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Bioremediation of heavily hydrocarbon-contaminated drilling wastes by composting

G. Paladino[1,2] · J. P. Arrigoni[2] · P. Satti[2,3] · I. Morelli[4,5] ·
V. Mora[5] · F. Laos[2]

Abstract Oil-based drilling cuttings comprise a large and hazardous waste stream generated by oil and gas wells drilling operations. Oil-based cuttings are muddy materials with high contents of salts and hydrocarbons. Composting strategies have shown to be effective in the biodegradation of petroleum hydrocarbons, and it offers numerous advantages in comparison with other bioremediation methods. In order to assess the effectiveness of drilling cuttings bioremediation by composting with food and garden wastes, an experiment was conducted in 60-L reactors for 151 days. Four treatments were carried out: only oil-based cuttings, two proportions (in a volume basis) of organic wastes to drilling cuttings (33 and 75 %) and only organic wastes (as a traditional composting reference), with pine-tree woodchips as bulking agent. High degradation percentages of total hydrocarbons (≈ 82 %), n-alkanes (≈ 96 %) and the 16 USEPA-listed polycyclic aromatic hydrocarbons (≈ 93 %) were reached in the treatment with 75 % of organic wastes, and applying 33 % of organic wastes was not more effective than not applying organic wastes for the drilling cuttings hydrocarbons biodegradation. Furthermore, in the treatment with 75 % of organic wastes, alkanes half-life and polycyclic aromatic hydrocarbons half-life were about 10 times and four times lower, respectively, than those in the treatment with 33 % of organic wastes. Possibly, lower hydrocarbons and salts initial concentrations (i.e., lower toxicity), higher microbial counts, adequate nutrient proportions and water content supported a high biological activity with a consequent elevated biodegradation rate in the treatment with 75 % of organic wastes.

Keywords Drilling wastes treatment · Hydrocarbons biodegradation · Oil-based drilling cuttings · Organic wastes

Introduction

Oil-based drilling cuttings are one of the largest fractions of the hazardous wastes generated by oil and gas wells drilling operations. This waste stream is composed of spent drilling fluids and borehole rock cuttings. Oil-based cuttings are muddy consistency materials with high contents of salts and hydrocarbons, which come from drilling fluid additives and the reservoir geological formation (Arce-Ortega et al. 2004; Ball et al. 2012). Proper management of drilling cuttings is a current concern for oil companies and environmental protection authorities, since toxicity and high rate of generation of this waste make it difficult to achieve effective treatment solutions at acceptable costs (Onwukwe and Nwakaudu 2012).

Composting bioremediation strategies rely on organic wastes (i.e., composting feedstock) application to contaminated materials, with the aim of promoting biological

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activity and, consequently, the biodegradation of pollutants. Organic wastes application provides a broad range of microorganisms and readily available nutrients and improves structure and water retaining capacity of the material undergoing treatment. In addition, this low-cost strategy allows processing of large volumes of wastes, with the extra benefit of simultaneous treatment of more than one waste streams (Savage and Díaz 2007; Chen et al. 2015). In oilfields staff offices and accommodation camps, available wastes are food, gardening and wood refuses (Elshorbagy and Alkamali 2005). Thus, using these types of organic wastes for the remediation of drilling cuttings could greatly cooperate with oilfields waste management programs.

Governing factors affecting composting bioremediation (i.e., nutrients content, pH and oxygen and water availability) depend on the amount and type of the organic wastes applied. In heavily hydrocarbon-contaminated materials, high-carbon concentration can lead to a C/N ratio imbalance, due to nitrogen deficiency, greatly affecting microbial activity. Thus, the amount of N supplied by organic wastes is of vital importance. However, if large amounts of organic wastes are applied, this carbon source could be preferentially degraded over the target compounds and hydrocarbon biodegradation may be delayed (Namkoong et al. 2002; Antizar-Ladislao et al. 2005). Likewise, even though water provided by organic wastes is an advantage in composting bioremediation strategies, it is essential that the water content of the composting mass does not affect oxygen flow (Joo et al. 2007).

On the other hand, the adsorption/desorption processes of the contaminant to the matrix are regulated not only by pollutants volatility, water solubility and affinity for organic matter, but also by matrix porosity and composition. These factors, which are highly dependent on the mixtures to be composted, and therefore on the type and the amount of organic wastes applied, will regulate contaminants bioavailability and biodegradability (Huesemann et al. 2004; Grace Liu et al. 2013).

Oil-based drilling cuttings are a biologically impoverished and cohesive oil-rich silts and clays admixture (Ball et al. 2012), very different from a hydrocarbon-contaminated soil. Bioremediation of contaminated soils by composting has been extensively reported in scientific literature, and these methods have proven to be effective in petroleum hydrocarbons degradation (Van Gestel et al. 2003; Antizar-Ladislao et al. 2004; Moretto et al. 2005; Joo et al. 2007; Zhang et al. 2011; Laos et al. 2012; Chen et al. 2015). However, drilling cuttings composting bioremediation reports are scarce in scientific literature. In the few studies found, only two types of organic wastes were used: poultry manure (Saretsky et al. 2002; Ayotamuno et al.

2009) and straw with the addition of inorganic fertilization (Rojas-Avelizapa et al. 2007). In these trials, high hydrocarbons removal efficiency was attained (60–90 %). Nevertheless, to the best of our knowledge, there are no reports of trials using food and gardening organic wastes for the bioremediation of drilling cuttings by composting.

The overall objective of this work was to assess the remediation of heavily hydrocarbon-contaminated drilling cuttings through composting, using food and garden wastes. Particularly, we attempted to study the effect of applying different proportions of organic wastes on hydrocarbons biodegradation according to their type and molecular weight.

This study was carried out from December 2013 to April 2014, in the Environmental Sciences Laboratory of the Universidad Nacional de Río Negro—Sede Andina.

Materials and methods

Collection and pretreatment of drilling cuttings and organic wastes

Oil-based drilling cuttings (OBCs) were collected in an oilfield located in the north of Argentine Patagonia region. In order to prevent mixing with contaminated soil, OBCs were taken directly from the well site, before they were transported to the storage repositories. Source separated organic wastes were collected from a company staff buffet. These consisted of refuses from raw vegetables, cooked meals and napkins paper. Fresh organic wastes (OW) were shredded (rough particle size < 3 cm), in order to increase its specific surface, homogenized and mixed with 20 % by volume of grass clippings. Pine-tree woodchips (WChs), with a prevailing diameter of 1–3 cm and made from untreated wood, were used as bulking agent. Representative samples of the three raw materials (OBCs, OW and WChs) were taken for chemical analyses.

Experimental design and monitoring

Twelve plastic drums with lid (60 L) were used as reactors for the experiment. Reactors were thermally insulated with a 3-cm-thick layer of polyurethane foam. A metal mesh was placed 10 cm up from the drum bottom to allow leachates separation and collection. Four treatments were conducted. In each treatment, 30 L of woodchips was mixed with 30 L of the following composting mixtures, to reach a final volume of 60 L: OBC alone (0 % OW), two proportions in volume of OBC and OW (33 and 75 % OW), and only OW (100 % OW). The last one was used as a traditional composting reference. Each treatment was run in triplicate. Treatments composition is detailed in Table 1.

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Table 1 Composting mixture proportions in performed treatments

Treatment (% OW)[a]	Volume (L)[b]				OBC:OW (v:v)	Dry weight (kg)[b]				OBC:OW (dw:dw)	Water content[b] (%)
	OBC	OW	WCh	Total		OBC	OW	WCh	Total		
0	30	0	30	60	1:0	30.3	0	4.9	35.2	1:0	27
33	20	10	30	60	1:0.5	20.0	1.2	4.3	25.5	1:0.1	35
75	7.5	22.5	30	60	1:3	7.0	2.8	3.7	13.5	1:0.4	55
100	0	30	30	60	0:1	0	3.6	4.3	7.9	0:1	70

[a] OW percentage in volume

[b] Values are the means of three replicates (i.e., reactors) per treatment

The composting experiment was conducted outside during 151 days, from December 2013 to April 2014 (summer and early autumn). Using temperature probes connected to a data logger, each reactor temperature was recorded automatically every 30 min. Ambient temperature was monitored with a maximum–minimum thermometer. In order to allow air exchange and homogenize, reactors were uncovered twice a week and composting mass was manually turned.

Sampling

One composite sample was taken from each reactor at 0, 4, 8, 15, 30, 61, 94 and 151 days, for hydrocarbons analysis and chemical characterization. Composite samples, of approximately 150 g each, consisted of three subsamples, taken at the bottom, in the middle and at the top of the reactor. Sampling was done with an Edelman-type auger. In addition, at the beginning of the experiment, one composite sample was taken under sterile conditions for microbiological analysis. In every sampling instance, gravimetric water content was determined by oven drying 10 g of sample at 70 °C (to avoid volatile compounds losses) to constant weight.

Chemical analysis

Air-dried samples were sieved (<1 cm) in order to remove woodchips. Electrical conductivity (EC) and pH were measured in 1:10 ratio water extracts. Phosphorus was extracted in $NaHCO_3$ 0.5 M (1:100) and determined by the molybdate–ascorbic acid method (Laos et al. 2002). Total nitrogen (TN: organic N + $N-NH_4$) was determined by semimicro Kjeldahl and total organic carbon (TOC) by the Walkley–Black method (Sparks et al. 1996).

Microbiological analysis

The enumeration of heterotrophic and hydrocarbon-degrading bacteria was performed in fresh unsieved samples, using selective culture methods. Serial tenfold sample dilutions were spread on plates with R2A agar medium supplemented with cycloheximide (7 % w/v), for cultivable heterotrophic aerobic bacteria count (Reasoner and Geldreich 1985). Enumeration of hydrocarbon-degrading bacteria was performed by the most probable number (MPN) technique, using a mineral liquid medium in 96-well microtiter plates. For total hydrocarbon, alkane and PAH-degrading bacteria counts, sterile diesel oil, n-hexadecane and a PAHs solution were used as a sole carbon source, respectively; 1 mL per liter of resazurin (0.1 % w/v) was used as a color indicator in the liquid medium, except for PAH counts. The plates were incubated at 25 ± 1 °C for 7 days for cultivable heterotrophic bacterial growth and for 21 days for hydrocarbon degraders (Wrenn and Venosa 1996; Morelli et al. 2005).

Hydrocarbons analysis

Hydrocarbons were analyzed only in 0, 33 and 75 % OW samples. Hydrocarbons were extracted by sonication and quantified by gas chromatography (GC) (US EPA 2007). Briefly, 5 g of moist and sieved (<1 cm) sample was mixed with 5 g of Na_2SO_4 (purified by heating at 400 °C for 4 h). Hydrocarbons were extracted with 15 mL of acetone:hexane 1:1 (v:v) in an ultrasonic bath (400 W at 30–40 °C for 30 min). Each sample extraction was repeated three times, and supernatants were combined in one. This hydrocarbon suspension was purified on a 100 % activated silica gel column (60–120 mesh), in order to retain polar extracted compounds from organic wastes (British Columbia MELP Canada 2004); 5 μL aliquot of purified extract was splitless injected (250 °C) into the Perkin-Elmer *Clarus 500* GC, equipped with a PE-5HT column (30 m × 0.25 mm × 0.10 μm) and a flame ionization detector (FID). Helium was used as the carrier gas at a flow of 2 ml/min. The GC column temperature program was 4 min at 50 °C, 4 °C/min up to 150 °C, 10 °C/min up to 280 °C, and hold for 13 min. Stock solutions were used as external standards for the identification of 18 n-alkanes (NJEPH Aliphatics Frac. Check Mix, Restek, Bellefonte, PA, USA) and the 16 USEPA-listed PAHs (Calibration Mix #5, Restek, Bellefonte, PA, USA) (Table 2).

Table 2 Identified and quantified n-alkanes and PAHs

n-alkanes	
<C10	n-nonane
C10–C21	n-decane; n-dodecane; n-tetradecane; n-hexadecane; n-octadecane; n-eicosane; n-heneicosane
C22–C35	n-docosane; n-tetracosane; n-hexacosane; n-octacosane; n-triacontane; n-dotriacontane; n-tetratriacontane
C36–C40	n-hexatriacontane; n-octatriacontane; n-tetracontane
PAHs	
2–3 rings	naphtalene; acenaphthylene; acenaphthene; fluorene; phenanthrene; anthracene; fluoranthrene
4–6 rings	pyrene; benzo(a)anthracene; crysene; benzo(b)fluoranthene; benzo(k)fluoranthene; benzo(a)pyrene; indeno(1,2,3-cd)pyrene; dibenz(a,h)anthracene; benzo(g,h,i)perylene

Dibenzothiophene 98 % and n-hexadecane 99 % (Sigma-Aldrich, St. Louis, MO, USA) were employed as internal standards for compounds quantification once identified. In each sample chromatogram, the concentration of extracted total hydrocarbon (TH) was quantified by the area under the curve between retention times corresponding to n-nonane (C9) and n-tetracontane (C40).

Statistical analysis

Longitudinal datasets were modeled using generalized linear model (GLM). Days, OW percentage (i.e., treatments) and time–OW % interaction were specified as fixed effects. Main effects means differences were analyzed by LSD Fisher test, with a confidence limit ≥95 %. For non-longitudinal data, one-way ANOVA was used to determine significant differences ($p < 0.05$) between treatments and post hoc Tukey tests ($\alpha = 0.05$) were applied for means separation. All analyses were performed with INFOSTAT v. 2015 software (Di Rienzo et al. 2015).

Results and discussion

Raw materials and composting mixtures characterization

Chemical characteristics and hydrocarbons content

Raw materials characteristics are detailed in Table 3. Both OW and OBC showed high EC values, considering that EC was measured in a tenfold dilution. Organic wastes shredding may have contributed to the release of soluble salts. In cooked meals, added salt could also account for high EC values that were measured in OW. Organic wastes TH, total alkanes and total PAH concentrations were around 15–20 % of those determined in OBC, whereas woodchips hydrocarbon concentrations were negligible. Alkanes <10 carbons (potentially volatile) were not detected in any of the three primary materials. Alkanes of high molecular weight (C36-C40) were not detected in

Table 3 Drilling cuttings, organic wastes and bulking agent characterization

	OBCs	OW	Woodchips
Water content (%)	18	79	54
pH (H₂O) 1:10	8.5	8.9	6.0
EC 1:10 (dS m⁻¹)	5.0	7.1	0.1
TOC (g kg⁻¹)	72	393	485
TN (g kg⁻¹)	0.4	31.2	4.2
Extractable P (ug g⁻¹)	5	802	64
C/N	180	13	116
Alk < C10 (mg kg⁻¹)	ndᵃ	nd	nd
Alk C10–C21 (mg kg⁻¹)	4577	461	40
Alk C22–C35 (mg kg⁻¹)	2158	182	157
Alk C36–C40 (mg kg⁻¹)	nd	419	nd
Total alkanes (mg kg⁻¹)	6735	1062	197
PAHs 2–3 rings (mg kg⁻¹)	439	33	18
PAHs 4–6 rings (mg kg⁻¹)	188	86	1.3
Total PAHs (mg kg⁻¹)	627	119	19
TH (mg kg⁻¹)	49,372	10,615	2799

Values are expressed on a dry weight basis

EC electrical conductivity, *TOC* total organic carbon, *TN* Organic N + N-NH₄; *TH* total hydrocarbons

ᵃ nd = no detectable

OBC and woodchips. However, a prominent signal was observed in OW chromatogram, which matched to n-hexatriacontane (36 carbons) standard retention time (Fig. 1). Probably, these compounds are large biomolecules (i.e., biopolymers) from vegetables and grass clippings that were not retained during the extract cleanup process. This signal was also observed in 33 and 75 % OW samples.

Initial composting mixture characteristics are presented in Table 4. EC values were around 3.5 dS m⁻¹ in all composting mixtures. Thus, organic waste application had no positive effect on electrical conductivity values. In 0 and 100 % OW initial mixtures, average EC was quite different from OBC and OW alone. This could be attributed to a sample dilution effect owed to woodchips that were not retained during sample sieving. The C/N (TOC/
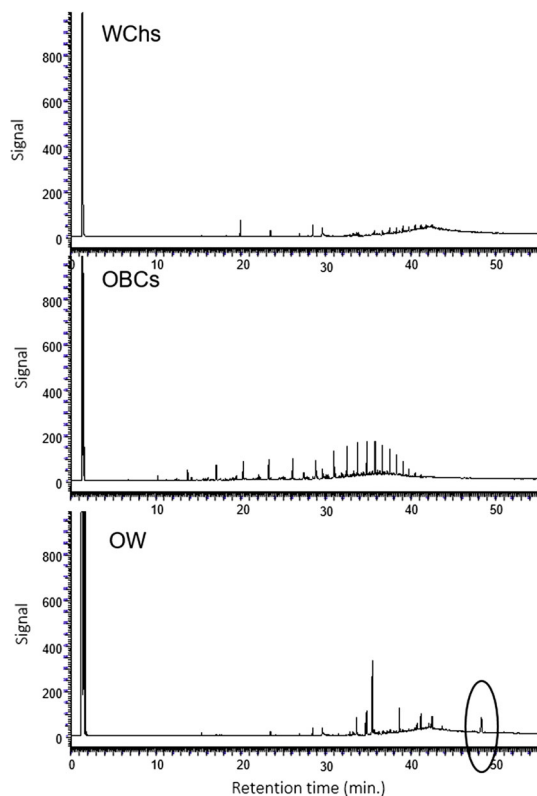
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Fig. 1 Woodchips (WChs), drilling cutting (OBCs) and organic waste (OW) chromatograms (GC-FID). n-hexatriacontane signal is circled in OW chromatogram

TN) ratio of 75 % OW was the closest to the recommended range (25–30) for composting (Rynk et al. 1992). High C/N ratios in 0 and 33 % OW suggest a nitrogen deficit in these mixtures, since a C/N ratio > 40 could imply an important reduction in the biological activity because of the lack of N for protein synthesis (Márquez et al. 2008).

Organic waste incorporation promoted a pollutant dilution effect in 75 % OW initial composting mixture, even though OW extractable compounds did contribute to TH values. In 75 % OW, TH concentration was about one half of that in 0 % OW, while initial TH value in 33 % OW was not significantly different from that in 0 % OW. In some cases, dense toxic matrices can inhibit microbial growth, and thus, dilution should be carried out prior to biological treatment. Besides other important benefits, the application of organic wastes to highly contaminated materials produces a pollutant "dilution effect" that reduce initial matrix toxicity (Vallini et al. 2002; Joo et al. 2007).

On the other hand, it is also noticeable that hydrocarbons measured in the initial composting mixtures are not proportional to the sum of the hydrocarbons contribution of each mixture component alone (OW or OBC), in a dry weight basis. This difference, of about 40 %, could be attributed to a sample dilution effect owed to woodchips

not retained during sample sieving, as it was indicated before for initial EC values.

Reasonably, C10–C35 alkanes concentration was greater in the treatment with the higher OBC proportion (0 % OW). On the contrary, the concentration of C36–C40 alkanes was about four times higher in 75 % OW, ratifying the contribution of such compounds by the organic wastes. Light aromatic fraction (2–3 rings) was also reasonably higher in 0 % OW. However, there were no differences in the initial concentrations of these compounds between 33 and 75 % OW, and heavier PAH (4–6 rings) concentrations were the same for all systems. This shows the contribution of mostly high molecular weight PAHs by the organic wastes.

It can be seen that a comprehensive characterization of the substrates to be composted provides valuable and necessary information in order to determine optimal environmental conditions for successful degrading microbial activity. In addition, organic wastes hydrocarbon-like compounds contribution should be considered in composting bioremediation processes, mainly when general parameters like "total hydrocarbons" or TPH (total petroleum hydrocarbons) are used to monitor biodegradation.

Enumeration of heterotrophic and hydrocarbon-degrading bacteria

In 33 and 75 % OW treatments, the initial counts of heterotrophic, total hydrocarbon-degrading and aliphatic-degrading bacteria were approximately threefold higher than 0 % OW bacteria counts (Table 5). These values show that biodiversity and abundance of microorganisms present in organic wastes ensure the contribution of populations with the metabolic potential to break down the target contaminant. On the other hand, PAH degraders showed low counts ($<10^3$ MPN g^{-1}) in all initial composting mixtures. This confirms the recalcitrance of such compounds and the higher metabolic specificity required for their biodegradation (Antizar-Ladislao et al. 2004). Nevertheless, it should be considered that in such complex samples, culturable bacteria enumeration is limited. In fact, it is estimated that less than 1 % of environmental isolates are culturable (Chikere et al. 2011), though these techniques only allow a comparative approach.

The composting process

Temperature and moisture content monitoring

During the experiment, none of the reactors reached typical composting thermophilic temperatures (>45 °C), as it would be expected in the treatments with the highest

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Table 4 Composting mixtures initial characterization

	0 % OW			33 % OW			75 % OW			100 % OW		
pH (H_2O) 1:10	8.3	(0.1)	a	8.0	(0.2)	ab	7.0	(0.2)	c	7.6	(0.3)	bc
EC 1:10 (dS m^{-1})	3.6	(0.1)	a	3.4	(0.5)	a	3.6	(0.3)	a	3.5	(0.2)	a
TOC (g kg^{-1})	65	(4)	c	69	(6)	c	92	(15)	b	320	(10)	a
TN (g kg^{-1})	0.3	(0.1)	c	0.9	(0.3)	c	3.8	(0.6)	b	31	(5.9)	a
Ext. P (ug g^{-1})	8	(1)	c	18	(3)	bc	76	(21)	b	804	(176)	a
C/N	208	(6)	a	81	(21)	b	24	(2)	c	11	(2)	c
N/P	39	(5)	a	48	(11)	a	52	(10)	a	40	(15)	a
Alk < C10 (mg kg^{-1})	nd^a			nd			nd			nm^b		
Alk C10–C21 (mg kg^{-1})	2897	(888)	a	2264	(280)	ab	1329	(327)	b	nm		
Alk C22–C35 (mg kg^{-1})	1156	(67)	a	875	(93)	b	696	(56)	b	nm		
Alk C36–C40 (mg kg^{-1})	39	(4)	b	42	(12)	ab	146	(44)	a	nm		
Total alkanes (mg kg^{-1})	4092	(956)	a	3181	(453)	ab	2171	(298)	b	nm		
PAHs 2–3 rings (mg kg^{-1})	283	(33)	a	191	(45)	b	195	(51)	b	nm		
PAHs 4–6 rings (mg kg^{-1})	97	(25)	a	118	(45)	a	130	(19)	a	nm		
Total PAHs (mg kg^{-1})	380	(9)	a	309	(37)	a	325	(62)	a	nm		
TH (mg kg^{-1})	29,186	(2827)	a	21,840	(3733)	ab	17,165	(2794)	b	nm		

Values are expressed on a dry weight basis and are the means of three replicates per treatment. SD is indicated in parenthesis

Different letters indicate significant differences ($p < 0.05$) between treatments

[a] nd = not detectable/[b]nm: not measured

Table 5 Heterotrophic and hydrocarbon-degrading bacteria counts in initial composting mixtures

	0 % OW	33 % OW	75 % OW	100 % OW
Heterotrophs (UFC g^{-1})	nc^a	3.6×10^8	3.0×10^9	3.8×10^{10}
TH degraders (MPN g^{-1})	3.6×10^5	1.3×10^8	9.3×10^8	1.7×10^{10}
Alk degraders (MPN g^{-1})	9.7×10^5	9.8×10^7	5.2×10^8	4.6×10^9
PAH degraders (MPN g^{-1})	<1500	<1500	<1500	<1500

All values are expressed on dry weight basis

[a] no count: number of colonies < 30

proportion of organic wastes (i.e., in 75 and 100 % OW) (Fig. 2). All reactors temperature fluctuated between 15 and 30 °C during the first 65 days and then started a gradual temperature decrease, reaching average values of 10–15 °C at the end of the experiment. As the same temperature pattern was observed in all treatments, including 100 % OW, it could be supposed that the amount of composting mass could not generate and retain enough heat to reach thermophilic temperatures. Consequently, the effects on hydrocarbons biodegradation of typical high temperatures of the composting process could not be assessed in this study.

Nevertheless, in the context of composting as a bioremediation strategy, high temperatures (>45 °C) are not always desired as they are in traditional composting for meeting regulatory requirements in pathogen control (Antizar-Ladislao et al. 2007). In fact, several authors report higher hydrocarbon degradation rates, particularly of PAHs,

at mesophilic (25–45 °C) than at thermophilic temperatures. This would be associated with the variety of microorganisms, and the proper functioning of the enzymatic systems related to the degradation of target compounds, within mesophilic temperature range (Van Gestel et al. 2003; Antizar-Ladislao et al. 2004, 2007; Sayara et al. 2010).

The water incorporated along with the organic wastes can regulate moisture for proper biological activity, reducing or even avoiding the need for irrigation, when appropriate wastes proportions are applied. In this study, no irrigation was performed and reactors moisture content was monitored during the entire experiment (Fig. 3), in order to evaluate this effect. In 75 % OW moisture content remained within the recommended range for composting 50–70 % (Márquez et al. 2008), and in 0 and 33 % OW, moisture content was below 40 % during the entire process. Therefore, the biological activity in 0 and 33 % OW treatments might have resulted limited.

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Fig. 2 Temperature profiles during composting. Data series are the mean of temperatures recorded in each reactor per day. Values are the average of three replicates per treatment
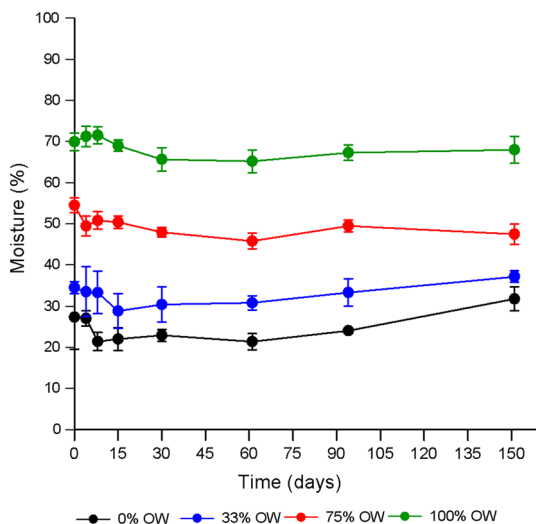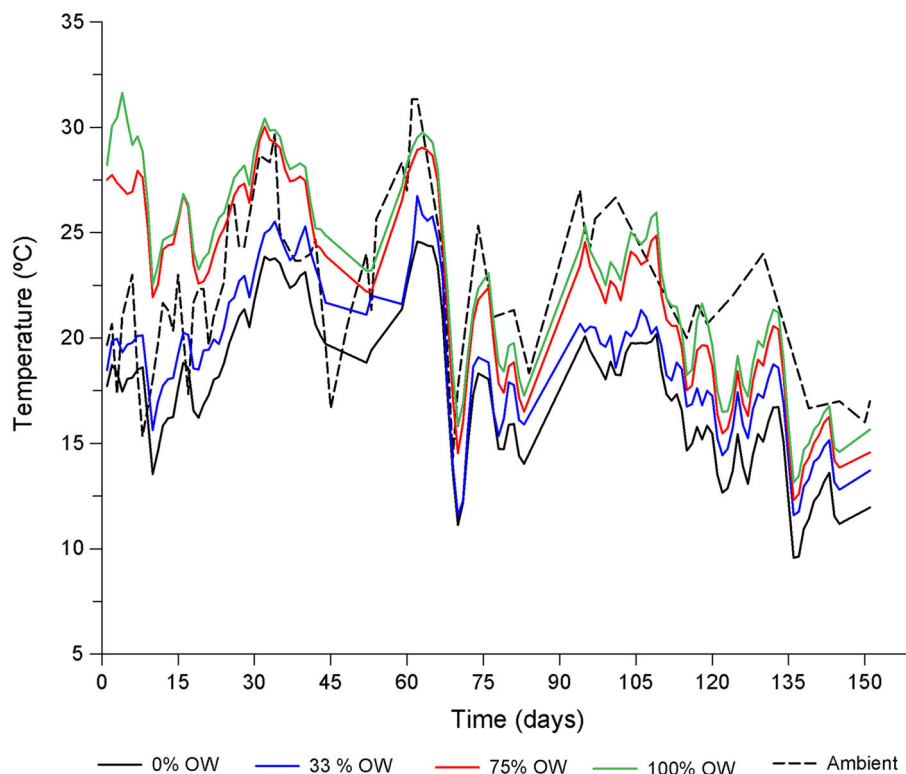

Fig. 3 Moisture profiles during composting process. Values are the average of three replicates per treatment and *bars* indicate standard deviation

pH and electrical conductivity

In 75 % OW, pH values remained within 7.0–7.5 throughout the experimental period and were significantly different ($p < 0.05$) from pH values in 0 and 33 % OW, which remained between 8.0 and 8.5 (Fig. 4a). Nevertheless, these pH values are not considered restrictive since,

due to the buffering capacity of the process and the broad spectrum of the microorganisms involved, composting may work over a wide pH range (5.5–9) (Rynk et al. 1992).

After 151 days of composting, EC values started at 3.5 dS m^{-1} in all treatments with drilling cuttings, as was stated previously, and ended around 2.5 dS m^{-1}, with no significant differences between treatments ($p > 0.05$) (Fig. 4b). Differently, in 100 % OW final average EC value was significantly lower ($p < 0.05$), reaching approximately 1.8 dS m^{-1}.

During composting, salts loss is mainly owed to the leaching of the water contained in primary materials or owed to irrigation (Laos et al. 2002). In this study, leachates were collected in large amounts in 100 % OW, but practically no leachates were accumulated in reactors with OBC. Probably, OBC clayey nature could have increased water absorption, preventing leaching and therefore the washing out of soluble salts.

Hydrocarbons removal

Hydrocarbons degradation percentage

In 75 % OW treatment, the highest degradation percentages of TH (≈ 82 %), total alkanes (≈ 96 %) and PAHs (≈ 93 %) were reached after 151 days of composting (Fig. 5a). Between 0 and 33 % OW treatments, there were

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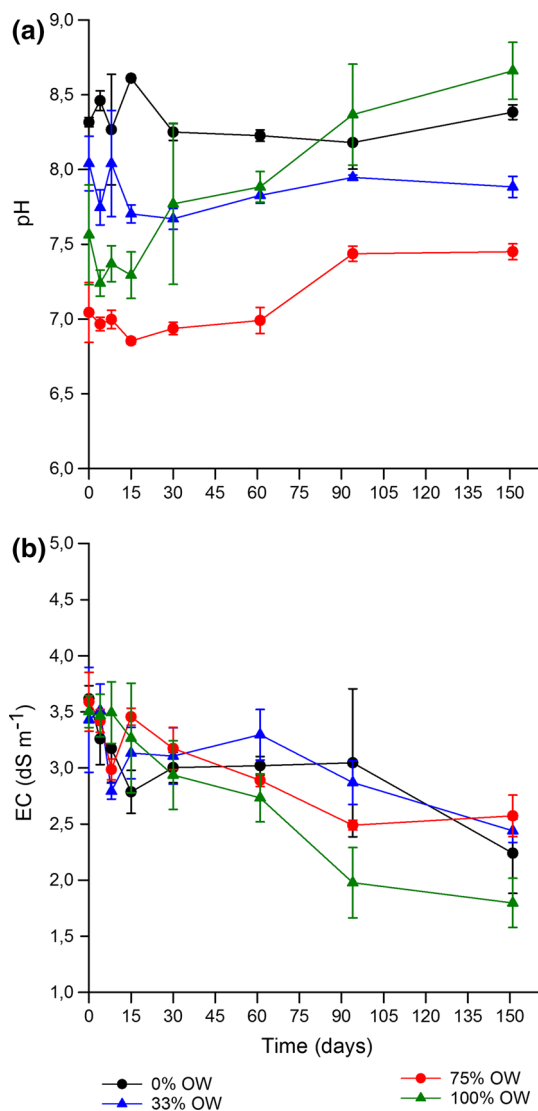Int. J. Environ. Sci. Technol. (2016) 13:2227–2238

Fig. 4 Evolution of **a** pH and **b** electrical conductivity. Values are the average of three replicates per treatment and *bars* indicate standard deviation

Fig. 5 Hydrocarbons degradation percentage per treatment: **a** total hydrocarbons, total alkanes and total PAHs; **b** alkanes and PAHs grouped by molecular size. Values are the average of three replicates per treatment, and *bars* indicate standard deviation. *Different letters* indicate significant differences ($p < 0.05$) between treatments

no significant differences in hydrocarbon degradation percentages. Both treatments reached 40–50 % of TH and PAHs degradation and 55–70 % removal of alkanes. The tendency was the same for the alkanes and aromatics grouped by molecular size (see Table 2), except for the C36–C40 alkanes removal percentages, which showed a different tendency (Fig. 5b). Degradation of these compounds reached 80–100 % in 0 and 33 % OW. This may be attributable to low initial concentrations of this aliphatic fraction in these treatments (see Table 4), since this fraction derived mainly from organic wastes.

Because of different contaminated matrices studied and organic wastes applied, a comparative analysis of hydrocarbons biodegradation efficiency with other composting bioremediation studies is difficult. Nevertheless, the results
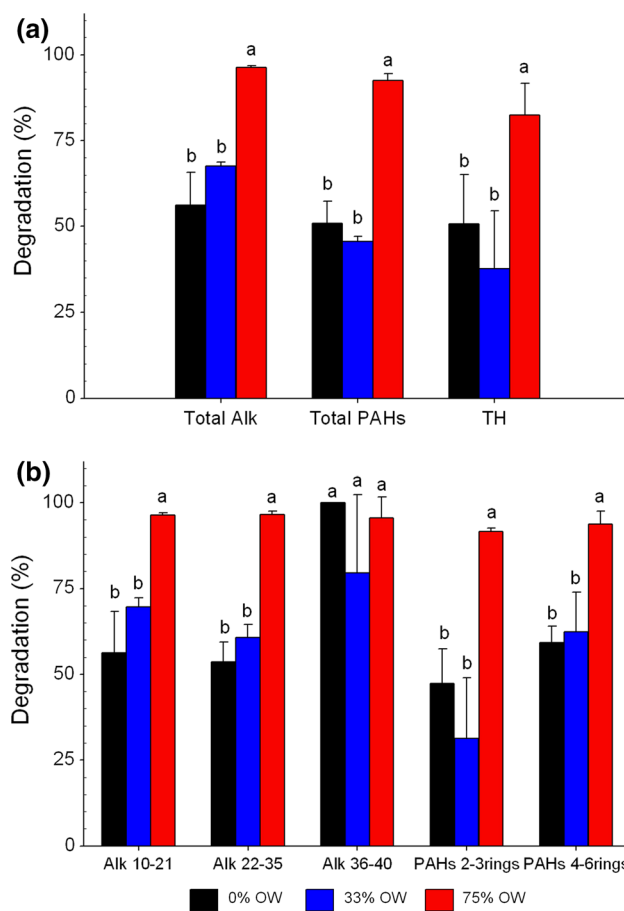
obtained in this work support other authors reports, in which organic waste small proportions, such as 33 % v/v (equivalent to 1:0.1 OBC:OW, in a dry weight basis), did not improve biodegradation (Namkoong et al. 2002; Antizar-Ladislao et al. 2005; Joo et al. 2007).

Finally, it should be made clear that, since several authors reported that hydrocarbon losses due to volatilization were not significant with respect to biological degradation (2–5 % of the initial concentration) (Namkoong et al. 2002; Hesnawi and McCartney 2006; Sayara et al. 2010), it was not considered necessary to measure abiotic hydrocarbon losses, in order to assess the actual composting impacting factors in drilling cuttings hydrocarbons removal efficiency.

Hydrocarbons degradation rates

Total hydrocarbons, total alkanes and total PAHs degradation were modeled using a three-parameter logistic

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Table 6 Model parameters of total hydrocarbons (TH), total alkanes and total PAHs biodegradation

	Total alkanes			Total PAHs			TH		
	b (mg kg^{-1} day^{-1})	$t_{1/2}$ (days)	r	b (mg kg^{-1} day^{-1})	$t_{1/2}$ (days)	r	b (mg kg^{-1} day^{-1})	$t_{1/2}$ (days)	r
0 % OW	5.8 ± 0.7	144 ± 3	0.9907	na[a]	na	na	6 ± 1	148 ± 5	0.9723
33 % OW	5 ± 1	123 ± 9	0.9407	3.6 ± 0.5	107 ± 4	0.9857	4 ± 2	143 ± 15	0.8819
75 % OW	1.0 ± 0.3	16 ± 6	0.9768	1.0 ± 0.3	25 ± 7	0.9584	13 ± 7	133 ± 9	0.9931

b slope parameter, $t_{1/2}$: hydrocarbons half-life, r correlation coefficient

[a] PAHs concentration could not be adjusted to the model used

function. The model is described by the following equation $C = C_0/1 + (t/t_{1/2})^b$, where C is TH, alkanes or PAHs concentration (mg kg^{-1} dw); C_0 is the hydrocarbons initial concentration; t is time (days); $t_{1/2}$ is hydrocarbons half-life time (days); and b is the slope parameter (mg kg^{-1} day^{-1}) (Ibarrolaza et al. 2011).

The adjustment was obtained by nonlinear regression using Sigma Plot V10, Systat Software Inc. Table 6 details model parameters for each treatment. The differentiation of the estimated degradation model equation allowed approximating hydrocarbons degradation rates (mg kg^{-1} day^{-1}).

Pollutant half-life is essentially related to the existence and length of a lag phase in pollutant concentration decay. Alkanes half-life was about 10 times lower in 75 % OW than in 0 % OW and in 33 % OW. PAHs half-life in 75 % OW was about one-fourth of that in 33 % OW. Unfortunately, due to broad intrinsic variability, PAHs data of 0 % OW could not be adjusted to the model used.

The lag phase, which shows the microbial adaptation time, is an interesting biodegradation parameter, and it is suggested as a good indicator of a microbial community catabolic potential (Couling et al. 2010). In 75 % OW, there was not a lag phase, and thus, alkanes and PAHs biodegradation started immediately. On the contrary, in 0 and 33 % OW both alkanes and PAH concentrations started to decay after 60 and 90 days of composting, respectively (Fig. 6a, b).

Consistently, alkanes and PAHs degradation rates showed that reduction in these compounds was faster within the first 15 days in 75 % OW (Fig. 6d, e) and that a lag phase did not occur. However, alkanes degradation was about ten times faster than PAHs degradation in this treatment, as it would be expected. After this period, 75 % OW degradation rate declines, probably because of the run out of substrate and nutrients already consumed in the first phase of high biological activity, like usually occurs in traditional composting systems.

In 0 and 33 % OW treatments, alkanes biodegradation rate increased only after 60 days of composting, which confirms the time needed for microbial adaptation. In 33 % OW, also alkanes degradation was around ten times faster

than PAHs degradation. Even after overcoming the lag phase, 0 and 33 % OW biodegradation rates were not as high as in 75 % OW. This probably responds to the lack of adequate environmental conditions for the stimulation of biological activity, such as nutrient and water content, in 0 and 33 % OW, as was stated in previous Sects. (3.1.1 and 3.2.1).

Even though hydrocarbons biodegradation efficiency depends on many factors, the evidence shows that the one of the main principles controlling biodegradation degree is molecular configuration. Biodegradability sequence is recognized near to: n-alkanes > branched alkanes > n-alkyl low molecular weight aromatics > monoaromatics > cyclic alkanes > polynuclear aromatics (Chikere et al. 2011). These assumptions are confirmed by the differences observed between alkanes and PAHs biodegradation rates within each treatment.

TH degradation curves (Fig. 6c, f) show a different situation. TH decay starts after about 60–90 days of composting for all treatments. The extended lag phase observed for TH degradation in 75 % OW could be attributed to the contribution of extractable recalcitrant compounds, such as lignin, from lignocellulosic organic wastes (see Sect. 3.1.1). Lignin is difficult to degrade and is chemically bonded with hemicellulose. In addition, this complex enwraps cellulose, slowing down these carbohydrates degradation (Huang et al. 2010). Despite the fact that TH half-life is similar for all treatments, degradation rate was also relatively higher in 75 % OW than in 0 and 33 % OW.

Conclusion

In heavily contaminated oil-based drilling cuttings, the effect of applying appropriate proportions of organic wastes has been relevant for hydrocarbons removal efficiency. Applying a 75 % of organic wastes in a volume basis (equivalent to a proportion of 1:0.4 OBC:OW in a dry weight basis) was highly effective in hydrocarbons removal efficiency, including recalcitrant compounds, such as heavy PAHs, despite salts concentration. In contrast, the application of 33 % of organic wastes by volume (1:0.1

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Fig. 6 Modeled evolution of hydrocarbons concentration and degradation rate: **a**, **d** total alkanes, **b**, **e** total PAHs and **c**, **f** total hydrocarbons. Values are the average of three replicates per treatment. *Bars* indicate standard deviation in concentration versus time graphics. Due to broad intrinsic variability, PAHs data of 0 % OW could not be adjusted to the model used
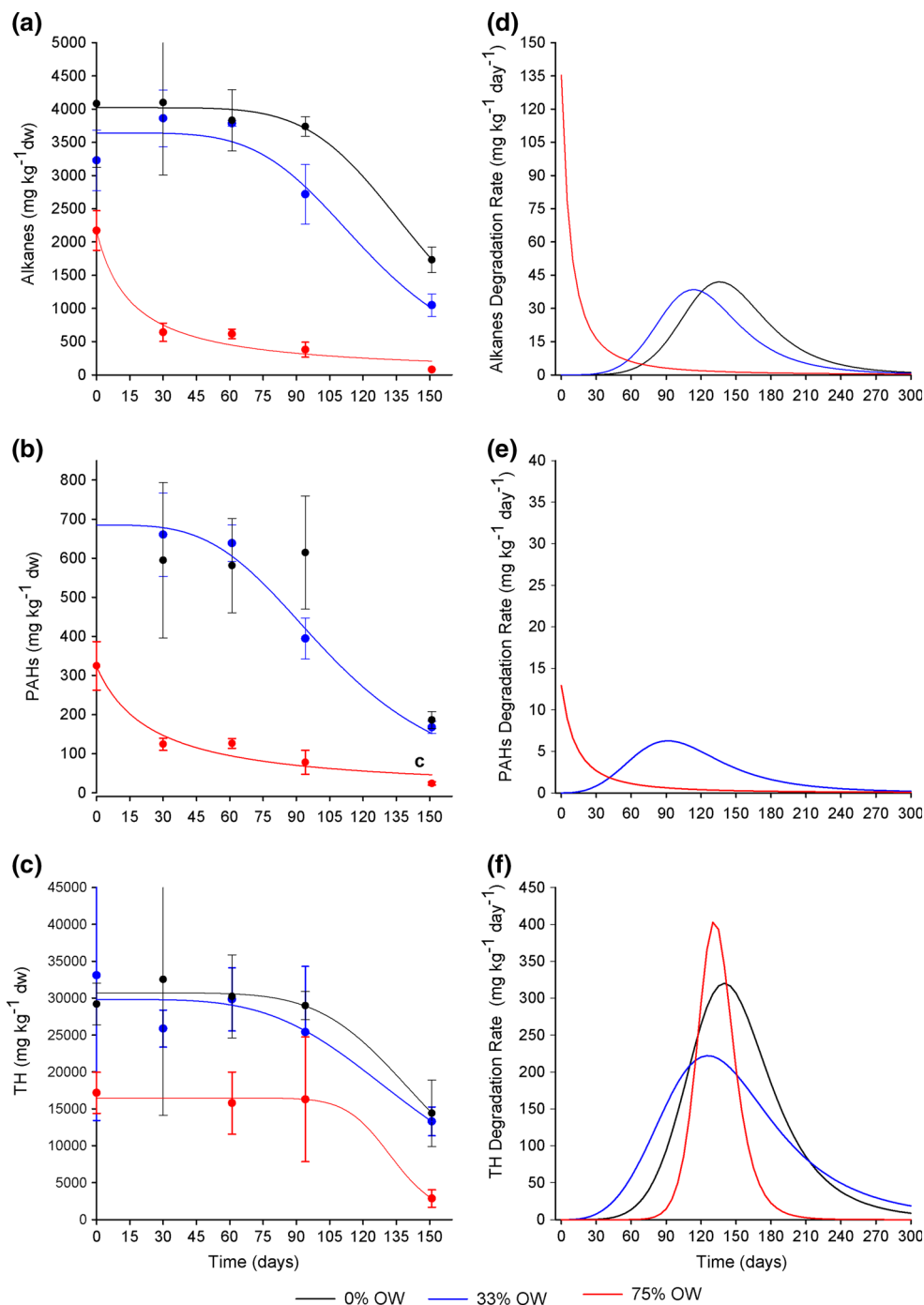
OBC:OW, dry weight basis) was not more effective for hydrocarbon removal than not applying organic wastes. Microorganisms incorporated along with the organic waste, adequate nutrients proportions, suitable water content and a lower initial concentration of hydrocarbons probably supported a high biological activity and a consequent high biodegradation rate in 75 % OW.

Similar degradation percentages were observed for light and heavy alkanes and aromatics within each treatment.

This shows that experimental time (151 days) was sufficient in order to detect the potential removal of both hydrocarbon types, according to each treatment particular environmental conditions, despite the different biodegradation rates observed for alkanes and PAHs. Given this difference, shorter experimental times probably would have resulted in measuring different degradation percentages between the more and the less recalcitrant compounds. This is an important aspect to take into consideration, since

treatment time consumption is a major factor affecting the choice of biological methods as a remediation alternative, and widely influences associated costs.

We consider that composting is a promising strategy for the treatment of heavily contaminated oil-based drilling cuttings. Future efforts should be associated with the assessment of using composted material (nutrients rich) for soil regeneration and revegetation of degraded areas, which are very common in oilfields, as an alternative for proper final disposal.

References

Antizar-Ladislao B, Lopez Real JM, Beck AJ (2004) Bioremediation of Polycyclic Aromatic Hydrocarbon (PAH)-Contaminated waste using composting approaches. Crit Rev Env Sci Tec 34:249–289

Antizar-Ladislao B, Lopez-Real J, Beck AJ (2005) In-vessel composting-bioremediation of aged coal tar soil: effect of temperature and soil/green waste amendment ratio. Environ Int 31:173–178

Antizar-Ladislao B, Beck AJ, Spanova K, Lopez-Real J, Rusell NJ (2007) The influence of different temperature programmes on the bioremediation of polycyclic aromatic hydrocarbons (PAHs) in a coal-tar contaminated soil by in-vessel composting. J Hazard Mater 144:340–347

Arce-Ortega JM, Rojas-Avelizapa NG, Rodríguez-Vázquez R (2004) Identification of recalcitrant hydrocarbons present in a drilling waste-polluted soil. J Environ Sci Heal A 39:1535–1545

Ayotamuno JM, Okparanma RN, Araka PP (2009) Bioaugmentation and composting of oil-field drill-cuttings containing polycyclic aromatic hydrocarbons (PAHs). J Food Agric Environ 7:658–664

Ball AS, Stewart RJ, Schliephake K (2012) A review of the current options for the treatment and safe disposal of drill cuttings. Waste Manag Research 30:457–473

British Columbia Ministry of Environment, Lands and Parks (MELP) (2004). CSR-Analytical Method 10, Silica Gel Clean Up of EPH, Version 1.0, Canada, 15 pp

Chen M, Xu P, Zeng G, Yang C, Huang D, Zhang J (2015) Bioremediation of soils contaminated with polycyclic aromatic hydrocarbons, petroleum, pesticides, chlorophenols and heavy metals by composting: applications, microbes and future research needs. Biotechnol Adv 33:745–755

Chikere CB, Okpokwasili GC, Chikere BO (2011) Monitoring of microbial hydrocarbon remediation in the soil. 3 Biotech 1:117–138

Couling NR, Towell MG, Semple KT (2010) The simultaneous effects of PAH concentration, contaminant mixture and repeated application on the development of catabolic activity in soil. Environ Pollut 158:3411–3420

Di Rienzo JA, Casanoves F, Balzarini MG, González L, Tablada M, Robledo CW (2015). InfoStat v. 2015. InfoStat Group, FCA, Universidad Nacional de Córdoba, Argentina. URL: http://www.infostat.com.ar

Elshorbagy W, Alkamali A (2005) Solid wastes generation from oil and gas industries in United Arab Emirates. J Haz Mat B120:89–99

Grace Liu P-W, Chang TC, Chen C-H, Wang M-Z, Hsu H-W (2013) Effects of soil organic matter and bacterial community shift on bioremediation of diesel-contaminated soil. Int Biodeter Biodegr 85:661–670

Hesnawi RM, McCartney DM (2006) Impact of compost amendments and operating temperature on diesel fuel bioremediation. J Environ Eng Sci 5:37–45

Huang DL, Zeng G-M, Feng C-L, Hu S, Lai C, Zhao M-H, Su F-F, Tang L, Liu H-L (2010) Changes in microbial population structure related to lignin degradation during lignocellulosic waste composting. Bioresour Technol 101:4062–4067

Huesemann MH, Hausmann TS, Fortman TJ (2004) Does bioavailability limit biodegradation? A comparison of hydrocarbon biodegradation and desorption rates in aged soils. Biodegradation 15:261–274

Ibarrolaza A, Coppotelli BM, Del Panno MT, Donati ER, Morelli IS (2011) Application of the knowledge-based approach to strain selection for a bioaugmentation process of phenanthrene and Cr(VI)-contaminated soil. J Appl Microbiol 111:26–35

Joo H-S, Shoda M, Phae C-G (2007) Degradation of diesel oil in soil using food waste composting process. Biodegradation 18:597–605

Laos F, Mazzarino MJ, Walter I, Roselli L, Satti P, Moyano S (2002) Composting of fish offal and biosolids in northwestern Patagonia. Bioresource Technol 81:179–186

Laos F, Mazzarino MJ, Roselli L, Satti P (2012) Petroleum hydrocarbons-contaminated soils remediation. In: Mazzarino MJ, Satti P (eds) Composting in Argentina: production, quality and use experiences. Orientación Gráfica Editora, Buenos Aires, pp 257–270 **(In Spanish)**

Márquez PB, Díaz Blanco MJ, Cabrera Capitán F (2008). Factors affecting the composting process. In: Moreno Casco J, Moral Herrero R (eds) Composting. Ediciones Mundi-Prensa, Madrid, España, pp 93–109. (In Spanish)

Morelli IS, Del Panno MT, De Antoni GL, Painceira MT (2005) Laboratory study on the bioremediation of petrochemical sludge-contaminated soil. Int Biodeter Biodegr 55:271–278

Moretto LM, Silvestri S, Ugo P, Zorzi G, Abbondanzi F, Baiocchi C, Iacondini A (2005) Polycyclic aromatic hydrocarbons degradation by composting in a soot-contaminated alkaline soil. J Haz Mat B126:141–148

Namkoong W, Young E-Y, Park J-S, Choi J-Y (2002) Bioremediation of diesel-contaminated soil with composting. Environ Pollut 119:23–31

Onwukwe SI, Nwakaudu MS (2012) Drilling wastes generation and management approach. Int J Environ Sci Dev 3:252–257

Reasoner D, Geldreich E (1985) A new medium for the enumeration and subculture of bacteria from potable water. Appl Environ Microb 49:1–7

Rojas-Avelizapa N, Roldán-Castillo T, Zegarra-Martínez H, Muñoz-Colunga A, Fernández-Linares L (2007) A field trial for an ex situ bioremediation of a drilling mud-polluted site. Chemosphere 66:1595–1600

Rynk R, Van de Kamp M, Willson GB, Singley ME, Richard TL, Kolega JJ, Gouin FR, Laliberty Jr. L, Kay D, Murphy DW, Hoitink HA, Brinton WF (1992). On-farm composting handbook. Natural resources, agriculture, and engineering service. NRAES-54, Cooperative Extension, Ithaca, NY, USA, 186 p

Saretsky M, Wilson M, Wyse S (2002). Bioremediation of drill cuttings in an arid climate. 9th Annual International Petroleum Environ. Conference (IPEC) Proceedings, Albuquerque, New

2238

Int. J. Environ. Sci. Technol. (2016) 13:2227–2238

México, USA, 8 p. http://ipec.utulsa.edu/Conf2002/saretsky_3.pdf. last access Sept 2015

Savage GM, Díaz LF (2007) Bioremediation. In: Díaz LF, De Bertoldi M, Bidlingmaier W, Stentiford E (eds) Compost science and technology, 10 ed., Waste Management Series 8, Elsevier Science, Amsterdam, pp 159–175

Sayara T, Sarrá M, Sánchez A (2010) Effects of compost stability and contaminant concentration on the bioremediation of PAHs-contaminated soil through composting. J Hazard Mater 179:999–1006

Sparks DL, Page AL, Helmke PA, Loeppert RH, Soltanpour PN, Tabatabai MA, Johnston CT, Sumner ME (1996) Methods of soil analysis, part 3, chemical methods, SSSA bookSeries No 5, SSSA, ASA, Madison, USA, 1390 p

United States Environmental Protection Agency (US EPA) (2007). SW-846, Method 3550c, Ultrasonic extraction, Rev. 3, USA, 17 p

Vallini G, Di Gregorio S, Pera A, Cunha Queda ACF (2002) Exploitation of composting management for either reclamation of organic wastes or solid-phase treatment of contaminated environmental matrices. Environ Rev 10:195–207

Van Gestel K, Mergaert J, Swings J, Coosemans J, Ryckeboer J (2003) Bioremediation of diesel oil-contaminated soil by composting with biowaste. Environ Pollut 125:361–368

Wrenn BA, Venosa AD (1996) Selective enumeration of aromatic and aliphatic hydrocarbon degrading bacteria by a most probable number procedure. Can J Microbiol 42:252–258

Zhang Y, Zhu Y-G, Houot S, Qiao M, Nunan N, Garnier P (2011) Remediation of polycyclic aromatic hydrocarbon (PAH) contaminated soil through composting with fresh organic wastes. Environ Sci Pollut Res 18:1574–1584