The effect of sand composition on the degradation of buried oil

Sandra Fernández-Fernández, Ana M. Bernabeu, Daniel Rey, Ana P. Mucha, C. Marisa R. Almeida, Frédéric Bouchette

A GEOMA.NET, Dpt. Geociencias Marinas, Universidad de Vigo, 36310 Vigo, Spain
B CIMA/CEMARE – 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

A R T I C L E   I N F O

Article info
Available online 17 July 2014

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

A B S T R A C T

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.

© 2014 Elsevier Ltd. All rights reserved.

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. (2006) 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
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°00′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):

\[
\Delta E_{ab} = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2} \quad (1)
\]

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).
The mineralogy of the sand was analysed with a PANalytical X’Pert PRO X-ray diffractometer (XRD). The data were processed using the PANalytical X’Pert HighScore software. The crystalline compounds were identified using the JCPDS-ICDD database. The semi-quantitative concentrations were determined using the adiabatic principle (Chung, 1974), the RIR (Reference Intensity Ratio) factors and the intensity of the lines, which coincides with the identified standards. In the present work, the RIR values used were as follows: quartz: 5, calcite: 2, aragonite: 1, microcline: 3.5, albite: 3.5, muscovite: 2.5 and orthoclase: 1.7.

The experiment was monitored over 120 days, at which time one of the microcosms developed a grey sand halo over the entire sand column. The temperature and the description de visu of the changes in the sand surrounding the tar-ball were recorded daily. The expansion of the grey sand halo was measured, and photographic reports were obtained out weekly. The colour was measured monthly on clean and grey sand halos (oil coatings).

During the experiment, two sub-samplings were obtained. The first sub-sampling was carried out when the grey sand halo had been developed enough to surround the tar-ball (day 46). Samples of clean sand were collected in Eppendorf tubes to analyse the abundance of microorganisms. The second sub-sampling was carried at the end of the experiment (day 120). Samples of clean and grey sand were collected to assess the changes in the microbial abundance. The grey sand samples were extracted in dark glass jars to quantify the amount of oil transferred from the tar-ball to the sand using a total petroleum hydrocarbon (TPHs) analysis and to Petri dishes to examine their morphology and surface texture through SEM.

The estimated microbial abundance in the samples, which was called the Total Cell Counts (TCC), was obtained using the DAPI (4,6-diamidino-2-phenylindole) direct counting method (Porter and Feig, 1980; Kepner and Pratt, 1994). Toward that purpose, 0.1 g of a homogenised sample was added to 2.5 ml of a saline solution (0.2 l m^{-1} filtered, 9 g l^{-1} NaCl), and 200 l l of Tween 80 (0.2 l m^{-1} filtered, 12.5% (v/v)) before being fixed with 1 ml of formaldehyde (0.2 l m^{-1} filtered, 4% (v/v)). The samples were stirred at 150 rpm for 15 min followed by sonication for 20–30 s at a low intensity (0.5 cycles, 20% amplitude). The subsamples of sediment were then stained with DAPI and incubated in the dark for 12 min (Porter and Feig, 1980). The samples were filtered using black Nucleopore polycarbonate filters (0.2-l m pore size, 25-mm diameter, Whatman, UK) under gentle vacuum and washed with autoclaved, 0.2-l m-filtered distilled water. The membranes were placed on glass slides and the cells were counted at 1875 X on an epifluorescence microscope (Labphot, Nikon, Japan).
The TPHs concentrations were determined using the method described by Couto et al. (2014). Three replicates of each sample were analysed. The sediment samples were mixed with tetrachloroethylene (>99% spectrophotometric grade from Sigma–Aldrich) and ultrasonically extracted (Elma, Transsonic 460/H model). The extracts were cleaned with deactivated silica gel and analysed by Fourier transform infrared spectrophotometry (Jasco FT/IR-460 Plus) using a quartz cell with a 40 mm path length (Infrasil I, Starna Scientific).

The grain morphology and surface texture were examined on a SEM (JEOLJMS6700 F) with a 3.5-nm resolution while using 20 kV for acceleration. The qualitative microanalyses were performed using energy-dispersive X-ray analysis systems (EDS). The samples were embedded in epoxy resin, polished and covered with a thin homogeneous layer of gold.

The Pearson correlation analysis was carried out using an IBM SPSS (v.19) to assess the relationships between the variables. Previously, the Kolmogorov–Smirnov test for normality was applied. The Pearson’s product-moment correlations coefficient (PPMCC) was calculated for the expansion rate, daily halo appearance, sedimentary characterisation (D50, sorting), percentage of TOC, carbonates and mineralogical components, as well as the TPHs and colour variations. In the present work, the correlations were considered significant at \( p < 0.05 \).

### 3. Results

The grain size of the samples matched that of medium sand (after Wentworth, 1922, Table 1). The D50 varied between 291 \( \mu \)m (São Pedro) and 499 \( \mu \)m (A Lanzada). The Folk and Ward (1957) sorting index varied between 1.27 (very well sorted) at São Pedro and 2.11 (moderately sorted) at A Lanzada. Most of the samples were moderately sorted (Table 1).

Both the TOC and carbonate content separated São Pedro (TOC and CaCO3 were below the detection limit and were 0.05% and 0.4%, respectively) from the rest of the samples (TOC = 0.46–0.79%, CaCO3 = 40–70.8%, Table 1). The high percentage of CaCO3 in the northernmost sand samples is directly related to the intensive coastal upwelling present in this area and the associated primary production. These concentrations agreed with the results of other works in the area (Rodríguez et al., 1987; Álvarez-Vázquez et al., 2003; Flor et al., 2004; Bernabeu et al., 2006, 2012).

The XRD analysis revealed that the main compositional differences were attributed to the relative contribution of siliciclasts (56.4–100%) and bioclasts (0–43.5%). In the bioclastic fraction, only the carbonates were considered because opal represents less than 0.5%, as reported by Bernárdez et al. (2005). These differences in mineralogy represent the variations in the provenance and coastal transport conditions (Fig. 2). Typically, the bioclastic constituents
are associated with the relative proportion of upwelling, which is related to their production in the subtidal factory. The siliciclastic constituents arise from longshore sediment transport and local coastal erosion effects.

According to their mineralogical composition, the samples can be classified in three groups: (1) quartzitic sands (quartz >90%) solely represented by the São Pedro sample, (2) siliciclastic sands with more than 70% of siliciclastic constituents, which include almost 60% quartz on average and were represented by the Nemiña, Montalvo and A Lanzada samples, and (3) carbonate-rich sands containing more than 30% biogenic carbonate compounds and less than 70% siliciclastic compounds, which contain less than 40% quartz

Fig. 4. Photographs (A and C) and SEM microphotographs (B and D) showing the two types of halos. Type 1 halo from O Rostro (A) and Type 2 halo from São Pedro (C). The occurrence of oil spots coating the surface of a bioclastic grain associated to Type 1 halos can be clearly seen in the SEM microphotograph (B). The siliciclastic grains of Type 2 halos do not develop this feature (D).

Fig. 5. (A) Time evolution of the room temperature. The mean temperature is also shown (grey line). (B) Absolute growth in centimeters of the halo thickness during the experiment.
and are represented by the O Rostro, Carnota and América samples. The quartzitic sands primarily reflect the influence of the Douro and Vouga drainage areas in the Portuguese continental shelf and the corresponding northwards transport of recycled sediments along a lineal and energetic coast (Abrantes et al., 1994; Cascalho, 2000). The exclusively siliciclastic composition of São

---

**Fig. 6.** Analysis of the halo expansion rates with time for every microcosm. The line shows the cumulative percentage of change in the halo thickness during the experiment. The bars indicate the weekly change in thickness expressed as the expansion rate in cm day$^{-1}$. Note the almost uniform expansion rate in São Pedro. Temperature is plotted for reference.

**Fig. 7.** Microbial abundance for each sample estimated from the total cell counts (log TCC g$^{-1}$, mean and standard deviation, n = 3) at two moments of the experiment: day 46 (clean sand) and day 120 (clean sand and grey sand). Note the absence of differences between samples.
Pedro is related to the local provenances associated with the current dune erosion (Granja et al., 2008; Costa and Coelho, 2013). The siliciclastic group reflects the more local provenances that are primarily associated with pocket beaches (IGME, 1994; Vilas et al., 2005), while the carbonate-rich sands reflect the more wave-exposed beaches with important contribution of present-day upwelling, which is associated with subtidal biogenic carbonates (Flor, 1977).

The results revealed the formation of grey halos around the buried oil in every microcosm during the 120-day observation period (Fig. 3). However, the differences in the formation process distinguished the two types of halos. Type 1 halos (T1) resulted from the assemblage of oil-coated grains (Fig. 4A and B). T1 halos were identified in all of the microcosms except in São Pedro. In contrast, type 2 halos (T2) resulted from the migration of discrete oil microparticles that separated from the buried tar ball (Fig. 4C and D), concentrating on top of the tar ball and forming a black band (Fig. 3). T2 halos only occurred in São Pedro (Fig. 4D).

The first sample to develop a T1 halo was from Nemiña (day 8), and the last one was from Carnota (day 30) (Table 1). The colour change in the sand associated with the halo was quantified using the colour variation parameter $\Delta E_{\text{clean-grey}}$ ranging between 5.6 (Carnota) and 14.4 (A Lanzada). The intensified colour associated with the halo development over time was also evaluated using the parameter $\Delta E_{\text{grey initial-end}}$, which varied between 2.9 (América) to 10.6 (Montalvo) (Table 1). The halo growth remained independent of temperature (Fig. 5A). The temperature varied by 10.9°C during the experimental period: between 27.0°C (day 42) and 17.9°C (day 120) with a mean temperature of 23.3 ± 2.0°C.

The rate of the development and intensity of the halos during the experiment was different for each type of halo and sample, varying between the T2 halo of São Pedro microcosm (quartzitic sand) to the fully developed T1 halo in the Carnota microcosm (carbonate-rich sand) (Figs. 5 and 6B–H). At the end of the experiment, the halo thickness reached a maximum value of 5 cm in Carnota and a minimum value of 1 cm in São Pedro (Fig. 5). The daily halo expansion rate varied during the experiment; most of the samples showed periods of stagnation (Fig. 6B–H). However, the halo growth over the timescale of the experiment was linear and was consequently estimated. The halo expansion rate estimated through linear regression (least-squares) varied between 18 cm year$^{-1}$ in Carnota and 4.5 cm year$^{-1}$ in São Pedro. O Rostro and Montalvo showed similar expansion rates, which were approximately 9.5 cm year$^{-1}$ (Table 1).

The microbial abundance showed no significant differences between the sand samples during the experiments, remaining between 6.8 and 7.3 log TCC g$^{-1}$ (Fig. 7). The concentration of the TPHs found on the grey sands samples fluctuated between 0.048 mg g$^{-1}$ in São Pedro and 0.630 mg g$^{-1}$ in A Lanzada (Table 1). In Nemiña, Carnota, A Lanzada and America samples, the standard deviations for the TPHs were elevated because at least one replicate had a significantly higher value than the other two due to the heterogeneity of the samples, which is related to the random distribution of oil microparticles in the sand column. Consequently, it was difficult to obtain three identical replicates.

The sand grains recovered from the halo area of each microcosm were examined using SEM. These observations revealed that the oil preferentially adhered to the bioclastic carbonate grains, where oil residues were common (Figs. 8 and 9A–F). The oil preferentially occurred as randomly distributed and isolated areas of very thin lamina that stained the bioclast surface. In Nemiña (Fig. 9A), the oil spots were abundant and similar in size (10–15 μm). In Carnota (Fig. 9C), the oil spots were less abundant and varied in size (1–15 μm). The oil spots are more abundant in the bioclastic grains that are more altered. Oil spots were rarely observed on siliciclastic grains among our samples. When they were, the oil appeared to cover another grain that had settled on the silicilastic grain surface (Fig. 9G–H).

Elemental mapping through EDS was used to characterise the composition and the oil residues. Fig. 10A shows the oiled surface of a bioclastic grain and the element maps for Ca and S from the same area. Sulphur, which exhibited concentrations up to 2.28%...
in the POS oil (Albaigés et al., 2003), was used as a proxy for the oil residue. The EDS maps of calcium showed a uniform distribution on this type of grain surface. Therefore, the electron beam can pass through the area shown on the SEM image. In the sulphur maps, the higher S concentrations coincide with an area that is likely to be oil residue. Similarly, Fig. 10B shows the surface of a silicilastic grain under a scanning electron microscope in backscattering (BS) mode and the corresponding EDS mapping of Si and S. In contrast to the former example, the Si maps show a black shadow that approximately coincides with the area containing higher sulphur content. In this case, the oil residues coat a smaller grain (white area on the oil particle) that had settled on the silicilastic grain. The oil acted as an adhesive between the grains.

The Pearson correlation aimed to document the influence of the sedimentary composition on halo development. Accordingly, the carbonate concentrations had a significantly ($p < 0.05$) positive Pearson product-moment correlation coefficient (PPMC) at the beginning of the halo growth ($r = 0.868$) and the expansion rate ($r = 0.862$). Furthermore, the halo growth and the expansion rate showed a highly negative PPMC with the variations in colour (clean-initial grey sand) ($r = -0.889$, $r = -0.910$, respectively) (Table 2).

**Fig. 9.** Representative SEM microphotographs of samples where oil was associated to carbonatic (A–F) and silicilastic (G–H) grains. Microscope operated on backscattering mode (BS, YAG detector) (A) Nemiña, (B) O Rostro, (C) Carnota (D) Lanzada (E) Montalvo (covering salt crystals), (F) América (G) Lanzada (oil-covered micro grain settled a top a larger grain), and (H) São Pedro (two oil-covered micro grains).
4. Discussion

All microcosms were subjected to the same environmental conditions (no flow, room temperature and seawater salinity), and a microbial analysis revealed similar abundances on all of the sand samples (approximately 7 log TCC g⁻¹). Because any microorganism can use petroleum as a source of carbon and energy for growth (Van Hamme et al., 2003; Atlas and Hazen, 2011; Pontes et al., 2013; Reis et al., 2014), both biodegradation and physicochemical processes should degrade the buried oil to the same extent during all of the experiments. However, significant differences have been detected between the microcosms. These differences in oil degradation can be primarily attributed to factors associated with the sediment.

Two stages of the buried oil degradation were established by Bernabeu et al. (2010), specifically emulsification and diffusion, and both were completed in all of the microcosms. Emulsification is induced by the surfactant-like action of the polar asphaltene and resin compounds (Fingas, 2014) present in the Prestige oil in concentrations up to 28% (Albaigés et al., 2003). This process gives forms oil microparticles at the oil–water interface. Although the concentration of oil microparticles increases near the surface of the tar ball, the diffusion processes is active (Atkins, 2009; Bernabeu et al., 2010), expanding concentrically in the sand column. The size of the oil microparticles varied but needed to be smaller than the intergranular effective porosity to diffuse. These particles were detected during all of the experiments over a short time interval and were particularly conspicuous in the São Pedro microcosm where the oil microparticles reached the sediment surface, forming a concentrated black layer (Fig. 3).

The presence of these oil microparticles highlighted the activation of the degradation processes in the buried oil. The TPHs analysis also supported this assertion, revealing detectable levels of hydrocarbons in the sand samples next to the buried tar-ball. Based on our measurements and experience, the TPHs analysis is a good proxy for establishing the presence or absence of oil in the sediment; however, this method fails to evaluate the total buried oil. Quantifying the total buried oil is very difficult because different oil morphologies are distributed randomly in the sand column. Consequently, the data from a single sand sample is not representative of the total buried oil.

The formation of oil coatings began concurrently with these degradation steps. This type of oil morphology reinforced the halo formation and promoted a fast halo expansion (Fig. 3). Our experiments revealed that oil coatings primarily developed on the carbonate sand microcosms and that the halo in the São Pedro microcosm is produced by a high concentration of oil microparticles (Fig. 4).

### Table 2

Results of statistical analysis showed the Pearson correlations between day of halo appearance and halo rate expansion (cm/year) with compositional parameters such as carbonates and silica, colour variation (clean-initial grey) and total petroleum hydrocarbons (TPHs).

<table>
<thead>
<tr>
<th></th>
<th>Day</th>
<th>Expansion rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonates</td>
<td>0.868</td>
<td>0.862</td>
</tr>
<tr>
<td>Silica</td>
<td>-0.697</td>
<td>-0.740</td>
</tr>
<tr>
<td>Colour (clean-initial grey)</td>
<td>-0.889</td>
<td>-0.910</td>
</tr>
<tr>
<td>TPHs</td>
<td>0.260</td>
<td>0.209</td>
</tr>
</tbody>
</table>

* Correlation is significant at the 0.05 level.

**Fig. 10.** (A) BS image of the surface of a carbonate grain showing an oil spot (left), and corresponding elemental map for Ca and S (right) estimated from their EDS spectrum. (B) The same for a siliciclastic grain in which two oil-covered micro grains can be observed on the grain surface; and corresponding Si and S element maps.
the microscopic scale, the grey sands correspond to sedimentary grains that are irregularly covered by oil spots, as shown in Figs. 8 and 9. Bioclasts present a rougher and more highly altered surface than the siliclasts, as observed in the different SEM images; these data might indicate that the oil microparticles stain the grain surfaces while diffusing along the sand column. Although all of the microcosms composed of bioclastic sands developed the T1-halos associated with the formation of oil coatings, which varied from the poorly developed halo in the América microcosm to the well-developed halo in the Carnota microcosm, non-bioclastic sand (São Pedro microcosm) developed a T2-halo associated with a high concentration of oil microparticles because they do not accommodate oil coatings. Siliclastic grain surfaces only showed oil residues when smaller oil-coated grains were affixed to them. In this case, the oil was the adhesive binding the grains.

The carbonate content in the sand also seems to affect when the T1 halo forms and how fast it expands. Overall, the higher the carbonate concentration, the sooner the T1 halo appears and the faster their expansion. This effect might be modulated by other sedimentary variables, such as compaction or poropermeability, which have not been considered during this experiment.

Previous works (Bernabeu et al., 2010) indicated that the formation of oil coatings was the last step during the degradation of buried oil, and they provided a temporal scale for the arrival and burial of the oil. If oil coatings were found, the tar-ball had been buried long enough to complete the degradation sequence. However, the present outcomes suggest that oil coatings are not always present for subsurface contamination because siliclastic sands hinder the formation of oil coatings. Therefore, the beaches primarily composed by siliciclastic sand would exhibit contamination by particulate buried oil more than the grey sand layers. Consequently, the sedimentary composition reveals is a new factor affecting oil degradation process in sandy beaches.

5. Conclusions

The sedimentary composition clearly influences the degradation process for oil buried in a beach and, consequently, the conditions indicating the fate of the oil by depth. Mixed carbonate siliciclastic sands favour oil degradation starting from tar balls and forming oil coatings. The typical oil morphologies in the mixed carbonate siliciclastic sand beaches are grey sand layers in clean sands. In contrast, the most abundant oil morphologies in siliciclastic carbonate sands could act as a remediation tool by retaining the oil in a predetermined site to limit its expansion toward more sensitive areas. This approach has the additional advantage of creating a confined environment in which nutrients can be added to enhance the activity of oil degrading microorganisms (Swannell et al., 1996).

Acknowledgements

This work was financially supported by the MICINN of Spain (CTM 2008-02699E) and the FCT of Portugal (ERA-AMPERA/0003/2007) in the framework of the EU AMPERA. The authors gratefully acknowledge N. El Mekadem and M.A. Otero for their help in the field and I. Reis for the microbial counts. The constructive comments of the anonymous reviewers are greatly appreciated. S.F.-F. was awarded a FPU grant by the Ministry of Spanish Education.

References
