/L in one surface water sample (depth not reported) collected on May 11, 2010 at a site near and above the wellhead. By contrast, Boehm et al. (2011) summarized TPAH data for over 6,000 unfiltered water samples taken across all depths and directions. TPAH concentrations in 2,536 samples taken in the upper 200 m of the water column ranged from <0.1 to >100 µg/L. Most of these samples (81 %) had TPAH concentrations below detection (0.1 µg/L), while only a few (0.2 %) had concentrations exceeding 100 µg/L. Of the remaining samples, 18 and 0.75 % had TPAH concentrations in the 0.1–10 and 10–100 µg/L range, respectively (Boehm et al. 2011). Thus, the data presented here were well within the range of a large mass of upper water column concentration data.

Characterization of effects from a dispersant constituent

In the present analysis, DPnB concentrations were within the ranges measured in Gulf-wide water samples during the response (OSAT 2010), and below chronic levels of concern. Yet, information on the acute and chronic toxicity and environmental persistence of DPnB and other dispersant-related chemicals (2-butoxyethanol, dioctylsulfosuccinate) is limited, although they are expected to biodegrade in a short time frame (days to weeks).

Small particle distribution

The analysis of particles in the water column showed a clear shift in the distribution of small particles (<70 µm diameter) across sample categories, with generally higher concentration in samples collected after surface dispersant applications. A high concentration of small

particles was also found in wave tank experiments with dispersed source oil (JAG 2011, unpublished). An increased concentration of these small particles is environmentally relevant because the exposure of water column biota to particulate oil droplets may have a different mode of toxicity (e.g., physical coating of body surfaces, gill uptake, ingestion) than dissolved oil (primarily narcosis). Yet, little empirical information exists on the ecological and toxicological implications of increased concentration of small oil droplets. Nevertheless, oil droplets are within the normal food size range of naturally occurring food particles ingested by suspension feeding zooplankton (Berggreen et al. 1988; Conover 1971; Paffenhöfer 1984), and can adhered to feeding appendages interfering with normal feeding (Hansen et al. 2009). A more recent work by Olsvik et al. (2011) found that exposure of Atlantic cod (*Gadus morhua*) larvae for 4 days to media containing oil droplets in the 11–13 µm range induced gene expression in treatments with 10.41 µg TPAH/L, but oil droplets did not have a strong effect on survival. Recently, Lee et al. (2012) found that tunicates ingested chemically dispersed oil droplets (1–30 µm in diameter) only when food particles were present in the exposure media, and that oil droplets were readily eliminated in the form of fecal pellets. This study did not report adverse effects resulting from the ingestion of oil particles.

While the results presented here and elsewhere (JAG 2011, unpublished) showed a clear increase in the concentration of small particles after dispersant applications during the DWH oil spill, the ecological and toxicological implications remain unresolved and represent a significant knowledge gap.

Summary and implications

One of the contributions of this work was the comparison between analytical data and its correlation with SMART-Tier III field assessments of dispersant effectiveness following surface dispersant applications. However, this work highlighted that other contributing factors may have added uncertainty to the analyses presented here. For example, oil slicks at the water surface had various degrees of oil weathering (Brown et al. 2011), possibly influencing the effectiveness of some, but not all, surface dispersant applications. In fact, a retrospective power analysis of samples collected at 1 m suggested that given variability in TPAH and

TPH concentrations between naturally dispersed and “effective” and “very effective” (pooled) dispersant applications, a much larger sample size (at least 30 samples for a 0.8 power) may have been needed to detect statistical differences between these two groups. Furthermore, field conditions may have added variability to this dataset, which may have over- or underestimated dispersant effectiveness and assessments of potential risks of acute effects from exposures to oil constituents. It is possible that potential risks to water column biota from oil constituents may have been higher in areas where dispersants were applied to less weathered slicks. But as stated previously, the primary goal of the SMART program is to provide scientific support to the response concerning dispersant effectiveness, and not to evaluate statistically based hypotheses or to answer specific questions regarding biological effects. Yet, samples collected during the DWH by the special mission onboard the *M/V International Peace* were valuable in generating information that went well beyond the scope of the SMART program.

Efforts emerging post-DWH have recommended improvements to the SMART program, particularly for future oil spills of national significance. Key recommendations relevant to the analyses presented here include: (1) effective coordination between application of dispersants and sample collection of treated oil slicks by SMART-Tier III field assessment teams (BenKinney et al. 2011b); (2) increased availability of vessels equipped with a dispersant spray system and SMART-Tier III capabilities (BenKinney et al. 2011b); (3) a more rigorous selection of background or unimpacted areas (Levine et al.⁴ unpublished); and (4) improved consistency and standardization of data collected by the SMART program (Levine et al. unpublished). Implementation of these and other recommendations into future revisions to the SMART program could facilitate data collection and interpretation, and may enhance the use of quantitative data during future oil spill incidents. In addition to those recommendations, the results presented here highlight the need for a more robust and rigorous collection of samples, both in space and time. However, this may only be feasible under special missions, like the *M/V*

International Peace, not mandated under regulatory requirements. These missions would facilitate hypothesis testing of relevant scientific questions without sacrificing the goals of the SMART program and related sampling efforts. Hence, providing more scientific validity to this program and generating information of interest not only to the response but also to the public and the scientific community. Consequently, lessons emerging from this research include: the need to prepare for an expanded sampling effort proportional to the geographic area where dispersant use is intended; and increased collection of samples at intermediate depths (between 1 and 10 m) and at different time intervals post-dispersant application, at least at selected locations. Furthermore, chemical analysis on both unfiltered and filtered samples would allow for more realistic characterizations of risk, although these may not be necessary on all samples as the goals of the SMART program are not directly related to risk characterization and damage assessment. Analysis should also include a more systematic collection of LISST data as it provides a quantitative measure of dispersant effectiveness and can help validate the assessments made via fluorometry. Unlike fluorometry and LISST data, collection of samples for chemical analyses (oil constituents and dispersant makers) during dispersant monitoring efforts may not have an immediate real-time value to dispersant management decisions because of the processing time associated with these analyses. Nevertheless, and as shown here, these data are useful in allowing quantitative analyses that can help improve monitoring efforts, and can provide valuable information for environmental impacts assessments and other oil spill science outside of the scope of the SMART program. The strengthening of the SMART program, particularly during oil spills of national significance, is vital to provide reliable information to the Unified Command, and can also serve a dual purpose by generating information of interest to a larger scientific audience.

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⁴ An internal report by NOAA reviewed the use of SMART during aerial dispersant operations. This report was prepared for the USCG, but it is not currently available in the public domain.

not those of their associated institutions. This publication does not constitute an endorsement of any commercial product or intend to be an opinion beyond scientific or other results obtained by NOAA.

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