

# Bioremediation of a Diesel-contaminated Soil: Effect of Compost Addition

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## ABSTRACT

Organic waste derived compost is usually viewed as a soil amendment. However, mature and stable composts can be used as a media to aid in the bioremediation of hazardous wastes. The goal of this study was to investigate the effect of compost addition on the degradation of a diesel-contaminated soil. A municipal solid waste-derived compost and an olive pulp-derived compost were used in this study. The former compost was more stable than the latter. A total of 18 experiments were performed in 1 L manometric respirometers and the biodegradation process was followed through measurements of net O<sub>2</sub> consumption and net CO<sub>2</sub> generation for 170 days. Results of the work showed that the addition of both composts increased the net respiration activity due to the degradation of diesel in the compost amended samples. The addition of municipal solid waste compost at a ratio of 2: 1 (dry soil: dry compost) led to the highest net microbial activity and the highest diesel removal (94%). The olive pulp-derived compost resulted in the highest net microbial activity when added at a ratio of 5: 1 but with a diesel removal of approximately 73%. The diesel contaminated soil alone had a low microbial respiration activity and a relatively high diesel removal (84%).

**Keywords:** soil contamination, soil bioremediation, diesel biodegradation, compost, respirometry

## INTRODUCTION

Organic waste-derived compost is usually viewed as a soil amendment. However, mature and stable composts can be used as a media to aid in the bioremediation of hazardous wastes (USEPA 1998). Mixtures of composts with hazardous organic wastes (HOW) have been successfully used in bioremediation projects to remove hazardous pollutants (USEPA 1998). Composts can provide nutrients, microorganisms as well as an organic substrate (energy amendment) that will enhance overall HOW degradation. Composts can originate from various sources and can have different stabilities. Both are likely factors that may affect the removal of the hazardous pollutants. Researchers experimented on the use of either mixtures of biowaste with contaminated soil in an aerobic environment (Van Gestel *et al.* 2003) or the use of mixtures of composted organic material with contaminated soil to remediate the hazardous compounds in the soil (Jørgensen *et al.* 2000; Park *et al.* 2001; Namkoong *et al.* 2002; Rivera and Dendooven 2004; Ouyang *et al.* 2005; Faundez *et al.* 2008; Godoy *et al.* 2008; Farrell and Jones 2010; Gandolfi *et al.* 2010; Sayara *et al.* 2010a, 2010b). Researchers have shown that the addition of compost to the contaminated soil enhanced the removal of the pollutant compared with a contaminated soil without the addition of compost. In a recent work, Sayara *et al.* (2010a) showed that the more stable a municipal solid waste (MSW) compost was (as judged based on a dynamic respiration index), the higher the degradation of the organic pollutant (pyrene) was. In another similar work, Sayara *et al.* (2010b) adopted the central composite design principles and concluded that maximum pyrene degradation occurred at ratios of 1: 3 (soil: compost) using a medium stability compost at a 1.3 g kg<sup>-1</sup> pollutant concentration level. The adequate use of compost as a biofiltration media to treat gasoline vapors has been also demonstrated by Namkoong *et al.* (2003).

It appears that there is a lack of information on the effect of MSW-derived compost produced after an extended

period of curing (5 years) on the remediation of diesel-contaminated soils (DCS). In addition, the olive pulp derived compost, which can be produced from the solid residue of two-phase olive mills, does not appear to have been studied as a potential remediation media to treat diesel-contaminated soils.

Based on the above, the objective of this research work was to investigate the influence of the addition of two different composts (a 5-year old MSW-derived compost and an olive pulp-derived compost) on the degradation of a diesel contaminated soil. Both composts were added at 3 different mixing ratios with the DCS. Diesel degradation was indirectly studied via the calculation of net respiration activities (oxygen consumption and carbon dioxide generation) over a 170-day period using air tight 1 L static manometric respirometers. Final diesel contents (quantified as total petroleum hydrocarbons) were measured in the runs that contained diesel contaminated soil. No diesel measurements were performed in the single composts and in the uncontaminated soil.

## MATERIALS AND METHODS

### Soil and composts

Approximately 4 kg of soil were collected from the university area and were screened through a 3 mm screen to remove large particles. Sieve analysis was performed according to Komilis *et al.* (2010). Undersized material was then air-dried for 7 days and was then spiked with automobile diesel purchased from a local gasoline station at an initial content of 2% (i.e. 20000 mg kg<sup>-1</sup> air dried soil). The artificially diesel-contaminated soil (DCS) was further air-dried under a hood for an additional 3 day period to remove readily volatile compounds. The municipal solid waste-derived compost (MSWC) was obtained from 5-year old compost curing piles from a MSW composting facility in Kalamata (Greece). The olive pulp-derived compost (OLPC) was obtained from a two-phase olive milling facility from Thassos Island (Greece). Both

composts had been characterized in Komilis and Tziouvaras (2009) using a static respirometric assay. The MSWC had a total 7-day O<sub>2</sub> consumption and a total 7-day CO<sub>2</sub> generation equal to 2.0 g O<sub>2</sub> kg<sup>-1</sup> dry matter (DM) and 1.0 g C-CO<sub>2</sub> kg<sup>-1</sup> DM, respectively; the OLPC had a total 7-day O<sub>2</sub> consumption and a total 7-day CO<sub>2</sub> generation equal to approximately 5 g O<sub>2</sub> kg<sup>-1</sup> DM and approximately 2.5 g C-CO<sub>2</sub> kg<sup>-1</sup> DM, respectively (Komilis and Tziouvaras 2009). Therefore, the MSWC was more stable compared to the OLPC.

### Analytical methods

The moisture content of all materials was measured by evaluating the weight difference at 75°C until constant weight. The volatile solids (VS) or the organic matter (OM) was measured by the loss on ignition after 2 h at 550°C. Analyses of total carbon (C) and total nitrogen (N) of ground dry samples were performed with an elemental analyzer (CE Instruments, EA 1110, Italy) according to Komilis and Tziouvaras (2009). The water holding capacities (WHC) of soil and composts were measured based on weight difference following systematic saturations of dry soil samples (approximately 5 g) and a drainage period of 2 h. The particle density of the soil solids was measured via water displacement of a known mass of dry soil.

The diesel content in the soil was quantified as total petroleum hydrocarbons (TPHs) according to Karamalidis and Voudrias (2007). A 4-step sequential extraction with dichloromethane was adopted. Two (2.0) grams of composite wet samples of soil or compost/soil mixtures were received for analysis. The final volume of dichloromethane after the sequential extraction procedure was accurately measured with a graduated cylinder. The extract was then analyzed by a gas chromatograph (HP Agilent® 6890N) equipped with a flame ionization detector. The GC column was a capillary HP-5 (30 m × 0.32 mm i.d.). Temperature programming comprised an initial 50°C oven temperature which was kept constant for 1 min and then increased to 250°C at a rate of 15°C/min. A final bake out at 280°C for 5 min followed. Injector and detector temperatures were 280 and 290°C, respectively. Helium was the carrier gas at a constant flow of 1.2 ml/min. One (1) µL of sample was injected into the GC in a splitless mode. A 5 point calibration was performed by preparing standards of diesel in dichloromethane at concentrations equal to 10, 50, 100, 200 and 400 mg L<sup>-1</sup>. TPHs were quantified via integration of the total hump area above the baseline. Results were expressed in mg TPH kg<sup>-1</sup> dry material.

### Manometric respirometers

The materials used in this research (soil, composts) were placed in 1 L respirometers equipped with Oxi-Top® manometric heads that were acquired from WTW®. The dry weights of the materials or mixtures placed in each respirometer are shown in **Table 1**. Deionized water was added to the materials within each respirometer to achieve moisture contents corresponding to 60% of their WHC. The cumulative mass of O<sub>2</sub> consumed in each respirometer was calculated on the basis of the ideal gas law taking into account the pressure drops recorded and logged at regular time intervals (Komilis *et al.* 2011). The gross cumulative oxygen consumption was finally expressed in g O<sub>2</sub> dry kg<sup>-1</sup> of material placed in the respirometer. The mixtures of compost and contaminated soil were prepared according to the ratios mentioned in **Table 1**.

Runs were performed at 22°C in order to keep diesel volatilization minimized throughout the experiment (Komilis *et al.* 2010). Fifty (50) ml of a KOH solution was placed within each respirometer to trap the CO<sub>2</sub> generated. The alkaline solutions were periodically titrated with a 0.2 N H<sub>2</sub>SO<sub>4</sub> solution to quantify the C-CO<sub>2</sub> trapped in the solution, as described in Komilis *et al.* (2011). The CO<sub>2</sub> measurements were performed on day 22, 71, 108, 145 and 170 (end of runs) from the initiation of the experiments. The alkaline traps were replaced with new ones after each titration. CO<sub>2</sub> generation was expressed in g C-CO<sub>2</sub> kg<sup>-1</sup> DM of mixture or individual material. Respirometers were opened once per week to aerate their contents and to adjust the pressure inside the respirometer back to atmospheric pressure. The material in the respirometer was manually stirred to aid aeration.

### Experimental design

Each of the two composts used in this study was mixed with the DCS in 3 ratios which were 2: 1, 5: 1 and 10: 1 (dry contaminated soil: dry compost), according to **Table 1**. A total of 18 respirometers were used in this study and runs lasted 170 days. All runs with mixtures were performed in duplicate, except for the MSW2:1 run (see **Table 1**). The biodegradation of the composts was studied under the same conditions using duplicate runs as well. One single run was performed with the DCS (control) and one run was performed with the uncontaminated soil (UCS) alone (blank) to quantify soil respiration. The C/N ratios were calculated by accounting the total C and N contents of compost, soil and diesel, separately. Diesel was assumed to be represented by hexadecane (Walecka and Walworth 2006; Komilis *et al.* 2010) to calculate its carbon content; therefore, diesel carbon was 85% of the diesel mass.

### Net respiration activities

The net O<sub>2</sub> consumption due to the degradation of the DCS in the mixtures was calculated according to the equation:

$$O_{2\text{DCSMIX}} = \frac{O_{2\text{MIX}} \cdot DM_{\text{MIX}} - O_{2\text{COMPOST}} \cdot DM_{\text{COMPOST}}}{DM_{\text{SOIL}}} - O_{2\text{SOIL}} \quad (1)$$

where: O<sub>2DCSMIX</sub>: net cumulative oxygen consumption due to the degradation of the DCS contained in the mixture (g O<sub>2</sub> kg<sup>-1</sup> dry soil); O<sub>2MIX</sub>: gross cumulative oxygen consumption of the mixture (compost and DCS) (g O<sub>2</sub> kg<sup>-1</sup> dry mixture); DM<sub>MIX</sub>: dry mass of the mixture (compost and DCS) placed in the respirometer (kg); O<sub>2COMPOST</sub>: cumulative oxygen consumption of the compost (g O<sub>2</sub> kg<sup>-1</sup> dry compost); DM<sub>COMPOST</sub>: dry mass of the compost contained in the mixture (kg); O<sub>2SOIL</sub>: cumulative oxygen consumption of the uncontaminated soil due to soil respiration (g O<sub>2</sub> kg<sup>-1</sup> dry soil); DM<sub>SOIL</sub>: dry mass of the contaminated soil contained in the mixture (kg).

The net cumulative CO<sub>2</sub> generation due to the degradation of the DCS in the mixtures was calculated with a similar equation:

$$CO_{2\text{DCSMIX}} = \frac{CO_{2\text{MIX}} \cdot DM_{\text{MIX}} - CO_{2\text{COMPOST}} \cdot DM_{\text{COMPOST}}}{DM_{\text{SOIL}}} - CO_{2\text{SOIL}}$$

where: CO<sub>2DCSMIX</sub>: net cumulative carbon dioxide generation due to the degradation of the DCS contained in the mixture (g C-CO<sub>2</sub> kg<sup>-1</sup> dry soil); CO<sub>2MIX</sub>: gross cumulative carbon dioxide generation of the mixture (compost and DCS) (g C-CO<sub>2</sub> kg<sup>-1</sup> dry mixture); CO<sub>2COMPOST</sub>: carbon dioxide generation of the compost (g C-CO<sub>2</sub> kg<sup>-1</sup> dry compost); CO<sub>2SOIL</sub>: carbon dioxide generation of the uncontaminated soil due to soil respiration (g C-CO<sub>2</sub> kg<sup>-1</sup> dry soil); other parameters as defined earlier.

## RESULTS AND DISCUSSION

### Initial properties

The soil used in this work was a sandy soil which was characterized in Komilis *et al.* (2010). The initial properties of all mixtures, the individual composts and the soil are included in **Table 1**. According to **Table 1**, the initial C/N ratios achieved for all mixtures ranged from 14.3 to 24.5. The uncontaminated soil (UCS) alone had a C/N ratio of 4.14. The OLPC had the highest organic matter content, which was 78.1% (dry matter basis – DM). The WHC of both composts were 1.2 ml dry g<sup>-1</sup> while the soil alone had a WHC of 0.35 ml g<sup>-1</sup>. The initial concentration of the diesel (TPHs) in the DCS, prior to the initiation of the runs, was measured at approximately 11000 mg kg<sup>-1</sup> of dry soil. The removal of approximately 9000 mg/kg of dry soil was due to an apparent vaporization of the volatile fraction of the diesel during the 3 day air-drying period under the hood. The initial TPH contents of the mixtures ranged from 7500 mg kg<sup>-1</sup> DM (in the runs with mixing ratios of DCS: compost equal to 2: 1) to 10200 mg kg<sup>-1</sup> DM (in the runs with mixing ratios of DCS: compost equal to 10: 1). The initial TPH contents of the mixtures varied, since composts contained no TPH; therefore, as the ratio of the DCS: compost

**Table 1** Initial properties of the mixtures and of the individual materials.

Run	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
MSW 2:1 *	2:1	292	27.1%	11.4%	12.2%	6.2%	0.41%	14.3	7500
MSW 5:1 **	5:1	353	22.1%	6.4%	7.4%	3.8%	0.22%	16.0	9400
MSW 10:1 **	10:1	323	19.7%	4.2%	5.2%	2.8%	0.13%	18.4	10200
OLP 2:1 **	2:1	293	27.1%	27.0%	27.7%	13.2%	0.58%	22.1	7500
OLP 5:1 **	5:1	235	22.1%	14.2%	15.2%	7.3%	0.30%	23.1	9400
OLP 10:1 **	10:1	323	19.7%	8.4%	9.5%	4.7%	0.18%	24.5	10200
MSWC **	-	75	42.0%	31.5%	-	15.7%	1.2%	13.1	N/M
OLPC **	-	85	42.0%	78.1%	-	36.5%	1.7%	21.5	N/M
DCS * (control)	-	294	16.5%	1.47%	2.6%	1.5%	0.022%	47.6	11200
UCS * (blank)	-	292	16.5%	1.47%	-	0.091%	0.022%	4.14	N/M

OLPC: olive pulp-derived compost; MSWC: municipal solid waste-derived compost; DCS: diesel-contaminated soil; UCS: Uncontaminated soil; Ratio A:B indicates dry mass (A) of diesel contaminated soil per dry mass (B) of compost; \*: single run; \*\*: duplicate runs;

(1): Ratio (dry diesel-contaminated soil: dry compost);

(2): Weight (g) of dry mixture or material placed in the respirometer;

(3): Moisture content (% WW) that was achieved after addition of deionized water. The moisture contents achieved correspond to approximately 60% of the water holding capacities (WHC) of the mixtures or individual materials;

(4): Initial organic matter content (% DM) of mixture (without including the diesel);

(5): Initial organic matter content (% DM) of mixture (including diesel);

(6): C content of mixture including the diesel (% DM);

(7): N content (% DM);

(8): C/N ratio of the whole mixture;

(9): Initial TPH concentration achieved in the mixture (mg dry kg<sup>-1</sup> of mixture).

**Table 2** Average degradation indices after 170 days.\*

Run <sup>s</sup>	Final OM content of mixture (% DM)	Final moisture content (% WW)	Dry mass reduction of mixture (%)	Net cumulative O <sub>2</sub> consumption (g O <sub>2</sub> dry kg <sup>-1</sup> soil)**	Net cumulative CO <sub>2</sub> generation (g C-CO <sub>2</sub> dry kg <sup>-1</sup> soil)**	Final TPH concentration (mg dry kg <sup>-1</sup> of mixture) <sup>sss</sup>	TPH removal (%) <sup>sss</sup>
MSW 2:1	11.0%	24.8%	1.36%	9.13	3.51	490	94%
MSW 5:1	6.42% (0.01%)	20.0% (0.28%)	1.02% (0.01%)	6.01 (0.16)	2.06 (0.029)	3954, 4593	58%, 52%
MSW 10:1	4.42% (0.04%)	17.2% (0.16%)	0.84% (0.04%)	7.19 (0.26)	2.16 (0.010)	2447, 5177	76%, 50%
OLP 2:1	25.7% (0.16%)	26.6% (2.5%)	2.72% (0.21%)	-6.90 (1.06) <sup>ss</sup>	-2.95 (0.20) <sup>ss</sup>	759, N/M	90%
OLP 5:1	13.5% (0.02%)	21.9% (3.9%)	1.91% (0.02%)	9.81 (0.16)	2.04 (0.15)	2367, 2686	75%, 72%
OLP 10:1	8.57% (0.24%)	17.4% (1.8%)	0.96% (0.26%)	5.69 (0.22)	1.26 (0.019)	2924, 4916	72%, 52%
MSWC	30.6% (0.16%)	39.1% (0.16%)	1.20% (0.23%)	13.8 (1.06) <sup>^^</sup>	3.94 (0.038) <sup>^^</sup>	N/M	N/M
OLPC	77.6% (1.13%)	43.0% (2.0%)	2.70% (3.8%)	42.3 (3.0) <sup>^^</sup>	19.4 (0.33) <sup>^^</sup>	N/M	N/M
DCS	1.83%	13.6%	1.29%	1.58	0.22	1858, 1831 <sup>&amp;</sup>	84%
UCS	N/M	N/M	N/M	0.95	0.20	N/M	N/M

\*: Values in parentheses are standard deviations based on n = 2;

\*\* : Net O<sub>2</sub> consumption (or CO<sub>2</sub> generation) due to diesel degradation only; it was calculated after subtracting the O<sub>2</sub> consumed (or CO<sub>2</sub> generated) due to soil respiration and due to compost degradation from the corresponding gross amounts recorded from the mixture;

<sup>ss</sup>: Negative value indicates that the O<sub>2</sub> consumed or CO<sub>2</sub> generated from the compost in the mixture was higher than the overall O<sub>2</sub> consumed/CO<sub>2</sub> generated from the mixture;

<sup>sss</sup>: Each value shown is based on the analysis of one composite sample received from each respirometer;

<sup>&</sup>: Two (2) composite samples were obtained from the same respirometer;

<sup>^^</sup>: Amounts are per dry kg of compost;

N/M: not measured.

increased, the initial TPH content of the whole mixture increased as well.

## Final properties

**Table 2** shows the final OM and moisture contents of the mixtures. According to **Table 1** and **2**, no major moisture losses occurred during the 170 day period within all respirometers. The dry matter (DM) reduction is also included in **Table 2** and was calculated using the principle of ash conservation. DM reductions were higher in the mixtures with the OLPC, since this compost was more degradable than the MSWC. OLPC alone had 2.70% of DM reduction over the 170 days compared to 1.20% for the MSWC. The standard deviations from the duplicate runs that contained OLPC mixtures were higher compared to the standard deviations from the duplicate runs that contained MSWC mixtures (see **Table 2**). This difference is attributed to the higher heterogeneity of the OLPC compared to the MSWC.

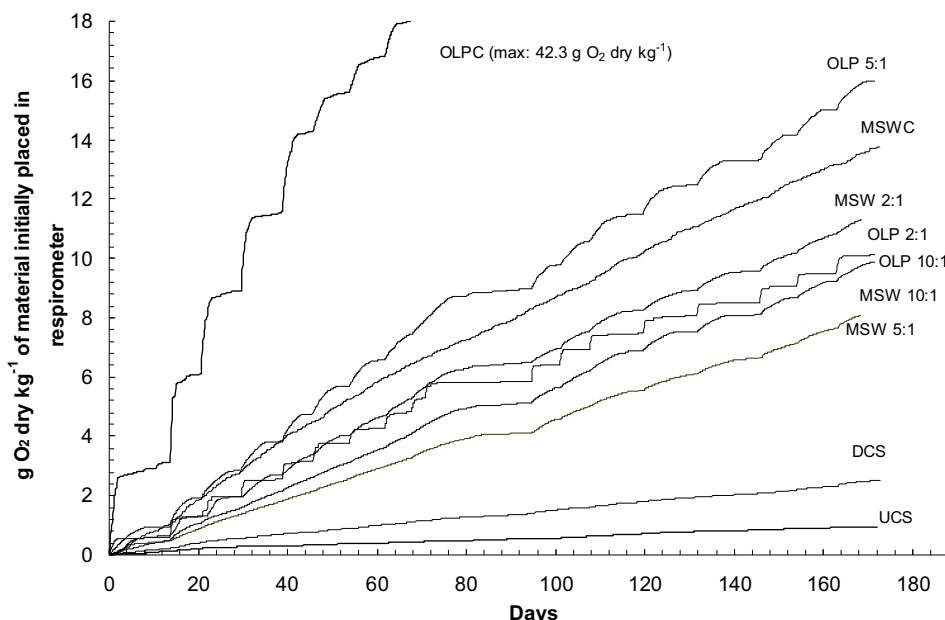
## Microbial respiration activities

**Fig. 1** illustrates the gross cumulative O<sub>2</sub> consumption from all runs during the 170 day period. As indicated in **Fig. 1**, OLPC was the material that consumed the highest oxygen amount, i.e. 42.3 g O<sub>2</sub> dry kg<sup>-1</sup> (not fully shown in **Fig. 1**) from all other runs. MSWC consumed 13.8 g O<sub>2</sub> dry kg<sup>-1</sup>. CO<sub>2</sub> generation from the OLPC and MSWC were 19.4 and

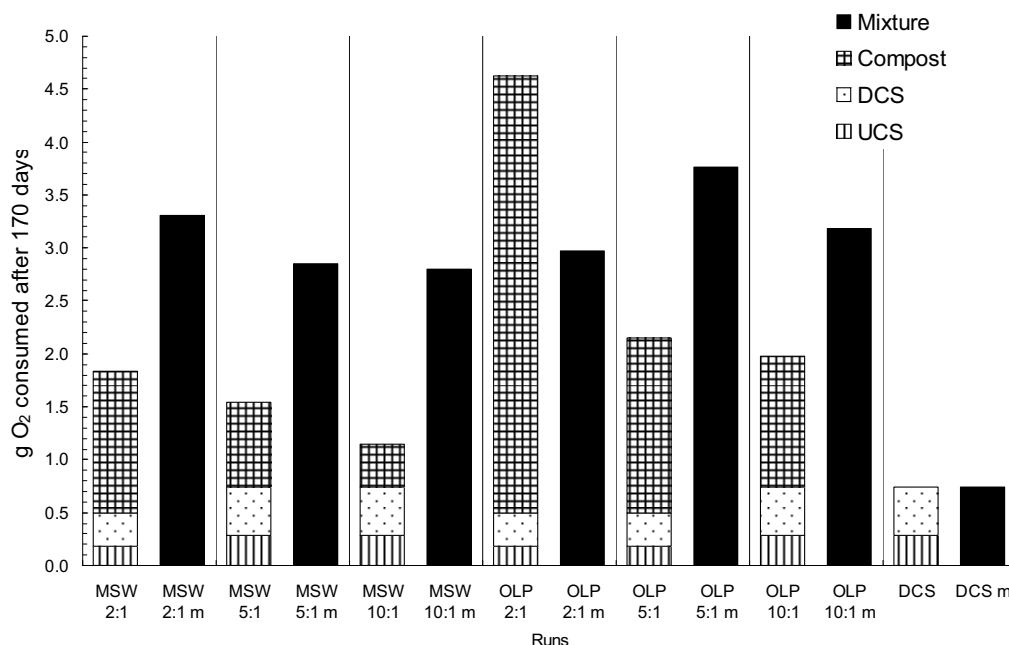
3.94 g C-CO<sub>2</sub> dry kg<sup>-1</sup>, respectively. MSWC was, therefore, more stable than OLPC, as had been also shown in Komilis and Tziouvaras (2009). All other mixtures / materials consumed from approximately 2.5 (DCS) to 16 (OLP 5: 1) g O<sub>2</sub> dry kg<sup>-1</sup> of mixture. Soil respiration led to the consumption of approximately 0.95 g O<sub>2</sub> dry kg<sup>-1</sup> dry soil after 170 days. The DCS consumed 2.53 g O<sub>2</sub> dry kg<sup>-1</sup>, which is a gross oxygen consumption that includes the O<sub>2</sub> consumption due to soil respiration.

**Fig. 2** illustrates the gross mass (g) of oxygen consumed after the 170-day incubation period (black bars) from each mixture in a run. The bars to the left of the black bars illustrate the gross cumulative masses of oxygen (g) that were expected to be consumed by each of the individual components contained in the mixture (compost, DCS, uncontaminated soil) after the 170-d period. According to **Fig. 2**, the gross oxygen consumptions of the mixtures are always greater than the sum of the oxygen consumptions of the individual components, except for the OLP 2:1 run. Therefore, a synergistic effect is evident in all runs, except the OLP 2:1 run. This synergistic effect could be attributed to an enhanced degradation of the DCS in most of the mixtures. In the case of the OLPC 2:1 run, an antagonistic effect was obtained, since a negative net O<sub>2</sub> consumption and a negative net CO<sub>2</sub> generation were calculated (see **Table 2** and **Fig. 3**).

According to equations (1) and (2), the net O<sub>2</sub> consumptions for all runs are illustrated in **Fig. 3A** and the net CO<sub>2</sub>



**Fig. 1 Average gross cumulative O<sub>2</sub> consumptions.** OLPC: olive pulp-derived compost; MSWC: MSW derived compost; DCS: diesel-contaminated soil; UCS: Uncontaminated soil; Ratio A:B indicates dry mass (A) of diesel contaminated soil per dry mass (B) of compost.



**Fig. 2 Average gross oxygen consumption (g) from a mixture (black bar with indication “m”) and the expected oxygen consumptions by the individual components contained in the mixture (bar left to black bar).** O<sub>2</sub> masses (black bars) should not be compared to each other, since they correspond to different masses of materials placed in the respirometer.

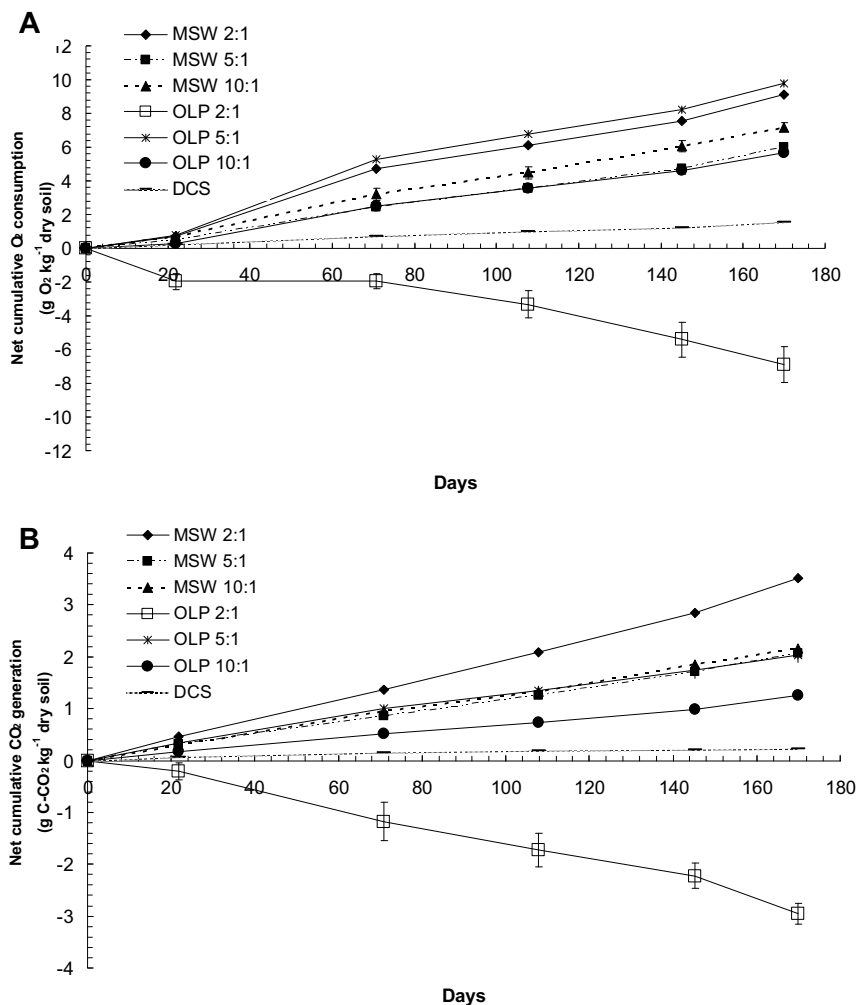
generations are illustrated in **Fig. 3B**.

According to **Fig. 3A**, the OLPC 5:1 run had the highest net O<sub>2</sub> consumption (9.8 g O<sub>2</sub> dry kg<sup>-1</sup> soil), followed by the MSW 2:1, the MSW 10: 1, the MSW 5: 1 runs and the OLPC 10: 1 runs. The net CO<sub>2</sub> generated, from higher to lower, were from runs MSW 2: 1, MSW 10: 1, MSW 5: 1, OLPC 5: 1 and OLPC 10: 1. Therefore, the 2 microbial respiration activity indices do not precisely agree on which mixture had the highest microbial activity. As stated in Brook *et al.* (2001), oxygen consumption and carbon dioxide generation rates do not always agree in diesel degradation soil studies due to incomplete TPH mineralization, the incorporation of diesel carbon in biomass and soil carbonate interactions. Based on the net CO<sub>2</sub> production, it can be indirectly indicated that the MSWC led to a higher diesel degradation compared to the OLPC. Therefore, the more stable compost (MSWC) led to a higher diesel biodegradation compared to the less stable compost (OLPC); this agrees to the findings

of Sayara *et al.* (2010a, 2010b), who used pyrene as the model organic contaminant.

The negative net O<sub>2</sub> consumption and net CO<sub>2</sub> generation from run OLPC 2: 1 has no practical meaning, but is still illustrated in **Fig. 3**. A likely explanation is that the mixing of the DCS with compost in that run inhibited the degradation of the compost which led to these negative net respiration activities.

Average values and standard deviations of the respiration activities are included in **Table 2**. The relative standard deviations (RSD) from the duplicate measurements of O<sub>2</sub> consumption after 170 days ranged from 1.6% (OLPC 5: 1 run) to 15.4% (OLPC 2: 1). The relative standard deviations from the duplicate measurements of CO<sub>2</sub> generation after 170 days ranged from 0.45% (MSW 10: 1 run) to 7.1% (OLPC 5: 1 run).



**Fig. 3 Means  $\pm$  one standard deviation.** (A) Average net cumulative O<sub>2</sub> consumption due to DCS degradation; (B) Average net cumulative C-CO<sub>2</sub> generation due to the DCS degradation.

## Respiratory quotients

The respiratory quotient (RQ) is defined as the moles of CO<sub>2</sub> generated per moles of O<sub>2</sub> consumed during a process. **Fig. 4A** illustrates the gross RQs versus time for all runs. RQs were calculated based on the gross amounts of CO<sub>2</sub> generated and O<sub>2</sub> consumed from the whole mixture (**Fig. 4A**). The RQs corresponded to the time intervals between the sampling times. For example, the RQ shown on day 71 was calculated from the total amount of CO<sub>2</sub> generated and the amount of O<sub>2</sub> consumed from day 22 up to day 71. According to **Fig. 4A**, RQs remained stable during the process in most of the cases. A slight diminishing trend was evident for the DCS and the MSWC, whilst an increase of the RQ was observed for the OLPC up to day 71. The diesel-contaminated soil alone had the lowest gross RQ which remained between 0.4 and 0.6 indicating that CO<sub>2</sub> generation was less than the O<sub>2</sub> consumption. This agrees to the findings of Moller *et al.* (1996) who showed that RQ values in diesel-contaminated soils are always <1. On the other hand, Aspray *et al.* (2008) found that diesel-contaminated soils had RQs > 1. In particular, Aspray *et al.* (2008) calculated RQs during aerobic degradation of three hydrocarbon contaminated soils that ranged from 1.2 (for the sandy gravel and sandy loam soils) to approximately 3 (for the silty clay soil). The lower than 1 RQ indicate the presence of oxygen poor compounds in the organic substrate (Moller *et al.* 1996), which is true for diesel.

The uncontaminated soil had the next lowest RQ values (<0.8). The mixtures that contained OLPC, and the OLPC alone, had some of the highest RQ values during the whole process, with 1.6 being the maximum value. The higher val-

ues of RQ in OLPC compared to that of MSWC are attributed to the higher degradability (lower stability) of that compost compared to MSWC (Gea *et al.* 2004). The lower stability of OLPC compared to MSWC was also clearly shown by the higher values of the respiration indices (O<sub>2</sub> consumption and CO<sub>2</sub> generation) of the former compost compared to the latter.

Net RQs are shown in **Fig. 4B**. They were calculated from the net O<sub>2</sub> consumed and the net CO<sub>2</sub> generated from the diesel in the contaminated soil. The profiles of the net RQ versus time are more obvious than that of the gross RQ. **Fig. 4B** indicates that a clear diminishing trend of RQ took place during the first 70 days for all runs; RQs remained either stable later on, or had a slight increasing trend. In general, there was a diminishing trend of the RQ after day 21. This trend is particularly obvious for the net RQ of the DCS alone that started from approximately 0.8 and reduced steadily to 0.3 after 170 days.

## Diesel removal

The final diesel (TPH) contents were measured for all runs, except for the composts and the UCS, and the results are included in **Table 2**. The dry matter at the end of the process was calculated by the ash conservation principle. Based on the dry matter of the mixtures at the end of the experiment, and the corresponding TPH contents, the total TPH removals within the respirometer were calculated.

The highest TPH removals occurred in the MSW 2: 1 and OLP 2: 1 runs. Although the high TPH removal of the MSW 2: 1 run agrees with its relatively high net O<sub>2</sub> consumption and net CO<sub>2</sub> generation, this is not true for the

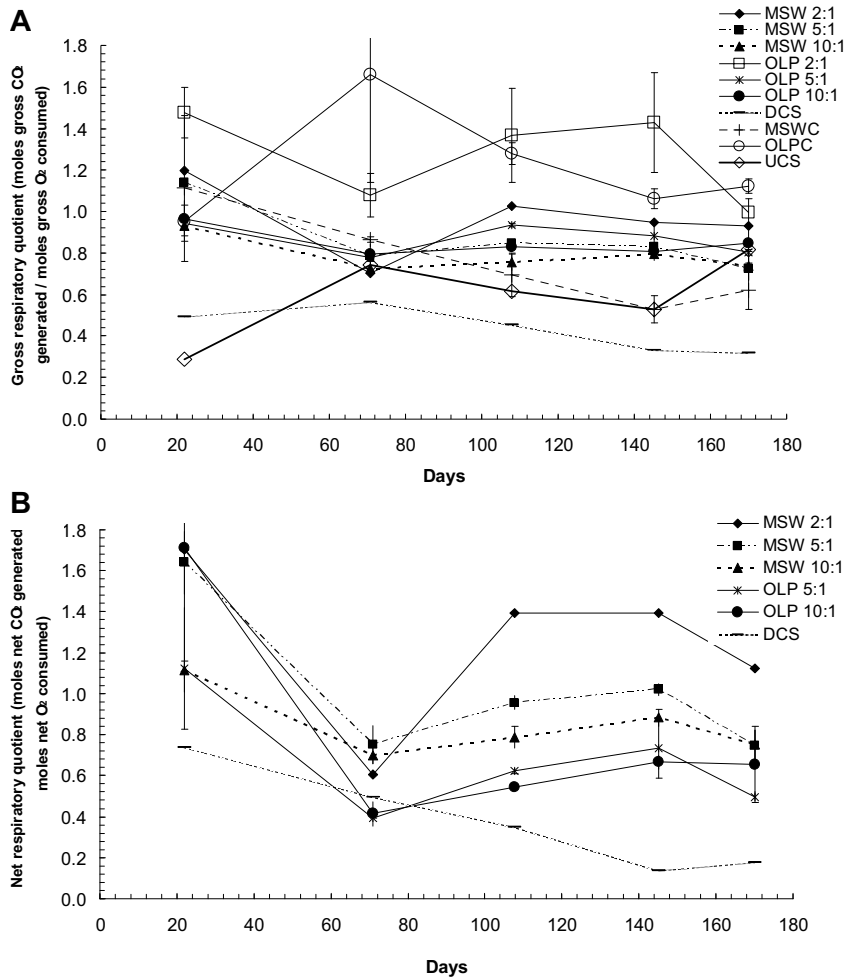


Fig. 4 Gross (A) and net (B) respiratory quotients versus time. Values are means ± one standard deviation.

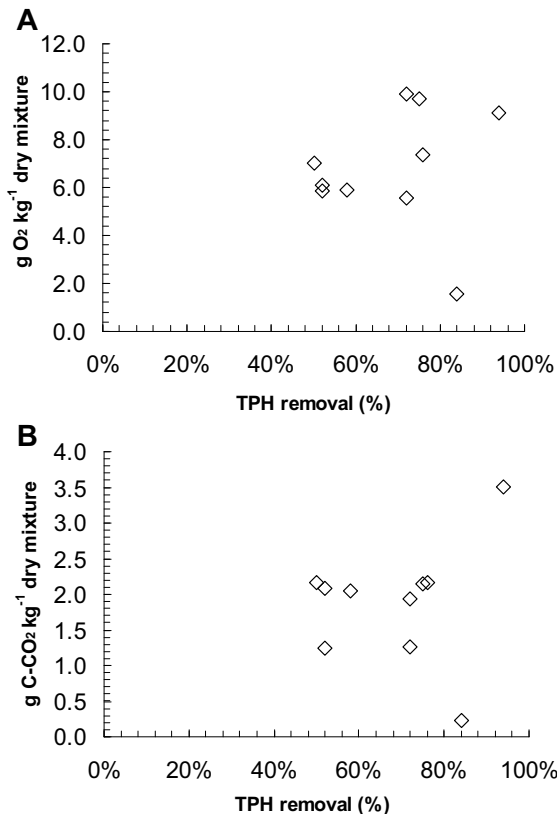


Fig. 5 Net oxygen consumption (A) and net CO<sub>2</sub> generation (B) versus TPH removal after 170 days.

OLP 2: 1 run that had a negative net respiration activity. Net respiration activities and TPH removals were both higher in the MSW 10: 1 run compared to the MSW 5: 1 run. The OLP 5: 1 run had a higher respiration activity and a higher average TPH removal compared to the OLP 10: 1 run.

The positive effect of compost addition on diesel degradation can be attributed to the addition of an active microbial population as well as to the addition of a source of nutrients to support microbial growth (Gandolfi *et al.* 2010). The compost addition to the contaminated soil can also lead to sorption of the toxic compounds, which are produced during diesel metabolism, on the compost organic matter, and, therefore, to a toxicity reduction (Gandolfi *et al.* 2010). An additional beneficial effect of compost addition in soils contaminated with organics can be related to the presence of humic matter. Compost humic compounds can aid in the desorption of hydrophobic organic contaminants from the soil (i.e. reduction of the bonds between soil and the organic contaminant), so that the contaminant is eventually available for degradation (Jansen *et al.* 1996; Sayara *et al.* 2010a, 2010b). Finally, the addition of an organic substrate in the mixture could enhance the co-metabolic degradation of diesel by the microbial population present in the compost. Strangely, the DCS alone had one of the highest TPH removals among all runs, which does not agree with its low microbial respiration activity. The diesel removal in that run can be likely attributed to volatilization and not decomposition. This speculation needs further investigation, since volatilization was not quantified in this work.

Fig. 5A shows the net O<sub>2</sub> consumed versus TPH removal and Fig. 5B illustrates the net C-CO<sub>2</sub> generation versus TPH removal. The negative net values are not included in the plots. According to Fig. 5, the correlations are poor, primarily, due to the DCS related values (lowest value in y

axis). If this value is excluded, there appears to be some trend that indicates that as the net microbial respiration activity increases, the TPH removal increases too. This trend is more evident when the net O<sub>2</sub> consumption is used (Fig. 5A) as opposed to the net CO<sub>2</sub> generation (Fig. 5B). According to Table 2, TPH removals were greater than 50% for all mixtures.

## CONCLUSIONS

The addition of both composts to the diesel contaminated soil led to net respiration activities greater than the respiration activity of the DCS alone. This can be likely attributed to an enhanced diesel degradation in the compost amended soils. The addition of MSWC to the diesel contaminated soil, in particular, led to higher net microbial activities compared to the OLPC. In the case of the MSWC, the ratio of 2:1 (dry soil: dry compost) led to the highest net microbial activity and the highest TPH removal (94%). In the case of the OLPC, the ratio 5:1 led to the highest net microbial activity and to an approximately 73% TPH removal. The diesel-contaminated soil alone had the lowest microbial respiration activity and an 84% TPH removal.

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