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Spatial and temporal distribution of water column total polycyclic aromatic hydrocarbons (PAH) and total petroleum hydrocarbons (TPH) from the Deepwater Horizon (Macondo) incident

Terry L. Wade *, José L. Sericano, Stephen T. Sweet, Anthony H. Knap, Norman L. Guinasso Jr

Geochemical and Environmental Research Group (GERG), Texas A&M University, 833 Graham Rd. College Station, TX 77845, USA

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ABSTRACT

Pre-spill background concentrations of TPH and PAH in water samples from the Gulf of Mexico are compared with samples (over 20,000) collected during and after the Deepwater Horizon incident (13,000 stations). Samples were collected by multiple response agencies, trustees and BP and reported in the Gulf Science Data. The samples were collected from a few m to over 800 km in all directions from the wellhead. During the incident, samples with the highest concentrations of hydrocarbons were collected proximal to the wellhead or in samples collected from surface slicks and dispersant use. Of the 13,172 water sample TPH concentrations reported, 84% were below 1 μg/L (background). Of the 16,557 water sample PAH concentrations reported, 79% were below 0.056 μg/L (the median field blank, background). The percentage of samples below background increased rapidly after the well was capped. The spatial and temporal distributions of these hydrocarbon data are presented.

1. Introduction

The Deepwater Horizon incident occurred on April 20, 2010 and the well was capped on July 15, 2010. During that time a large amount of oil (ruled to be 3.19 million barrels by a court, though disputed by the parties) was released to the surrounding environment at a depth of ~1500 m. There was an unprecedented number of water samples collected (over 20,000) during and after the release of oil from the Deepwater Horizon oil spill. Total petroleum hydrocarbons (TPH) and total polycyclic aromatic hydrocarbon (PAH) concentration data from water samples published on the Gulf Science Data web site in May 2014 (file W-01v02-01.csv available at gulfsciencedata.bp.com) were downloaded and converted into an R data base (R Core Team, 2013) for this analysis.

Some of the oil was transported to the surface while some was transported and degraded in subsurface intrusion layers (Socolosky et al., 2011). The presence of oil components was confirmed by detection in separate sub surface intrusion layers at depths ranging from 800 to 1400 m (Camilli et al., 2010; Diercks et al., 2010; Hazen et al., 2010; Kujawinski et al., 2011; Sammarco et al., 2013; Spier et al., 2013; Valentine et al., 2010). The last date documented with potentially recoverable oil on the surface was August 3, 2011 (OSAT, 2011). These data are publically available in the Gulf Science Data (file W-01v02-01.csv available at gulfsciencedata.bp.com) which had undergone an extensive quality assurance/quality control validation process prior to release.

Total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH) included in the data base form the basis for our analysis. TPH provide an estimate of the concentration of higher molecular weight hydrocarbons present in the samples, and PAH provide an estimate of some of the more toxic components of oil as well as components responsible for its fluorescent characteristics (Wade et al., 2011a, 2011b).

Following introduction into the environment, petroleum or petroleum products are subject to a number of processes that affect their composition (NRC, 2003). These processes are generally called "weathering" and include evaporation, dissolution, biodegradation, dispersion, photolysis and sedimentation. The amount and type of "weathering" process can be assessed by the use of diagnostic ratios of selected oil components.

Overall, the objectives of the present report are to provide the scientific community a detailed description of the Gulf Science Data, an overview of the spatial and temporal distributions of higher molecular weight TPH and PAH in water samples collected during and after the spill, and a website that contains the "R" code generated to analyze this database so other investigators can better use these data in the future. We also compare these data to water samples collected before the incident.

* Corresponding author.
E-mail addresses: terry@gerg.tamu.edu (T.L. Wade), jlsericano@geos.tamu.edu (J.L. Sericano), sweet@gerg.tamu.edu (S.T. Sweet), tknap@tamu.edu (A.H. Knap), guinasso@gmail.com (N.L. Guinasso).

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2. Methods

2.1. Data

The water sample and quality assurance data were downloaded from The Gulf Science Data Water Chemistry Data File (http://gulfsciencedata.bp.com/go/doc/6145/1942326/) containing water sample hydrocarbon concentrations. These Gulf Science Data were made publically available first on November 18, 2013 and updated in May 2014. The updated data was used for the analysis after conversion into a format compatible with the data-sorting program "R". The data transfer into "R' was verified to ensure this process did not alter the original data or create artifacts during the transfer. In addition to the water samples themselves, the Gulf Science Data contained results for field blanks, rinsate blanks, trip blanks and equipment blanks. These quality assurance samples were analyzed separately.

2.2. R and RStudio

Most of the data and figures presented in this paper were prepared using R and RStudio. R is a programming language that is similar to S originally developed at Bell Laboratories (R Core Team, 2013). The R language is widely used in the finance, statistics, and chemistry communities and is especially adept at dealing with large data sets. RStudio is a development system for R that is freely available, although some commercial uses may require a license.

RStudio works by creating a R Markdown Document containing R code interspersed with content. A program called knitr converts the R markdown document to a webpage html document, a pdf document, a Microsoft Word document, or slides suitable for presentations (Xie, 2015).

We started with the BP Water Chemistry Data set (BP, 2014), and created a R Markdown Document to read this data set, prepare analyses, figures and tables. R package reshape2 (Wickham, 2007) permits easy arrangement of the water chemistry data table into a table where rows represent each sample. The R packages dplyr (Wickham and Francois, 2014) and data.table (Dowle et al., 2014) facilitate preparation of summaries. R package ggplot2 (Wickham, 2009) makes elegant graphics.

The R Markdown Document can be run by anyone to reproduce the results, a process often referred to as "reproducible research" (Peng, 2011).

The RStudio R Markdown Document we used for this paper is available at www.gerg.tamu.edu/MacondoDataAnalysis. Archived and updated versions will be maintained at https://github.com/nguinasso/Macondo.

2.3. Filtered samples

There were also records in the database from special studies which included both filter and filtrate results from each sample. Although these samples contain important data they were not included in the analyses reported here as they were not directly comparable to the majority of the samples.

The water samples were 1 L discrete samples extracted by accepted solvent partitioning methods. Water samples, including those from the intrusion layers can contain dissolved hydrocarbons, oil droplets, dispersant, metastable gas hydrate, precipitated waxes and polar petroleum compounds (Valentine et al., 2014). Aside from the special projects, the water samples reported in the Gulf Science Data were not filtered so reported concentrations represent both the particulate and dissolved phase of hydrocarbons.

2.4. Procedural and field blanks

Procedural blanks were analyzed with each sample batch to determine contamination during the laboratory analyses. Field blanks were analyzed with selected sample batches to determine possible contamination during sample collection and transport. The mean and median concentrations for field, rinsate (sampling equipment rinsed with clean water), trip and equipment blanks were determined (Table 1). Generally, more sample sets contained field blanks compared to the trip, rinsate, or equipment blanks. Higher median concentrations were detected in the equipment blanks compared to the other blanks. The higher of the procedure and field blanks was used to qualify the data for each analyte in the Gulf Science Data. Any analyte found in the procedure or field blank above the contract required detection limit (CRDL) or method detection limit (MDL) was qualified with a "U" as analyzed for but was not detected (U.S. EPA, 2008). For the analyses reported here data designated as "U" was set to zero which has the same result as if the higher of the field or procedural blank were subtracted from all the specific analytes or group concentrations (i.e. blank corrected).

Table 1
Blank TPH and PAH concentration means and medians.

Sample type	Number	Mean µg/L	Median µg/L
PAH field blanks	394	0.22	0.056
PAH trip blanks	21	0.14	0.049
PAH equipment blanks	875	0.31	0.099
PAH rinsate blanks	15	94.7	0.229
TPH field blanks TPH (C9-C44)	235	49	0
TPH trip blanks TPH (C9-C44)	14	0	0
TPH equipment blanks TPH (C9-C44)	98	65	0
TPH rinsate blanks TPH (C9-C44)	12	0	0
TPH field blanks total extractable matter	132	29	0
TPH equipment blanks total extractable matter	98	103	0
TPH rinsate blanks total extractable matter	2	170	170

2.5. Total petroleum hydrocarbons (TPH) and total polycyclic aromatic hydrocarbons (PAH)

TPH and PAH included in the Gulf Science Data form the basis for this present analyses. There are differences in analytical methods and laboratory detection limits for the different compounds for the many participating laboratories.

2.6. TPH

The term total petroleum hydrocarbons (TPH) are used to include total higher molecular weight hydrocarbons determined by a range of different methods. There were a total of 13,172 water samples where TPH concentrations were reported. This includes 5012 samples designated as TPH (C9-C44); 6286 sample results designated as TEM (total extractable matter)[1]; 1048 samples designated as TPH, Total; 778 samples designated as TEH (total extractable hydrocarbons); 48 samples designated as TPH, Total (C9-C40). While different methods were used to determine TPH, with different detection limits (0.02 to 2500 µg/L) all the data reported were used without regard to the method or laboratory providing the analyses. The mean and median TPH concentrations for the various blanks are reported in Table 1. The medians are all zero except for TEM rinsate blanks. The field blank mean is 49 µg/L (TPH C9-C44) and 29 µg/L (TEM) with a weighted average of 42 µg/L (Table 1).

2.7. PAH

Total polycyclic aromatic hydrocarbons (PAH) include the sum of all the two to six ring aromatic hydrocarbons including alkylated PAH

[1] Methods used to determine total extractable matter may include non-petroleum organic components and may be biased high.

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