

This article was downloaded by: [Univ Politec Cat]

On: 31 December 2011, At: 04:46

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Chemistry and Ecology

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gche20>

### Soil texture affects adsorption capacity and removal efficiency of contaminants in ex situ remediation by thermal desorption of diesel-contaminated soils

P. P. Falciglia<sup>a</sup>, M. G. Giustra<sup>a</sup> & F. G.A. Vagliasindi<sup>a</sup>

<sup>a</sup> Department of Civil and Environmental Engineering, University of Catania, Catania, Italy

Available online: 18 Feb 2011

To cite this article: P. P. Falciglia, M. G. Giustra & F. G.A. Vagliasindi (2011): Soil texture affects adsorption capacity and removal efficiency of contaminants in ex situ remediation by thermal desorption of diesel-contaminated soils, *Chemistry and Ecology*, 27:S1, 119-130

To link to this article: <http://dx.doi.org/10.1080/02757540.2010.534087>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Soil texture affects adsorption capacity and removal efficiency of contaminants in *ex situ* remediation by thermal desorption of diesel-contaminated soils

P.P. Falciglia\*, M.G. Giustra and F.G.A. Vagliasindi

*Department of Civil and Environmental Engineering, University of Catania, Catania, Italy*

*(Received 13 January 2010; final version received 19 October 2010)*

Five soil-size aggregate fractions, corresponding to coarse (500–840  $\mu\text{m}$ ), medium (200–350  $\mu\text{m}$ ), fine (75–200  $\mu\text{m}$ ) sand, silt (10–75  $\mu\text{m}$ ) and clay ( $<4 \mu\text{m}$ ), were artificially contaminated with diesel fuel, and thermally treated using a laboratory-scale apparatus to investigate the effects of soil texture on contaminant removal. Specifically, an *ex situ* thermal process was simulated using helium as carrier gas at a pressure of 1.0 atm, a flow rate of 1.5 L·min<sup>-1</sup> and different temperatures (100–300 °C). Soil specimen and carrier gas temperature in different experimental apparatus sections were monitored. The amount of contaminant sorbed and contaminant residual concentration in soil (as *n*-alkanes compounds C<sub>10</sub>–C<sub>25</sub>) were determined by gas chromatography. The main results show that soil texture influences contaminant sorption phenomena and remediation processes in thermal desorption treatment. Contaminant removal was affected by soil texture (variation up to 37.1%), and fine sandy soil exhibited the highest desorption extent of diesel fuel for a thermal treatment of 30 min. Results are of practical interest and may be used in scaling-up and designing of desorption systems for preliminary cost and optimal condition assessment.

**Keywords:** diesel contamination; soil remediation; soil texture; thermal desorption.

### 1. Introduction

The occurrence of soils and groundwater contaminated by petroleum hydrocarbons is a widespread and relevant environmental problem. Investigators have devoted a great deal of effort towards developing efficient and cost-effective remedial technologies, such as biological ones, to deal with hydrocarbon polluted soil [1–3]. Among hydrocarbons, diesel fuel, a complex mixture of saturated (60–80% *n*-alkanes and naphthenes) and aromatic hydrocarbons (20–40%), is often present in environmental matrices as the result of leakage from storage tanks and pipelines or accidental spills.

Although organic compounds could be partially removed by microbial action, biological treatments are not time-effective, particularly at high pollutant concentrations [4,5].

When remediating hydrocarbon polluted soils, *in situ* or *ex situ* thermal desorption [6,7] might represent a viable alternative to attain regulatory limits, especially with respect to efficiency,

---

\*Corresponding author. Email: ppfalci@dica.unict.it

cost and necessary time. According to the treatment temperature, thermal treatments can be classified as low-temperature (100–350 °C) or high-temperature (350–600 °C) thermal desorption, both involving the physical separation of contaminants from the soil, or thermal destruction (600–1000 °C), involving the chemical modification of contaminants. Several studies on thermal desorption treatment have been performed in order to understand the fundamentals of contaminant release [8–10] and to investigate the effects of process physical parameters on the remediation efficiency of hydrocarbon contaminants such as polychlorinated biphenyls (PCBs) [11,12], pentachlorophenols (PCPs) [13], chlorinated solvents [14,15] or several single polycyclic aromatic hydrocarbons (PAHs) [16,17].

However, limited studies have been carried out on thermal desorption of diesel-contaminated soils. Thermal treatment of soil artificially contaminated with fuel oil under rapid heating conditions and high temperatures was investigated by Bucalà et al. [18], assessing the effects of heating rate, final temperature and degree of contamination on per cent removal calculated as weight loss, presenting modelling kinetic data. Piña et al. [19] also studied the effect of the final temperature on the weight loss of uncontaminated and diesel-contaminated soil (2.5% w/w) during thermal desorptive and destructive treatments (200–900 °C). It was found that soil composition and temperature strongly influence the quantity and composition of volatile compounds. Merino and Bucalà [20] assessed the influence of treatment temperature on contaminant removal from a *n*-hexadecane artificially contaminated soil thermally treated at different final temperatures (150–800 °C) for 30 min. Analysis of the light gas released during the treatment indicated that no pyrolysis reaction takes place, confirming that evaporation–desorption of the contaminant is the process that governs the removal phenomena from the soil, and that at ~ 300 °C the contaminant can be removed almost completely from the soil matrix. Moreover, Lee et al. [21], for fluidised thermal desorption treatment of diesel-polluted soil, studied the effects of temperature and heating time on contaminant per cent removal. Results showed that time to achieve the available efficiency depended on temperature and that maximum removal was achieved in 30 min.

The above-mentioned studies were based on the assessment of contaminant removal by means of gravimetric analysis; in addition, the factors affecting the removal of diesel by low temperature have not been thoroughly investigated.

Moreover, it has been shown that the specific surface area of soil fractions, as well as soil texture, influences contaminant soil interaction, sorption phenomena and consequently contaminant removal during biological and chemical–physical decontamination processes. Amellal et al. [22] found that soil texture influenced the bioavailability of PAH within aggregates of polluted soil and consequently their remediation, whereas Lee et al. [23] showed that the effectiveness of surfactant-based remediation could be limited by the presence of fine soils such as silt and clay. Since aspects linked to soil texture have not yet been investigated in thermal treatment of diesel-polluted soil, more laboratory work is needed to understand the limitations of thermal desorption processes.

The objectives of this study were to test a bench-scale apparatus in order to predict optimum conditions for *ex situ* thermal desorption treatment of diesel-polluted soil and to assess the influence of treatment temperature and soil texture on diesel removal in order to guide the design and the scale up of low-temperature desorption systems.

## 2. Materials and methods

### 2.1. Materials

Commercially available diesel fuel (Esso, Italy) (Table 1) was used to artificially contaminate the soils. All chemicals used in the experiments were of analytical reagent quality. Anhydrous sodium

Table 1. Properties of commercial diesel fuel used to artificially contaminate the soil.

Parameter	Value
Density at 25 °C (kg·m <sup>-3</sup> )	900.6
Flash point (°C)	55
Water content (mg·kg <sup>-1</sup> )	200
Evaporation at 250 °C (% v/v)	64
Evaporation at 350 °C (% v/v)	85
Evaporation at 370 °C (% v/v)	95
<i>n</i> -alkanes fraction C <sub>10</sub> –C <sub>25</sub> (%)	39.9
<i>n</i> -alkanes fraction C <sub>10</sub> –C <sub>13</sub> /C <sub>10</sub> –C <sub>25</sub> (%)	37.1
<i>n</i> -alkanes fraction C <sub>14</sub> –C <sub>17</sub> /C <sub>10</sub> –C <sub>25</sub> (%)	41.7
<i>n</i> -alkanes fraction C <sub>18</sub> –C <sub>21</sub> /C <sub>10</sub> –C <sub>25</sub> (%)	16.7
<i>n</i> -alkanes fraction C <sub>22</sub> –C <sub>25</sub> /C <sub>10</sub> –C <sub>25</sub> (%)	4.5

sulphate (Na<sub>2</sub>SO<sub>4</sub>, purity 99%) and *n*-hexane (C<sub>6</sub>H<sub>14</sub>, purity 99%) were purchased from Merck KGaA (Darmstadt, Germany). Activated carbon (RB1) used for the volatile compounds capture system of the experimental apparatus were supplied by Norit Italia S.p.A. (Ravenna, Italy).

## 2.2. Preparation of diesel contaminated soils

Because soil texture influences the contaminant soil interaction in sorption and desorption processes, soils with a wide range of textures were selected for the experiments. Specifically, five soil-size aggregate fractions, corresponding to coarse (500–840 μm), medium (200–350 μm), fine (75–200 μm) silica sand, silt as silica flour (10–75 μm) and clay as kaolin (<4 μm) were used. Soil properties are given in Table 2.

Selected soils were artificially contaminated by diesel fuel at different rates. The contamination procedure [19,24,25] was performed by introducing a pollutant solution of diesel fuel (80 mL) in *n*-hexane (200 mL) into a 500 mL round-bottom flask containing the selected soil samples (120 g) to obtain a representative contaminant concentration for each type of soil. Soil and pollutant solution were shaken for 48 h using an orbital shaker, then the *n*-hexane solvent was removed in 1 h, using a rotary evaporator, under slight vacuum, to obtain a homogeneous powdered soil. The contaminated soils were kept in a closed vessel and stored in a dark room at 4 °C then analysed by *n*-hexane extraction and subsequently by gas chromatography (GC) for contaminant content, before being thermally treated. Triplicates of the contamination procedure were carried out, and mean and standard deviation values of sorbed contaminant concentration were calculated.

Table 2. Properties and characteristics of selected soils.

Parameter	Coarse sand (500–840 μm)	Medium sand (200–350 μm)	Fine sand (75–200 μm)	Silt (10–75 μm)	Clay (<4 μm)
Soil mineral	Silica sand	Silica sand	Silica sand	Silica flower	Kaolin
pH	8.31	8.73	8.72	8.65	8.39
Bulk density (g·cm <sup>-3</sup> )	1.23	1.42	1.36	1.30	1.00
Porosity (%)	35.0	42.5	32.5	33.3	60.2
Specific surface area (m <sup>2</sup> ·g <sup>-1</sup> )	0.6	2.11	3.45	12.7	20.01
Hydraulic conductivity (cm·s <sup>-1</sup> )	0.67	1.2 × 10 <sup>-2</sup>	5.0 × 10 <sup>-2</sup>	2.1 × 10 <sup>-4</sup>	10 <sup>-6</sup>
Organic matter (g·kg <sup>-1</sup> )	3.40	2.62	3.55	3.84	3.29
Moisture content (%)	0.9	1.0	1.2	1.8	2.1

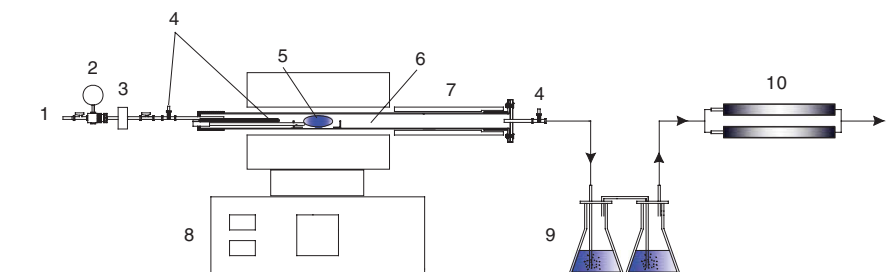


Figure 1. Schematics of the experimental apparatus. (1) Gas carrier inlet, (2) pressure gauge, (3) flowmeter, (4) gas type-K thermocouple, (5) soil sample, (6) quartz tube, (7) post-heater, (8) tubular electric furnace, (9) hexane traps, (10) activated carbon.

### 2.3. Experimental apparatus and procedures

Contaminated soil samples were treated simulating *ex situ* thermal process conditions using a bench-scale apparatus (Figure 1), which included the components listed below:

- input gas transport section in pressure (with flowmeter and pressure gauge);
- tubular electric furnace (Carbolite MTF 12/38/400, maximum power 1.5 kW) that could reach a maximum temperature of 1200 °C;
- quartz cylindrical tube (inner diameter: 30 mm, length: 450 mm), where the polluted soil sample was placed into an axially isothermal temperature region of the oven;
- heating electric band at post heater section;
- volatile organic compounds (VOCs) capture system (*n*-hexane traps and Norit RB1 activated carbon filters);
- 4 k-type thermocouples system to measure soil and gas carrier temperature connected to a laptop for data recording.

A preliminary test was carried out, using a sandy soil (75–200  $\mu\text{m}$ ) and helium as carrier at a temperature of 25 °C and a pressure of 1.0 atm, in order to assess the influence of the gas flow rate on removal process. A gas carrier flow ( $Q$ ) range of 0.2–2.5  $\text{L}\cdot\text{min}^{-1}$  and an oven temperature ( $T$ ) of 100, 175 and 300 °C for a treatment time ( $t$ ) of 30 min (close to the minimum value recommended for indirectly heated desorber units) were used. Gas and soil temperatures were monitored. After treatment (in triplicate), mean and standard deviation values of contaminant residual concentrations ( $C_r$ ) were calculated for each selected soil.

After preliminary tests, all selected soils were thermally treated using the bench-scale laboratory at  $Q = 1.5 \text{ L}\cdot\text{min}^{-1}$  (25 °C), at a pressure of 1.0 atm and temperatures of 100, 150, 175, 250 or 300 °C, to assess the influence of soil texture on diesel removal. A flow rate of 1.5  $\text{L}\cdot\text{min}^{-1}$  was selected because, based on preliminary tests results, it assures minimal residual contaminant concentration and optimal gas temperature conditions inside the quartz tube.

In the experiments, once the electric oven reached the desired temperature (100, 150, 175, 250 or 300 °C), the quartz tube was purged with helium for 10 min, maintaining the selected temperature without cooling the tube, then 5 g of the polluted soil sample was placed inside the oven and heated for 30 min. After treatment, soil samples were removed from the apparatus, cooled at room temperature (20 °C) and stored in a dark cold room at 4 °C prior to analysis. During the experiments, soil and gas temperature in three different sections of the apparatus (inlet section, inside the quartz tube, outlet section) were monitored by means of the k-thermocouples system. Triplicates of the thermal treatment procedure were carried out and mean and standard deviation values of contaminant residual concentrations ( $C_r$ ) as a function of the treatment temperature were calculated for each selected soil.

Percent removal ( $R$ ) was also calculated by the following expression:

$$R(\%) = \frac{C_i - C_r}{C_i} \times 100, \quad (1)$$

where  $C_i$  is the initial contaminant concentration in soil ( $\text{mg}\cdot\text{kg}^{-1}$ ) and  $C_r$  is the residual concentration of contaminant in soil after the thermal treatment ( $\text{mg}\cdot\text{kg}^{-1}$ ).

#### 2.4. Extraction and analysis

For each 5 g sample treated, a 2 g subsample was analysed for hydrocarbon concentration. The subsample was mixed with anhydrous sodium sulphate (4:5 w/w), then placed with  $n$ -hexane in a Soxhlet extractor for 6 h. Five millilitres of effluent were mixed with 2 mL of  $n$ -hexane in a separate funnel, stirred for 2 min then left at rest for separation. The supernatant phase was mixed with internal standard (ISM-560 Ultra Scientific, USA) and analysed by GC.

Owing to their high proportion (40%) in diesel fuel,  $n$ -alkanes ( $C_{10}$ – $C_{25}$ ) were chosen as representative components [26], and their total concentration in spiked and treated soil samples was taken as that of diesel fuel and expressed as  $\text{mg}\cdot\text{kg}^{-1}$  soil.

The concentration of  $n$ -alkanes in soil samples was measured by GC (Agilent Technologies 6890N) equipped with a mass spectrometer (Agilent Technologies 5975) using the US-EPA 8270-C method. A capillary column (HP-5, 30 m length  $\times$  0.32 mm ID  $\times$  0.25  $\mu\text{m}$  film thickness) was used. The GC was operated with a helium carrier gas flow rate of  $1.5 \text{ mL} \cdot \text{min}^{-1}$  and the oven temperature programme starting at  $40^\circ\text{C}$  (held for 4 min) and increasing at a rate of  $10^\circ\text{C} \cdot \text{min}^{-1}$  to a maximum temperature of  $310^\circ\text{C}$ . The temperature of the injector was  $270^\circ\text{C}$ .

### 3. Results and discussion

#### 3.1. Preliminary test

Preliminary test results highlight that the diesel residual concentration in soil ( $C_r$ ) at different oven temperatures (100, 175 and  $300^\circ\text{C}$ ) (Figure 2) was dependent on the gas flow rate ( $Q$ ) and, for all tested temperatures, residual diesel concentration function has a parabolic shape versus gas flow rates. Lowest  $C_r$  variation was observed for  $t = 100^\circ\text{C}$ , and minimal values of  $C_r$  were observed, for all tested temperatures, at  $Q = 1.5 \text{ L} \cdot \text{min}^{-1}$ .

Such behaviour may be attributed to a gas ventilation effect that increased the contaminant desorption, which, for values  $> 1.5 \text{ L} \cdot \text{min}^{-1}$ , reduced the temperature inside the quartz tube during treatment, causing an increase in the residual concentration. A tube gas temperature decrease (Figure 3) was indeed observed with an increasing gas flow rate with temperature values, at the end of treatment, over a wide range ( $225$ – $260^\circ\text{C}$ ). Based on the obtained results, the gas flow rate used in the main thermal treatments was  $1.5 \text{ L} \cdot \text{min}^{-1}$ .

#### 3.2. Temperature monitoring

Figure 4 shows the temperature profiles recorded during thermal treatment for all tested soils, considering an oven temperature ranging from 100 to  $300^\circ\text{C}$ . In all cases, soil temperature increased with treatment time, reaching the oven temperature in relatively less time the higher the oven temperature. For all tested temperatures, highest values were observed for clayey soils, whereas the lowest values were for coarse sand, with a difference up to  $20^\circ\text{C}$  being observed during the

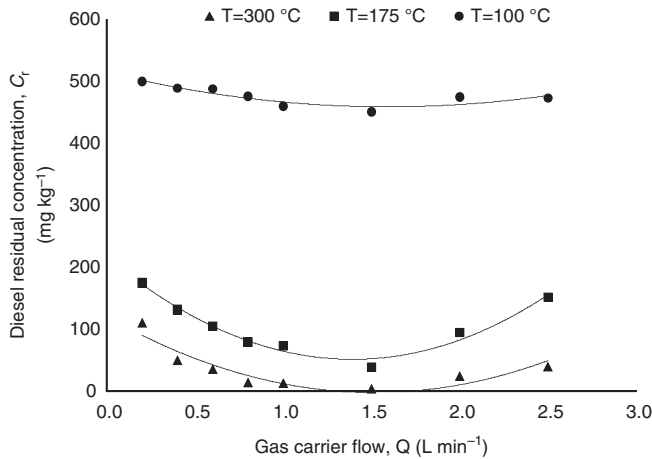


Figure 2. Influence of gas carrier flow ( $Q$ ) on diesel residual concentration ( $C_r$ ) in preliminary thermal treatment at  $T = 100$ ,  $175$  and  $300$  °C (pressure 1 atm).  $T = 100$  °C:  $y = 21.974x^2 - 69.892x + 514.75$  ( $R^2 = 0.8033$ );  $T = 175$  °C:  $y = 85.078x^2 - 236.99x + 216.64$  ( $R^2 = 0.9683$ );  $T = 300$  °C:  $y = 53.381x^2 - 161.82x + 120.65$  ( $R^2 = 0.8598$ ).

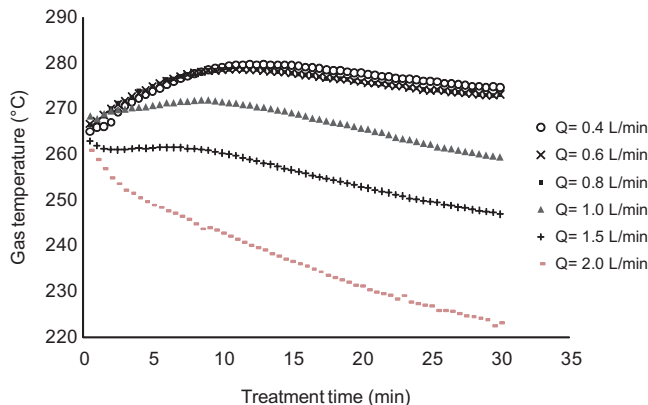


Figure 3. Influence of gas carrier flow ( $Q$ ) on tube gas temperature in preliminary thermal treatment at  $300$  °C (pressure 1 atm).

pre-equilibrium phase (in which none of the soils reached the temperature of the oven). This specific behaviour might be due to the thermal transfer capability, defined as specific heat capacity  $C_s$ , which is highest for fine particles soils such as clays ( $0.92 \text{ KJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ) and lowest for sand ( $0.80 \text{ KJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ). Highest hydraulic conductivity of coarse sand ( $10^{-2} \text{ cm}\cdot\text{s}^{-1}$ ) further influenced the cooling process of the soil sample during the thermal treatment resulting in a limitation of the heat transfer and consequently a decrease in the soil temperature.

### 3.3. Contaminant removal

After the contamination procedure, sorbed diesel on soil ( $C_i$ ), as  $n$ -alkanes fractions ( $C_{10}$ – $C_{25}$ ), for all spiked soils was measured and the results are illustrated in Table 3. Moreover, for all the investigated soils, the percentage distribution of single  $n$ -alkanes fractions (calculated as the ratio between the concentration of the single  $n$ -alkanes fraction  $C_n$  and the total concentration  $C_{10}$ – $C_{25}$ ) presented the highest percentage for the fractions ranging from  $C_{14}$  to  $C_{17}$  with a typical

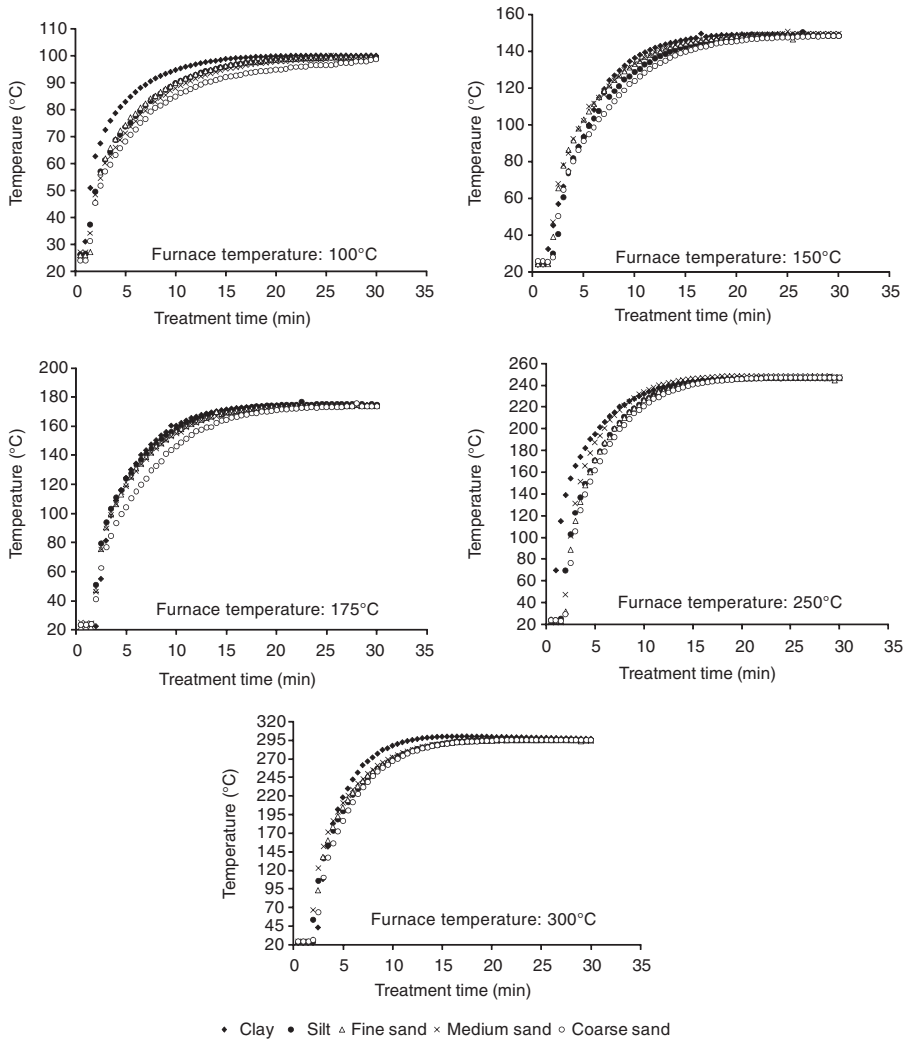


Figure 4. Soil temperature profiles of the five soil size aggregate fractions for 100, 125, 150, 175, 250 and 300 °C oven treatment temperature ( $T$ ).

'bell-curve type' shape. However, it did not reflect the percentage composition of diesel used for the contamination procedure ( $C_{10}$ – $C_{13}$  fraction was 37.1% for diesel and ranged between 13.9 and 28.2% for soils). This indicated that all fractions did not adsorb similarly onto the different soil matrices and affinity was observed between specific  $n$ -alkanes fraction and soil. The  $C_{10}$ – $C_{11}$  fraction was adsorbed much more in silty and clay soils compared with sandy soils.

Residual diesel concentration on soil ( $C_r$ ) and the diesel per cent removal ( $R$ ) at temperatures of 100, 150, 175, 250 and 300 °C are reported in Figure 5. Residual diesel concentration ( $C_r$ ) as  $n$ -alkanes fractions after the treatment are also reported in Table 4. Residual contaminant concentration decreased with increasing temperature for all cases, and it is clear that exposure to a temperature of 250 °C eliminated diesel from the soil. At lower temperatures,  $C_r$  was higher for fine material than for coarse sand. A temperature of 175 °C was sufficient to reach low  $C_r$  values ( $\sim 100$  mg·kg $^{-1}$ ) for all types of soil except clay. For all tested temperatures, maximum  $R$  values were observed for fine sandy soils, whereas the lowest values resulted for coarse sand.



Table 3. Distribution of sorbed diesel ( $C_i$ ) as  $n$ -alkanes fractions in all soils.

$n$ -alkanes fraction	Coarse sand (500–840 $\mu\text{m}$ )		Medium sand (200–350 $\mu\text{m}$ )		Fine sand (75–200 $\mu\text{m}$ )		Silt (10–75 $\mu\text{m}$ )		Clay (<4 $\mu\text{m}$ )	
	$\text{mg}\cdot\text{kg}^{-1}$	%	$\text{mg}\cdot\text{kg}^{-1}$	%	$\text{mg}\cdot\text{kg}^{-1}$	%	$\text{mg}\cdot\text{kg}^{-1}$	%	$\text{mg}\cdot\text{kg}^{-1}$	%
C <sub>10</sub>	0.0 ± 0.0	0.0	0.0 ± 0.0	0.0	16.7 ± 4.7	0.9	180.5 ± 9.7	6.1	295.2 ± 47.6	7.4
C <sub>11</sub>	19.3 ± 2.1	2.8	9.3 ± 0.7	1.1	63.2 ± 14.0	3.4	168.7 ± 6.1	5.7	239.3 ± 32.3	6.0
C <sub>12</sub>	42.0 ± 3.2	6.1	39.8 ± 3.8	4.7	113.4 ± 24.6	6.1	207.1 ± 4.4	7.0	279.2 ± 36.0	7.0
C <sub>13</sub>	57.9 ± 4.5	8.4	68.5 ± 2.9	8.1	150.6 ± 28.6	8.1	233.8 ± 1.7	7.9	311.1 ± 38.1	7.8
C <sub>14</sub>	75.8 ± 6.0	11.0	93.9 ± 6.5	11.1	198.9 ± 37.1	10.7	295.9 ± 16.0	10.0	398.9 ± 45.9	10.0
C <sub>15</sub>	83.4 ± 5.1	12.1	101.5 ± 5.1	12.0	223.6 ± 40.2	12.0	319.6 ± 7.2	10.8	434.8 ± 54.3	10.9
C <sub>16</sub>	77.2 ± 2.9	11.2	96.4 ± 4.8	11.4	206.3 ± 32.6	11.1	298.9 ± 7.5	10.1	398.9 ± 48.5	10.0
C <sub>17</sub>	66.8 ± 2.9	9.7	87.1 ± 5.4	10.3	182.2 ± 30.4	9.8	254.5 ± 10.2	8.6	335.5 ± 37.6	8.4
C <sub>18</sub>	57.2 ± 5.0	8.3	73.7 ± 4.2	8.7	154.3 ± 24.5	8.3	216.0 ± 14.4	7.3	287.2 ± 38.0	7.2
C <sub>19</sub>	49.6 ± 2.3	7.2	65.1 ± 2.2	7.7	133.8 ± 19.4	7.2	189.4 ± 6.8	6.4	247.3 ± 27.8	6.2
C <sub>20</sub>	45.7 ± 3.1	6.6	60.1 ± 5.1	7.1	119.0 ± 17.2	6.4	171.6 ± 11.5	5.8	223.4 ± 37.9	5.6
C <sub>21</sub>	37.2 ± 2.3	5.4	49.1 ± 3.9	5.8	96.7 ± 13.3	5.2	139.1 ± 8.4	4.7	179.5 ± 26.5	4.5
C <sub>22</sub>	29.6 ± 1.6	4.3	39.8 ± 3.1	4.7	78.1 ± 10.2	4.2	112.4 ± 5.8	3.8	139.6 ± 16.0	3.5
C <sub>23</sub>	22.7 ± 1.2	3.3	29.6 ± 1.6	3.5	61.3 ± 8.6	3.3	85.8 ± 4.4	2.9	107.7 ± 10.8	2.7
C <sub>24</sub>	15.2 ± 1.2	2.2	20.3 ± 0.9	2.4	39.0 ± 3.5	2.1	53.4 ± 2.4	1.8	67.8 ± 6.2	1.7
C <sub>25</sub>	9.6 ± 0.9	1.4	11.8 ± 0.6	1.4	22.3 ± 2.6	1.2	32.5 ± 1.7	1.1	39.9 ± 3.5	1.0
C <sub>10</sub> –C <sub>25</sub>	689.2	100.0	846.0	100.0	1859.4	100.0	2959.2	100.0	3985.3	100.0

Note:  $\pm$  represents the standard deviation based on triplicate experiments.

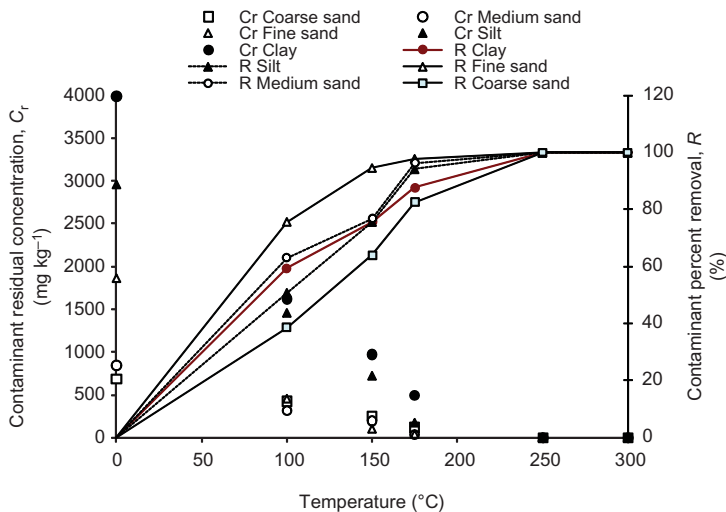


Figure 5. Residual contaminant concentration ( $C_r$ ) and per cent removal ( $R$ ) for sandy, silty and clayey soils and for 100, 125, 150, 175, 250 and 300 °C oven treatment temperature.  $C_r$  at  $T = 0$  °C is the initial concentration ( $C_i$ ) before thermal treatment.

Overall, a maximum change in  $R$  (37.1%), due to the variation of soil texture, was observed at the lowest treatment temperature (100 °C). Specifically, for fine sand, high  $R$  was reached also at lower temperatures (i.e. 76% at 100 °C and 95% at 150 °C). The lowest value of  $R$ , observed for coarse sand, might be due to the cooling process, resulting in a limitation in the heat transfer and consequently, as reported in monitoring data, in lowest soil temperature for coarse sand. Thus  $R$  was not directly proportional to soil texture.

Table 4 shows that a preferential effect of the thermal treatment on the various  $n$ -alkanes present in diesel occurred. The distribution of the  $n$ -alkenes in soil after heating at different temperatures did not reflect the initial distribution ( $C_i$ ) of sorbed diesel in all soils. Therefore, the

Table 4. Distribution of residual diesel ( $C_r$ ) as  $n$ -alkanes fractions after the treatment ( $T = 100, 150, 175$  and  $250^\circ\text{C}$ ) in all soils.

$n$ -alkanes fraction	Coarse sand (500–840 $\mu\text{m}$ ) ( $\text{mg}\cdot\text{kg}^{-1}$ )				Medium sand (200–350 $\mu\text{m}$ ) ( $\text{mg}\cdot\text{kg}^{-1}$ )			
	$T$ ( $^\circ\text{C}$ )							
	100	150	175	250	100	150	175	250
$C_{10}$ – $C_{11}$	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0
$C_{12}$ – $C_{13}$	15.1 $\pm$ 2.1	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	2.7 $\pm$ 0.4	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0
$C_{14}$ – $C_{15}$	89.3 $\pm$ 8.4	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	38.0 $\pm$ 4.1	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0
$C_{16}$ – $C_{17}$	107.8 $\pm$ 9.2	24.7 $\pm$ 0.9	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	69.5 $\pm$ 5.1	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0
$C_{18}$ – $C_{19}$	84.6 $\pm$ 6.5	63.9 $\pm$ 3.3	10.9 $\pm$ 1.1	0.0 $\pm$ 0.0	71.3 $\pm$ 6.1	13.8 $\pm$ 1.4	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0
$C_{20}$ – $C_{21}$	66.3 $\pm$ 5.5	77.5 $\pm$ 6.9	43.7 $\pm$ 3.2	0.0 $\pm$ 0.0	64.4 $\pm$ 5.8	54.8 $\pm$ 5.6	2.7 $\pm$ 0.1	0.0 $\pm$ 0.0
$C_{22}$ – $C_{23}$	41.2 $\pm$ 3.6	55.9 $\pm$ 6.3	42.3 $\pm$ 3.9	0.0 $\pm$ 0.0	45.2 $\pm$ 3.3	78.7 $\pm$ 6.4	10.2 $\pm$ 1.3	0.0 $\pm$ 0.0
$C_{24}$ – $C_{25}$	18.6 $\pm$ 2.1	26.1 $\pm$ 2.2	23.0 $\pm$ 3.1	0.0 $\pm$ 0.0	21.1 $\pm$ 1.7	48.5 $\pm$ 5.8	18.7 $\pm$ 1.4	0.0 $\pm$ 0.0
$C_{10}$ – $C_{25}$	422.9	248.2	119.9	0.0	312.3	195.8	31.6	0.0
	Fine sand (75–200 $\mu\text{m}$ ) ( $\text{mg}\cdot\text{kg}^{-1}$ )				Silt (10–75 $\mu\text{m}$ ) ( $\text{mg}\cdot\text{kg}^{-1}$ )			
$C_{10}$ – $C_{11}$	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	5.5 $\pm$ 0.6	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0
$C_{12}$ – $C_{13}$	27.9 $\pm$ 1.8	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	95.0 $\pm$ 8.7	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0
$C_{14}$ – $C_{15}$	93.8 $\pm$ 7.2	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	287.6 $\pm$ 27.1	2.3 $\pm$ 0.4	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0
$C_{16}$ – $C_{17}$	109.7 $\pm$ 9.1	6.9 $\pm$ 4.2	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	350.3 $\pm$ 33.9	57.7 $\pm$ 4.8	6.1 $\pm$ 0.5	0.0 $\pm$ 0.0
$C_{18}$ – $C_{19}$	88.4 $\pm$ 6.8	22.5 $\pm$ 3.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	286.0 $\pm$ 26.6	179.9 $\pm$ 14.8	26.1 $\pm$ 3.7	0.0 $\pm$ 0.0
$C_{20}$ – $C_{21}$	68.5 $\pm$ 5.6	30.2 $\pm$ 2.0	2.8 $\pm$ 0.2	0.0 $\pm$ 0.0	223.2 $\pm$ 24.1	220.7 $\pm$ 20.7	47.1 $\pm$ 5.5	0.0 $\pm$ 0.0
$C_{22}$ – $C_{23}$	43.2 $\pm$ 5.1	25.6 $\pm$ 1.8	16.4 $\pm$ 1.1	0.0 $\pm$ 0.0	145.1 $\pm$ 13.5	177.2 $\pm$ 20.0	56.3 $\pm$ 5.9	0.0 $\pm$ 0.0
$C_{24}$ – $C_{25}$	19.5 $\pm$ 1.2	13.8 $\pm$ 0.7	19.6 $\pm$ 1.3	0.0 $\pm$ 0.0	62.7 $\pm$ 4.8	82.5 $\pm$ 5.5	35.4 $\pm$ 2.7	0.0 $\pm$ 0.0
$C_{10}$ – $C_{25}$	451.0	99.1	38.8	0.0	1455.5	720.2	171.0	0.0
	Clay (<4 $\mu\text{m}$ ) ( $\text{mg}\cdot\text{kg}^{-1}$ )							
$C_{10}$ – $C_{11}$	51.9 $\pm$ 3.6	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0				
$C_{12}$ – $C_{13}$	177.2 $\pm$ 13.2	3.0 $\pm$ 0.1	0.0 $\pm$ 0.0	0.0 $\pm$ 0.0				
$C_{14}$ – $C_{15}$	369.6 $\pm$ 25.5	55.4 $\pm$ 5.6	8.4 $\pm$ 8.9	0.0 $\pm$ 0.0				
$C_{16}$ – $C_{17}$	364.8 $\pm$ 39.9	187.4 $\pm$ 16.5	52.0 $\pm$ 3.8	0.0 $\pm$ 0.0				
$C_{18}$ – $C_{19}$	271.7 $\pm$ 31.7	249.1 $\pm$ 22.8	92.9 $\pm$ 7.6	0.0 $\pm$ 0.0				
$C_{20}$ – $C_{21}$	200.1 $\pm$ 20.8	237.6 $\pm$ 23.6	131.4 $\pm$ 14.7	0.0 $\pm$ 0.0				
$C_{22}$ – $C_{23}$	130.6 $\pm$ 14.6	166.5 $\pm$ 12.4	136.9 $\pm$ 14.6	0.0 $\pm$ 0.0				
$C_{24}$ – $C_{25}$	54.4 $\pm$ 3.3	73.8 $\pm$ 5.9	73.2 $\pm$ 7.9	0.0 $\pm$ 0.0				
$C_{10}$ – $C_{25}$	1620.3	972.8	494.8	0.0				

Note:  $\pm$  represents the standard deviation based on triplicate experiments.

thermal treatment of the soil produced a total desorption of the lightest  $n$ -alkanes fractions and the range of  $n$ -alkanes fractions removed depended on the treatment temperature and the nature of the soils. For example, the treatment of the fine sandy soil at  $175^\circ\text{C}$  produced a total removal up to  $C_{18}$ – $C_{19}$  fractions, whereas the same treatment of the clayey soil produced a removal up to  $C_{12}$ – $C_{13}$  fractions. This indicates that a very low temperature might also remove the lightest  $n$ -alkanes fractions, which presents the higher risk for the environment.

Our results are in agreement with Merino and Bucalà [20] and Lee et al. [21] who showed that at  $\sim 300^\circ\text{C}$ ,  $n$ -hexadecane and diesel can be removed completely from a fine sandy soil.

The influence of soil texture on organic contaminant removal observed for the performed experiment is in the same range as that reported in previous literature findings on biological and chemical physical treatments. Lee et al. [23] demonstrated that the remediation efficiency of a clayey soil polluted by toluene or TCB was reduced by  $\sim 30\%$  with respect to a sandy soil, whereas Jung et al. [27] reported a variation in  $n$ -hexadecane removal of  $\sim 40\%$  between sandy and clayey soils for an integrated ozonation and biodegradation treatment.

Our results confirm that thermal desorption reduced hydrocarbon concentration to a very low level in a short time, and this is hardly achievable by other treatments such as oxidation with chemical agents or ozone. Comparable removal efficiencies can be reached using technologies that require a long time, e.g. bioremediation or high consumption of energy or costs, e.g. soil washing by surfactants [26], electrokinetic–Fenton oxidation [28] or microwave thermal remediation [29]. For example, Wan Namkoong et al. [30] observed very high per cent removal (up to 99.6%) for the bioremediation of diesel-contaminated soil with composting over a 30-day treatment period, whereas Li et al. [31] reported that for a sandy soil spiked with diesel fuel at different rates ranging from 500 to 50,000 mg·kg<sup>-1</sup>, the percentage of total petroleum hydrocarbon (TPH) natural biodegradation, for an incubation period of 110 days, reached a maximum value of ~ 73% for the lowest contamination levels. Do et al. [32] showed that an *in situ* chemical oxidation treatment of a diesel-polluted soil at 5000 mg·kg<sup>-1</sup>, using peroxymonosulphate/cobalt (PMS/CoII), was characterised by a maximum contaminant degradation around 47% and that a sequential injection treatment using high amount of chemicals was needed to reach a contaminant degradation of 88%. Moreover, Lee et al. [4] found that a diesel removal of 40% was obtainable by ozonation of a heavily contaminated sandy soil (17,000 mg·kg<sup>-1</sup>).

In terms of costs, the US Environmental Protection Agency [33], for the treatment of VOC hydrocarbon polluted soil, reported costs from US\$ 24 to 380 ton<sup>-1</sup> for *ex situ* bioremediation and from US\$ 75 to 560 ton<sup>-1</sup> for thermal desorption. Therefore, for the high removal and the energy required (that based on our findings could be further minimised), low temperature thermal desorption appears to be a better choice for remediation of the types of soils tested here and for the interventions where brief periods of time are required.

#### 4. Conclusions

To investigate the effects of soil texture on contaminant sorption and removal, five soil-size aggregate fractions, corresponding to coarse, medium, fine sand, silt and clay, were artificially polluted with diesel fuel, and thermally treated at different temperatures, using a laboratory-scale apparatus. The following conclusions have been drawn based on experimental results and discussion:

- (1) The developed bench-scale apparatus can be used to optimise operating conditions of thermal desorption processes for the treatment of organic contaminants-polluted soil.
- (2) Desorption efficiency was affected by the soil texture (variation up to 37.1%), and fine sandy soil exhibited the highest desorption extent of diesel fuel for a thermal treatment of 30 min.
- (3) A temperature of 175 °C was sufficient to reach low residual concentration (~ 100 mg·kg<sup>-1</sup>) for all types of soil except for clay, which needs a temperature of 250 °C.
- (4) For remediation interventions in which brief periods are required, low-temperature thermal desorption appears to be a better choice for remediation of diesel-polluted soils due to their high removal and costs, which may be reduced further by low temperatures and time required.
- (5) Results are of practical interest and may be used in scaling-up and designing desorption systems for preliminary cost and optimal condition assessment.

#### Acknowledgements

This research was funded by the Italian Ministry of Education, University and Research (MIUR), 'Research Program of Relevant National Interest', Fiscal year 2006 (Criteria and tools for environmental remediation and functional regeneration of contaminated sites) and partially by Catanzaro Costruzioni S.r.l., Italy.

## References

- [1] L.M. Barahona, R.R. Vazquez, M.H. Velasco, C.V. Jarquin, O.Z. Pérez, A.M. Cantú, and A. Albores, *Diesel removal from contaminated soils by biostimulation and supplementation with crop residues*, Appl. Soil Ecol. 27 (2004), pp. 165–175.
- [2] F.M. Bento, A.O. Camargo, B.C. Okeke, and W.T. Frankenberger, *Comparative bioremediation of soil contaminated with diesel oil by natural attenuation, biostimulation and bioaugmentation*, Bioresour. Technol. 96 (2005), pp. 1049–1055.
- [3] R. Boopathy, *Anaerobic biodegradation of no. 2 diesel fuel in soil: a soil column study*, Bioresour. Technol. 94 (2004), pp. 143–151.
- [4] B.T. Lee and K.W. Kim, *Ozonation of diesel fuel in unsaturated porous media*, Appl. Geochem. 17 (2002), pp. 1165–1170.
- [5] L. Bonomo, *Bonifica di siti contaminati – Caratterizzazione e tecnologie di risanamento*, McGraw-Hill, Milan, 2005.
- [6] US EPA, *In-situ treatment technologies for contaminated soil, EPA/542/F-06/013*, Soil Waste and Emergency Response, US EPA, Washington DC, 2006.
- [7] US EPA, *Innovative SITE remediation technology, Thermal desorption, EPA/542/B-97/008*, US EPA, Washington DC, 1998.
- [8] J.S. Lighty, G.D. Silcox, and D.W. Pershing, *Fundamentals for the thermal remediation of contaminated soils. Particle and bed desorption models*, Environ. Sci. Technol. 24 (1990), pp. 750–757.
- [9] P. Gilot, J.B. Howard, and W.A. Peters, *Evaporation phenomena during thermal decontamination of soils*, Environ. Sci. Technol. 31 (1997), pp. 461–466.
- [10] R.B. Keyes and G.D. Silcox, *Fundamental study of the thermal desorption of toluene from montmorillonite clay particles*, Environ. Sci. Technol. 28 (1994), pp. 840–849.
- [11] V. Risoul, V. Renaud, G. Trouvé, and P. Gilot, *A laboratory pilot study of thermal decontamination of soil polluted by PCBs. Comparison with thermogravimetric analysis*, Waste Manage. 22 (2002), pp. 61–72.
- [12] E.E. Uzgiris, W.A. Edelstein, H.R. Philipp, and I.E.T. Iben, *Complex thermal desorption of PCBs from soil*, Chemosphere 30 (1994), pp. 377–387.
- [13] K.K.C. Tse and S.L. Lo, *Desorption kinetics of PCP-contaminated soil: effect of temperature*, Water Res. 36 (2002), pp. 284–290.
- [14] V. Risoul, C. Pichon, G. Trouvé, W.A. Peters., P. Gilot, and G. Prado, *Thermogravimetric study of thermal decontamination of soil polluted by hexachlorobenzene, 4-chlorobiphenyl, naphthalene, or n-decane*, J. Hazard. Mater. B64 (1999), pp. 295–311.
- [15] C.E. George, D.E. Azwell, P.A. Adams, and G.V.N. Rao, *Evaluation of steam as a sweep gas in low temperature thermal desorption processes used for contaminated soil clean up*, Waste Manage. 15 (1995), pp. 407–416.
- [16] R.C. Chawla, A. Pourhashemi, *Contaminant removal from dry and wet sands by thermal desorption*, Int. J. Environ. Waste Manage. 1 (2006), pp. 39–48.
- [17] V. Risoul, H. Richter, A.L. Lafleur, E.F. Plummerb, P. Gilot, J.B. Howard, and W.A. Peters, *Effects of temperature and soil components on emissions from pyrolysis of pyrene-contaminated soil*, J. Hazard. Mater. B126 (2005), pp. 128–140.
- [18] V. Bucalá, H. Saito, J.B. Howard, and W.A. Peters, *Thermal treatment of fuel oil-contaminated soils under rapid heating conditions*, Environ. Sci. Technol. 28 (1994), pp. 1801–1807.
- [19] J. Pina, J. Merino, A.F. Errazu, and V. Bucalá, *Thermal treatment of soil contaminated with gas oil: influence of soil composition and treatment temperature*, J. Hazard. Mater. B94 (2002), pp. 273–290.
- [20] J. Merino and V. Bucalá, *Effect of temperature on the release of hexadecane from soil by thermal treatment*, J. Hazard. Mater. 143 (2007), pp. 455–461.
- [21] J.K. Lee, D. Parka, B. Kimb, J. Dongb, and S. Lee, *Remediation of petroleum-contaminated soils by fluidized thermal*, Waste Manage. 18 (1998), pp. 503–507.
- [22] N. Amellal, J.M. Portal, and J. Berthelin, *Effect of soil structure on the bioavailability of polycyclic aromatic hydrocarbons within aggregates of a contaminated soil*, Appl. Geochem. 16 (2001), pp. 1611–1619.
- [23] D.H. Lee, R.D. Cody, D.J. Kim, and S. Choi, *Effect of soil texture on surfactant-based remediation of hydrophobic organic-contaminated soil*, Environ. Int. 27 (2002), pp. 681–688.
- [24] B.T. Lee and K.W. Kim, *Ozonation of diesel fuel in unsaturated porous media*, Appl. Geochem. 17 (2002), pp. 1165–1170.
- [25] S.N. Chesler, A.P. Emery, and D.L. Duerwer, *Recovery of diesel fuel from soil by supercritical fluid extraction-gas chromatography*, J. Chromatogr. 790 (1997), pp. 125–130.
- [26] R. Khalladi, O. Benhabiles, F. Bentahar, and N. Moulai-Mostefa, *Surfactant remediation of diesel polluted soil*, J. Hazard. Mater. 164 (2009), pp. 1179–1184.
- [27] H. Jung, K.D. Sohn, B. Neppolian, and H. Choi, *Effect of soil organic matter (SOM) and soil texture on the fatality of indigenous microorganisms in integrated ozonation and biodegradation*, J. Hazard. Mater. 150 (2008), pp. 809–817.
- [28] T.T. Tsai, J. Sah, and C.M. Kao, *Application of iron electrode corrosion enhanced electrokinetic–Fenton oxidation to remediate diesel contaminated soils: a laboratory feasibility study*, J. Hydrol. (2009), pp. 4–13.
- [29] D. Li, Y. Zhang, X. Quan, and Y. Zhao, *Microwave thermal remediation of crude oil contaminated soil enhanced by carbon filter*, J. Environ. Sci. 21 (2009), pp. 1290–1295.
- [30] W. Namkoong, E.Y. Hwang, J.S. Park, and J.Y. Choi, *Bioremediation of diesel-contaminated soil with composting*, Environ. Pollut. 119 (2002), pp. 23–31.

- [31] H. Li, Y. Zhang, I. Kravchenko, H. Xu, and C.G. Zhang, *Dynamic changes in microbial activity and community structure during biodegradation of petroleum compounds: a laboratory experiment*, J. Environ. Sci. 19 (2007), pp. 1003–1013.
- [32] S.H. Do, J.H. Jo, Y.H. Jo, H.K. Lee, and S.H. Kong, *Application of peroxymonosulfate/cobalt (PMS(Co(II))) system to treat diesel-contaminated soil*, Chemosphere 77 (2009), pp. 1127–1131.
- [33] US EPA, *Remediation technology cost compendium – year 2000*, Solid Waste and Emergency Response, EPA-542-R-01-009, US EPA, Washington DC, 2004.