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## Chronology and backtracking of oil slick trajectory to source in offshore environments using ultraspectral to multispectral remotely sensed data

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#### ABSTRACT

Offshore natural seepage confirms the occurrence of an active petroleum system with thermal maturation and migration, regardless its economic viability for petroleum production. Ocean dynamics, however, impose a challenge for correlation between oil seeps detected on the water surface and its source at the ocean floor. This hinders the potential use of seeps in petroleum exploration. The present study aims to estimate oil exposure time on the water surface via remote sensing in order to help locating ocean floor seepage sources. Spectral reflectance properties of a variety of fresh crude oils, oil films on water and oil-water emulsions were determined. Their spectral identity was used to estimate the duration of exposure of oil-water emulsions based on their temporal spectral responses. Laboratory models efficiently predicted oil status using ultraspectral (>2000 bands), hyperspectral (>300 bands), and multispectral (<10 bands) sensors covering near infrared and shortwave infrared wavelengths. An oil seepage recorded by the ASTER sensor on the Brazilian coast was used to test the designed predictive model. Results indicate that the model can successfully forecast the timeframe of crude oil exposure in the ocean (i.e., the relative "age" of the seepage). The limited spectral resolution of the ASTER sensor, though, implies less accurate estimates compared to higher resolution sensors. The spectral libraries and the method proposed here can be reproduced for other oceanic areas in order to approximate the duration of exposure of noticeable natural oil seepages. This type of information is optimal for seepage tracing and, therefore, for oceanic petroleum exploration and environmental monitoring.

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#### 1. Introduction

With the high demand for energy resources, still founded on fossil fuels, petroleum exploration has migrated to deeper waters, particularly along the South American Atlantic coast. In view of its certified deep-water reserves, Brazil is set to become a top world oil producer and net oil exporter by 2017, possibly reaching the world's sixth-largest oil production by 2035 (IEA, 2013).

In deep-water conditions, and consequently far from the coastlines, optical remote sensing is an essential tool for the detection and analysis of oil traces in the ocean. Such traces, when related to the natural escape of hydrocarbons (HCs) from the sea bottom to the surface (i.e., seepage), are of interest to oil exploration for ensuring, at least, that there is generation and migration of HCs in

http://dx.doi.org/10.1016/j.jag.2015.03.007 0303-2434/© 2015 Elsevier B.V. All rights reserved. the sub-surface. The traces could also result from leakages of oil tankers, pipelines or rigs and their early detection helps to control marine pollution, which is the aim of environmental monitoring agencies.

Recent remote sensing studies have provided advances in the analysis of the compositional features (i.e., API gravity degree) of oil seepages found in the ocean (e.g., Wettle et al., 2009; Clark et al., 2010; Lammoglia and Souza Filho, 2011, 2012; Leifer et al., 2012; Prelat et al., 2013). Inverse modelling has also been tested as an attempt to identify areas in the seafloor from which petroleum seeped (Mano et al., 2011). This type of information enriches the remotely detection of seepages or leaks and, furthermore, can assist the exploratory or oceanic monitoring workflow.

Considering modern positive results achieved through the use of optical remote sensing data to estimate the composition of trace oil in the ocean, this work now seeks further science advances in remotely estimating the duration of oil exposed at the ocean surface based on spectral signatures.

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#### 2. Material and methods

#### 2.1. Oil samples and spectroscopy measurements

Three crude oil samples were selected from the oil collection of the University of Campinas (UNICAMP). Oil samples 1–3 have API degrees of 19.2°, 19.4° and 27.7°, respectively. The API classification is inversely proportional to the oil's specific gravity (density). Viscosities of samples 1–3 at 50 °C are 84.9, 78.5 and 20.4 mm<sup>2</sup>/s, correspondingly.

Experiments to analyze the spectral characteristics of crude oil, oil film and oil emulsions were carried out separately for each type of oil. Approximately 5 ml of oil was placed in Erlenmeyer flasks with 15 ml of water (Fig. 1). The water solution used in the experiment was prepared with a commercial ocean sea salt mixture (Instant Ocean Sea Salt – Aquarium Systems Inc., Sarrebourg, France), using 35 mg of salt to 1 l of water, aiming to simulate actual sea water. Once prepared, the samples were partially immersed in water inside a Dubnoff shaking water bath. The water inside the equipment was maintained at a temperature of 20–24 °C, which simulated the temperature range of seawater observed along the coast of Sao Paulo and Rio de Janeiro States, Brazil.

At regular intervals (i.e., 24 h, 48 h, 72 h, ...days, ... weeks.), the samples were carefully and quickly transferred from the Erlenmeyer flasks to Petri dishes and measured for reflectance with a FieldSpec-3High Resolution spectrometer (ASD), which operates within the 350-2500 nm range, with ultraspectral resolution (>2000 channels). The measurements were performed with a  $5^{\circ}$ foreoptics, some 10 cm distant from the sample, yielding a spot with a diameter of 0.87 cm. Each measured spectrum resulted from an average of 100 consecutive measurements. Besides, at least three different spectra were retrieved for each sample to account for possible heterogeneities (e.g., bubbles). The light source was positioned about 90° opposite from the optical fiber. The spectra were measured relative to a Spectralon<sup>®</sup> panel. The measurements were executed using a spectral featureless black bench and a black mask covering the borders of the Petri dish. Replicates were not produced, but several spectra were determined for each sample and the experiment repeated with different crude oils to validate the observations.

#### 2.2. Data analysis with chemometric techniques

Several published studies demonstrate the applicability of chemometric techniques to interpret spectral transmittance or absorbance of HCs (e.g., Kallevik et. al., 2000; Aske et al., 2001; Pasquini and Bueno, 2007), but fewer discuss their use on reflectance spectra of crude oils for remote sensing purposes. The partial least square regression (PLS regression) is a technique that combines features of principal component analysis with multiple regression with the objective of relating the variations of the responses (Y variables) to the variations in the prediction parameters (X variables). This type of regression correlates components of the X variables (in this case, reflectance values), which are also relevant to the predicted variables (Y) (i.e., exposure duration of the oil emulsion). In this process, scores and loadings are computed to simultaneously decompose X and Y with the premise of explaining the maximum covariance between these variables. Subsequently, a regression is performed between the latent variables (i.e., scores and loadings) and the response (see also Workman, 2000; Aske et al., 2001). The purpose of using this technique is to calculate the unknown response value, using a regression model. Moreover, it is particularly suitable for correlated and/or redundant data, like spectral data, and for nontrivial relations, like reflectance spectra and duration of exposure of oil-water emulsions.

In order to evaluate the quality of the models, the root mean square error was calculated for calibration (RMSEC) and prediction (RMSEP). These RMSEs, expressed by the same units as the original parameters (i.e., in hours), can be taken as an average of errors in calibration and prediction (Geladi and Kowalski, 1986; Beebe and Kowalski, 1987; Workman, 2000; Aster et al., 2005). At least three spectra representative of each phase of the experiments were employed for the modeling. For example, for oil 1, 63 spectra measured at different times (i.e., hours, days and weeks apart) were employed, in addition to spectra of pure oil and oil films.

#### 2.3. Simulation of spectral responses to operational sensors

Once registered, the full resolution reflectance spectra were convolved to the spectral resolution of the following sensors, currently in operation: (i) the ProspecTIR VS (Specim AISA Eagle &



Fig. 1. Samples of oil with an API degree of 19.4 as (a) oil film on water, (b) oil-water emulsion after 48 h in the Dubnoff shaker, and (c) emulsion after 72 h in the Dubnoff shaker.

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