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Estimating Incident Ultraviolet Radiation Exposure in the Northern Gulf of Mexico during the *Deepwater Horizon* Oil Spill[1]

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Abstract

Millions of barrels of oil were released into the Gulf of Mexico following the 2010 explosion of the *Deepwater Horizon* oil rig. Polycyclic aromatic hydrocarbons (PAHs) are toxic components of crude oil, which may become more toxic in the presence of ultraviolet (UV) radiation, a phenomenon known as photo-induced toxicity. The *Deepwater Horizon* spill impacted offshore and estuarine sites, where biota may be co-exposed to UV and PAHs. Penetration of UV into the water column is affected by site-specific factors. Therefore, measurements and/or estimations of UV are necessary when one is assessing the risk to biota posed by photo-induced toxicity. We describe how estimates of incident UV were determined for the area impacted by the *Deepwater Horizon* oil spill, using monitoring data from radiometers near the spill, in conjunction with reference spectra characterizing the composition of solar radiation. Furthermore, we provide UV attenuation coefficients for both near- and offshore sites in the Gulf of Mexico. These estimates are specific to the time and location of the spill, and fall within the range of intensities utilized during photo-induced toxicity tests performed in support of the *Deepwater Horizon* Natural Resource Damage Assessment (NRDA). These data further validate the methodologies and findings of phototoxicity tests included in the *Deepwater Horizon* NRDA, while underscoring the importance of considering UV exposure when assessing possible risks following oil spills.

Keywords: Photo-induced toxicity, Polycyclic aromatic hydrocarbon, *Deepwater Horizon*, ultraviolet attenuation

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INTRODUCTION

On the morning of 20 April 2010, the *Deepwater Horizon*, a Transocean mobile drilling unit chartered by British Petroleum, exploded, sank, and released millions of barrels of oil into the Gulf of Mexico. During the 87 active days of the spill, the cumulative footprint of the surface slick was detected over 112 100 km^2 of open surface waters (Rice 2014; Nixon et al. 2016). Surface slicks subsequently migrated into coastal estuaries, exposing 2100 km of wetland/marsh shoreline to oil released from the spill (Rice 2014; *Deepwater Horizon* Natural Resource Damage Assessment Trustees 2016; Nixon et al. 2016).

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic contaminants composed of 2 or more fused carbon rings. Analytes of this class are common toxic components of crude oils and petroleum products (King 1988; MacFarland 1988; Cram et al. 2004). They have high lipophilicity, persist long after releases, and become more toxic in the presence of sunlight, a phenomenon known as photo-induced toxicity (Oris and Giesy 1987; Weinstein 1996; Xue and Warshawsky 2005).

Photo-induced toxicity may occur through 2 different mechanisms: photosensitization and photomodification. Photosensitization is thought to be the most important such mechanism in aquatic environments (Arfsten et al. 1996; Diamond et al. 2003). Organisms that lack sufficient pigmentation to prevent ultraviolet (UV) radiation from penetrating tissues, including many early life stages of aquatic biota, are particularly sensitive to photosensitization (Finch and Stubblefield 2016). Following absorption of PAHs from the external environment, photodynamic PAHs in tissues may interact with UV radiation, generating reactive oxygen species and free radicals (Roberts et al. 2017). The consequence is oxidation of biomolecules, oxidative stress, and tissue damage (Choi and Oris 2000; Roberts et al. 2017). Photomodification of PAHs by UV radiation occurs in the external (aquatic) environment, and results in modified compounds that

may exert greater toxicity than parent PAHs (Arfsten et al. 1996; Lampi et al. 2007). Because photomodification of PAHs occurs prior to absorption by aquatic biota, this mechanism of photo-induced toxicity is not affected by pigmentation.

Adverse effects of photo-enhanced or photo-induced PAH toxicity have been well documented in aquatic vertebrate (Alloy et al. 2016, 2017; Finch and Stubblefield 2016), invertebrate (Alloy et al. 2015; Finch and Stubblefield 2016; Damare et al. 2018), and aquatic plant species (Huang et al. 1997), and such effects occur at very low concentrations under both laboratory and field conditions. Organisms in early life stages exhibit increased sensitivity to photo-induced PAH toxicity, compounding the risk of adverse effects in embryos and larval fish (Incardona et al. 2004; Alloy et al. 2015, 2017; Sweet et al. 2017).

To accurately characterize the potential for photo-induced toxicity to occur in a given aquatic ecosystem, it is important to understand the UV exposure within the water column. The rate of UV attenuation is significantly affected by physical characteristics of the water column including turbidity, dissolved organic carbon (DOC) content, and the type/source of DOC (Tedetti and Sempéré 2006; Weinstein and Diamond 2006). In addition, the spectral composition of incident sunlight itself can be affected by time of day, latitude, and changing atmospheric conditions. A change in any one, or a combination, of the aforementioned factors may lead to changes in UV penetration (Alloy et al. 2017; Roberts et al. 2017).

Penetration of UV radiation within the water column is often described using the rate of UV attenuation per meter of water, or K_d, calculated from vertical irradiance data collected by underwater radiometers (Kirk 1994; Tedetti and Sempéré 2006). In the present study we describe how we derived UV attenuation coefficients for the period during, and immediately following, the *Deepwater Horizon* incident in the Gulf of Mexico. We obtained solar data collected during

the spill from weather stations and analyzed them in tandem with UV irradiance data sets generated during subsequent measurements in impacted areas of the Gulf of Mexico. Given the extensive number of photo-induced toxicity studies precipitated by the *Deepwater Horizon* spill, it is critical to generate site-specific UV exposure data/estimations to validate test methodologies and conclusions, as well as inform future risk assessments following oil spills.

MATERIALS AND METHODS

Transparency measurements

Radiometers (Biospherical Instruments) were used to measure several wavelengths of UV light (305, 313, 320, 340, 380, and 395 nm, and photosynthetically active radiation (400–700 nm) during *Deepwater Horizon* Natural Resource Damage Assessment (NRDA) photo-induced toxicity testing. The 380-nm wavelength was utilized to quantify photo-induced toxicity during laboratory bioassays, because it has been shown to potentiate the toxicity of photodynamic PAHs, and to penetrate seawater more deeply than shorter wavelengths of UV light (Oris and Giesy 1987; Arfsten et al. 1996; Jeffrey et al. 1996; Vasilkov et al. 2001). In addition, a submersible Biospherical radiometer was used to collect depth profiles of UV irradiance at both nearshore and offshore sites during and after the spill to account for changes in attenuation due to site-specific characteristics of the water column. Nearshore UV profiles were collected in Barataria Bay (LA, USA) in 2013 and 2014, and offshore UV profiles were collected by the *Walton Smith* sampling cruise in 2010 (French-McKay et al. 2010; Stratus Consulting 2013, 2014). Vertical profiles of UV intensity were collected by lowering the radiometer to depth from a starting position just beneath the surface, while the instrument recorded multiple measurements of UV intensity per second. Therefore, UV intensity in the Gulf of Mexico, including UV_{380}, was measured during several different data collections in the laboratory and in the field.

Surface UV estimates during the Deepwater Horizon *spill*

To characterize surface UV in the Gulf of Mexico during the *Deepwater Horizon* incident, we obtained spectral data from 2 stations that recorded light intensity data during the spill. These included the National Oceanic and Atmospheric Administration (NOAA)–Environmental Protection Agency Brewer Spectrophotometer UV and Ozone Network (NEUBrew; Earth System Research Laboratory 2015a) station at Houston (TX, USA; 29.718°N, 95.341003°W; Earth System Research Laboratory 2015b**<ZAQ;1>**) and NOAA buoy 42040 (29.212°N, 88.207°W; National Data Buoy Center 2015) located approximately 55 km northeast of the wellhead. The Houston station collected measurements of UV_{363} approximately every 30 min. Because the Biospherical radiometer does not record UV_{363} we could not directly compare measurements from the radiometer with those collected by the Houston NEUBrew station during the spill. Therefore, we used a standardized reference table (ASTM International 2012), which describes the spectral makeup of sunlight on the Earth's surface, to estimate surface UV_{380} from the UV_{363} data measured by the Houston NEUBrew station during the oil spill (Figure 1; Earth Systems Research Laboratory 2015). Although the spectral makeup of sunlight varies with many factors, this reference spectrum provides a good estimate of the relationships among different wavelengths under a variety of sunny conditions in the United States.

<ZAQ;2>A direct comparison between the data obtained by the LI-COR meter used on NOAA buoy 42040 and data from the Houston station was not possible. The LI-COR radiometer measured average intensities across a broad band of visible light wavelengths (400–1100 nm) each hour. However, buoy 42040 is close to the wellhead, so data from the LIC-COR radiometer provided a reference point for the amount of sunlight received near the spill. Readings from the LI-COR radiometer (55 km northeast of the wellhead) were visually compared with incident UV

data from the Houston station, located approximately 690 km northwest of the wellhead. Comparison of light intensity data provided information regarding the similarity of weather conditions between locations. We excluded dates with dissimilar light intensities from our estimate of UV_{380} (Figure 2). Three people examined the data, and consensus was reached for excluded dates.

UV intensity estimates at depth and attenuation coefficients

Profiles of UV irradiance at various depths collected by a Biospherical radiometer were used to generate regressions of log-transformed UV_{380} intensity against depth, for both nearshore and offshore sites (French-McKay et al. 2010; Stratus Consulting 2013, 2014). From this regression, site-specific attenuation coefficients (K_d) were determined as the slope of the line (Kirk 1994; Diamond 2003; Weinstein and Diamond 2006).

Attenuation by oil–water and oil–water-dispersant mixtures

To characterize potential attenuation of UV by oil present in the water column, we examined the attenuation of UV_{380} by various oil and water preparations in the laboratory (Diamond 2003; Weinstein and Diamond 2006). We prepared high-energy water accommodated fractions (HEWAFs) of 2 oil samples (slick A and slick B) using the methods previously described in Alloy et al. (2015, 2016). The slick A oil sample was collected on 29 July 2010 from the hold of barge number CTC02404, a repository for oil recovered by various skimming vessels near the wellhead. Slick B oil was collected on 19 July 2010 from the US Coast Guard skimmer *Juniper*. Slick A was less weathered than slick B and had 68% loss of the sum of 50 PAHs (tPAH50) relative to hopane, whereas slick B samples had 85% loss (Forth et al. 2017a, 2017b; see those studies for additional details on oil and HEWAF chemistry and for a list of PAHs included in tPAH50 sums).

Test solutions were prepared by diluting HEWAFs in synthetic seawater to nominal concentrations ranging from 2 to 100% HEWAF for slick A, and 20 to 100% HEWAF for slick B. To account for potential UV attenuation by dispersant used during the spill response, a chemically enhanced water accommodated fraction (CEWAF) treatment (one using slick A and one using slick B) was also included in attenuation testing. The CEWAF was prepared by mixing each oil type (1:1000 oil-to-synthetic–seawater ratio) with dispersant (Corexit 9500, 1:10 dispersant-to-oil ratio) on a stir plate (25% vortex) for 24 h. Thin surface sheens of both oil types were also prepared, to assess the potential of surface oil to attenuate UV_{380}. Surface sheens were prepared by applying a thin layer of each oil type to the inside rim of a polyvinyl chloride coupler, which was then placed in contact with the surface of the test chamber water for 4 h. Oiled couplers were removed immediately before testing. All test chambers (250-mL Pyrex crystallizing dishes) contained 200 mL (35-mm depth) of their respective solutions, prior to testing.

Testing was performed at the University of North Texas (Denton, TX, USA). The indoor component was performed under UV-A light banks, which are routinely used for indoor phototoxicity testing (Sweet et al. 2017; Wormington et al. 2017). Intensities of UV_{380} representative of those measured during outdoor photo-induced toxicity testing were obtained by adjusting the height of the light banks above the sensor on a Biospherical radiometer (Figures 3 and 4; Alloy et al. 2015, 2016, 2017). Baseline intensities of UV_{380} emitted from the light banks were recorded before each replicate**<ZAQ;3>**, followed by placement of a test chamber on top of the UV sensor to obtain a second reading. From these 2 values, we calculated attenuation (i.e., % reduction in transmittance) as the ratio of the second UV_{380} intensity to the initial UV_{380}

intensity. We corrected all values for a 4% attenuation due to synthetic seawater and glass dishes.

RESULTS AND DISCUSSION

Surface UV estimates

The spectral composition of sunlight hitting surface waters varies according to latitude, time of day, and changing atmospheric conditions. However, the relative power of each wavelength of light is well characterized in various reference spectra for a variety of conditions. The ASTM International G173-03 reference table values for direct and reflected sunlight at a 37° global tilt were used to relate surface UV_{380} (present during the oil spill) to the UV_{363} data from the Houston NEUBrew station (**<ZAQ;4>**ASTM International 2012; Earth System Research Laboratory 2015b). We selected these values because they provided the best comparison with data recorded by instruments during depth profile measurements of UV. Using this relationship, UV_{380} was estimated at 116.42% of UV_{363} (Table 1). This relationship corresponds to a mean energy of 1550 ± 372 mW s/cm^2 (range: 370–1980 mW s/cm^2) for UV_{380} (Table 1). Because the radiometer did not measure UV_{363}, estimates were further validated by measuring the ratios of UV_{380} to 2 other wavelengths (UV_{395} and UV_{340}) recorded by the radiometer over the course of 2 d of toxicity testing (Table 2). The relative ratios of these wavelengths measured during toxicity testing were then compared with estimated ratios for the corresponding wavelengths from the reference spectrum table (ASTM International 2012), yielding an average relative percentage difference of 6.2% (Table 2).

The visible light readings from buoy 42040 were used to confirm similarity in weather conditions between the Houston NEUBrew station and the spill site (Figure 2). Following visual comparison of light intensities from buoy 42040 with those from the Houston NEUBrew station,

it was determined that weather conditions between locations varied considerably on 6 separate dates, which were excluded from the estimate. For 5 of these 6 d, the Houston NEUBrew station showed evidence of cloudy days based on the relatively low average incident UV_{363}, whereas data from buoy 42040 indicated fair conditions. Because buoy 42040 did not record data before 1 May 2010, we were unable to perform this comparison for all dates. However, we did exclude Houston NEUBrew station data from 30 April 2010, because it was very dissimilar from the buoy 42040 data for 1 May 2010, which had the second lowest UV_{363} measurement taken over the duration of the spill. Finally, we excluded 25 May 2010 because some Houston NEUBrew station data were missing.

UV intensity estimates at depth and attenuation coefficients

As previously discussed, UV attenuates with water depth, at a rate that varies according to site-specific characteristics within the water column. Estuarine and bay waters generally attenuate UV more quickly with depth, because changing tides increase particle suspension and tidal creeks increase DOC relative to open-water sites (Weinstein and Diamond 2006). The slope of the fitted line for a regression of log-transformed UV_{380} irradiance against depth is the coefficient of attenuation with depth, or K_d. We calculated K_d for specific sites by fitting these regression lines separately. Attenuation of UV_{380} in Barataria Bay was considerably higher than in offshore waters sampled during the *Walton Smith* cruise in 2010. The K_d calculated from profiles in Barataria Bay collected during 2013 and 2014 ranged from 3.99 to 18.68, with a mean of 11.55 ± 4.02. The K_d values at offshore sites ranged from 0.04 to 0.11, with a mean of 0.06 ± 0.02. Based on these measurements, we estimated that average incident UV_{380} in the Gulf of Mexico during the spill (1550 mW s/cm^2) penetrated well beneath the water surface in open water near the wellhead, exposing organisms as deep as 20 m below the surface to approximately

33% of incident UV_{380} (Figure 5). This percentage corresponds with a UV_{380} intensity of 512 mW s/cm^2, which may be sufficient to cause photo-induced toxicity in sensitive organisms concurrently exposed to PAHs (Alloy et al. 2016, 2017). These findings suggest that a wider range of aquatic organisms in the Gulf of Mexico may be at risk for photo-induced toxicity than previously thought. Furthermore, they highlight the need for studies examining the effects of photo-induced toxicity using a lower range of UV intensities to represent depths down to 20 m, because these types of toxicity studies focus almost exclusively on the risk posed to organisms at or near the surface.

Attenuation by oil–water and oil–water-dispersant mixtures

Both the CEWAF and the surface slick treatments showed extremely little UV attenuation through test chambers, with UV_{380} attenuation of 3% or lower (Figure 6). A 100% slick A HEWAF had the highest attenuation of all solutions tested, at 58% of incident UV_{380}. The 100% slick B (more weathered) HEWAF attenuated 23% of incident UV_{380} (Figure 6). In spite of the considerable attenuation in the 100% HEWAF test chambers, it should be noted that exposure to much lower nominal HEWAF (slicks A and B) concentrations resulted in full mortality in phototoxicity tests that included a 50% UV treatment (obtained using UV–filtering screens (Alloy et al. 2017; Damare et al. 2018). Therefore, UV attenuation is unlikely to ameliorate adverse outcomes in biota at these high concentrations, which are sufficient to cause injury via other modes of action (e.g., narcosis, cardiotoxicity) even in the absence of UV (Incardona et al. 2014; Mager et al. 2014).

The attenuation of UV for both slick A and slick B was less than 14% in test chambers containing 20% HEWAF (Figure 6). Photo-induced toxicity testing performed as part of the NRDA found that dilutions well below 20% HEWAF led to significant mortality in a number of

early life stage organisms (Alloy et al. 2015, 2017; Morris et al. 2015; Travers et al. 2015; *Deepwater Horizon* Natural Resource Damage Assessment Trustees 2016). In fact, the least sensitive organism tested, Mississippi blue crab (*Callinectes sapidus)* zoea, still exhibited significantly increased mortality in treatments containing 2% or more (slick A) HEWAF, when co-exposed to solar radiation (Alloy et al. 2015). Given the linear relationship between HEWAF strength and attenuation, a nominal concentration of 2% (slick A) HEWAF should attenuate less than 4% of incident UV_{380} (Figure 6). The highest nominal concentration used in the Mississippi blue crab larval exposures was 10% (slick A) HEWAF, a concentration that can be expected to attenuate approximately 10% of UV_{380} (Alloy et al. 2015). In spite of this reduction in UV exposure, complete mortality was still observed following co-exposure with solar radiation (Alloy et al. 2015).

Because UV increases the toxicity of oil by several orders of magnitude, photo-induced toxicity can lead to injury in sensitive organisms at PAH concentrations insufficient to induce other modes of toxicity (Alloy et al. 2017; Roberts et al. 2017; Sweet et al. 2017). Therefore, attenuation of UV by oil and/or dispersant itself is negligible within the range of PAH concentrations in which photo-induced toxicity is the expected mode of action. For example, the speckled sea trout *(Cynoscion nebulosus)* displayed significantly increased mortality at a tPAH50 concentration of only 0.18 μg/L (Alloy et al. 2017). This amount corresponds with a nominal concentration of less than 0.01% HEWAF, in which UV attenuation due to oil would be expected to be insignificant. Although speckled sea trout are the most sensitive species tested to date, early life stages of other fish species native to the Gulf of Mexico, including mahi-mahi (*Coryphaena hippurus)* embryos, and red drum (*Sciaenops ocellatus)* larvae, also displayed considerable sensitivity to photo-induced toxicity (Alloy et al. 2016, 2017; Sweet et al. 2017).

Significant mortality following co-exposure to *Deepwater Horizon* oil and solar radiation occurred in mahi-mahi embryos after treatment with 4.3 µg/L or more tPAH50, and in red drum larvae after treatment with 2.27 µg/L or more tPAH50 (Alloy et al. 2016, 2017; Sweet et al. 2017).

These PAH concentrations are generally below those required to cause acute mortality through other modes of toxicity; however, developmental exposure to similar concentrations of oil has been shown to lead to physiological abnormalities associated with long-term fitness costs, most notably cardiotoxicity (Incardona et al. 2004, 2014; Mager et al 2014; Khursigara et al. 2017; Sweet et al. 2017). Cardiotoxicity has been observed in early life stages of a variety of ecologically and commercially important fish species in the Gulf of Mexico, at concentrations less than 15 µg/L tPAH50 (equivalent to a nominal concentration of 0.75%) in the absence of UV (Incardona et al. 2014; Khursigara et al. 2017). Sensitive organisms include amberjack (*Seriola dumerili*), yellowfin tuna (*Thunnus albacares*), mahi-mahi, and bluefin tuna (*Thunnus thynnus*; Incardona et al. 2014; Mager et al. 2014; Sweet et al. 2017). Although concentrations of less than 15 µg/L tPAH50 (in the absence of UV) may not initially lead to significant mortality, developmental cardiac abnormalities have implications for delayed mortality and fitness costs (e.g., impaired swimming performance) that greatly reduce the odds of survival in the wild (Incardona et al. 2014; Mager et al. 2014). However, it is important to note that Sweet et al. (2017) report that UV co-exposure may exacerbate cardiotoxicity in embryonic mahi-mahi exposed to *Deepwater Horizon* oil, eliciting effects at even lower PAH concentrations than previously described. Findings from the aforementioned studies, and the attenuation data from the present study, indicate that the concentrations of oil capable of substantially attenuating UV are beyond the threshold concentrations required to initiate additional modes of toxicity.

Therefore, cumulative damage would almost certainly far outweigh any benefits offered by reduced UV exposure.

Comparison with photo-induced toxicity tests

The majority of photo-induced toxicity testing conducted as part of the *Deepwater Horizon* NRDA used natural sunlight as a light source for UV exposure. To reduce the environmental variability associated with outdoor testing (e.g., passing clouds, different cloud cover, etc.), an increasing number of phototoxicity tests are being conducted indoors using light banks as a source of UV-A radiation. The solar radiation that reaches the earth's surface contains a broad spectrum of wavelengths, ranging from infrared to UV (Lay et al. 2015). However, only specific wavelengths of light can be absorbed by photodynamic PAHs, the most notable of which are in the UV-A spectrum (315–400 nm; Roberts et al. 2017). Because UV_{380} falls within the UV-A spectrum, is absorbed by photodynamic PAHs, and penetrates seawater to deeper depths than shorter UV-A wavelengths, this wavelength can serve as a useful indication of the potential for UV-enhanced toxicity in the presence of photodynamic PAHs (Jeffrey et al. 1996; Tedetti and Sempéré 2006; Lay et al. 2015). The UV-A light banks used for indoor phototoxicity testing emit UV wavelengths between 350 and 400 nm (Figure 4). Intensities of UV_{380} similar to those measured in outdoor toxicity tests can be achieved by adjusting the height of light banks above exposure chambers. This exposes test chambers to the range of UV-A wavelengths typically implicated in photo-inducing toxicity in photodynamic PAHs (Figure 4). Results of indoor and outdoor toxicity tests evaluating the phototoxic effects of *Deepwater Horizon* oil on the hatching success of mahi-mahi embryos yielded comparable phototoxic median effect concentration (EC50) values, as follows: outdoors, 6.77 µM/L mW s/cm^2 (95% confidence interval [CI] 5.91–7.64 µM/L mW s/cm^2); and indoors, 9.8 µM/L mW s/cm^2 (95% CI 6.4–13.2 µM/L mW s/cm^2).

These data validate the use of indoor UV-A light banks as a reliable substitute for solar radiation (Alloy et al. 2017; Sweet et al. 2017).

The mean estimates of surface UV_{380} near the wellhead during the spill fall within the range of integrated doses utilized to conduct photo-induced toxicity tests in support of the *Deepwater Horizon* NRDA (Figure 3). In view of the estimated UV penetration in the Gulf of Mexico (Figure 5), it is likely that photo-induced toxicity was a relevant mechanism of toxicity for a wide range of ecologically important species in the Gulf of Mexico during the spill. For instance, Alloy et al. (2017) reported significantly increased mortality in both larval red drum (phototoxic median lethal concentration [LC50] 1.41 µM/L mW s/cm^2) and speckled sea trout (phototoxic LC50 0.516 µM/L mW s/cm^2) embryos co-exposed to tPAH50 concentrations of 2.40 µg/L or more (slick A), and solar radiation. These results were obtained with a daily integrated UV_{380} dose of only 706 mW s/cm^2 over the course of a 5- to 6-h solar exposure. Significant reductions in hatching success were observed in mahi-mahi embryos (phototoxic EC50 6.77 µM/L mW s/cm^2) exposed to tPAH50 concentrations of 4.3 µg/L or more (slick A) following 2, 7-h solar exposures (UV_{380} dose range: 607–2423 mW s/cm^2; Alloy et al. 2016). Mississippi blue crab zoea showed significantly decreased survival (phototoxic LC50 20.6 µM/L mW s/cm^2) in all exposures of 44.02 µg/L or more tPAH50 (slick A), using the same 2-d solar exposure scenario with daily UV_{380} doses of 908.2 and 1570.3 mW s/cm^2, respectively (Alloy et al. 2015). Maryland blue crab zoea from the same study were considerably more sensitive (phototoxic LC50 9.5 µM/L mW s cm^{-2}), with all tested tPAH50 concentrations (14.71 µg/L or more, slick A) exhibiting more than 80% mortality except for the control group (Alloy et al. 2015). During the active phase of the spill, tPAH50 concentrations of up to 84.8 µg/L were detected in the oiled areas of the Gulf of Mexico (*Deepwater Horizon* Natural Resource Damage

Assessment Trustees 2016). These maximum measured concentrations are well above those required to significantly increase mortality in the presence of UV, even for the least sensitive early life stage organisms tested (Alloy et al. 2015). In light of the UV estimates provided in the present study, the penetration depths measured in the Gulf of Mexico, and the results of toxicity tests incorporating similar intensities of UV, it is likely that photo-induced toxicity of *Deepwater Horizon* oil led to adverse outcomes for some aquatic organisms (residing in the upper water column) in the Gulf of Mexico (Alloy et al. 2015, 2017; Morris et al. 2015; Travers et al. 2015; *Deepwater Horizon* Natural Resource Damage Assessment Trustees 2016; Finch and Stubblefield 2016; Sweet et al. 2017; Damare et al. 2018).

CONCLUSIONS

Estimates of surface UV were determined for the area impacted by the *Deepwater Horizon* oil spill between 20 April and 11 August 2010. The UV_{363} data from the Houston NEUBrew station was compared with that from a radiometer located on buoy 42040 near the *Deepwater Horizon* wellhead, to determine similarity in weather conditions prior to all calculations. Information from reference spectra was used to determine the relationship between UV_{380} and UV_{363} intensities. Solar data collected by radiometers during outdoor toxicity testing was used to further validate the estimate of UV_{380}. In addition, we have provided site-specific data for UV attenuation and extinction coefficients for nearshore and offshore sites in the Gulf of Mexico impacted by the *Deepwater Horizon* incident. The estimates of incident UV_{380} also fall within the range of measurements reported in various outdoor toxicity tests that used solar exposures as a source of UV (Alloy et al. 2015, 2016, 2017; Morris et al. 2015; Damare et al. 2018). This finding supports our assertion that the UV doses applied during photo-induced toxicity testing as part of the *Deepwater Horizon* NRDA were representative of those in the Gulf

of Mexico during the *Deepwater Horizon* spill. Given the importance of photo-induced toxicity in estimating damages from oil spills, we recommend increasing the number of direct measurements of insolation at the surface and under slicks during oil spills, and deploying light meters as part of a coordinated spill response.

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Data Availability—Data are available on request (aproberts@unt.edu).

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Figure 1. Reference spectrum (ASTM G-173-3, black line; ASTM International 2012) compared with wavelengths measured by various devices. The red line shows ultraviolet $(UV)_{380}$ irradiance quantified during phototoxicity testing. The gray line represents UV_{363}, as measured by the Houston NEUBrew station. The yellow area shows the wavelengths recorded by buoy 42040.

Figure 2. Comparison of the light readings from 1 May through 11 August 2017 from the Houston NEUBrew station (blue lines, right axis) and buoy 42040 (green lines, left axis), which were used to identify dates to be excluded from surface ultraviolet (UV) estimates due to dissimilarity (indicated by arrows below graph) or missing data (indicated by arrow above graph). The incident UV_{380} energy at the spill site was estimated as 116% of the UV_{363} measured at the Houston NEUBrew station (20 April 2010–11 August 2010).

Figure 3. Irradiance (black line) and energy (gray area under the curve) of the 380-nm wavelength of ultraviolet (UV) radiation (UV_{380}) measured during a summer day in Auburn, AL (USA).

Figure 4. The red line shows the solar irradiance by wavelength, as measured at noon on a sunny April day at the University of North Texas (Denton, TX, USA). The black line shows the irradiance by wavelength of the indoor light setup at the University of North Texas, used during indoor toxicity testing. Irradiance for each light source was measured using an Ocean Optics Jaz radiometer.

Figure 5. Estimated depth of penetration of ultraviolet $(UV)_{380}$ given average attenuation estimated from measurements collected in offshore areas during the 2010 *Walton Smith* cruise (French-McKay et al. 2010) and estimate of average incident UV_{380} in the Gulf of Mexico during the spill (1550 mW s/cm^2).

Figure 6. Effect of preparation method and oil type on ultraviolet $(UV)_{380}$ attenuation in phototoxicity test chambers. PAH = polycyclic aromatic hydrocarbon; HEWAF = high-energy water accommodated fraction; CEWAF = chemically enhanced water accommodated fraction.

<<ENOTE>>AQ1: Earth System Research Laboratory 2015b: the first ESRL reference (2015a) is to the general website. But this one, for data from the Houston station, needs to have the full URL for those data. See entry in the reference list.

<<ENOTE>>AQ2: is the sense of the sentence OK as edited? “A direct comparison between the data obtained by the LI-COR meter used on NOAA buoy 42040 and data from the Houston station was not possible[0]”

<<ENOTE>>AQ3: please clarify “before each replicate”.

<<ENOTE>>AQ4: are these references correct?

<<ENOTE>>AQ5: is it OK to reword this as “Trustee Council”? This is how NOAA refers to it.

<<ENOTE>>AQ6: ASTM International. 2012: please give date accessed prior to the present study’s acceptance.

<<ENOTE>>AQ7: [0]Damare L, Bridges K, Forth H, Lay C, Morris J, Stoeckel J, Curran T, Soulen B, Alloy M, Roberts A. 2018: please update if possible.

<<ENOTE>>AQ8: *Deepwater Horizon* Natural Resource Damage Assessment Trustees. 2016: please give date accessed.

<<ENOTE>>AQ9: Earth System Research Laboratory, National Oceanic and Atmospheric Administration. 2015a: please give date accessed.

<<ENOTE>>AQ10: Earth System Research Laboratory, National Oceanic and Atmospheric Administration. 2015b: please give date accessed. Also for Earth System Research Laboratory 2015b: please give the full URL for the Houston data.

<<ENOTE>>AQ11: Finch et al. 2016: please cite in text or delete.

<<ENOTE>>AQ12: Morris J, Krasnec, MO, Carney M, Forth H, Lay C, Lipton I, McFadden A, Takeshita R, Cacela D, Holmes JV, Lipton J. 2015: please give date accessed. Also, instead of the section number, please give the full URL where the report can be found.

<<ENOTE>>AQ13: [0]National Data Buoy Center, National Oceanic and Atmospheric Administration. 2015: please give data accessed.

<<ENOTE>>AQ14: Rice S. 2014: please give date accessed.

<<ENOTE>>AQ15: Travers C, Wobus C, Morris J, Lay C, Rissing M, Forth H, Holmes J. 2015: please give the date accessed. Also, rather than giving the section, please give the full URL where the report can be found.

<<**ENOTE**>>**AQ16:** Weinstein 1996: are the changes OK?

Table 1. The UV_{363} energy (mW s/cm^2) measured at the Houston NEUBrew station between 20 April and 11 August 2010, and UV_{380} light estimated as approximately 116% of UV_{363} light[a]

	UV_{363} light (mW s/cm^2; measured)	UV_{380} light (mW s/cm^2; estimated)
Mean (± 1 SD)	1330 ± 320	1550 ± 372
Range	320–1700	370–1980

[a] The maximum estimated UV_{380} light during the spill (1980 mW s/cm^2) is similar to that measured during toxicity testing (2184 mW s/cm^2).

UV = ultraviolet: NEUBrew = National Oceanic and Atmospheric Administration–Environmental Protection Agency Brewer Spectrophotometer UV and Ozone Network; SD = standard deviation.

Table 2. Comparison of the estimated ratios for ultraviolet (UV) wavelengths with the measured ratios (using the Biospherical radiometer) from laboratory toxicity testing[a]

UV wavelengths compared	Date	ASTM G173-3 global tilt ratio	Measured ratio (Biospherical)	Relative difference (%)
UV 380:395 nm	5/22/2013	0.879	0.957	8.477
	8/17/2011	0.879	0.908	3.209
UV 380:340 nm	5/22/2013	1.397	1.390	–0.457
	8/17/2011	1.397	1.586	12.714
Mean relative percentage difference (absolute)				6.2

[a] The estimated ratios were from ASTM International table G173-3, global tilt ratio (ASTM International 2012). Laboratory testing was conducted at the Gulf Coast Research Laboratory (Ocean Springs, MS, USA; 17 August 2011), and the University of North Texas (Denton, TX, USA; 22 May 2013) The relative percentage difference between the estimate and the measurement for these days and wavelengths was 6.2%.