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An Integrated Approach to Assess Smart Passive Bioventing as a Sustainable Strategy for the Remediation of a Polluted Site by Persistent Organic Pollutants

Mariangela Triozzi, Maria Silvia Binetti, Claudia Campanale, Vito Felice Uricchio and Carmine Massarelli *

National Research Council of Italy—Water Research Institute, CNR-IRSA, Address F. De Blasio, n. 5, 70132 Bari, Italy

* Correspondence: carmine.massarelli@ba.irsa.cnr.it

Abstract: Recently modern methodologies allowed the improvement of conventional bioventing strategies in an engineering technology known as smart passive bioventing (S-PBv). The latter is an increasingly used application to reduce the concentrations of organic contaminants below the relative value of contamination threshold concentration (CSC). The S-PBv exploits the natural fluctuations of atmospheric pressure, which allow air to enter into the subsoil, to facilitate natural remediation processes. In this way, the efforts in terms of economics resources in the remediation process are minimised, the risk of pollutants volatilization is drastically reduced, and the degradation favoured by microorganisms is promoted. Our study aims to provide the essential information to plan a series of in situ tests (pilot test) to verify the applicability of this remediation technology, through the use of intelligent sensors designed and engineered using open-source hardware and software.

Keywords: smart passive bioventing; bioremediation; pilot test; polluted site; organic pollutants; open source

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1. Introduction

The relationship between environmental degradation and pollution is becoming more and more marked. This can be an inevitable consequence of massive industrialization, often conducted with unsustainable and not environmentally friendly practices. The excessive use of pesticides applied to agricultural land, the exploration and extraction of mineral resources, the spillage of crude oil, and the improper disposal of waste are among the human and industrial activities that involve a reduction of arable land for agriculture [1] and a reduction in the availability of drinking water [2–4].

As part of the environmental remediation strategies, the reclamation practices for the recovery of contaminated areas assume considerable importance for human and environmental health [5].

In the European context, there is no specific common legislation on the protection and rehabilitation of contaminated sites or soils, unlike other environmental sectors, such as water and air. In order to fill this legislative gap, the European Union has, over the years, incorporated many operational principles in the environmental field into certain community treaties. Europe has often applied other sectoral directives that help define recovery strategies, e.g., the Nitrates Directive [6]. Towards the end of the last century, the European Union adopted as its environmental policy the adoption of programs based on priority missions to be carried out over a certain time.

In particular, for remediation, the reference is the seventh environmental action program.

The European Union has set itself the objective of drawing up a common action plan for all Member States on land reclamation and soil protection. In the absence of specific legislation, Directive 2004/35/EC [7] is a valid reference for solutions concerning the rehabilitation of polluted sites [8].

The current Italian legislation applies this directive in the Environment Code. In particular, previews that, as a result of a preliminary environmental characterization and the consequent detection of a violation of the normative limits of reference—contamination threshold concentrations (CSC), whether it is necessary to determine the Site Concentration Risk Threshold (CSR), or for small areas, proceed to the remediation of the area [9].

Over time, bioremediation strategies have been demonstrated to be effective, ecological, and economic compared to physiochemical remediation practices which are rather expensive and sometimes ineffective [10–12]. Bioremediation includes ex situ and in situ methods. The former (e.g., Solid-phase treatment, Slurry-phase bioremediation) implies the transport of polluted matrices from the site of origin to the treatment area with the risk of spreading contaminants into the environment. The second (e.g., bioventing, bioslurping, biosparging, phytoremedetion) provides an in situ treatment of polluted matrices, reducing the risk of spreading pollutants and the costs of transport [13].

Bioslurping is a technique suitable for the reclamation of soils with high permeability and less suitable for those with low ones. Biosparging is applied for the treatment of water polluted by diesel and kerosene, but its efficiency depends greatly on the biodegradability of contaminants and the degree of soil permeability [13]. Phytoremediation is an economical, ecological, and not invasive technique that takes advantage of the action of different plant species that can purify the air from pollutants. However, the remediation technique is slower than other repair processes and strongly depends on the growth conditions of plants [14].

Among the last strategies cited, bioventing has become very popular over time. It is a microbiological remediation strategy, feasible exclusively in situ, typically in the vadose or unsaturated area, which exploits the metabolism of native bacteria present in soil and the subsoil, to degrade the organic contaminants adsorbed to the organic and mineral fractions of the soil. Bioventing technology enhances microbial degradation activity (aerobic, anaerobic, or co-metabolic depending on the type of gas injected) through the introduction of air, gas, and in some cases nutrients [15], to the native bacterial community to stimulate its growth and metabolic activity. Conventional bioventing provides an air injection with a blower to promote the bacterial degradation of organic compounds, minimizing volatilization. In some cases, the biodegradation of contaminants can also occur naturally in other cases, it is necessary to stimulate the activity of natural degradation, as pollutants can negatively impact the bacterial communities (active bioventing) [16].

The technology of bioventing, therefore, involves the injection of air, oxygen, or other gases through blowers connected to vertical and horizontal wells aimed to favour the aerobic catabolism of organic compounds. Through these wells, the gases reach a depth that depends on the spatial distribution of the contamination. By changing the type of gas, it is possible to change the degradation process [16,17].

The feasibility of a bioventilation system depends on various physical, chemical, and biological processes that can affect the site to be reclaimed. They include the activity of bioventilation, the diffusion and distribution of pollutants in soil, the area of oxygen influence, and the permeability of the soil to gases. A traditional bioventing plant is certainly a quick and easy installation; however, frequent periodic checks and replacements for filters, flowmeters, or indicators are required. Moreover, if we install an extraction or extraction and reinjection system, this will probably require more intensive maintenance. All these requirements involve a greater expenditure of economic resources in addition to increasing the time of the bioremediation of a polluted site. All these efforts are considerably reduced in the design of a passive bioventing system.

Passive technology does not use electric blowers to force the entry of air into the soil but variations in atmospheric pressure to allow gas exchange between the atmosphere and the subsoil through vent wells [18]. This translates into a remediation strategy with a strong eco-sustainable and affordable character. Nonetheless, even today, it has few applications in design scale, perhaps due to the uncertainties related to the challenges of scale-up for applying this technology in the field. The atmospheric pressure can vary daily with the weather conditions. A significant change in atmospheric pressure cannot, on its own, ensure the development of sufficient gradients between the atmosphere and the subsoil and ensure the airflow necessary to stimulate biodegradation activity effectively. In order to create the right gradient that can ensure sufficient airflow to the biodegradation process, it is also necessary to consider the characteristics of the soil and the lithology of the site to be restored.

Passive bioventing is a technology still little used but surely of greater interest if combined with systems able to acquire timely weather–climate data and local monitoring. In light of this, the National Research Council-Water Research Institute (CNR-IRSA) improved a strategy of PBv coupled to an intelligent sensor system.

The objective of the present work is to assess the application of the smart passive bioventing, for the definition of a remediation strategy for the biodegradation of organic pollutants. A pilot test with a set of in situ investigations coupled with the use of smart customized sensors (S-PBv) has been set up to evaluate the technique as a remediation strategy. Our work consists of direct and indirect investigations for the acquisition of specific parameters of the site to be reclaimed. In the preliminary phase, the execution of perforations, sampling, and field tests allowed the assessment of the technology to the specific site and the type of contamination. In the second phase, based on previous results, it has been possible to set up an environmental remediation strategy aimed at reducing the concentrations of organic soil contaminants below the CSC.

On-site investigations allowed the definition of the design of the passive ventilation system. The use of smart sensors in our work represents an optimized system to improve data management, thanks to the possibility of being able to use and develop ad hoc programming code. In addition, the implementation of S-Pbv to assess the applicability of the remediation strategy to a real site allowed us to enhance new aspects related to the topic of bioventing, still poorly deepened in the relevant literature.

2. Pilot Test Set-Up

An essential premise in setting up the pilot test is the need to characterize (identification, nature, and extent of contamination) and frame the site to remediate (location and use of the site, regulatory framework, and technical–administrative reconstruction) with the smart passive bioventing (S-PBv) application.

This is important to have the spatial and environmental data useful to reconstruct the technical–administrative remediation process. In addition, it is necessary to evaluate a series of parameters (geological, hydrogeological, geochemical, and biological) with field tests to determine them. It is required to deepen the degree of knowledge of these parameters for a correct operational design and subsequent application of the S-PBv.

2.1. Framing of the Study Area

The investigation area selected for a hypothetical application of the S-PBv is located in the Apulia region, southern Italy, in the urban–industrial-site in the province of Taranto. This is a strongly industrialized area with several industries, the largest steel plant of companies in Europe, and a shipyard [19]. According to the declaration of urban use, provided by the General Plan of the Municipality of Taranto, the area is considered a “Commercial and Industrial Site”. In this area, there is a large tank for storing fuel for vehicles. In the past, accidents have occurred due to fuel losses in soil, which have led to the assessment of chemical risk by measuring concentrations of pollutants in the area concerned. In fact, In August 2010, following the finding of a leak from an underground tank, soil samples were collected for pollutant investigations. Four excavations have been carried out and four samples were collected (S1-1, S1-2, S1-3, S1-4) (Figure S1). Moreover, in the same period, to verify the soil quality around the tank, three other composite samples were collected with a core barrel of 101 mm in diameter until a depth of about five metres

(SA-1, SA-2, SA-3) (Figure S1). Based on the initial soil surveys, further analysis had to be carried out and an operational land reclamation project was developed and submitted to the competent authorities. The Services Conference, on August 2011, asked to integrate the surveys already provided with the collection of further samples called SB from 1 to 9 and SC1 and SC2 (Figure S1), and required for all cores, three sampling depth intervals.

On the basis of the environmental investigations, for the analytes examined, the concentrations exceeding the limits provided for by Legislative Decree no. 152/06 and ss.mm.ii were highlighted. In particular, the samples S1-1, S1-2, S1-3 and S1-4, showed exceedances for ethylbenzene, styrene, toluene, light and heavy hydrocarbons, PCB, and BTEX summation. As regards PCBs, the values observed for S1-1, S1-2 and S1-3 do not exceed the legal limit. For heavy hydrocarbons, the values observed for S1-2, S1-3 and S1-4 do not exceed the legal limit (Table S1). Pollutant values vary with the sampling depth, as can be seen in Table S2. In fact, for some analytes for some depths, the legal limit is not exceeded.

Investigations of other samples referred to SB-1, SB-2, SB-3, SB-4, SB-5, SB-6, SB-7, SB-8, SB-9 and SC-1 and SC-2 (Figure S1), allowed to exclude the presence or exceedance of the analytes examined in almost all the excavations studied. For some samples, non-compliance with the legal limit was found only for light and heavy hydrocarbons (Tables S3–S6).

The formulation of the risk analysis, scheduled by the Italian National System for Environmental Protection (ISPRA), determined the source surface in the deep ground (SP) and in the topsoil (SS) (Tables S7–S8). The source surface in the deep ground (SP) was defined across the construction of the polygons of influence (Thiessen polygons). The source of contamination in deep soil was determined considering the set of polygons where the contamination threshold concentrations were found in excess in the survey campaigns. As regards the surface soil (SS), only one sampling was carried out (SA 2—0.50 m and 0.70 m from the surface) which detected exceedances of BTEX and light and heavy hydrocarbons. The considered source of contamination in the surface soil (SS) has an equivalent shape and size to deep ground (SP). References (Figure S1 and Tables S1–S8) are cited in the Supplementary Materials.

2.2. Smart Sensors and Design Scheme

The construction of a smart sensor system is essential to continuously monitor the parameters for the applicability of the remediation technique. The use and implementation of intelligent technologies allow optimisation of the management of the system's data, achieving an efficient result. The monitoring system shall comprise several devices capable of measuring different environmental parameters (temperature, pressure, oxygen and carbon dioxide, and wind speed). These sensors are designed in blocks independently from each other but can communicate and transmit the measured data to a central recorder. Each block consists of the following sensors: one temperature sensor (on the ground surface), two pressure sensors (about fifty cm from the surface and underground), one oxygen and carbon dioxide sensor, one wind speed sensor (transducer), one Bluetooth module, one control board based on Arduino technology.

The temperature sensor is used to estimate and monitor the temperature on the ground surface. The aforementioned depends on biodegradation kinetics.

The implementation of the system used was made with open-source hardware and software. The device is a new prototype solution designed and engineered by CNR-IRSA (National Research Council-Water Research Institute). In a process of aerobic biodegradation, microorganisms constantly consume oxygen and produce carbon dioxide as a by-product. The biological activity in the soil can be best monitored by measuring the site condition for a long period during the bioventing process. The following figure shows the design scheme with which to implement the technology in the field (Figure 1).

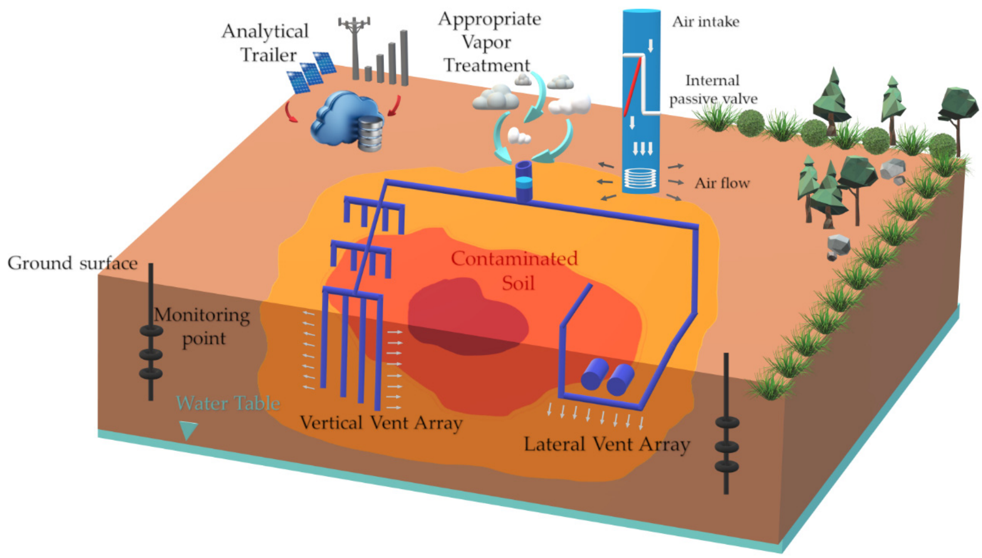

Figure 1. Schematic diagram of a smart passive bioventing (S-PBv) system.

2.3. Definition of the Environmental Parameters Influencing the S-PBv Process

The availability of the proposed technology for site remediation is closely linked to certain site-specific parameters. In fact, the lithological, physical, chemical, and biological properties of the soil are fundamental to assessing both the applicability and the effectiveness and efficiency of the remediation technology. The choice of remediation technique to be implemented is also influenced by the type of contamination.

The applicability of the S-PBv technology is related to definite site-specific geological, hydrogeological, geochemical, and biological parameters. These settings are described in the sections below.

2.3.1. Geological, Hydrogeological, Geochemical, and Biological Parameters

The parameters characterizing the lithological, chemical, physical, and biological properties of the soil are fundamental to understanding both the behaviour of contamination and assessing the applicability of the S-PBv. These parameters are:

Parameters Influencing the Chemicophysical Soil Properties

- Grain size and soil bulk density (mm—g/cm^3). The grain size is the diameter of individual grains of sediment. The bulk density is a measure of soil compaction, which is defined as the dry weight of many particles of the material (soil at 105 °C) divided by its total volume.
- Intrinsic permeability (kg—cm^2) of soil to gas. It is a measure of the capacity of soils to transfer fluid. The intrinsic permeability intervals of the soil vary according to its characteristics (Figure 2). The intrinsic permeability ranges over amounts to $10^9 \div 10^8$ cm^2; the soil must have high hydraulic conductivity and low humidity. It must permit air motion and oxygen availability. The ability of soil to transmit air is decreased by the presence of soil water, which can stop the soil pores and decrease airflow. The configuration of the ventilation shafts (distance, centre distance) derives from the soil permeability.
- The moisture of the soil and the water retained in the soil outline a limit for the S-PBv process. Excessive moisture reduces the air permeability of the soil and wards off the gas transmission, while too low moisture inhibits biomass metabolism and microbial activity.
- Pollutants concentration. Minimal concentrations of pollutants in the soil can excessively reduce the rate of biodegradation. At the same time, excessive concentrations of them can be lethal to microorganisms, e.g., excessively high concentrations of

petroleum hydrocarbons limit the potential for biodegradation [20]; on the contrary, if their amount is very low there is not enough carbon input to promote the growth and activity of microorganisms [21]. The biodegradation rate is in an inverse proportionality relationship with the chemical complexity of the hydrocarbon molecule and its molecular weight. Thus, there will be an increase in this rate with the reduction of the structural complexity of the molecule and its molecular weight [22]. The environmental characterization surveys allow knowing the type and the number of pollutants present in the site to be subjected to remediation. Moreover, through studies, it is possible to relate the parameters of contamination with the most suitable remediation technology and therefore more effective for the type of contamination present in the investigated site.

- pH. Soil pH changes can affect the bioremediation process because they have an important influence on biological processes. Microorganisms have a different optimal pH range and therefore pH changes can reduce the efficiency and rate of total microbial degradation in a site, although generally, this parameter may have adverse effects within a range of 5–9. In the case of metals, pH changes can determine structures and states of toxic valence for microorganisms. High pH values reduce the bioavailability of metals and can change the organic component of the soil, affecting the existence of microorganisms in that site. Moreover, these variations can negatively affect the adsorption reactions of metals in soil and their mechanisms of absorption by plants [23]. It is important to measure the pH of the samples submitted for the lithological examination.
- Temperature. Soil temperature affects the growth of microorganisms and is directly proportional to biodegradation kinetics. Generally, the biodegradation rate is doubled every time the temperature increases by 10,000 °C. However, an extreme increase in temperature can cause irreversible damage to microorganisms due to excessive heat. Temperature changes affect the adsorption and desorption reactions of pesticides and heavy metals to soil and microorganisms [24] and can change the chemical–physical characteristics of contaminants, e.g., when the temperature increases, there is an increase in the solubility of hydrophobic contaminants and therefore their bioavailability. Conversely, low temperatures hinder the passage of contaminants from the solid phase to the liquid phase [21]. The temperature will be evaluated in situ and on the samples through special equipment, and during the execution of the pilot test will be constantly monitored in order to correctly assess the speed and time of evolution of the biological process.

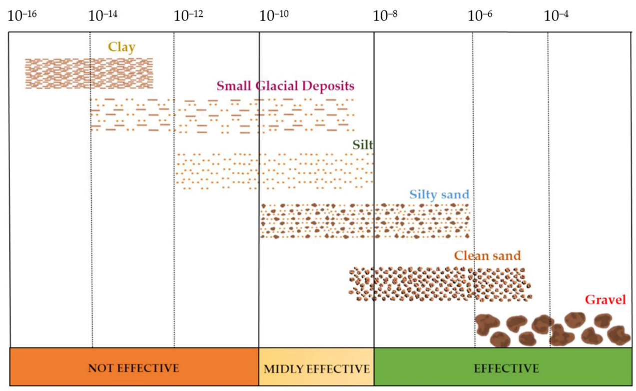

Figure 2. The intrinsic permeability ranges of soil, with different grain sizes, according to their characteristics.

Parameters Influencing the Biological Soil Properties

The microbial activity may be influenced by several biotic and abiotic factors during the process of bioremediation in soil. The efficiency of this process depends, first of all, on the survival of microorganisms and consequently on their biological activity. This activity is closely related to the microbial species present in a site, their density, the presence of nutrient sources, at appropriate intervals of temperature, pH, humidity, and the amount and bioavailability of pollutants [23].

There are microorganisms with specific biodegradative polluting potential. The following are examples of microorganisms with their substances that they can catabolize:

1. *Pseudomonas* spp.—benzene, anthracene, hydrocarbons, PCBs;
2. *Alcaligenes* spp.—halogenated hydrocarbons, sulphates, PAH, PCBs;
3. *Flavobacterium* spp.—naphthalene, aromatic biphenyls;
4. *Azotobacter* spp.—benzene, cycloparaffin;
5. *Rhodococcus* spp.—aromatic hydrocarbon.

Presence and type should be evaluated in the laboratory through the study of site-specific microcosms.

The greatest limiting factor of microbial activity in biodegradation processes is represented by oxygen (O_2). The measurement of this chemical element in the soil is an index of the biodegradation activity of contaminants and therefore can be taken as a measure to assess the need and suitability of applying a bioventing technology.

The increase in the concentration of O_2, which in saturation conditions of the unsaturated medium can reach values of about 21%, comparable with those of atmospheric air, determines in fact the acceleration of the natural process of biodegradation in aerobic metabolic conditions of organic substances by the native bacteria.

For the development of the aerobic processes in the subsoil minimum values of oxygen equal to about 3% of the soil gas (v/v) are necessary even if for prudence this minimum limit is fixed at about 5%. The maximum value available under saturation conditions corresponds to the atmospheric value of 20.9%.

The concentration of O_2 in contaminated soils undergoing a natural biodegradation process is close to 5%, which is lower than the typical concentration of uncontaminated soil (about 20%); this reduction is due to metabolic activity and is assessed by comparison with the O_2 concentration in uncontaminated soil areas. However, in porous soils, high concentrations of O_2 can also occur in the presence of biodegradable contaminants, because the O_2 consumption of biomass is compensated by atmospheric rearrangement. In this case, the soil is aerated naturally, so it is not necessary to resort to the installation of systems (piezometers, trenches, etc.) to allow entry of area into the soil.

In the event of an extreme oxygen shortage, anaerobic degradation of contaminants in soil, e.g., in the catabolism of petroleum hydrocarbons, microorganisms have electron acceptors other than oxygen (carbon dioxide, iron, sulphate, etc.). Providing these electron acceptors is less expensive from an economic point of view, but this type of microbial degradation could be complex due to the difficulties of detecting anaerobic microbes that efficiently catabolize hydrocarbons [25].

It is important to constantly monitor this gas, on samples in the laboratory and in situ during the execution of the pilot test, in order to correctly assess the speed and time of evolution of the biological process.

A significant measure of biological activity is represented by the concentration of carbon dioxide (CO_2) due to the production of carbonates that leads to the reduction of CO_2 in gaseous form (situation possible for pH > 7.5 and high alkalinity). In contaminated soils, CO_2 is even greater than 10%, therefore higher than that of uncontaminated soils (less than 0.5%); this increase is due to metabolic activity (catabolite).

It is also important to evaluate the fraction of organic carbon (foc-g-C/g-soil) in unsaturated soil, subject to reclamation. The organic carbon content in soil is conventionally correlated with that of the organic substance present; in fact, the latter is equal to 1724 times the organic carbon content.

Microorganisms require nitrogen, carbon, and phosphorus to increase biomass. It is important to check the presence of nutrients and water availability. They represent limiting factors beyond oxygen for the biodegradation process; in case they are scarce, it is necessary to dose with an irrigation system water additive with nutrients, which is also useful to regulate soil moisture (humidity rates not appropriate to the life of the microorganisms do not make the bioremediation efficient).

Studies have shown that the adequate ratio of nutrients, carbon, nitrogen, and phosphate (C:N:P), to promote the growth of microorganisms, is 100:10:1 [26–28]. The biodegradation of hydrocarbon pollutants is supported by excessive amounts of nutrients. Moreover, high amounts of phosphate, nitrogen, and potassium can reduce the amount of oxygen present in the soil because they imbalance the C:N:P ratio [22,29–31].

The availability of nutrients and water should be assessed on samples taken for each lithology investigated.

The success of the remediation process is conditioned by the availability of contaminants and their concentration. Bioavailability represents the ability of the contaminant to participate in biodegradation processes. This ability can be influenced by abiotic and biotic factors: chemical properties of pollutants, in particular their composition, volatility, and hydrophobicity in addition to the physicochemical properties of the soil, environmental conditions, and biological activity [25].

Pollutants are generally not accessible to microorganisms when they are adsorbed on solid particles or when they are in the gaseous or water-insoluble phase. They are accessible when dissolved in water. Studies have shown that the unavailability of hydrocarbons in the remediation process due to the low solubility of the pollutant in the aqueous medium can be resolved by adding biostimulant-producing microorganisms. These molecules promote the solubilization, de-absorption, or emulsion of hydrocarbon contaminants [25].

The implementation of unsustainable practices in industrialization and agriculture has favoured the phenomenon of soil pollution combined with the action of organic pollutants, such as pesticides, with toxic inorganic elements, such as heavy metals. In these cases, the application of bioremediation technologies can be very complex because the bioavailability of co-existing pollutants can undergo alteration due to additional actions, synergistic or antagonists of contaminants [23].

2.3.2. Climate Analysis

The geological, hydrogeological, geochemical, and biological parameters influence the smart passive bioventing technology. A climate analysis will be conducted to determine the operational parameters for the design and development of S-PBv wells. The study site is a Mediterranean climate region according to the Köppen, and a semiarid to sub-humid climate based upon De Martonne aridity index. The winters are mild but relatively wet, summers are hot and dry. Average annual precipitation values range from 450 to 1775 mm, concentrated between fall and winter. The mean annual T range is 12 to 17 °C [32]. Climate analysis will be performed: thermometric analysis (averages, dispersion and shape indices, frequencies, trends); rainfall analysis (averages, shape indices, frequencies, SPI, trends), rainfall events can have a significant effect on the S-PBv technique, hence, water levels should be under surveillance in the area to determine the amount of up-flow resulting from the applied vacuum; barometric variations analysis in different time scales. The study will be employed the stations of Grottaglie and Taranto [33].

3. Results

3.1. Unsaturated Soil Field Test and Pilot Tests

In order to proceed to the definition of the remediation project through the application of S-PBv technology, it is necessary to proceed to the determination of all design variables, for some of which it is necessary to perform a pilot test—field tests.

The field checks, proposed below, will allow for evaluating the full applicability of the system to the site in question as well as to provide information on the final sizing type in a full-scale implementation.

The preliminary execution of field tests must therefore provide the data to be taken for the elaboration of the project in terms of efficiency and duration of remediation, in particular, the rays of influence of the system—radius of influence (ROI)—defined as the maximum distance from the axis of the well within which the effect of the air inlet is affected, distinguishing in:

- ROIp: pressure influence radius, equal to the distance from the axis of the well at which the pressure change induced by the injection/extraction system (P ≅ Patm), is negligible, in our case of natural input;
- ROIox: oxygen influence radius, equal to the distance from the axis of the well, at which the change in concentration of O_2 induced by the insufflation/extraction system is negligible, in our case of natural input.

Both the influence rays of the system must be determined experimentally considering the natural pressure gradients with which the system will work and the rate of biodegradation:

- Air permeability test (to determine the permeability of the soil to gas kg and ROIp);
- Respirometric test (for the determination of the consumption rate of oxygen ko, the biodegradation rate of the contaminant Kb and ROIox).

The factors influencing the ROI, which will depend on the number of wells necessary for the remediation of the site, are:

1. The presence of impermeable surfaces (asphalt, concrete)
2. The depth of the window section of the well
3. Ventilation modes (ROIox in injection modality is > of that in intake)

The above elements constitute, in fact, the conditions defining the conditions of applicability provided for in the technical literature of reference [34–37].

3.2. Perforations Executions

To achieve a correct perforations execution, it is essential to define the topographic model of the site. The number of environmental studies should be sufficient to paint a full picture of the measured endpoint. The execution will be used for characterizing site conditions, monitoring pilot tests, and developing a bioventing technique. For the environmental study, eight vertical wells have been carried out, among them two piezometers. The excavations are 5 m deep, 101 to 219 sizes, and executed with the drilling method. A sampling of soils found during drilling enhances understanding of the underground. The casing used is composed of a Polyvinyl chloride (PVC) coating of 4″, all filtered. The PVC pipe must resist the suppression of the backfill and compaction apparatus.

3.3. Characteristics of the Pilot Plant and Instrumentation

A pilot plant is a pre-commercial production system that utilizes new production techniques principally to gain an understanding of the new technology. Pilot plant scale tests of the S-PBv process usually measure pressures, flow rates, contaminant concentrations, and other parameters [38]. It consists of a system of piezometers that can measure positive and negative pore water pressures. The assembly of the valves, located at the head of the piezometers, allows the entry and exit of air in the monitoring points. This is required to intercept the stream to be sampled. Additionally, a nutrient injection system will be needed, if necessary. The test will use the smart sensor, a portable photoionizer (PID), and active carbon vials for adsorption of the extracted gas (HC vapours) for subsequent laboratory analysis. The portable photoionizer measures volatile organic compounds by indicating the extent of the contamination. The sensors will be installed according to the specific needs related to the site and the monitored parameters.

The real-time data acquisition service will be implemented using an open-source software platform developed by CNR-IRSA. The platform enables the continuous delivery of information streams for the application of storage, analysis, and visualization methodologies. Data traffic is optimized through smart control and configuration systems based on C, C++, Python, JavaScript, SQL programming languages. The data transmitted are archived in databases and displayed in real-time via the Web with an interoperable geographical platform based on Geoserver and Open layers. The procedures, methodologies, and protocols to be used can be customized and verified according to the characteristics of the context to which they apply. There will be prepared an ad hoc web space with various access profiles to log in to display the recorded data during monitoring and subsequent corrective actions.

3.4. Air Permeability and Respirometric Tests

The air permeability test is carried out to determine the permeability of the soil to gas (kg) and the distance from the well beyond which it is not affected by pressure changes induced by this and subsequent evaluation of the ROIp.

Normally in the case of a bioventing application (active), a flow step test (stepped-rate test) is carried out, with the aim of identifying the optimal injection/extraction flow rate, derived from the reading of the intersection of the vacuum/overpressure curves—the flow of the blower and the well, useful for deciding the size of the blower, which will be used in subsequent tests at constant flow, in order to determine kg and ROIp.

In our case (S-Pbv), the inlet flow rates, having the same characteristics as the inlet piezometers, will depend exclusively on the daily variations of atmospheric pressure and the regulation of the inlet valve. This induces an instant-by-instant variable negative gradient, measurable at the monitoring points in the form of a vacuum, between the atmosphere and the subsoil (soil–gas).

In our study, appropriate hypotheses will be used to apply the calculation model, possibly modified, of a constant flow test under transient conditions, suitable for poorly permeable soils. For them, the stationary condition would be reached in a too long time, and/or in the case of the power of a high unsaturated zone (>3 m). In this case, the pressure measurements made in the monitoring wells can be interpreted with the Cooper–Jacob rough expression/solution valid for the (radial) 1-D model [39], from which soil permeability to gas can be obtained.

The respirometric test is performed to assess the biodegradation potential of the site pollutants. They estimate O_2 consumption or CO_2 production of microbial biomass. The rate of biodegradation is estimated based on the changes in O_2 and CO_2 measured in soil gases in the soil after allowing ventilation by air.

The test shall be performed non-stationary and at the entry points, using the associated monitoring points. Before the test, it will be necessary to determine the starting conditions of the system in terms of O_2 and CO_2 concentration in interstitial gases both in the area outside the contamination zone (bottom) and in the ventilation well, and at the monitoring points.

The first part of the test is to allow ventilation of the soil to oxygenate it, allowing free entry of air, for a time that will be evaluated during the tests themselves; this is only if the O_2 concentration is far from the saturation values or at least with a differential of less than 10% with respect to the initial value.

The test will therefore begin at the end of the ventilation (carried out in natural intake), so at a closed pilot plant, after the oxygen concentration at the monitoring points, measured expeditiously, has reached values close to saturation (possibly 20.9%).

If this objective is not achieved, so that the results of the tests can be considered reliable, there must be at least one difference between the oxygen concentration in natural conditions and that in stable conditions as a result of ventilation of the order of 10% of the total must be obtained. If with calculated natural intake rates, it is not possible to achieve an acceptable level of oxygenation at monitoring points, an increase in input piezometers will be required.

The test consists of monitoring and analysis of the variation of CO_2 and O_2 at ventilation and monitoring points at a certain distance.

The atmospheric pressure and air temperature will also be monitored during the test and, initially, the readings will be performed every 2 h; during the test, the sampling frequency will increase progressively and measurements will be made at 12-h intervals and in any case, during the ongoing tests, these intervals may be varied.

However, the measuring frequency should be related to the rate of decrease observed by oxygen: in the presence of a rapid decrease, the readings should be more frequent; conversely, in the case of low decreasing rates, the time intervals may be longer. The test will be interrupted by the achievement of O_2 concentrations below 5%, below which the degradation kinetics of the contaminant is greatly slowed down.

At the end of the test, the temporal trends of oxygen and carbon dioxide concentrations for each input point and control point will be shown in the table and graphically. Starting from the curve of decreasing oxygen over time it will be possible to calculate the initial rate of oxygen consumption and interpret the measures for the calculation of the rate of oxygen consumption, KO, and then the rate of biodegradation (or removal) of the contaminant Kb and the ROIox.

It is reported in the literature that values of the biodegradation rate above 1% of O_2/day are indicators of the potential applicability of bioventing to the site [34].

The value of the ROI for the sizing of the remediation system is chosen as an average among those determined as ROIox and ROIp, possibly repeated for the different depths at which the measurements were performed. The distance "r" between the wells is 1.2–1.5 ROI. The number of wells N can be calculated by covering the entire contaminated area A (m^2) by placing the wells with the reciprocal distance "r" (m) fixed.

Summary of the project parameters to be calculated for the subsequent processing of the Remediation Operational Project through the S-PBV:

1. Air permeability kg (with permeability test)
2. Ray of influence ROIp (with permeability test)
3. KO oxygen consumption rate (with respirometric test)
4. Removal rate of contaminant Kb (idem)
5. Ray of influence ROIox (with respirometric test);
6. Number of wells N
7. Natural air flow Q (field measurements)
8. Duration of the intervention T
9. Verification of air changes

3.5. Soil Analyses

Soil sampling shall be carried out using three continuous core drillings, without core destruction. Taking three samples, in three aliquots, at different depths, involving both the surface soil and the deep soil. In particular, we will collect the following samples from the polls: SA, SB, and SC.

These surveys, to be set up subsequently in the piezometer, will be carried out in the same manner as provided in the paragraph Perforations Executions.

The samples taken will be analysed for the analytes shown in the Table 1, which also shows the hypothetical sampling rates.

The analytical determinations shall be carried out on the soil fraction with a particle size of less than 2 mm, observing the results for both this last soil fraction and all the dry materials, including the skeleton. The skeleton shall therefore be analysed using a 2 mm sieve and the moisture by drying at 105 °C. In addition, undisturbed samples (both for deep and superficial soil) representative of the intercepted lithologies shall be taken, to determine geological, hydrogeological, and biological parameters.

Table 1. Analytes to be investigated, methods, and sample identification.

Samplem from c.p. / Analyte	SA-1 SB-1 SC-1 (0.5)	SA-2 SB-2 SC-2 (2.5)	SA-3 SB-3 SC-3 (4.5)	Limits (*) (mg/kg)
	Method	Technique	L.R.	
Ethylbenzene	EPA 5035A 2002 + EPA 8260C 2006	GC-MS	0.01	50
Styrene	EPA 5035A 2002 + EPA 8260C 2006	GC-MS	0.01	50
Toluene	EPA 5035A 2002 + EPA 8260C 2006	GC-MS	0.01	50
Hydrocarbon C $\leq$ 12 (**)	EPA 3545A 2007 + EPA 8270 D 2007	GC-MS	1.0	250
Hydrocarbon C > 12 (**)	EPA 3545A 2007 + EPA 8270 D 2007	GC-MS	10	750

(*) D.Lgs. 152/2006 Title V All. 5 Part IV Table 1 Column B—Sites for commercial and industrial use. (**) MADEP speciation will be performed.

3.6. Identification of the Areas to Be Reclaimed and Delimitation of the Sources of Contamination

The procedure for the delimitation of one or more sources within a contaminated site on the basis of the characterization data was obtained from the document Risk Assessment Guidance for Superfunds [40], still considered a fundamental guide for these activities. The procedure must be performed separately for surface soil and deep soil, which constitute two distinct secondary sources of contamination as each could have its remediation objective (these aspects are defined by the regulations).

This procedure can be summarized as follows. The first step consists of subdividing the area under investigation into polygons of influence, according to the sampling strategy adopted. In the case of reasoned sampling, i.e., with knowledge of the facts and based on very advanced knowledge of the area and the potential processes of contamination, it is better to proceed according to the Thiessen polygons. In the case of systematic sampling, which is performed when poor information is available, regular mesh cells are created. For reasons of synthesis, we will analyse the case of a single source of contamination with well-known information on what happened. A single source is defined as a source with spatial continuity which can cause risks for the same receptor in the same area of exposure and the source in which, even in the case of patchy contamination, it is impossible to establish a solution of continuity. In Figure 3, let us see how the subdivision of the polygons has been applied by carrying out a reasoned sampling. Each point represents the exact point where the sample was taken and the coloured polygons depend on the concentration values of the contaminants found: if red, the greater the risk threshold concentration value and therefore it is necessary to clean up, if yellow, the values are between contamination and risk concentration threshold and therefore it is necessary to proceed with a characterization project for monitoring over time.

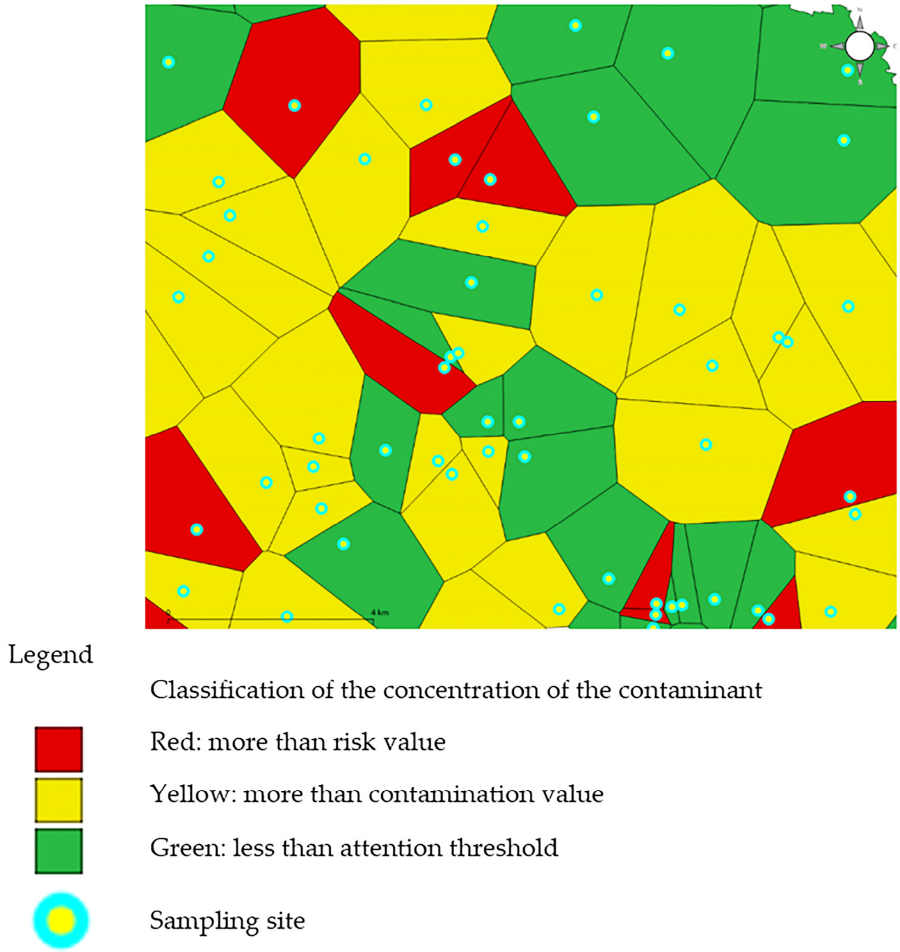

Figure 3. Example of subdivision of areas into Thiessen polygons functional to the identification of monitoring or remediation programs.

On the basis of this classification, it is now possible to identify the areas to be reclaimed and to be paid attention to. Subsequently, we proceed with the determination of the spatial continuity of the sources, for example, if between two red sources, there is a green or yellow one, the latter is considered red, and if there is a green one between two yellow ones, it is considered yellow. We thus proceed according to a hierarchical scale from the cell with the most pollution to the one with the least pollution.

4. Discussion

Bioventing in active form has been considered by some authors as an adaptation of soil vapour extraction (EVS) because it couples the bioremediation with a volatilisation process [41]. Some authors [42] conducted an experimental set-up in which 4 mg g^{-1} (soil) of toluene was reduced by 99% between 11 and 24 days, with a constant gas flow of 40 cm^{-1} h^{-1}. In this case, we are talking about air injection bioventing (AIBV) carried out by injecting air into the soil subsoil [14], optimizing the natural biodegradation in situ. In particular, the aerobic bioremediation process is encouraged and, at the same time, VOC emissions are minimised [43–45]. In order to achieve significant biodegradation rates, the microorganisms mineralising the hydrocarbons must be present naturally in soil and sufficiently large quantities [45]. Tsao et al. [45] showed high percentages of xylene, benzene and toluene removal (52–68%), with high rates of degradation of 6.1–8.0% g of $soil^{-1}$ day^{-1}. Österreicher-Cunha et al. [43] observed the results obtained with BV or AIBV applied to soil polluted from petrol. In 60 days, the contaminant was removed, 95% of gasoline (initial concentration of about 117 mg g of $soil^{-1}$), through the application of a constant air pressure of 2 psi.

Depending on the specific conditions of the sites to be reclaimed, treatment by application of BV or AIBV technology may also take several years. This is an inconvenience associated with the previously mentioned technologies [46]. To reduce the time required for BV or AIBV technology, very high air flows are often used. This promotes the volatilization of pollutants from the treated site and therefore the need to treat these gases. In addition, energy costs must be considered. A detailed analysis is reported below.

S.M.C. Magalhães et al., have studied a combination of AIBV technology with a biotrickling filter that has the function of treating the gases resulting from the remediation process. In this way, soil polluted by toluene with two different concentrations (2 and 14 mg g^{-1} of soil) was reclaimed efficiently (AIBV with a constant airflow of about 0.13 dm^3 min^{-1}), reaching in 5 days the elimination of about 99% of the contaminant. The biotrickling filter has achieved the removal of about 86% of the outgoing gases [41].

However, passive bioventing has proven to be a more easily applicable and cost-effective alternative to active bioventing in sites showing favourable conditions. It is known that passive technology exploits pressure variations for aeration, but the vadose zone must be sufficiently permeable. Remediation experiments using passive bioventing have been carried out at the Marine Corps Air Ground Combat Center (MCAGCC) in Twentynine Palms, California. These studies showed biodegradation rates ranging from 0.3 to 2.1 mg/kg/day with increases in O_2 concentrations from about 2 to 15%. The survey showed that the radius of influence of the vent wells may limit ventilation at many monitoring sites. In addition, the inability to reach elevated airflows to achieve efficient biodegradation rates is one of the major disadvantages of passive bioventing [47].

In light of these considerations, very accurate studies should be conducted on the atmospheric parameters that come into play with passive bioventing. Liu et al. [48] analyse a new Flexible Resistance Temperature Detector. The sensor turns the applied temperature into an electrical signal with a wide range of features, such as flexibility, elasticity, sensitivity, resolution, and lightness. Further, a pressure sensor is a device that detects the surface pressure and converts it to an electronic signal. The goal is to calculate the natural pressure gradients between the surface and the underground. The oxygen and carbon dioxide sensors allow us to correctly evaluate the speed and time of evolution of the biological process. Santonico et al. [49] presented a pilot study with low-cost, low-power, and connectivity CO_2 and O_2 sensors. Finally, the wind speed sensor, or a transducer, is an optical photo coupler that converts the rotation speed into an impulsive signal. Zhi et al. [50] propose an innovative wind speed monitoring system based on an optical fibre curvature sensor.

Another example of passive bioventing equipment is shown by the study conducted by M.H. Liu et al., on the relationship between the microbial degradation process and the efficiency of diesel degradation in the soil during remediation by wind bioventing. In addition, a comparison is made between the indicators of cumulative oxygen absorption and 24-h rate of absorption of this gas, with the results of diesel concentration analyses (analyses performed with GC/FID). The pilot test of eolic ventilation for soils heavily contaminated by diesel (about 20,000 mg kg^{-1}) had provided the use of a self-built eolic ventilation device and a bubble respirometer arranged according to the bioslurry method, to supervise microbial activity in the soil. The survey shows a positive link between the catabolism efficiency of diesel and the mean rate of oxygen uptake by microorganisms for 24 h. Thus, this result suggests that we could use as an indicator of microbial activity the average 24-h oxygen uptake rate. Moreover, the test shows how the activity of diesel-degrading microorganisms, in particular *Bacillus subtilis* and *Pseudomonas putida*, could be bioaugmented for two consecutive weeks [51].

In the work that we present, the execution of the pilot test will determine the applicability of the technology to the specific site and the specific type of contamination and the parameters useful for the final design of remediation interventions. In particular, the field test will allow the determination of the radius of influence ROI (radius of influence—defined as the maximum distance from the axis of the well where the effect of air is affected), the number of wells necessary for the rehabilitation of the site, taking into account the natural pressure gradients, which will be calculated experimentally, the rate of biodegradation (respirometric tests) and any other elements that will allow the assessment of the applicability of the technology, the timing and the costs of recovery.

The advantage of this technique of remediation of contaminated sites is essentially in the low costs of plant construction and management. It exploits a completely natural condition without risk of dispersion of contaminants in the environment.

The advantage of the use of open source hardware and software is that it is possible to adapt the monitoring devices in the best way and according to the specific characteristics of the site, so that the position can be modified according to, for example, the various grain sizes of the soils and the time taken data position, with the not negligible possibility of being able to carry out maintenance interventions in very fast times. Moreover, the adoption of open components makes the system easily expandable both from a hardware point of view, through the integration with additional sensors, and in terms of software functionality, having the availability of the source codes used for the realization of the platform.

S-PBv, like bioventing, can be widely used for the remediation of soils contaminated by compounds of organic origin of medium weight, such as petroleum hydrocarburs [46], in particular of the less volatile fraction of gasoline and gas oils and, with appropriate precautions, for the depollution by non-chlorinated solvents, some pesticides, and wood preservative. It is potentially applicable to all biodegradable contaminants more or less adsorbed to soil particles; however, while not degrading inorganic compounds, biodegradation can also be used to modify the valence of inorganic compounds causing adsorption, absorption, accumulation, and concentration of inorganics in macro or microorganisms [52].

The application of passive bioventing through the use of smart sensors, smart passive bioventing (S-PBv) exploits the natural daily variations of atmospheric pressure, determining a negative gradient between the atmosphere and the subsoil (soil–gas). These sensors, based on open-source hardware and software, can be programmed according to one's needs and the characteristics of the site, according to any changes that may arise during the reclamation phase. These changes can be made in real-time and are practically free of charge. Only the presence of personnel capable of programming is required. Traditional sensors cannot be reprogrammed so quickly as it is necessary to send them back to manufacturing companies.

This gradient pushes the air through a unidirectional valve mounted at the head of a suitably windowed well, deep into the unsaturated subsoil, preventing the flow in the opposite direction and stimulating the natural process of bioremediation implemented by native microorganisms. In fact, the increase in the amount of oxygen in the unsaturated subsoil (it can reach values of 21%) accelerates the processes of biodegradation under aerobic conditions. Taking advantage of atmospheric pressure fluctuations, the most expensive use of energy-intensive machineries, such as blowers, is not used and sufficient air flows can be guaranteed (which translate into sufficient quantities of electron-acceptors/donors to activate an efficient bacterial degradation of the contaminant). In addition, injections take place at low pressures and in this way, the most volatile contaminants are prevented from passing into the vapour phase both if they are strongly adsorbed to soil particles and if they are dissolved in interstitial liquids. At the same time, the biodegradation process is enhanced and the problem of treating the extracted vapours is eliminated. Surely the driving force of the process is the natural rate of variation of atmospheric pressure. This, together with the porosity of the subsoil, the depth of the vadose zone and the permeability to the air, determine the efficiency and effectiveness of the reclamation technology [47].

5. Cost Estimates of a Passive Bioventing System

In this section, an evaluation of the expected installation and operation costs for a full-scale passive bioventing system is reported. The costs have been compared with those of a conventional bioventing system using the second-level work breakdown structure coding system detailed for a single demonstration in a fuel farm area site of ten hectares [53] using this guideline for cost estimator [54]. The costs have been calculated considering data analysis, pilot testing, site inspections, analytical sampling, work plan and report preparation, well installation, regulatory approval, full-scale system installation, various maintenance, and disassembly of the system.

The bioventing cost estimator [54] calculated that the conventional bioventing system would require three vent wells, five vapour-monitoring points, and one 255 m^3/h blower to treat the site and everything you need to run the blower. The cost estimated for the passive bioventing system did not include a blower, electrical system upgrade, or trenching and surface repair; however, one-way passive valves and six vent wells to treat the site were included. The time from initial installation to closure sampling after remediation has been conventionally estimated to be 3 years for both the conventional and passive bioventing systems.

The total estimated cost, for a 3-year intervention, for a passive bioventing system is approximately 2.2 EUR/m^3, unlike conventional bioventing, which is valued at 2.6 EUR/m^3. Obviously, if more time were available for remediation, the cost of passive bioventing would be even lower than that of traditional bioventing.

Now, let us consider a real case study with an extension of the affected area of 0.03 hectares, where there was a fire brigade filling station and where the contamination of diesel oil affected a sandy-gravel particle size soil [55,56]. The available data indicate that the diesel concentration before the implementation of the bioventing technology was 7000 mg/kg in the zones of maximum accumulation. After 59 months, the minimum concentration of diesel dropped to 100 mg/kg, with intervention effectiveness between 93% and 99%. The cost of the operation estimated at EUR 60,000 allows us to say that the remediation cost 33 EUR/m^3 which reflects the average estimates reported in other European countries which are between EUR 25 and 80 EUR/m^3 [57,58].

One very important thing to report is that initially, the original passive bioventing concept was to convert existing groundwater monitoring wells. Although this idea was certainly cost-effective, it did not prove to be viable due to limitations in the construction of existing groundwater monitoring wells, which may be constructed in ways that make reconversion impossible for this application. Therefore, a first suggestion that could be performed is that in those areas where such applications are quite common, as petroleum, oils, and Lubricants Fuel Farm Area (PFFA), to envisage the construction of easily reconvertible monitoring wells. Obviously we should carefully analyse the depth of the aquifer and know if there are unconfined or phreatic aquifers.

In general, the point at which the cost to install additional vent wells under a passive bioventing approach offsets the blower capital and maintenance costs under a conventional bioventing approach will be site-specific and dependent on the following:

- Differences in the radius of influence between conventional and passive bioventing;
- Installation of electrical systems;
- Drilling costs affected primarily by contamination depth, soil type, and location;
- The time frame required to achieve the remediation objectives.

We should, however, consider that there is limited applicability to shallow groundwater sites and that higher pore water saturation corresponds to lower air permeability in these sediments and, therefore, to lower airflow rates. Soil, gas or air permeability is one of the key parameters determining the suitability of both passive and conventional bioventing, to this reason, it is better to conduct in situ air permeability test to know this parameter with certainty to avoid using soil boring logs to estimate the air permeability [59].

In addition, it is recommended to use buried oxygen sensors that provide good-quality data and are relatively simple to install. These oxygen sensors may also be very cost-competitive at conventional bioventing sites because, with the use of a data logger, in situ respiration tests can be performed remotely.

If the times required for the remediation can be 3 years or more, then passive bioventing is convenient both from an economic and from environmental point of view. In case of a need to reuse the area as soon as possible, it is also necessary to appropriately evaluate the higher costs of traditional bioventing compared to the expected revenues from the commercial activity.

6. Conclusions

Considering the environmental remediation technologies, biological-based recovery processes, focused on the ability of living organisms to partially or completely transform/degrade contaminants, are an emerging issue of collective interest.

Technological development and scientific progress have made it possible to achieve important results aimed at ever-greater protection of the environment and human health, obtaining ambitious objectives through innovative tools and common strategies.

In the last few years, non-invasive and cheaper technologies for an in situ remediation of polluted sites under community legislation, have been preferred.

Among the most environmentally sustainable innovative technologies, there is smart passive bioventing. It exploits the natural variation of atmospheric pressure to facilitate the entry of oxygen into the polluted site favouring the growth of indigenous aerobic microbial communities and their degradation activity. Fundamental to consider is the site-specificity of the contaminated area, taking into account the lithology of the site and the soil's properties.

In our work, we have planned a series of integrative surveys with in situ tests (pilot test) able to verify the applicability of the remediation technology coupling the traditional passive bioventing through the use of a smart sensor (S-PBv). The intelligent sensors based on *open-source* software and hardware demonstrated the ability to support better data management, offering a more efficient and sustainable way to achieve results. The optimized combined strategy represents an eco-friendly technology to remediate a polluted site in field applications, with reasonable costs and without wasting resources and time. This work contributed to show a feasibility study for a recovery technique that currently still has few full-scale applications.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su15043764/s1, Figure S1. Scheme of survey points and secondary sources of contamination. Table S1. Analyte concentration values in soil samples taken from excavation walls S1-1, S1-2, S1-3, S1-4. Table S2. Concentration values in soil samples taken from SA-1, SA-2, SA-3. Table S3. Concentration values in soil samples taken from SB-1, SB-2, SB-3. Table S4. Concentration values in soil samples taken from SB-4, SB-5 and SB-6. Table S5. Concentration values in soil samples taken from SB-7, SB-8, and SB-9. Table S6. Concentration values in soil samples taken from SC-1 and SC-2. Table S7. Contaminants Index and Maximum Values of SP Source Concentrations; Table S8. Contaminants Index and Values of Representative Concentrations at source SS.

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