Source identification of beached oil at Al Zubarah, Northwestern Qatar

Nasser S. Al-Kaabi[a,b], Mette Kristensen[c,*], Nabil Zouari[a], Theis I. Solling[d], Steffen S. Bach[b], Mohammed Al-Ghouti[a], Jan H. Christensen[c]

[a] Department of Biological and Environmental Sciences, College of Arts and Sciences, Qatar University, P.O. Box 2713, Doha, Qatar
[b] Maersk Oil Research and Technology Centre, TECH 2 Building, Level 1, Unit 107, Al Gharrafa Street, Al-Rayyan, Education City, P.O. Box 22050, Doha, Qatar
[c] Department of Plant and Environmental Sciences, University of Copenhagen, Thorvaldsensvej 40, 1871 Frederiksberg C, Denmark
[d] Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark

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ABSTRACT

The Gulf was contaminated with a large quantity of crude oil during the Gulf War in 1991. Some of the oil beached on the shorelines of the Northwest coast of Qatar. It was discovered, during a sampling campaign in 2015, that the shorelines were contaminated with both fresh oil and heavily weathered oil that could be originating from the Gulf War. A total of 38 oil spill samples were collected during two sampling campaigns and analysed with gas chromatography - mass spectrometry (GC–MS). The chemical fingerprints of petroleum biomarkers and C0-C4 alkyl-substituted polycyclic aromatic compounds for these spill samples were compared to those of more than 250 crude oils from around the world applying the CHEMSIC method (chemometric analysis of selected ion chromatograms). The weathering degree varied significantly between samples, and relatively unweathered oil from the Gulf War oil spill is still found in the Al Zubarah area together with oil from more recent spills. The spill samples were found to originate from at least two sources with most resemblance to oils from Kuwait and Saudi Arabia.

1. Introduction

During the 1991 Gulf War, around 10 million barrels of oil were deliberately spilled into the Gulf (Massoud et al., 1996; Tawfiq and Olsen, 1993). Large quantities reached the shorelines and some beached on the northwest coast of Qatar where the Al Zubarah UNESCO site is located. During a sampling campaign in June 2015 it was discovered that the coast was heavily contaminated with both old highly weathered asphalt-like oil that could originate from the Gulf War oil spill but also with more fresh oil that most likely originates from recent oil spills in the Gulf. The latter was confirmed after discussions with locals in the area. In this study, the term weathering will be used to describe any removal of compounds due to physical weathering and/or biodegradation.

Oil pollution along the coastline are problematic for the area, especially due to tourism and visual perception since Al Zubarah is on the UNESCO World Heritage list and is of great importance to the Qatari history (UNESCO). Tar deposits on the Qatari coastlines have previously been analysed and quantified by Al-Madfa et al. (1999). They concluded that tar deposits in the north - northwestern coast of Qatar most likely originated from both previous oil spills and from fresh tar deposits, whereas the eastern coast were mainly impacted by fresh tar (Al-Madfa et al., 1999). Several field surveys (Massoud et al., 1996; Bejarano and Michel, 2010; Hayes et al., 1993) have been conducted following the Gulf War oil spill in 1991, but no studies have identified whether the tar deposits, currently found on Qatari coastlines, originates from recent oil spills or are very persistent and highly weathered oil tar deposits from the Gulf War. The objective of this study is therefore to assess whether the spilled oil at northwestern Qatar originates from multiple sources and to identify the most probable source(s) of the oil spill by comparing with oils in the oil database at University of Copenhagen (UCPH). For source identification we also aim at describing whether the spill samples are heavy fuel oils from bunker flushes (HFO's) or crude oils.

Several methods, based on specific diagnostic ratios and assessment of selected ion chromatograms (SICs), has been used in oil spill identification. In 2005, Christensen et al. proposed a novel method for oil hydrocarbon fingerprinting of gas chromatography-mass spectrometry selected ion monitoring data (GC–MS SIM) (Christensen et al., 2005). The method has been applied to several case studies, e.g. assessment of bioremediation (Soleimani et al., 2013), source differentiation of polycyclic aromatic hydrocarbons (PAHs) from multiple

sources (Gallotta and Christensen, 2012) and assessment of biodegradation and weathering effects (Kristensen et al., 2015). The method has, however, not been tested on real samples originating from multiple oil spills with different degrees of weathering.

To identify the source(s) of spilled oil in northwestern Qatar, several steps have been taken. First step was to build a database with crude oils and heavy fuel oils from all over the world, including oils from the Gulf. Oils in the database and oil samples, collected from two main areas along the beach in the Al Zubarah area, were analysed using GC–MS SIM. Source identification of the beached oil was performed with the CHEMSIC oil hydrocarbon fingerprinting method using the C0-C4 alkyl-substituted phenanthrene, C1-C2 pyrene, C0-C1 chrysene and the petroleum biomarkers hopanes and steranes.

2. Materials and methods

2.1. Chemicals

Dichloromethane (HPLC grade, Rathburn) was pro analysis grade. Anhydrous sodium sulphate (pro analysis) was purified by heating at 400 ℃ for 4 h and allowed to cool in a desiccator. For instrument performance assessment a GC–MS tune mixture was used. This was composed of benzidine (99.9%, Sigma), 4,4-DDT (99.7%, Sigma), pentachlorophenol (99.9%, Sigma, Supelco) and decafluorotriphenyl-phosphine, dftpp (99.3%, Sigma, Supelco) (50 µg/mL of each).

2.2. Sampling

On June 10th, 2015, fresh and heavily weathered stranded oil as well as surface and subsurface sediments were collected from two main areas at Al Zubarah, northwestern Qatar. Samples were collected by hand using a sterile spatula. The soil samples were collected into sterilized glass bottles, properly sealed, labeled and warped with foil to prevent any further light reactions. All collected samples were temporally stored in an icebox at 4 ℃ and transferred to the laboratory for further analysis. Temperature of collected soils ranged from 25 to 26 ℃. 10 oil/sediment samples from Al Zubarah were analysed in a pilot study (collected March 29th, 2014). Five of these were found to contain oil and were also included in the study (samples named X-01 to X-05). Samples and sampling sites are described in details in supporting information.

2.3. Chemical analysis

Oil samples were weighed and dissolved in dichloromethane to reach a total oil concentration of 2500 µg/mL. The extracts were analysed using an Agilent 7890A/5975C GC–MS operating in electron ionization (EI) mode. The GC was equipped with a 60 m ZB-5 (0.25 mm inner diameter, 0.25 µm film thickness) capillary column (Phenomenex, USA). Helium was used as carrier gas with a flow rate of 1.1 mL/min. Aliquots of 1 µL were injected in pulsed splitless mode with an inlet temperature of 315 ℃. The column temperature program was as follows: Initial temperature 40 ℃ held for 2 min, 25 ℃/min to 100 ℃ then followed by an increase of 5 ℃/min to 315 ℃ (held for 13.4 min). The transfer line, ion source and quadrupole temperatures was 315 ℃, 230 ℃ and 150 ℃, respectively. A total of 55 mass-to-charge ratios (m/z) were acquired in SIM mode (cf. Table S2 in supporting information). The method is described in details in Gallotta and Christensen (2012) (Gallotta and Christensen, 2012).

2.4. Data set

The data set consists of retention time windows of 55 selected ion chromatograms (SICs) for each sample (cf. Table S2 in supporting information). A total of 267 samples were analysed and split into four training sets (TrainSet), used to construct the models, and three

Table 1
Training (TrainSet) and validation (ValSet) sets used in PCA model 1–4. Sets in italic are subsets.

Sets	No. of samples	Model 1	Model 2	Model 3	Model 4
Global	153	TrainSet		TrainSet	TrainSet
M. East	35	TrainSet		TrainSet	TrainSet
Gulf 2	*11*		TrainSet		
HFO's	18				
Qatar Spill	34	ValSet	ValSet	ValSet	
Qatar Spill UW	*13*				ValSet
QC	27	ValSet			ValSet

validation sets (ValSet), predicted onto the model. The four training sets consist of 153 global samples ('Global'), 18 heavy fuel oils (HFO's), 35 Middle East samples ('M. East') and a subset of 11 of the Middle East samples ('Gulf 2'). The three validation sets consist of 27 quality control samples ('QC'), 34 spill samples collected in Northwestern Qatar ('Qatar Spill') and a subset with 13 of the Qatar Spill samples that were found to be relatively fresh ('Qatar Spill UW'). The training and validation sets used for each model can be seen in Table 1.

2.5. CHEMSIC

2.5.1. PCA modelling and data processing

Data were processed following the CHEMSIC method, described by Christensen et al. (2005; Christensen and Tomasi, 2007), to eliminate any variation between samples not related to chemical composition. The CHEMSIC method includes baseline removal, retention time alignment and data normalisation. Four PCA models, with various datasets, were made (see Table 1). For all models, baseline was removed by the Savitzky–Golay function using first order derivative, third order polynomial and a filter width of 5 data points (Savitzky and Golay, 1964). After baseline removal, retention times were aligned using correlation optimal warping (COW). The COW algorithm aligns sample chromatograms to a target chromatogram by stretching or compressing the samples along the retention time axis (Nielsen et al., 1998). The optimal warping parameters (i.e., the length of the segments in which the signals are divided and how much it is allowed to change) were determined by the use of a grid search in the parameter space followed by a discrete simplex-search (Skov et al., 2006).

The grid search were between 50 and 200 scan points for segment length (with 37.5 point increments) and 1–3 for the slack parameter, followed by at most 50 simplex iterations. The fraction of maximal deviation from the center in the COW alignment was 5%. The nine m/z's were aligned separately to the SICs of a quality control sample with intermediate shift.

For PCA model 1,153 global samples ('Global') and 35 samples from the Gulf ('M. East') were used to construct the model based on hopane, m/z 191. 34 spill samples ('Qatar Spill') and 27 QC ('QC') samples were predicted onto the model to ensure that the PCA model explain differences in the oil hydrocarbon fingerprints that are not only due to extensive weathering of the spill samples. 10 samples from the Middle East and 1 sample from Syria ('Gulf 2') were used to construct a local model (model 2) (m/z 191) and all spill samples ('Qatar Spill') were predicted onto this model. Data in both model 1 and 2 were normalized to unitary Euclidean norm within each SIC before SICs were combined (Gallotta and Christensen, 2012). This was done to focus the analysis on variations within each SIC.

A subset of unweathered spill samples ('Qatar Spill UW') were defined from a model of C1–C3 alkyl substituted polycyclic aromatic hydrocarbons (model 3) (Christensen and Tomasi, 2007; Christensen et al., 2005). The PAHs included in the model were: phenanthrene and