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Characterization of the particulate emissions from the BP Deepwater Horizon surface oil burns

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ABSTRACT

Sampling of the smoke plumes from the BP Deepwater Horizon surface oil burns led to the unintentional collection of soot particles on the sail of an instrument-bearing, tethered aerostat. This first-ever plume sampling from oil burned at an actual spill provided an opportunistic sample from which to characterize the particles' chemical properties for polycyclic aromatic hydrocarbons (PAHs), organic carbon, elemental carbon, metals, and polychlorinated dibenzodioxins/dibenzofurans (PCDDs/PCDFs) and physical properties for size and nanostructure. Thermal–optical analyses indicated that the particulate matter was 93% carbon with 82% being refractory elemental carbon. PAHs accounted for roughly 68 μg/g of the PM filter mass and 5 mg/kg oil burned, much lower than earlier laboratory based studies. Microscopy indicated that the soot is distinct from more common soot by its aggregate size, primary particle size, and nanostructure. PM-bound metals were largely unremarkable but PCDD/PCDF formation was observed, contrary to other's findings. Levels of lighter PCDD/PCDF and PAH compounds were reduced compared to historical samples, possibly due to volatilization or photo-oxidation.

1. Introduction

The British Petroleum (BP) Deepwater Horizon drilling platform caught fire on April 20, 2010, releasing an estimated 4.2 million barrels of crude oil (McNutt et al., 2012) into the Gulf of Mexico over the next three month period. In one effort to limit the spread of oil and keep it from reaching the beaches, the U.S. Coast Guard undertook a program of deliberate collection and burning of the oil on the sea surface. A total of 410 in situ burns were estimated to have combusted 260,000 barrels of oil (Anon.). Surface oil was collected by pairs of fishing trawlers, moving in parallel and each towing one end of a fireproof boom. The collection booms moved through surface oil slicks, accumulating oil. Smaller "igniter" boats placed an incendiary starter charge (gelled diesel in a plastic container with foam flotation and a road flare) in the collected oil pool to initiate combustion. When conditions of the oil and the sea/wind state were suitable, the collected oil would ignite, burning for times varying from minutes to hours.

In situ oil burning has long been considered as a means to reduce the environmental threat of oil spills. It has the benefit of minimizing contamination of coastal marine environments as well as the water and seabed. Likely the largest negative aspect of the burning is the resultant emissions from incomplete combustion of the oil, as indicated by the large volumes of black, particle-laden smoke. Efforts have been undertaken to characterize the emissions from burning oil, most notably from wells during the Mideast Gulf War (Okita et al., 1994; Amin and Husain, 1994; Husain and Amin, 1994). However, these efforts consisted largely of identification of a small number of pollutants and determination of volumetric concentrations, rather than quantification of source strength, limiting the ability to conduct dispersion modeling and risk assessments. More relevant simulations of emissions from oil spill burns at sea have been quantified in laboratory, tank pools, and at-sea simulations (Fingas et al., 1996; Evans et al., 2001). These results have looked at pollutant concentrations and, in limited cases, have determined source strength through emission factors, which express the pollutant mass per mass of oil burned, allowing for pollutant predictions in similar situations. The most comprehensive at-sea simulation was likely the Newfoundland offshore burn experiments (Environment Canada, 1997). A variety of methods were used (Fingas et al., 1996) to characterize particle and gas concentrations for emission factors (Ross et al., 1996a), including airborne sampling and samplers aboard remote controlled marine vessels.

During the BP Gulf disaster limited duration sampling was conducted by the U.S. National Oceanic and Atmospheric Administration (NOAA) (Middlebrook et al., 2012; de Gouw et al., 2011) and the U.S. Environmental Protection Agency (EPA) via airplane (http://www.epa.gov/bpspill/air.html#aspect) and by EPA via aerostat-lofted instrumentation (Aurell and Gullett, 2010). NOAA conducted aircraft measurements of trace gases and aerosols (de Gouw et al., 2011) with a focus on secondary organic aerosol formation. A WP-3D aircraft sampled gaseous and aerosol species above the DWH site and the in situ surface oil burns (Middlebrook et al., 2012) for two days. Flights collected a broad

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array of samples and gas concentration values, determining that 4% of the oil mass was emitted as soot particles. The preponderance of aerosol mass, however, was secondary organics with 8 ± 4% of the surface oil converted to SOA within 3 h of transport.

EPA also collected data using its remote-sensing aircraft known as ASPECT (Airborne Spectral Photometric Environmental Collection Technology) employing a Fourier transform infrared spectrometer. Daily flights for three months over the Deepwater Horizon platform and the in situ burns detected only low concentrations of acetaldehyde, methanol (60 ppb detection limit, DL, estimate), CO (100 ppb DL), and O_3, with a single trace detection of 1,3-butadiene (http://www.epa.gov/bpspill/air.html#aspect, open via Google Earth). However, the 24 chemicals targeted are, with the exception of CO, not commonly associated with combustion emissions.

EPA also used a helium-filled, tethered aerostat to collect air samples from the at-sea, in situ burn plumes to determine whether the combination of incomplete combustion and Cl (from the oil or the seawater) resulted in polychlorinated dibenzodioxin/dibenzofuran (PCDD/PCDF) formation (Aurell and Gullett, 2010). Measurements were made by maneuvering an aerostat-lofted instrument package into the plume and collecting a sample with a quartz filter and polyurethane foam (PUF)/XAD™/PUF (PXP) sorbent. Filter samples were collected of total particulate matter. The plumes of 27 surface fires of varied size and duration were sampled over a period of four days. The resultant filter and PXP sample were analyzed for PCDD/PCDF. During this sampling, a second, unintentional sample was collected that consisted of a solid catch from the filter-like sail of the aerostat (see Fig. 1). The sail is used to stabilize the aerostat by movement of the wind through the porous fabric; its shape helps it maintain the aerostat's directional heading. The opportunistic sail solids catch provided a much larger solids catch than was collected in 2010, affording an opportunity to conduct additional pollutant analyses and to verify the previous PCDD/PCDF results. While the sample was collected in a non-standard and non-conservative manner, the presence of the solids catch afforded an opportunity to characterize the minimum possible levels of pollutants and conduct sample analyses on a heretofore undocumented source. The work reported here characterizes these samples for polycyclic aromatic hydrocarbons (PAHs), metals, physical structures, organic carbon (OC), elemental carbon (EC), and PCDDs/PCDFs, presenting the sample data in terms of emission factors, and providing preliminary characterization of emissions from in situ oil burns.

2. Experimental

A 4.0 m diameter, helium-filled aerostat (Kingfisher model, Lighter Than Air Systems Corp., FL) was used to loft an instrument package (termed the "Flyer") into the in situ oil fire plumes in the Gulf of Mexico to collect a sample for determination of PCDD/PCDF (Aurell and Gullett, 2010). Unexpectedly, the sail from the aerostat filtered a large amount of particulate matter (PM) from the plume. When the aerostat was retrieved shipboard, the PM from the sail was saved. While the openings in the sail fabric were relatively large (>100 μm), the overall porosity of the sail was low (approximately 36%) facilitating collection of fine particles. Preliminary analysis on this sample was conducted prior to PCDD/PCDF analysis by Aurell and Gullett (2010). Subsequently, the remaining sample, along with five 47 mm PM Teflon filters from the 2010 sampling were available for additional characterization. The solids from the sail ("Sail Solids Catch") and the five filter-collected PM samples ("PM Filter") were subject to further analysis, documented herein, and pictorially displayed in Fig. 2.

At the completion of the 2010 sampling effort, the sail was carefully folded and placed within a plastic bag for transport back to the EPA laboratory. At the laboratory, 2.18 g of the solids were vacuum-collected from the sail, extracted in toluene through a thimble, and the extract (termed the "Sail Extract") was concentrated to 1 mL and stored in a refrigerator near 0 °C in an amber vial. The solvent on the thimble was allowed to evaporate and the thimble and solid residue were placed in an amber 1 L jar and stored in a laboratory refrigerator. The Sail Extract was divided for subsequent analysis. One part was further extracted and subjected to a PAH analysis ("Sail PAH Extract"). The other part was subjected to further cleanup, resulting in a "Sail Dioxin Extract", and then analyzed for polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDDs/PCDFs). The post-extraction solid residue from the thimble, termed "Extracted Sail Solids," was also divided; one fraction was analyzed for OC/EC/total carbon (TC), a second fraction was subjected to a second extraction with hexane/isopropanol/benzene (HIB) and analyzed for PAHs, and another fraction was analyzed for metals via ICP-MS. The PM Filter samples were analyzed for OC/EC/TC and also subjected to an extraction with HIB prior to PAH analysis.

2.1. PCDD/PCDF analysis

Analysis of the solids recovered from the aerostat sail for PCDD/PCDF followed previously documented procedures (Agency, U. S. E. P. Method 8290A, 2007). Pre-extraction and recovery standards were used to determine quality metrics and sample quantification via the isotope dilution procedure. The normal pre-sampling standard was added to the sample prior to extraction rather than a sorbent media, as the sample was fortuitously collected and, in any event, the sail fabric was an inappropriate substrate for the standards. The recovered material was Soxhlet-extracted overnight with toluene, concentrated to about 100 mL, and concentrated further with flowing N_2. The extract was split and half was cleaned and fractionated using an automated, multi-column liquid chromatography system (Power Prep Dioxin System, FMS Fluid Management Systems, Inc., USA) consisting of acidic/basic/

Fig. 1. Aerostat with sampling instruments and solids-laden aerostat sail.

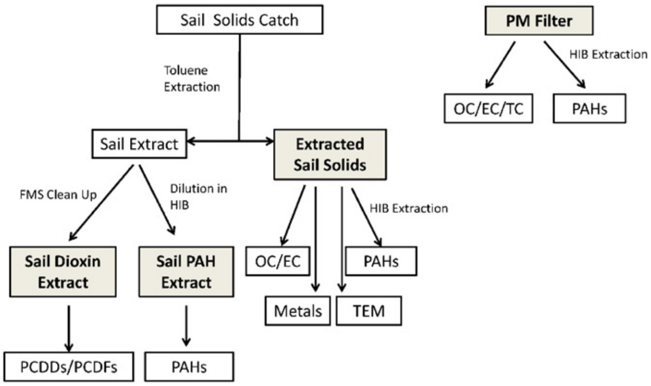

Fig. 2. Schematic of samples (shaded boxes) and their analyses.