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Remediation of a Petroleum Hydrocarbon-Contaminated Site by Soil Vapor Extraction: A Full-Scale Case Study

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Abstract: Spills, leaks, and other environmental aspects associated with petroleum products cause hazards to human health and ecosystems. Chemicals involved are total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAHs), solvents, pesticides, and other heavy metals. Soil vapor extraction (SVE) is one of the main in-situ technologies currently employed for the remediation of groundwater and vadose zone contaminated with volatile organic compounds (VOCs). The performance of an SVE remediation system was examined for a petroleum hydrocarbon-contaminated site with attention to remediation targets and final performance. The study assessed: (1) the efficiency of a full-scale remediation system and (2) the influence of parameters affecting the treatment system effectiveness. Results showed how VOC concentration in soil was highly reduced after four year treatment with a global effectiveness of 73%. Some soil samples did not reach the environmental threshold limits and, therefore, an extension of the remediation period was required. The soil texture, humidity, permeability, and the category of considered pollutants were found to influence the amount of total extracted VOCs.

Keywords: clean-up; contamination; hydrocarbons; PAHs (polycyclic aromatic hydrocarbons); risk; soil vapor extraction; volatile organic compounds and Taranto

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1. Introduction

Petroleum represents one of the most important energy resources and raw materials of the chemical industry. Nevertheless, oil spills during exploration, transportation, and refining can cause serious environmental problems. This is mainly due to leaking underground and aboveground storage tanks, inappropriate disposal of petroleum wastes, and accidental spills [1,2]. Unfortunately, the dynamic movements of hydrological transport cycles to groundwater aquifers could lead to wide hazardous contamination. The liquid petroleum, once released into the ground, generally partitions into dissolved, liquid, and gas phases [3], spreading out in all ecosystems and posing a serious threat to human health and the environment.

Common remediation technologies employ a range of physical, chemical, biological treatments, and thermal approaches [4–6]. Among the in-situ technologies, soil vapor extraction (SVE) has gained in efficiency and popularity for volatile (VOC) and semi-volatile organic compound (SVOC) removal [7]. However, heavier fuels, such as mid-weight petroleum products like diesel fuel, heating oils, and kerosene, are not always completely removed by SVE, which performs better with light hydrocarbons [8]. SVE treatment involves the installation of vertical and/or horizontal wells in the vadose zone, pumping air to strip the contaminants from the soil matrix [9]. Extracted vapors are then treated using sorbent materials (commonly activated carbon) before being released into the atmosphere [10]. SVE performs better in highly permeable and homogeneous soils [11], and it is recommended to cover the site surface with an impermeable layer to minimize airflow short-circuiting and infiltration [12,13].

Although SVE is a conventional technology, the literature review has shown limited full-scale case studies documenting its application to soils and subsoils contaminated by petroleum hydrocarbons. Albergaria et al. [14] reached respectable efficiencies (above 92%) with an SVE process performed in column experiments with sandy soils and different soil water contents (SWCs) with benzene, toluene, ethylbenzene, xylene, trichloroethylene, and perchloroethylene as targets. An increase of the SWC led to a more time-consuming remediation procedure with longer periods for contaminants with lower vapor pressures and lower water solubilities. The most efficient airflow rate was identified within the range of 0.50 and 5.3 cm^3/s at standard temperature and pressure [8]. Additionally, Chuan-yu et al. [15] conducted a series of one-dimensional column experiments to analyze the factors influencing the SVE as a remedial technique. The outcomes showed that the higher the vapor flow rate was, the higher the contaminant removal efficiency was as well. Furthermore, the soil grain size was found to influence chlorobenzene removal efficiency in that the coarser the sand was, the higher the removal rate was. Additionally, organic and water content in the soil had impacts on the process, with a decrease in the removal efficiency with high organic content. Behar et al. [16] presented the results from a calibrated flow and transport model to simulate 1,1,1-trichloroethane concentrations for the Los Alamos National Laboratory liquid waste disposal facility. Simulations showed that SVE can be started three years following drum failure and remain a viable remediation tool.

However, if high levels of removal need to be reached (efficiency > 95%), a pilot study is recommended to evaluate the appropriateness of integrating bioventing (BV) at that site or if another technology should be considered [17,18]. The critical problem of tailing during SVE operation could be addressed with a conversion to a properly designed BV system [18]. Based on pilot trials, Lee et al. [19] concluded that contaminants with high concentration can be initially treated using SVE and then with a BV process as soon as the volatilization rate becomes smaller than the biodegradation rate. It was concluded that it would take about 100 days to treat 130 kg of toluene at this location with this combined system, considering the characteristics of this very volatile and biodegradable pollutant.

This investigation quantified the effectiveness of an SVE remediation treatment of a full-scale plant in a real case study contaminated by petroleum products. In particular, the site to remediate was located in a strongly compromised industrial area in Taranto (Southern Italy). The industrial area was included in the Italian most contaminated sites of national interest (SIN in Italian) with the Italian Ministerial Decree of the 10 January 2000 [20], and it represents one of the most polluted sites in Europe. The main objectives of this study were to analyze the correlations between performance and process parameters and to interpret monitoring data about soil coring and air quality. The framework of the experimentation was based on: (a) development of a soil and subsoil remediation plan through the SVE treatment and (b) assessment of remediation performances and interpretation of data.

2. Materials and Methods

2.1. Background Information

2.1.1. Site Description

In operation since 1967, the 275 hectare Taranto Eni refinery supplies the petroleum product market in South-East Italy (Figure 1).

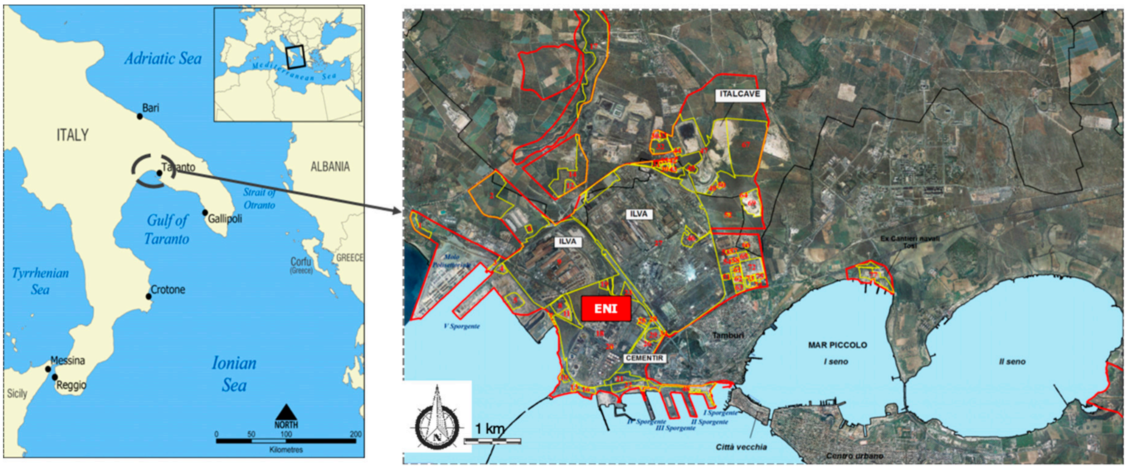

Figure 1. Area of ENI refinery in Taranto, South of Italy. The red line shows the perimeter of the SIN area and the yellow line indicates the localization of factories.

The refinery produces propane, butane, liquefied petroleum gas (LPG) blend, gasoline, diesel, jet fuels, fuel oils, and bitumen, with an authorized processing capacity of 6.5 million tons of crude oil per year [21]. ENI petroleum refinery represents the second industrial plant in the industrial district of Taranto in Apulia, and it treats up to 4 Mt/y on average of imported crude oil [22]. For several decades, this industrial area of Taranto has been subjected to chemical pollution deriving from different industrial activities, such as the steel plant ILVA, the concrete factory Cementir, the Eni station, and the Military Arsenal in the Taranto port [23]. The perimeter of the SIN area is shown in Figure 1.

2.1.2. Previous Environmental Investigations

In compliance with the current legislations about protection and safeguard of soil, subsoil, and ground waters [24,25], from the year 2000, ENI started to present a site characterization plan, after which remediation activities were needed. The environmental characterization (EC) included 1100 soil coring samples and 110 piezometers for the groundwater monitoring, and it allowed refinement of the conceptual model of a contaminated site (i.e., sources, types, and concentrations of contaminants, potentially contaminated media, potential exposure pathways, and final receptors).

As stated by Calabrese et al. [26] and as confirmed by the EC, from a geological perspective, the area is characterized by a middle-upper Pleistocene “terraced marine deposits”. These terraces consist of an incised substrate composed of marine clay (Argille Subappennine) overlain by Holocene sandy, gravelly sandy and alluvial sandy silty and coastal deposits outcrops. This area is also characterized by great variability, moving from calcareous and calcarenitic outcrops to flat alluvial deposits near the seacoast (Figure 2). The local hydrography appears to be characterized by the tributaries of the Bradano and the Lato rivers in the hinterland of the Gulf of Taranto. The groundwater is divided into two aquifer systems, one more deeply located in the Mesozoic carbonate basement (about −55 m from sea level) and a surface one in the terraced marine deposits (about −2 m from sea level) reflecting the seasonality of the rainfall regime [27].

The results of the EC, shown spatially in Figure 3, demonstrated contamination of top and deep soil. Chemical analysis showed how most samples had heavy hydrocarbon-related contamination, some with short-chain hydrocarbons and some with benzene, ethylbenzene, and xylene.

After the site characterization was completed, an environmental-health risk analysis (EHRA) was performed. The main pollutants investigated were BTEX (Benzene, Toluene, Ethylbenzene and Xylenes), classified as priority pollutants regulated by many environmental organizations around the world. Since the industrial use of the area, the human target considered in the analysis was “worker”. The pathways considered in the analysis included: (i) outdoor dust inhalation, (ii) outdoor vapors from top soil, (iii) outdoor vapors from deep soil, and (iv) soil runoff towards groundwater. The remediation targets (RTs) considered for this specific case in deep soil were obtained using GIUDITTA software and are described below: (1) RT for C<12 = 891 mg/kg; (2) RT for C>12 = 365 mg/kg.

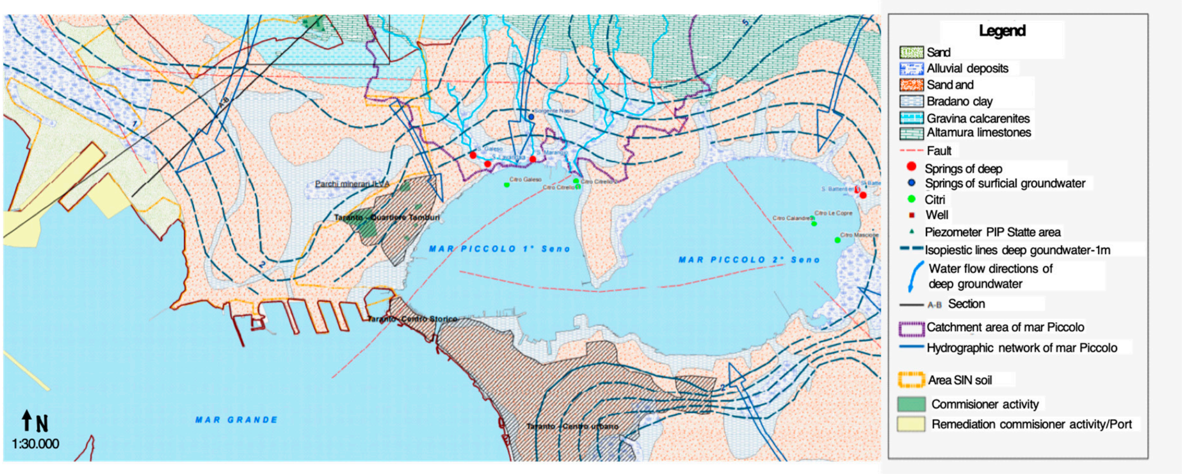

Figure 2. Hydrogeological map of Taranto and mar Piccolo area.

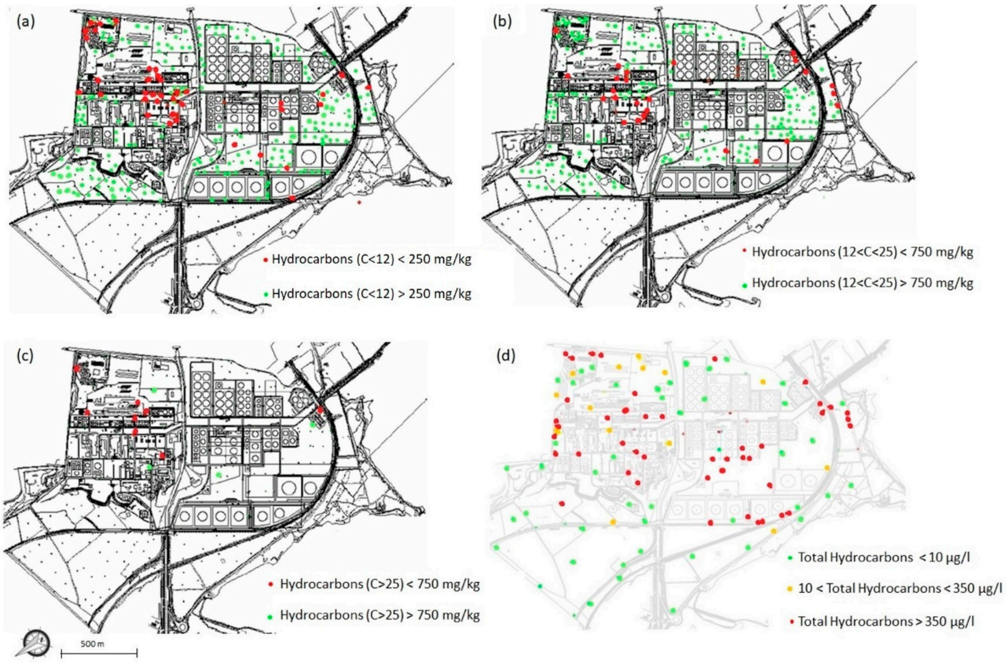

Figure 3. Environmental characteristics (EC) map of concentration of hydrocarbons in (**a**–**c**) soil (1 to 5 m below ground surface) and (**d**) groundwater.

2.1.3. Remediation Plan

In 2005, soil (SRP) and groundwater (GRP) environmental remediation plans were submitted to the competent authority after a pilot field study. The total area was divided into six sub-areas according to geomorphological characteristics and contamination type. In this work, we focused the attention on one of the above-mentioned sub-areas with remedial activities carried out from 2014 to 2018 (Figure 4a). The treatment consisted of SVE applied to the vadose zone section of the area. Table 1 shows the characterization parameters of the soil. All the concentrations above the Italian environmental regulation limits (RL) [28] are shown in red.

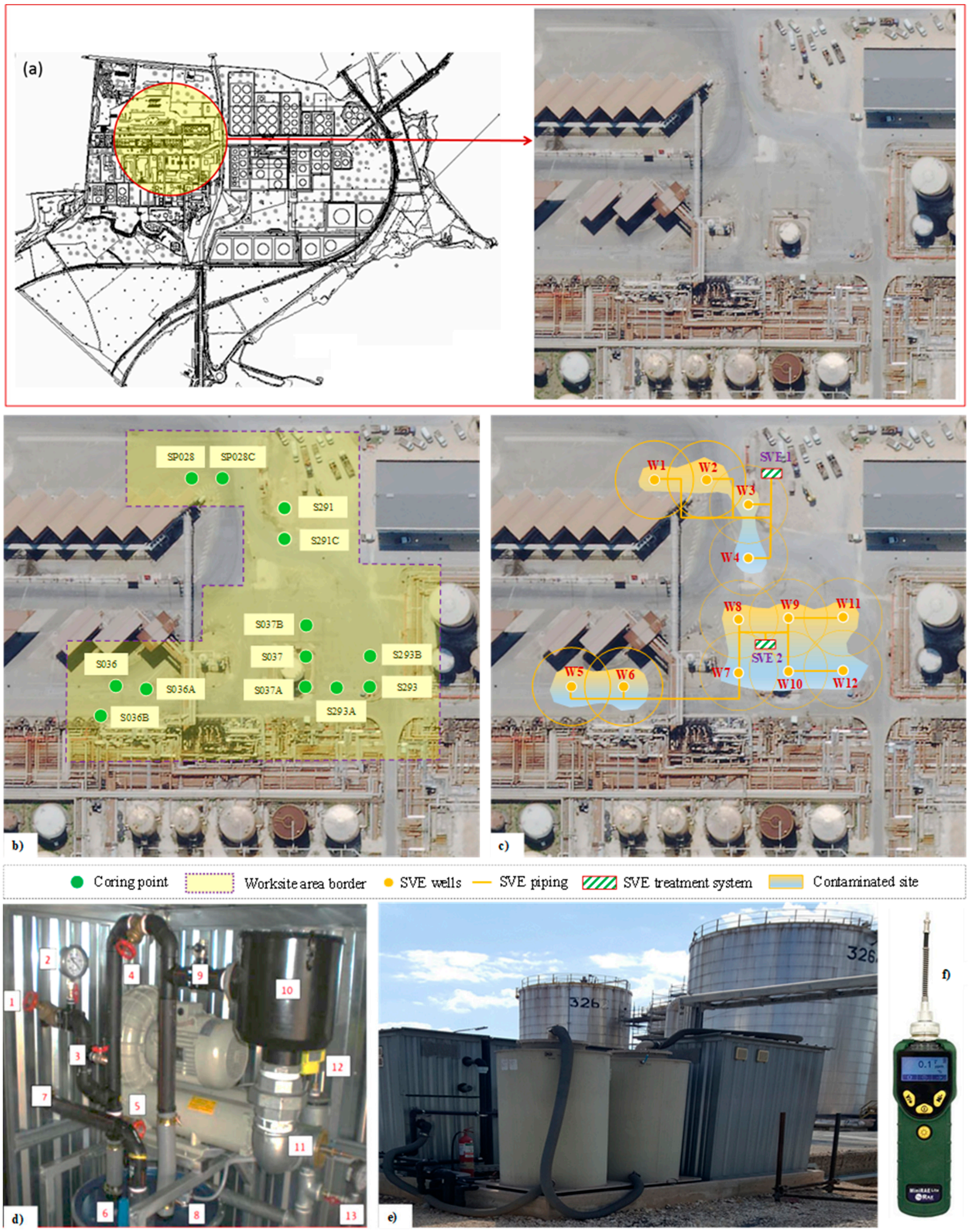

Figure 4. (**a**) Study area; (**b**) map of the coring campaign, (**c**) layout of soil vapor extraction (SVE) plant, (**d**) SVE system components, (**e**) SVE system seen from the outside, (**f**) photoionization detector.

Table 1. Soil concentration measurements from the environmental characterization (EC) in 2005. RL: regulation limits.

	Units	**RL**	**S291**	**S291C**	**S293**	**S293A**	**S293B**	**S037**	**S037A**
Sampling Depth	**m**	**-**	**4**	**4**	**4**	**4**	**4**	**4**	**1**
Humidity at 105 °C	%	-	32.5	21.2	8.2	17.2	12.6	15.2	5.2
Residues at 105 °C	%	-	67.5	78.8	91.8	82.8	87.4	84.8	94.4
Fraction < 2 mm	%	-	92.6	93.9	67.7	94.3	68.3	71	-
C>12	mg/kg	750	119.4	445.2	525	404.4	406.5	658	34,177
C<12	mg/kg	250	1156	908	7108	1855	569	1608	<0.1
Benzene	mg/kg	2	<0.005	0.226	0.524	7.63	1.64	1.82	<0.001
Ethylbenzene	mg/kg	50	<0.005	7.59	11.3	62	6.73	19.9	<0.001
Xylene	mg/kg	50	<0.005	12.1	<0.005	184	16	95.4	<0.001
	Units	**RL**	**S037B**	**S037B**	**SP028**	**SP028C**	**P036**	**P036A**	**P036B**
Sampling depth	**m**	**-**	**4**	**1**	**5**	**5**	**1**	**3**	**4**
Humidity at 105 °C	%	-	17.6	6.3	21.1	17.1	14	18.2	20.8
Residues at 105 °C	%	-	82.4	93.7	78.9	82.9	86	81.8	79.2
Fraction < 2 mm	%	-	-	-	85.8	-	89.8	-	-
C>12	mg/kg	750	3642	4128	749	9812	0.2	52	10,026
C<12	mg/kg	250	408	<0.1	410	333	<0.1	785	1276
Benzene	mg/kg	2	1.37	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ethylbenzene	mg/kg	50	24.4	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Xylene	mg/kg	50	99.8	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

2.2. Full-Scale SVE System

The soil remediation plan (SRP) considered for this full-scale case study was based on an SVE treatment.

Due to the type of pollutants present in the vadose zone, the main SVE goals were (a) to intercept any produced vapor preventing it from rising up to the ground level and (b) to treat the contaminants in air collected via SVE.

For the SVE design, a stepped-rate test was conducted with the pilot plant first to determine the actual capacity of the vent and then to select a flow rate for conducting constant-rate tests. The latter were conducted to evaluate the actual area of influence and efficiency of a given well or combination of wells [29]. Figure 4b,c show the site area with the core points and the position of the SVE air extraction wells with their radius of influence of 13 m, as it is known from the previous pilot field study.

The total surface of the area was about 13.000 m^2.

The project installations for this area included two main system lines with:

- 12 extraction wells of SVE to a maximum depth of 3 m from the ground level with a slotted section between 1.3 and 3 m;
- 4 activated carbon vessels to treat the VOCs pumped out.

In Figure 4d, all the mechanical parts of the SVE plant (overview in Figure 4e) are shown, in particular: 1. well intake regulation valve; 2. vacuum gauge; 3. predisposition for flowmeter; 4. bypass valve; 5. inlet valve for moisture separation; 6. valve on moisture separator for purging cylinder; 7. external connection for purging cylinder; 8. level switch for moisture separation; 9. dilution valve; 10. dust filter; 11. PSV vacuum-breaking valve; 12. temperature and moisture gauge; 13. manometer; 14. socket for Rilsan® tube.

The remediation technological plants were installed in compliance with the authorized SRP. Completed in August 2013 and working from October 2013, they were subjected to a phase of functional tests until 2014 with the subsequent stabilization of the operating conditions.

In the period 2014–2018, the air quality was analyzed with a site-specific VOC investigation campaign, based on IN-OUT VOC measurements. The trend value of VOCs extracted from the two

SVE lines is shown and discussed in the results section. The VOC IN sample is where the volatile hydrocarbons enter the granular activated carbon (GAC) units, while the VOC OUT sample represents the gasses leaving the systems, expecting to be low and under the remediation threshold limits. VOCs were measured through a photoionization detector (MiniRAE Lite, RAE Systems by Honeywell) with an accuracy of ±5% and resolution of 0.1 $\mu g/Nm^3$ (Figure 4f). Moreover, VOC samples were collected monthly for laboratory analysis to verify permit vapor treatment requirements.

For the monitoring phase, the daily measured parameters were: vacuum/pressure in extraction wells (mbar), gas flow rate in extraction wells and manifolds (m^3/h), VOC concentrations in extraction wells and treatment system compliance data ($\mu g/Nm^3$), and system data for the maintenance (e.g., temperature (°C), frequency (Hz), and working hours (h) of vacuum pumps). The monitoring of these parameters was necessary to obtain the hydrocarbon mass removal rates (kg/d), calculated using the Equation (1) [11]:

$$Mass\ Removal\ Rate = Q \times C \times \frac{273}{T} \times P \tag{1}$$

where Q is the measured flow rate in the exhaust stack, C is the hydrocarbon concentration, T is the exhaust temperature in Kelvin, and P is the pressure in the exhaust.

Moreover, the daily control of the moisture in the condensation water tank was necessary to ensure the system reliability watching for excessive condensation as the groundwater rises and falls with rainfall.

The SVE remediation began in June 2014 and ran continuously (except for brief interruptions due to power failures and technical issues) using all the extraction wells. No rebound testing was performed.

In 2016, pre-acceptance tests were carried out in order to understand if the mitigation targets were achieved. A new coring campaign based on 13 samples was carried out with a variable depth (from 1 to 5 m from the ground level) in correspondence with the same cores considered during the environmental characterization, specifically S291, S291C, S293, S293A, S293B, S037, S037A, S037B, SP028, SP028C, P036, P036A, and P036B (Figure 4b). The organic contaminant concentrations were obtained by gas chromatography in accordance with the EPA method 8015D (standard deviation of measurements ±5%) [30]. In addition, in 2018, another coring survey to monitor the performance of the remediation system was carried out. The efficiency rate, identified as hydrocarbon reduction in soil over the years, was calculated for each sample as:

$$\%Eff = \frac{C_{in} - C_{fin}}{C_{in}} \times 100 \tag{2}$$

with C_{in} the initial concentration at the EC in 2005 and C_{fin} as the final concentration at the preliminary test (PT) in 2018.

3. Results

3.1. Air Monitoring

The SVE system was constantly monitored to perform with the best efficiency.

The VOC IN-concentration trend allows us to evaluate the efficiency of the extraction system, where a reduction of VOCs pumped over time could presumably indicate a decrease of hydrocarbons in the vadose zone. The SVE system removed an estimated 540 kg of VOC from the subsurface during about 1300 days of continuous (24 h/day) operation, as shown in Figure 5. The contaminant removal was characterized by a high initial rate (1.5 kg/day) to a value approximately ten times lower (0.15 kg/day) after one year of operation. A general trend when using an SVE treatment consisted of initially high VOC removal rates (Figure 5a) due to flushing and evaporation, then a drop of the VOC removal rate occurred, reaching a steady state in which the mass transfer of VOC contamination was controlled only by diffusion [24]. For this reason, it was chosen to analyze and present the data about the GAC facility efficiency in two periods: (i) one related to the first working year, where concentrations of treated pollutants were high (range 5000–50,000 µg/Nm^3) (Figure 5b), and (ii) one for the last three working years, where concentrations dropped and reached values lower than 5000 µg/Nm^3 (Figure 5c).

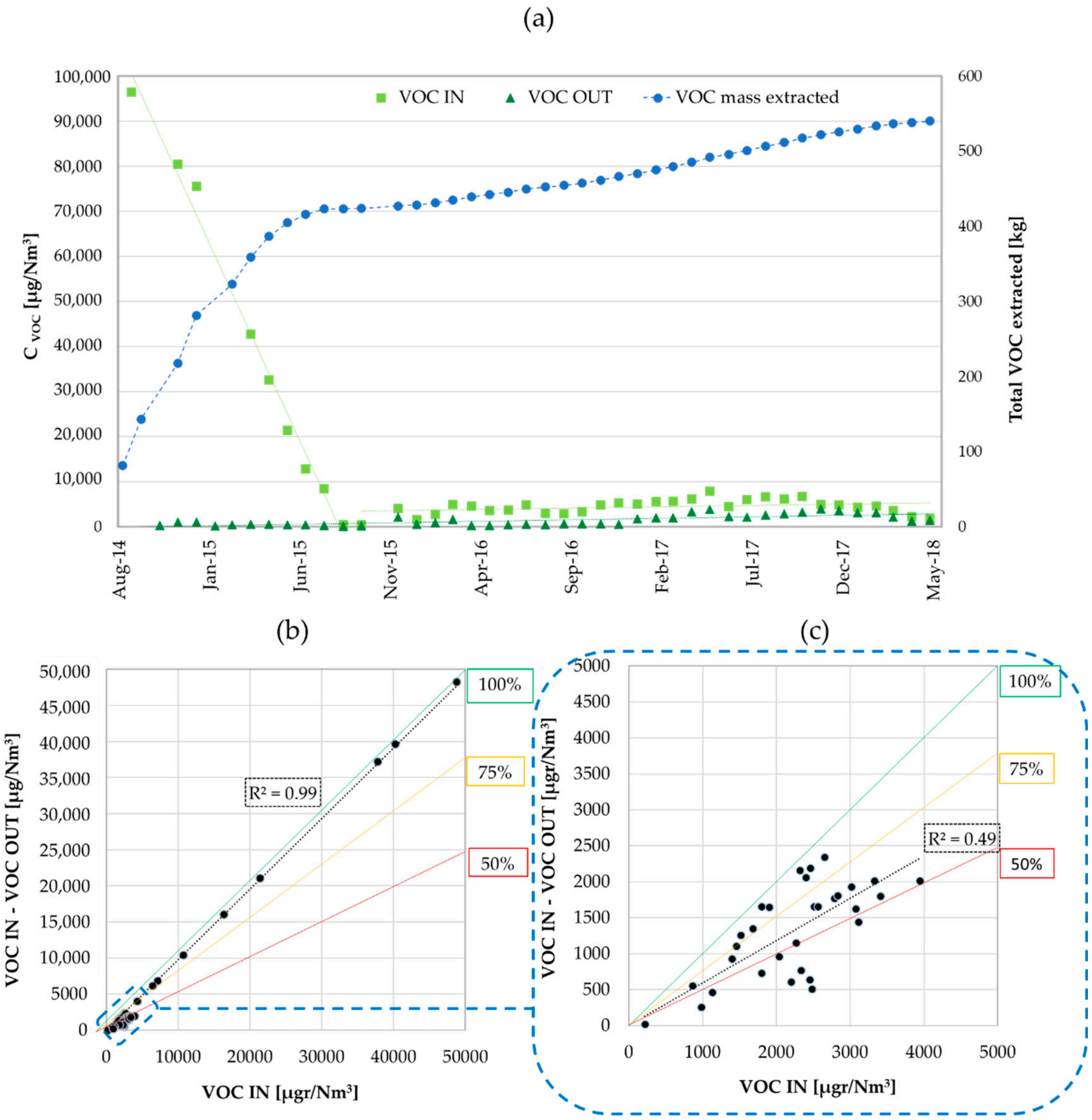

Figure 5. (**a**) Linear trend estimation of distribution for volatile organic compounds (VOC) IN, VOC OUT, and VOC mass extracted, (**b**) correlation trend and VOC removal efficiency (%), (**c**) overview of 5b in the range [0–5000] µgr/Nm^3.

During the first year of remediation with the SVE system, the GAC facility performance initially followed linearly the trend of 100% efficiency (Figure 5), but in the later years, the general trend fell between 50% and 100% efficiency lines. It could be explained by the fact that the easily removable VOCs (already in the soil gas, readily transferrable from soil pore or readily transferred from organic matter) were already removed in the first year, and GAC efficiency decreased as less volatile components were treated. In fact, GAC adsorption capacity is based on VOC type, vapor temperature, and relative humidity.

VOCs OUT concentrations recorded over the treatment period were below the permitted limit and followed an almost-linear distribution for all the four years of remediation, showing the efficacy of the GAC system.

Another reason for monitoring the system is related to the GAC treatment unit, which needs to be replaced as soon as the total saturation occurs. In fact, the IN-OUT difference evaluates the

GAC vessel efficiency, showing that a GAC unit is saturated and needs to be replaced immediately when IN and OUT have about the same value. However, the best time to change out the GAC unit is when a breakthrough is first noticed and verified. In addition, two GAC beds are aligned in series to prevent contaminant emissions from exceeding local regulatory requirements if saturation in the primary treatment vessel occurs.

In correspondence with a facility downtime due to a strong rainfall event, occurring in November 2015, no IN-OUT VOC concentrations were recorded. After that event, an increase of VOCs was observed. The groundwater level (i.e., soil moisture), which varies with the rainfall [31], can strictly affect the volatilization of hydrocarbons.

The rainfall distribution over time demonstrates that a significant soil moisture produces a drop in the extracted VOC amount that increases again as soon as the precipitation event ends. As stated by Morgan and Atlas [25], since oxygen diffusion through the air is around 10^4 times faster than that through water, an increased soil moisture corresponds to a reduced porosity for available gases. The soil moisture content plays a key role by determining whether the diffusion is relatively fast (primarily through pore space occupied by air) or relatively slow (primarily through pore space occupied by water). The lag time in VOC extraction may be associated with higher moisture contents due to the infiltration of rainfall into the soil; the raising of the water table in soil limits the flow of gas from the underground and leads to the introduction of water into the SVE system, reducing the efficiency of the treatment. In Figure 6, the VOC concentration is plotted on a log scale to illustrate the rapid initial decay followed by a rebounding and slower decay. These observed trends display the classic decay and rebound expected from the operation of SVE when a significant fraction of the VOC mass is removed from the soil. It is assumed this period of dormancy allowed the site to re-equilibrate fully to ambient conditions.

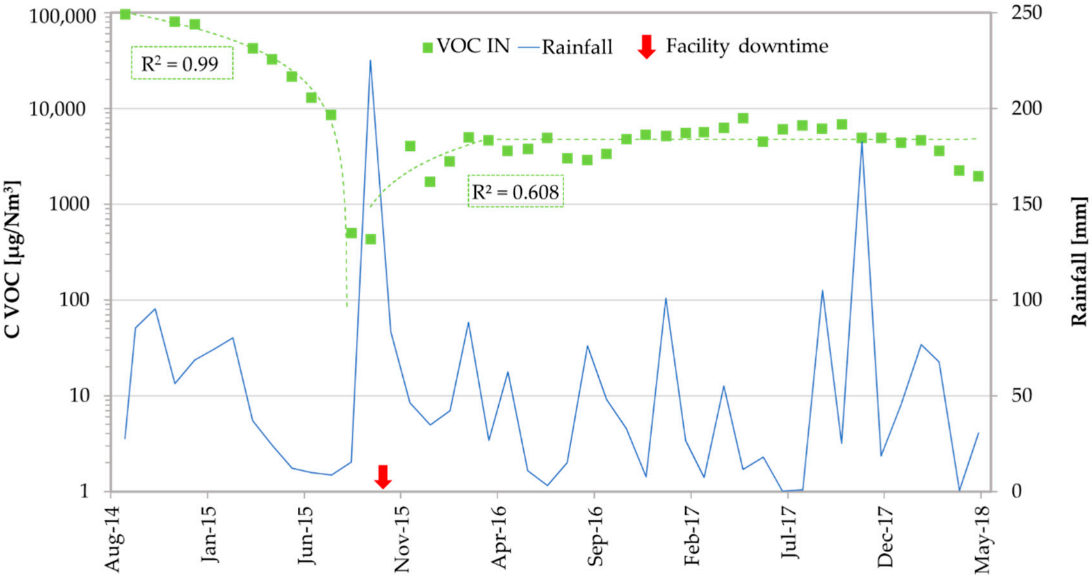

Figure 6. VOC IN and rainfall distributions over time.

3.2. Coring Survey

C<12 and C>12 hydrocarbon concentration is depicted in Figure 7, where it is noticeable how many samples were still above the remediation threshold limits after the monitoring campaign in 2018. A reduction of the initial concentration over the years was observed in all the soil samples.

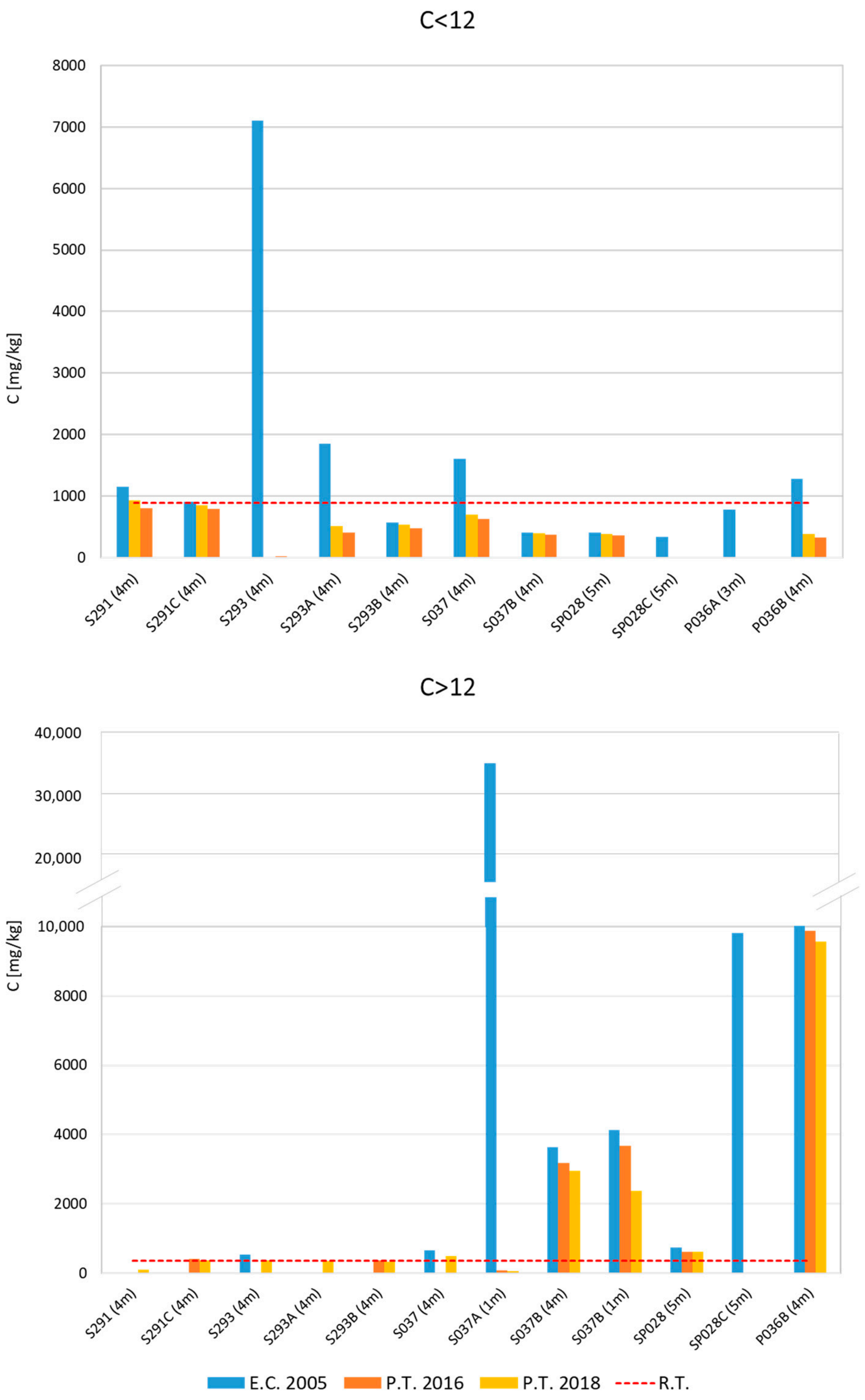

Figure 7. Concentration of C<12 and C>12 compounds in samples over time.

It is also visible in Figure 7 that the highest contamination reduction was obtained in the first two years of treatment.

Except for six samples still above the remediation limit for C>12 hydrocarbons, the RT was reached everywhere within four working years (Table 2) for all light hydrocarbons. The samples with concentrations still above the threshold limit values are shown in red in Table 2. Samples with an initial concentration lower than 0.5 mg/kg (S037A (1 m), S037B (1 m), P036 (1 m) for C<12 and P036 (1 m) for C>12) and lower than 4 mg/kg (P036A (3 m) for C>12) are not indicated.

Table 2. Efficiency of the remediation treatment for C<12 and C>12 hydrocarbons.

Core Sample n.	Sampling Depth (m)	C<12			C>12		
		RT = 891 mg/kg			RT = 365 mg/kg		
		EC 2005 (mg/kg)	PT 2018 (mg/kg)	Efficiency (%)	EC 2005 (mg/kg)	PT 2018 (mg/kg)	Efficiency (%)
S291	4	1156	800	30.8	119.4	99.2	16.9
S291C	4	908	786	13.4	445.2	362	18.7
S293	4	7108	25	99.6	525	367	30.1
S293A	4	1855	412	77.8	404.4	350	13.5
S293B	4	569	478	16.0	406.5	335	17.6
S037	4	1608	623	61.3	658	491	25.4
S037A	1	<0.1	-	-	34,177	50	99.9
S037B	1	<0.1	-	-	4128	2381	42.3
S037B	4	408	366	10.3	3642	2953	18.9
SP028	5	410	360	12.2	749	622	17.0
SP028C	5	333	15	95.5	9812	<5	99.9
P036A	3	785	<5	99.4	52	<5	99.9
P036B	4	1276	330	74.1	10,026	9572	4.5
Total	-	16,416	4195	74.4	65,096	17,582	72.4

The global efficiency for the reduction of total hydrocarbons (C<12 + C>12) was found to be 73%, but the global treatment cannot be considered concluded and needs an extension for additional 24 months from the official end, as planned in the SRP. As expected, the efficiency related to short-chain hydrocarbons reached a slightly higher level than long-chain ones. The total efficiency for the reduction of C<12 was about 74.4% (calculated on the totals of C<12); instead, the total efficiency for the reduction of C>12 was about 72.4% (calculated on the totals of C>12). In fact, the SVE is more effective with smaller aliphatic compounds, which are more volatile and therefore represent generally the primary component in vapors in the petroleum source.

It is worth mentioning that the efficiency rate covers a wide range, e.g., from a minimum of 4.5% (P036B) to a maximum of 99.9% (SP028C) for C>12, indicating that the remediation performance can deeply vary in the area, even considering the same contaminant. Moreover, it is interesting to notice that, in the same sample (e.g., P036B (4 m)), the final efficiency reached 74.1% for light hydrocarbons and 4.5% for the heavy ones. In general, extraction efficiency decreased with the increase of contaminant molecular weight. However, concentration reduction rates greater than 90% were difficult to achieve [7].

4. Data Interpretation and Future Implications

By the vapor concentration data and the cumulative mass extracted (Figure 5), several considerations can be drawn concerning the success and the general performance of the SVE system.

Extracted concentrations show an initial spike (96,000 $\mu g/Nm^3$) followed by a rapid decline towards concentrations ranging from 3–5% of the initial concentration (2800 ÷ 4800 $\mu g/Nm^3$). As the time of SVE operation increased, the less mobile phases (i.e., more strongly adsorbed forms) or gasses from greater distances were removed. In fact, two primary physical mechanisms in SVE operations are mass transfer (as the partition of one phase to another) and mass transport. Desorption phenomenon from the soil particles may occur for long time [32]. During the Phase I, mass transfer provides little contribution until the extracted concentration decreases significantly as the advective soil volume is swept. At later times (Phase II), the extracted concentration changes very slowly.

As described above, the early rapid decay in concentration (Phase I) corresponds to the permeable soil volume holding volatilized vapors easily accessible. Instead, the mass removal from low-accessibility domains entails a mass transfer lower rate (Phase II). This implies that, during the first year of SVE treatment (Phase I), over 420 kg of VOCs were extracted, which corresponds roughly to the 78% of the total mass extracted (540 kg) in four years of treatment (Phase I + Phase II).

In this case study, a small contaminant "rebound" effect was observed during the monitoring period. VOC IN concentration showed a spike (4000 µg/Nm^3) after the facility shutdown. The compounds retained in the stagnant regions escaped slowly by diffusion and resulted in rebounding of concentrations in the gaseous phases.

Experimental results indicated that the water saturation from rainfall is one of the important factors for contaminant volatilization; in fact, high water table causes significant mass transfer limitations. Consequently, the limited rate of mass transfer may be attributed to the reduction of the interfacial area available for VOC volatilization.

Therefore, it is clear how variable the remediation performance could be according to different environmental conditions.

Cross-sections of subsoil and permeability are illustrated in Figure 8. Figure 8a shows how the moisture influences the VOC extraction in mostly uniform and permeable soils. In the borehole P036B, the water reduced the permeability to gas flow by occupying more pore space. Therefore, when the water saturation is high (on the order of 70% to 80% of the pore space), the gas phase is mostly disconnected into bubbles, and the gas flow is orders of magnitude less than the flow through dry soil. This involves a reduction of the system effectiveness.

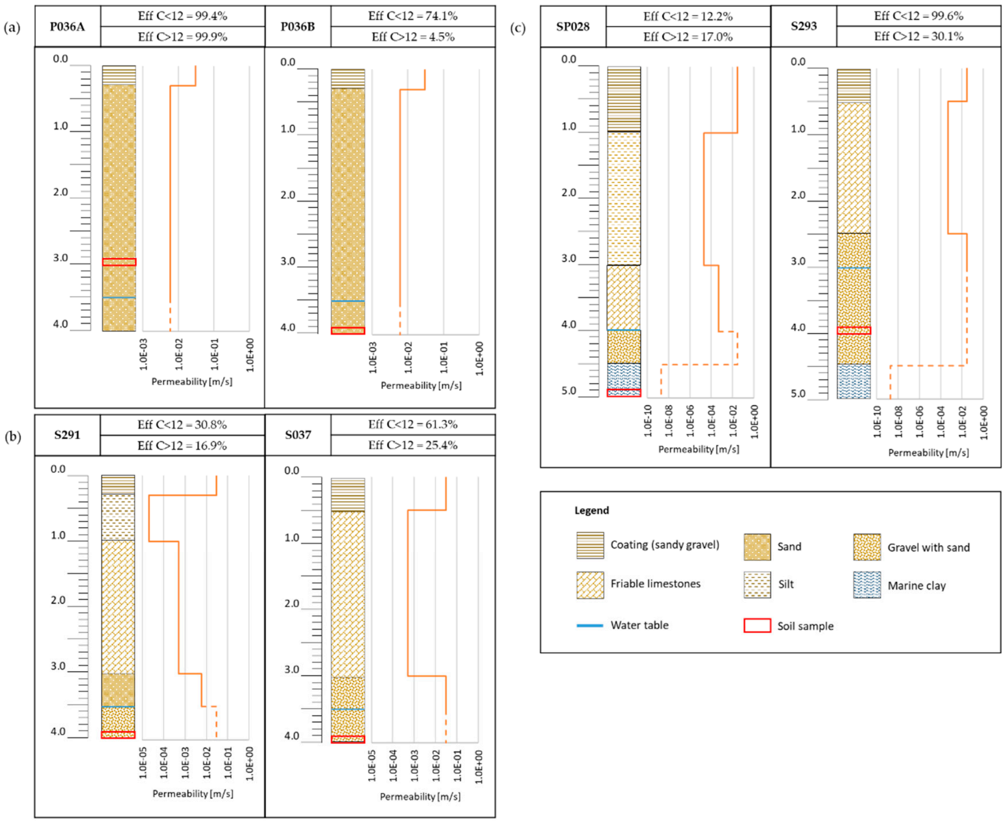

Figure 8. Stratigraphic column description for samples P036A, P036B, S291, S037, SP028, and S293 (uncertainty in the profiles at the bottom of the wells are indicated by dashed lines).

It was observed that heterogeneous geologic conditions, with the presence of low permeability layers overlying zones of higher permeability, could reduce the system effectiveness. In Figure 8a, it is shown how layers with different permeability could affect the total remediation efficiency for both light and heavy hydrocarbons. For boreholes with interbedded sand, silt, or clay (such as S291 and SP028) (Figure 8b,c), SVE induces flow through the sand that bypasses silt and clay lenses because of their higher moisture contents and lower absolute permeability. In other terms, sand is dominated by a significant airflow, while a much slower process of diffusion dominates the contaminated silts and clays, if any gas flow occurs. The ability of SVE to remove volatile contaminants from highly permeable soils (intrinsic permeability $K > 10^{-8}$ cm^2) is well established in literature [33–35]. In these cases, the extracted concentrations may fall rapidly during the initial SVE operations, but once the SVE operations cease, contaminant vapor concentrations slowly reach the initial condition by diffusion from the silty/clay (i.e., less permeable soils act as a secondary source of contamination). In such cases, the removal can often be improved by modifying the extraction strategy (e.g., operating different or new wells, transitioning to a lower extraction rate, pulsing SVE operation). In particular, the rebound test provides valuable data for assessing the time of operation to achieve performance objectives as well as a benchmark for assessing progress toward cleanup during subsequent operations [36]. Consequently, soils with low air permeability are more difficult to remediate and exhibit reduced removal efficiency [35]. SVE is generally most effective in uniform soils with good conductivity and low moisture content. Furthermore, an excess of moisture can also cause a decrease in the microbiological activity. Glascoe et al. [37] demonstrated through laboratory measurements and mathematical simulations that even small changes in temperature and moisture content can influence microbial activity, affecting the overall efficiency of the remediation operation.

5. Conclusions

This study aimed to illustrate the key factors involved in an SVE remediation treatment. The effectiveness of the SVE system was evaluated as the removal rate of organic pollutants from soil and air matrices. SVE was used for the reduction of short and long-chain hydrocarbons, allowing us to obtain the following main results.

- Soil texture affects air rate and vapor movement through the ground and, subsequently, the total VOC removal. The higher the soil permeability is, the more effective the SVE system is. The presence of low permeability layers overlying zones of higher permeability reduces the global effectiveness of the remediation system; however, in low permeable sediments, the removal rate reached values of efficiency >12%.
- The SVE remediation system was effective at reducing VOCs in the vadose zone with a total final efficiency equal to 73%. The remediation targets were reached within four working years for all light hydrocarbons, highlighting how SVE is more effective with smaller and lighter organic compounds. Six samples showed concentrations still higher than the remediation target for heavy hydrocarbons and, thus, an extension of the treatment was planned for 24 months more.
- During the first year of SVE operations, over 420 kg of VOCs were extracted, corresponding to approximately 80% of the total mass extracted (540 kg) in four years of treatment.
- To evaluate the SVE performance for completion or transition to another technology, a full rebounding test may be performed.

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