

***Characterization and flux of marine oil snow settling toward the seafloor in the northern Gulf of Mexico during the Deepwater Horizon incident: Evidence for input from surface oil and impact on shallow shelf sediments***

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**Abstract**

Sediment trap samples from the shelf edge area (400-450m water depth), 58 km northeast of the failed Macondo well, were collected before, during and after the *Deepwater Horizon* oil spill. Detailed chemical analyses of particulates revealed that fluxes of spill-derived TPH (2,356  $\mu\text{g}/\text{m}^2/\text{day}$ ), total PAH (5.4  $\mu\text{g}/\text{m}^2/\text{day}$ ), and hopane (0.89  $\mu\text{g}/\text{m}^2/\text{day}$ ) settling to the seafloor directly beneath the surface-plume were 19- to 44-times higher during the active spill than pre- and post-spill background values. The oil was variably biodegraded, evaporated and photo-oxidized indicating that it derived from the sinking of surface oil. The hopane-based oil flux that we calculate (10 bbl/ $\text{km}^2$ ) indicates that at least 76,000 bbl of Macondo oil that reached the ocean surface subsequently sank over an area of approximately 7600  $\text{km}^2$ . We explore how this flux of sunken surface oil contributed to the total volume of oil deposited on the seafloor following the *Deepwater Horizon* incident.

**Keywords:**

Sediment trap  
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## **1. Introduction**

Between April 20 and July 15, 2010 the *Deepwater Horizon* oil spill introduced approximately 4 million barrels of oil to the northern Gulf of Mexico (GoM) at a depth of approximately 1500m (Crone and Tolstoy, 2010). One fraction of the Macondo crude oil that was released remained at depth in the ocean in a combination of dissolved material and physically- or chemically-dispersed droplets, all of which were advected away from the source in the form of a laterally dispersing non-buoyant plume centered at approximately 1000-1300m depth (Camilli et al. 2010; Socolofsky et al. 2011). Importantly, however, a second fraction of the oil released from the Macondo well was sufficiently buoyant to rise all the way to the ocean surface where it was dispersed by wind and currents over vast areas of the northern GoM over a period of nearly three months (Graettinger et al., 2015).

Some fraction of the dispersed oil from the deep-sea plume and/or buoyant oil from the sea surface was ultimately deposited on the seafloor as evidenced by the widespread accumulation of oily “floc” in sediments (Valentine et al., 2014; Brooks et al., 2015; Chanton et al., 2015; Hastings et al., 2015; Romero et al., 2015; Schwing et al., 2015; Stout et al., 2016a,b) and on deep-sea corals (White et al., 2012; Hsing et al., 2013; Fisher et al., 2014a,b). Although impingement of oil from the dispersing deep-sea plume directly onto topographic obstacles likely occurred, the dominant mechanism by which the oily “floc” was carried to the seafloor is hypothesized to have been the formation and sinking of marine oil snow (Kinner et al., 2014). The marine oil snow formed from aggregates of oil with microbially-mediated, mucous-rich marine snow particles that formed following the proliferation of oil-degrading bacteria, in both the deep-sea and near the ocean surface, in response to the spill (Hazen et al., 2010; Valentine et al., 2010; Baelum et al., 2012; Passow et al. 2012, Ziervogel et al., 2012; Passow 2014; Fu et al., 2014; Daly et al., 2016; Passow and Ziervogel, 2016).

The numerous sediment and coral studies mentioned above have already established the impact of sinking marine oil snow on seafloor sediments and coral communities found at depths greater than 1000m. This initially had led to a broad expectation that oil dispersed through the deep-sea plume, which never penetrated upward shallower than 1000m, was the overwhelming and perhaps exclusive source of oil found in the oily floc. Evidence that marine oils snow formed at the surface had impacted the shallower seafloor less than 1000m deep (i.e., above the depth of the deep sea plume) was varied.

For example, two colonial coral sites shallower than 1000m and immediately north of the Macondo wellhead (VK906 and VK826; Fig. 1) did not exhibit visible signs of impact (Fisher et al., 2014). Hydrocarbon analysis of sediment cores collected at less than 1000m depth, while limited in number and only sparsely distributed across the northern GoM (Fig. 1), had indicated no obvious evidence for impact by Macondo oil (Valentine et al., 2014; Stout et al., 2016a,b) whereas radio-carbon analysis of sediment cores collected near and east of DeSoto Canyon indicated some impact had occurred (Chanton et al., 2015). This disparity was, at least in part, likely attributable to the difficulty of collecting and measuring what, if present, was likely only a thin layer of marine oil snow that was deposited onto, and then potentially bioturbated into, the surficial layers of these shallow marine seafloor sediment.

Unfortunately, sediment trap studies during oil spill events are limited with respect to their location and/or the time of deployment relative to a spill. Two such studies were conducted during the *Deepwater Horizon* oil spill. In the first, a sediment trap deployed after the spill had ended (Aug-2010 to Oct-2011), and in deep water (1540m) 7.4 km southwest of the failed Macondo well, showed some sinking marine oil snow persisted in the deep sea for at least five months after the spill ended (Yan et al., 2016). In the second study, comparison of sediment traps deployed in shallower water near VK826 and VK906 (Fig. 1) prior to (Oct-2008 to Sept-2009) and after the spill (Oct-2010 to Sept-11) showed a reduction in primary production after the spill (Prouty et al., 2016).

Neither of these sample-collection studies, however, were active during the period of the spill and, hence, neither were able to confirm and measure any sinking marine oil snow from the sea surface onto shallow (<1000m) shelf sediments caused by the *Deepwater Horizon* oil spill.

Here we present new evidence for the formation and sinking of marine oil snow formed at the ocean surface and deposited to the shallow GoM seafloor. Specifically, we present results of chemical analysis of marine oil snow captured in sediment traps in the Viosca Knoll area (VK906 and VK826, the latter in particular) that show an impact from the *Deepwater Horizon* spill on shallow shelf sediments in the northern GoM. The traps were located approximately 37 and 58 km from the Macondo well in water depths of approximately 400-450m (Fig. 1) and proximal to *Lophelia* reef ecosystems that were already known to exist in both areas. The VK826 samples collected span the time from September 2009 to September 2011, a two year time-series that extends from before and during, until more than 12 months after, the *Deepwater Horizon* oil spill. The results

provide an unequivocal basis upon which to recognize the presence, weathering characteristics, sedimentation rate and duration of the Macondo-derived marine oil snow deposited in the Viosca Knoll area during the spill. The results demonstrate that (1) Macondo oil from the ocean surface sank to the seafloor and (2) the process by which this phenomenon impacted shallow (<1000m) benthic ecosystems in the Viosca Knoll area, most probably recurred widely across the northern GoM shelf.

## **2. Samples and Methods**

### *2.1 Sediment Trap Samples*

Fig. 1 shows the locations of the Viosca Knoll sediment traps and additional details are given in Table 1. All of the (McLane Mark-7 type) sediment traps had a 0.5 m<sup>2</sup> collection area and had 13 or 21 collection cups. A complete inventory of 71 individual samples from these traps is given in Table S-1 (Supporting Information). Prior to the start of the *Deepwater Horizon* oil spill on April 20, 2010, a sediment trap was deployed in the VK826 area as part of on-going NOAA and Minerals Management Service (now Bureau of Ocean Energy Management) *Lophelia II* research program concerning the well-studied *Lophelia pertusa* cold-water reef ecosystem that exists in the area (e.g., Sulak et al. 2008). After the spill began, additional sediment traps were deployed in the VK826 and VK906 areas through funding provided by the National Science Foundation's Rapid Response Research grant and from NOAA's NRDA (Table 1). In addition, a limited number of samples collected before the start of the spill were available from a sediment trap located in the Mississippi Canyon (MC751) area approximately 153 km southwest of the Macondo well (Fig. 1).

Of greatest relevance to this study, the three individual traps deployed in the VK826 area provide a near-continuous sample set (n=47) that, with a 14- or 15-day temporal resolution, spans 733 days. These 733 days include 221 days before the *Deepwater Horizon* oil spill commenced, the 87 days of the active spill (April 20, 2010-July 15, 2010), and 426 days after the well was shut-in (Table 1). The two individual traps deployed in the VK906 area provide a smaller sample set (n=20) spanning 90 days beginning two weeks after the Macondo well was capped and overlapping, temporally, with a subset of the samples collected at the adjacent VK826 site, increasing the lateral extent of our survey for that time-period (Fig. 1, Table 1).

## 2.2 Sample Preparation

The sediment trap samples were preserved *in situ* during collection with 20% buffered dimethyl sulfoxide (DMSO) and upon retrieval were stored cold (5°C) and dark until processing at the Woods Hole Oceanographic Institution (WHOI) laboratory. Each sample was wet sieved through 5-mm (intended to remove “swimmers”) and then 1-mm sieves. All sample fractions were visually inspected as there was an *a priori* expectation that some oil could be present. However, there was no visual evidence for oily snow particles and/or adhered oil in the < 1 mm, 1-5 mm, or > 5 mm fractions; i.e., by visual accounts the samples appeared typical of sediment trap samples unrelated to any oil spill. On average, the < 1 mm fraction represented >95% of the total mass and therefore, our analytical efforts were focused on this fraction, as is standard practice for ocean biogeochemical studies using sediment traps (Honjo et al., 2014).

Aliquots of the <1 mm size fraction were wet-split into 10 parts (RSD of 5%) with four splits being used for multiple analyses at WHOI, including particulate organic carbon (POC) and particulate organic nitrogen (PON) and sample dry weight (hence, mass flux) determinations following standard methods (Honjo et al., 1995). The remaining six aliquots of each sample were individually prepared for hydrocarbon analysis by rinsing with distilled water over a 0.3 µm pore, 47 mm diameter glass fiber filter (GFF) in order to remove any (operationally-defined) dissolved hydrocarbons. The six aliquots for each sample were then stored wet in a 10% buffered DMSO solution sealed in six 50 mL polypropylene centrifuge tubes and refrigerated (5°C). The individual sample masses for the 71 samples (< 1 mm) available for the chemical analysis described herein ranged from 26 mg to 9.8 g dry weight, of which approximately 80% was used for the analyses described below.

## 2.3 Sample Extraction

The six aliquots for all 71 sediment trap samples (< 1 mm) for chemical analysis were transferred from WHOI to Alpha Analytical Laboratory (Mansfield, MA) under full chain-of-custody on September 12, 2013. Samples were stored cold (4°C) and dark until sample preparation. Five of the six aliquots from each sample were centrifuged at 3500 RPM for 5 minutes and the supernatant was decanted and archived. (The sixth aliquot for each sample was archived and later returned to WHOI.) Particulates from each of

the five aliquots representing a single trap sample were rinsed from each vial with deionized water and composited upon transfer to an extraction jar. The extraction jar was then centrifuged at 3000 RPM for 5 minutes and the supernatant was filtered through pre-cleaned (baked 400°C for 1 hour, rinsed in dichloromethane and air-dried) 0.4 µm pore 47 mm diameter GFF. The filter was then transferred back into the extraction jar to be extracted along with the particulate. The filtrate was archived.

The composited particulate/filter from each sediment trap sample was then spiked with recovery internal surrogates (RIS; 5 $\alpha$ -androstane, acenaphthene-d<sub>10</sub>, chrysene-d<sub>12</sub>) and serially-extracted (3x) using fresh dichloromethane (DCM). Each sample's serial extracts were combined, dried with sodium sulfate, and concentrated to 1 mL using Kuderna Danish apparatus and nitrogen blow-down. The concentrated extracts were then processed through silica gel, eluting with DCM, following adaptations of EPA Method 3630 and re-concentrated to 1 mL (as above). The concentrated silica-cleaned extracts were then spiked with surrogate internal standards (SIS; *o*-terphenyl, *n*-tetracosane-d<sub>50</sub>, 2-methylnaphthalene-d<sub>10</sub>, pyrene-d<sub>10</sub>, benzo(b)fluoranthene-d<sub>12</sub>, and 5 $\beta$ (H)-cholane) prior to instrument analysis.

#### 2.4 Instrument Analysis

All sample extracts were analyzed using (1) modified EPA Method 8015B and (2) modified EPA Method 8270 as described in the following paragraphs. Additional details of these methods are described elsewhere (Douglas et al. 2015).

Modified EPA Method 8015B was conducted via gas chromatography-flame ionization detection (GC-FID; Agilent 6890) equipped with a Restek Rtx-5 (60 m x 0.25 mm ID, 0.25 µm film) fused silica capillary column. Extracts were injected (1 µL, pulsed splitless) into the GC programmed from 40°C (1 min hold) and ramped at 6°C/min to 315°C (30 min hold) using H<sub>2</sub> (3 mL/min) as the carrier gas. This analysis was used to determine the concentrations of GC-amenable total petroleum hydrocarbons (TPH; C<sub>9</sub>-C<sub>44</sub>) and individual *n*-alkanes (C<sub>9</sub>-C<sub>40</sub>) and (C<sub>15</sub>-C<sub>20</sub>) acyclic isoprenoids. Prior to sample analysis a minimum five-point calibration was performed to demonstrate the linear range of the analysis. The calibration solution was composed of selected aliphatic hydrocarbons within the *n*-C<sub>9</sub> to *n*-C<sub>40</sub> range. Analyte concentrations in the standard solutions ranged from 1 ng/µL to 200 ng/µL. Target analytes that were not in the calibration solution had the average response factor (RF) of the nearest eluting

compound(s) assigned as follows: RF of  $n$ -C<sub>14</sub> assigned to C<sub>15</sub> isoprenoids,  $n$ -C<sub>15</sub> assigned to C<sub>16</sub> isoprenoids;  $n$ -C<sub>17</sub> assigned to nor-pristane, and  $n$ -C<sub>40</sub> assigned to  $n$ -C<sub>39</sub>. All calibration solution compounds that fall within the window were used to generate the average RF for TPH. TPH was quantified by integrating the total C<sub>9</sub>-C<sub>44</sub> area after blank subtraction. Calibration check standards representative of the mid-level of the initial calibration and a procedural (solvent) blank were analyzed every 10 samples. The check standard's response was compared versus the average RF of the respective analytes contained in the initial calibration. All authentic samples and quality control samples were bracketed by passing mid-check standards.

Modified EPA Method 8270 was conducted via gas chromatography-mass spectrometry (GC-MS; Agilent 7890 GC with 5975c MS) with the MS operated in the selected ion monitoring (SIM) mode for improved sensitivity. Extracts were injected (1  $\mu$ L, pulsed splitless) into the GC containing a 60 m x 0.25 mm ID, 0.25  $\mu$ m film, Phenomenex ZB-5 capillary column and the oven programmed from 35°C (1 min hold) and ramped at 6°C/min to 315°C (30 min hold) using He as the carrier gas (1 ml/min). This analysis was used to determine the concentrations of 62 parent and alkylated decalins, polycyclic aromatic hydrocarbons (PAH), sulfur-containing aromatics, and 54 petroleum biomarkers (i.e., tricyclic and pentacyclic triterpanes and steranes, and triaromatic steroids (Table S-3). Prior to sample analysis, the GC-MS was tuned with perfluorotributylamine (PFTBA) at the beginning of each analytical sequence. A minimum 5-point initial calibration consisting of selected target compounds was established to demonstrate the linear range of the analysis. Analyte concentrations in the standard solutions ranged from 0.01 to 10 ng/ $\mu$ L for PAH and from 0.01 to 20 ng/ $\mu$ L for biomarkers. Quantification of target compounds was performed by the method of internal standards using average response factor (RF) determined in the initial calibration. Alkylated PAHs were quantified using the RF of the corresponding parent, triterpanes were quantified using the RF's for 17 $\alpha$ (H),21 $\beta$ (H)-hopane, and steranes and triaromatic steroids were quantified using the RF of 5 $\beta$ (H)-cholane. Biomarker identifications were based upon comparison to selected authentic standards (*Chiron Laboratories*), elution patterns in the peer-reviewed literature, and mass spectral interpretation from full scan GC/MS analyses conducted in our laboratory. Sample dry weights were determined separately and all concentrations are reported on a dry weight basis ( $\mu$ g/kg<sub>dry</sub>).

All sediment trap samples' surrogate-corrected concentration data are publically available through NOAA *Deepwater Horizon* NRDA data portal, DIVER (Data Integration Visualization Exploration and Reporting), available at <https://dwhdiver.orr.noaa.gov/>. Several samples had TPH concentrations reported below the sample specific reporting limit (i.e., reported concentrations were J-qualified and considered estimates; Table S-2); these were converted to non-detected in DIVER, but were utilized as reported herein. TPAH50 represents the total concentration of the 50 2- to 6-ring PAH analytes ranging from naphthalene to benzo(*g,h,i*)perylene, excluding perylene (Table S-3). All concentrations used herein have been converted to non-surrogate values.

The relative (hopane-normalized) concentrations of PAH and biomarkers in the sediment trap samples studied are compared to those of fresh Macondo oil and floating Macondo oils (n=62) collected during the active spill (Stout et al., 2016c). Those data are also publically available through the DIVER database. In addition, publically-available data obtained from the DIVER database for six sediment cores collected in the VK826 and VK906 areas in October 2011 (R/V *Holiday Chouest 3* cruise, Oct. 1-25, 2011) are presented herein.

## 2.5 Flux Calculations

Hydrocarbon sedimentation rates (flux) for TPH, TPAH16, TPAH50, and hopane ( $\mu\text{g}/\text{m}^2/\text{day}$ ) were calculated by multiplying the concentration of these hydrocarbons in trap samples ( $\mu\text{g}/\text{g}_{\text{dry}}$ ) by the total mass of particles (< 1 mm) in the trap samples ( $\text{g}_{\text{dry}}$ ) divided by 0.5  $\text{m}^2$  (surface area of the trap) then divided by the number of days during which each sequential sample cup was rotated into the open collection position (days):

$$\text{Flux } (\mu\text{g}/\text{m}^2/\text{day}) = [(\text{Conc } \mu\text{g}/\text{g}_{\text{dry}}) \times (\text{Mass } \text{g}_{\text{dry}})] \div 0.5 (\text{m}^2) \div \text{days} \quad \text{Eq. (1)}$$

Hopane (17 $\alpha$ (H),21 $\beta$ (H)-hopane) was one of the targeted petroleum biomarkers (Table S-3) and is recognized to be highly recalcitrant to oil weathering processes (Prince et al. 1994). After correcting for any pre-spill deposition of hopane, the sedimentation rate of hopane in those trap samples recognized to contain Macondo oil was used to estimate the sedimentation rates of Macondo oil on a mass basis ( $\text{kg}/\text{km}^2/\text{day}$ ) and volume basis ( $\text{barrels}/\text{km}^2/\text{day}$ ) using the previously-determined concentration of hopane (68.8  $\mu\text{g}/\text{g}$ ) and density (0.856  $\text{g}/\text{ml}$  at 5°C) of fresh Macondo oil (Stout et al., 2016c). The



sedimentation rates, mass, and volumes of Macondo oil calculated are considered conservative as they reasonably assume hopane was not weathered within the few months of our study.

### **3. Results and Interpretation**

Tabulated concentration data and corresponding sedimentation rates for the 71 sediment trap samples discussed herein are found in Tables S-1 and S-2.

#### **3.1 Conventional Flux Metrics**

Fig. 2 shows the temporal trend in sedimentation rates of sinking particulate mass (<1 mm fraction) and associated particulate organic carbon (POC) fluxes and bulk composition for the sediment trap samples studied, which are described in the following paragraphs. The shaded area spans the time interval of the *Deepwater Horizon* oil spill (April 20-July 15, 2010).

Total mass fluxes (Fig.2A) show high values in Winter 2009-10 for the Viosca Knoll (VK826) site, consistent with peak sedimentary discharge from the Mississippi River into the northern Gulf of Mexico (Snedden et al., 2007). Additional though lesser peaks in total mass flux are also observed coincident with the timing of the *Deepwater Horizon* oil spill in Spring 2010 and, at an even higher mass flux rate, in the Spring of 2011 (note that our time series lacks a complete data set for Winter 2010-11). Superficially, the POC fluxes at the VK826 location show a similar trend with peaks in accumulation rates in Winter 2009-10 and again in Spring 2010 and Spring 2011 (Fig.2B). Note, however, that the peak POC fluxes in all three cases are very similar (60-70 mg/cm<sup>2</sup>/day) even though total mass fluxes in Winter 2009-10 are almost double those observed in Spring 2010 and 2011 (Fig.2A).

The same variations are also apparent when one considers the bulk composition of the material arriving in the VK826 sediment trap over this two year time series (Fig.2C). During the Winter months the concentration of POC, as represented by the percent mass of POC of the total mass (%POC) of material reaching the traps, typically falls in the range 3-6% by mass whereas in the Spring/Summer windows is regularly >8% by mass (Fig. 2C). Although the POC concentration and total mass data do not correlate

directly, the elevated POC flux and concentration observed in Spring 2010 could be associated with settling of biomass and/or oil associated with the oil spill. However, comparable increases in both parameters were also observed at a similar time of year in 2011, between April and July. Thus, one could argue, conversely, that these data alone (for both Spring 2010 and Spring 2011) may be related to some natural “spring bloom” event. We note however, the C:N ratios of organic material in the particulate matter collected in the VK826 sediment trap in Spring 2010 reveal excess carbon is present during the period of the *Deepwater Horizon* oil spill compared to the organic matter collected at all other times across our 2 year time series (Fig.2D). While elevated POC:PON ratios in marine sediment trap samples are known to be consistent with more highly matured sinking biogenic matter, the extreme values reported here (>9 g/g) exceed the range typically expected from marine biogeochemical cycles (Honjo et al., 1995). It was this trend in bulk composition data, coincident with the dates of the *Deepwater Horizon* oil spill that first motivated us to further examine our sample suite using detailed hydrocarbon analyses for any evidence of marine oil snow in the Viosca Knoll area; the results of which are described below.

### 3.2 Hydrocarbon Concentrations

Fig. 3 shows the temporal trends in the concentrations of TPH, TPAH50, and hopane in the same trap particulate samples over the entire study period. The largely uninterrupted sample set for the VK826 site provides a complete record spanning from up to 221 days before to 512 days after the *Deepwater Horizon* disaster on April 20, 2010. A smaller sample set exists for the nearby VK906 site for 14 to 104 days after the Macondo well was shut-in and the leak stopped on July 15, 2010.

At the VK826 location trends for all three hydrocarbons show dramatic increases, approaching two orders of magnitude in the concentrations of TPH, TPAH50, and hopane in trap particulates coincident with the *Deepwater Horizon* oil spill (Fig. 3). Specifically, hydrocarbon concentrations increased sharply between the samples collected April 9 to 23, 2010 and April 23 to May 7, 2010, which coincides with the *Deepwater Horizon* explosion on April 20 and subsequent sinking of the rig on April 22, 2010. Elevated concentrations of hydrocarbons persisted throughout the 87-day spill but showed two distinct maxima, or “pulses”, separated by an interval of lower concentrations (Fig. 3). Possible causes for these “pulses” are discussed further below.

Finally, there was a rapid decrease in hydrocarbon concentrations in the sediment trap samples from VK826 soon after the spill ended on July 15, 2010. Low concentrations then persisted throughout the post-spill sampling interval (Fig. 3).

### 3.3 Hydrocarbon Flux

When calculating fluxes of any given parameter, it is important to remember that the deposition rate to the seafloor is a product of both the concentration of any given parameter per unit mass in the material settling through the ocean and the total mass flux of material sinking toward the seabed. Thus, while revealing, the hydrocarbon concentrations in our trap samples (Fig. 3) only reflect variations in the amounts of *both* oil and any non-oil (e.g., biomass or mineral matter) components present in the sediment trap samples. To understand the impact of this deposition, however, it is more appropriate to examine any temporal trends using hydrocarbon sedimentation rate, or *flux*. (All individual samples' calculated sedimentation rates are found in Table S-2.)

The fluxes calculated for TPH, TPAH50, and hopane for the sediment trap samples from the VK826 site are plotted in Fig. 4. Table 2 provides the average sedimentation rates for the VK826 trap samples representing the pre-spill, spill, and post-spill periods. Hydrocarbon flux rates calculated for the VK906 and MC751 trap samples (Table S-2) are not discussed due to their limited durations which we know, from comparison with the VK826 data, fall outside the window of spill-impacted sediment-trap flux. As noted above, however, hydrocarbon concentrations at both of these additional sites, at the times for when data are available, generally matched those present at VK826 both prior to (MC751) and following (VK906) the spill (Fig. 3).

Markedly higher sedimentation rates of TPH, TPAH50, and hopane existed at the VK826 site during the active *Deepwater Horizon* oil spill (Fig. 4). The seven trap samples collected during the active spill (points B through H; Fig. 4) had average sedimentation rates for TPH, TPAH50, and hopane of  $2,356 \pm 1,919$ ,  $5.4 \pm 5.7$  and  $0.89 \pm 1.0$   $\mu\text{g}/\text{m}^2/\text{day}$ , respectively (Table 2). These average sedimentation rates during the spill are 19- to 44-times higher than existed prior to the spill (Table 2), which clearly reveals that the deposition of oil in the VK826 area was coincident with the active *Deepwater Horizon* oil spill. By extension, it is reasonable to believe that sedimentation of oil was

occurring across and beneath a much larger area than represented by the VK826 sediment trap alone. Additional discussion of this is given in Section 4.2 (below).

During the active spill there were two distinct “pulses” of hydrocarbon sedimentation (Fig. 4), which were also apparent in the hydrocarbon concentration data (Fig. 3) – i.e., the material sinking through the water column was richer in these hydrocarbons per unit mass during the second pulse (Table S-2). The first “pulse” of oil occurred during the first four weeks of the spill (April 23-May 21; sample points B and C; Fig. 4), before declining slightly over the next four weeks (May 21-June 18; sample points D and E; Fig. 4). A second “pulse” of oil was then observed (June 18-July 25; sample points F to H; Fig. 4). The second “pulse” exhibited measurably higher oil sedimentation rates than the first “pulse”, with the second “pulse” exhibiting maxima of 5,756, 17.5, and 2.9  $\mu\text{g}/\text{m}^2/\text{day}$  of TPH, TPAH50, and hopane, respectively (sample point G, Fig. 4).

Further discussion as to the cause(s) for the two “pulses” of oil arriving at the VK826 trap is warranted. Comparison of Figs. 2 and 4 reveal that the first “pulse” of oil (sample points B and C) was accompanied by only slight increases in both the total mass of particles and POC (Fig.2) whereas the second “pulse” of oil (sample points F and G) was accompanied by larger increases in mass flux by a factor of >2, in addition to increases in hydrocarbon concentration per unit mass. Thus, the increase in flux between the two “pulses” (Fig.4) is even more pronounced than the variations in composition observed between the two (Fig. 3). This relationship between the fluxes of oil, total mass and POC can be more easily seen in Fig. 5, which shows the flux of hopane *versus* those for total particulate mass (Fig. 5A) and POC (Fig. 5B) for the VK826 sediment trap samples before, during, and after the active spill. The markedly higher fluxes of oil (represented by hopane) during the active spill, at any given value of total particulate mass or POC flux, are clearly evident – and are at their highest during the second “pulse” of oil (sample points F, G and H; June 18-July 25), which also coincide with the highest mass and POC flux values for samples collected during the period of the active spill (samples B through H).

Thus, there is a clear relationship between the amounts of total particulate mass or POC sinking through the water column and the amount of oil being transported to the seafloor. We attribute this relationship to the formation of mucus-rich marine snow that was observed to form *in situ* at the sea surface during the active spill (Passow et al., 2012). Specifically, phytoplankton under stress produce a mucus-like, sticky (extracellular

polymeric) substance that promotes their aggregation and sinking, a process which is hypothesized to have carried spill oil from the surface to the seafloor (Passow, 2014) or to have scavenged chemically dispersed oil from the water column (Fu et al., 2014).

The marine oil snow hypothesis is clearly supported by the VK826 sediment trap results, which demonstrate that two distinct marine oil “snow storms” occurred in the VK826 area resulting in two “pulses” of oil being transported to the seafloor (Fig. 4). A combination of factors were likely involved in promoting these two marine oil snow “storm” events in the VK826 area during the course of the active spill. These factors likely included temporal variations in: (1) the persistence of floating oil in the area (i.e., oil days); (2) the surface application of chemical dispersants in the area that released oil back into the water column; (3) plankton and bacterial populations; (4) abundances of mineral matter, perhaps due to a resuspension event; and (5) the hydrodynamic conditions affecting the collision rates among oil and any (organic and/or inorganic) particles in the water. Based upon the sediment trap results, we can infer that some combination of these factors must have been most favorable for the formation and sedimentation of marine oil snow in the VK826 area during the second “pulse” of oil that occurred later in the spill, between June 18-July 25 (sample points F, G and H; Figs. 4 and 5). Notably, only shortly after this second “pulse” of oil, sedimentation rates dropped quickly to rates that were directly comparable to those observed prior to the spill (Fig. 4; Table 2). The average post-spill flux for hopane is only marginally higher than what had existed prior to the spill (Fig. 4), and given the error among these average rates (Table 2) provides equivocal evidence for the persistence of any “lingering” oil following the end of the active spill. The fingerprinting results presented in Sections 3.4 to 3.6, however, further address this possibility.

The obvious temporal relationship between hydrocarbon fluxes in the Viosca Knoll 826 area and the duration of the *Deepwater Horizon* oil spill (Fig. 4; Table 2) provides strong preliminary evidence that Macondo oil (and not some “other” oil) was responsible for the fluxes of hydrocarbons settling through the water column at that time. Additional evidence for the presence of Macondo oil and its degree of weathering is provided in the detailed characteristics of these hydrocarbons, as discussed in the following sections.

### 3.4 Total Petroleum Hydrocarbons

Fig. 6 shows a series of GC/FID chromatograms that reveal the nature of the TPH found in trap samples collected before, during, and after the *Deepwater Horizon* oil spill. Prior

to the spill (Fig.6A) the sediment trap samples' TPH chromatograms were dominated by discrete, resolved peaks and no unresolved complex mixture (UCM). GC/MS analysis revealed some of the smaller resolved peaks were odd-carbon *n*-alkanes typical of epicuticular higher plant waxes (Fig. 6A; Eglinton and Hamilton 1967). The larger peaks, however, were tentatively identified as cyclic terpenoids (see triangles; Fig. 6) likely associated with recent marine biomass – not petroleum.

The GC/FID chromatograms for the TPH in the seven samples collected during the spill exhibit clear evidence for the presence of crude oil. However, the extent of weathering of the oil varies progressively over time (Fig. 6B-H). The earliest sample collected during the spill contains crude oil that exhibits a relatively small unresolved complex mixture (UCM) atop of which are a series of *n*-alkanes ranging from *n*-C<sub>15</sub> to *n*-C<sub>40</sub>, reaching a maximum around *n*-C<sub>20</sub> (Fig. 6B). Pristane and phytane are present, though in lower concentrations than the corresponding *n*-alkanes. The features of this “first arriving” oil are consistent with Macondo oil that has experienced evaporative losses of most compounds below *n*-C<sub>15</sub> while evidence for biodegradation is not (yet) evident.

Over time, the crude oil present in the trap samples exhibits signs of increased weathering, particularly biodegradation (Fig. 6C-H). There is a progressive loss in *n*-alkanes, which are the hydrocarbons in crude oil that have long been recognized to be those most highly susceptible to biodegradation (Peters and Moldowan, 1993). Eventually, only the longer chain *n*-alkanes (*n*-C<sub>28</sub> to *n*-C<sub>45</sub>, reaching a maximum around *n*-C<sub>33</sub>) are retained (Fig. 6H). The more resistant acyclic isoprenoids, pristane and phytane, are initially preserved (Fig. 6B-F), but they too are depleted or absent due to biodegradation in the later trap samples (Fig. 6G-H). Over time the shape of the UCM progressively shifts toward higher and higher boiling range material, reflecting an increasing loss of smaller, lower boiling hydrocarbons. This steady progression in weathering represented by the first four samples collected during the spill (Fig. 6B-E) is interrupted, however, by the somewhat “fresher” character of the oil present in the fifth sample collected (Fig. 6F), which exhibits higher proportions of both resolved (*n*-alkanes, pristane and phytane) and unresolved mass below *n*-C<sub>25</sub> compared to the immediately preceding sample (Fig.6E). Importantly, the arrival of this slightly less weathered oil (compare Figs. 6E to 6F) coincides with the onset of the second “pulse” of oil that arrived at the VK826 trap later in the oil spill (Fig. 4).

There is a notable variation in the relative abundance of the biomass-related compounds *versus* oil among the chromatograms containing oil (see triangles; Fig. 6B-H) that also follows the “two pulse” trend. Specifically, the samples represented by the first “pulse” of oil (Fig. 6B-D) contain a greater relative (to oil) abundance of biomass-related compounds than the samples represented by the second “pulse” of oil (Fig. 6F-H). Although the higher concentrations of oil in the latter may play a role, it is also possible that the abundance of these particular biomass-related compounds may reflect different types of biomass within the samples. Specifically, the particulate biomass that contributed to the first “pulse” of marine oil snow may have been different from the biomass that participated in the second “pulse”. Because the oil in the first “pulse” was less biodegraded than the oil in the second “pulse” one could speculate that the dominant biomass promulgating these two marine oil snow events might have been (non-oil-degrading) phytoplankton and oil-degrading bacteria, respectively.

As noted above, the flux of TPH after the active spill, on average, returned to levels comparable to those that existed prior to the spill (Table 2). However, while TPH flux rate alone cannot be used to argue that there was any continuing effect of oil being transported to the seafloor post-spill, the character of the TPH arriving at the trap after the spill does exhibit some evidence in support of that possibility. For example, Figure 6I shows that the sediment trap TPH exhibits a trace UCM and minor longer chain *n*-alkanes (with no odd-carbon dominance) that were not present prior to the spill (Fig.6A). Both of these features suggest that some traces of oil may have continued to be delivered to the seafloor in the weeks following the end of the active spill.

What is more notable from our data, however, is the clear evidence for progressive biodegradation of the oil arriving at the trap throughout the duration of the spill (Fig. 6; see above). No biodegradation was observed among the population of 62 Macondo surface slicks, mounds, and sheens collected at the sea surface between May 10 and June 20, 2010 (Stout et al., 2016c). The lack of biodegradation among those floating oils was attributed to the inability for biodegradation to advance quickly within the coalesced surface slick and sheen samples analyzed in that study. The sediment trap results reported here, however, indicate that biodegradation was able to affect marine oil snow particles as they sank through the water column, perhaps facilitated by chemical

dispersants. If true this suggests that, as intended, dispersants applied to surface oil allowed biodegradation to proceed within dispersed oil droplets. Because the “first arriving” oil reaching the trap was not biodegraded (Fig. 6B) it seems possible that there may have been an initial lag in the ability of indigenous bacteria to respond to the oil’s presence within the water column. Throughout the course of the 87-day spill, however, biodegradation of the settling oil within the water column appears to have progressed aggressively (Fig. 6B-H).

### 3.5 PAHs

Fig. 7 plots hopane-normalized histograms showing the relative abundance and distributions of PAHs in the trap samples collected before, during, and after the *Deepwater Horizon* oil spill. Prior to the spill only low fluxes of TPAH were evident in the VK826 trap samples (Fig. 4B) that averaged  $0.20 \pm 0.16 \mu\text{g}/\text{m}^2/\text{day}$  TPAH50 (Table 2). These were comprised predominantly of numerous Priority Pollutant PAHs (Fig. 7A), which are likely associated with “background” inputs of atmospheric fallout or riverine inputs of combustion-derived PAH. Also prominent in the pre-spill PAHs is perylene (Fig. 7A), which has been long associated with biomass precursors (Venkatesan, 1988). (As noted above, perylene is excluded from the calculation of TPAH50.)

During the oil spill, the flux of TPAH50 dramatically increased (Fig. 4B), and averaged  $5.4 \pm 5.7 \mu\text{g}/\text{m}^2/\text{day}$  throughout the spill (Table 2). The character of the PAH present in the VK826 trap samples demonstrates the clear presence of petroleum-derived (petrogenic) PAHs (Fig. 7B-H). These PAHs are initially dominated by 3-ring alkylated phenanthrenes with lesser amounts of alkylated fluoranthenes, pyrenes, benz(a)anthracenes, and chrysenes and sulfur-containing alkyl-dibenzothiophenes and naphthobenzothiophenes (Fig. 7B). Two-ring naphthalenes, which are the dominant PAHs present in fresh Macondo oil (Stout et al., 2016c), are markedly reduced in the sediment trap samples. Notably, the retention of decalins (D0-D4) in the face of reduced amounts of the comparably volatile but more soluble naphthalenes suggests that dissolution and/or biodegradation (and not just evaporation) had already affected the “first arriving” oil at the trap (Fig. 7B). Over the course of the spill the character of the PAHs exhibits an overall weathering trend, as was observed in the TPH chromatograms. The PAHs in the trap samples become increasingly dominated by higher molecular weight alkylated chrysenes (Fig. 7B-E) which themselves become



increasingly dominated by the C<sub>4</sub>-alkylated homologue (Fig. 7E). The shift in PAHs toward higher molecular weight PAHs and more highly alkylated homologues is consistent with the effects expected from biodegradation (Elmendorf et al., 1994), although dissolution may also contribute.

Coincident with the second “pulse” of oil that arrived at the trap during the oil spill (Fig. 4), and just as was observed for the TPH (Fig. 6F), the PAHs become somewhat “fresher” midway through the oil spill period. For example, in sample F, decalins are again present and alkylated phenanthrenes are again dominant (see D0-D4 in Fig. 7F). Continued weathering of these late-arriving oils then, once again, shifts the PAHs toward higher molecular weight PAHs and more highly alkylated homologues (Figs. 7G and 7H).

After the well was capped the flux of PAHs quickly dropped to pre-spill levels (Fig. 4, Table 2), and averaged only  $0.14 \pm 0.12$  and  $0.28 \pm 0.25$   $\mu\text{g}/\text{m}^2/\text{day}$  (Post-spill periods A and B, respectively; Table 2). These post-spill fluxes approximate the TPAH50 flux that had existed prior to the spill ( $0.20 \pm 0.16$   $\mu\text{g}/\text{m}^2/\text{day}$ ; Table 2). The distribution of PAHs measured in trap samples after the spill was also relatively enriched in Priority Pollutant PAHs (and perylene; Fig. 7I), providing no evidence for continuing oil deposition to the seafloor, after the active spill ceased.

Notably, detailed features among PAH isomers provide evidence that the oil reaching the VK826 trap samples during the active spill originated from oil that was once at the sea surface, rather than from oil derived from any deep sea plume. Specifically, it is well known that photo-oxidation can preferentially affect aromatic compounds in petroleum released into the environment (Garrett et al., 1998; Plata et al., 2008). Isomers of some of the C<sub>1</sub>-fluoranthrenes/pyrenes and benzofluorenes are particularly susceptible (CEN, 2012) and, thus, evaluating these compounds’ isomer patterns can reveal evidence of photo-oxidation. Fig. 8 shows the partial extracted ion profiles (EIPs) for methyl-fluoranthrenes and methyl-pyrenes ( $m/z$  216) for fresh Macondo crude oil and for the sediment trap samples at the beginning and end of the spill (i.e., samples “B” and “H”, per Figure 4). Inspection reveals that the oils from the trap samples have experienced a preferential loss of 1-methylpyrene (1MPy) and all three benzofluorene isomers (BaF, BbF, BcF) relative to 2-methylpyrene (2MPy) and 4-methylpyrene (4MPy), consistent

with photo-oxidation (Fig. 8). This indicates that the oil found in the sediment traps had previously been at the sea surface where it was exposed to *UV* radiation.

Finally, it is worth noting that between April 28 and July 19, 2010 approximately 220,500 to 310,400 barrels (bbls) of floating Macondo crude oil were consumed, reportedly, in 411 separate *in situ* burn events (Mabile and Allen, 2010; Perring et al., 2011). At least some fraction of the uncombusted emissions from these fires might be reasonably expected to have returned to the sea surface and settled through the water column. Priority Pollutant PAHs (i.e. non-alkylated parent PAHs) are known to be abundant in partially combusted organic matter (Blumer and Youngblood, 1975). The sediment trap samples collected at VK826 and VK906 have only trace amounts of Priority Pollutant PAHs and thus do not appear to show any evidence for settling through the water column of combustion-derived particulates resulting from *in situ* burning.

### 3.6 *Petroleum Biomarkers*

As noted above, hopane fluxes showed a dramatic increase in the VK826 trap samples immediately following the start of the *Deepwater Horizon* oil spill, remained high and exhibited a double pulse over the duration of the spill, and then exhibited a sharp decline immediately after the well was shut-in (Fig. 4C). Hopane, of course, is only one of the targeted biomarkers present in crude oil – but in the case of the sediment trap samples studied, hopane was the most abundant biomarker detected and, hence, most easily monitored. The distribution, or “fingerprint” of all targeted biomarkers provides an important means to distinguish among different petroleums (Wang et al., 2006). In this instance, the distribution of biomarkers is another means to confirm the presence of Macondo oil (*versus* any “other” oil) within the sediment trap samples.

Fig. 9 shows hopane-normalized histograms of all targeted biomarkers – triterpanes, regular and dia-steranes, and triaromatic steroids (TAS) – in the same suite of trap samples shown in Figs. 4 to 7. For comparison, also shown in Fig. 9 are the average biomarker distributions for fresh Macondo oil and for floating Macondo oils from 2010 (Stout et al., 2016c).

Prior to the spill sinking particulates from the VK826 area contained very low concentrations of biomarkers, most being undetectable (Fig. 9A). On average, the flux

of hopane was only  $0.02 \pm 0.01 \mu\text{g}/\text{m}^2/\text{day}$  prior to the spill (Table 2). The most prominent compounds detected in the pre-spill samples (which plot off-scale in Fig. 9A) are four interfering compounds that happen to co-elute with targeted triterpenoids, (T11a, T20, T26, and T35). These interferences are commonly recognized in marine sediments and are believed to be biomass- (bacterial- or plant- ) derived (Simoneit 1986; Kennicutt and Comet 1992; Hood et al. 2002; Dembicki and Harry 2010). Most of these compounds are unidentified triterpenoids that produce a  $m/z$  191 fragment during mass spectrometry; the interferant present at T20 (which co-elutes with the targeted  $17\beta(\text{H}), 21\alpha(\text{H})$ -moretane) is likely  $17\beta(\text{H}), 21\beta(\text{H})$ -30-norhopane.

Immediately following the start of, and throughout the duration of the *Deepwater Horizon* oil spill, the VK826 sediment trap samples exhibited high fluxes of hopane (Fig. 4C) that averaged  $0.89 \pm 0.95 \mu\text{g}/\text{m}^2/\text{day}$  (Table 2) with complete suites of triterpanes, steranes, and TAS being present (Fig. 9B-H). The profiles of these biomarkers closely match those of the fresh Macondo oil and floating Macondo oils collected in the spring and summer of 2010 for surface waters in the northern GoM (Fig. 9B-H). The distributions of triterpanes and steranes match very well, except for differences due to the aforementioned interfering triterpenoids (light blue bars; Fig. 9). However, all four TAS congeners in the trap samples are present in relatively lower concentrations than in fresh or (on average) floating Macondo oil (see yellow bars; Fig. 9B-H), which we can attribute to weathering.

Specifically, the floating Macondo oils had, on average, also experienced a reduction in TAS relative to fresh oil (Fig. 9), with the most severely weathered floating oils containing TAS in abundances comparable to the trap samples (Stout et al., 2016c). This reduction in TAS was also observed by other researchers who attributed it to photo-oxidation of these photo-reactive (polycyclic aromatic) biomarkers (Aeppli et al., 2014; Radovic et al., 2014), although some dissolution or, perhaps even biodegradation, of these aromatic biomarkers also seems possible. Regardless, this difference in biomarker fingerprints of the trap samples *versus* fresh or floating Macondo oil is readily attributable to weathering, and does not indicate the presence of a “different” oil. Assuming photo-oxidation caused (or, at least, contributed to) the observed reductions in TAS, provide further evidence that the oil reaching the VK826 sediment trap during the period of the *Deepwater Horizon* spill had previously been present at the ocean surface

where they were exposed to *UV* radiation (see previous discussion on photo-oxidation of PAH isomers in Section 3.5; Fig. 8).

After the well was shut-in on July 15, the sediment trap samples exhibited average flux rates of hopane that, within error, were indistinguishable from those recorded prior to the spill ( $0.03 \pm 0.02$  versus  $0.02 \pm 0.01$   $\mu\text{g}/\text{m}^2/\text{day}$ ; Table 2). The triterpanes in these post-spill samples became increasingly dominated by the interfering triterpenoids associated with biomass, although a full suite of regular and diasteranes mostly consistent with Macondo oil were still present (Fig. 9I). In fact, trap samples exhibiting suites of steranes and diasteranes persisted in VK826 trap samples until mid-November 2010, i.e., four months after the well was shut-in, before finally becoming undetectable. Because such suites of steranes and diasteranes were not present in trap samples collected prior to the spill (Fig. 9A), their persistence suggests that some “lingering” vestiges of the Macondo oil may have still been settling to the seafloor in the VK826 area for up to four months after the end of the active spill. Yan et al. (2016) similarly reported the presence of “lingering” oil settling to the seafloor in a deep-sea location 7.4 km southwest of the well for five months after the spill ended.

#### **4. Significance of Results**

##### *4.1 Volume of Macondo oil deposited to the seafloor in the Viosca Knoll area*

Converting the observed sedimentation rates for Macondo oil-derived hydrocarbons during the active spill (Table 2) into the volume of Macondo oil deposited to the seafloor in the VK826 area in the shallow northern GoM is best achieved using the sedimentation rate for hopane, which is considered a conservative marker for Macondo oil within the trap samples. Specifically, because the concentration of hopane in the fresh liquid Macondo oil is known ( $68.8$   $\mu\text{g}/\text{g}$ ; Stout et al., 2016c), and because hopane is not considered to have been lost due to weathering, the mass of liquid Macondo oil represented in the samples collected in the sediment traps can be calculated from the hopane fluxes for each sampling interval throughout the spill. In addition, because the density of fresh Macondo oil is also known ( $0.856$   $\text{g}/\text{cm}^3$  at  $5^\circ\text{C}$ ; Stout et al., 2016c), the calculated *mass* of oil deposited can also be converted to *volume*. The results of these calculations are given in Table 3. The total volume calculated assumes that the oil deposited was fresh Macondo oil (which we know was not the case; see above) and

therefore does not include the volume of any expelled oil that was lost to weathering *before* reaching the VK826 sediment traps/seafloor. Nonetheless this calculation provides information on the total oil budget for the *Deepwater Horizon* oil spill.

The average “background” hopane sedimentation rate at the VK826 site (0.02  $\mu\text{g}/\text{m}^2/\text{day}$ ; Table 2) must first be subtracted from the total (“background” plus spill) hopane sedimentation rates for each of the seven samples (B to H; Fig. 4) collected during the active spill (and which clearly contained Macondo oil; see above). The mass and volume of Macondo oil represented by each sample can then be summed to provide an estimate of the unit-area fluxes of mass and volume of Macondo oil deposited in the over the course of the active spill. The results of our calculations show that during the active spill a total of approximately 10 barrels (bbls) of Macondo oil per  $\text{km}^2$  was delivered to the seafloor in the VK826 area (Table 3).

#### 4.2 *Implications of VK826 Sediment Trap Results*

The VK826 (*Lophelia* reef) location, at a depth of  $\sim 450\text{m}$ , was too shallow to have been impacted by oil transported laterally within the dispersing deep-sea plume that never penetrated to water depths shallower than  $1000\text{m}$  (Camilli et al. 2010). Consistent with this, our new VK826 sediment trap results provide clear evidence that throughout the duration of the *Deepwater Horizon* oil spill, some fraction of Macondo oil sinking to the seafloor at this location was being delivered vertically from the overlying ocean surface (as evidenced by photo-oxidation of the oil; Fig. 8). Thus, marine oil snow formed within the deep-sea plume was clearly not the only source of oil to reach the seafloor of the northern GoM.

Further, it is clear that the phenomenon of Macondo oil sinking from the ocean surface to the seafloor at the VK826 site would not have been unique to this specific location considering the lateral extent of the surface oil slicks that overlay that sediment trap mooring. Rather, logic dictates that the process of oil sinking to the seafloor, after once having reached the ocean surface, must have been widespread and occurred over large regions of the northern GoM, providing a mechanism – previously unrecognized – of delivering Macondo oil to shallow shelf and shelf-edge sediments across the northern GoM.

*How widespread might this phenomenon have been?* As described above, a combination of factors likely controlled the flux of oil from the ocean surface to the seafloor at any given location. The most critical factor in this process would likely have

been the presence and abundance of surface oil above any given location, a parameter that was assessed continuously throughout the northern GoM during and after the spill (April 25-July 28, 2010) using a variety of satellite sensors (Graettinger et al., 2015).

Fig. 10 shows the cumulative oil days for the region from April to mid-August 2010 reported by Graettinger et al. (2015). The VK826 (and VK906) sediment trap(s) occur within an approximately 7600 km<sup>2</sup> “footprint” indicated to have experienced more than 30 days of oil present at the surface, which we have enclosed by the dashed line shown (Fig. 10). As can be seen, some areas inside this 7600 km<sup>2</sup> area, including the VK906 site, experienced more (above 40 or even 50) oil days while areas outside of this 7600 km<sup>2</sup> area experienced fewer (but still greater than zero) oil days.

It is reasonable to assume that flux of oil from the surface to the seafloor occurred over this entire region, but were likely higher in areas that experienced more oil days and *vice versa*. To establish a minimum flux, therefore, we conservatively assume that surface oil sank to the seafloor for a minimum of 30 days within the 7600 km<sup>2</sup> footprint that encompasses the VK826 (and VK906) site(s) at a rate represented by the VK826 fluxes reported here. Notably, approximately half of this 7600 km<sup>2</sup> area occurs in water depths less than 1000m and even extends onto portions of the shelf (< 200m; Fig. 10).

Even considering the 7600 km<sup>2</sup> area as conservative (we have not included any fluxes for oil sinking to the seafloor outside the >30 oil day region in our calculations) the dashed envelope shown in Fig.10, is much larger than the area of seafloor previously-recognized to have been impacted by sunken Macondo oil. For comparison, using kriging of non-background/non-seep hopane concentrations in surface sediments (as established through chemical fingerprinting; Stout et al., 2016a), Stout et al. (2016b) had previously calculated that only between 1030 and 1910 km<sup>2</sup> of deep seafloor had been measurably impacted by Macondo oil (see Fig. 10). Thus, the 7600 km<sup>2</sup> minimum area of seafloor calculated to have been impacted by marine oil snow settling via the surface ocean, in this study, represents a 4- to 7-fold increase over all seafloor “footprint(s)” previously recognized to have been impacted by fall-out from the *Deepwater Horizon* oil-spill based on conventional geochemical analysis of sediments collected from beneath the dispersing deep-sea plume. Notably, our results are quite comparable to Chanton et al. (2015) who, based upon radiocarbon results for surface sediments concluded that seafloor oiling had occurred over 8400 km<sup>2</sup>.

One might reasonably ask: *Why didn't prior sediment-based studies from the shallow Northern GoM (e.g., Valentine et al., 2014; Stout et al., 2016a) recognize the large benthic "footprint" we demonstrate here?* We believe the answer to this question is two-fold. First, existing sediment studies were constrained by the sediment core data available. Most of the 728 sediment cores collected in the course of the NRDA were collected from the deep sea (>1000m) with only a few collected on the slope or shelf (Fig. 1). The low sample density of sediment cores that were collected from these shallower areas provided low spatial resolution that precluded the ability to statistically recognize any impact in areas of low sampling density, even where some impact was suspected (Valentine et al., 2014). Second, the fluxes reported here for VK826 were transient and would not be so readily detectable from the time-integrated sampling that sediment coring represents – even at locations, including VK906 and VK826, where some sediment cores *were* collected. Consequently, the effects of dilution on the concentration of any Macondo oil deposited to the seafloor, where cores were sampled at resolutions of between 0-1 cm and 0-2 cm sediment intervals, undoubtedly impeded the ability to recognize excess hopane or to chemically fingerprint the hydrocarbons present in areas where only Macondo oil had sunk (i.e., outside the “footprints” recognized by Stout et al., 2016b; Fig. 10). Notably, however, a limited number of ultra-high resolution cores (analyzed at 0-2 or 0-5 mm intervals) collected in the DeSoto Canyon area (east of VK826) exhibited elevated concentrations of PAH and biomarkers at their surfaces that *were* attributed to marine oil snow from the *Deepwater Horizon* oil spill (Romero et al., 2015; Brooks et al. 2015). By contrast, recognizing an impact to the surface from the lower resolution (0-1 cm) sampling of the majority of the hundreds of NRDA cores collected, was beyond the sensitivities of the standard analytical protocols employed.

To illustrate this point, concentrations of Macondo-derived TPAH50 and hopane in the surface (0-1 cm) sediment layer can be predicted using the average sedimentation rates for each parameter, as obtained from the VK826 trap data (Table S-4). These calculations reveal the predicted concentrations of Macondo-derived TPAH50 and hopane deposited as marine snow in the VK826 area during the active spill in the upper 0-1 cm of sediment to be  $19.8 \pm 21.7 \mu\text{g/g}$  and  $3.3 \pm 3.6 \mu\text{g/g}$ , respectively. Although these low concentrations are above the typical analytical reporting limits for sediments, in practice their impact may be difficult to recognize, let alone attribute to Macondo oil using chemical fingerprinting.

Despite these practical considerations, some of the six sediment cores collected in October 2011 from the VK826 and VK906 sites do show increases (albeit slight) in the concentrations of TPAH50 and/or hopane in the surface layers, while other cores show quite consistent concentrations of TPAH and hopane throughout (Fig. 11). The increased concentration at the top of some cores and lack of increases in others likely speaks to the heterogeneities consistent with particle (marine oil snow) deposition. Those cores exhibiting increases, however, when viewed in light of the VK826 sediment trap data presented here (and the higher-resolution sediment-sampling results of Romero et al., 2015), suggest that Macondo oil-derived PAH and hopane did contribute to the total hydrocarbons in the surface sediments. Of course, it is also notable that the sediment cores that were collected from VK826 and VK906 were only collected in October 2011, more than a year after the Macondo marine oil snow was deposited during the active spill. Over the intervening 18 months, multiple chemical, biological, or physical processes may have acted to reduce the Macondo-derived hydrocarbon concentrations that were initially deposited to the seafloor in these locations. To conclude this section, we argue that sediments in any shallow (< 1000m) setting in the northern GoM, underlying areas that experienced frequent oil days, are likely to have been impacted by Macondo-derived hydrocarbons associated with marine oil snow sinking from the ocean surface in a manner similar to that documented here for VK826.

*How much oil was deposited on the seafloor through marine oil snow formed at/near the surface?* If it is assumed, conservatively, that the volume of oil deposited near the VK826 site (10 bbl/km<sup>2</sup>; Table 3) is representative of the whole 7600 km<sup>2</sup> of the northern GoM seafloor that underlay 30+ cumulative surface oil days, it can be estimated that approximately 76,000 bbl of oil that had once been part of the surface oil slicks resulting from the *Deepwater Horizon* accident may have sunk within the 7600 km<sup>2</sup> footprint indicated (Fig. 10). Of course, this estimate remains highly conservative: it is more likely that the volume of surface-slick oil that sank closer to the wellhead, in the area that experienced more than 30 oil days (>40 or >50 days; Fig. 10) was significantly higher. In addition, some additional volume of surface oil likely sank beyond the 7600 km<sup>2</sup> area (i.e., in the area that experienced < 30 oil days but >0 oil days; Fig. 10). Therefore, although only roughly estimated, we consider our prediction that 76,000 bbl of surface oil sank to the northern GoM seafloor to be a conservative minimum.

*How does this volume compare to the volume of oil on the seafloor derived from the deep-sea plume?* Using the same hopane-based method to estimate oil volume



employed herein, Stout et al. (2016b) estimated that between 152,000 bbl and 173,000 bbl of Macondo oil was present in the 0-1cm layer of seafloor sediments within their minimal (1,030 km<sup>2</sup>) and maximal (1,910 km<sup>2</sup>) deep-sea “footprints”, respectively.<sup>1</sup> Because these deep-sea, surface sediment “footprints” mostly fall within the 7600 km<sup>2</sup> area over which we predict that at least 76,000 bbl of surface-slick oil was deposited (Fig. 10) it is now clear that some portion of the total Macondo oil (i.e., 10 bbl/km<sup>2</sup>) within each of these deep-sea sediment-surface “footprints” must have been derived from the sinking of surface oil.

Assuming spatial homogeneity across the 76,000 km<sup>2</sup> area of >30 oil days, we calculate that 7 to 11 percent (by volume) of the total Macondo oil found *inside* the previously-recognized (minimal and maximal) deep-sea, surface sediment “footprints” was derived from oil that had sunk from the surface (Table 4). Conversely, of course, that implies that 89 to 93 percent of the Macondo oil found within these deep-sea, impacted “footprints” was derived from the deep-sea plume (Table 4). While we consider those ranges, updated from those reported by Stout et al. (2016b,c) to be representative over the whole of their deep-sea “footprints” we might expect that the relative contributions from sinking surface oil would be lowest at stations closest to the well and *vice versa*. Regardless, overall and within the previously-established deep-sea surface sediment “footprints” (Stout et al., 2016b, c) our results indicate that the dominant source of oil reaching the seafloor was the deep-sea plume (89 to 93%) – this is also consistent with the previously-recognized southwesterly-skewed geometry of those deep-sea sediment-surface “footprints” (Valentine et al. 2014; Stout et al. 2016b). What is new here, rather, is that there is both a larger area of GoM seafloor, and one that extends to depths shallower than the deep sea plume could reach, which has also been impacted by Macondo Oil fall-out.

Subtracting the fluxes attributable to the already-recognized deep-sea footprint areas from our total surface-derived oil deposition volumes, we now calculate (Table 4) that an additional 56,900 to 65,700 bbl of sunken surface-derived oil was deposited to the seafloor *outside* of the previously-recognized deep-sea “footprints”, spread across the

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<sup>1</sup> Stout et al. (2016b) also determined approximately 67,000 to 74,000 bbl of Macondo oil was deposited in subsurface (> 1 cm) sediments near the well. These volumes are envisioned to have been overwhelming deposited by direct fallout from the well, and not from marine oil snow. As such they are excluded from the discussion here, which is focused on marine oil snow contributions to surface sediments outside the immediate fallout zone around the well. Those additional volumes, nonetheless, *should* be included in any total “sunken” oil estimates.

7600 km<sup>2</sup> area shown in Fig.10 (Table 4). These additional and substantial volumes of sunken surface oil were unrecognized prior to this work. While we would contend that our estimates remain conservative, they simultaneously represent significant volumes of previously-unrecognized sunken surface oil, increasing the total volume of Macondo oil that had previously been recognized to have been deposited to the GoM seafloor by more than 33% (Table 4). When combined with prior work that focused on impacts in the deep-sea at depths greater than 1000m (Stout et al., 2016b) we can now calculate that a total of at least 217,700 to 229,900 bbl of oil was deposited in the form of marine oil snow over an area of at least 7600 km<sup>2</sup> of seafloor surface (0-1 cm) following the *Deepwater Horizon* accident (Table 4). This range in the volume of oil deposited on the seafloor, either directly from fallout near the well, deposition of oil from the sub-sea plume, or sinking of marine oil snow from the sea surface represents 6.8 to 7.2 % of the 3.19 million barrels of oil spilled that was not recovered or burned (per U.S. District Court, 2015; Table 4).

## **5. Conclusions**

Sediment trap samples from the Viosca Knoll (*Lophelia* reef) shelf edge area (VK826), approximately 60 km northeast of the failed Macondo well, were collected over a 2-year time series extending from before and during until more than 12 months after the *Deepwater Horizon* oil spill. Detailed chemical analyses were performed on the <1 mm particulate fraction in order to assess the presence, character and sedimentation rate of any Macondo oil impacting the reef ecosystems in this area. This study contributes to the understanding of the marine oil snow phenomenon caused by the *Deepwater Horizon* oil spill. The following conclusions are reached:

[1] The sedimentation rates of conventional metrics, *viz.*, total mass of particulate (<1 mm) and particulate organic carbon (POC) provided no immediate basis upon which to recognize an impact of the *Deepwater Horizon* oil spill in the Viosca Knoll area. However, elevated POC:PON ratios during the spill suggested sinking oil may have been present, warranting a more detailed study of hydrocarbons.

[2] Sedimentation rates of hydrocarbons – measured as total petroleum hydrocarbons (TPH), total polycyclic aromatic hydrocarbons (TPAH50), and hopane – in the same samples showed dramatic increases, more than an order of magnitude

higher than pre- and post-spill background values, coincident with the active *Deepwater Horizon* oil spill (April 20 to July 15, 2010).

[3] During the active spill period, all seven samples from the VK826 site exhibited average sedimentation rates for TPH, TPAH50, and hopane of 2356, 5.4 and 0.89  $\mu\text{g}/\text{m}^2/\text{day}$ , respectively. These values are 19- to 44-times higher than were measured prior to the spill. After the active spill, hydrocarbon fluxes returned to values that, on average, were directly comparable to pre-spill conditions.

[4] From both the timing of its appearance and its chemical fingerprint (e.g., biomarkers) it is clear that the oil detected in the trap samples during April-July 2010 was Macondo oil released during the *Deepwater Horizon* oil spill.

[5] Further, because all of the settling Macondo oil collected in this area had been partially evaporated and exhibited evidence of photo-oxidation of susceptible PAHs and triaromatic steroids, we can conclude that this material originated from oil that had been delivered via the ocean surface, rather than through upwelling of oil dispersed within the deep-sea (1000-1300m) plume.

[6] Two distinct maxima, or “pulses” of oil deposition were recognized during the active spill that can be attributed to factors including the persistence of floating oil in the area (oil days), surface application of dispersants, algal/bacterial populations, abundance of mineral matter, and the hydrodynamic conditions affecting the collision rates among oil and any (organic and/or inorganic) particles present. Within the duration of each of these “pulses” the oil settling into the sediment trap showed evidence of becoming increasingly biodegraded.

[7] Based on the measured sedimentation rates for hopane, a presumed conservative marker, it is estimated that a minimum of ~10 barrels (bbl) per  $\text{km}^2$  of Macondo oil was deposited in the VK826 area during the 87-day active spill. From this, we conservatively estimate that > 76,000 bbl of oil once present at/near the ocean surface sank to the seafloor over the ~7600  $\text{km}^2$  area of the northern GoM that has previously been shown to have experienced at least 30 surface oil days (the value estimated for ocean waters overlying the VK826 site).

[8] This 7600  $\text{km}^2$  area includes, but is 4- to 7-times larger than, the previously-recognized area of seafloor in which core-top sediments (0-1 cm) have revealed a Macondo Oil “footprint”. Notably, about half of the 7600  $\text{km}^2$  area calculated here

covers relatively shallow (<1000m) regions (including the Viosca Knoll *Lophelia* reefs) where Macondo oil had not previously been considered to have been deposited.

[9] The volume of previously-unrecognized sunken surface oil calculated from this work (56,900-65,700 bbl) increases the total volume of Macondo oil believed to have been delivered to the GoM seafloor surface by more than 33 vol%, to a total sunken oil volume of 217,700 to 229,900 bbl, which represents 6.8 to 7.2 % of the 3.19 million barrels spilled that was not recovered or burned.

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**Table 1: Inventory of sediment trap samples studied.** Locations shown in Fig. 1. Complete listing of samples from each trap is provided in Table S-1.

Trap ID	Distance to Macondo (km)	Lat (N)	Long (W)	Sea-floor (m)	Trap Depth (m)	Start Date	End Date	Interval (days)	Samples available for study
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**VK826 Site**

NOAA/BOEM	GOMEX M2 VK01	58	29°09.55'	88°01.13'	463	457	11-Sep-09	2-Jul-10	14	21
NSF	RR1 M2 VK02		29° 09.62'	88°01.13'	452	426	25-Jun-10	7-Jan-11	15	13
NRDA	RR3		29°09.61'	88°01.12'	450	424	16-Mar-11	14-Sep-11	14	13

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**VK906 Site**

NRDA	RR2 M1*	37	29°04.17'	88°22.64'	427	401	29-Jul-10	27-Oct-10	6	6
NRDA	RR2 M2		29°06.44'	88°23.09'	332	306	29-Jul-10	15-Oct-10	6	13

\*incomplete suite; missing some intervals

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**MC751**

NOAA/BOEM	GOMEX M1 MC01	153	28°11.64'	89°47.90'	436	430	11-Sep-09	20-Nov-09	14	5
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**Table 2: Sedimentation rates (mean and standard deviation;  $\mu\text{g}/\text{m}^2/\text{day}$ ) of TPH, TPAH50, and hopane in sediment trap particulates from Viosca Knoll (VK826) collected before, during and/or after the *Deepwater Horizon* oil spill. Calculated from data in Table S-2.**

n	TPH		TPAH50		Hopane	
	mean	$\sigma$	mean	$\sigma$	mean	$\sigma$

**VK826 Site**

Pre-Spill	16	124	144	0.20	0.16	0.02	0.01
Spill	7	2356	1919	5.4	5.7	0.89	0.95
Post-Spill A <sup>1</sup>	11	108	53	0.14	0.12	0.03	0.02
Post-Spill B <sup>2</sup>	13	142	116	0.28	0.25	0.03	0.02

<sup>1</sup> late July 2010 to early Jan. 2011

<sup>2</sup> mid-March to mid-Sept. 2011

**Table 3: Hopane-based sedimentation rate for Macondo oil for the seven trap samples collected during the active spill showing the total volume (bbl/km<sup>2</sup>) of Macondo oil deposited in the VK826 area during the *Deepwater Horizon* oil spill.** Total is corrected for “background” oil as represented by the average for 16 pre-spill samples (from Table 3). Note nearly half of the total oil (4.6 of 9.5 bbl/km<sup>2</sup>) was deposited during the 15-day period (June 25-July 10, 2010), i.e., the second “pulse” of oil (see text; RR1 M2 VK02-01).

Sample	Figure Label	Total Hopane Flux (ug/m <sup>2</sup> /day)	"Pre-Spill" Hopane Flux (ug/m <sup>2</sup> /day) (Avg; n=16)	Macondo Hopane Flux (ug/m <sup>2</sup> /day)	Macondo Oil Flux-Mass (kg/km <sup>2</sup> /day)	Macondo Oil Flux-Volume (bbl/km <sup>2</sup> /day)	Macondo Oil Volume (bbl/km <sup>2</sup> per deployment period)
GOMEX M2 VK01-17	B	0.18	0.02	0.16	2.35	0.02	0.2
GOMEX M2 VK01-18	C	0.62	0.02	0.60	8.68	0.06	0.9
GOMEX M2 VK01-19	D	0.19	0.02	0.17	2.45	0.02	0.3
GOMEX M2 VK01-20	E	0.32	0.02	0.30	4.41	0.03	0.5
GOMEX M2 VK01-21	F	1.00	0.02	0.98	14.20	0.10	1.5
RR1 M2 VK02-01	G	2.90	0.02	2.88	41.88	0.31	4.6
RR1 M2 VK02-02	H	1.02	0.02	1.00	14.57	0.11	1.6

<sup>1</sup> Fresh Macondo contains 68.8 mg/kg hopane

<sup>2</sup> Fresh Macondo density at 5°C 0.856 g/ml; 42 gall = 1 bbl

**Macondo Oil Deposited at VK826 During Spill: 10 bbl/km<sup>2</sup>**

**Table 4: Calculations of the volumes (percentages) of Macondo oil found on the seafloor based upon results of a previous study of deep-sea sediments (Stout et al., 2016b) and the new VK826 sediment trap results. See text for description.**

<b>Deep-Sea Surface Sediment Footprint</b>	Minimal	Maximal
Area (km <sup>2</sup> ) <sup>1</sup>	1030	1910
Volume oil - Total on seafloor within deep-sea "footprint" (bbl) <sup>1</sup>	152,000	173,000
Volume oil - Sunken surface oil contribution to the deep-sea "footprint" (bbl) <sup>2</sup>	10,300 (7%)	19,100 (11%)
Volume oil - Sunken deep-sea plume oil within deep-sea "footprint" (bbl) <sup>3</sup>	141,700 (93%)	153,900 (89%)

**Sunken Surface Oil Footprint**

Area (km <sup>2</sup> ) <sup>4</sup>	7600	7600
Volume oil - Total sunken surface oil within sunken surface oil "footprint" (bbl) <sup>2</sup>	76,000	76,000
Volume oil - Sunken surface oil contribution to the deep-sea "footprint" (bbl) <sup>2</sup>	10,300	19,100
Volume oil - Sunken surface oil deposited outside deep-sea "footprint" (bbl) <sup>3</sup>	65,700	56,900

**Summary**

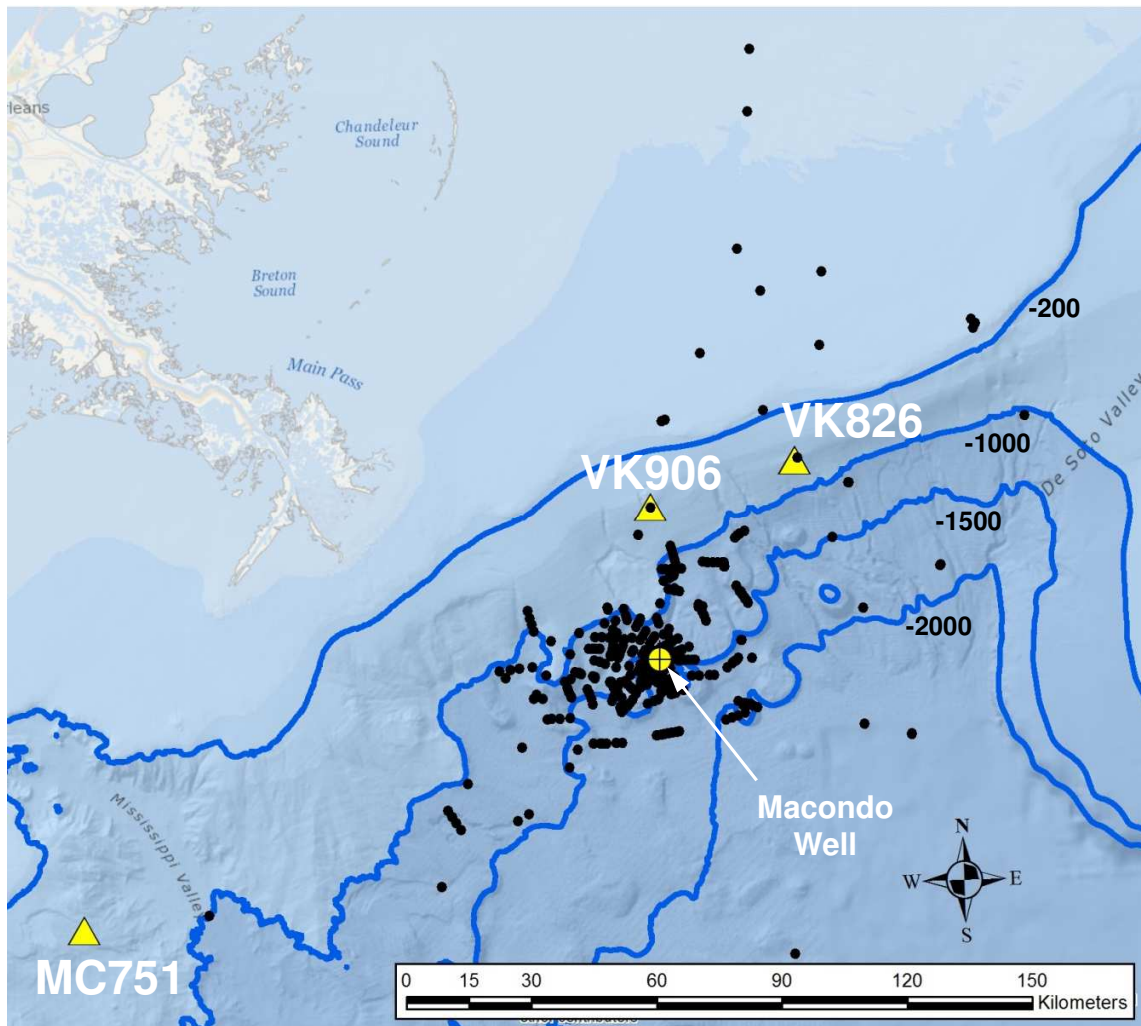
Volume oil - Total on seafloor within deep-sea "footprint" (bbl) <sup>1</sup>	152,000 (70%)	173,000 (76%)
Volume oil - Total sunken surface oil outside deep-sea "footprint" (bbl) <sup>2</sup>	65,700 (30%)	56,900 (24%)
Volume oil - Total oil reaching the seafloor within 7600 km <sup>2</sup> area (bbl) <sup>4</sup>	217,700	229,900
Percent of total oil released (3.19 M bbl) reaching the seafloor within 7600 km <sup>2</sup> area	6.8	7.2
Percent Increase in total oil reaching the seafloor due to sinking surface oil	43	33

<sup>1</sup> Stout et al. (2016b); excludes seep oil and subsurface (> 1 cm) Macondo oil nearest the well

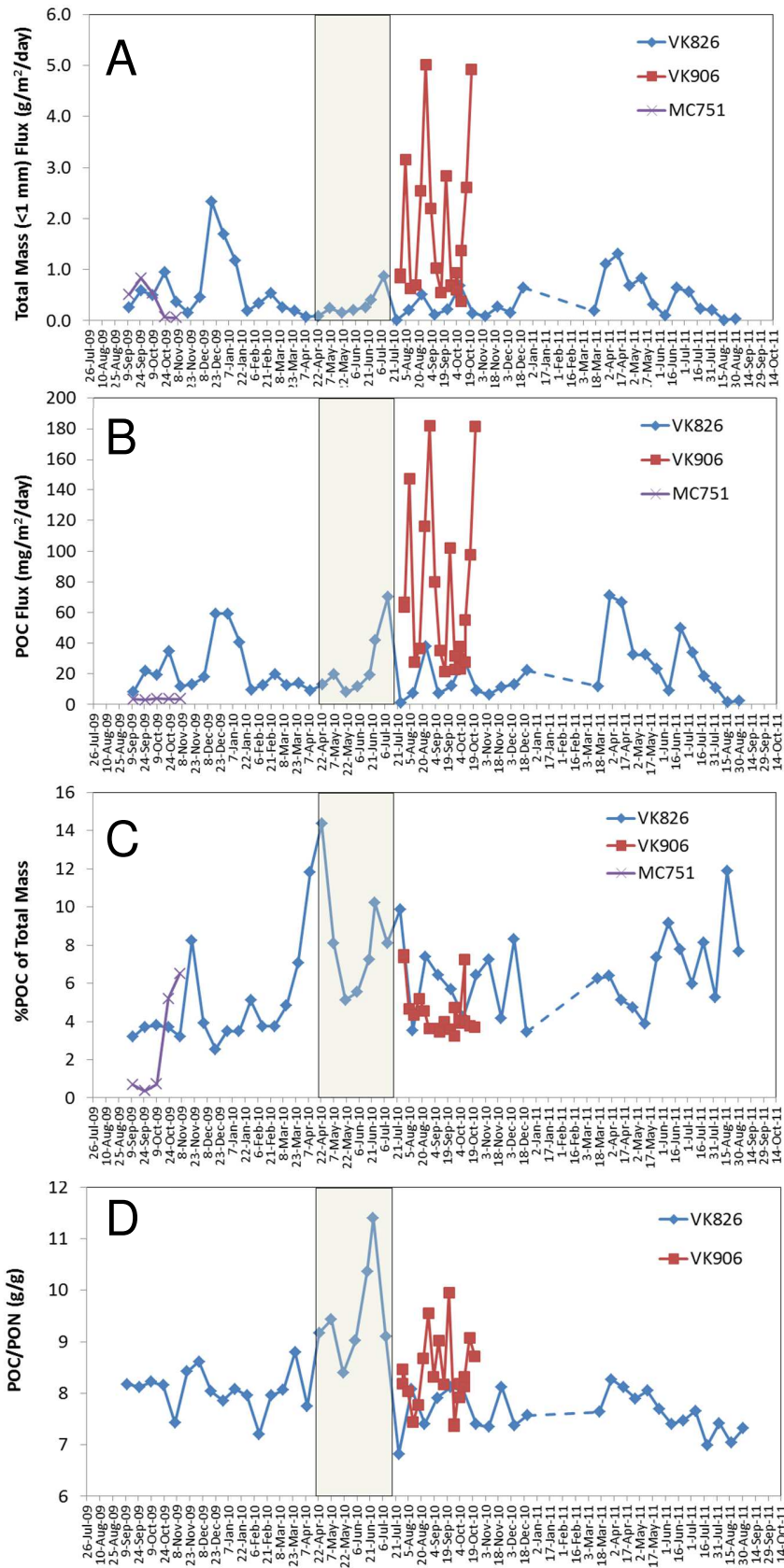
<sup>2</sup> as calculated using 10 bbl/km<sup>2</sup> per VK826 trap results

<sup>3</sup> by difference

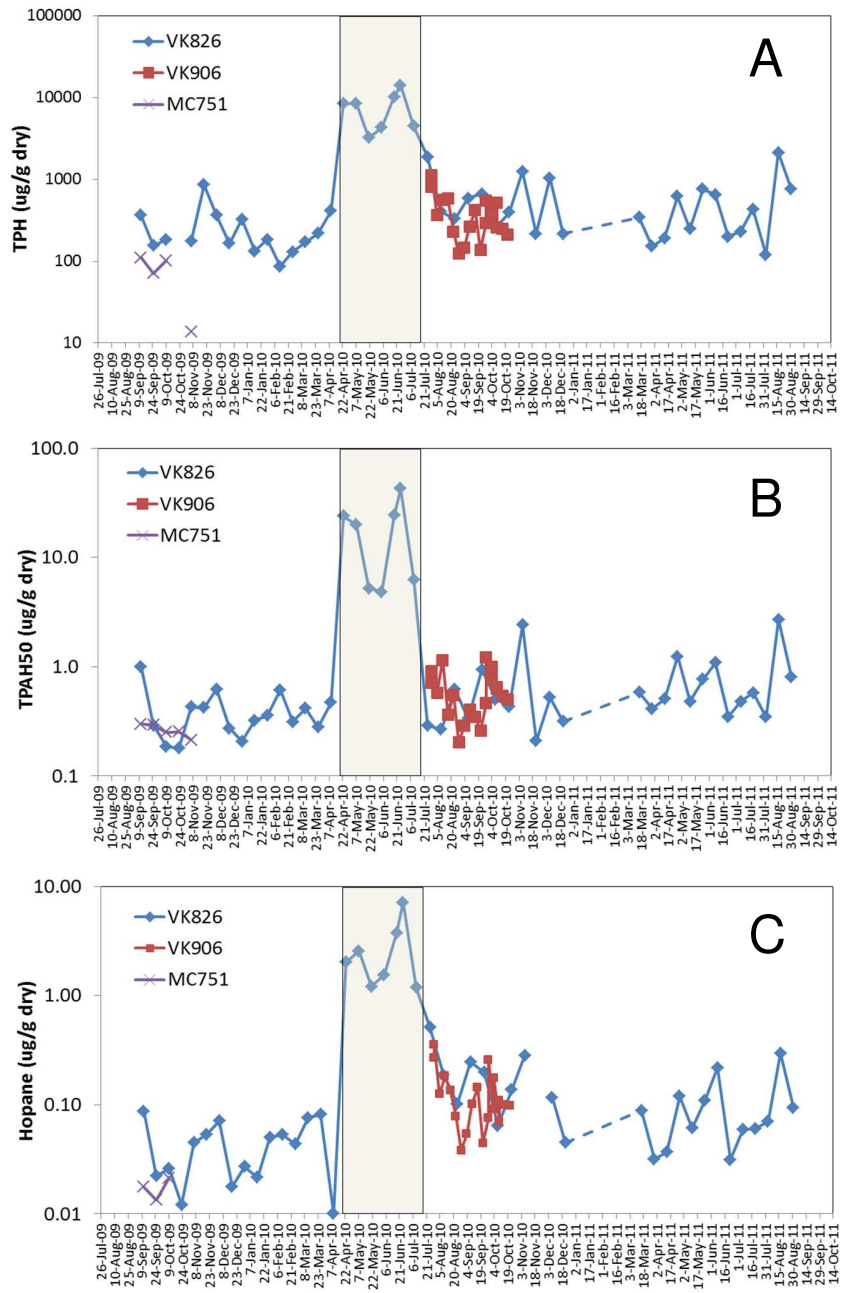
<sup>4</sup> 30+ oil days (Fig. 10)



**Fig. 1: Map showing the location of the Viosca Knoll (VK906 and VK826) and Mississippi Canyon (MC751) sediment traps (triangles). Bathymetric contours (m) and locations of 728 sediment cores collected as part of the NRDA investigation (black dots) are indicated. Note only a limited number of sediment cores were collected at depths less than 1000 m with only very few located at the Viosca Knoll sediment trap sites.**

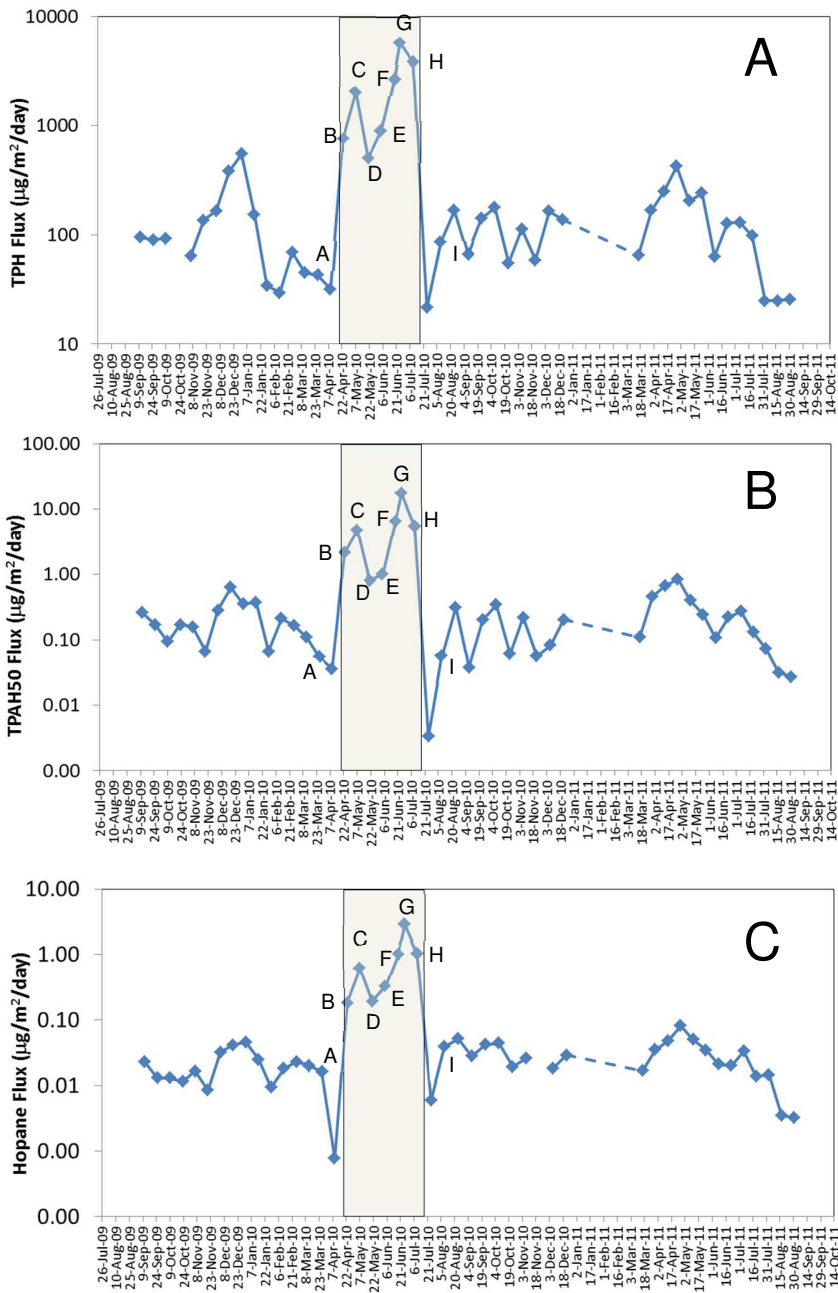


**Fig. 2: Plots showing the temporal trends in (A) sedimentation rate of total mass of particulate (< 1 mm), (B) sedimentation rate of particulate organic carbon (POC), (C) percent POC of total by mass, and (D) POC/PON by mass in the sediment trap samples studied. Trap “open date” plotted on x-axis. All data from Table S-1. Shaded area depicts time span of the *Deepwater Horizon* oil spill (April 20-July 15, 2010) and includes sample B through H as shown in Figs. 4 to 7.**

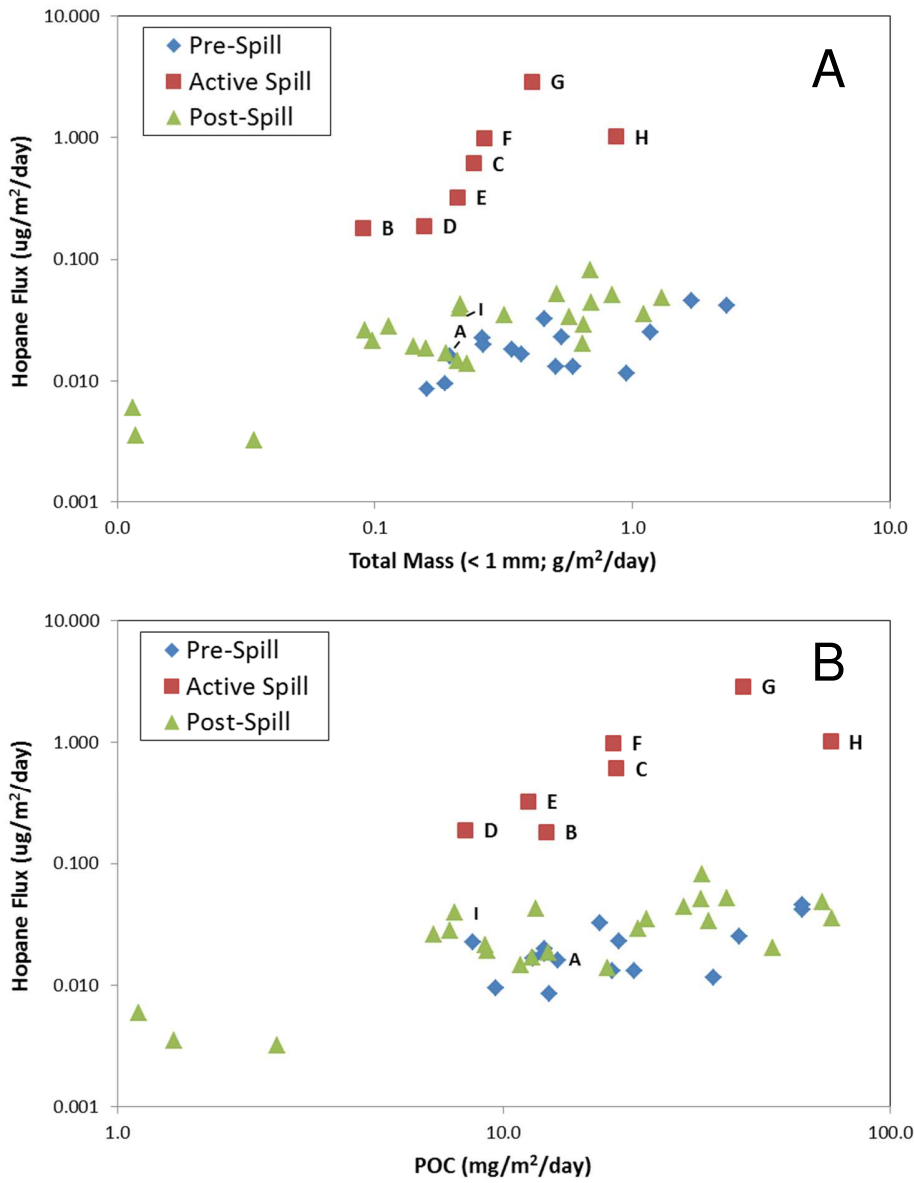


**Fig. 3: Plots showing the temporal trends in the concentrations of (A) TPH, (B) TPAH50, and (C) hopane in particulates (< 1 mm) in the sediment trap samples studied.** Trap “open date” plotted on x-axis. All data from Table S-2. Shaded area depicts time span of the *Deepwater Horizon* oil spill (April 20-July 15, 2010) and includes sample B through H as shown in Figs. 4 to 7. Note log-scale on each.

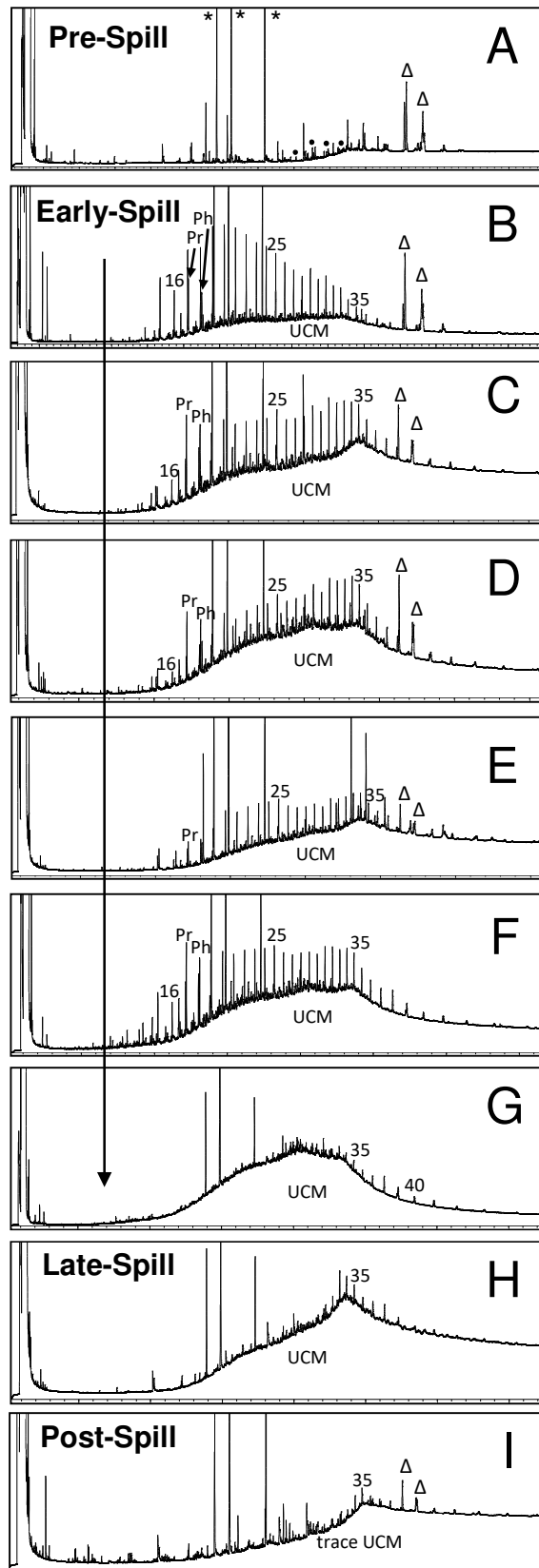




**Fig. 4: Plots showing sedimentation rates for (A) TPH, (B) TPAH50, and (C) hopane in Viosca Knoll 826 sediment trap samples studied.** Trap “open date” plotted on x-axis. All data from Table S-2. Shaded area depicts time span of the *Deepwater Horizon* oil spill (April 20-July 15, 2010). Note log-scale on each. Small letters (A through H) refer to individual sample data shown in Figs. 5, 6, 7 and 9.

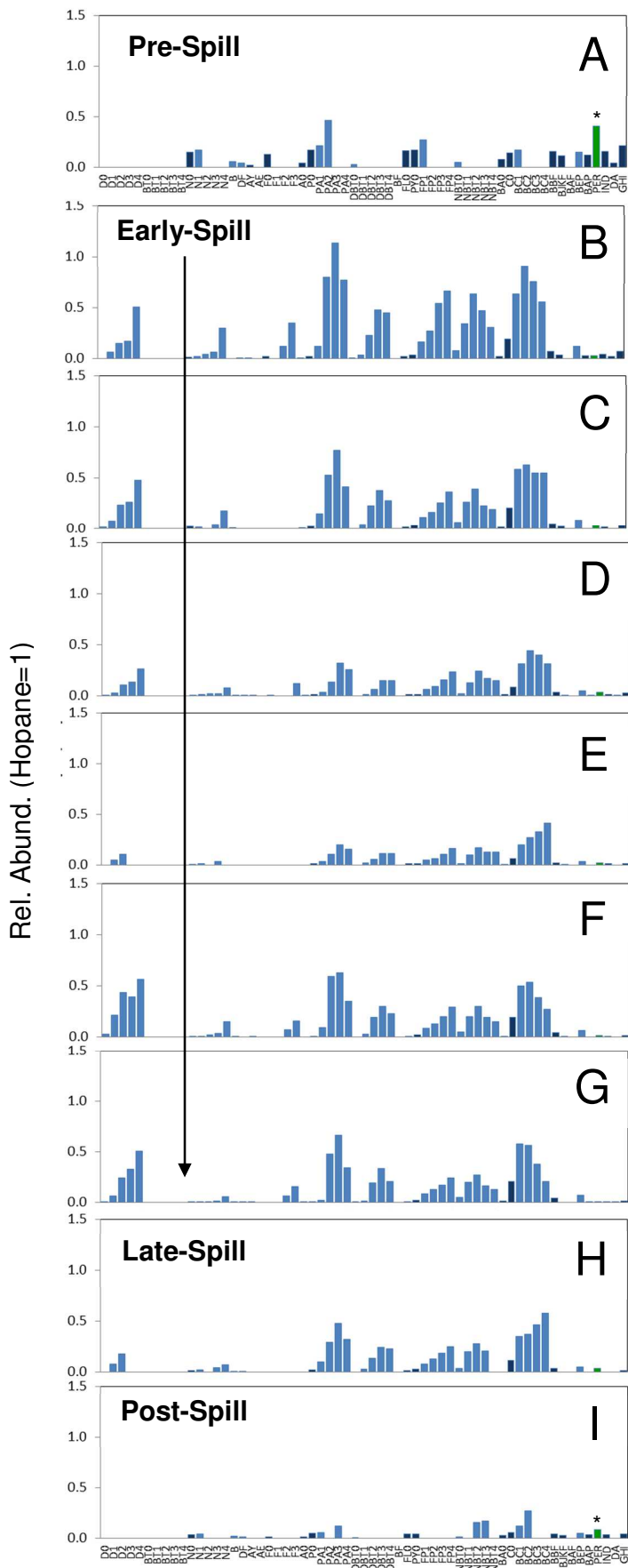


**Fig. 5: Plots showing relationships between the sedimentation rates for hopane and (A) total mass of particulate <1 mm and (B) POC in VK826 the sediment trap samples studied.** All data from Table S-2. Sample labels (A-I) correspond to those shown in Fig. 4. Note log-scale on each.

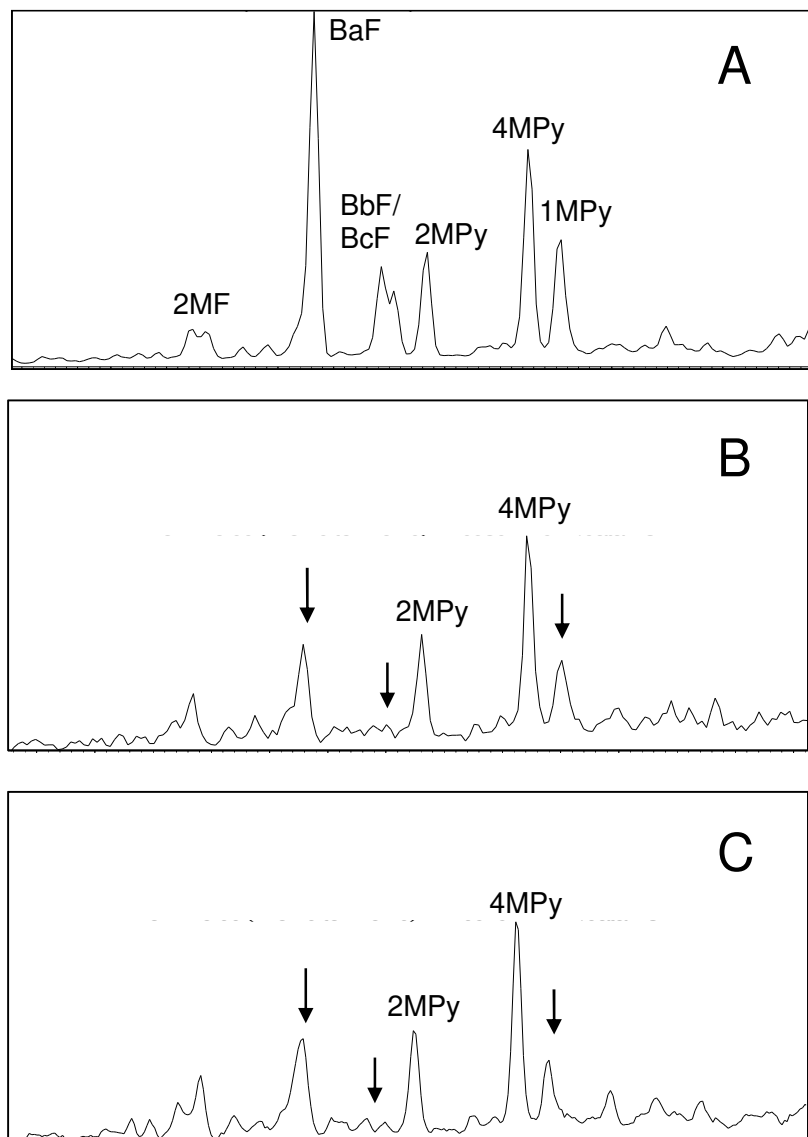


**Fig. 6: GC/FID chromatograms for TPH in sediment trap samples from VK826 site. (A) pre-spill (March 26, 2010), (B) through (H) represent the samples collected during the active spill, and (I) post-spill (Aug. 9, 2010). Refer to Fig. 4 for labels (A) through (I). \* - internal standards; Δ - unknown marine snow constituents attributed to biomass (not oil); # - n-alkane carbon number; Pr-pristane; Ph-phytane; • - odd n-alkanes (27-33); UCM – unresolved complex mixture.**

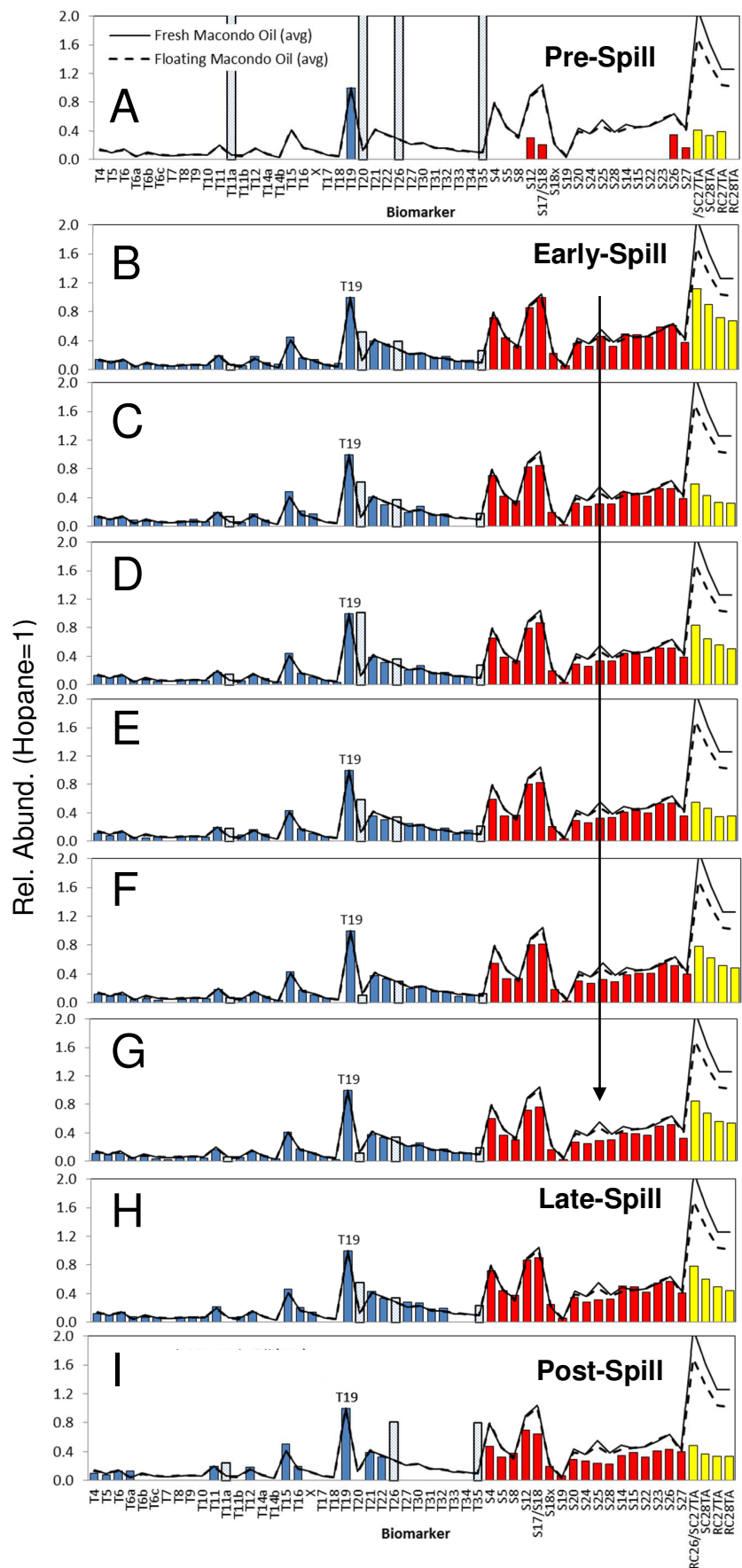
Label	Sample/Open Date
A	GOMEX M2 VK01-15 3/26/2010
B	GOMEX M2 VK01-17 4/23/2010
C	GOMEX M2 VK01-18 5/7/2010
D	GOMEX M2 VK01-19 5/21/2010
E	GOMEX M2 VK01-20 6/4/2010
F	GOMEX M2 VK01-21 6/18/2010
G	RR1 M2 VK02-01 6/25/2010
H	RR1 M2 VK02-02 7/10/2010
I	RR1 M2 VK02-04 8/9/2010



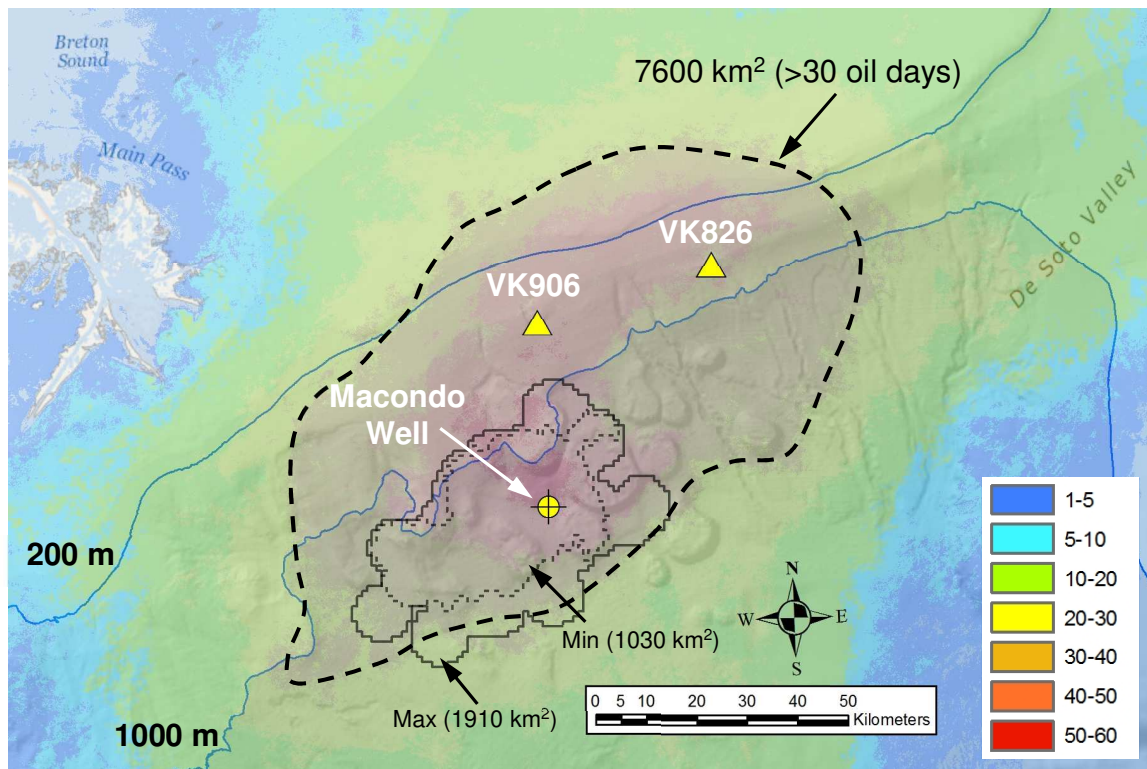
**Fig. 7: Hopane-normalized histograms showing relative concentrations and distributions of PAH in sediment trap samples from VK826 site. (A) pre-spill (March 26, 2010), (B) through (H) represent the samples collected during the active spill, and (I) post-spill (Aug. 9, 2010). Refer to Fig. 4 for labels (A) through (I); Caption to Fig. 6 contains sample identifications. See Table S-3 for compound abbreviations. Asterisk indicates perylene.**



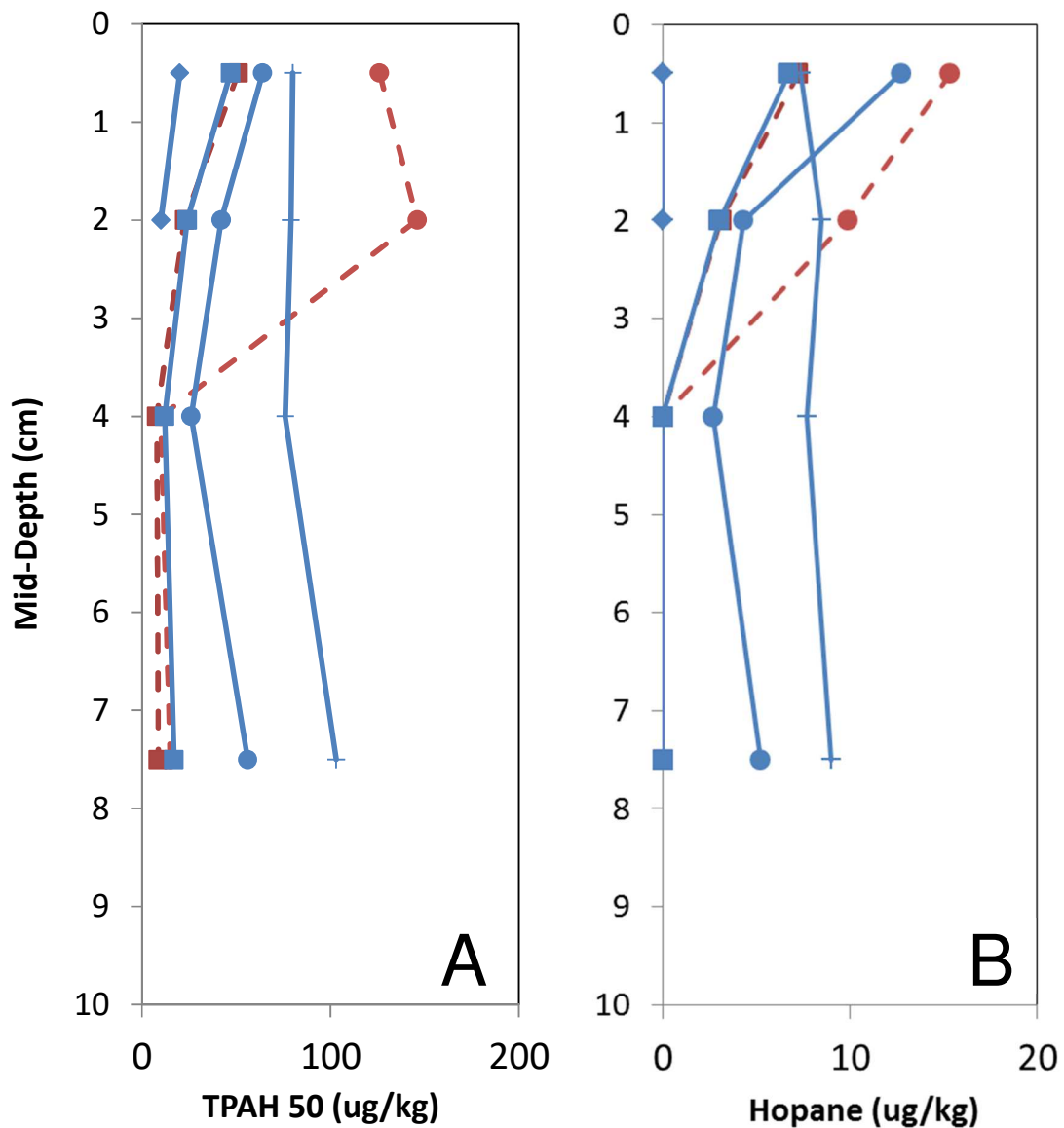
**Fig. 8: Partial EIPs ( $m/z$  216) showing methyl-fluoranthrenes/pyrenes isomer patterns in (A) fresh Macondo crude oil, (B) "first arriving" oil from VK826 sediment trap (Sample "B" in Fig. 4; GOMEX M2 VK01-17) and (C) later arriving oil from VK826 sediment trap (Sample "H" in Fig. 4; M2 VK02). Isomer specific reductions (arrows) are attributed to photo-oxidation indicating the oil reaching the sediment trap had previously been at the sea surface.**



**Fig. 9: Hopane-normalized histograms showing relative concentrations and distributions of biomarkers in sediment trap samples from VK826 site. (A) pre-spill (March 26, 2010), (B) through (H) represent the samples collected during the active spill, and (I) post-spill (Aug. 9, 2010). Average fresh and floating Macondo oils given for comparison (Stout et al.2016c). Refer to Fig. 4 for labels (A) through (I). Caption to Fig. 6 contains sample identifications. Blue: triterpanes; Red: dia- and regular steranes; Yellow: triaromatic steroids; See Table S-3 for compound abbreviations.**



**Fig. 10: Map showing cumulative surface oil days (April 25 to July 28, 2010) as determined by Graettinger et al., 2015 relative to the Viosca Knoll sediment traps, Macondo well, and 200 and 1000 m bathymetry contours.** Key refers to total number of days when surface oil was determined to be present using multiple remote sensing methods (Graettinger et al., 2015). The ~7600 km<sup>2</sup> area which experienced > 30 oil days is indicated (dashed line) along with previously-recognized deep-sea “footprints” (min. and max.) of seafloor sediments containing Macondo oil based upon chemical results of more than 700 sediment cores (Stout et al., 2016b). The sediment trap results indicated 10 bbl/km<sup>2</sup> of surface oil that sunk near the VK826 site indicating, by extension, at least 76,000 bbl of surface oil likely sunk within the entire 7600 km<sup>2</sup> area that had experienced 30 or more days of surface oil. See additional discussion in text.



**Fig. 11: Plots showing the concentration profiles of (A) TPAH50 and (B) hopane in sediment cores collected from the VK826 (dashed; n=2) and VK906 sites (solid; n=4).** Profiles show either an increase in concentration at the uppermost layer(s) or no change throughout the cores. All six cores collected on R/V *Holiday Chouest* 3 NRDA cruise (Oct. 1-25, 2011). Non-detected concentrations of hopane are plotted as zeros. Core identities and data provided in Table S-5.