



Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Oil residue contamination of continental shelf sediments of the Gulf of Mexico

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ARTICLE INFO

Article history:

Received 25 February 2016

Received in revised form 10 May 2016

Accepted 23 July 2016

Available online xxxxx

Keywords:

Oil contamination

BP oil spill

Gulf of Mexico

Pyrolysis

ABSTRACT

We have investigated the distribution of a heavy oil residue in the coastal sediments of the Gulf of Mexico. The amount of the contamination was determined by high-temperature pyrolysis coupled with the Gas Chromatography–Mass Spectrometry (GCMS) of air-dried sediments. The pyrolysis products contain straight-chain saturated and unsaturated hydrocarbons, such as dodecane and 1-dodecene, resulting in a very characteristic pattern of double peaks in the GCMS. Hydrocarbons containing 8 to 23 carbon atoms were detected in the pyrolysis products. Using thermal pyrolysis we have found that the sediment samples collected along Texas, Louisiana, and Mississippi shores contain no detectable traces of oil residue, but most of the samples collected along Alabama and Florida shores contain ~200 ppm of heavy oil residue.

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1. 1. Introduction

The Gulf of Mexico BP oils spill in April 2010 is very well documented in numerous reports and research publications (Lustgarten, 2012; Bergin, 2012; Konrad and Schroder, 2011; DOC/NOAA, 2010; Hayworth et al., 2011; Kujawinski et al., 2011). In this paper we concentrate on thermogravimetric and pyrolysis GCMS analysis of oil residue in benthic sediments of the Gulf of Mexico after the Macondo Mississippi Canyon Block 252 (MC252) well disaster. Classical GCMS or Gas Chromatography and Flame Ionization Detector (GC-FID) techniques are widely used in analysis of petroleum products and oil residues in environmental studies. These methods are described in detail in the EPA protocols and industrial standards (EPA analytical methods 3450C and 8275A; Wang and Fingas, 1997). While these analytical methods are very powerful in analysis of fresh samples, the analysis of heavily weathered samples is much more difficult. The weathered oil residue samples contain only small amounts of GCMS identifiable compounds and the unique identification of these samples is based on the GCMS studies of degradation of resistant biomarkers, such as terpanes, seohopanes, steranes, and monoaromatics (Peters et al., 2005; Stout and Wang, 2008; Wang and Brown, 2009). Unfortunately, direct GCMS methods are not suitable for the identification of very heavily weathered samples containing only negligible amounts of biomarkers and GCMS-identifiable compounds. These samples contain mostly high molecular weight asphaltene and resins (Sheu, 2002), which are not suited for direct GCMS analysis. Various pyrolysis methods of asphaltene fractions have been developed to analyze these samples. In one of these methods (Oudot and Chaillan, 2009), the asphaltene are separated from maltene by precipitation

with hexane and then pyrolyzed in a closed glass ampoules at temperatures above 300 °C for several hours. Then the pyrolysis products were extracted with hexane and analyzed using GCMS. Various modifications of the pyrolysis method have been developed for specific applications, such as analysis of degradation mechanisms of plastic waste, environmental studies, soil contamination, or forensic analysis (Wampler, 2006; Pasadakis and Xekoukoulotakis, 2007; White et al., 1998).

In this paper we use direct pyrolysis of dried sediment samples to determine the amount of the oil residue. Volatile pyrolysis products were collected under nitrogen flow and solidified in a glass ampoule immersed in liquid nitrogen. This method is especially suitable for a fast analysis of raw samples. The procedure does not require extracting the residue from raw samples and separation of the extracted residue into aliphatic, aromatic and asphaltene fractions. This direct approach is much faster than the traditional Saturates, Asphaltenes, Resins and Aromatics (SARA) protocol (Sheu, 2002; Klein et al., 2006).

2. Materials and methods

2.1. Chemicals

Dichloromethane (DCM), pentane, and methanol (analytical grade) were purchased from VWR International. Alkane and PAH standards were obtained from Restek. The ISOLUTE SPE (1.45 g, EPH 3 mL) fractioning columns were acquired from Biotage. Approximately 100 mL of the Mississippi Canyon 252 (MC252) oil and 1000 mL of the Louisiana Sweet crude oil were provided by the BP Exploration & Production. GC gases (ultrapure nitrogen and helium) were purchased from a local supplier.

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2.2. Sample collection

The sediment samples were collected in October/November 2010 and October/November 2011 using a Shipek grab sampler operated from the NOAA research vessels R/V *Pisces* in 2010 and R/V *Gordon Gunther* in 2011. The samples were collected from ~25 cm upper layer of the continental shelf sediments at depths between 35 and 200 m. Several samples were acquired at depths between 200 and 400 m. Approx. 0.5 kg of mud from the Shipek sampler were transferred into glass jars, sealed, and stored at ~5 °C in a cold room. Total 44 samples were collected in 2010 and 33 samples were collected in 2011.

2.3. Residue extraction and pyrolysis

Wet sediment samples were first homogenized and then approximately 100 g of wet sediment was dried under nitrogen or air for 2 to 3 days. On average, about 30% to 45% of the sample mass was lost in this process due to water evaporation. Dried samples were ground in a mortar and stored in air-tight polyethylene centrifuge tubes. Approximately 20 g of dried sediment was used for extraction of oil residue following standard 3540C EPA procedure using dichloromethane and pentane (5:1 ratio by volume). The combined extracts were cooled to –20 °C, then centrifuged (at 5000 to 7000 rpm and temperature –20 °C). Next, the pentane-dichloromethane fraction was filtered using PTFE 0.45µ filters, concentrated by evaporation under nitrogen from an initial volume of approximately 50 mL to ~5 mL, and then analyzed using GCMS. The completeness of the extraction of the organic residue was checked by spiking the sample with 10 µL of Restek 31,222 hydrocarbon standard and the percentage of recovered C12–C44 hydrocarbons was determined using GCMS. We have found that at least 98% of spiked amount was extracted in the process. The volume of extracts of two samples (sample 15, Fig. 1 and sample 77, Fig. 3) was further reduced by evaporation to 1.0 mL. We have found that GCMS patterns of more concentrated extracts were almost the same as the chromatograms of extracts evaporated to 5 mL.

The pyrolysis of dried sediments was carried out in a quartz tube under stream of nitrogen. A U-tube was attached to the quartz tube for collection of pyrolyzates. Approximately 20 to 25 g of dried sample was loaded into the tube, and the apparatus was flushed with nitrogen. After nitrogen flushing, the sample was heated at 10 degrees per minute to 500 °C and then kept at 500 °C for 30 min. Water and volatile pyrolysis products were captured in the U-tube immersed in liquid nitrogen. After cooling, the U-tube was disconnected from the apparatus and immediately ~5 mL of dichloromethane was added to the U-tube. The solidified pyrolyzates thawed under dichloromethane releasing hydrogen and small amounts of gaseous hydrocarbons, which were captured into vials and later analyzed. After thawing, dichloromethane was transferred into a vial, and then the U-tube was rinsed again with dichloromethane. A small amount of methanol (~2 mL) was used to rinse the U-tube in order to collect water and polar compounds. Combined dichloromethane and methanol extracts were cooled to –20 °C. At this temperature, water containing fractions separate from dichloromethane. After separation, 0.5 to 1.0 mL of dichloromethane fraction (out of ~6.5 mL of total volume) was carefully transferred into GC vial, sealed, and analyzed.

The pyrolysis/GCMS method is specifically tailored to detect non-volatile petroleum contamination only. Upon pyrolysis, the petroleum contamination yields a mixture of unsaturated and saturated hydrocarbons. Then, the post-pyrolysis mixture is GCMS analyzed and the amount of the petroleum contamination in the sample is determined using asphaltene and tar ball extracts as standards as described in detail in Section 3.2. This method does not determine non-petroleum, bioorganic contamination in the sample, because bioorganic substances yield different GSMS chromatograms upon the pyrolysis. Therefore, this method is used to determine non-volatile petroleum contamination

called *heavy oil residue* in the presence of bioorganic material in the sediment samples.

2.4. Extraction of asphaltene fraction from the Louisiana Sweet crude

The asphaltene fraction of the Louisiana Sweet crude was extracted using slightly modified SARA protocol (Cruz et al., 1997). 400 mL of pentane cooled to –20 °C was dropwise added to 10 mL of Louisiana crude with constant stirring using a magnetic stirrer. After addition, the pentane solution was kept at –20 °C for 12 h, and then the solution was centrifuged at –20 °C. The solid product was isolated, washed with cold pentane and dried. The yield was 3.9%. This product still contained higher saturated hydrocarbons (C25 to C44). It was further purified using ISOLUTE SPE columns. Saturated hydrocarbons were eluted with pentane, and aromatics with pentane-toluene. Then the asphaltene fraction was eluted with dichloromethane and dried under nitrogen. The final yield of asphaltenes was 0.58% with respect to the Louisiana Sweet crude.

2.5. Thermogravimetric (TGA) and GCMS analysis

Approximately 30 to 40 mg of dried and powdered sediment sample was loaded into an alumina cup and analyzed using a TA Q600 simultaneous thermal analyzer. The sample was equilibrated at 30 °C and then heated at 20 °C/min to 900 °C under 100 mL/min flow of nitrogen. The Agilent 6890N GC equipped with low polarity Restek Rxi-5ms column and coupled with the Water Micromass spectrometer, was used for all runs. The injector was set up at 275 °C for splitless injection and constant 1 mL/min flow of helium. After equilibration for 2 min at 30 °C, the temperature of the GC oven was increased at 10 °C/min to 300 °C, and then at 2 °C/min to 320 °C, following by 1 min holding time at 320 °C. Total GC runtime was 40 min per run. The Perkin-Elmer Clarus 500 GCMS coupled with Turbomatrix Headspace sampler was used to test all samples for the presence of volatile petroleum compounds using headspace GCMS method. The TIC MS scans were used for quantification with the MS set up to scan m/z from 40 to 400 in 0.15 s with 0.10 s interscan delay. For low oil contaminated samples, the SIM scans at $m/z = 57$ and 71 were acquired to check the accuracy and the sensitivity of the method.

2.6. Accuracy and the detection limit of the method

The major source of errors in this procedure is due to grab sampling used to collect the sediments. The oil residue from the spill would be most likely deposited as a thin layer on the floor of the Gulf. During the grab sampling, such oil film could be separated from the bottom sediments and leak out from the sampler. Therefore, it is very possible that the grab collection could reduce the amount of the residue in the sample. The loss of the residue during storage and drying was negligible because of extremely low volatility of the residue. We have found that the thermal decomposition of the residue and subsequent extraction of the pyrolysis products did not introduce measurable errors into the procedure. The completeness of the pyrolysis was checked with TGA runs of heavy oil residue, tar ball extracts, and asphaltenes. The TGA data show that these materials entirely decompose into volatile products between 450 and 500 °C, leaving less than 1% of glossy carbon residue.

To determine the detection limit of the method, we spiked 50.0 g samples of pure sand (previously dried at 500 °C in a muffle furnace) with 0.05 to 1.0 mL of asphaltene solution (1 mg/mL of asphaltene in dichloromethane). The spiked sand sample was homogenized and then pyrolyzed and analyzed as described above. We have found that contamination as small as 1 ppm could still be detected, but reliable results were obtained for contaminations higher than 10 ppm.

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