Marine Pollution Bulletin 86 (2014) 391–401

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

The effect of sand composition on the degradation of buried oil

Sandra Fernández-Fernández[a], Ana M. Bernabeu[a,*], Daniel Rey[a], Ana P. Mucha[b], C. Marisa R. Almeida[b], Frédéric Bouchette[c,d]

[a] GEOMA.NET, Dpt. Geociencias Marinas, Universidad de Vigo, 36310 Vigo, Spain
[b] CIMAR/CIIMAR – Centre of Marine and Environmental Research, University of Porto, 4050-123 Porto, Portugal
[c] Institute of Mathematics, cc 51, University of Montpellier/CNRS, 34095 Montpellier, France
[d] Geosciences-Montpellier, cc 60, University of Montpellier/CNRS, 34095 Montpellier, France

ARTICLE INFO

Article history:
Available online 17 July 2014

Keywords:
Oil spill
Buried oil
Sandy beaches
Mineralogical composition
Oil degradation
Scanning electron microscope

ABSTRACT

The potential effects of the mineralogical composition of sediment on the degradation of oil buried on sandy beaches were investigated. Toward that purpose, a laboratory experiment was carried out with sandy sediment collected along NW Iberian Peninsula beaches, tar-balls from the Prestige oil spill (NW Spain) and seawater. The results indicate that the mineralogical composition is important for the physical appearance of the oil (tar-balls or oil coatings). This finding prompted a reassessment of the current sequence of degradation for buried oil based on compositional factors. Moreover, the halo development of the oil coatings might be enhanced by the carbonate concentration of the sand. These findings open new prospects for future monitoring and management programs for oiled sandy beaches.

1. Introduction

The monitoring programs carried out on the Galician beaches after the Prestige oil spill (POS) (NW Spain) highlighted the existence of subsurface oil pollution (Bernabeu et al., 2006, 2009, Bernabeu et al., 2013; González et al., 2009; Lorenzo et al., 2009), with some differences from what had been described after other oil spills (Holme, 1978; Vandermeulen et al., 1979; Long et al., 1981; Gundlach et al., 1983). Two different oil morphologies occurring at depths of up to 4 m were reported by Bernabeu et al. (2006): tar-balls in different sizes that are similar to the surficial oil and oil coatings on sand grains that form grey-coloured sand layers up to 1 m thick. Both the tar balls and the oil coatings constitute a portion of the degradation sequence for buried oil. The temporal scale for this process was established by Bernabeu et al. (2010) from a set of experiments performed in the laboratory under different environmental conditions. Their results indicate that the degradation process can also occur in the absence of microorganisms. The degradation begins when the required chemical compounds (resin and asphaltene) are present and the viscosity conditions are met (Fingas, 2014), which enhance the emulsification processes. These processes act on the tar-ball surface and release oil microparticles smaller than the inter-granular porosity of the sand medium. These oil microparticles expand in the sand through diffusion and/or by flow advection in the presence of water. The adsorption of these oil microparticles on the sediment grains occurs via an oil retaining mechanism that forms oil coatings during the final stage of degradation. Furthermore, the experiments were performed using the same type of oil and sediment across all microcosms. These studies revealed that various environmental conditions, such as the flow generated by oscillation of groundwater associated with tidal variations and the salinity, are important factors during oil degradation (Bernabeu et al., 2010).

The oil coatings identified in the beach samples oiled by POS were also examined using scanning electron microscopy (SEM) (Bernabeu et al., 2006). The preliminary SEM results revealed that the oil coatings are discontinuous oil coverings on the sand grains; these results also revealed that the oil residues are more common on carbonate grain surfaces than on the detrital grains. Other authors have explored the effects of the sand composition on oil degradation. Rowland et al. (2000) found that the total calcium content of the beach sand seems to affect the oil degradation process because the Ca in carbonate bioclasts buffers against the acidification of the environment, favouring a more effective oil breakdown.

In the present work, we report on a new set of laboratory experiments designed to assess the influence of the sedimentary composition on the degradation process for buried oil. In contrast to previous studies, the new experiments involve burying oil tar balls in sands with different compositions under the same environmental

* Corresponding author. Tel.: +34 986 812005; fax: +34 986 812556.
E-mail address: bernabeu@uvigo.es (A.M. Bernabeu).

http://dx.doi.org/10.1016/j.marpolbul.2014.06.040
0025-326X/

conditions. The results yielded important information regarding the assessment and management of future oil spills on sandy beaches.

2. Materials and methods

The experimental design involved seven 600-ml glass beakers from Ilmabor (12.5-cm height and 8.8-cm diameter) representing microcosms. Every microcosm contained approximately 600 g of medium-grained sands with nearly 35 g of oil (Prestige tar-balls) buried 2–3 cm from the surface against the beaker wall, which facilitated our observations, and 300 ml of seawater (salinity = 35 ppm, filtered to 1 μm and UV treated). The microcosms were covered with a black cloth to prevent photooxidation. Each microcosm experienced the same environmental conditions: no flowing seawater and room temperature.

Sand samples were collected in sterile bags from seven exposed sandy beaches during the spring of 2011 on the intertidal beach area during low tide. The sampling sites were distributed along 250 km of the NW Atlantic coast of the Iberian Peninsula, representing a sufficiently wide range of sand compositions (IGME, 1994) within the area affected by the Prestige oil spill. The sampled beaches were as follows from North to South: Nemiña (43°0′N, 9°15′W), O Rostro (42°57′N, 9°16′W), Carnota (42°49′N, 9°6′W), A Lanzada (42°26′N, 8°52′W), Montalvo (42°23′N, 8°50′W), América (42°8′N, 8°49′W), which are all on the NW Spanish coast, and São Pedro da Maceda, which is referred to as São Pedro (40°55′N, 8°39′W) and is the only sample from the NW Portuguese coast (Fig. 1). The first three beaches are the most affected by Prestige oil spill (Junoy et al., 2005) where the occurrence of buried oil has been reported even several years after the spill (Bernabeu et al., 2006; González et al., 2009; Lorenzo et al., 2009). A Lanzada and América beaches are considered as slightly polluted (Junoy et al., 2005). The São Pedro beach is a clean beach because no significant oil pollution event has been reported at that location (Almeida et al., 2013; Pontes et al., 2013). The tar balls used in the experiment were collected in April 2011 on the intertidal area of the O Rostro beach in dark glass jars. The hydrocarbon analysis confirmed the origin of the samples POS (Bernabeu et al., 2013).

The physical properties (grain size and colour) and composition (total organic carbon, carbonate content and mineralogy) of the sand samples were analysed to characterise the sediment.

The grain size was measured by dry sieving through a battery of sieves spaced at 0.5 phi units in a sieve shaker (CISA RP-03). The data were processed using the Gradistat software (v. 4) (Blott and Pye, 2001). The median grain size (D50) and sorting were calculated using the method of Folk and Ward (1957).

The colour was computed directly using a portable spectrophotometer (Konica Minolta CM-2600 d) through the Spectra Magic Nx software (v. 1.6). The recorded colour parameters correspond to the uniform colour space CIELAB, which was designed by CIE (Commission Internationale de l'Eclairage) in 1976. Briefly, this system provides a psychometric index of lightness L^* and two colour coordinates, which are a^* (green–red continuum) and b^* (blue–yellow continuum). The colour variations were assessed using the following formula (1):

$$\Delta E * ab = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{\frac{1}{2}} \quad (1)$$

The total carbon (TC) content and total inorganic carbon (TIC) were determined using a LECO analyser (CNS2000). The total organic carbon (TOC) was estimated by subtracting TIC values from the TC values. The $CaCO_3$ percentage was obtained after multiplying the TIC values by 8.33 (the ratio between the molecular weight of $CaCO_3$, which is 100.9 g mol^{-1} and the C atomic mass, which is 12.01 u).

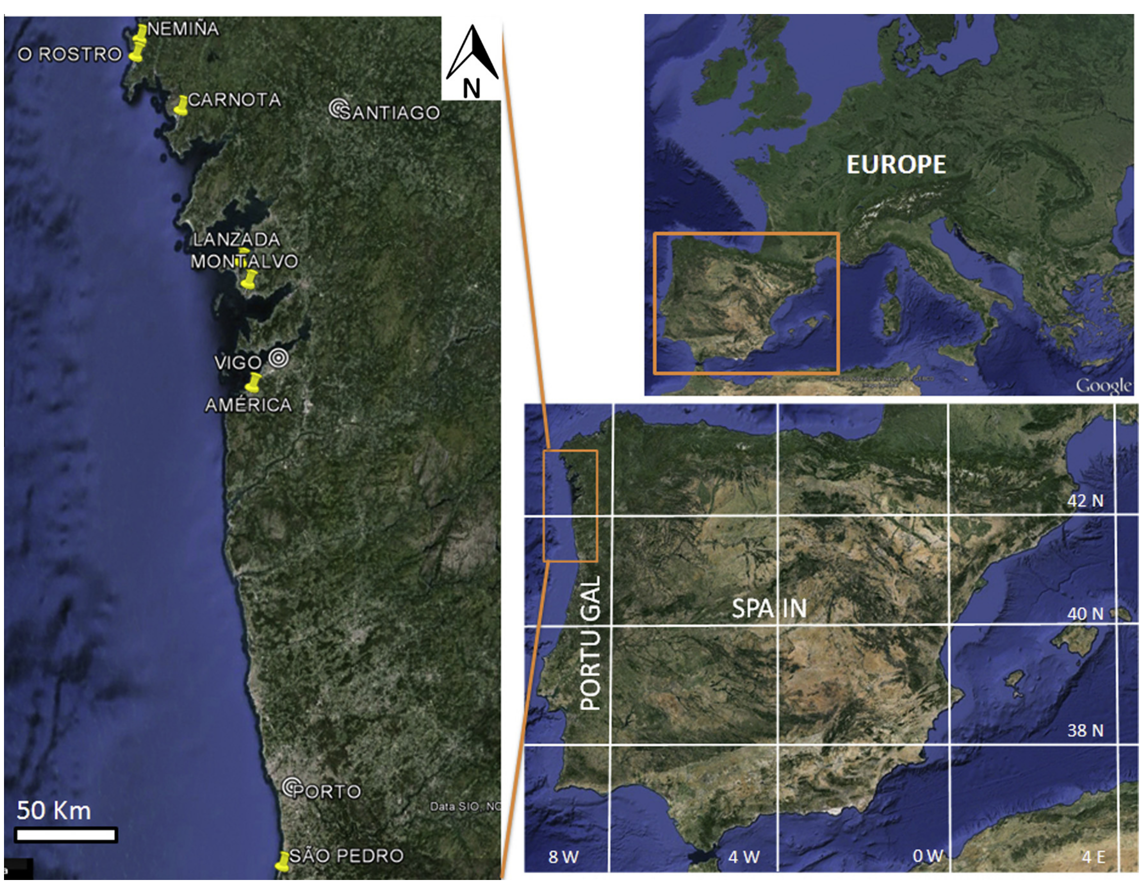

Fig. 1. Localization map showing the position of the sampled beaches along the Atlantic coast of the Iberian Peninsula (SW Europe) (courtesy of http://earth.google.com).