Assessment of photochemical processes in marine oil spill fingerprinting

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ABSTRACT

Understanding weathering processes plays a critical role in oil spill forensics, which is based on the comparison of the distributions of selected compounds assumed to be recalcitrant and/or have consistent weathering transformations. Yet, these assumptions are based on limited laboratory and oil-spill studies. With access to additional sites that have been oiled by different types of oils and exposures, there is a great opportunity to expand on our knowledge about these transformations. Here, we demonstrate the effects of photooxidation on the overall composition of spilled oils caused by natural and simulated sunlight, and particularly on the often used polycyclic aromatic hydrocarbons (PAHs) and the biomarker triaromatic steranes (TAS). Both laboratory and field data from oil released from the *Macondo* well oil following the *Deepwater Horizon* disaster (2010), and heavy fuel-oil from the *Prestige* tanker spill (2002) have been obtained to improve the data interpretation of the typical fingerprinting methodology.

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1. Introduction

Over one million metric tonnes of petroleum enter the marine environment annually from municipal and industrial sources, marine transport, natural oil seeps and accidental oil spills (GESAMP, 2007). Although the number of the latter has decreased significantly during the past decades, catastrophic accidents such as the sinking of the *Prestige* tanker near the coast of Galicia (Spain) and the *Deepwater Horizon* (*DWH*) platform blowout in the Gulf of Mexico, still pose an important threat to marine and coastal ecosystems, causing extensive environmental (Albaigés et al., 2006; White et al., 2012) and economical (Garza-Gil et al., 2006; McCrea-Strub et al., 2011) damages. And while the past history has been promising, new environmental concerns arise as the oil industry is venturing to recover oil into more hostile, challenging and dangerous regions such as ultra deep-water, Arctic and along national boundaries that lack the infrastructure to respond effectively to any mishaps.

Identifying the source of oil releases, acute or chronic, is the primary step in assessing their consequences and better defining the response strategies. Efficient and unambiguous analytical methods for the characterization of these spillages are also needed from the standpoint of the enforcement of the pollution-control laws, designed to protect the public health and the environment. The most mature methodology for oil-spill characterization is based on the chemical fingerprinting approach, where a series of petroleum hydrocarbons can be profiled by gas chromatography fitted with a flame ionization detector or coupled to mass spectrometry (GC–FID and GC–MS) (Albaiges and Albrecht, 1979; Wang et al., 2007). Characteristic distributions and ratios of selected 'diagnostic' compounds generate an oil 'fingerprint' that can be used to identify the source of the spilled oil. This methodology has been extensively used (Wang and Fingas, 2003) and has recently been standardized (CEN, 2012). In past few years comprehensive two-dimensional gas chromatography (GC × GC) coupled to flame ionization detector (FID) or time-of flight mass spectrometry (TOFMS) has also demonstrated great potential for oil fingerprinting due to its unprecedented resolving capability and excellent sensitivity (Eiserbeck et al., 2012). It has been successfully applied for fingerprinting oil samples (Aeppli et al., 2012; Lemkau et al., 2010; Ventura et al., 2010).

However, once in the marine environment, any spilled oil undergoes a variety of physical, chemical, and biological processes (weathering), including evaporation, dissolution, microbial degradation and photooxidation that modify the original oil compositional patterns (NRC, 2003). A fundamental understanding of these processes is essential to refine the diagnostic value of the source recognition indices and interpret the profiles in tracking oil sources. This is particularly important for identifying the sources in areas of heavy traffic (Diez et al., 2007) or with natural oil seeps, such as in some areas of the Gulf of Mexico (Anderson et al., 1983; MacDonald, 2002), where misinterpretations may arise by the concurrence of other sources.

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The physical and biological processes are well studied and have been reviewed in detail (Fingas, 1995; Prince, 1988; Yang and Wang, 1977), but photooxidation is still poorly characterized (Nicodem et al., 2001; Payne and Phillips, 1985; Plata et al., 2008). Oil beached above the high tide mark is more exposed and more affected by direct sunlight (Douglas et al., 2002; Prince et al., 2003). In the sea surface microlayer, the process is thought to be driven by a series of radical reactions due to the presence of photosensitizers (e.g., dissolved organic matter), which can be excited by light to form various reactive species (RO·, HO$_2$·, HO·, etc.) (Liss et al., 2005; Schwarzenbach et al., 2005). Deeper in the euphotic zone, dissolved or particulate-associated oil molecules, such as polycyclic aromatic hydrocarbons (PAHs), can be photooxidized directly by absorbing UV radiation (Lee, 2003). A number of studies have been focused on the increase of toxicity of oil residues after photooxidation (Maki et al., 2001; Lee, 2003; Barron et al., 2005). The coupling of photooxidation with biodegradation has also been studied (Dutta and Harayama, 2000; Maki et al., 2001), but the information on the oil photochemical transformations at molecular level is limited (Jacquot et al., 1996; Bobinger and Andersson, 2009; Charrie-Duhaut et al., 2000).

In this respect, it is well known that oil weathering leads to an increase of polar components, akin in basic characteristics to resins and asphaltenes found in crude oils (Albaiges and Cuberes, 1980; Garrett et al., 1998; Maki et al., 2001; Prince et al., 2003; Aeppli et al., 2012). Moreover, there is evidence that methyl-substituted aromatic molecules photochemically oxidize at a faster rate than the parent compounds (Garrett et al., 1998). Some previous reports have also suggested that particular biomarker molecules used in oil forensics, such as triaromatic steranes (TAS), can be unexpectedly depleted due to field or simulated weathering (Barakat et al., 2002; Charrie-Duhaut et al., 2000; Jacquot et al., 1996). However, a more comprehensive research on the effects of photooxidation on the reliability of the oil fingerprinting methodology is still lacking.

The goal of this paper is to investigate compositional changes of marine oil spills that can be attributed to photooxidation and how they may affect the diagnostic ratios commonly used in oil spill fingerprinting. To this end, laboratory and field data have been obtained from two different oils, *Macondo* well (*MW*) oil from the 2010 *Deepwater Horizon* disaster in the Gulf of Mexico (SE USA), and heavy fuel-oil from the 2002 *Prestige* tanker spill off the Galicia coast (NW Spain) that were analyzed using GC × GC–FID and GC–MS fingerprinting methodologies. These included the analyses of PAHs and TAS diagnostic compounds in weathered field samples from the Gulf of Mexico and the Galicia coast, and irradiated samples in two laboratory-scale experiments, using natural sunlight and a Xe lamp. Target compounds in original and weathered oil samples were compared to calculate their losses, which in turn were used to calculate commonly used fingerprinting ratios to test if they can be reliably employed in environmental forensics in their current fashion.

2. Materials and methods

2.1. Chemicals

All solvents (dichloromethane, *n*-hexane, toluene and methanol) were obtained from Merck (SupraSolv®) (Darmstadt, Germany). Neutral alumina and anhydrous sodium sulfate were also obtained from Merck and activated at 400 °C overnight.

2.2. Samples and sample preparation

The fuel oil sample was obtained from the *Prestige* cargo tanks and the *MW* oil from the gushing well using an isobaric gas-tight

(IGT) sampler, in June 2010, deployed from a remotely operated vehicle (ROV) (Reddy et al., 2012).

Field sampling of *Prestige* oil was focused not on the major oil paths or the recently oiled shorelines, but on the lumps appearing at sea or arriving at the coast from time to time during 2003 and 2004. Samples were collected with a metal spoon, placed in pre-cleaned amber glass jars and stored in a portable refrigerator for transport to the laboratory.

The *MW* oil was recovered from oil splashes on jetty rocks ("rock scrapings") collected at two time points, first in April 2011 (350 days after the spill) at Buckaneer State Park (30°15′65″, −89°24′22″) and Waveland (30°16′55″, −89°22′07″), MS and second in August 2012 (750 days after the spill) at Fort Gaines, AL (30°14′47″, −88°4′32″). They were found above the sea level, and were exposed to sunlight.

Prestige samples (80–150 mg) were dissolved or extracted (in the case of field samples) with hexane and cleaned-up in an open glass-column, over anhydrous Na$_2$SO$_4$, and neutral alumina (5% water deactivated), eluting with hexane. The eluate was reduced in volume under a nitrogen stream to provide a concentration suitable for injection into the GC–MS.

The samples of fresh *MW* oil and field rock scraping samples were prepared as described previously (Aeppli et al., 2012). Briefly, the *MW* oil sample was dissolved in dichloromethane (DCM) at concentrations of 10–50 mg mL^{-1}. The rock scrapings were extracted three times with DCM/methanol (80/20), by vigorously shaking and centrifuging (1600 rpm for 5 min), and the combined extracts were dried over anhydrous Na$_2$SO$_4$ and used for further analysis by TLC-FID and GC × GC–FID.

2.3. Irradiation experiments

Both natural and simulated solar irradiation was used to investigate the photooxidation of the two oils. In the first experiment, approximately 80 mg of the *Prestige* oil was placed in an uniform thin layer in Petri plates and irradiated using a SUNTEST® CPS flat-bed Xe-exposure system (Atlas, Chicago, USA), equipped with a 1500B NrB4 Xe lamp that was operated at the potential of 507.5 W/m^2 to simulate natural irradiation. The system is equipped with a ventilator to maintain a constant temperature and prevent sample overheating. Control plates covered with Al foil were irradiated simultaneously. Samples were collected after 12 h, a time span found adequate for simulating moderate field conditions. The oil was washed off the plates with 3–5 mL of DCM, the solvent was then evaporated under gentle nitrogen stream, and the oil was finally cleaned-up for injection to GC–MS as described in Section 2.2.

For the *MW* oil experiments, approximately 50 mg of oil was added to each quartz glass tube to form relatively uniform thin layer. Control tubes were wrapped in Al foil. The tubes were mounted horizontally on an Al foil wrapped surface and exposed to sunlight on the top of a 3-m high cargo container in the Woods Hole Oceanographic Institution Quisset Campus (Woods Hole, MA). The duplicate tubes were collected every day during the first week, then after 20 and 70 days when the experiment finished (18 samples in total). Oil was extracted with DCM/methanol (80/20) and dried over anhydrous Na$_2$SO$_4$ for further analysis. Experiment was performed from May to August 2012, and the average irradiation potential during this period was 750 W/m^2 as recorded by the nearby solar station (41°42′38″, −70°4′31″).

2.4. Instrumental analysis

Samples were characterized by Fourier transform infrared spectroscopy (FT-IR) with a Nicolet Avatar 360 Thermo Scientific Spectrometer (Waltham, MA, USA) and by thin layer chromatography