

Oil refinery sludge and green waste simulated windrow composting

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Abstract Oil refinery sludge (ORS) was mixed with shredded green wastes (GW) at ratios of 1:1 v/v (RI) and 1:3 v/v (RII). The mixtures, of approximately volumes of 1,020 l and 990 l respectively, were introduced in metal cubic containers of 1.0 m³ volume, opened at the top and with small holes punctured in the bottom and the side. The containers were additionally insulated with a layer of rockwool (20 mm). The boxes were emptied, the mixtures were turned and water was added occasionally, in one to two weeks intervals, simulating a windrow composting system. Temperature, physiochemical characteristics, mineral oil and grease (MOG) concentration, polycyclic aromatic hydrocarbons (PAHs) concentration, carbon dioxide emission, methane emission and microorganisms presence were recorded either daily or every time the mixtures were turned, for a period of 120 days. RII recorded temperatures as high as 62°C, reaching 56°C in Day 6 and retained temperatures above 50°C for more than 40 days. RI recorded its highest temperature

of 53°C in Day 77. The reason why the two mixtures behaved so differently can be explained by: (i) extended co-digestion phenomena by the microorganisms decomposing the GW in RII, (ii) toxic effect of ORS in RI due to the far larger amounts used (840 kg in RI in comparison with the 460 kg in RII). After Day 36 temperature increased gradually in RI and MOG and PAHs reduction was first noted. At the end of the experiment MOG concentration in RI was 57.2 mg/kg dry weight (dw) (52.1% reduction) where in RII was 34.3 mg/kg dw (62.1% reduction). Emissions of methane and carbon dioxide support the concept of the toxic effect and the delay ignition of the decomposing process in RI. In total, CO₂ and CH₄ emissions from RI were recorded to be 30.8 kg and 18.5 g, respectively, where from RII 59.6 kg of CO₂ and 6.4 g of CH₄ were emitted. An effort was made to determine the effect of temperature alone (as an abiotic treating parameter) in both mixtures. It can be supported that about least 15% of the MOG and PAHs removal.

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Introduction

Petroleum storage and transportation facilities have often been a source of environmental pollution as they generate a number of hazardous wastes during the

operation. Oily refinery sludge (ORS) is produced mainly from the accumulation of waste oily material in storage tank bottoms and from the water-oil separation systems. Due to its content of harmful organic compounds, ORS has been recognized as a potentially dangerous waste product (Karr and Lysyj 1983; Yang et al. 1991; Olajire et al. 2005). Particularly, petroleum-based oil wastes consist mainly of alkanes, paraffins, cycloalkanes, and aromatic hydrocarbons (Overcash and Pal 1979; Kirchman and Ewnetu 1998). Polycyclic aromatic hydrocarbons (PAH) constitute a small but important class of aromatic hydrocarbons, which are highly persistent compounds in the environment, recalcitrant to biodegradation and highly lipophilic, while some of them cause acute carcinogenic and mutagenic toxicity (Blanchard et al. 1999) and as a result, have been listed by regulatory agencies such as U.S.E.P.A. as top priority pollutants.

One of the most popular ORS treating method, due to its low cost and the simplicity of the treatment, was landfarming. Landfarming has traditionally been the biological treatment method chosen to dispose ORS (Wilson and Jones 1993; Persson and Welander 1994), even though low efficiencies in removing most toxic pollutants were achieved (Ferrari et al. 1996). Furthermore, the large surface area required for landfarming turned research to alternative biological methods such as composting (Williams and Keehan 1992; Kirchmann and Ewnetu 1998; Marin et al. 2006). Beaudin et al. (1996) showed that composting resulted in degradation of 77% of the mineral oil and grease (MOG) of a petroleum-hydrocarbon contaminated soil in six months while landfarming degraded less than 30% of the MOG in the same period. Studies were also performed by composting hydrocarbon-contaminated soil with other materials as biowaste (Van Gestel et al. 2003), activated sludge (Juteau et al. 2003) and tree leaves (Beaudin et al. 1999). A similar number of researches examined the composting of raw ORS with pig slurry (Marin et al. 2006); peat (Bengtsson et al. 1998) and horse manure (Kirchmann and Ewnetu 1998).

Green wastes (GW) have historically been disposed in landfills (Stentiford 2001). However, last years many governments have been trying to change this practice. In the EU, garden waste has been targeted for recycling, since a high proportion of civic-amenity waste is organic and it is produced free

from contaminants relatively easily (Keeling et al. 1995).

The aim of this work is to examine systematic the composting treatment of oily waste sludge with GW in a pilot scale windrow system. The influence of mixing ratio to the reduction of oil content, PAHs concentration, microbial population and the production of greenhouse gases were examined.

Material and methods

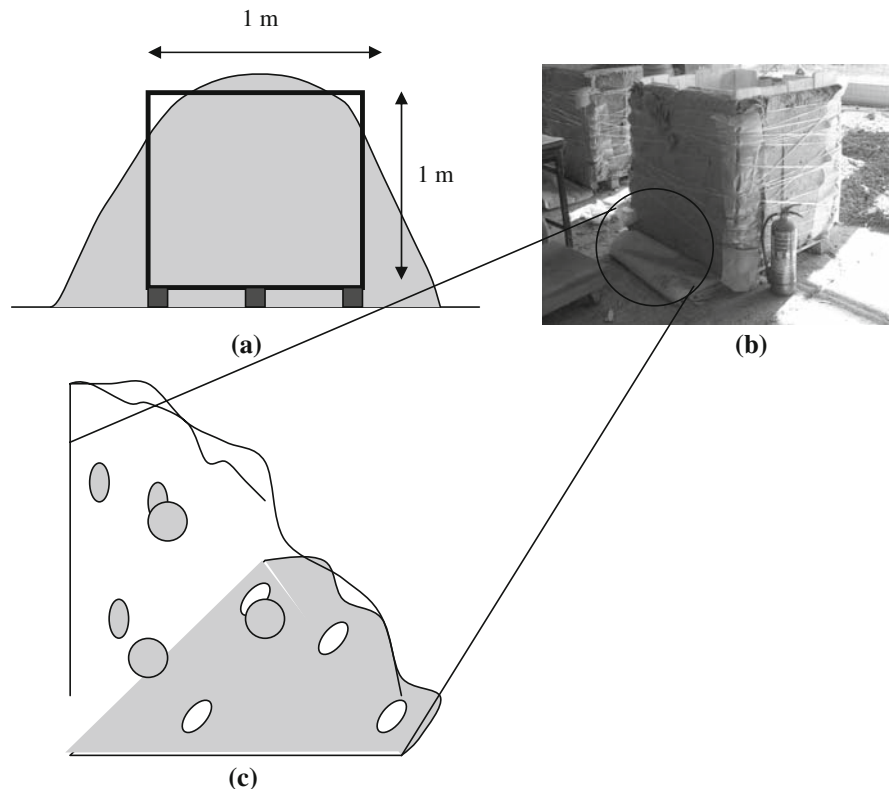
Composters

Two 1 m³ volume cubic shape (length × width × height, 1 × 1 × 1 m) metal containers were used as aerobic bioreactors, also known as composters. The boxes were completely opened at the top and small holes were punctured in the bottom and the sides. A layer of rockwool (20 mm) was used as additional insulation of the sides which however did allow the passive aeration through the holes. The boxes were introduced on the top of a small wooden structure that allowed air to enter from the bottom through the above mentioned small holes. As the mixtures inside the boxes were emptied and turned in one to two weeks intervals and water was occasionally added these systems simulated the windrow composting method. A presentation of the composters imitating the windrow composting system is provided in Fig. 1.

The mixtures

Oil refinery sludge (ORS) from the oil storage facilities in the outskirts of the city of Heraklion, in the island of Crete in Greece, was used together with shredded GW from the parks and roads of the city of Heraklion. Two mixtures were composed, one with a ratio of 1:1 v/v of ORS and GW named RI and a second with a ratio of 1:3 v/v respectively, named RII. During the synthesis of the mixtures the weights and volumes of each component added was measured and recorded. The mixtures were emptied from the composters and turned manually in 1–2 weeks intervals for a period of 120 days. In total 13 turnings took place. The initial moisture content of ORS and GW was found 34.7 and 43.1%, respectively. In order to maintain moisture levels between 50 and 60% which is identified for many investigators as suitable for

Fig. 1 Representation of the composter; (a) which parts of the windrow pile it simulates, (b) the composter, and (c) the holes in the sides and bottom



efficient composting (Liang et al. 2003; Tiquia et al. 1996; Haug 1993; Suler and Finstein 1977), water was occasionally added in the mixtures manually.

Abiotic trials

Approximately 5 l of each mixture were further treated with 2% by weight HgCl_2 in an effort to kill all the microorganisms present, as previous work on composting of oily sludge (Bengtsson et al. 1998). Each mixture was introduced in a drying oven with a digital temperature control. Each day, the temperature measured in each composter was used in each oven, achieving a very realistic temperature representation of the process. During the 120 days five samples were collected from the ovens (approximately in month intervals) and analyzed for MOG and PAHs.

MOG analysis

Oil and grease was determined by a gravimetric method. The sample was dried overnight at 60°C and

homogenized by passing through a 20 mesh sieve in a grind (Pulverisette 14, Fritsch). Exactly 10 g of homogenized sample was mixed with 10 g anhydrous sodium sulfate in a mortar. The mixture was pulverized and 10 g of them were placed in an extraction thimble. The oil and grease were extracted in a Soxhlet apparatus using petroleum ether at a rate of 12 cycles h^{-1} for 8 h. The extraction solvent was filtered through glass wool containing anhydrous sodium sulfate, placed in a pre-weighed flask and evaporated. Mineral oil and grease was calculated by weighing the dry residue after solvent evaporation.

PAHs analysis

Concentrations of individual PAHs were determined by HPLC-DAD coupled with a fluorescence detector. The HPLC system consisted of a Solvent Delivery System from Agilent 1200 Series. The chromatographic separation was done using a reversed-phase Supelcosil LC-18 analytical column of 250×4.6 mm and 5 μm particle diameter from Supelco. The mobile phase initially consisted of 70% acetonitrile

and 30% water. The analysis was run isocratically for 15 min and then programmed to 100% acetonitrile between 15 and 20 min. The mobile phase flow rate was 1.0 ml/min. The detection on the fluorescent detector was carried out at λ_{ex} : 250 nm and at λ_{em} : 370 nm from 0 to 12 min and λ_{ex} : 234 nm and at λ_{em} : 420 nm from 12 to 20 min.

Gas analysis

The closed chamber technique was used for estimating the emission rate from the composters. The specifically designed and constructed chambers were introduced in the top of the composters and were left open. The lead was introduced when sampling was conducted, in most cases in daily intervals. Four samples were collected (0, 15, 30, and 60 min) in gas tight syringes and were transferred to the gas chromatograph by sealing the needle with a butyl rubber stopper. Twenty microliters were injected into a gas chromatograph (Agilent 6890 N GC System) for analysis of methane and carbon dioxide. A thermal conductivity detector and a capillary column (GS Carbonplot, 30 m \times 0.32 mm, 3 μm) were used. The column operated isothermally at 80°C and the detector port was operated at 150°C. Helium was used as the carrier gas at a flow rate 15 ml/min.

Mean values of the gas concentration measurements obtained between consecutive turnings for both piles, were calculated and used for further statistical analysis, according to Manios et al. (2007). Two-Way ANOVA on log-transformed gas concentration data was used in order to test the significance of differences in the mean gas concentration values between the two piles. Post Hoc Tukey tests were used to further investigate these differences ($P < 0.05$).

Microbial analysis

From the sample collected during turnings 10 g of were suspended in 90 ml sterile 0.1% ringer solution and agitated for 20 min on a reciprocal shaker at ambient temperature. One milliliter of each serial dilution of the suspensions was filter and the membrane was placed in triplicate on Rose Bengal Agar and Pseudomonas Agar, for enumeration of mesophilic fungi, and *Pseudomonas* after incubating at 25°C from 3 to 5 days and 37°C for 1 day, respectively.

Other physiochemical analysis

Temperature in the composters was measured in a daily bases at the core, meaning a depth of 40–60 cm. During turning composite samples were taken randomly at different places from the composting mixtures, were manually homogenized and used for further analysis. Percentage of humidity was estimated by determining the loss of weight of the sample after drying at 105°C (APHA 1985). The pH and electrical conductivity (EC) were measured in 1/1.5 solid/liquid aqueous extract (extraction time equal to 24 h). Volatile solids and total organic carbon (TOC) were analyzed by the ignition of sample at 600°C for 16 h (FCQAO 1996). Total nitrogen (TN) was determined by the micro-Kjeldal method (APHA 1995).

Results and discussion

The raw materials and their mixtures

Table 1 provides adequate information for the characterization of the two raw materials and their derived mixtures. For GW the physiochemical parameters are within the expected margins (Manios 2004). Regarding ORS it seems that there is a significant presence of soil together with oil residues since both TOC and MOG content (as well as TN) was smaller than that presented by other authors for similar materials (Marin et al. 2006). Since the ORS was not collected directly from the tanks, but from an exposed, temporary storage area, this was expected. The question was how the 12.5% TOC and the 0.51% TN of the ORS will affect the mixtures and their composting process.

Both RI and RII presented high electrical conductivity (especially RI) which even though will not effect the process considerably; it will affect the end product (Lasaridi et al. 2006). The pH value was also acceptable and the TOC was increased to 293 and 351 g/kg approximately for RI and RII, respectively. Organic matter wise there was a substantial substrate for the decomposing microorganisms to utilize in both mixtures, even though the TN content remained low (5.4 and 6.2 g/kg, respectively). MOG concentration drops also considerably in the mixtures, to 122 and 78 mg/kg, respectively. According to Table 1;

Table 1 Characteristics of the oil refinery sludge, GW, and mixtures

Parameters	ORS	GW	RI	RII
pH	7.5	5.4	7.3	6.6
Electrical conductivity (mS/cm)	14.87	0.97	9.46	4.81
Mineral Oil and Grease (mg/kg)	203.8	7.7	122.4	77.5
Total organic carbon C (g/kg)	125.1	526.3	292.5	350.8
Total nitrogen (g/kg)	5.1	7.1	5.4	6.2
Phenanthrene (mg/kg)	26.3	n.d	14.5	13.0
Fluoranthene (mg/kg)	1.2	n.d	0.67	0.63
Pyrene (mg/kg)	14.7	n.d	7.8	7.3

Fig. 1 the probable limiting factors for successful composting of both mixtures in Day 1, were; (i) the relatively low moisture level, approximately 36 and 40% respectively for RI and RII, (ii) the very low carbon—nitrogen rate, and (iii) the unknown toxic effect of the petroleum hydrocarbons found in the two mixtures.

The C:N rate was approximately 54:1 for RI, where for RII (due to the larger presence of GW) was 56:1 where the optimum rate for composting is about 30:1 (Huang et al. 2004). Data from GW composting (shredded branches and leaves) indicate that the process can proceed with such high rates without the necessity of nitrogen addition (Manios and Stentiford 2004; Tai and He 2007). So that, it was decided to allow the process to develop before a final decision would be made.

Moisture levels for both ORS and GW were known the day when RI and RII were established and it was estimated that the mixture would have lower than the optimum moisture level, which is considered about 50–60% as previous reported. Furthermore, Antizar-Ladislao et al. (2006) studied the degradation of PAHs in an aged coal tar contaminated soil under in vessel composting conditions found that the optimal operational conditions occurred at moisture content of 60%. For this reason it was decided to add water during mixing as had happened with numerous other organic wastes in the past (Manios 2004). However, the texture of the ORS which looked extremely moist, far more than just 40%, confused the water addition process, which is in a large part rather empirical. As a result the water added was less

than that required resulting to moisture levels presented in Fig. 2. Moisture loss was prominent throughout the composting as expected for open windrow systems (Haug 1993; Mohee et al. 2008). Adjustments of the water content performed and the moisture losses during experiment resulted to moisture content fluctuations among 30.3–53.4% and 38.6–58.7% for RI and RII, respectively. The mean moisture content value and the standard deviation for RI was $41.4 \pm 6.7\%$ and for RII was $46.9 \pm 5.1\%$. Several researchers showed that as moisture content increased from 30% to 60% the metabolic and physiological activities of microorganisms were enhanced.

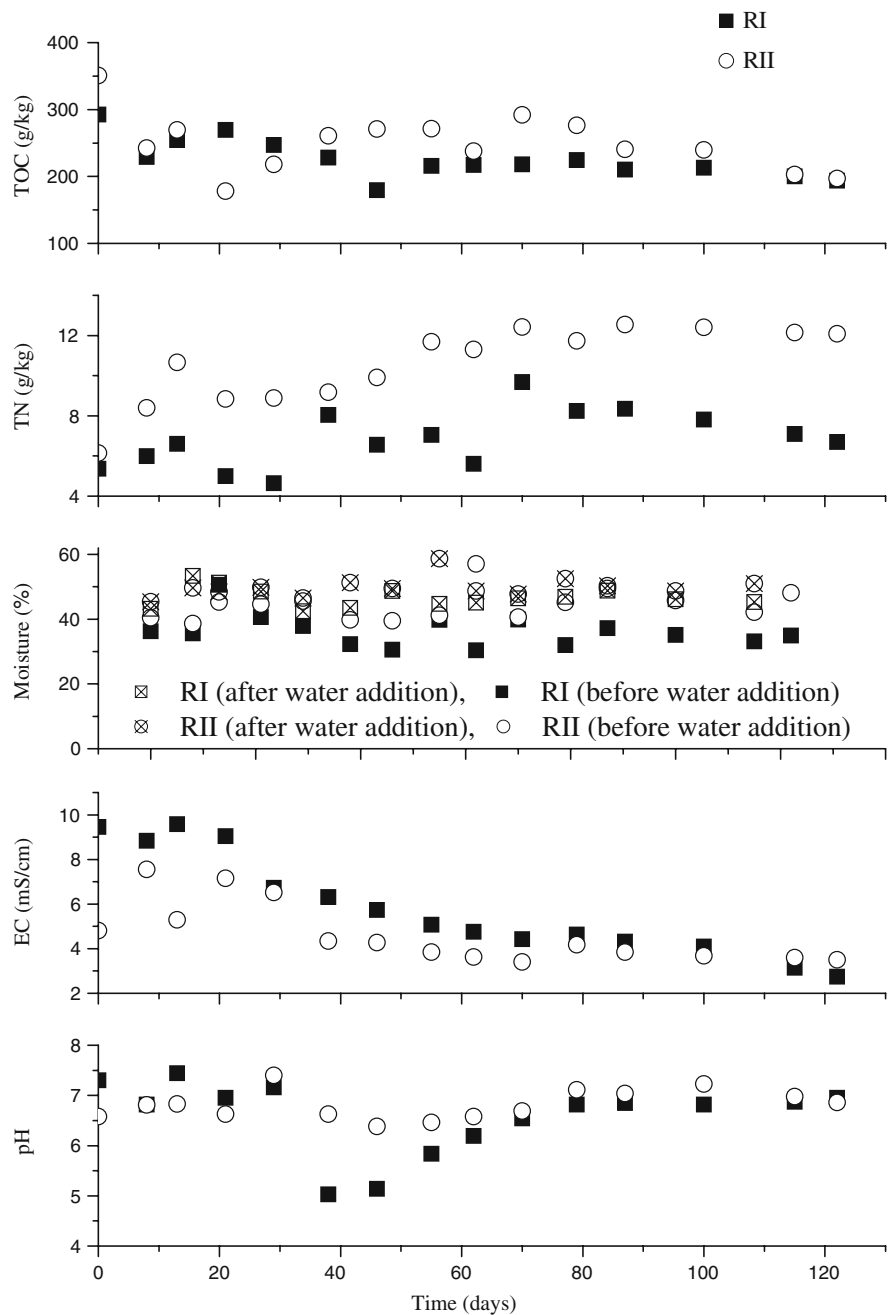
MOG concentration and its effect in the process was the biggest question mark since there was limited experience with ORS. The relevant literature as for example work conducted by Kirchmann and Ewnetu (1998); Van Gestel et al. (2003) and Marin et al. (2006) provide contrary results regarding a threshold value of MOG that would be able to delay or even cancel the composting process.

The composting behavior of RI and RII

Figure 3 presents the temperature fluctuation in the core of the two mixtures with time. Four days after establishment the temperature in RII was 50°C, a very good value for any organic waste in such short period of time. From that point onward RII behaved as most organic wastes both as temperature wise—recording more than 40 days with temperatures above 50°C and a maximum temperature of 62°C in Day 35—as well as pH, EC, TN, and TOC fluctuation (Fig. 2). RI behaves differently with the first 35 days straggling to increase temperature above 35°C. It does retain a medium temperature of above 40°C for a long period of time from that point onwards (as RII), These findings are in complete accordance to work presented by Marin et al. (2006) found that there are different thermal behavior between compost containing bulking agent and the other with no additives.

The presence of GW in larger amount in RII than in RI (Table 2) provides the bases for explaining the significant differentiation in the composting profile of the two mixtures. Better structure, provided by the 1:3 v/v rate of the bulking agent, allowed more air entrapment increasing the aerobic biodegradation of the mixture. This is strongly supported by the gases

Fig. 2 Physiochemical parameters fluctuation during the composting process for RI (■) and RII (○)



emission presented in Fig. 4 and statistically analyzed in Table 3. During the first 30 days of composting carbon dioxide flows out of RII in significant larger rates than in RI. Specifically until that day 13.6 kg of CO₂ have been released from RII, in comparison with 2.2 kg of RI. Aerobic microorganisms in RII are predominant even though some anaerobic pockets exist producing small amounts of methane (and part of

the carbon dioxide) as suggested by relevant published work (Atkinson et al. 1996; Ryckeboer et al. 2003).

If however density and absence of oxygen were the main reasons for the lower temperature, then as anaerobic microorganisms would become predominant methane and carbon dioxide should be produced and emitted from the RI composter. However, as can

Fig. 3 Temperature profile during composting. Arrows indicate turnings

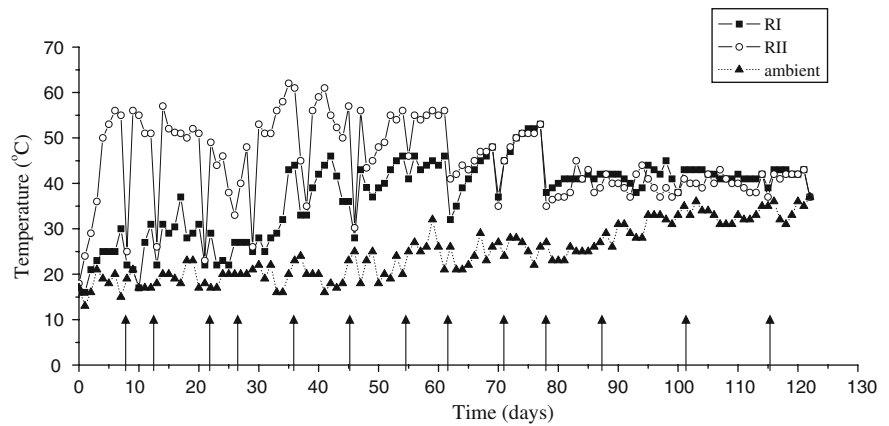


Table 2 Mass and volume composition of the two mixtures prior and after the end of the thermophilic phase

	ORS		GW		Total	
	Mass (kg)	Volume (l)	Mass (kg)	Volume (l)	Mass (kg)	Volume (l)
Initially						
RI	860	850	140	840	1,000	1,020
RII	480	460	195	1,200	675	990
Finally						
RI	–	–	–	–	540	670
RII	–	–	–	–	410	550

be easily spotted again through Fig. 4 and Table 3, this is not the case. The methane emission was higher but not significant than in RII. A simple and direct explanation to this phenomenon is the toxicity of MOG found in the ORS.

When used in the smaller rate (RII) the more easily decomposable GW managed to start their decomposing process. As temperature increased due to their decomposition two phenomena took place probably at the same time. First the thermophilic decomposing microorganisms co-digest the difficult to be decomposed and under ordinary situations toxic molecules. The use of co-substrate in order to enhanced biodegradation process has been well studied for various wastes under aerobic and anaerobic conditions (Rajaguru et al. 2000; Mata-Alvarez et al. 2000; Marin et al. 2006) and especially for oil refinery wastewaters in aerobic bioreactors (Lee et al. 2004). Slowly (or not) bacteria and fungi decompose the toxic molecules (here represented by the MOG and PAHs) as shows in Figs. 5 and 6. As these molecules decompose produce

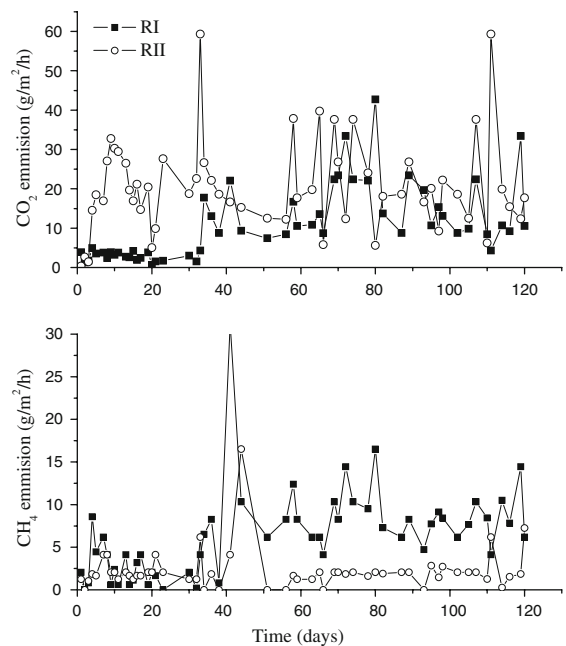


Fig. 4 Methane and carbon dioxide emissions during composting

easier decomposable molecules (less toxic) providing additional substrate to the microorganisms (Antizar-Ladislao et al. 2004) and sustaining the co-digestion phenomenon.

Research into bioremediation of PAH contaminated wastes shown that fungi are an important microbial group for composting of a contaminated soil (Sasek et al. 2003; Bhatt et al. 2002). More specifically, the majority of these belong to the *Basidiomycota*, which contain the fungal genera responsible for wood decomposition and hence possess the necessary complex array of ligninolytic enzymes and nonenzymatic

Table 3 Mean methane and carbon dioxide emissions for both piles during various stages of the composting process

Piles	Mean emission rates	
	RI	RII
Between day 1 and 38		
CH ₄ (mg/m ² /h)	2.683 ± 0.759 a	1.943 ± 0.226 a
CO ₂ (g/m ² /h)	3.955 ± 1.892 a	20.313 ± 7.945 b
Between day 38 and 78		
CH ₄ (mg/m ² /h)	9.791 ± 3.066 a	2.401 ± 1.467 b
CO ₂ (g/m ² /h)	15.275 ± 4.868 a	21.252 ± 2.129 a
Between day 0 and 120		
CH ₄ (mg/m ² /h)	6.805 ± 3.631 a	2.205 ± 0.841 b
CO ₂ (g/m ² /h)	11.509 ± 6.783 a	20.127 ± 5.776 b

Mean values in the same line followed by different letter are significantly different ($P < 0.05$)

mechanisms for the degradation of lignin whose basic chemical structures are similar to the PAHs. Microorganisms degrading PAHs include fungi, such as *Phanaerochaete chrysosporium*, *Bjerkandera* sp. and *Pleurotus ostreatus* (Antizar-Ladislao et al. 2004; Canet et al. 2000). According to Fig. 6, fungi population in RII is larger than in RI, at least until Day 60. This observation may be explain the higher PAH degradation in RII than in RI. However, several researchers indicated that most common effect of fungi on PAHs degradation is not mineralization but mainly the activation and solubilization of PAHs by non-specific fungal enzymes (Johnsen et al. 2002). In addition, recent research on in-vessel composting of aged coal-tar contaminated soil showed no correlation between fungal to bacteria ratios and PAH losses (Antizar-Ladislao et al. 2008).

The heat released from the decomposing GW and the slowly decomposing ORS is entrapped inside the pile by the insulating capacity of the GW (Tai and He 2007). Temperature by its self as an abiotic treating parameter plays a part in the process as suggested by the relevant finding of the abiotic experiments presented in Table 4. The moderate abiotic treatment is added to the significant biotic in RII reducing the toxicity effect of the hydrocarbon pollutants to the decomposing microorganisms. As a result and as it is recorded in Figs. 5 and 6, pollutants are decreased faster and to lower final concentrations.

The toxic effect of the hydrocarbon pollutants can be further supported by the simultaneous MOG

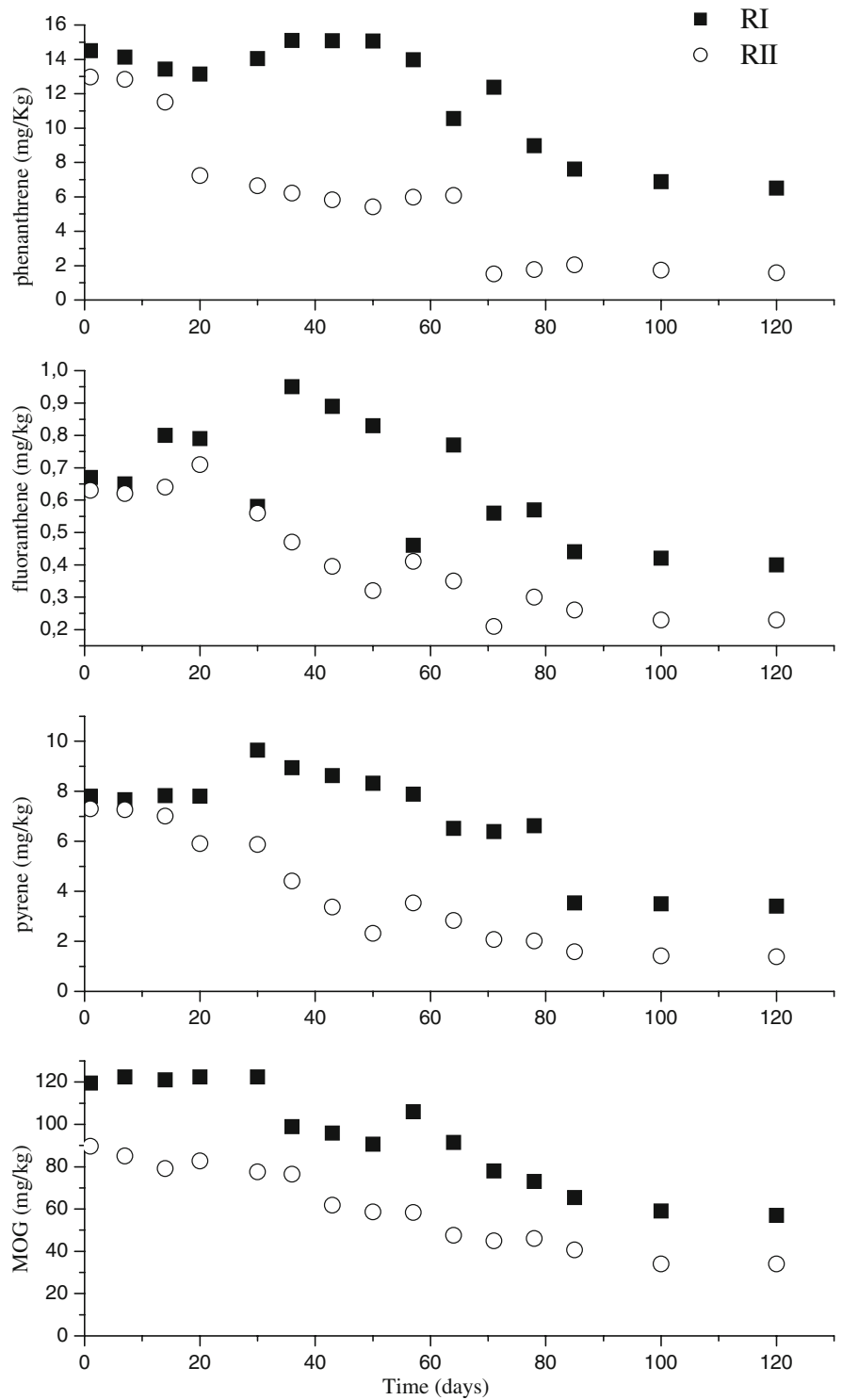
reduction and temperature increase in RI following the fourth turning. In Fig. 5 the concentration of MOG between the 29th day and the 38th day records a significant drop of approximately 20%, to a concentration lower than 100 g/kg. It is after that sudden drop that both the temperature profile and gases emissions change dramatically. From that point onwards RI records temperatures above 40°C and carbon dioxide and methane starting recording some important values (Fig. 4). Specifically and according to Fig. 4, carbon dioxide emission is increased almost to the level of RII where methane emission is now significant higher than RII (Table 4). Few days after PAHs concentration in RI starts dropping (Fig. 6) and finally *Pseudomonas* spp. and fungi population, both related to PAHs decomposition, do record a slight increase (especially the fungi).

It is rather clear that after more than 35 days of abiotic (temperature) and biotic (microorganisms) treatment, the toxicity level in RI has been reduced, probably through decomposition to simpler and less toxic molecules, in such way that allowed a larger variety of decomposing microorganisms to act. The capability of microorganisms to biodegrade specific contaminants depends on different reasons. The elevated temperatures of composting can increase the enzyme kinetics involved in biodegradation processes. Co-oxidation may be enhanced due to the range of alternative substrates present or modifications in the physical and chemical microenvironments within the composting mass can serve to increase the diversity of the microflora to which the contaminant is exposed (Williams and Keehan 1993).

Removing PAHs and MOG through composting

Tables 4 and 5 (the last was produced through Tables 1–3 as well as Fig. 2) together with Figs. 5 and 6 describe in a detailed manner the removal of MOG as well as phenanthrene (PHE), fluoranthene (FLU) and pyrene (PYR), constituting the PAHs monitored in these trials. According to them the reduction of MOG is 52.1% in RI and 62.1% in RII, where for PHE these values are 55.2% and 87.7%, for FLU 40.3 and 63.5% and for PYR 56.4% and 81.1% respectively. These removals were statistically significantly different (ANOVA—Tukey test) both for MOG and PAHs ($P = 0.05$). It is rather difficult

Fig. 5 MOG and PAHs concentration reduction during the composting process for RI (■) and RII (○)



to make direct comparison of these findings, with data published by other authors due to the quality of the ORS used and the nature of the bulking agent. For

example Marin et al. (2006) reported 60% degradation of hydrocarbon content in similar ORS mixed with wood shavings. Since though, their mixtures

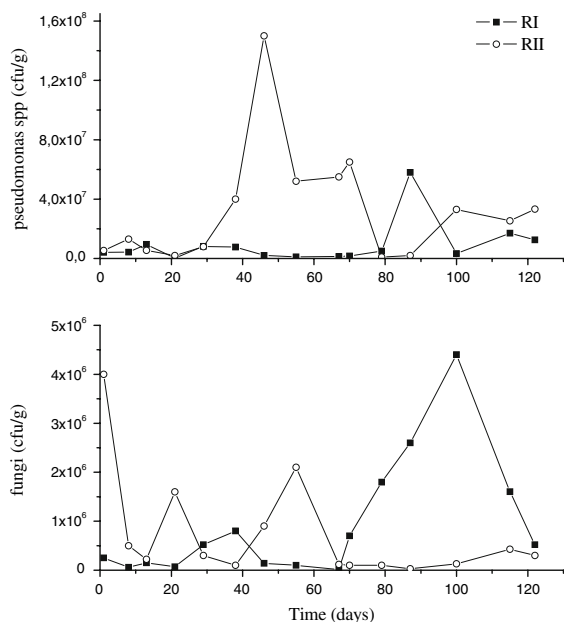


Fig. 6 *Pseudomonas* spp. (a) and fungi (b) populations during composting for RI and RII

were made based in mass rates and not volume rates, the comparability of the results is rather limited. However the removal percentage achieved at least in RII should be considered high compared with other composting efforts (Antizar-Ladislao et al. 2004).

As far the net amount of MOG removed, though composting, RI has a significant precedence with more than 41 g, where RII only slightly more than 17 g (Table 5). If the amount removed is compared with the volume of the mixture (or the volume of the bioreactor) then the efficiency rate is 0.41 for RI where for RII is 0.18. Also if the same amount is compared with the mass of GW required in each case (important for a cost benefit analysis) then again the efficiency rate for RI (0.30) is far better than for RII

(0.09). Its obvious that this difference is a result of the initial concentrations, however does indicate in a rather strong way that if the aim is to remove/decompose/evaporate as much MOG as possible then mixtures like RI are far more productive. This is not the picture with PAHs. According to Table 5, there is rather small difference between the two mixtures, with RI recording slightly better values.

However, RII is superior to RI in regarding final concentration which more or less will determine how the end product will be handled further. In this case RII (Table 4) records far smaller values allowing the easier handling of the end product. The fact though that there was no total degradation of oil content, indicates (a) that there is some weakness in the composting treating process and (b) that the residual quantity is highly recalcitrant to biodegradation due to possible strong biosorption to the solids (non-bio-available fraction) or to the nature of the remaining molecules (Artola-Caricano et al. 2003; Leonardi et al. 2007).

The abiotic treatment

Table 4 and Fig. 5 present some information regarding the effect of the temperature increase as a direct part of the treating process. According to the table MOG reduction due to temperature increase and the subquential evaporation of the lighter hydrocarbon is 15.3% for RI and 23.2% for RII. For all three PAHs the percentage removals were lower with the expectance of FLU which recorded similar values (14.1% and 19.4%, respectively). Antizar-Ladislao et al. (2005) found that abiotic losses of total PAH using non-amended soil was 20.8%, 42.0% and 66.3% at 38, 55 and 70°C, respectively. The mean temperature during experiment in RI was 37.2°C and for RII was

Table 4 Final concentration and percentage reduction for MOG and PAHs after 120 days of composting and abiotic experiments

Parameters	Composting experiments				Abiotic experiments			
	Final value (mg/kg)		% removal		Final value (mg/kg)		% removal	
	RI	RII	RI	RII	RI	RII	RI	RII
MOG	57.2	34.3	52.1	62.1	103.7	59.52	15.3	23.2
Phenanthrene	6.51	1.59	55.2	87.7	12.98	11.69	10.5	9.8
Fluoranthene	0.42	0.23	40.3	63.5	0.57	0.51	14.1	19.4
Pyrene	3.40	1.38	56.4	81.1	6.92	6.67	11.2	8.6

Table 5 Amount of MOG and PAHs prior and after the thermophilic period

Parameters	RI			RII		
	Initially (mg)	Finally (mg)	Lost (mg)	Initially (mg)	Finally (mg)	Lost (mg)
MOG	78,336	36,608	41,728	31,126	13,776	17,350
PHE	9,280	4,166	5,114	5,221	0,639	4,583
FLU	0,429	0,269	0,160	0,253	0,092	0,161
PYR	4,992	2,176	2,816	2,932	0,554	2,378

44.7°C. According to these temperatures, the observed abiotic losses are relatively close to this reported from Antizar-Ladislao et al. (2005). The effect of the abiotic parameter can be explained through the MOG composition. Many volatile compounds are part of the MOG. As temperature increase and remains high these molecules evaporates allowing a reduction in the overall MOG concentration (Bengtsson et al. 1998).

What however must be taken under consideration is the fact that during the abiotic experiments the mixtures were exposed to the temperature from the oven, where during composting the temperature was recorded in the core of the simulated windrow pile (Fig. 1). In the first case there was no physical barrier to the substances evaporation, where in the reality both the piled above materials as well as the drop of temperature in the outer layers might reduce the importance of abiotic treatment. Kirchman and Ewnetu (1998) support this idea showed that gaseous losses of oil compounds through volatilization from composts were not significant. It would be safe to suggest that microorganisms (similar to those monitored here—Fig. 6) are the main decomposing reason either by direct decomposition of the hydrocarbons and the decomposed bio-products or through co-digestion phenomena.

Previous research on remediation of PAH contaminated soil by in-vessel composting (Antizar-Ladislao et al. 2005) found that the biocidal effect of 2% $HgCl_2$ were reduce over time, thus some foreign microorganisms may have been able to colonise the medium again. General, the technique of in-vessel composting providing in the reactors constant air-flow with air pump resulting to higher expose of medium to foreign microorganisms transported via air-flow. On the other hand in this experiment the $HgCl_2$ -inhibited reactor introduced in the oven without air or water supply amendment. So that, the abiotic losses represented by a

non-amended medium as suggested (Antizar-ladislao et al. 2005) plus $HgCl_2$ addition.

Conclusions

The 1:3 v/v mixing rate (RII) for the co-composting of ORS with GW should be considered as optimum, comparable to the 1:1 v/v (RI) mainly due to its overall behavior during the thermophilic stage of the process, as well as the lower final concentration of the MOG and PAHs. However, what seems more important than just the mixing rate, as a criterion for examining the composting potential of a mixture, is the concentration of the MOG that potentially inhibits the composting process. According to the findings presented, MOG concentration above 100 mg/kg of dry weight might potentially limit and delay composting. Mixing rates like 1:2 v/v should also be tested, as well as 1:3 v/v rates in which the initial MOG concentration would be higher than the above mentioned limiting value. Further investigation in the toxic effect of each MOG/PAHs component should also be conducted.

If and when this concentration is no longer a limiting factor, the ability of composting to remove MOG and PAHs should be considered as significant, with rates spreading between 50% and 85% depending the mixture and the pollutant. Most of this removal should be considered as a result of the decomposing microorganisms' action, with a far smaller part as a result of the temperature increase and the consequent evaporation of the lighter hydrocarbons. This is difficult to be estimated accurately since it would be possible evaporated molecules due to temperatures in the core to be condensed in outer colder layers as flowing vertically.

Finally, monitoring methane and carbon dioxide emission during composting should be considered an important part of the process evaluation. In this case

the emission profile of the two piles provided the required information for determining the toxic threshold of the MOG concentration.

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