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Characterization of a crude oil weathering series by ultrahigh-resolution mass spectrometry using multiple ionization modes

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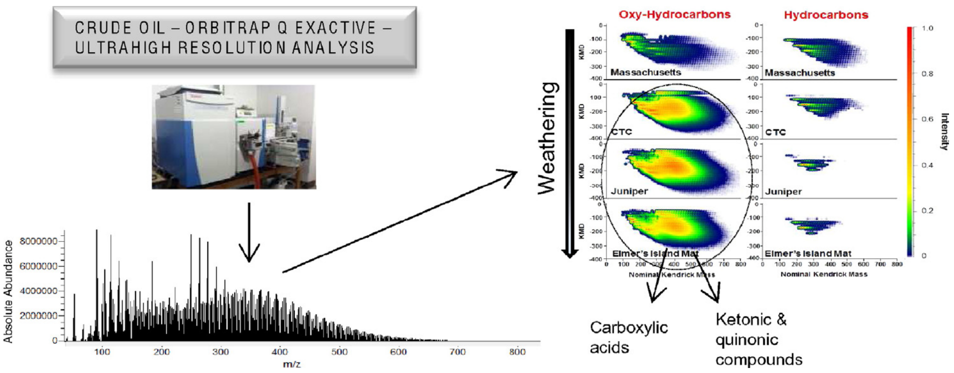
HIGHLIGHTS

- A crude oil weathering series is analyzed using ultrahigh-resolution mass spectrometry.
- An increase in oxidation products is observed with increased weathering.
- Formation of acidic, ketonic and quinonic compounds is suggested.
- Preferential ionizations of specific compounds may significantly skew results.

GRAPHICAL ABSTRACT



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ABSTRACT

Accidental crude oil releases, such as the *Deepwater Horizon* (*DWH*) accident, are always a potential threat to pristine marine ecosystems. Since the toxicity of crude oil heavily depends on its variable composition, the comprehensive characterization of crude oil compounds as a function of weathering is an important area of research. Traditional gas chromatography-based characterization presents significant limitations, and the use of ultrahigh-resolution mass spectrometric (UHRMS) techniques (that allow for the assignment of molecular formulae) has been shown to be better equipped to address the complex nature of crude oils. This study used an Orbitrap Q Exactive mass spectrometer operated at a resolving power of 140,000 FWHM with both electrospray ionization (ESI) and atmospheric pressure photoionization (APPI) sources, in order to characterize a crude oil weathering series of the Macondo oil released during the *DWH* incident (the source oil, two differently weathered surface slicks, and a beached residue). Preliminary gas chromatography mass spectrometry (GC–MS) and gas chromatography flame ionization detection (GC–FID) results suggested that the four oils comprised a true weathering series (including biodegradation and photodegradation in addition to other well-known processes such as dissolution and evaporation). UHRMS results showed a clear increase in oxygenated compounds with weathering, and further suggested a significant gain of acidic compounds, as well as the transformation of phenols to ketonic and quinonic compounds with weathering. A complementary study on a weathered oil sample amended with selected model compounds contributed additional insight into the functional group types that are accessible in each ionization technique.

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1. Introduction

In a society that is highly dependent on energy derived from petroleum, constant crude oil extraction and transportation lead to virtually unavoidable releases into the environment (Wang et al., 2013). On April 20, 2010, a turbulent mixture of gas and a light, sweet (Macondo type) crude oil was released into the Gulf of Mexico as a result of the *Deepwater Horizon* (*DWH*) drilling rig incident in the Mississippi Canyon Block 252 (MC252) (Camilli et al., 2012; McNutt et al., 2012; Aeppli et al., 2012). In the days following the accident, some of the escaped Macondo oil rose 1500 m to the surface of the ocean, creating oil slicks some of which ultimately reached the coast (Liu et al., 2012). In the event of crude oil discharges into marine environments, weathering processes such as dissolution, dispersion, emulsification, evaporation, biodegradation, and photo-oxidation (Wang et al., 2013; Aeppli et al., 2012) constantly modify the oil composition (Wang et al., 2013; Jordan and Payne, 1980). Weathering, thus, adds compositional complexity to what is already one of the most complex natural mixtures known to mankind (Hsu et al., 2011). The thousands of compounds present in crude oil can be divided into four main classes: saturated hydrocarbons (straight, branched, and cyclic alkanes), aromatic compounds (containing one or more rings), resins (relatively high molecular weight and polar compounds, which are soluble in the oil, and contain heteroatoms such as nitrogen, sulfur, and oxygen), and asphaltenes (highest molecular weight and most polar compounds, also containing heteroatoms such as nitrogen, oxygen and sulfur but unlike resins insoluble in the oil) (Garrett et al., 1998; Speight, 2004). These different compound types are affected differently by oil weathering as each of the weathering processes is selective towards specific compounds. For example, evaporation and emulsification deplete the oil of its volatile compounds, while water washing removes water-soluble compounds (Mansuy et al., 1997), and biodegradation affects primarily n-alkanes followed by branched and cyclic hydrocarbons, closely followed by naphthenic compounds (Wang et al., 2013). Photo-oxidation has been shown to primarily modify select polycyclic aromatic hydrocarbons (PAHs), and in addition to other oxidation mechanisms (including biodegradation) to be responsible for the increase of the oxygen content in the remaining oil (McKenna et al., 2013; Prince et al., 2003). Since several constituents in crude oil have been associated with some degree of toxicity, the characterization of fresh and especially of the modified weathered crude oil is crucial in order to understand the potential environmental effects.

Conventional oil characterization by gas chromatography flame ionization detection (GC–FID), or gas chromatography mass spectrometry (GC–MS) (Maki et al., 2001), has been able to elucidate weathering related compositional changes of hydrocarbons and PAHs. However, coelution and the inability to analyze polar, nonvolatile, or thermally unstable compounds (Wang et al., 2013; Garrett et al., 1998; McKenna et al., 2013; Burns, 1993; Charrie-Duhaut et al., 2000), limit the amount and type of analytes that can be detected (McKenna et al., 2013). Consequently, both techniques tend to overlook the analysis of oxygenated hydrocarbons (Aeppli et al., 2012), which is particularly problematic for weathered oil that has a lower amount of low-boiling and nonpolar compounds that are GC amenable, and has a higher amount of high-boiling and polar compounds (Aeppli et al., 2012). The characteristic oil “hump” or unresolved complex mixture (UCM), which is a raised baseline due to the coelution of numerous compounds and is observed in GC analysis and is most prominent in weathered oils, is an indication of the limitations of these previously described techniques (Gough and Rowland, 1990). In order to resolve a larger fraction of the components present in oil, more advanced techniques need to be used, such as two-dimensional gas chromatography mass spectrometry (GC × GC–MS) or Fourier transform mass spectrometry (FT–MS). GC × GC–MS somewhat expands the accessible analytical window and allows for isomer differentiation (McKenna et al., 2013); however, it is still limited to volatile compounds that are GC amenable (up to C_{45}). FT–MS, on the other hand, provides the possibility to extend this range up to C_{100} (McKenna et al., 2013), and to analyze nonvolatile and/or highly polar compounds (Qian et al., 2001a, 2001b; Mapolelo et al., 2009). Moreover, FT–MS analysis provides ultrahigh-resolution (Kaiser et al., 2011; Podgorski et al., 2013), and mass accuracy of less than 1 ppm (with internal calibration) (Savory et al., 2011), which leads to the possibility of assigning elemental compositions (Rodgers et al., 2005). The ability to couple several different ionization techniques to FT-MS is also crucial in the analysis of complex and diversified mixtures such as crude oil. Common sources that have been used are electrospray ionization (ESI) and atmospheric pressure photo ionization (APPI) (McKenna et al., 2013), but others such as atmospheric pressure chemical ionization (APCI) (Roussis and Fedora, 2002), and atmospheric pressure laser ionization (APLI) (Schrader et al., 2008) have also been employed. APPI is particularly useful to characterize nonpolar or slightly polar species, while ESI offers the advantage of accessing more polar species while avoiding interferences of the hydrocarbon matrix. As a result, comprehensive characterizations of weathered oils must be achieved by a combination of multiple techniques, aimed at accessing the maximum possible number of compounds.

A big portion of the previous studies on the Macondo oil released during the *DWH* accident have focused mainly on common analytes that are GC amenable, such as PAHs, alkanes, and hopane and sterane biomarkers (Aeppli et al., 2012; McKenna et al., 2013). Unsurprisingly, reports have shown that, with increased weathering, the oil was depleted of most of its saturated and aromatic compounds (Aeppli et al., 2012; Atlas and Hazen, 2011; Carmichael et al., 2012; Kostka et al., 2011; Lima et al., 2005; Liu et al., 2012). However, McKenna et al. (2013) estimated that in surface slicks only about 40% of the total mass of hydrocarbons could be analyzed by conventional GC-based techniques, while Reddy et al. (2012) estimated that for weathered Macondo oil traditional analytes only account for less than 25% of the oil mass. Moreover, an increase in oxygenated hydrocarbons with a concurrent decrease in saturated hydrocarbons and aromatics was reported in weathered oil deposited at the shoreline (Aeppli et al., 2012). Hall et al. (2013) further predicted by GC × GC–MS analysis that this oxygenated fraction is largely due to the oxidation of saturates, which has only recently been shown to be a significant process during oil weathering (Hall et al., 2013). FT-ICR analysis of oiled sands has shown a similar trend, more specifically detecting the possible formation of carboxylic acids, ketones, and alcohols (Ruddy et al., 2014), all being consistent with photo-oxidation and biodegradation transformation products. However, a significant portion of the currently available knowledge originates from GC × GC–MS analysis, and thus only applies to a limited amount of compounds. Data currently available from ultrahigh-resolution mass spectrometry (UHRMS) is limited, which evidences a strong need to expand the knowledge on weathering products of the Macondo crude oil by FT–MS techniques. This study, therefore, aims to characterize and identify compositional changes that occurred in a weathering series (fresh crude oil, two distinct oil slicks, and a beached oil mat) of the Macondo crude oil. UHRMS coupled with APPI and ESI in both positive and negative ionization mode are used in order to expand the range and type of compounds that can be detected.

2. Materials and methods

2.1. Samples and preparation

Four different field-collected oils were characterized in this study. The unweathered Macondo oil (denoted as Massachusetts oil from hereon) was collected by a production vessel on August 15, 2010 directly at the MC-252 wellhead, and transferred to the Massachusetts oil barge. Two weathered oils originating from two distinct surface slicks were skimmed from the Gulf of Mexico, and were collected by the USCG Cutter Juniper and Barge No. CTC02404 on July 19, 2010 and July 29, 2010, respectively (referred to as Juniper and CTC oil from