

Thermal desorption of a PAH-contaminated soil: a case study

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Abstract

Thermal desorption was tested to remediate a soil contaminated by PAHs (Polycyclic Aromatic Hydrocarbons) from a former Manufacturing Gas Plant site in northern Italy. Lab-scale experiments were carried out to assess the feasibility of this technology; in particular, the minimum desorption temperature required to reach the Italian soil standards was sought, as well as interferences of the natural organic matter on the on-line process control, performed by a Flame Ionization Detector (FID).

The matrix was a sandy gravel; experiments were carried out on the fraction having particle size lower than 2 mm, whose PAH contamination was nearly 2700 mg/kg (total benzo-PAHs: 1100 mg/kg), and the fraction of organic carbon f_{oc} 2.4% w/w. The apparatus was equipped with an indirectly-heated quartz reactor placed into a cylindrical furnace. In a typical experiment, a measured amount of soil was loaded into the reactor. Soil temperature was increased according to a linear schedule under an air flow, followed by a hold (60 min) at the final temperature T_{max} , from 250 to 650 °C, depending on the test being performed. Gases exiting from the reactor were analyzed by an on-line FID. Soil analysis was also performed following each test.

The obtained results showed that remediation of soil could be accomplished with a maximum temperature between 300 °C and 350 °C, depending on the remediation limits to be reached. Removal efficiencies above 99.7% were obtained for all PAHs, when T_{max} above 300 °C was applied. In the case of T_{max} = 250 °C, the abatements decreased to values between 87.0% and 99.9%, depending on the PAH being measured. The on-line FID monitoring of the process fit the purpose, exhibiting results comparable with those obtained by chemical analyses carried out on the treated soil.

1 Introduction

Soil pollution by xenobiotic compounds is a fairly diffused problem, mainly due to occasional and continuous sources related to industrial activities. Dismissed Manufacturing Gas Plant (MGP) sites, rather diffused and active in the past years, are a serious problem all over the industrialized countries. Among the environmental issues related to these sites, soil pollution by Polycyclic Aromatic Hydrocarbons (PAHs) prompts one to explore high performance technologies, such as thermal desorption processes, in order to reach the low remediation limits often associated to these compounds, due to their toxicity [1, 2].

Thermal desorption is a process applied to separate mainly organic contaminants from waste matrices, typically soils, sludges, or sediments. As shown in the schematic diagram of Figure 1, contaminants and water are volatilized in the thermal desorber and swept into a carrier gas (e.g. air, a combustion or an inert gas). The off-gas is then treated in an emission control system, where the organic contaminants are either collected by wet scrubbers, condensers, or activated carbon traps, for subsequent recovery or off-site treatment/disposal, or destroyed in an afterburner [3].

Thermal desorbers can be characterized in several ways, according to [3]:

- the heating method (direct or indirect: in the first case heat is transferred through radiation and convection from the gas to the solids; in the second one, solids are heated by conduction from the desorber shell or by electrical resistance heaters);
- the operating pressure (atmospheric or under vacuum);
- the maximum solid treatment temperature (low: 150-315 °C, medium: 315-540 °C, high: 540-650 °C).

Performances of a thermal desorption process are affected by matrix and process parameters, such as boiling points and concentrations of organics in the material fed, soil type (clay content, material size, moisture content, etc.), and solid treatment temperature, residence time and mixing degree [3, 4].

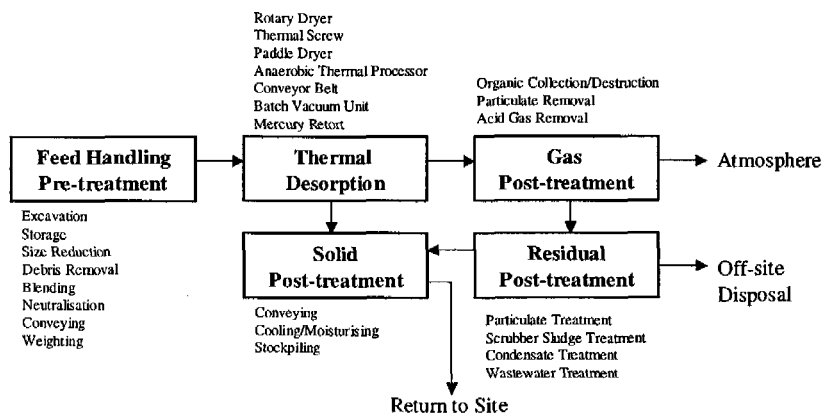


Figure 1: Thermal desorption system schematic diagram.

In this paper, lab-scale experiments are presented, performed in order to assess the feasibility of the thermal desorption technology for the remediation from PAHs of a MGP site (Italy) soil, used for over 80 years for coal gasification processes. Other types of technologies (bioremediation and surfactant-aided soil washing) have been tested on soils from this area [5, 6], but the application of these systems did not provide adequate removal efficiencies at affordable costs.

2 Materials and methods

2.1 Soils

Two soils (A and B) were excavated at the same depth from different areas at the brownfield (soil A from a contaminated area, soil B from a non polluted location) and dry-sieved to 2 mm. Quartering provided sub-samples with suitable weight; for each soil, homogeneity was assessed by comparing particle size distribution and PAH concentration of five sub-samples, resulting in a standard deviation lower than 5%.

The mean particle size distributions are reported in Table 1; soil B had larger percentages of particle size fractions below 0.212 mm. PAH concentrations (C_{in}) are reported in Table 2; in soil A, PAHs above pyrene exceeded Italian remediation limits from 4.4 to 2070 times, depending on the compound being considered and the future use of the area (either commercial/industrial or green/residential). Soil B was not contaminated by PAHs or other organic compounds. Both soils had a low content of organic carbon (2.4% w/w for soil A and 1.0% w/w for soil B respectively).

Table 1: Mean particle size distribution of soils (<2 mm).

Fraction (mm)	1-2	0.6-1	0.212-0.6	0.106-0.212	0.063-0.106	< 0.063
Soil A - % w/w	21.3	20.1	49.0	7.4	1.4	0.7
Soil B - % w/w	19.6	12.7	32.1	20.5	11.0	4.1

Table 2: PAH¹ concentration on soils (<2 mm) A ($C_{in,A}$) and B ($C_{in,B}$), and Italian remediation limits for green/residential (C_g) and commercial/industrial (C_c) purposes. Data are reported in mg/kg on dry weight basis (d.w).

	N	Acl	Ace	Fluo	A	Phen	F	P	C	B(a)A	B(a)P	B(b)F	B(k)F	I	B(ghi)P	DA
$C_{in,A}$	21	44	5	26	101	199	527	393	302	282	207	196	161	108	89	44
$C_{in,B}$	<0.05 each															
C_g^2	-	-	-	-	-	-	-	5	5	0.5	0.1	0.5	0.5	0.1	0.1	0.1
C_c^2	-	-	-	-	-	-	-	50	50	10	10	10	10	5	10	10

¹: N: naphthalene; Acl: acenaphthylene; Ace: acenaphthene; Fluo: fluorene; A: anthracene; Phen: phenanthrene; F: fluoranthene; P: pyrene; C: chrysene; B(a)A: benz(a)anthracene; B(a)P: benzo(a)pyrene; B(b)F: benzo(b)fluoranthene; B(k)F: benzo(k)fluoranthene; I: indeno(1,2,3-cd)pyrene; B(ghi)P: benzo(g,h,i)perylene; DA: dibenzo(a,h)anthracene.

²: Not established.

2.2 Thermal desorption system

A lab-scale indirectly-heated thermal desorber unit was used in this study. A schematic picture of the unit is shown in Figure 2. The desorption unit consisted in a horizontal tubular furnace (length: 68 cm, \varnothing_{in} : 3 cm) equipped with a Proportional-Integral-Derivative (PID) temperature controller-programmer which allowed heating of the furnace according to a linear schedule. Soil to be treated was contained in a cylindrical quartz reactor (length 65 cm, \varnothing_{out} : 16 mm, \varnothing_{in} : 12 mm) inserted inside the furnace. The reactor inlet was connected to an electronic gas supplier (Brooks 5850 TR) equipped with a digital control unit (Brooks Instruments 0154), whereas the outlet of the reactor was connected to a Flame Ionization Detector (FID) controlled by an electronic unit (Fisons Instruments EL980). The reactor outlet was tapered for fast transfer of the desorbed species to the analyzer; the lines connecting the reactor to the detector were heated at 250 °C to minimize condensation of desorbed products. The temperature of the soil was monitored by a K-type thermocouple directly immersed in the soil bed; an acquisition data system was used to record soil and furnace temperatures and FID signal.

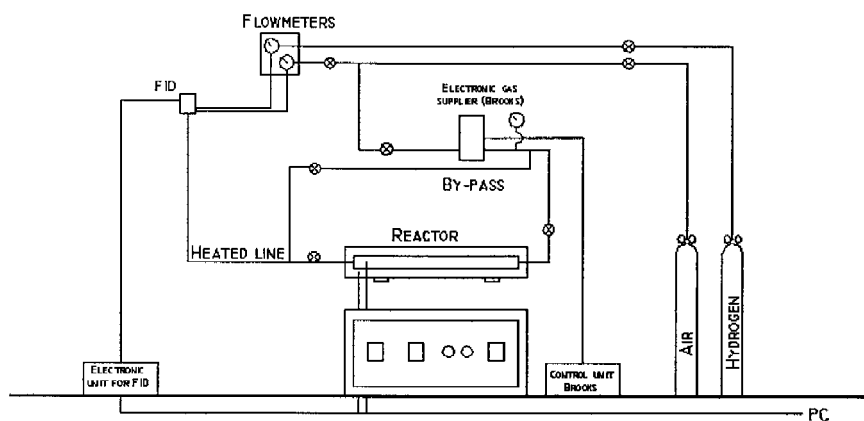


Figure 2: Schematic picture of the thermal desorber unit used in this study.

2.3 Tests performed

Several thermal desorption experiments have been performed in this study. In a typical run, nearly 10 g d.w. of soil were loaded in the reactor. Desorption treatments of soil A included heating (according to a linear schedule, 3 or 5 °C/min) from room temperature to the desired final temperature (T_{max}), ranging from 250 to 650 °C, followed by an hold (60 min) at T_{max} . For soil B, analogous tests were performed, with T_{max} equal to 650 °C. Contaminants desorbed upon

heating were swept away by the carrier gas (air, 150 Ncm³/min), and their concentration was continuously monitored by the FI detector. This allowed the determination of the desorption spectrum, i.e. of the concentration vs. temperature curve. At the end of each experiment, after switching off the FID detector and stopping the gas supply system, the treated soil was downloaded from the reactor, placed into a vial and kept at 4 ± 1 °C for subsequent analysis. All tests were performed in duplicate.

In selected runs, the FID detector was not employed and the reactor outlet was connected to a condensation section equipped with one or more cooled glass traps (~ -50 °C) followed by adsorption traps (ORBOTM 609 for PAH and Anasorb CSC for other organic compounds). Accordingly the nature of the desorbed species could be assessed in this case.

2.4 Chemical analyses

All chemicals were analytical grade purity (99.0 %). The fraction of organic carbon was determined by ISO/DIS 10694 methods [7]. Moisture content of soil was determined by the EPA 160.3 method (coefficient of variance CV: $\pm 0.5\%$) [8]. PAH extraction from soils was carried out by EPA SW 3540 B, clean up by EPA SW 3630 B, GC-MS analysis by EPA SW 8270 B [8]. The overall variation of PAH determination in soil was between 9% and 15%, depending on the compound being measured [9]. FID calibration was performed by loading known amounts of solid naphthalene in the reactor (without soil) and performing tests analogous to those already described ($T_{\max} = 650$ °C). Quali-quantitative analysis of the products condensed/adsorbed in the condensation unit of the thermal desorption apparatus was performed by GC-MS analysis. The GC/MS was equipped with an HP-5 MS column (30 m, 0.25 mm, 0.25 μ m), a split injector and a mass selective detector (40-350 a.m.u.). Analytical conditions for analysis of these products were: i) injector temperature = 250 °C; ii) ionization energy: 70 eV; iii) detector temperature = 290 °C; iv) thermal ramp: from 40 °C to 140 °C in 23.8 min, from 140 °C to 250 °C in 11 min, from 250 °C to 280 °C in 1.5 min.

3 Results and discussion

Figure 3 shows the FID signals acquired during the thermal desorption tests performed with $T_{\max} = 650$ °C on equal amounts of soils A and B. In the case of the contaminated soil (A), the concentration of desorbed species started to increase slightly above 100 °C. The desorption profile showed two maxima near 180 °C and 250 °C, followed by a long tail which extended up to 550 °C. On the other hand, for soil B the FID profile was nearly flat. The integral of the curve of soil B, ascribed to the natural organic matter present in it, was about 1.6% of the value obtained for soil A, suggesting that the contribution of the natural organic matter to the FID signal acquired during thermal desorption tests of soil A could be neglected.

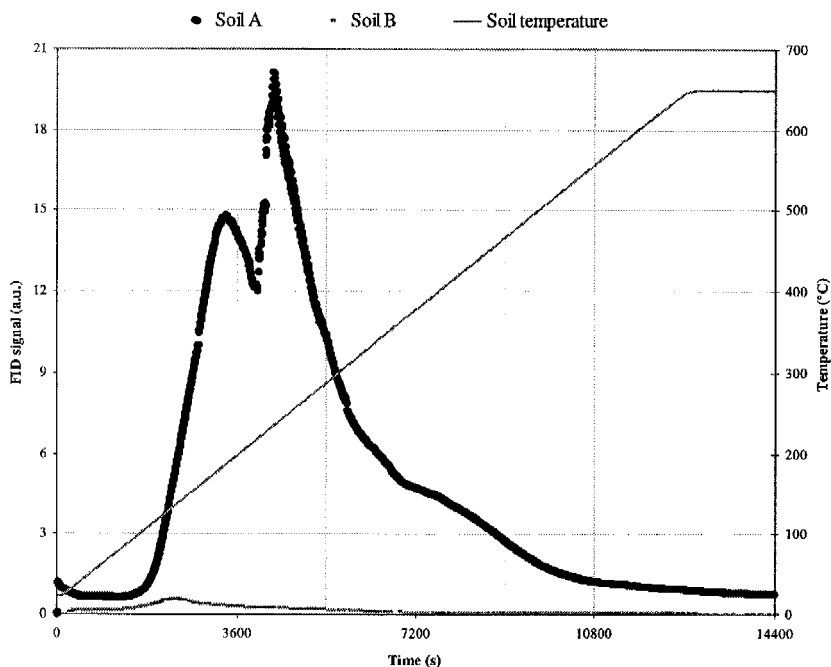


Figure 3: FID signals acquired during thermal desorption tests performed at 3 °C/min on equal amounts of soils A and B.

It is worth noticing that the FID signal corresponds to the desorption of all organic contaminants present in the soil, i.e. not only the sixteen standard PAHs. As a matter of fact, analysis of the condensate/adsorbed indicated the presence of other PAHs and of oxygenated molecules as well (e.g. furans). Some of these compounds, not present in the untreated soil, were likely formed via decomposition/oxidation of the original contaminants upon heating.

Desorption experiments were also performed with different T_{\max} , down to 250 °C. For comparison purposes, Figure 4 shows examples of FID signals obtained during thermal desorption tests performed on soil A with $T_{\max} = 250$ and 300 °C. In both cases similar results were obtained, thus suggesting that high desorption of contaminants could be achieved already at 250 °C. The absence of two separate desorption maxima (see Figure 2) was possibly related to the different heating rate used in this case (5 vs. 3 °C/min). As a matter of fact, the integral values of the two curves corresponded to nearly 2350 and 2540 mg naphthalene equivalents per kg of dry weight soil, respectively.

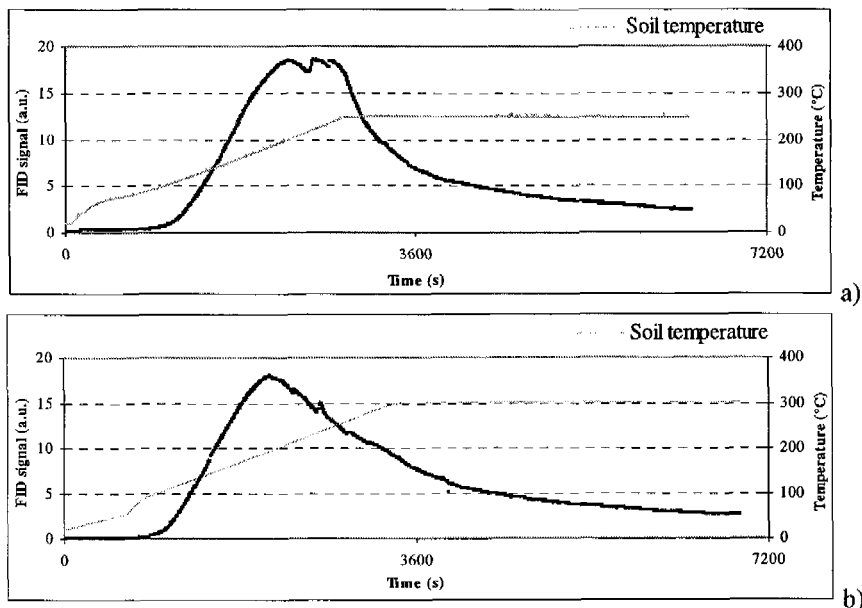


Figure 4: FID signals obtained during thermal desorption tests performed at 5 °C/min with $T_{\max} = 250$ (a) and 300 (b) °C on soil A.

The PAH concentrations on soil A following thermal desorption treatment at different T_{\max} ($C_{\text{out},A}$) are reported in Table 3.

Table 3: PAH¹ concentration (mg/kg d.w.) on soil A, following thermal desorption treatment at different T_{\max} . Gray cells represent values below the quantification limit of the analytical method adopted (0.05 mg/kg d.w.).

T_{\max} (°C)	N	Acl	Ace	Fluo	A	Phen	F	P	C	B(a)A	B(a)P	B(b)F	B(k)F	I	B(ghi)P	DA
250					1.2	0.8	5.2	3.6	9.9	7.6	5.5	14	12	11	8.8	5.7
300							0.2	0.2	0.5	0.3	0.2	0.6	0.3	0.2	0.2	0.1
350									0.1	0.1	0.1	0.2	0.1	0.1	0.1	
400	0.4		0.1													
≥450																

¹: N: naphthalene; Acl: acenaphthylene; Ace: acenaphthene; Fluo: fluorene; A: anthracene; Phen: phenanthrene; F: fluoranthene; P: pyrene; C: chrysene; B(a)A: benz(a)anthracene; B(a)P: benzo(a)pyrene; B(b)F: benzo(b)fluoranthene; B(k)F: benzo(k)fluoranthene; I: indeno(1,2,3-cd)pyrene; B(ghi)P: benzo(g,h,i)perylene; DA: dibenzo(a,h)anthracene.

Table 3 shows that for maximum temperatures above 450 °C, the PAH concentration on the treated soil was below 0.05 mg/kg d.w. for all compounds. For $T_{\max} = 400$ °C, only small amounts of naphthalene and acenaphthene could

be detected in the treated soil; however for these compounds no regulatory limits are established, and soil could be reused for both green/residential and commercial/industrial purposes (see Table 2). Detection of naphthalene and acenaphthene in tests with $T_{\max} = 400\text{ }^{\circ}\text{C}$ was ascribed to cracking of higher molecular weight molecules into lighter compounds, which could not be further removed during the treatment. For maximum treatment temperatures between $300\text{ }^{\circ}\text{C}$ and $350\text{ }^{\circ}\text{C}$, compounds from fluoranthene and chrysene respectively could be detected. In particular, for $T_{\max} = 350\text{ }^{\circ}\text{C}$ the treated soil could respect green/residential limits. For $T_{\max} = 300\text{ }^{\circ}\text{C}$, benzo(a)pyrene, benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene concentrations the exceeded green/residential limits; however soil treated at this maximum temperature could still be used for commercial/industrial purposes. A further decrease in T_{\max} ($250\text{ }^{\circ}\text{C}$) caused an increase of the residual concentrations of PAHs heavier than anthracene; for benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)perylene the commercial/industrial limits were exceeded. In Figure 5, concentrations of some PAHs before and after treatment at different T_{\max} are compared to the remediation limits (C_g and C_c). Different situations are shown: pyrene values were always below regulatory limits regardless of the land use; dibenzo(a,h)anthracene never exceeded commercial/industrial limits, but for T_{\max} equal to $250\text{ }^{\circ}\text{C}$ its residual concentration in soil was above the green/residential limit; indeno(1,2,3-cd)perylene concentration exceeded the limit for green/residential purposes, from a maximum temperature above $350\text{ }^{\circ}\text{C}$, and for $T_{\max} = 250\text{ }^{\circ}\text{C}$ its concentration was also above the commercial/industrial limits.

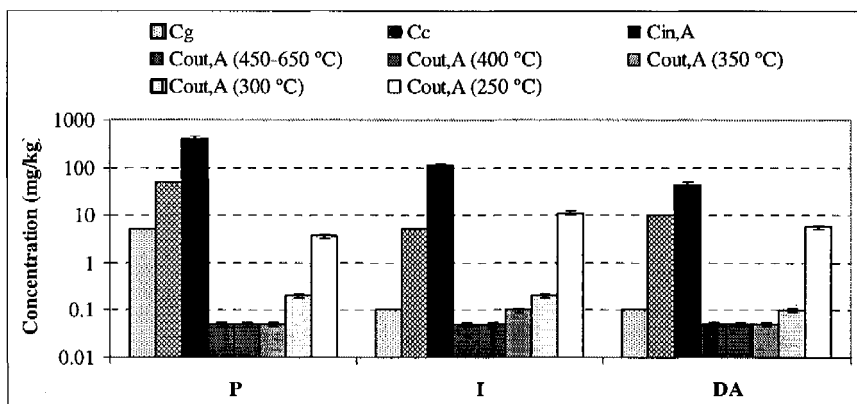


Figure 5: Concentrations of some PAHs (P: pyrene; I: indeno(1,2,3-cd)pyrene; DA: dibenzo(a,h)anthracene) before ($C_{in,A}$) and after treatment ($C_{out,A}$) at different T_{\max} , compared to green/residential (C_g) and commercial/industrial (C_c) regulatory limits.

For maximum temperatures above $450\text{ }^{\circ}\text{C}$, removal efficiencies were over 99.9 % for all PAHs except for light polyaromatic hydrocarbons, such as naphthalene and fluorene (99.8%) and acenaphthene (99.0%). Operating the

thermal desorption system at maximum temperatures between 250 °C and 350 °C, the removal efficiency for PAHs above anthracene decreased as T_{\max} decreased; the heavier was the compound, the greater was this effect, as shown in Figure 6 for some compounds taken as examples.

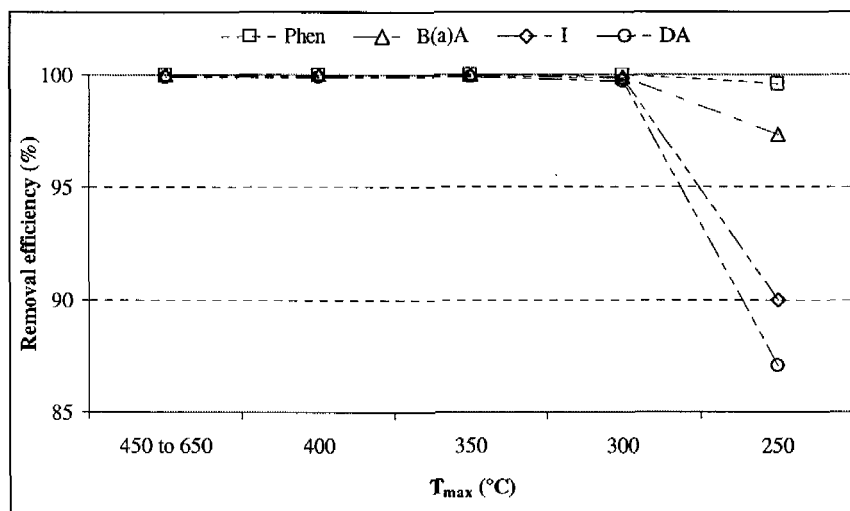


Figure 6: Removal efficiency for some PAHs (Phen: phenanthrene; B(a)A: benz(a)anthracene; I: indeno(1,2,3-cd)pyrene; DA: dibenzo(a,h)anthracene) as a function of the maximum temperature T_{\max} .

4 Conclusions

In this paper, lab-scale experiments were presented, performed in order to assess the feasibility of thermal desorption treatment for the remediation from PAHs of a MGP site soil.

The signal acquired by the on-line FID monitoring system could be properly used to locate the temperature range where desorption of contaminants occurred. Calibration of the system provided semi-quantitative results of the PAHs desorbed, matching with the total polyaromatic hydrocarbon concentration on soil before treatment; the contribution of the natural organic matter to the desorption profile could indeed be neglected.

This study indicated that high removal efficiencies could be obtained for all PAHs, ranging from 87% (for dibenzo(a,h)anthracene, with $T_{\max} = 250$ °C) to nearly 100% (for fluoranthene and pyrene, with T_{\max} above 350 °C).

Italian regulatory limits for green/residential and commercial/industrial uses could be achieved setting the maximum operating temperature at 350 °C and 300 °C respectively.

Furthermore, tests carried out with off-gas contaminant condensation showed that furans and other PAHs could be formed during the thermal process; therefore, further studies are on going in order to better investigate this aspect.

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