European Union Network for the Implementation and Enforcement of Environmental Law

NICOLE
Network for Industrially Co-ordinated Sustainable Land Management in Europe

Working Group Contamination

Multi Phase Extraction (MPE) report

Final Report

Date of report: 21 November 2022
Report number: 2022/10 MPE EN

Introduction to IMPEL

The European Union Network for the Implementation and Enforcement of Environmental Law (IMPEL) is an international non-profit association of the environmental authorities of the EU Member States, acceding and candidate countries of the European Union and EEA countries. The association is registered in Belgium and its legal seat is in Brussels, Belgium.

IMPEL was set up in 1992 as an informal Network of European regulators and authorities concerned with the implementation and enforcement of environmental law. The Network's objective is to create the necessary impetus in the European Community to make progress on ensuring a more effective application of environmental legislation. The core of the IMPEL activities concerns awareness raising, capacity building and exchange of information and experiences on implementation, enforcement and international enforcement collaboration as well as promoting and supporting the practicability and enforceability of European environmental legislation.

During the previous years IMPEL has developed into a considerable, widely known organisation, being mentioned in a number of EU legislative and policy documents, e.g. the 7th Environment Action Programme and the Recommendation on Minimum Criteria for Environmental Inspections.

The expertise and experience of the participants within IMPEL make the network uniquely qualified to work on both technical and regulatory aspects of EU environmental legislation.

Information on the IMPEL Network is also available through its website at:www.impel.eu

Suggested citation:
Falconi M. et al. (2022), Multi Phase Extraction (MPE) report. IMPEL, COMMON FORUM, EIONET, NICOLE report no 2022/10 MPE, 123 pages. Brussels, ISBN 978-2-931225-29-5

ISBN 978-2-931225-29-5
9 782931 225295

Title of the report: Multi phase extraction (MPE) report	**Number report:** 2022/10 MPE EN
Report adopted at IMPEL General Assembly Meeting: 29-30 November 2022, Prague (Czech Republic)	**Total number of pages:** 136 **Report:** 36 pages **Annexes:** 100 pages

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Executive Summary

Keywords

Multi phase extraction, Dual Phase Extraction, Sustainable Remediation, Soil, Groundwater, Soil Policy, Remediation, Environment, No net land take, Pollution, Polluted sites, Contamination, Contaminated sites, Monitoring, In field test.

Target groups

Competent authorities for remediation technology approval/application/monitoring, industrial operators, environmental protection agencies, nature protection bodies, environmental inspectorates, environmental monitoring, and research institutions, technical universities, environmental associations, NGOs, insurance companies and associations, environmental consultants.

As part of its 2020 Work Programme, the IMPEL Network set up this project Water and Land Remediation (2020/09), concerning the criteria for evaluating the applicability of remediation technologies.
The Water and Land Remediation project takes guidance on definitions and key steps of remediation technology application as a springboard and focuses on the technical procedures connected with the remediation technologies. The ultimate goal of the project is to produce a document proving criteria for the assessment of the proposal of remediation technology application, to understand the applicability, what to do in the field tests, and in the full-scale application. Annex 1 covers a number of case studies, that may help the reader to anticipate any problems they may encounter and see if the provided solution applies to their site, knowing that every contaminated site differs from others and it is ever needed a site-specific approach.
The Water and Land Remediation project for 2020-2021 has the objective was to concentrate on two remediation technologies, Multi Phase Extraction and Soil Washing.
Finally, Water and Land Remediation project intends to contribute to promoting the application of in situ and on-site remediation technologies for soil and groundwater, and less application of Dig & Dump and Pump & Treat that are techniques widely used in Europe but not sustainable in the middle-long term. Soil and water are natural resources and, when it is technically feasible, should be recovered not wasted.

Acknowledgements

This report has been peer reviewed by a wider IMPEL project team and by the IMPEL Water and Land Expert Group, Common Forum network, NICOLE network, EIONET WG Contamination and a group of external reviewers.

Disclaimer

This publication has been prepared within the IMPEL Water & Land Remediation project with the support of partner networks interested in Contaminated Land Management. Written and reviewed by a team of authors the document on hand intends to serve as primary information source to bridge and broaden knowledge among European countries and regions. In aiming support for a joint understanding the potentials of the specific remediation technology it seeks to facilitate.

The content reported here are on the basis of relevant bibliography, the authors' experience, and case studies collected. The document may not be extensive in all situations in which this technology has been or will be applied. Case studies (see annex) are acknowledged voluntary contributions. The team of authors had no task like evaluating or verifying case study reports.

As well some countries, regions, or local authorities may have launched particular legislation, rules, or guidelines to frame technology application and its applicability.

This document is NOT intended as a guideline or BAT Reference Document for this technology. The pedological, geological and hydrogeological settings of contaminated sites across Europe show a broad variability. Therefore tailor-made site-specific design and implementation is key for success in remediating contaminated sites. So the any recommendation reported could be applied, partially applied, or not applied. In any case, the authors, the contributors, the networks involved, cannot be deemed responsible.

The opinions expressed in this document are not necessarily those of the individual members of the undersigned networks. IMPEL and its partner networks strongly recommend that individuals/organisations interested in applying the technology in practice retain the services of experienced environmental professionals.

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Glossary

TERM	DEFINITION	SOURCE	PARAGR.
‘compliance point’	location (for example, soil or groundwater) where the assessment criteria shall be measured and shall not be exceeded	ISO EN 11074	3.4.5
‘compliance or performance control’	investigation or program of on-going inspection, testing or monitoring to confirm that a remediation strategy has been properly implemented (for example, all contaminated have been removed) and/or when a containment approach has been adopted, that this continues to perform to the specified level	ISO EN 11074	6.1.5
‘contaminant’[1]	substance(s) or agent(s) present in the soil as a result of human activity	ISO EN 11074	3.4.6
‘contaminated site’[2]	site where contamination is present	ISO EN 11074	2.3.5
‘contamination’	substance(s) or agent(s) present in the soil as a result of human activity	ISO EN 11074	2.3.6
‘effectiveness’[3]	<remediation method> measure of the ability of a remediation method to achieve a required performance	ISO EN 11074	6.1.6
‘emission’	the direct or indirect release of substances, vibrations, heat or noise from individual or diffuse sources in the installation into air, water or land;	IED	Art. 3 (4)
‘environmental quality standard’	the set of requirements which must be fulfilled at a given time by a given environment or particular part thereof, as set out in Union law;	IED	Art. 3 (6)
‘Henry's coefficient’	partition coefficient between soil air and soil water	ISO EN 11074	3.3.12
‘*in-situ* treatment method’ [4]	treatment method applied directly to the environmental medium treated (e.g. soil, groundwater) without extraction of the contaminated matrix from the ground	ISO EN 11074	6.2.3
‘leaching’	dissolution and movement if dissolved substances by water	ISO EN 11074	3.3.15

[1] There is no assumption in this definition that harms results from the presence of contamination

[2] There is no assumption in this definition that harms results from the presence of contamination.]

[3] In the case of a process-based method, effectiveness can be expressed in terms of the achieved residual contaminant concentrations.

[4] Note: ISO CD 241212 suggests as synonym: ‘in-situ (remediation) technique’ [Note 1 to entry: Such remediation installation is set on site and the action of treating the contaminant is aimed at being directly applied on the subsurface.] ISO CD 24212 3.1

'pollutant'	substance(s) or agent(s) present in the soil (or groundwater) which, due to its properties, amount or concentration, causes adverse impacts on soil functions	ISO EN 11074	3.4.18
'pollution'	the direct or indirect introduction, as a result of human activity, of substances, vibrations, heat or noise into air, water or land which may be harmful to human health or the quality of the environment, result in damage to material property, or impair or interfere with amenities and other legitimate uses of the environment;	IED	Art. 3 (2)
'remediation objective'	generic term for any objective, including those related to technical (e.g. residual contamination concentrations, engineering performance), administrative, and legal requirements	ISO EN 11074	6.1.19
'remediation strategy'[5]	combination of remediation methods and associated works that will meet specified contamination-related objectives (e.g. residual contaminant concentrations) and other objectives (e.g. engineering-related) and overcome site-specific constraints	ISO EN 11074	6.1.20
'remediation target value'	indication of the performance to be achieved by remediaton, usually defined as contamination-related objective in term of a residual concentration	ISO EN 11074	6.1.21
'saturated zone'	zone of the ground in which the pore space is filled completely with liquid at the time of consideration	ISO EN 11074	3.2.6
'soil'	the top layer of the Earth's crust situated between the bedrock and the surface. Soil is composed of mineral particles, organic matter, water, air and living organisms;	IED	Art. 3 (21)
'soil gas'	gas and vapour in the pore spaces of soils	ISO EN 11074	2.1.13
'unsaturated zone'	zone of the ground in which the pore space is not filled completely with liquid at the time of consideration	ISO EN 11074	3.2.8

[5] The choice of methods might be constrained by a variety of site-specific factors such as topography, geology, hydrogeology, propensity to flood, and climate

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1 INTRODUCTION

Over the last decades, our awareness of the contamination of soil and groundwater has significantly increased. This type of contamination can either originate from source or diffuse pollution sources and can have impacts on human health and the environment. This knowledge has steered our efforts to confront and manage such pollution more efficiently and sustainably. It has also resulted in the development of several remediation approaches, either to be applied ex-situ or in-situ and, in the last, on-site or off-site. The choice and application of a specific remediation scheme depend on several factors, ranging from environmental, social and economical ones. In practical terms, and from a strictly practical perspective, the choice of a technology depends on eg on-site constraints, type and class of contaminants, contamination age (recent or weathered), time to perform the remediation and future use of the land. However, as with any remediation method, the efficiency of applying Multi-Phase Extraction (MPE), regarding its environmental performance and costs, depends on many site characteristics, such as the type and extent of contamination in soil and groundwater, the site geology, and potential technical structures on the site. In addition, the required remediation status will be determined by the site's current and future land use.

Today, taking into consideration the so-called source-pathway-receptor (S-P-R) approach, several methods and techniques exist that aim to remove the contamination or remove exposure to the pollutant. Each method is characterised by pros and cons, while its suitability is dependent on on-site conditions and the physicochemical properties of the target contaminants. Hence, to ensure the effectiveness of remediation, it is crucial to ensure that the selection and application of any method will properly acknowledge its technical feasibility and limitations.

In-situ soil and groundwater remediation techniques are often more cost-efficient than excavation and do not move the contamination to another location. However, the solitary use of those methods poses many limitations eg regarding the duration of the remediation, the contaminated phase and the zone to be treated (for example, Soil Vapour Extraction (SVE) and bioventing treat only the vadose zone, while groundwater pump-and-treat acts only in the saturated zone). Therefore, it is advisable to use a method that acts on more phases and zones, such as Multi-Phase Extraction (MPE).

MPE is an in-situ remediation technology for the simultaneous extraction of contaminants in the vapour phase, dissolved phase and separate phase. It is impacting the vadose zone, the capillary fringe, and the saturated zone soils and groundwater. It is a combination of soil vapour extraction (SVE), pump and treat, and bioventing, and its feasibility in site remediation has been confirmed by several case studies from moderate to low soil permeabilities. The soil vapour is extracted by creating negative pressure in the unsaturated zone using extraction wells or trenches connected to suction. All of this makes MPE an exceptional technique to tackle mixed contamination (e.g. inorganic and organic; water-soluble and non-soluble compounds; volatile and semi-volatile compounds) with the potential to use the residual for recalcitrant and/or semi-/non-volatile contamination remediation in the vadose zone. As so, MPE can be used to extract:

- Groundwater containing dissolved constituents from the saturated zone.
- Soil moisture containing dissolved components from the unsaturated zone.
- Light Non-Aqueous Phase Liquid (LNAPL) floating on the groundwater.
- Non-drainable LNAPL in soil.
- Soil gas containing volatile contaminants and
- under certain conditions perched or pooled Dense Non-Aqueous Phase Liquid (DNAPL).

MPE has also potential beyond its direct application (previously described) as, indirectly, it can also assist in:

- In-situ aerobic bioremediation via increasing oxygen flux to the contaminated region
- SVE via lowering the water table and exposing a larger area to SVE

- Pump-and-treat in a low transmissivity region with less steep water drawdown gradients via vacuum enhancement.

Under the right conditions, deploying MPE can significantly reduce contaminant mass and concentrations in a cost-effective way. It can be applied in the source zone and eliminate the consequent environmental and health risks of, e.g., diffusive plume contamination migration. As so, limiting the total time frame of the system operation and effectively removing a broad range of contaminants can reduce or eliminate potential future on-site and off-site liabilities [1].

The chapters of the report further below provide a state-of-the-art for this method and its practices. This report will focus on a specific type of *in situ*, *on-site* technology for site remediation, MPE, compiling the main principles of the technique, discussing its potential and challenges seeking a broader use and, simultaneously, capitalizing on the lessons learned from the field applications. This report is not exhaustive and seeks to provide a state of the art of this technique based and compiled on the last developments taken at the European level, by surveys and experiences shared with multiple stakeholders.

2 DESCRIPTION OF THE TECHNIQUE

2.1 General process description

In general, MPE consists of applying a high vacuum (relative to SVE systems) to a well that intersects the vadose zone, capillary fringe, and saturated zone. Because of the pressure differences, the groundwater rises and, if drawn into the well, may be extracted and treated above-ground [1].

MPE, being a remediation technique mainly developed for petroleum contaminated sites, can be designed and implemented in a variety of configurations. In the subsurface, the contaminants may be found as vapours in pore spaces, as liquids sorbed to solids, as liquids in pore spaces (also known as light, nonaqueous-phase liquids - LNAPLs), and in the dissolved phase. The extent of partitioning and distribution of petroleum products in different phases is governed primarily by the physical properties of the constituents of the petroleum hydrocarbon (e.g., density, viscosity, vapour pressure, solubility in water, interfacial tension, petroleum fraction, linear vs aromatic structure) and soil characteristics (e.g., organic carbon and/or clay content, porosity) [2, 3].

The three main configurations of MPE are:

- "Two-phase extraction" (TPE) - when the liquid and vapour phases are extracted together through the same conduit (used mainly for extraction of chlorinated solvents);
- "Dual-phase extraction" (DPE) – when separate conduits for vapour and liquids.
- "Bioslurping" – when the liquid, LNAPL and vapour phases are extracted together through the same conduit (used mainly for vacuum-enhanced LNAPL recovery), as with TPE, the mechanism includes biodegradation of the contamination as well.

2.2 Two-phase extraction (TPE)

In TPE configuration, as shown in Figure 2.1 and 2.2., a drop tube extracts a mixture of liquid and vapour from a well. One vacuum pump achieves the mixture lift (liquid-ring pumps, jet pumps, and blowers are typical). In theory, a vacuum lift pump can only lift water at a height equal to atmospheric pressure. Therefore, single pump configurations are used for shallow (less than 10 m) water-table remediation [4].

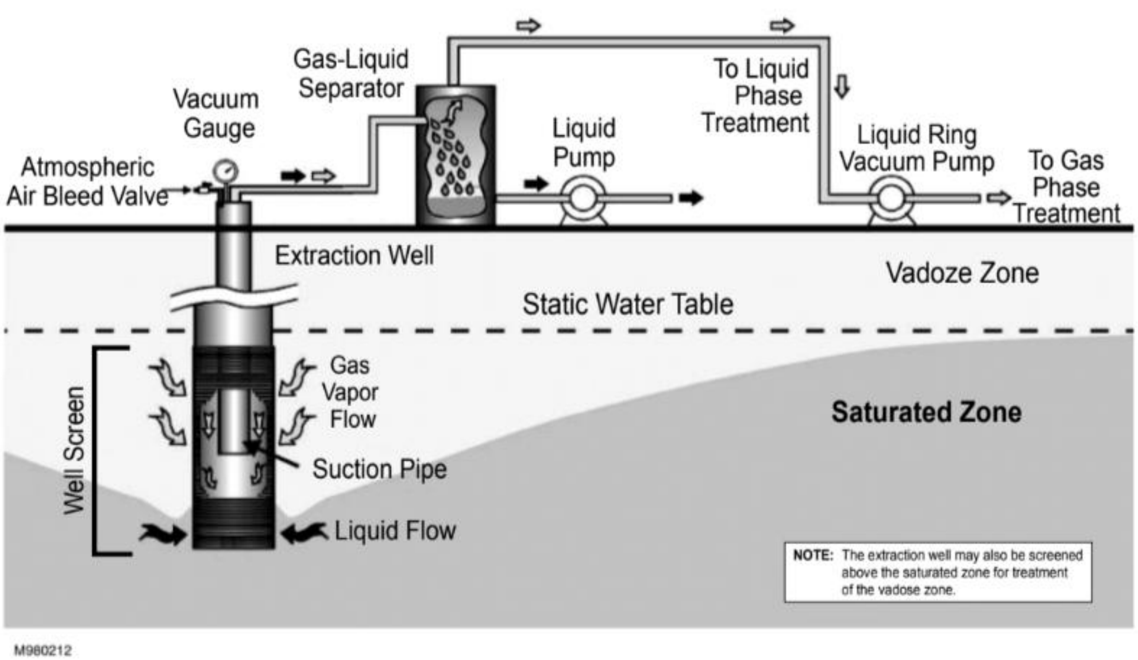
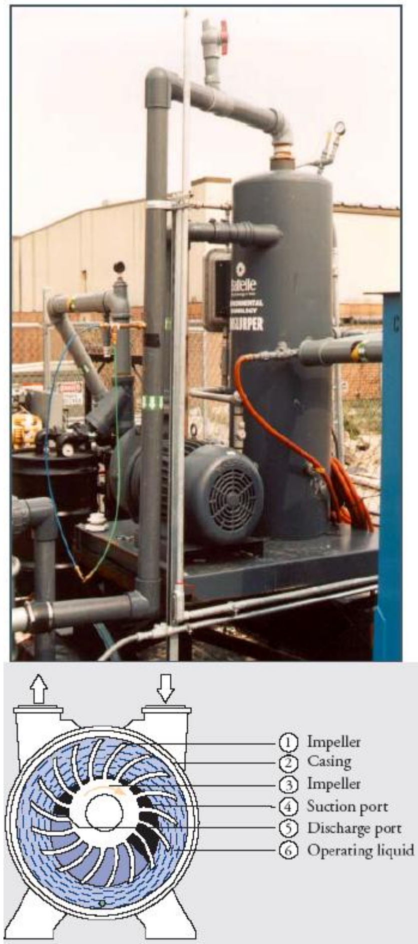


Figure 2.1.: **Schematic of TPE System [1]**



a) Liquid ring vacuum pumps

b) Air stripper to treat Vapor Phase Carbon

c) Chemical reaction and flocculation/Dissolved air flotation

Figure 2.2.: **Equipment used in TPE [2]**

The extracted mixture should be separated through a gas-liquid separator. Depending on the concentrations, the vapours are subject to different treatments such as thermal oxidation, recuperative oxidation, catalytic oxidating, or granular activated carbon. The liquid may be treated by one of the many existent technologies - E.g., first, it is passed through hydrophobic clay, then exposed to air stripping and to chemical reaction and flocculation/ dissolved air flotation, at the end being disposed of in a settling tank. From the tank, the clean liquid may be reinjected into the subsurface or discharged to surface water.

2.3 "Dual-phase extraction" (DPE)

Considering the depth limitations imposed by the TPE method was developed DPE which is shown in Figure 2.3. This configuration implies a submersible pump for groundwater recovery in conjunction with a separate vacuum applied at the sealed wellhead. Therefore, liquid and vapour streams are extracted separately.

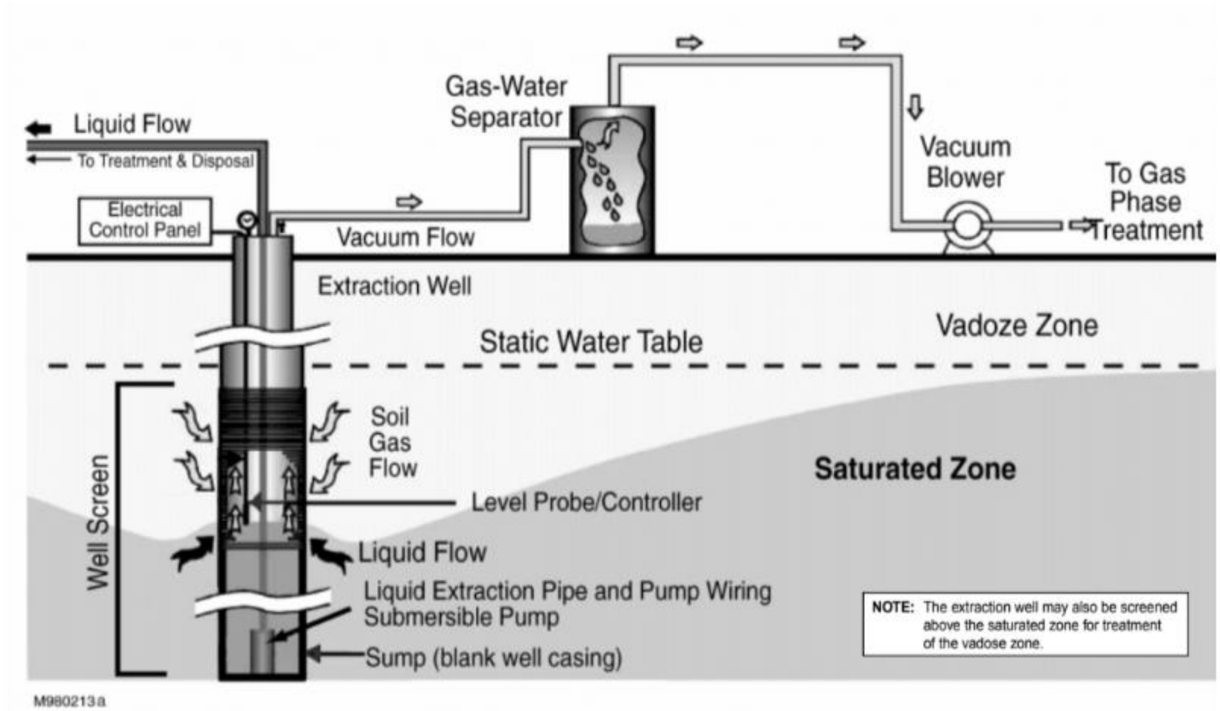


Figure 2.3.: **Schematic of DPE System [1]**

Level control with sensors might be necessary for preventing the vacuum from causing the pump to lose positive suction head and cavitate. The vacuum may be induced by two-pump systems that utilise electric or pneumatic submersible pumps for groundwater recovery and liquid ring pumps or blowers. For DPE wells using a submersible pump, a sump should be installed at the bottom of the well to prevent cavitation of the submersible pump. Under vacuum conditions, a net positive suction head may be maintained to avoid cavitation of the submersible pump, utilising a standing water column. Under high vacuum conditions, a 6 m deep sump may be required to provide a suitable water column at the pump intake.

The pump draws a mixture of air, water, and NAPL from the water surface. Therefore, the three phases should be separated on the surface in a series of separators, first liquid/vapour and then oil/water separators if needed [1, 6].

Practice showed that the oil/water separation might also be performed in-well (Figure 2.4). However, despite the obvious advantages (reduces the degree of oil/water emulsion; decreases hydrocarbon concentrations in off-gas), it is tricky to operate and requires more on-site labour.

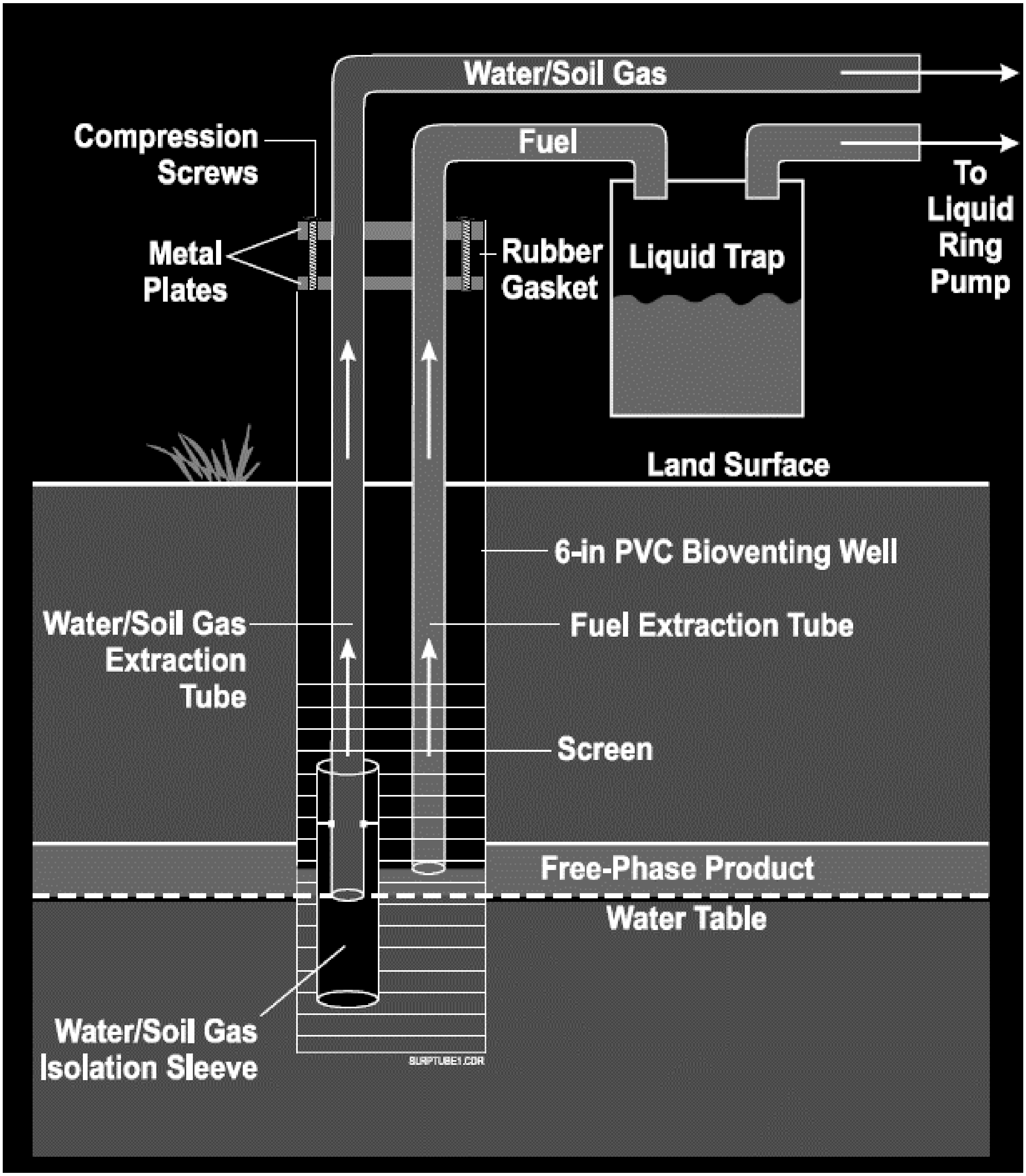


Figure 2.4.: **Schematic in-well water/oil separation [2]**

2.4 Bioslurping

Bioslurping is in fact a TPE where the focus is on the biodegration. It combines the two remedial approaches of bioventing and vacuum-enhanced dewatering technology to remediate hydrocarbon-contaminated sites. During fluid suction, the soil gas is replenished from the surrounding formation. Therefore, the vadose zone around the well is aerated. The role of bioventing is to stimulate the aerobic bioremediation of hydrocarbon-contaminated soils in situ. This is because most petroleum hydrocarbons' aliphatic and aromatic constituents are degradable under aerobic conditions. On the other hand, vacuum-enhanced free-product recovery extracts LNAPLs from the capillary fringe and the water table. Thus, bioslurping is a cost-effective in-situ remedial technology that combines free-product recovery, bioventing, and in-situ bioremediation for simultaneously accomplishing LNAPL removal and remediation of soil in the vadose (unsaturated) zone [2, 6].

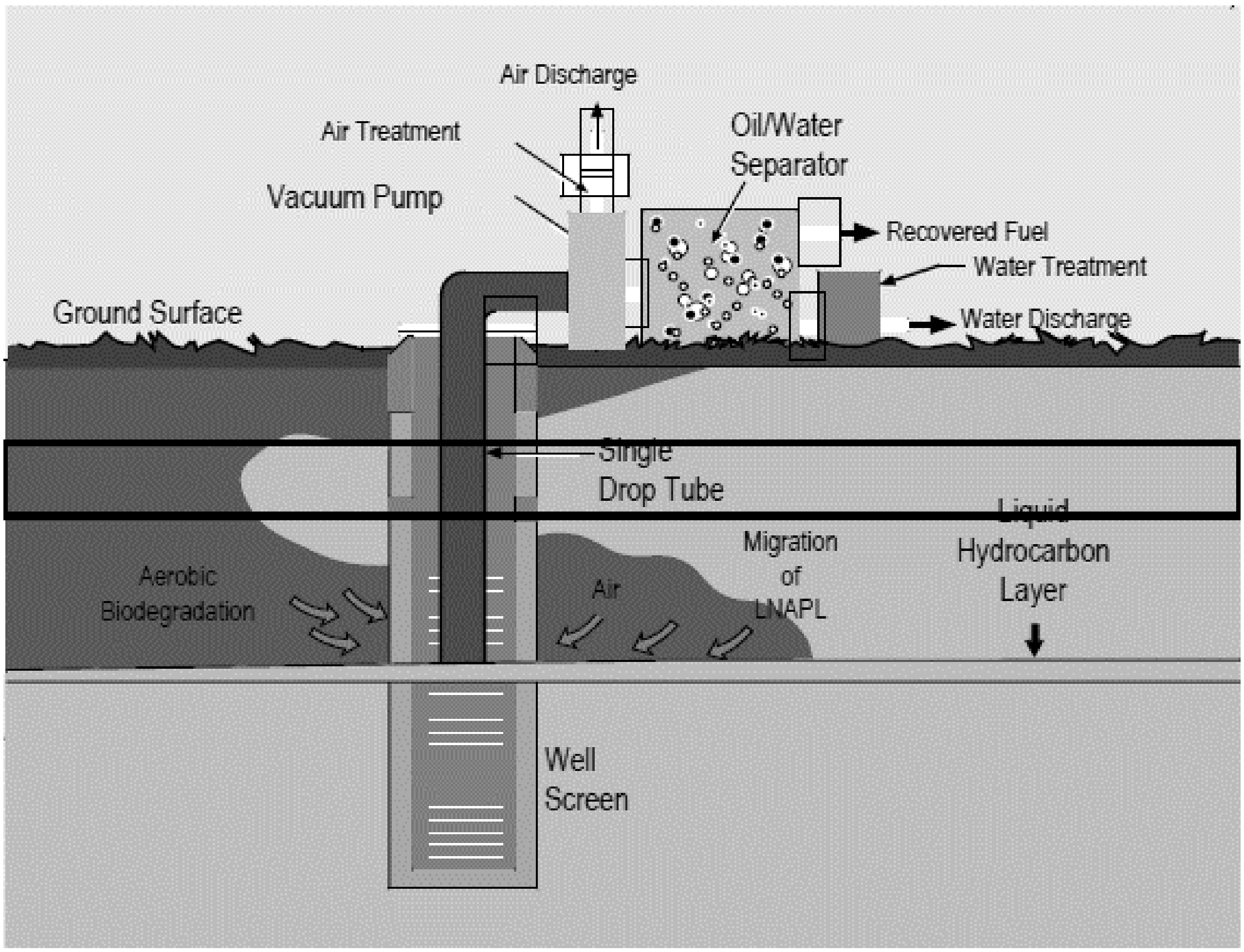


Figure 2.5.: **Schematic of Bioslurping**

a) Pilot-scale system

b) Full-scale system

Figure 2.6.: **Installed and operated bioslurper system [5]**

As bioslurping effectiveness is highly dependent on soil pore space (to guarantee aeration) it is applicable on medium to high permeability soils in sites with a deep groundwater table (> 10 m). However, adjustments to the system components, such as pump and pipe resizing, are required to increase the airlift needed to entrain LNAPL and water droplets.

2.5 MPE selection and implementation

MPE is an intensively used remediation technique due to the following advantages: it has greater LNAPL recovery rates compared to other pumping technologies; a single above-ground pump is necessary as opposed to a pump in each well; it may induce biodegradation of hydrocarbons in the vadose zone; air stripping of VOC from the vadose zone. Even though it is important to remember that it is not possible to recover all LNAPL from subsurface, it may appear channelling in the subsurface or create secondary waste streams that can be cost-prohibitive to treat.

Before starting the pilot study, it is recommended to verify the fulfillment of the requirements on which the efficiency of the remediation process depends:

1. Evaluate if air permeability at the site is conducive to vapour extraction.
2. Characterise soil gas and evaluate if the contaminant is present in concentrations amenable to MPE.

3. Evaluate liquid and vapour recovery rates as a function of vacuum.
4. Estimate the area of influence (vacuum response and groundwater capture)
5. Estimate liquid and vapour contaminant mass recovery rates [7]

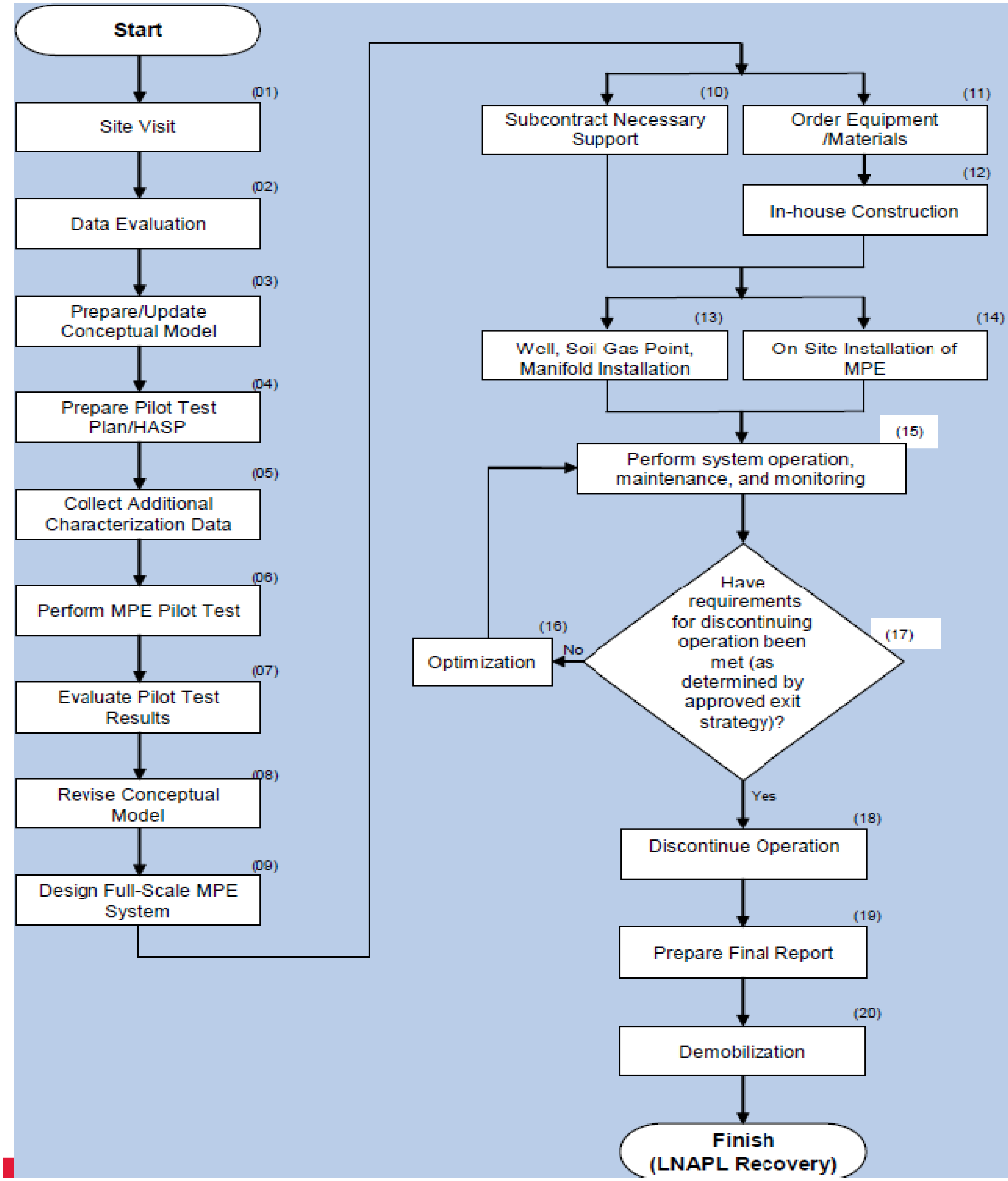


Figure 2.7.: **MPE implementation scheme**

After data evaluation, the conceptual model and the Pilot test plan may be elaborated. Having a well-structured Pilot test plan, the pilot test results will be trustful and valuable for further revision of the conceptual model, which is the basis of the MPE system's full-scale design.

3 SITE CHARACTERICS, CONTAMINANTS AND LABORATORY INVESTIGATION

The following sub-sections examine more in detail the site characteristics and contaminants amenable to remediated by MPE. Then, a note for the laboratory/bench scale and an overview of the technique are given.

3.1 Site Conditions and Site Conceptual Model

The MPE system is generally a good remediation alternative in sites requiring a combination and/or enhanced soil vapour extraction (SVE) and pump-and-treat system for the remediation of volatile contaminants, light non-aqueous phase liquids (LNAPL) and contaminants dissolved in groundwater adjacent/near the source area (instead of the plume). Another critical feat is its ability to lower the groundwater table and expose more sediment/soil to remediation (Figure **3.1**).

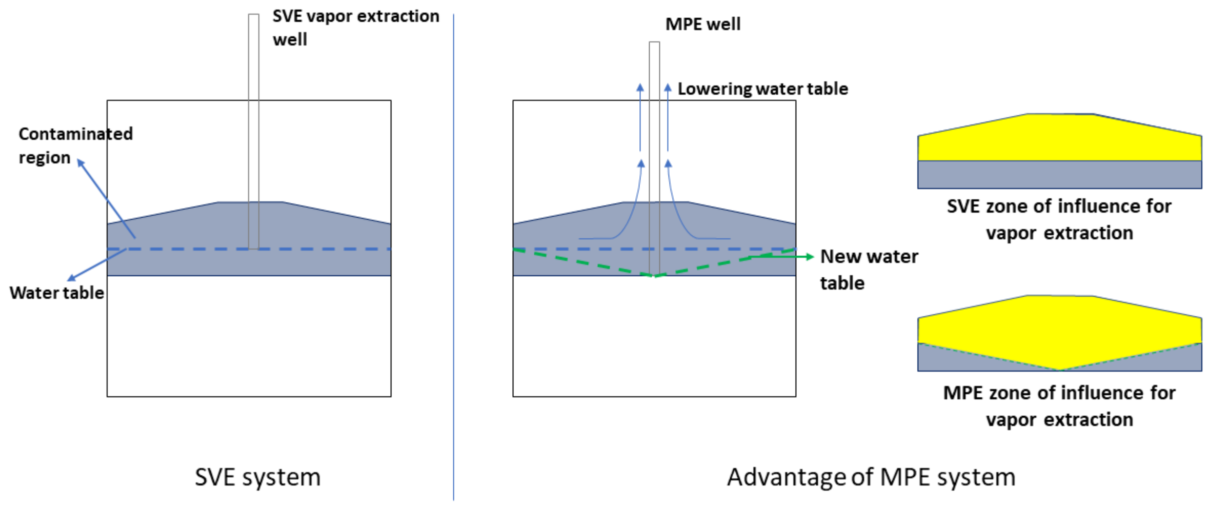


Figure 3.1.: **The advantage of MPE system over SVE in removing volatile contaminants**

Due to the fact that underpressures up to a several hundreds mbar can be applied, a surface cover can enhance the efficiency of the MPE system, by avoiding 'leak' flows.

Data need to be collected to consider a design of an MPE system as follows:

- Water table depth, fluctuations, gradient (MPE type selection, characteristics, or application methodology)
- Stratigraphy (potential hindrance of clay lenses, non-isotropic groundwater flow)
- Distribution and nature of contaminants, product saturation, solubility/vapor pressure, location, biodegradability (low or high vacuum systems, consideration of bioslurping)
- Hydraulic conductivity (type, design, application methodology)
- Groundwater geochemistry
- SVE properties, bacteriological nature (consideration of bioslurping)

The significant site and contaminant characteristics for MPE applicability are examined under separate sub-sections below.

3.2 Liquid and Gas Phase Movements

Both types of fluid movements, liquid and gas, will be overviewed in this section.

In Table 3.1 the general guidelines for choosing MPE for on-site remediation techniques are presented.

Table 3.1.: **MPE General guidelines (EPA 1997)**

Site conditions	Guideline
Contaminant	1. Halogenated VOCs 2. Non-halogenated VOCs and/or Total Petroleum Hydrocarbons (TPH)
Contamination location	1. Below groundwater table 2. Both above and below groundwater table
Henry's Law Constant of majority of contaminants	>0.01 at 20^o C (dimensionless)[a]
Vapor pressure majority of contaminants	>1.0 mm Hg at 20^o C
Geology below groundwater table	Sands to Clays
MPE application above the groundwater table	
Air permeability of soil above the groundwater table	Moderate and low permeability (k) soils

[a] Dimenssionless Henry's Law Constant in the form (concentration in gas phase) / (concentration in liquid phase)

[b] Soil gas permeability (k): = 10^{-14} m^2 [8]

3.2.1 Hydraulic Conductivity & Transmissivity

MPE is suitable for site settings with moderate to low conductivity, ranging from 10^{-5} to 10^{-7} m/s [12]. Especially in conditions where pump-and-treat systems start to be less effective or result in steep spatial gradients in groundwater table level near pumping well, vacuum application of MPE enhances the drawdown and reduces this drawdown gradient. This also makes MPE particularly useful for low transmissivity regions smaller than 7.18×10^{-5} m^2/s.

3.2.2 Vadose Zone Soil Permeability to Air

Air permeability is significant considering the MPE application for above the groundwater table regions. Dual-phase extraction setting low vacuum system (LVDPE) requires at least 10^{-15} m^2 air permeability to be feasible, while high vacuum dual-phase extraction (HVDPE) and two-phase extraction (TPE) can work in permeabilities lower than 10^{-14} m^2. As a remark, SVE is estimated to be infeasible in air permeabilities lower than 10^{-14} m^2 value [13], or 10^{-2} darcy. In other words, HVDPE and TPE can be chosen where SVE is inapplicable due to the low air permeability.

Considering these two related characteristics together, one study carried out by the U.S. Army Corps of Engineers [14] found that in sites with:

- high permeability and low air-entry pressure (<0.25 cm capillary fringe), the MPE wells with slurp tubes were flooded,
- moderate permeability and slightly low air-entry pressure (0.25-2.5 cm capillary fringe), the MPE system was seen as successful and cost-effective.
- Low-permeability and high air-entry pressure (>2.50 cm capillary fringe), no dewatering of the soil took place, with a minimal airflow pathway.

3.2.3 Geologic Setting

MPE applies to various geologic settings, from sands to clays [15]. This is possible via different types of Multi-Phase Extraction system settings. For example, LVDPE is suitable for sands to silty clays, whereas with TPE the geologic setting feasible for the remediation is sandy silts to clays with lower than 3×10^{-4} m^3/s groundwater production. The HVDPE system is also suitable for sandy silts to clays with a broader range of groundwater production.

3.2.4 Formation Characteristics

Feasible application range for MPE may occur in the following formation characteristics: fractured systems, interbedded sand and clay stringers, limited saturated thickness (otherwise flooding of TPE wells or high extraction costs), shallow water table (availability of multiple types of MPE), thick capillary zone (vacuum enhancement can break it), perched NAPL or groundwater layers.

3.2.5 Drawdown/Recovery Rate

The groundwater yield of the remediation system is also essential [9]. The experts have reported that groundwater yield values higher than 3.33×10^{-4} m^3/s result in flooding of wells and excess water drawdown for TPE. Hence, such locations would require DPE systems. An optimum point should be found without drawing too much groundwater with increasing operation costs or leaving considerable groundwater untreated.

3.2.6 Contaminant Location

The location of the contaminated region has a significant impact on the success of a specific remediation system. The same contaminant might be easy to clean in one part and difficult in another. When the contaminant is in the vadose zone, it should be in its volatile form before drawing it to the remediation well. Hence, vadose zone remediation systems are more useful when contaminants are volatile [12].

Another consideration, especially from cost-effectiveness, is that MPE technology is too aggressive to be used in plume treatments. Consequently, it is recommended to apply to source zones [16]. When the contaminant concentration reaches asymptotic levels, other relatively cheaper technologies can be used in lieu of MPE.

3.2.7 Contaminant Characteristics

Since MPE has two main types of actions soil vapour extraction and pumping, the type of contaminants that can be removed also changes. If the main action is soil vapour removal, the remediation of petroleum hydrocarbons (e.g. BTEX), chlorinated solvents, and degreasing agents by MPE is appropriate (see also Figure 3.1). On the other hand, if capillary zone fluids are to be removed via pumping and vacuum enhancement, LNAPL can be removed by MPE systems [12]. Lastly, MPE action can also enhance oxygen flow to the region of interest, hence stimulating the degradation of biodegradable non-volatile contaminants as well [17]. This approach was chosen in the bioslurping/bioventing system at Tinker Air Force Base with a broader spectrum of hydrocarbons to remediate (i.e. total petroleum hydrocarbons; TPH) contamination [18]. There were satisfactory results in dewatering and aerating the system in various geologic settings, including clay and silty clay layers, where adequate dewatering was observed, too, at the end.

MPE can also pump the dissolved phase contaminants in the groundwater. However, it might only be feasible if airflow and vacuum application in an MPE system also favour this treatment. Otherwise, the cheaper pump-and-treat system might be considered.

There were many cost-effective case studies on the removal of chlorinated ethenes [dichloroethylene (DCE), trichloroethylene (TCE), perchloroethylene (PCE)]; aromatic compounds (benzene), fluorinated aliphatic organic compounds (Freons), jet fuels and TPH with a range of water depth, lithology, contaminant concentration and applied vacuum [12, 15, 19]. Both volatile, water-soluble, and water-immiscible (LNAPL) contaminants can be treated by MPE systems [20].

Table **3.2** summarises the contaminants and the feasibility of being remediated by MPE in different configurations (compiled from [12, 15, 21].

Table 3.2.: **Summary of MPE configurations' effectiveness for specific contaminant groups***

	Group of Contaminant						
Configuration	VOC	HVOC	SVOC	HSVOC	Inorganics	LNAPL	DNAPL
Single Pump	√√	√√	√	√	-	√√	-
Low Vac DPE	√√	√√	√√	√√	-	√√	√
High Vac DPE	√√	√√	√√	√√	-	√√	√
Bioslurping**	√	√	√√	√√	-	√√	-

**Generally, MPE was applied for VOCs and LNAPLs, and in some cases, DNAPLs; on the contrary, no application was found for remediation of sites contaminated with inorganics*

***Mostly single pump configuration that is applied directly between or very near to the air-water intersection*

Legend: √ - limited effectiveness; √√ - demonstrated effectiveness

3.3 Note on Laboratory/Bench/Column scale Testing in MPE Remedial Design

The main issue in the feasibility test of an MPE system with bench-scale experiments is that they do not satisfactorily represent the field conditions. Even though [22] stated the utility of conducting laboratory-scale tests, such as the simulation of airflow within a soil column in the laboratory, significant size/scale issues are still to be resolved with pilot tests.

One relevant subject is preferential flow. The extraction rate for the liquid phase is impacted by permeability, which in turn is impacted by the presence/absence of preferential flows. This can result in 2 orders-of-magnitude lower permeability value readings in bench-scale tests compared to the field [23].

Another consideration is the flow direction. Usually, laboratory studies have only vertical, one-directional flow; on the contrary, field groundwater velocity is likely to have horizontal and vertical components [9].

3.4 MPE Feasibility Consideration /Overview

The MPE has been successfully applied in different situations and scenarios for several years. Part of its success is the potential to simultaneously remove different classes of contaminants that migrate/percolate through the soil profile, some reaching the groundwater.

The potential to cover three fronts - groundwater, free phase, and vapours - gives the technique enormous flexibility. Although there are common characteristics of the sites to be applied and the target contamination to be tackled (water-soluble, immiscible with water - LNAPL, vapours), there is great potential to extend the scope of MPE to other contaminant classes and environmental contexts, beyond the traditional applications. Additionally, MPE application will promote a unidirectional flow for contaminants removal which will, inherently, restrict the dispersion of the contamination plume. Another advantage is its combination with other remediation techniques. In addition to SVE designed to remove volatile organic compounds, bioventing has the potential to promote aerobic degradation in-depth, favouring the biodegradation of contaminants that have not been removed by MPE (e.g. those present in the solid fraction of the soil).

4 IN FIELD/LABORATORY TEST

As mentioned earlier, to design a pilot test for the large-scale installation of an MPE system, it is necessary to have already a well-structured conceptual model for the site and other preliminary information obtained during the characterisation phase.
The MPE pilot test should provide reliable data for the final system design in the following terms:

- definition of the treatment zone;
- mass removal rate;
- zone of influence;
- subsurface properties and parameters;
- effluent treatment technology;
- cost estimation.

In addition to providing data for full-scale system design, a properly conducted pilot test should help the consultant determine whether existing time constraints for project closure can be met with achievable removal rates.

4.1 Pilot test systems and conventional equipment for pilot tests

The following components are required to carry out a pilot test for a DPE system:

- n. 2 submersible pumps installed in groundwater extraction wells, placed at about 1 m from the bottom of the well. Depending on the geology a choice on the pump/flow rate has to be made (eg a 12 V pump with a maximum flow rate of 12 l/min and. This pump is connected with a manifold followed by an active carbon filter;
- n. 2 wellhead equipped with a vacuum gauge to control the depressions induced inside the well and a point of taking samples/measurements with portable tools;
- a lateral vacuum pump (eg with a flow of 100 m^3/h and a negative pressure of 150 mbar);
- potentially (dependent on the iron content) an iron separator air/water between the well and the vacuum pump, to avoid interaction with the mechanical compounds of the pump;
- an airline with active carbon filters for treatment of vapours extracted before discharge in the atmosphere through a chimney;
- a line with active carbon filters for treatment liquid phase before discharge in eg sewers line.

In case of a TPE system, the following components are required to carry out a pilot test for this technology, the description of the equipment to carry out a pilot test was used for this purpose and therefore, the technical characteristics of the various components: maximum flow, the voltage must be chosen according to the information in the conceptual site model.

- an ATEX vacuum pump that can generate depressions greater than 900 mbar
- a slurper of 1” HDPE piping directly connected to the well-head;
- wellhead equipped with a vacuum gauge to control the depressions induced inside the well and a point of taking samples/measurements with portable instrumentation;
- an ATEX vacuum pump that can generate depressions greater than 900 mbar;
- a condensate separator connected to the pump to allow separation of groundwater and sediment from the extracted vapors;
- an air line with active carbon filters for treatment of vapours extracted before discharge in the atmosphere through a chimney;
- a line with active carbon filters for treatment liquid phase before discharge in sewers line.

To follow up on the impact of the pumping, monitoring wells should be put in place. These wells have to be screened crossing the water table; the wellhead has to be equipped with a vacuum gauge to measure depressions and a sampling point. The monitoring piezometers can be arranged "helically" around the extraction well, i.e. at about 120° and with increasing distances the PM13 (2.9 m), PM12 (5.8 m) and PM02 (10.4 m), as indicated in the figure below (Figure 4.3). The test was performed by applying 3 different flow rate steps (30, 45 and 50 Nm3 /h) in PM03, while analysing the relative subsoil response (in the monitoring piezometers); the drop-tube was applied near the bottom of the hole.

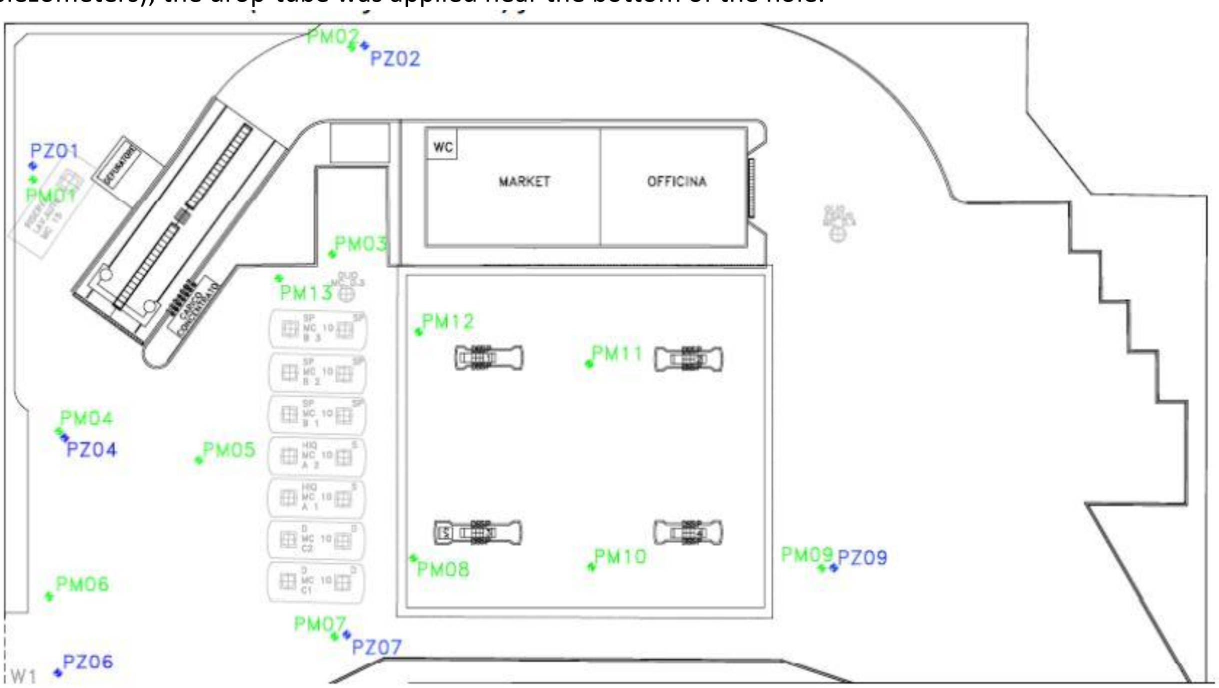


Figure 4.1.: **Site map and monitoring points (courtesy of Ing. Caldera F., Mares Italia)**

As a technology composed of several environmental remediation systems, the pilot tests to be performed are directly related to the chosen technology (TPE or DPE) and the type of instrumentation adapted to achieve the desired objectives (SVE, P&T, Bioslurping).

In a DPE-type system, pumping water into the well produces a large vacuum within the water column and draws new water; this effect, combined with the vacuum generated by a blower, creates a larger zone of influence than in the TPE system (Figure 4.4).

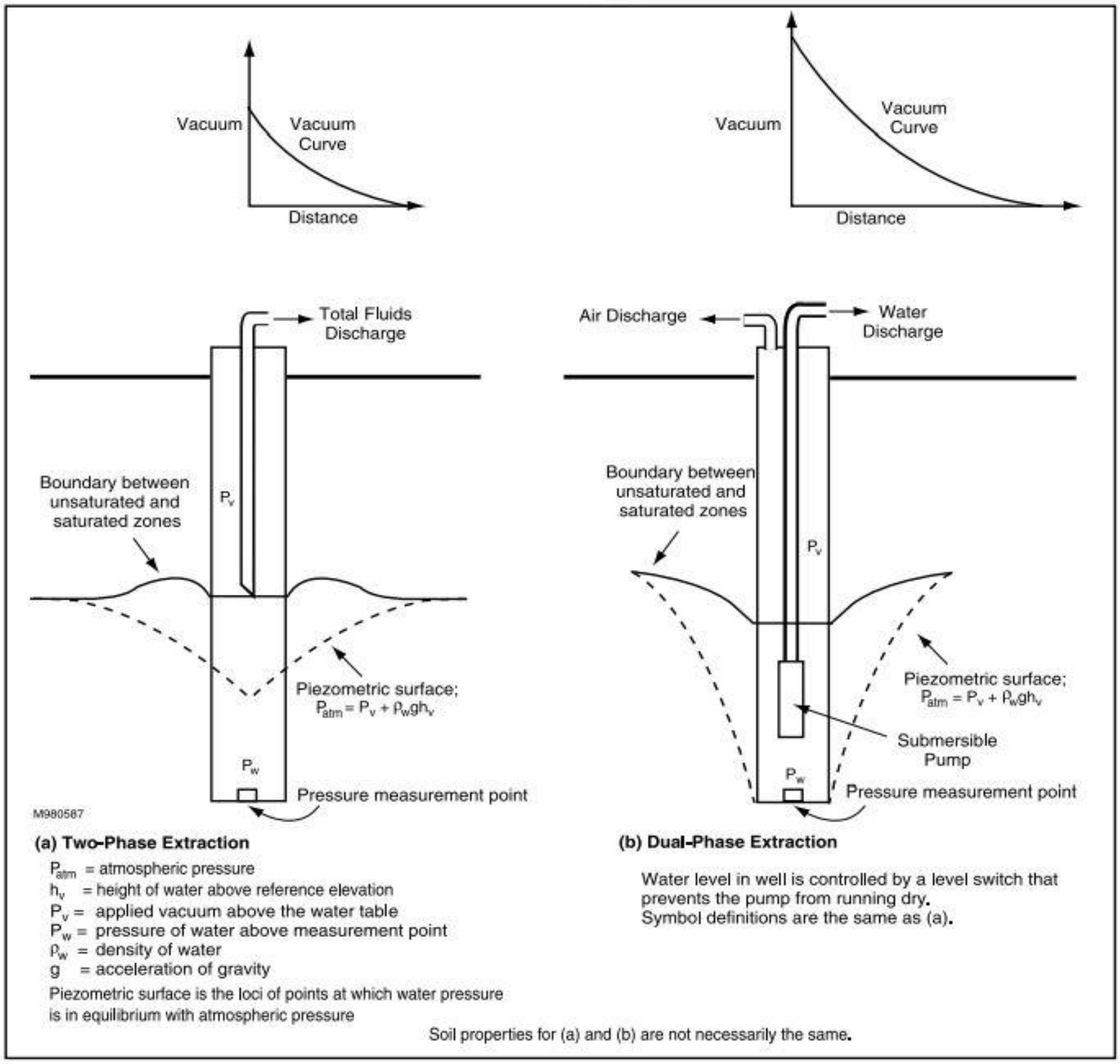


Figure 4.2.: **Scheme of groundwater depression and vadose zone effect in a TPE vs. DPE system [25]**

In addition to the two above-mentioned systems, particular attention must be paid to the study and understanding of the phenomena that are generated underground after the start-up of an MEP pilot system, which will be described below:

- mass removal effect - it must be expected that the efficiency in abating the concentrations of pollutants present in the subsoil and the reduction of their mass to be removed will decrease abruptly with the passage of time. This behavior is conditioned by the depletion of the most easily extractable fraction, which is removed from the subsoil by advection, after which mass of pollution transfer occurs only by simple diffusion effect;
- groundwater extraction - data collected during extraction will be useful for calculating hydrostatic responses, specific yield, extraction rate and permeability;
- soil gas extraction - data collected during extraction will be useful for calculating removal rates and mass and air extraction;
- Radius of Influence (ROI) - To calculate the ROI of an MPE system, it is necessary to consider both the vacuum at the wellhead and the water downhole as a function of distance and steam extraction rates. The case study described above produced, as shown in the figure below (Figure 4.5), an ROI of the extraction system (located in piezometer PM03) of 6.5 m with an airflow rate of 30 Nm3 /h and a

vacuum at the pump of -500 mbar; of 4.5 m with an airflow of 45 Nm^3 /h and a pump vacuum of -300 mbar; of 5 m with an airflow of 50 Nm3 /h and a pump vacuum of -15 mbar.

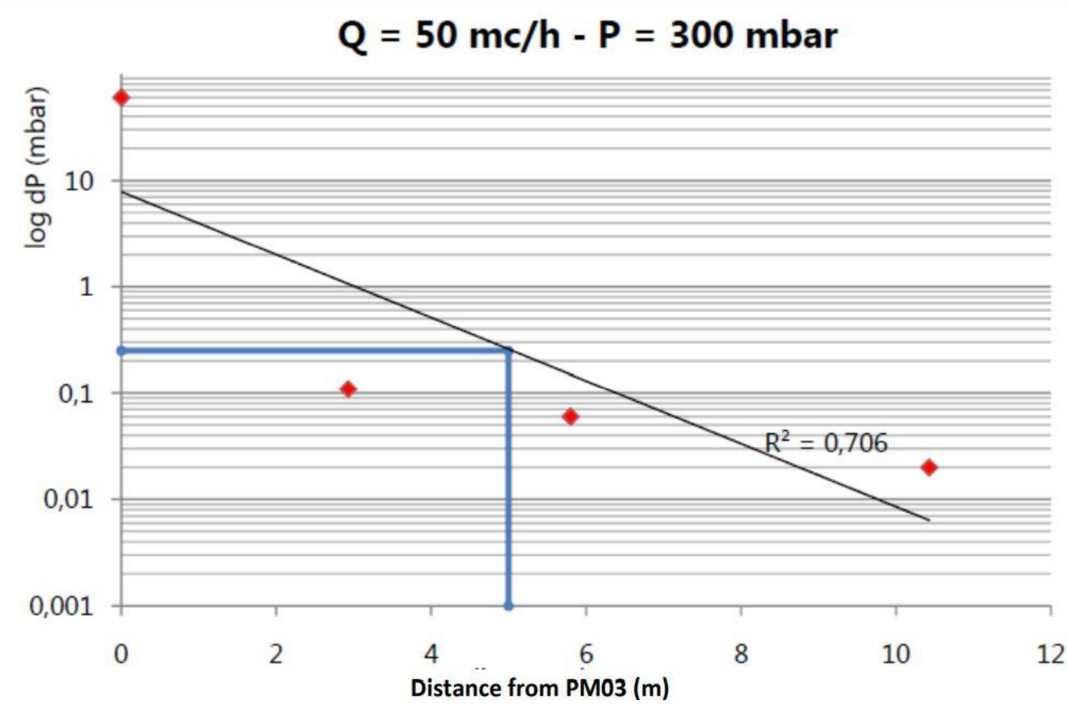


Figure 4.3.: **Graph of ROI test (courtesy of Ing. Caldera F., Mares Italia)**

In case of Bioslurping, the slurping action operates cyclically between the recovery of the liquid (supernatant product and/or groundwater) and the recovery of the soil gas, with a vacuum extraction (120 to 500 mm Hg) creating a pressure gradient that forces the movement of the supernatant product towards the well, inducing a slight lowering of the piezometric level of the aquifer and reducing the horizontal propagation of NAPL.

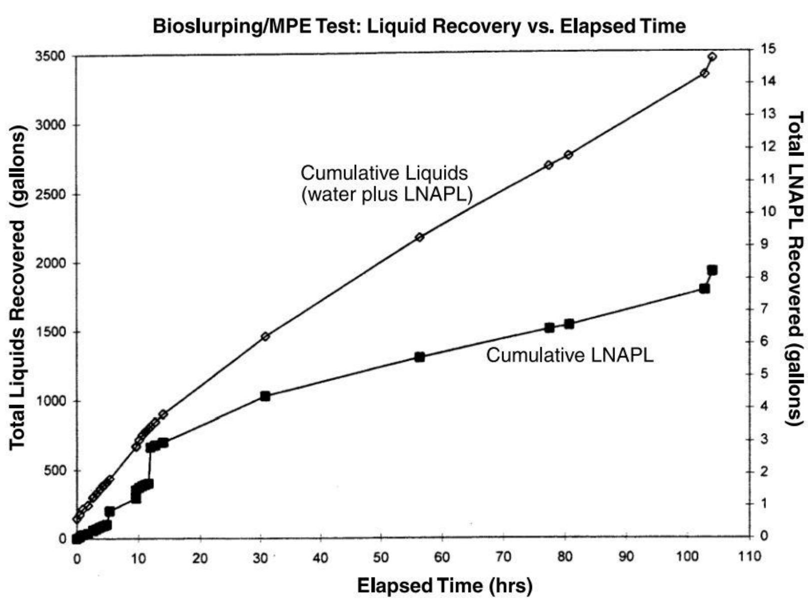


Figure 4.4.: **Liquid recovery vs elapsed time [25]**

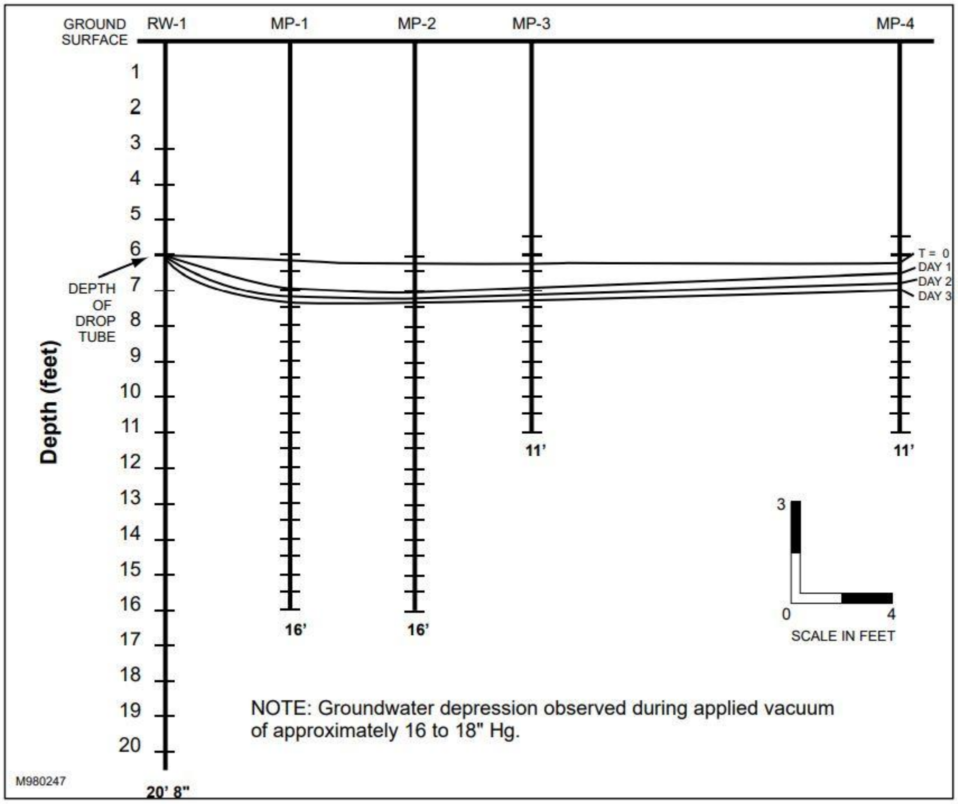


Figure 4.5.: Groundwater depression during bioslurping pilot test [25]

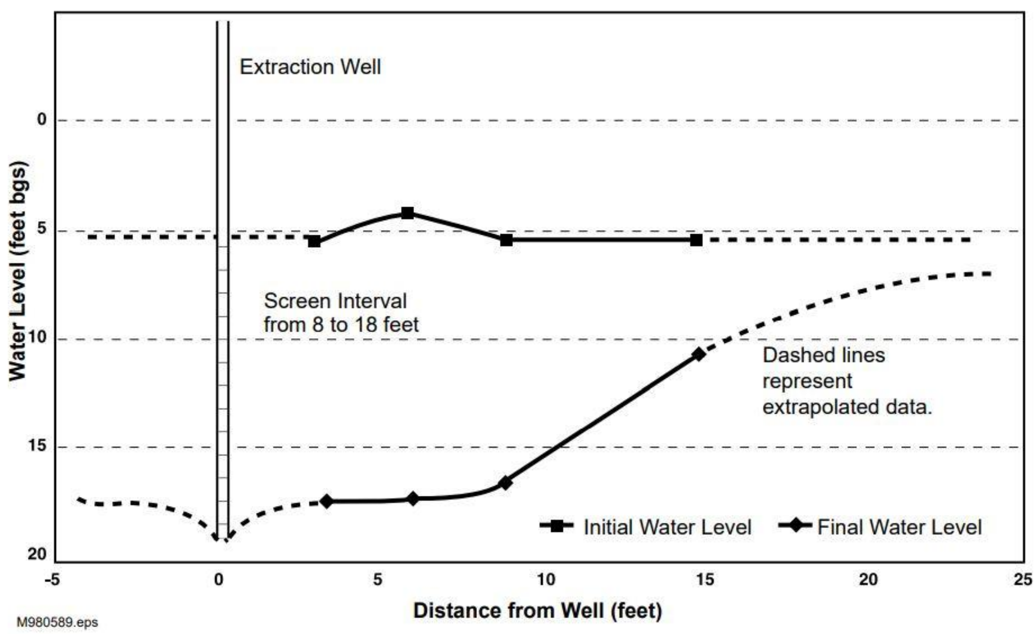


Figure 4.6.: **Shallow well Pilot test groundwater depression [25]**

4.2 Effluent treatment technology

As the MPE system is a complex system for treating different phases potentially polluted by other analytes, it presents a wide variety of possibilities for treating effluents once extracted from the subsoil. Therefore, from one case to another, a decision may be made to install:

- a groundwater treatment plant, not excluding from the system-specific components such as spiral decanters, chemical mixing tanks, stripping columns, sand and carbon filters, and others;
- a phase separator and at least one activated carbon filter for soil gas treatment;
- a double-walled tank or above a holding tank for LNAPL storage.

Depending on the national and local regulations in force at the site of installation of the MPE system and respecting the legal limits of the concentrations of contaminants present, it will be possible to release the effluents directly into a watercourse or canal or to feed them into the sewer system up to the possibility in some specific cases to release them underground upstream of the source.

4.3 Control parameters

The following parameters are to be monitored before the start and during the pilot test

- water/product;
- vacuum, temperature and flow rate of the extracted gases (on the high and low vacuum lines upstream of the sampling pump);
- the volume of water and product extracted;
- wellhead depression;
- VOC, CO_2, O_2 and CH_4 concentrations on high and low vacuum lines;

Vapours were also sampled on high and low vacuum lines using a sampling pump and activated carbon vials before the tests and at the end (60 minutes). Before starting the tests and at the end (60 minutes after starting) of each MPE test contaminants of interest were determined.
The data to be collected, depending on the type of MPE system (DPE or TPE) and the treatment goal to be achieved (NAPL, SVE/BV or groundwater), are summarised for convenience in the table below.

Table 4.1.: **Data to be collect and goal to achieve [25]**

GOAL / PARAMETERS	TWO-PHASE EXTRACTION			DUAL PHASE EXTRACTION			Comments
	LNAPL recovery	SVE/BV	GW recovery	LNAPL recovery	SVE/BV	GW recovery	
Extracted LNAPL/water ratio	X			X			Increasing level of applied vacuum favours the effect
Groundwater extraction rate	(X)	(X)	X	(X)	(X)	X	an increase in flow rates could increase the vacuum effect
Drop tube depth setting	X	X	X				Check the extraction rate according to the depth reached
Water table elevation changes	X		X	X		X	The changes are an indicator of the influence of pumping, greater depression, greater the recall of LNAPL
Vadose zone pressure changes		X			X		The changes are an indicator of the influence of vacum
Groundwater mass removal	X		X	X		X	an increase in the rate may mean that we are recalling the mass from the source area
O2, CO2, CH4 in soil gas	X		X	X		X	in bioslurping can be indicators of biological activity
Gas phase mass removal		X			X		Increasing level of applied vacuum favours the removal effect
X - parameters | **(X) -** optional parameters							

5 Monitoring of the performance

Monitoring is conducted during the operational phase to evaluate remediation progress and verify the achievement of cleanup criteria before the system shuts down. The objective of process and site monitoring is primarily to estimate the mass of hydrocarbons removed in the free phase (LNAPL), aqueous phase (dissolved in groundwater), and vapour phase. The monitoring plan should include more frequent sampling at system start-up and for cleanup confirmation. During operational phase monitoring, once the system is optimised, the sampling frequency and intensity may be reduced [26].
Below is a short description of the main parameters necessary to consider during routine monitoring.

5.1.1 Chemical parameters

Soil gas chemical monitoring is necessary to evaluate the effectiveness of the remedial process. Soil gas should be collected from individual extraction wells and soil gas probes.
During the operational phase, field instruments, such as flame- or photo-ionisation detectors, are often used for frequent or continuous measurements of total VOCs. Measurements performed with the aforementioned instruments should be considered as screening methods because of their nonspecific responses and the following other limitations [27]:

- The high ionisation potential of many common VOCs will result in nondetection using a conventional PID lamp.
- Gas matrix effects such as humidity, carbon dioxide, and alkenes (especially methane) may reduce PID response. However, when the relative humidity is very high, close to 100%, water vapour can condense on the sensor, causing a false-positive response. This signal is due to current leakage between the electrodes in the sensor [28].
- The high halogen content of many common VOCs will result in underestimation or nondetection of VOCs using an FID.

VOC and flow rate measurements in MPE system influent, and possibly in individual extraction wells, should be used to calculate the contaminant mass removal rates from the unsaturated soil.
Contaminant concentrations are usually measured at off-gas treatment influent and effluent (before and after carbon canisters) to assess the effectiveness of the air emission control system.
Groundwater chemical monitoring is necessary to evaluate the progress of groundwater remediation by the MPE system. The quality of the extracted groundwater may change over time; therefore, monitoring contaminant concentrations is necessary for calculating the mass removal of dissolved contaminants [9]. On top of that also (in case of presence) LNAPL thickness should be followed up. Effluent groundwater should also be analysed from time to time on parameters that can influence the efficiency of the treatment unit (eg Fe, carbonates,….).
Contaminant concentrations should be measured at groundwater treatment inlet, midpoint and effluent to calculate the contaminant mass removal rates from groundwater, estimate saturation times of the activated carbon filters, and check compliance with the discharge limits.

5.1.2 Physical parameters

Soil and vapour temperature measurement: vapour temperature data can help evaluate the efficiency of the vapour control system, and enable normalisation of flow rate data. Soil temperatures could be an indicator of biodegradation processes occurring in the vadose zone: in case of strong biodegradation, an increase in groundwater temperature of a few degrees can be measured.
Relative humidity: moisture content reduces the volume of pore space that contributes to fluid flow. Hence a high moisture level can reduce air permeability and airflow through the vadose zone; for the same reason, it may influence soil gas monitoring results. Furthermore, the relative humidity of the extracted gas can be

reduced to protect the blower and to promote the efficiency of the vapour emissions control system (the adsorptive capacity of activated carbon is decreased significantly when the relative humidity is greater than 50%). The relative humidity of the vapour stream can usually be decreased using an air heating system [26]. Often the installed blower delivers the needed heat. The heating of the vapour stream is limited by the highest permissible temperature while using activated carbon.

Water levels: it is necessary to pay particular attention to water table fluctuation because it could enhance mass contaminant transfer between solid, liquid and gas phases. Moreover, upwelling can cause an excess of moisture in the treatment zone, and can also lower the sorptive capacity of activated carbons in the treatment of the gases. This problem can be mitigated by improving moisture separation and/or actively pumping groundwater to counteract the upwelling in situ [26]. Applying a vacuum to the well will cause the zone of saturation to upwell (rise) in the recovery well upon vacuum application. However, in MPE, there is typically a drop tube or separate pump to remove groundwater and/or free phase product in the treatment part. Hence, this upwelling does not present the same problems encountered with SVE/BV systems of raising the top of the zone of saturation [9]. Monitoring the water levels also allows for evaluating the MPE system's effectiveness in terms of hydraulic containment of the contamination. A lower groundwater level is verified at the extraction well(s) due to the MPE system. The water level measured in an extraction well is typically lower than that in the adjacent aquifer due to well inefficiency and well losses [29]. Additional well losses may occur due to turbulent flow inside the well bore and through the well screen slots [30]. Using water levels at extraction wells can bias the interpretation of capture since the water levels at the extraction wells used for contouring may be much lower than water levels in the aquifer material just outside the well bore. Thus, the capture zone may be interpreted to be larger than it is when water levels at the extraction wells are used for contouring. To avoid these problems, EPA recommends installing a piezometer near each extraction well. It is also possible to install piezometers in the filter pack of extraction wells. However, this approach will not mitigate some causes of well inefficiency (e.g., formation damage due to poor well construction) [30].

Water flow rate: Groundwater recovery rates may be measured using flow rate meters, totalising flow meters, or by measuring accumulation in a holding tank over time after separation from NAPL. Initial flow rates will be very important for evaluating conditions in the recovery well(s) and should be monitored frequently, even hourly, on the first day. After separation, NAPL flow can generally be measured like that for groundwater. However, flow meters for NAPL measurement must be calibrated to the specific gravity of the NAPL [9].

Air flow rate measurement: flow rate data from each well, in conjunction with the corresponding applied vacuum, may provide information about the air permeability of the vadose zone. Normalising flow rates to a standard temperature and pressure is recommended so that data collected in different surveys can be easily compared.

Vacuum/pressure measurement: the measurement of observed vacuums at different locations and depths provides an indication of the airflow paths. Pressure gradients determined from the vacuum measurements should be coupled with horizontal and vertical air conductivity estimates to assess travel times or velocity [31].

NAPL thickness and drawdown in extraction wells and monitoring wells should be monitored for MPE system setting purposes (flow rate regulation at the single extraction well, drop tubes vertical position adjustment, filling of NAPL storage tank estimate of the) and to evaluate the progress of the groundwater remediation.

5.1.3 Meteorological

Meteorological data (e.g. precipitation, barometric pressure, ambient temperature) should be recorded and considered for a correct evaluation of monitoring results.

Precipitation: rainfall events limiting the transport of volatile contaminants in unsaturated soil can significantly affect MPE performance and soil gas monitoring results. Hence soil gas sampling should not occur after a significant rain event (1/2 inch or greater of rainfall during 24 hours). The waiting period should be based on soil drainage curves [32]. Precipitation could also affect the fluctuations in groundwater levels in the case of shallow, unconfined aquifers.

Barometric pressure: The atmospheric pressure fluctuations induce gas movement between the atmosphere and the subsurface. Gas movement in the unsaturated zone induced by natural fluctuations in atmospheric pressure is barometric pumping. When the atmospheric pressure falls, gases are drawn upward from the subsurface into the atmosphere. Conversely, fresh air is pushed downward into the subsurface [33]. Therefore, the effect of barometric pressure fluctuations on the transport of atmospheric gases may be more evident during shutdown periods.

5.2 Confirmation of clean-up and system shutdown

The objective of the remediation process is, in general, the attainment of predetermined quality standards for different environmental matrices. The ultimate shutdown criteria for an MPE system are usually based on the attainment of a regulatory or risk-based concentration standard for soil and groundwater, in some cases thickness of the LNAPL or reaching an asymptote in concentrations. However, soil sampling is both costly and potentially disruptive. Moreover, tracking residual contamination accurately requires analysing a large number of samples because soil, being an unmixed medium, is heterogeneous [26]. Hence before starting a large-scale soil sampling survey, other parameters (lines of evidence) can be considered/monitored to assess the remedial progress and to evaluate if the remediation goals are likely to have been met.

5.2.1 Possible lines of evidence to be considered for clean up confirmation

Soil sampling: the use of soil sampling for confirmation of cleanup and system shutdown must carefully consider the heterogeneous distribution of soil concentrations at a site and the uncertainties associated with sampling soils, particularly for VOCs [26].

Extracted water and vapour concentration trend: contaminant concentration in extraction wells can provide a gauge of contaminant mass removed and an indication of remedial progress. Usually, after a few months of operation data trend shows a rapid decline, after which concentrations approach asymptotic levels (see Fig. 5.1 and Fig. 5.2). In many cases, the attainment of an asymptotic condition is considered decisive in establishing technology performance limits and the closure of MPE systems. However, observation of low asymptotic vapour concentrations in effluent water gas is a necessary but not always sufficient condition to demonstrate progress in mass removal from contaminated areas. An effluent asymptote may as well be related to remediation system design (e.g., well spacing) or operating conditions (e.g. flow rate) separate or in addition to rate-limited transport [34]. Vapour extraction is more effective in soil portions near or between the wells that are thoroughly flushed. Hence contaminants concentrations may reach very low asymptotic levels while a significant quantity of contaminant mass remains in the soils, especially near-stagnation zones. The attainment of asymptotic concentration levels in extracted water/gas may imply that rate-limited mass transfer occurs during the operational phase. Suppose extraction rates exceed the rate of diffusive mass transfer between the phases (solid, liquid and gas) in the subsoil. In that case, contaminant concentrations can decrease without removing all of the contaminant mass from soil and water [26].

Soil gas monitoring: soil-gas samples are less expensive to collect and, since air is a mixed medium, generally represent more integrated (i.e., from a larger area) data. Hence VOC monitoring in soil gas probes is probably a more effective and efficient method to assess remediation progress than those previously described under points a) and b). Soil gas sampling should, however, follow a standard procedure that considers the influence of field conditions (e.g. lithology, humidity) and sampling parameters (e.g. sampling flow rate, sampling volume) on monitoring results. Soil gas probes should also be installed in areas far from the extraction wells that are more difficult to remediate and track residual contamination.

Groundwater monitoring: remediation in the vadose zone should not be conducted independently of groundwater conditions. Unsaturated soil may be recontaminated by capillary action and water table fluctuations. Contaminant concentrations in groundwater should also be monitored to evaluate the mass transfer from the aqueous phase to the soil gas. In particular, when LNAPL is present, the remediation efforts should focus on the so-called smearing zone. Accumulations of LNAPL at or near the water table are

susceptible to “smearing” from changes in water-table elevation such as those that occur due to seasonal changes in recharge/discharge and tidal influence in coastal environments, dewatering caused by pumping. LNAPL will be retained in the soil pores as the water table rises or falls, leaving behind a residual LNAPL “smear zone”. If smearing occurs during a decline in groundwater elevations, residual LNAPL may dissolve and recontaminate groundwater when elevations rise [35]. In the case of a light non-aqueous phase spill where groundwater concentrations within a “smear” zone are at much higher levels than beneath the “smear” zone, more aggressive dewatering and venting application should be considered [27].
Rebound: during the operational phase, a decrease in groundwater and soil gas contaminant concentrations is generally observed as a consequence of rate-limited mass transfer (starvation effect). Hence when the MPE system is turned off, concentrations may rise due to diffusion between different phases of subsoil, giving origin to the phenomenon usually described as a rebound. Furthermore, when NAPL is present, heterogeneities, such as layers or lenses of low permeable material, need longer to get flushed through the induced air or water flow. In addition, the contaminants may have spread into such layers, sorbed onto particle surfaces or present as a free product at residual saturations. Hence, in those cases, the rebound may be caused by NAPL dissolution, contaminant desorption, and back diffusion from low to high permeable parts of the subsoil [36]. For the aforementioned reasons, the rebound can be considered a reliable indicator of treatment effectiveness, minimal rebound or lack of rebound, neither in stagnant zones, after some period of system cessation indicates that available mass has probably been removed. The time period required to reach equilibrium is contaminant and soil-type specific. Sandy soils will generally reach equilibrium in several weeks, while several months may be required for highly-layered soils. Annual equilibrium (rebound) testing is recommended [37]. When contaminant rebound is observed, the following operational solutions can be considered: install additional wells, perform pulse MPE, and reduce flow rates.

5.2.2 Proposed shutdown sampling procedure

The ultimate shutdown criteria for an MPE system are usually based on the attainment of established soil, soil gas and groundwater concentration standards. However, as previously discussed, since soil sampling is both costly and potentially disruptive, before starting a large-scale soil sampling survey, other parameters (lines of evidence) are monitored to evaluate if the remediation goals are likely to have been met. Hence the following procedure for cleanup confirmation is proposed, based on a three steps verification process.

- attainment of a target groundwater and soil gas concentration during the operational phase;
- attainment of a target groundwater and soil gas concentration after a temporary system shutdown;
- comparison of soil sampling results with cleanup criteria.

6 Conclusions

MPE is one of the preferred remediation options in the case of the presence of LNAPL and in the case of contamination of volatile/semivolatile compounds in the saturated and the unsaturated zone of the soil. Quite often, only a single above-ground pump is necessary as opposed to a pump in each well. On top of those advantages, it may induce biodegradation of hydrocarbons in the vadose zone and air stripping of VOC from the vadose zone.

Mainly two ways of implementation exist: a DPE system with one pump (mostly a liquid ring pump to create enough depression) followed by a separating system to split between water gas and pure product; a TPE system with two pumps (one to lower the groundwater level, one for the pure product and the unsaturated zone, followed as well by a separating system).

Before implementation, a good understanding of the conceptual site model (geology, hydrogeology, type of contaminants,….) is required. For larger installations, a pilot test is recommended. In all cases good monitoring of the system is useful; this monitoring will have to be continued after the shut down of the system as well to measure potential rebound.

The success of MPE is dependent on (hydro)geology (heterogeneity, permeability) and the type of product. In general main mass can be removed, but a reduction of the mass by more than 1 to 2 orders of magnitude is hardly possible. Remediation targets can be based on LNAPL thickness, groundwater concentrations, and soil gas concentrations; the targets can be absolute values or reach the asymptote.

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European Union Network for the Implementation and Enforcement of Environmental Law

Annex 1

Multi Phase Extraction – Case studies

IMPEL Project no. 2022/10

1. Contact details - CASE STUDY: MPE n.1

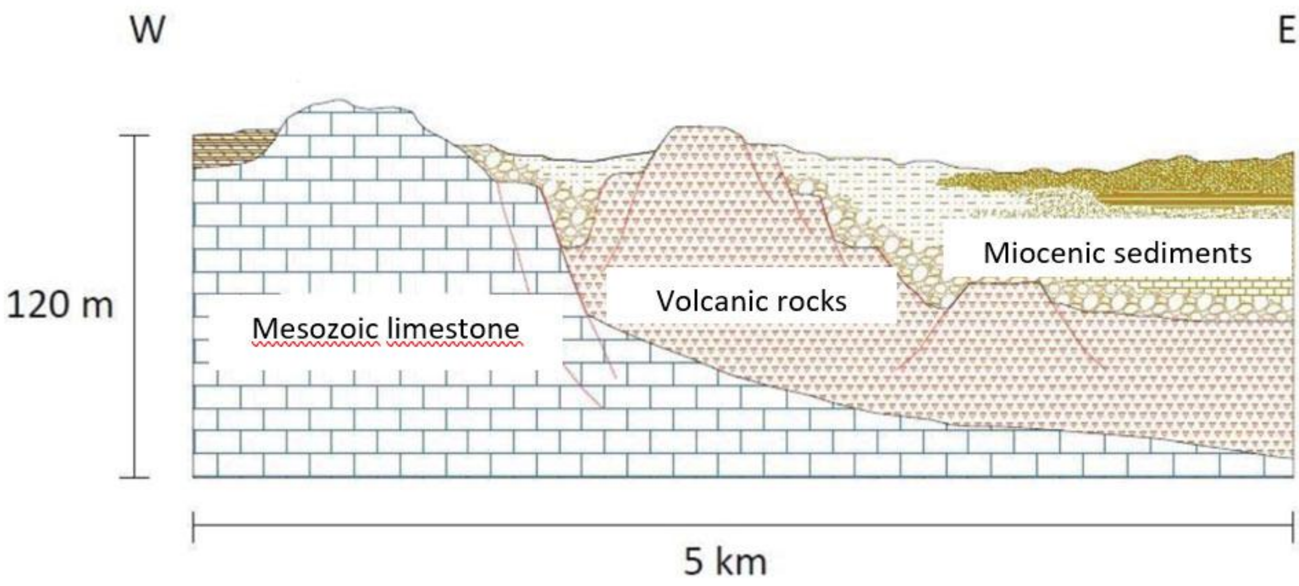
1.1 Name and Surname	Claudia Costanzo[1] Gianpiero Zaccone[2]
1.2 Country/Jurisdiction	Italy
1.3 Organisation	Golder Associates S.r.l.
1.4 Position	[1]Environmental engineer [2]Geologist
1.5 Duties	-
1.6 Email address	ccostanzo@golder.it – gzaccone@golder.it
1.7 Phone number	+39 011 2344211

2. Site background

2.1 History of the site

The Site is a petrochemical plant in Italy, built starting from the 1960s, was characterized by a differentiated production structure which has undergone considerable variations over time. The plant has a total extension of over 1100 ha.
During the first and second phase of development, production activities were started and subsequently, in 1965, those for the construction of the first Steam-Cracking plant (currently demolished), which allowed the construction of other plants for the subsequent use of Ethylene.
In 1967 was built the refinery. The refinery was then decommissioned in the 1980s.
At the end of the 1970s, the third phase of development of the plant began, which involved the construction of the chlorine and chlorine derivatives plants, the second steam cracking plant, the plants for the production of PVC, polystyrene and polyethylene, until 1976, the year of construction of the plant for the production of Acrylic Fibres.
From April 1982 the plant took a configuration almost similar to the current one.
Starting in the late 1990s, the productivity level dropped and the plant was slowly decommissioned.

2.2 Geological setting



Geology of the site consist in oligocenic volcanic/mesozoic limestone bedrock, underlies a thick miocenic sequence.

The depth to ground water changes as a function of the local stratigraphy. At site where MPE is installed, the depth to groundwater is approximately 10-15 meters below ground surface.

2.3 Contaminants of concern

The site is contaminated both in soil and in the aquifer.
MPE technology is used on site for groundwater remediation, currently in one of the plant areas, characterized by the presence of free phase product (LNAPL) and dissolved contamination.
The main exceedances of target limit (CSR) in groundwater, in correspondence of the areas where the MPE systems are installed, refer to:

- total hydrocarbons;
- aromatic hydrocarbons (benzene, toluene);
- organohalogen compounds (1,2-dichloroethane, 1,1,2-trichloroethane, vinyl chloride, trichlorethylene).

2.4 Regulatory framework

The main environmental law in Italy is the Legislative Decree no. 152/2006 (D.Lgs. 152/06) that in Part four, Title fifth sets specific rules for remediation of contaminated sites.
The reference legislation establishes some threshold limit values (CSC D.Lgs. 152/06) for the main existing contaminants both in soil and groundwater, if during the characterization there are one or more exceedance of these value, the site is defined "potentially contaminated", and a risk assessment can be elaborate to estimate the risks deriving from the potential sources of contamination detected on site (defined by the samples with exceedance). The legislature also fixes which are the values of acceptable risk to compare with the values derived from the site's risk assessment.
If the estimated risks are lower than acceptable values, the site is defined "not contaminated", and no remediation is needed. If the estimated risks are higher than acceptable values, the site is defined "contaminated", and remediation is needed. The legislation also allows to define, via risk assessment, new site-specific threshold limits (CSR defined by Italian law D.Lgs. 152/06), which becomes the remediation targets.
At the site specific threshold limits were available both in groundwater and soil.

3. Pilot-scale application in field

3.2 Feasibility study

The objective of conducting the MPE pilot test is to verify the applicability of the technology for site remediation and to define some process parameters. In particular, the pilot test will have the aim of:

- evaluate the removal capacity of the LNAPL product in the wells;
- measure the flow rates of extracted fluids;
- check the chemical characteristics of the extracted vapors;
- measure the induced depressions in the suction well;
- evaluate the effectiveness of MPE technology in the removal of fluids from wells with a depth of even more than 15 m;
- collect any other data useful for the design.

The system used for the pilot tests simulates the operation of the MPE plant designed for the site.

The extraction will take place through a well, which will be equipped with a sealed wellhead to which two pipes will be connected: one, at high depression, for multiphase suction (air / water / product), and the other, at low depression, for the aspiration of the air/VOC.

The wellhead will be equipped with a pressure gauge for measuring the depression in the well and a hole with suitable sealing for measuring the subsidence of water and product.

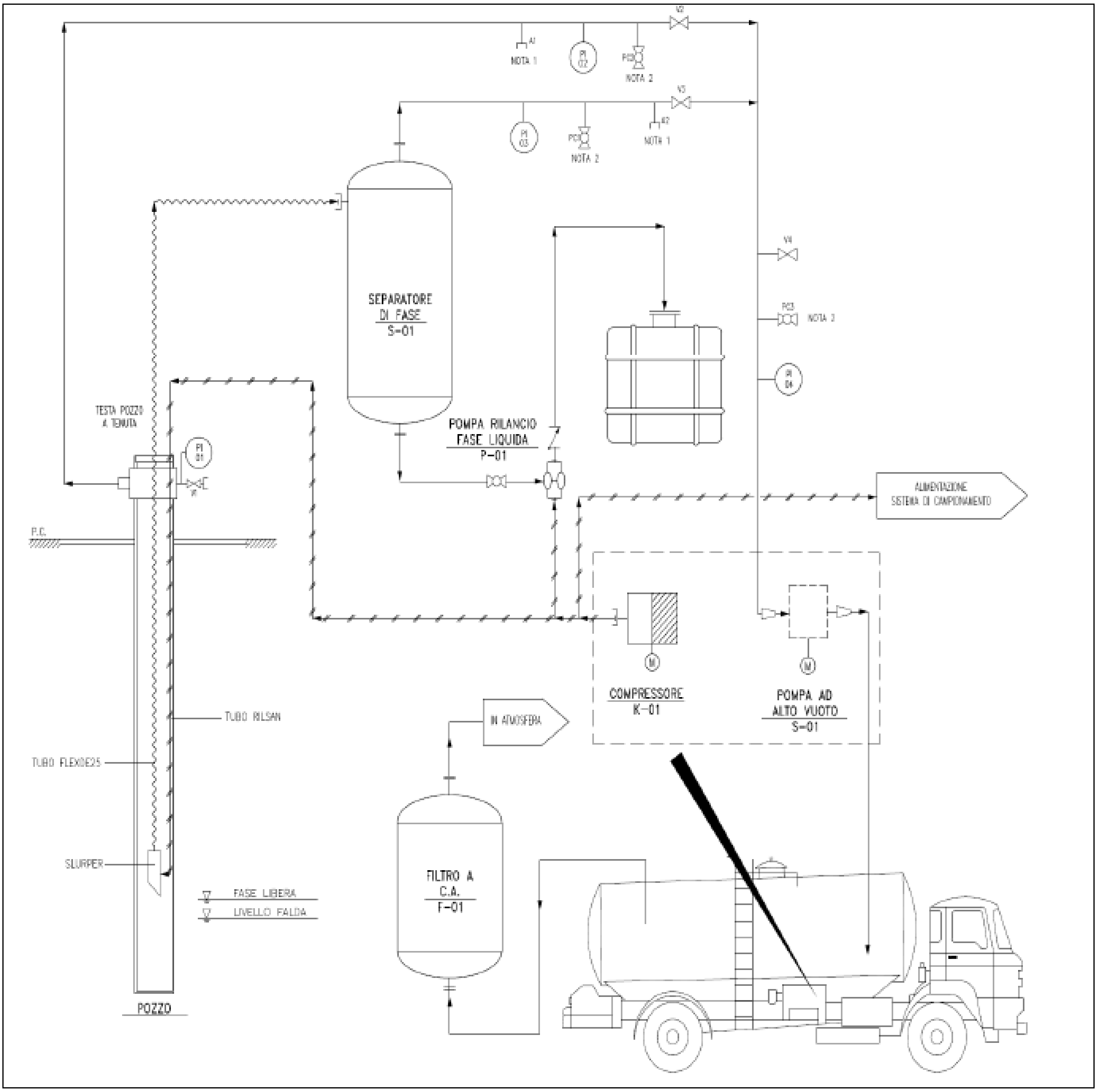
The suction will be generated with a high vacuum pump supplied with a self-purge device. This expedient will facilitate the logistics of the tests, avoiding the need to set up the connection to the system's electrical network and facilitate the management of the waste produced by the tests.

The flow extracted from the high-vacuum line will be passed through a phase separator where the air/fluid (water and product) separation of the high-vacuum flow will take place.

The aqueous phase and the product that will accumulate in the separator will be sent by means of a pneumatic diaphragm pump to a tank with a capacity of 1 m^3 for temporary storage before final disposal.

The compressed air for powering the pump will be generated by the generator supplied with the self purge.

Below some schemes and picture of the pilot test system.

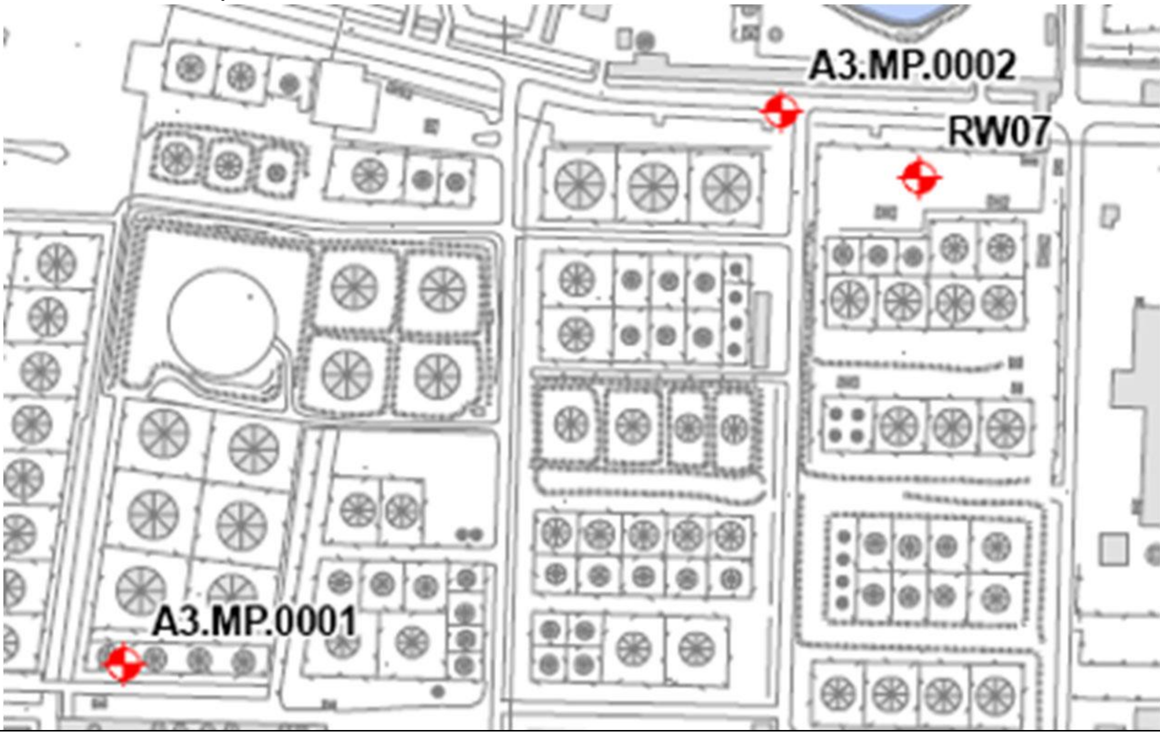


SEPARATORE DI FASE S-01
POMPA RILANCIO FASE LIQUIDA P-01
TESTA POZZO A TENUTA
P.C.
TUBO RILSAN
SLURPER
FASE LIBERA
LIVELLO FALDA
POZZO
FILTRO A C.A. F-01
IN ATMOSFERA
COMPRESSORE K-01
POMPA AD ALTO VUOTO S-01
ALIMENTAZIONE SISTEMA DI CAMPIONAMENTO
NOTA 1
NOTA 2


S13AM
S12AM
A01TD
S32 MR
MiniRAE Lite

3.3 Radius of influence

The pilot test did not foresee the drilling of new points to be equipped with extraction wells and / or monitoring piezometers.
Existing piezometers were used for the test and, not being present in the circumscribed surroundings of the points selected for the execution of the monitoring piezometers pilot test, it was not possible to define a radius of influence.



3.4 Off gas Treatment

The gases extracted during the test were sent to an activated carbon filter before being released into the atmosphere.

3.5 Water Treatment

The aqueous phase and the product that accumulated in the separator during the pilot test were sent by means of a pneumatic diaphragm pump to a tank with a capacity of 1 m^3 for temporary storage before final disposal.

3.6 Control parameters

During the pilot test the following parameters were monitored:

- water / product subsidence
- vacuum, temperature and flow rate of the extracted gases (on the high and low vacuum lines,
- upstream of the sampling pump)
- VOC
- CO_2, O_2 and CH_4 concentrations on high and low vacuum lines
- volume of water and extracted product
- wellhead depression

Vapors were also sampled on both the high and low vacuum lines using a sampling pump and activated carbon vials, before starting the tests and at the end (60 minutes after starting) of each MPE test for the determination of the contaminants of interest.

4. Full-scale application

4.1 Full design system

4 MPE modules were installed on the site, each consisting of 45 extraction wells 15 to 20 m deep.
The MPE system installed at the site was sized considering that:

- each MPE module has been designed so as to intervene on the areas characterized by the highest concentrations of hydrocarbon compounds in the dissolved phase, in the vapour phase and by the probable presence of LNAPL;
- the installation depth of the MPE wells is related in each installation area to the average depth of the groundwater level, the maximum oscillation of the groundwater level and the thickness of the capillary fringe;
- the radius of influence of the extraction wells was estimated to be around 5 meters.

The suction of low and high vacuum flows is achieved by generating a vacuum in the pipes by means of special suction modules, respectively equipped with blowers and high vacuum pumps.
The separation of the different phases (liquid and gaseous), which make up the flows extracted from the subsoil, starts through the passage in a special separation module, in which the condensate precipitates from the low depression flow and the air / aqueous phase separation. (water and product) of the high depression flow.
Each module making up the system consists of the following sections:

- 45 extraction wells: each well is equipped with 2 lines, one of which with high depression, for multiphase suction (steam / water / product) and one with low depression, for suction of the vapour phase only;
- 9 separation modules: each separation module manages 5 extraction wells and allows the precipitation of the condensate of the low-vacuum flow and the vapour / liquid (water and product) separation of the high-vacuum flow;
- 1 suction module (high and low depression lines): each suction module manages 9 separation modules and has the purpose of generating the air flow and the degree of vacuum required by the system;
- 1 treatment module: each module treats the vapour phase by means of 3 activated carbon filters and stores the liquid phase in a temporary storage system with subsequent re-launching for treatment;
- a module containing the compressed air production systems and the main management and

- Control unit of the treatment suction separation modules;
- Exhaust duct.
- The four suction modules deliver the liquid phase to a water / oil separator, where the LNAPL is separated and collected and the water phase is pumped to the groundwater treatment system.
- The hydrocarbon product leaving the oil separator is sent to the preliminary liquid deposit for subsequent disposal to an authorized external plant.

4.2 Different areas characteristics that affect the project

The 4 modules were installed in areas with similar geological and hydrogeological characteristics. The same inter distance has been maintained for all extraction points of each module.

4.3 Radius of influence

In the absence of specific site data, the radius of influence of the extraction wells was taken as a precaution, considering the geological and hydrogeological characteristics of the area, equal to about 5 meters, taken as a precaution, considering the geological and hydrogeological characteristics of the area, equal to about 5 meters.

4.4 Off gas Treatment

The gaseous flow leaving the MPE plant is treated by activated carbon filters connected in series.

4.5 Control parameters

The water extracted from the MPE system downstream of the oil separator is sent to the site groundwater treatment plant.
The current structure of the groundwater treatment plant to which the water extracted from the MPE systems (but not only) flows is composed of the following units:

- oil removal;
- chemical-physical treatment
- storage;
- sand filtration
- acidification;
- steam stripping
- activated carbon filtration;
- neutralization;
- sludge treatment (thickener and filter press);
- Vapour treatment (condensation and filtration on activated carbon).

4.6 Control parameters

MPE interventions are subject of a plant and environmental monitoring program aimed at keeping system functionality and evolutionary trends in terms of mass of contaminant removed under constant control, so as to determine the best performance obtainable in site-specific conditions.
As regards the environmental status, the plan provides for the following monitoring:

- phreatometric and the possible presence and thickness of free product (LNAPL), in correspondence with a network of 16 piezometers;
- the quantity of product recovered from each MPE module;
- hydrochemical of groundwater, at 24 points of the network of selected piezometers;
- Soil gases through field measurements, at 80 selected extraction wells;
- Soil gases by sampling and chemical analysis in the laboratory at 80 selected extraction wells.

From the plant engineering point of view, the following are detected:

- water / product subsidence in MPE wells
- vacuum, temperature and flow rate of the extracted gases (on the high and low

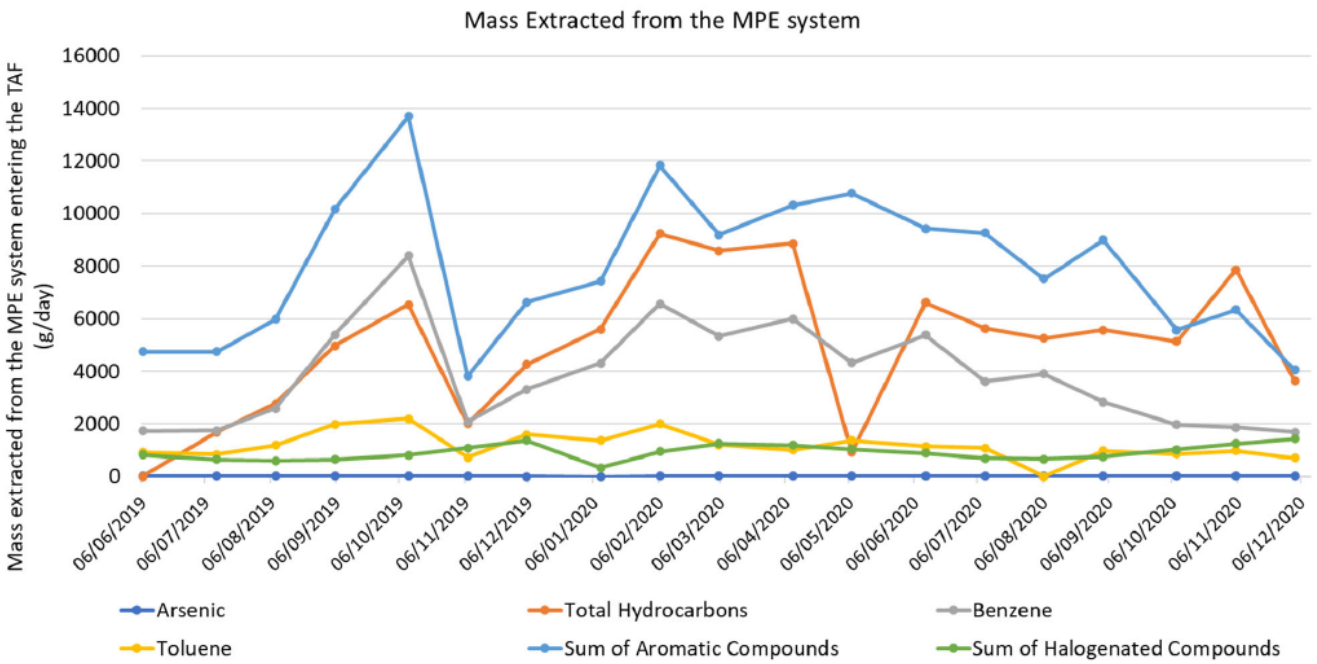
vacuum lines, upstream of the sampling pump)

- VOC at the wellhead
- concentrations of CO_2, O_2 and CH_4, VOC on high and low depression lines
- volume of water and cumulative extracted product
- wellhead depression.

5. Results

5.1 Removal rate

For the determination of the extracted mass, five index parameters are analyzed on the water drawn from the MPE system, such as arsenic, total hydrocarbons (expressed as n-hexane), benzene, toluene and the sum of the total and aromatic organohalogen compounds, using the results of the chemical analyzes performed monthly upon entry to the groundwater treatment system. The graph shows the trend of the mass of contaminant extracted, expressed in grams / day, in about a year and a half of operation of the MPE systems.



6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring
The MPE plant (4 modules) after carrying out the baseline monitoring, entered the start-up phase for about 6 months and starting from June 2019 was fully operational and is still in operation.

7. Additional information

7.1 Lesson learnt

In order to ensure optimal functioning of the systems, the following aspects are important:

- Carry out periodic routine and extraordinary maintenance
- Check the correct positioning of the slurper according to the depth to groundwater level and the depth to water / product interface
- Continuous operation of the system and constant adjustment of the process parameters.

Glossary of Terms

Term (alphabetical order)	Definition
CSC	Threshold limit values according to 152/06 Decree
CSR	Site-specific threshold limits according to 152/06 Decree
LNAPL	Light not acqueous phase liquid

1. Contact details - CASE STUDY: MPE n.2

1.1 Name and Surname	Federico Caldera
1.2 Country/Jurisdiction	Italy
1.3 Organisation	Mares S.r.l.
1.4 Position	Analista Sviluppo & Compliance
1.5 Duties	Sanitary and environmental risk assessment, innovative remediation and characterization technologies development
1.6 Email address	federicocaldera@maresitalia.it
1.7 Phone number	+39 3497616386

2. Site background

2.1 History of the site

The site is a gas station in a city of central Italy, where at least starting from 1968, the marketing of petroleum products for motor vehicles, refuelling of motor vehicles, sale of lubricants and oil change of cars have been carried out. A contamination of TPH affecting soil and TPH, Benzene, MTBE, ETBE, Lead affecting groundwater (with also LNAPL) was found there in 2010. So First Remediation Phase took place in 2012 and consisted of removing the contaminated soil simultaneously with the renovation of the mechanical system of the gas station. As Second Remediation Phase a groundwater and unsaturated soil remediation plant was installed using MPE and P&T technology in 2014.

2.2 Geological setting

The site is located in a hilly city, with the presence of some waterways characterized by a distinctly torrential regime.
The investigation carried out here has shown the presence of a succession of an alluvial nature at the site in which two units are identified: a superficial silty-clayey up to an average depth of about 5 m b.g.s., and a predominantly sandy underlying up to the maximum depth investigated (8 m b.g.s.).
The investigation carried out here showed the presence of an aquitard contained in the superficial part of the alluvial unit consisting of low permeability deposits.
The average piezometric level is about 2.0-2.5 meters deep from the ground level.
The presence of a confined aquifer with good permeability was found in the underlying sandy layer, whose piezometric level is about 3.0-3.5 m from the ground level.

2.3 Contaminants of concern

As anticipated the historical contamination affected both soil and groundwater, with TPH as CoCs in the first and TPH, Benzene, MTBE, ETBE and Lead as CoCs in the latter.
The residual contamination downstream of the remediation work carried out on the site in 2012 was present in the adsorbed phase in superficial and deep unsaturated soil and in the dissolved phase in the superficial aquitard and in the deep aquifer.

2.4 Regulatory framework

In Italy the environmental regulatory system is regulated by Legislative Decree No. 152/06 and for fuel stations by the Ministerial Decree No. 31/15. For the implementation of MPE and P&T technology (as well as for the implementation of any remediation plan) the approval by local authorities is needed.

3. Pilot-scale application in field

3.1 Extraction system

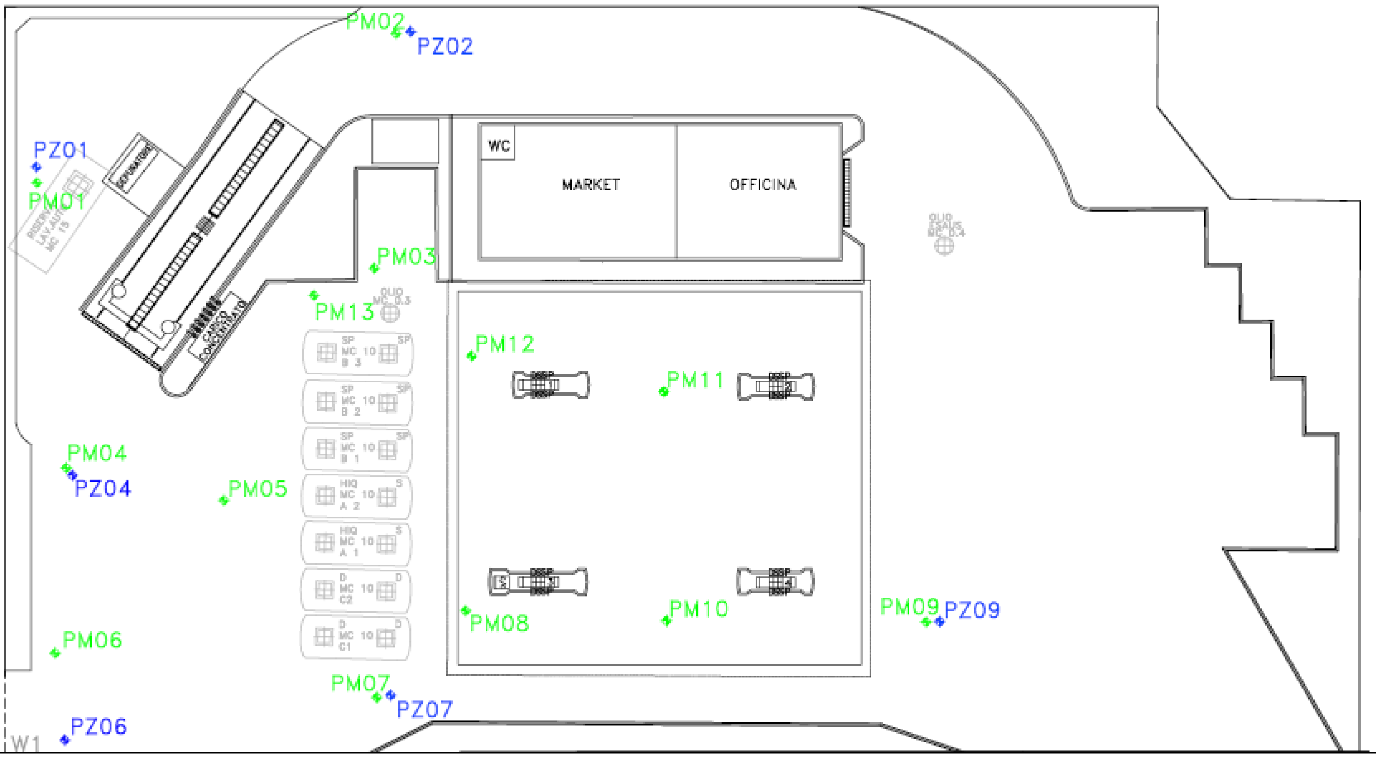
Single Pump configuration (extract air and liquid)

- Dual Pump configuration (submersible pump for groundwater recovery in conjunction with a separate vacuum applied at the sealed wellhead)
- Bioslurping (extraction at the interface air liquid)
- Other
    - High-Vacuum Dual Phase Extraction (HVDPE)
    - Low-Vacuum Dual Phase Extraction (LVDPE)
    - …….

For the pilot test, the PM03 and the monitoring piezometers arranged "helically" around the aforementioned piezometer were chosen as extraction piezometer, i.e. at about 120° and with increasing distances the PM13 (2.9 m), PM12 (5.8 m) and PM02 (10.4 m), as indicated in the figure below.

The test was performed by applying 3 different flow rate steps (30, 45 and 50 Nm^3/h) in PM03, while analyzing the relative subsoil response (in the monitoring piezometers); the drop-tube was applied near the bottom of the hole.

The drained waters were deposited on site and subsequently disposed of in accordance with current legislation, while the air was purified of any organic contamination contained in the flow by means of a granular activated carbon (hereinafeter GAC) filter.



3.2 Feasibility study

The pilot test was performed in order to:

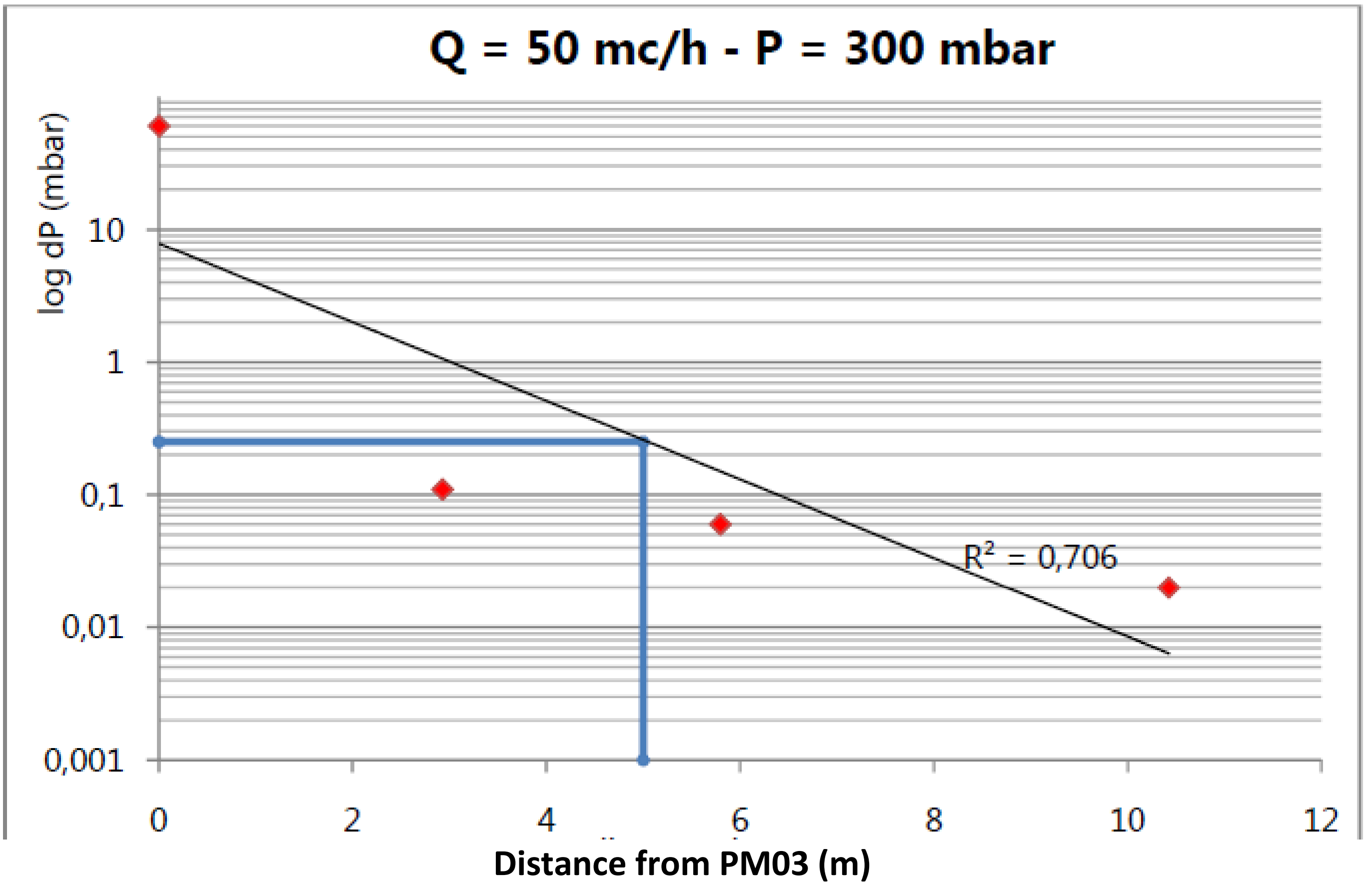
- verify the applicability of the MPE system in the geological, hydrogeological and environmental context of the specific site;
- determine the radius of influence of the depression (hereinafter ROI), conventionally defined as the distance, from the extraction point, where a relative depression of 0.25 mbar is recorded;
- determine the minimum depression to be applied for the extraction of the liquid phase;
- define the achievable extraction rates;
- estimate the concentrations of the Volatile Organic Compounds (hereinafter VOC) extracted.

The MPE pilot test demonstrated good applicability to the specific geological, hydrogeological and environmental context in terms of subsoil response to the stress induced by the system.

Simultaneously with the MPE pilot test, the step flow test was implemented, in order to obtain the characteristic curve of the well under test, while with the long-term pumping test the trasmissivity, the storage coefficient of the portion of the aquifer around the PZ04 well, as well as the radius of influence of the extraction.

3.3 Radius of influence

As shown in the figure here below, the ROI of the extraction system positioned in the PM03 piezometer, with an air flow rate of 30 Nm^3/h and a pump vacuum of -500 mbar, is approximately 6.5 m, with an air flow rate of 45 Nm^3/h and a vacuum at the pump of -300 mbar, the ROI becomes about 4.5 m, and with an air flow rate of 50 Nm^3/h and a vacuum at the pump of -150 mbar, it becomes about 5 m.



3.4 Off gas Treatment

For the abatement of any pollutants present in the extracted air, downstream of the air/liquid separation system, a pair of activated carbon filters for air in iron with epoxy treatment was provided, with a plating height of 1300-1500 mm and diameter 800-1000 mm.

3.5 Water Treatment

For the abatement of any pollutants present in the discharged water, a pair of activated carbon filters for water in iron with epoxy treatment was provided downstream of the water/oil separation system, with a plating height of 1100 mm and diameter 800 mm.

3.6 Control parameters

During the test, the following data were recorded, for each flow step applied on PM03:

- Flow rate of extracted air (Qa) and extracted water (Qw);
- Depression upstream of the pump (PIN) and induced on the wellhead;
- Concentration of extracted VOCs (VOCIN) and out of the GAC filter (VOCOUT);
- Temperature (TOUT) on the discharge line downstream of the pump.

At the same time, depressions (dP) and groundwater levels (Lgw) were recorded in the monitoring piezometers PM02, PM12 and PM13.

4. Full-scale application

4.1 Full design system

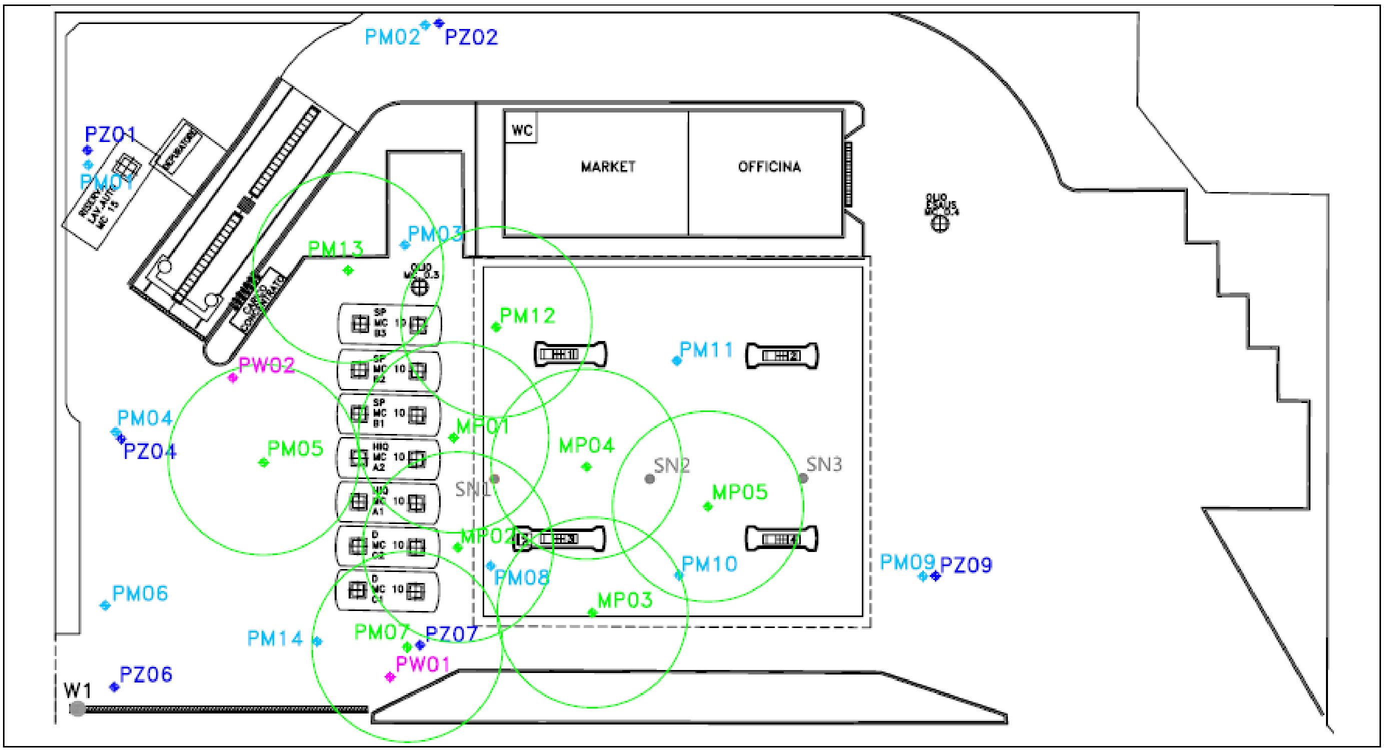
The MPE remediation system launched in 2014 consisted of n. 9 multi-phase extraction points (called PM05, PM07, PM12, PM13 and MP01÷MP05) in bio-slurping configuration (simultaneous aspiration of water, air and any product).
The MPE system provided that the emulsion extracted from the wells was conveyed inside a separator (S1) which separated the gaseous flow from the liquid one; the latter was collected, by gravity, inside an accumulation tank (T1).
The gaseous flow, once separated from the liquid phase, passed through the air handling unit (AT) consisting of a pair of filters in series, containing GAC.
At the exit of the AT unit, the air then passed through an anti-particulate filter before entering the vacuum pump and being discharged into the atmosphere.
The liquid flow accumulated in T1 was sent, by means of an electric pump (EP1), to an oil separator (S2) which guaranteed the separation of water and product.
Any product separated in S2, thanks to an overflow system, was collected by gravity inside a drum (T3).
The waters separated in S2 were collected by gravity inside a tank (T2); from here they were sent back to a treatment unit (WT), consisting of two filters in series containing GAC.
The water leaving the treatment was then discharged into the public sewer.

4.2 Different areas characteristics that affect the project

As anticipated within the site there are an aquitard contained in the superficial part of the alluvial unit consisting of low permeability deposits and a confined aquifer with good permeability in the underlying sandy layer.

4.3 Radius of influence

Radius of influence (ROI) was calculated around 4.5 m, obtained by cautiously dividing the ROI obtained with the pilot test by a safety factor of 1.3.



4.4 Off gas Treatment

Same of pilot test

4.5 Water Treatment

Same of pilot test

4.6 Control parameters

Periodic monitoring of the remediation system provided for:

- verification of the correct functioning of the system on a monthly basis;
- verification and reading of the operating parameters of the plant (flows, depressions, VOC concentrations, etc.) and possible fine-tuning, in the case of variations detected with respect to the operating parameters set;
- verification of the samples entering and leaving the water and air treatment plants on a monthly basis;
- monitoring of groundwater on a quarterly basis.

5. Results

5.1 Removal rate

The Phase 2 remediation testing activities aimed at verifying compliance with the regulatory limits of the respective environmental matrices (soil and subsoil and groundwater) or any residual contamination were carried out for groundwater and soil in 2019-2020. In particular, the following activities were carried out:

- sampling and analysis of groundwater on the entire piezometric network installed on the gas station;
- execution of 1 geognostic survey, pushed up to the maximum depth of 6.5 m b.g.s. and soil sampling and analysis.

The results of the samples taken showed full compliance with the remediation objectives for the soil, the surface aquitard and the confined aquifer.

6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring

Following the testing of the remediation, no further monitoring activities of the environmental matrices were carried out and in 2021 the region issued the certificate of successful remediation.

7. Additional information

7.1 Lesson learnt

In choosing the remediation technology to be adopted, the following aspects had to be taken into account:

- active fuel distribution system;
- presence of contamination in unsaturated and above all saturated soils, LNAPL and contamination in groundwater;
- technical limits of the intervention.

The environmental procedure started in 2010 was concluded in 2021 (11 years).
The remediation activities (first and second phase) and testing lasted from 2012 to 2020 (8 years).

7.2 Additional information

The keystone issue for a successful remediation is to gain a right conceptual site model, with a proper definition, in terms of extent, soil texture and presence of preferential flow pathways of the underground contamination source, in order to find adequate technology to properly address and remediate the CoCs.

7.3 Training need

E-learning/webinars in order to firstly understand the theoretical fundamentals of the technology (in terms of successful design and monitoring), but especially to be shown, through case studies, all the possible problems you can deal with during projecting, applying and monitoring the technology (lesson learnt by not perfect experiences).

Glossary of Terms

Term (alphabetical order)	**Definition**
GAC	Granular Activated Carbon
LNAPL	Light Non-Aqueous Phase Liquid
MPE	Multi Phase Extraction
P&T	Pump & Treat

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2. Site background

2.1 History of the site

Client facility in Province of Bergamo is a factory specialized in iron cabinets assembling and painting. The factory started its work in 1961 for the production of industrial shelves. In the first times, property included also the portion adjacent to the nearby river, currently owned by the Municipality. The preliminary characterization showed excedances for PCE in soils and groundwater, CHC and Metals only for groundwater.

2.2 Geological setting

Site area is made up of loose fluvioglacial deposits and colluvial soils with clayey sands, gravels and pebbles with silty and clay lenses; drainage ranges between medium and poor. The entire geological asset is extremely variable in the space of a few dozen meters. The bedrock (Dolomia) is detectable few centimetres below ground level (bgl) in NW area and at about 10 m bgl in the centre and in the eastern part of the site. We can split the area in two zones: in Zone A gravelly sands, silty clays, gravel mixed with sand and black limestone can be detected; in Zone B a distinct sequence of silt, clay, gravel, and gray limestone are identified. The depth to groundwater is approximately from 5 m to 7 m bgl detected in monitoring wells located to the eastern site boundary.

2.3 Contaminants of concern

Deep soil: PCE and Arsenic
Groundwater: Manganese, Chloroform, Vinyl Chloride, 1,1-DCE, TCE, PCE, Hexachlorobutadiene, 1,2-DCE, 1,2- Dichloropropane, 1,1,2-Trichloroethane, 1,2,3-Trichloropropane, 1,1,2,2-Tetrachloroethane, 1,2-Dibromoethane and Total hydrocarbons (mainly C5-C8 and C8-C12 detected by MADEP speciation).

Table 1. Maximum value for deep soil

Parameter	Concentration (mg/kg)
PCE	415

Table 2. Maximum values for groundwater

Parameter	Concentration (mg/l)
Chloroform	7,76E-04
Vinyl Chloride	2,33E-02
1,1-DCE	2,91E-03
TCE	2,58E-01
PCE	2,20E+01
Esaclorobutadiene	5,00E-04
1,2-DCE	6,29E-01
1,1,2-Trichloroethane	3,10E-03
1,2,3-Trichloropropane	5,00E-04
1,1,2,2-Tetrachloroethane	1,00E-03
1,2-Dibromoethane	5,00E-04
1,2-Dichloropropane	6,44E-04
Aliphatics Hydrocarbons C5-C8	1,07E+00
Aliphatics Hydrocarbons C9-C12	3,90E-02

Arsenic and Manganese are not included in this Table because they are not volatile compounds, and thus no active migration pathways were active.

2.4 Regulatory framework

Legislative Decree n. 152/2006 "Norme in Materia Ambientale" with its modifications and additions is the principal regulation for environmental characterization and remediation in Italy. Site-specific Human Health Risk Assessment (HHRA) has been developed in accordance with its content, with specific criteria and guidelines given by different Italian environmental agencies and the Ministry of Environment.

3. Pilot-scale application in field

3.1 Extraction system

- two pumps were installed in groundwater extraction wells, placed at about 1 m from the bottom of the well. The pumps were 12 V with a maximum flow of 12 L/min;
- the two pumps were connected with a manifold followed by an active carbon filter;
- in one of the wells, a lateral vacuum pump was installed with maximum flow of 100 m^3/h and maximum negative pressure of 150 mbar;
- between the well and the vacuum pump, an iron separator air/water was installed to avoid interaction with the mechanical compounds of the pump;
- air line was made up of two active carbon filters. Vapours extracted were treated and emitted in atmosphere through a chimney;
- liquid phase in the separator was released in active carbon filter by a pump;
- at the end of the process, water was collected in a 10k L tank with safety controls.

3.2 Feasibility study

The two options evaluated for the remediation of this site were P&T and MPE technologies. The choice of the MPE technology is due to:

- Enhanced groundwater flow rate recovery (more efficient than P&T);
- Enhanced radius of influence for every well than normal pumping;
- Recovering of volatile compounds from vadose zone and desaturated zone;

No explosiveness was detected.

Oxygen decrease (%) is under 1 % in the first 2 m bgl. The rate raises (over 10%) in the zone 2-4 m bgl.

CO_2 increase (%) is about 0,1 % in the first 2 m bgl. Its rate rises to 0,56 % in the zone 2-4 m bgl.

Reference values from 0,25 mbar to 4,63 mbar in the manometer are considered in order to have influence on the wells. No critical temperature was reached in the vacuum pump (only 10°C as a maximum).

Efficiency of water treatment was over 99,99 %. All the contaminants at the discharge are under detection limits for Italian Legislation. The output sampling for GAC filters showed values under detection limits.

3.3 Radius of influence

A useful parameter to measure ROI in a vacuum extraction is mounding effect (measure groundwater level increase inducted by air injection in an extraction well).
In the Table X results on Zone A are shown.
Table X: A Zone – Decrease of groundwater level with and without DPE.

Test Zone A			
Point of extraction	P2		
Extraction Flow	1 L/min (pumping only) 0.5 L/min (pumping + DPE)		
Monitoring well	**Distance (m)**	**Decrease with pumping only(m)**	**Decrease with DPE (m)**
PE4	5	0.05	0.13
P3	5	0.09	0.13
P1	9.3	0.04	0.06
P4	10	0.04	0.05

The test lasted 15 hours with a water flow of 0,5 l/min; water level was stable on extraction well and also on monitoring wells.
Analyzing data on inducted depressions, we can see possible influence from Extraction Point called P2 to Zone B (due to preferential ways).

Table Y: Daily average depressions (dP)

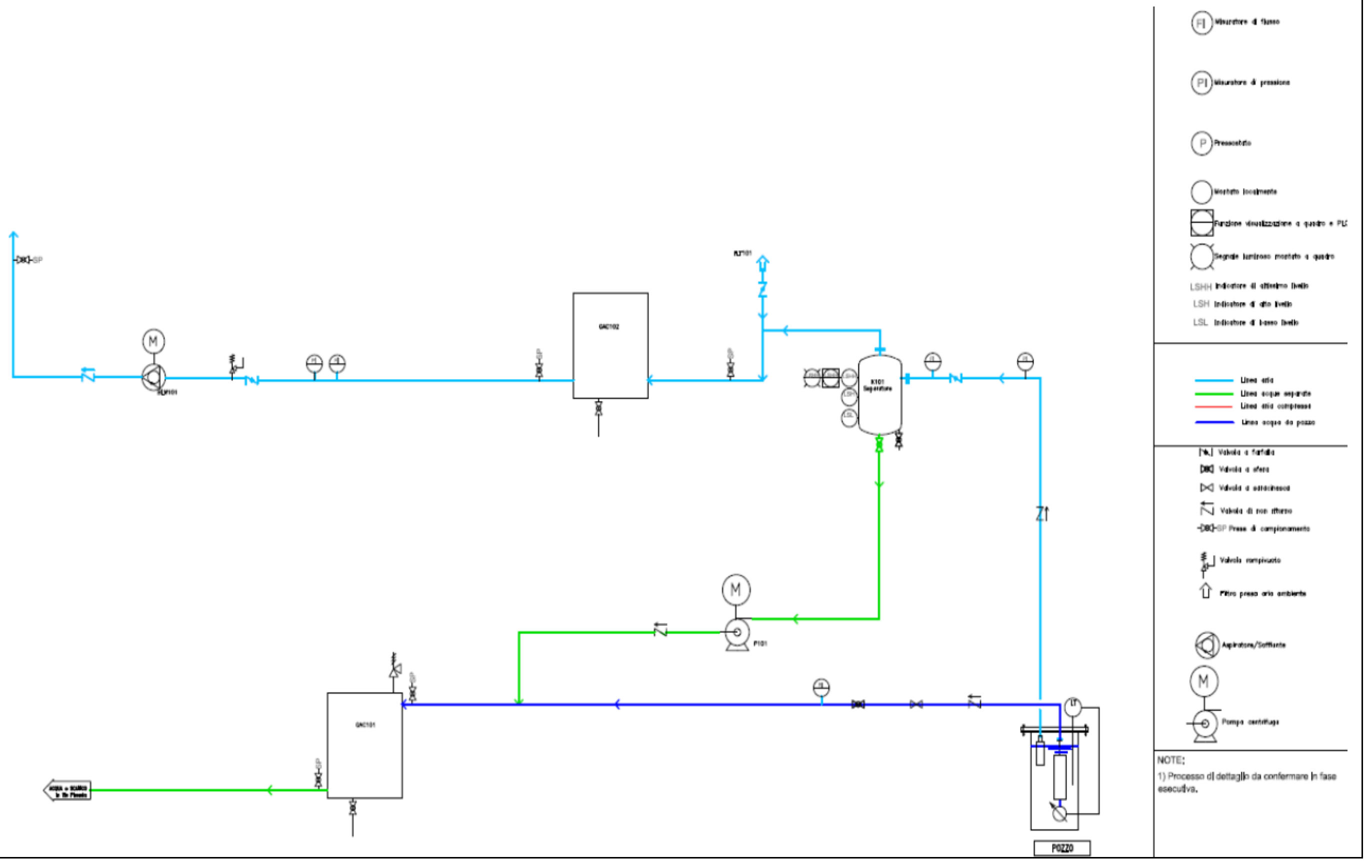
Monitoring well		Day of DPE test		Distance from extraction point – P2 (meters)
		24th of May 2018	25th of May 2018	
		Average inducted depression (mbar)		
A Zone	P1	5,43	0,96	9,37
	PE4	6,31	2,38	5,05
	P3	2,09	2,48	5,01
	P4	0,23	1,04	10
B Zone	P5	2,69	1,42	79
	P6	0,03	0,05	86
	PE5	0,00	0,00	91

At the end it has been decided to use a ROI of 8 m, as an average between 5 and 10 m.

3.4 Off gas Treatment

In one of the wells, a lateral vacuum pump was installed with maximum flow of 100 m^3/h and maximum negative pressure of 150 mbar; between the well and the vacuum pump, an iron separator air/water was installed to avoid interaction with the mechanical compounds of the pump; air line was made up of two active carbon filters. Vapours extracted were treated and brought out in atmosphere by a chimney;

In this case, it was calculated a contact timing of 10 seconds for air, considering PCE value of input and air flow of vacuum pump with a >90 % of adsorption on activated carbons until their exhaustion.



3.5 Water Treatment

In extraction wells, two pumps were installed, placed at about 1 m from the bottom of the well. The pumps were 12 V with a maximum flow of 12 L/min; the two pumps were connected with the manifold followed by an active carbon filter. At the end of the process, water was collected in a 10k L tank with safety controls.

For water treatment, usually the contact timing is between 10 and 30 minutes. In this case, as for the air treatment, it was calculated a contact timing of 20 minutes, considering the maximum input concentration of PCE and a >90% of adsorption rate.

3.6 Control parameters

During the test, the following parameters were monitored on the extraction wells and also in the closest monitoring wells:

- Groundwater depth
- Inducted vacuum pressure by manometer
- O_2, CO, % LEL with gas analyzer; VOCs with PID detector

A CO_2 detector was also used. Measurements were conducted at 2 and 4 m bgl in both zones A and B in order to evaluate changes.

Water contaminants compounds were analyzed by specialized laboratory: analytical set included CHCs, petroleum hydrocarbons and metals.

Air contaminants compounds were also analyzed: analytical set included only PCE compound.

4. Full-scale application

4.1 Full design system

- N.16 extraction wells, divided into 2 groups (n.10 Northern Area, n.6 Southern Area)
- N.3 monitoring wells
- N.16 pneumatic pumps
- N.1 lateral vacuum pump
- Maximum extraction flow: 480 m^3/h
- Maximum depression on the wellhead: 200 mbar
- Operative depression on the wellhead: 100 mbar
- Connection pipeline to the extraction system
- Connection pipeline from pneumatic pumps to water treatment system
- Condense separator before GAC filter for air treatment
- Oil separator, accumulation tank and bag filter for water treatment
- Water remediation system made up of n.2 GAC in-series filters
- Air treatment system made up of n.2 GAC in-series filters

All instruments, principal collectors and GAC filters have been collected in a dedicated container, acoustically isolated. Compressed air is provided by the client.
Groundwater is conveyed to treatment system by n.16 pneumatic total fluid bottom inlet pumps, in order to transport CHC, supplied by 8 bar compressed air. The pneumatic pumps have been chosen in order to respect the characteristic of the site. The piping lines have been realized above ground and are made up of pipes, connections, curves, valves, reductions, monitoring points and pressure measures. The piping and collector path has been realized in order to minimize digging operations. Air extraction needed a condense control system in order to minimize water accumulation in pipelines, in extraction system and in GAC filters.

4.2 Different areas characteristics that affect the project

The aquifer is not homogeneous: the geological asset is extremely variable in the space of a few dozen meters. This was managed in all phases of the project.

4.3 Radius of influence

The radius of influence has been determined in the pilot scale project: it has been established equal to 8 m, both for air and groundwater.

4.4 Off gas Treatment

In this project Granular Activated Carbons have been used for air treatment. Specific compounds of the air extraction system are:

- N.16 extraction wells, divided in 2 groups (n.10 Northern Area, n.6 Southern Area)
- N.1 lateral vacuum pump
- Maximum extraction flow: 480 m^3/h
- Maximum depression on the wellhead: 200 mbar
- Operative depression on the wellhead: 100 mbar
- Connection pipeline to extraction system
- Condense separator before GAC for air remediation
- Air remediation system made up of n.2 GAC filters in a series

Air extraction needed a condense control system in order to minimize water accumulation in pipelines, in extraction system and in GAC filters (280 kg each). On the pipeline, a LEL (%) sensor has been installed, with a flux meter and a sampling pump.

4.5 Water Treatment

In this project Granulated Activated Carbon Adsorption has been used for water treatment. Specific compounds of the GW extraction system are :

- N.16 extraction wells, divided in 2 groups (n.10 Northern Area, n.6 Southern Area)
- N.16 pneumatic pumps
- Connection pipeline from pneumatic pumps to water remediation system
- Oil separator, accumulation tank and bag filter for water remediation
- Water remediation system made up of n.2 GAC filters in a series

Discharge water pipeline has been realized with a HDPE 50 mm pipe, linking output GAC filters with the final point of discharge. A sampling point is just before discharging point. Remediated waters has to respect Italian surface water legal limits of Legislative Decree 152/2006 for contaminants of concern. On the discharge line there is a machanical totalizer in order to count treated water volume in output. The two iron GAC filters have been installed in-series (1500 kg of GAC each).

4.6 Control parameters

Parameters check and samples collection is performed monthly.
Activities performed periodically as follows:

- Collect sample from "In", "Intermediate" and "out" sampling points from water GAC filters (in order to evaluate adsorption rate and avoid excedances in the output values)
- Collect sample from "In" sampling point of air GAC filters (in order to evaluate the input value)
- Check input air flow speed
- Check of vacuum pump depression and collector depression
- Check water level on monitoring wells PE2, PE3 and PE8
- Check of discharge water counter

For air sampling, the analytical set is VOC calculated on 20 normalized litres (Q= 0,5 l/min; t = 51,4 min).
For water sampling (from filters), the analytical set is made up of CHCs, metals and total petroleum hydrocarbons.
A groundwater monitoring campaign on existing monitoring wells is planned (not started yet) as follows:

- quarterly for the first 3 years
- semi-annual for further 2 years
- annual afterwards.

Analytical set includes CHC and total petroleum hydrocarbons

5. Results

5.1 Removal rate

The last summary report is dated October 2021.

The water flow rate is always under 50% of the maximum authorized flow. The air extraction system do not have a maximum authorized emission limit, as the contaminant mass flow rate is under the threshold value defined by Italian legislation (it is considered a “not-significant emission point”).

Water treatment:

- CHC: PCE input to the system in a range between 370 – 5800 µg/L. The efficiency in contaminants reduction is close to 100%. Output values are always under detection limits. The rate of CHCs input is showing a constant decreasing trend;
- Hydrocarbons: concentration input ranges between 0 and 19,3 µg/L. The efficiency of contaminants reduction is close to 100 %. The rate of hydrocarbons is constantly under detection limit in the last year;
- Arsenic and Manganese: concentration always under threshold limits;
- Mass removal of CHCs estimated in 9,1 kg from groundwater stream in the period September 2019 – August 2021 from groundwater treatment;
- PCE mass removal estimated in 400 kg of PCE from air stream in the period September 2019 – August 2021 from air treatment.

6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring

There is not a post treatment or long term monitoring at the moment as the remediation design has been submitted as an Operational Safety Measure.

7. Additional information

7.1 Lesson learnt

Difficulties:

- Presence of a transient aquifer, never thicker than 4 m, highly influenced by meteorological phenomena. Indeed, the average water flow rate registered is 1-2 L/min;
- Heterogeneous bedrock, with 4-5 meters variations in depth in very close wells;
- Logistic difficulties: temporary closure of the public road was required to perform operational installation of the plant.

Strengths:

- High volatile removal rate (especially PCE) particularly from the air stream;
- Excellent comprehension of the conceptual model of the site that allowed addressing these results.

7.2 Additional information

High importance of an interdisciplinary characterization for defining the best remediation technology. The following investigations activities have been performed:

- tracer test (in order to evaluate direction and speed of the groundwater flow)
- pumping test,
- boreholes,
- MIP investigation,
- groundwater monitoring,
- soil gas monitoring,
- geophysical survey (in order to outline the bedrock surface)

All these surveys allowed defining the Site Conceptual Model with high accuracy. As a consequence, locations of the pumping points were defined targeting points with specific elevation of the bedrock, maximizing the contaminants removal rate.

7.3 Training need

The best way to understand this project is the training on-the-job.
The detailed characterization performed (exposed above) aimed at refining the site conceptual model required the involvement of a wide number of different professionals with specific technical skills.
The outcome allowed engineers to define at best the remediation strategy to adopt on site, given the complex hydrogeological setting.

7.4 Additional remarks

The best way to understand this project is the training on-the-job.
The detailed characterization performed (exposed above) aimed at refining the site conceptual model required the involvement of a wide number of different professionals with specific technical skills.
The outcome allowed engineers to define at best the remediation strategy to adopt on site, given the complex hydrogeological setting.

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2. Site background

2.1 History of the site

The site is located inside the Gela refinery and is a former industrial landfill used, until the 80s of the last century, for high viscous liquid waste and sludges disposal (oily waste) from refining process. It is a pool/basin with an internal footprint of about 60 x 60 m, external 80 x 80 m and a height difference between the ground level and the bottom equal to ≈ 12 m. In 2011, the removal of oily residues inside the tank was completed. In the 2013-2014, the remediation project for the unsaturated soil below the bottom of the pool was approved after requirements of the Ministry of the Environment and the public control agencies. Before the remediation activities, the perimeter of the pool was insulated with steel sheet piles and the walls waterproofed with HDPE sheets (see photo).

Site location in the south-eastern areas of Gela refinery (CL) – Italy.

The Gela Refinery areas are included in the list of Italian contaminated Sites of National Interest (SIN): for these sites, the administrative competence in remediation procedures is a responsibility of the Ministry for the Ecological Transition (MiTE).
Simam S.p.A. is the leader of the Joint Venture established with Haemers Technologies of Brussels and Icaro Ecology S.p.A. of Gela for the execution of the remediation project (2016 - in progress).

Site view, during the intervention phase with the installation of remediation systems (see Chapter 4) and Vapour Treatment Unit (upper edge of the basin).

The remediation project is based on the application of ISTD In Situ Thermal Desorption technologies with Smart Burners, patented by Haemers Technologies SA (the largest application of this technology in Europe, at the time). MPE application is a component of the remediation project and will be described below. According to the purposes of this work, ISTD technology by Smart-Burners® will not be described because the focus is on associated vapour extraction and treatment systems.

2.2 Geological setting

Site soil consists largely of silty sands interbedded with purely sand layers (from fine to medium grain size).
The depth of ground water is approximately 1,5 meters below unsaturated soil layers (-6,5 m from pool bottom ground surface).
The thickness of interest for remediation project concerns the saturated soil up to 5 m from the bottom of the basin.

2.3 Contaminants of concern

The CoCs for the soil (target of remediation projects), are represented in the summary table with average concentrations before treatment.
The concentrations are divided by intervention areas:

- Zone A (soil below the bottom of the basin);
- Zone B (soil below the strips surrounding the perimeter of the pool corresponding to the ground level of the Refinery).

Contaminants of Concern	***Zone – A (mg/kg)***	***Zone – B (mg/kg)***	***Remediation target concentrations (mg/kg)***
TPH (Total Petroleum Hydrocarbons) C≤12	*3.600*	*709*	*250*
TPH (Total Petroleum Hydrocarbons) C≥12	*19.800*	*7.723*	*750*
PAH (Polycyclic Aromatic Hydrocarbons)	*42*	*0*	*100*
Aromatic Hydrocarbons (without Benzene)	*277*	*27*	*100*
Benzene	*45*	*11*	*2*
Vinyl Chloride	*3*	*3*	*1.3*
1.2 - Dichloroethane	*49*	*2*	*0,46*
Chloromethane	*113*	*0*	*6,1*
Mercury	*11*	*20*	*-*

The remediation of unsaturated soil is the main objective of the project described in this case-study. The groundwater contamination derives from refinery activities and is widespread throughout the Gela area. The groundwater remediation interventions/safety measures are part of a specific project, not illustrated in this case study. The groundwater safety measures are an integration of the project for unsaturated soil.

The CoCs for groundwater are:

- Total Hydrocarbons (as n-hexane)
- PAH
- Vinyl Chloride
- Organ chlorinated compounds
- Aromatic compounds
- Heavy metals

2.4 Regulatory framework

As described below, the Gela Refinery areas are included in the list of Italian contaminated Sites of National Interest (SIN). The administrative competence in remediation procedures and in authorizations for the various remediation steps is a responsibility of the Ministry for the Ecological Transition (MiTE).

The reference legislation is represented by the Italian Decree n. 152/06 "Environmental regulations" and subsequent amendments / additions.

Part IV of the Decree regulates the technical-administrative procedures/step:

- Environmental characterization of the site and identification of contaminants of concern that exceed the contamination threshold values for water and soil, defined by the Decree;
- Safety measures for soils and groundwater;
- Environmental risk analysis to define if the site is contaminated and establish any target values for remediation;
- Remediation project;
- Testing and certification (achievement of remediation target).

Each procedural step is verified and validated by the Ministry and its technical bodies and public agencies such as ISPRA (Institute for Protection and Environmental Research), ARPA (Regional Environmental Protection Agency).

Program agreements for the site between local authorities, consortia of private companies and the Ministry, can be established in relation to the specificity of the site, to define some technical-administrative aspects (e.g. natural background values) and methods of intervention.

3. Pilot-scale application in field

3.1 Extraction system

Pilot scale application in field, not foreseen for this remediation project. The treatment area has been divided into no. 2 zones: A-Zone (internal, bottom of the pool), B-zone (external). Each zone is divided, in turn, into no. 12 batch with an average surface area equal to ≈ 290 m² for A-Zone and between 228 m² and 400 m² for B-Zone (see figure in this page). Batch A1 was used, in fact, as a full scale test to verify the response of the soils and to calibrate the extraction and treatment vapour systems.

This case study does not concern the application of MPE technologies in a narrow sense but the combined application of several techniques:

- ISTD - In Situ Thermal Desorption with Gas Extraction and treatment systems;
- Dual Pump Systems (submersible pump for groundwater recovery + pneumatic submersible pump – total fluid, installed on water/oil interface). The function is to maintain the safety lowering of the groundwater level of at least 1.5 m below the unsaturated soil subject to heating up to 550 ° C.

The batches refer to single applications of thermal desorption of which the extraction of the vapour phase is an essential component.

The combination of several technologies, applied to unsaturated soils, ISTD + SVE (vapour phase) and dual pump systems for the extraction of groundwater and the removal of LNAPL, can be assimilated to an overall MPE system, and normally installed on a single well.
The combined ISTD / SVE + Dual Pump systems were applied directly full scale.

3.2 Feasibility study

In this case, the feasibility study was not foreseen, because the Ministry has decided to proceed with the direct application of the ISTD + Soil Vapour Extraction technology for the soils and groundwater.

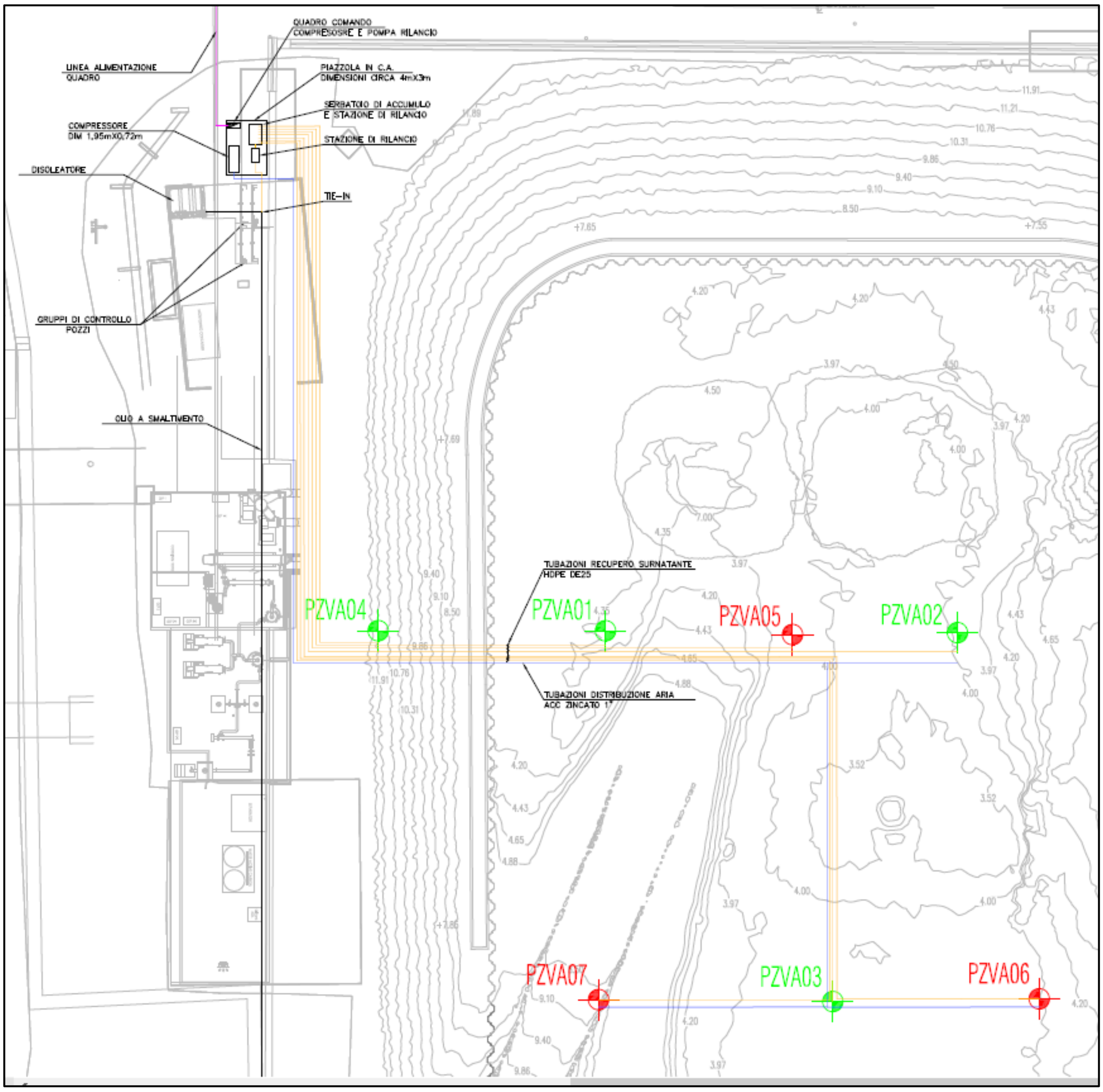
4. Full-scale application

4.1 Full design system

Components of the combined system for removing liquid phases from groundwater and vapour phase from the soil:

a) Phase liquid extraction - Dual Pump systems located at the bottom of the pool

- Submersible pump for groundwater recovery, installed on no. 7 piezometers (Ø 6’’) (PZVA01 ÷ 07) equipped with 4 '' submersible electric pumps and relaunch to the oil separation system, located close to the Vapour Treatment Unit (above the pool). Total project flow rate: 72 m^3/ day (established value to maintain the safety lowering of the groundwater level);



Dual pump wells design lay-out. This lay-out is modified based on the location of the single treatment batches to avoid interference with ISTD systems and SVE manifolds.

- Pneumatic pump/total fluid for LNPLs recovery

The process scheme provides:

- Product recovery by total fluid pneumatic pumps, top inlet, inside the existing piezometers, located at the oil-water interface level;
- Sending the product through single delivery lines to a storage tank located above the basin, near the oil separator;
- Re-launch of the product from the storage tank to the existing product delivery line (reintroduction into refinery cycles), downstream of the oil separator;
- Management systems simplified: self-regulating pneumatic pumps, air intake adjustment valve, level switch system that acts on the intake of air from the compressor, on the intake of air to the pumps, in case of too much full of the tank and on the booster pump from the storage tank;
- Dedicated power / control panel near the control panel of the groundwater pumping system.

Characteristics of the equipment

Pneumatic pumps data:

- Øext: 2''
- minimum air flow: 3 - 4 l/min
- carbon steel casing
- pressure range: 0,4 - 9 bar

Piping:

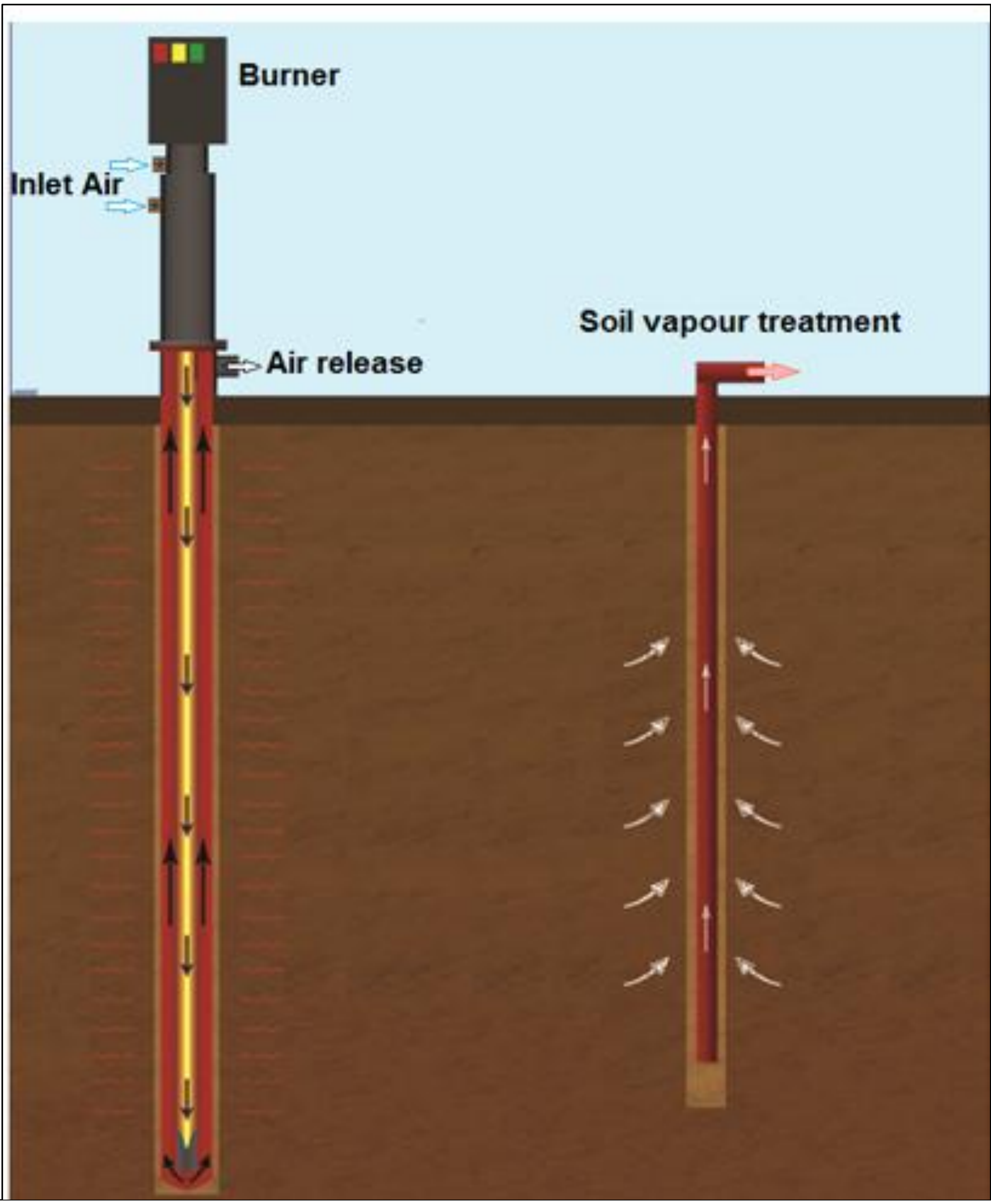
- 1'' galvanized steel pipes for the supply of air, from the compressor unit to the wellhead;
- air intake from the wellhead to the pump, Rilsan 3/8 '' pipe (ø 9.5 mm);
- Oil delivery pipes, HDPE DE20 up to the wellhead and then DE25, PN16 for the manifold up to the storage tank.
- Valves, fittings, etc.

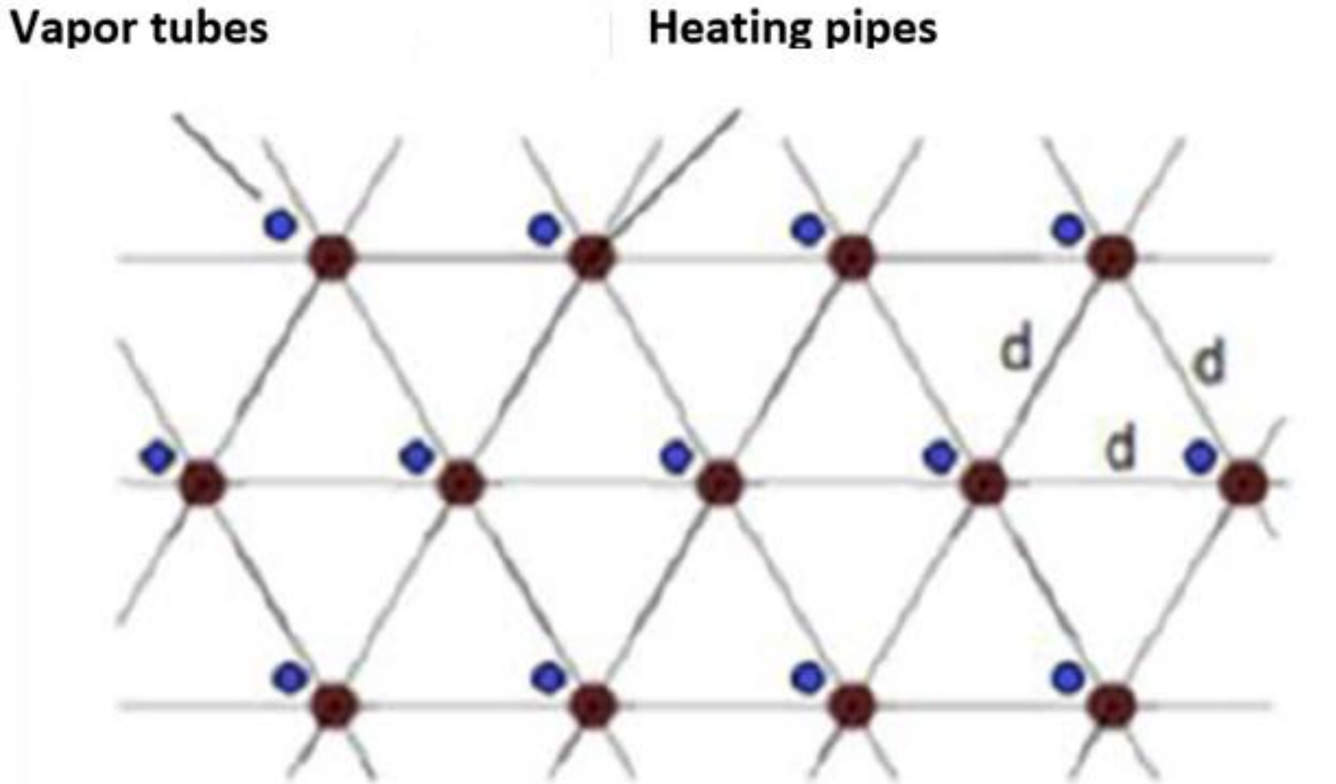
Electric compressor equipped with a compressed air tank (10 ÷ 13 bar rotary compressor, with 500 l tank, production: 780 l / min, 7.5 Kw, 15 HP);

The pneumatic pumps are raised and lowered by means of winches placed on the wellhead and after having measured the water / oil interface level by means of interface probes.

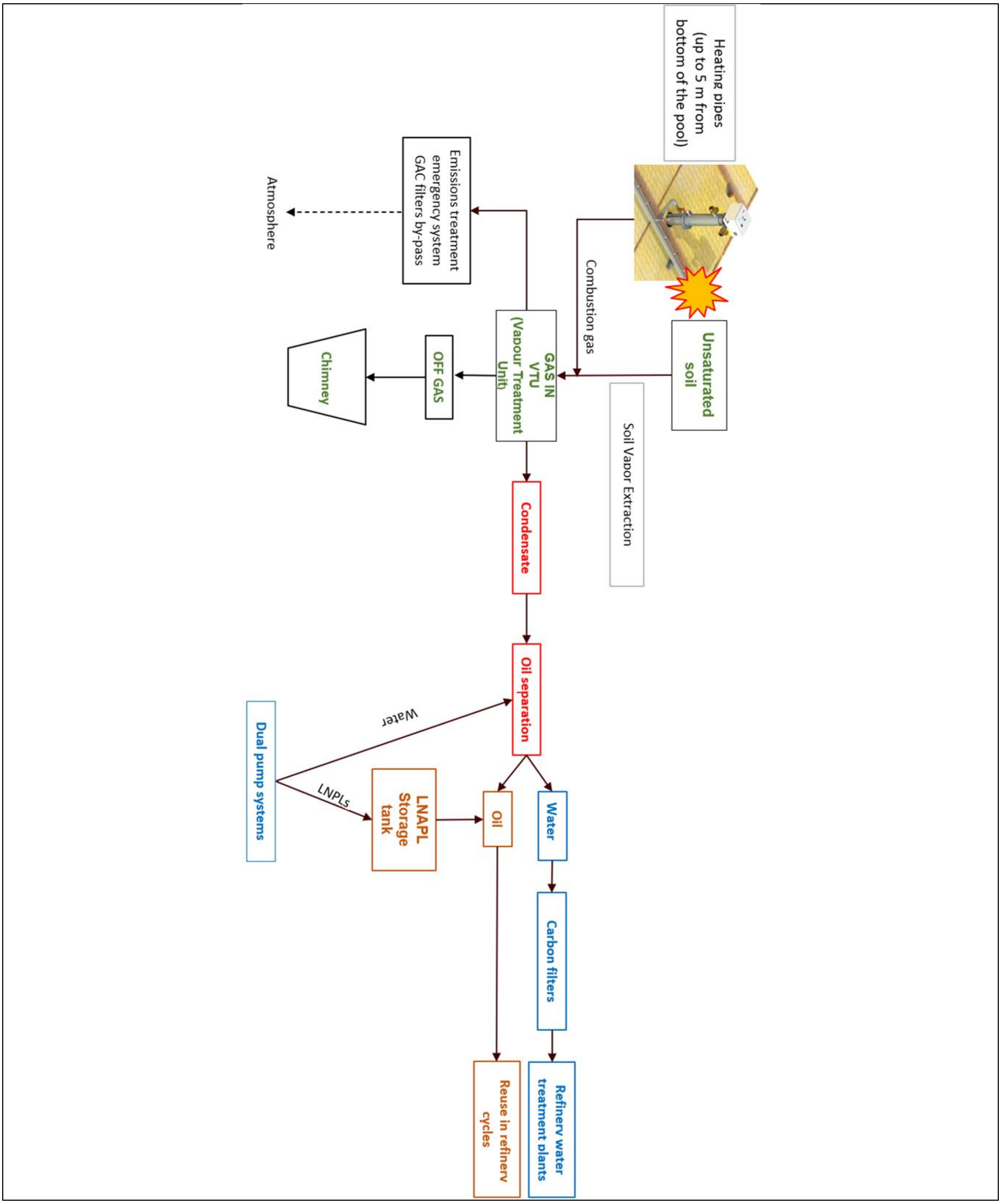
b) Phase Vapour extraction - Dual Pump systems located at the bottom of the pool

The vapour phase extraction system does not take place in the wells but uses a series of extraction probes placed inside the individual batches near the heating tubes of the thermal desorption system (see figures), according to a grid arrangement that must cover the entire surface of the batch. The soil surface is thermally insulated by laying a concrete slab and rockwool panels.





During the heating and for the entire treatment period, the contaminants, in gas phase, are extracted by steam extraction probes, positioned in the soil, near the heating points, to then be conveyed inside stainless steel pipes and sent to the vapour treatment unit. General scheme of remediation project is in the following page.


Heating pipes (up to 5 m from bottom of the pool)
Combustion gas
Unsaturated soil
Soil Vapor Extraction
GAS IN VTU (Vapour Treatment Unit)
Emissions treatment emergency system GAC filters by-pass
Atmosphere
OFF GAS
Chimney
Condensate
Oil separation
Water
Oil
Carbon filters
Refinery water treatment plants
Reuse in refinery cycles
LNAPL Storage tank
Water
LNPLs
Dual pump systems

4.3 Radius of influence

The application of Dual Pump for extraction of phase liquid (necessary to maintain, in safe conditions, the groundwater level, 1.5 m below the unsaturated soil subjected to heating).
It was requested as integration to the project for the soil remediation, in terms of no. of wells to be installed on the bottom of the pool, single and overall flow rate of groundwater extraction functional to ensure the required lowering of the level.
The project parameters were defined by another research body (University of Rome) on the basis of the hydrogeological model of the site.
Hydrogeological modelling was not included in the aims of the unsaturated soil remediation project.

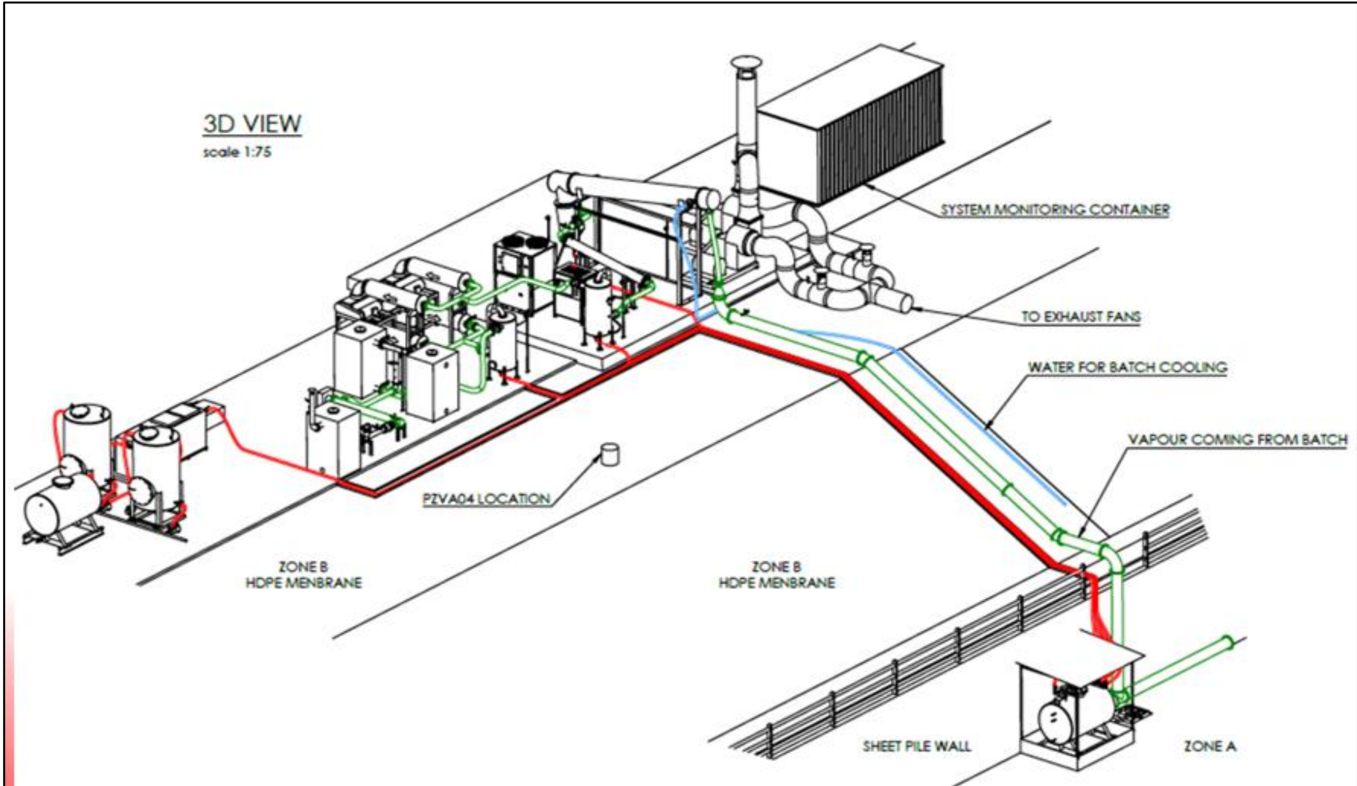
The sizing of the soil vapour extraction systems was based on:

- Volumes of soil to be treated;
- Physic-chemical characteristics of the contaminants;
- Soil characteristics (pore size, grain size, etc.);
- Vapour extraction rates.

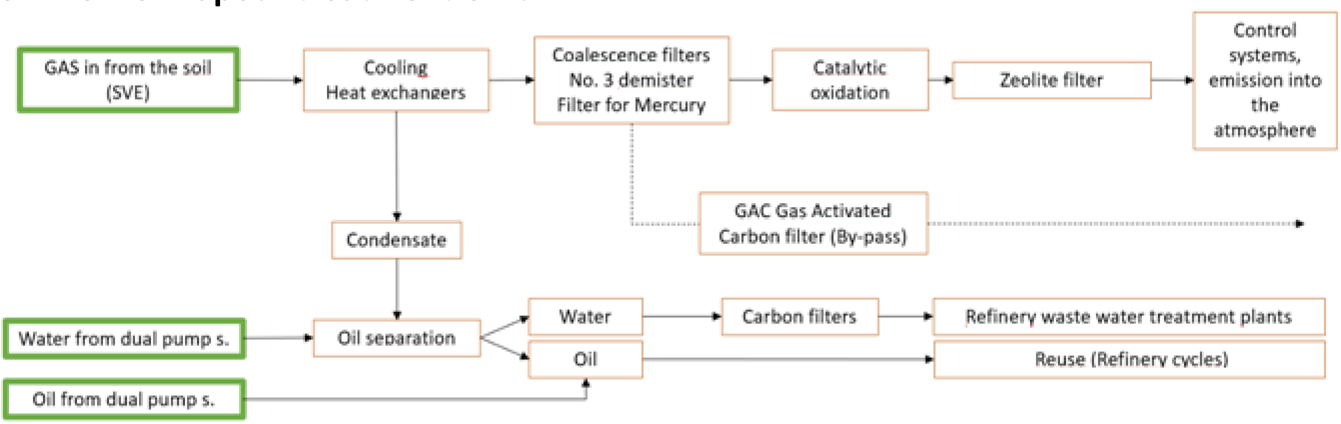
4.4 Off gas Treatment

The vapour treatment unit was installed next to basin A Zone 2. Due to the different nature of the compounds present in the extracted vapors (organic compounds, hydrocarbons, chlorinated organic compounds, mercury), it was decided to use a physical treatment system, which would allow to treat all organic contaminants and mercury by condensation of the gas extracted. This, to avoid different chemical reactions to extract the contaminants separately.
The treatment system is based on the cooling and condensation of the contaminants (operating at a temperature between 0 ° C and 5 ° C), with subsequent recovery of the same in the liquid phase (such as LNAPLs). In detail, the progressive heating of the soil causes the evaporation of contaminants and water and the destruction of part of the contaminants initially present in the soil. The vapors and gas produced are extracted by primary / secondary pipes of the SVE system and sent to a first heat exchanger with condensate collection. Subsequently, the circuit includes a second heat exchanger and a cooling unit (Chiller / Cooler).
The cycle continues with the passage through a regenerative absorber (catalyst) and

zeolitic carbon filters and from here to the chimney with a system for controlling the gas emission parameters into the atmosphere.
An additional treatment section was also installed on the by-pass of the main circuit, consisting of n. 2 filter boxes with GAC (Granular Activated Carbon Filter), to be used in case of emergency and / or maintenance of the main circuit, with the need to by-pass the flow.
Two blowers, placed in parallel with each other, ensure the depression in the soil and are a reserve to the other during the treatment of the batch.



3D view of Vapour treatment Unit

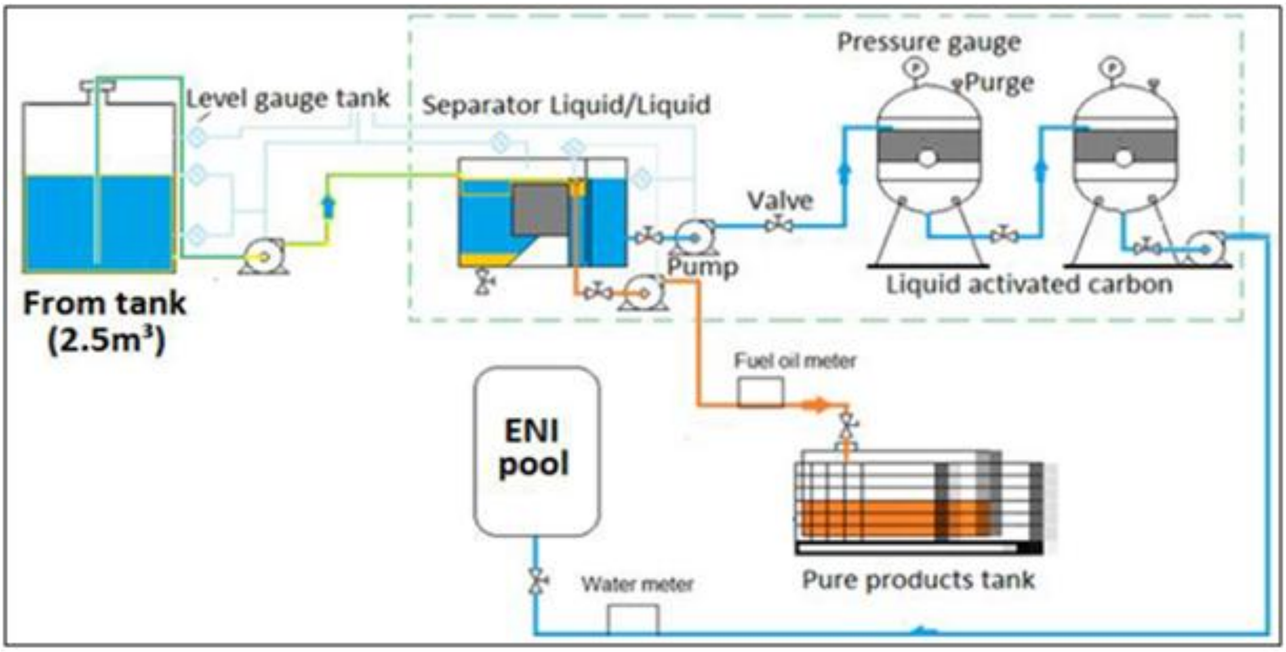


General scheme of liquid and vapour phase extraction and treatment

4.5 Water Treatment

The effluent (water from dual pump systems and condensate from vapour treatment unit, after oil separation) go to an existing refinery groundwater and wastewater treatment plants. The battery limit of MPE treatment is the delivery point of the water to the refinery piping network which collects all the water coming from the groundwater remediation and safety measures systems (hydraulic barriers).

The water, before being transferred to the treatment plant, are subjected to oil separation and passing over carbon filters, as shown in the following diagram (ENI Group is the Client/Owner of Refinery):



4.6 Control parameters

Field monitoring and sampling program that will adequately monitor the effectiveness of the treatment. As for example:

- Contaminant concentrations in groundwater compliance with the acceptability criteria of input parameters to the treatment plant;
- Oxygen, carbon dioxide, carbon monoxide, TOC, contaminant concentrations in SVE in-gas e off-gas or soil vapour;
    - continuous analyzers (in gas and off gas)
    - lab analyzes (daily) also with sampling from the probes on the ground
- Multilevel soil temperature;
- Air flow and extraction rates;
- Air pressure measurements;
- Water and oil levels (dual pump systems);
- Daily volumes of water discharged, condensates and oil recovered and progressive values from the start of remediation.

5. Results

5.1 Removal rate

It is not possible to define an efficiency value of the applied techniques since they must be verified considering the remediation target (residual concentrations of CoCs in the soil) and compliance with the legal limits required for the gas emission into the atmosphere. In this case, good contaminant removal efficiency can be defined, after soil analysis. The qualitative monitoring of In gas e off gas also allows to define the quantities of recovered contaminant and the recovery and vapour treatment efficiency, for each remediation batch. The efficiency of the treatment is also measured by verifying the degree of consumption of the filters and the trend of the parameters of the off gas, analyzed on the chimney. The parameters must comply with the legal limits, otherwise the system must be switched off to avoid the introduction of contaminants into the atmosphere. A system of by-pass filters makes it possible to carry out maintenance operations on the treatment system with autonomy of a few hours. As regards dual pump systems, the degree of recovery efficiency is measured through the volumes of water and LNPLs emitted and the maintenance of water levels, below the safety limit, and the LNPL thickness tending to 0.
The contaminants removal and treatment good efficiency, for each batch is based on following assumption:

- The temperature of 250 ° C has been reached - decisive criterion for switching off the heating system and start with cooling phase, before soil sampling;
- The temperature reached and the removal of the contaminant mass were also confirmed by the results of the monitoring of the concentrations in the condensates and in the vapors extracted from the soil;
- The average for the period, referring to the soil vapour extraction points, showed a general trend in concentrations consistent with that of temperature;
- The analysis of the parameters referring to emissions into the atmosphere and those of mass flows did not show that the regulatory thresholds were exceeded.

One of the criteria for establishing the achievement of the soil remediation target for a batch is the asymptotic trend of gas concentrations (maximum level of efficiency in gas extraction from the soil).
The main criterion is the achievement of temperatures of 250 ° C in the soil for at least 5 days, in the "cold" points, i.e. those furthest away from the heating pipes.
Temperature monitoring is also performed by thermocouples installed in the soil at different depths. The data is managed by a PLC with pc and dedicated software application.

6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring

After soil heating and during the cooling phase (vapour phase)

- Soil temperature trend
- Oxygen, carbon dioxide, carbon monoxide, TOC, contaminant concentrations in SVE in-gas e off-gas or soil vapour ;
- continuous analyzers (in gas and off gas)
- lab analyzes (daily) also with sampling from the probes on the ground
- Multilevel soil temperature;
- Air flow and extraction rates;
- Air pressure measurements;
- Water and oil levels (dual pump systems);
- Daily volumes of water discharged, condensates and oil recovered and progressive values from the start of remediation.

The extraction of vapors from the soil continues even during the cooling phase to avoid emissions from the ground and limit the rebound phenomena due to the presence of contaminants in the ground that have not yet been stripped by thermal desorption and SVE.

Once the soil has reached temperatures <70 ° C, soil sampling and analysis will be carried out to verify the residual concentrations and the achievement of the remediation target.

Dual pump systems

The operation of the dual pump systems proceeds in continuous even at the end of the heating of the soil and during the passage from one batch to another. The parameters are the same as already indicated in the point 4.6.

7. Additional information

7.1 Lesson learnt

1) Methodology and procedures

The procedures and methodologies are those codified in the final approved project, therefore an attempt was made to improve the design aspects in the development of detailed engineering and in the conditions of applicability, especially in relation to gas treatment systems. One of fundamental aspects regarding the lessons learnt concerns the response of the remediation and treatment systems in relation to the actual characteristics of the site, not foreseen in the approved project, especially in terms of concentrations of major pollutants, or heavy hydrocarbons, more difficult to remove and to be treated.

2) Technical aspects
What indicated in the previous point has translated into progressive technical improvements, especially after batch 1 which represented the full-scale pilot batch. It is important to underline that these methodologies had never been applied on a large scale in Italy. The lesson learnt on the technical aspects concerned the upgrading of the treatment system and the optimization of the consumption of electricity and methane to power the burners and treatment systems. Main difficulties: technological limit in the extraction of contaminants consisting of heavy hydrocarbons (concentration values higher than the project data), heterogeneity in the characteristics of the soil within the same batch, constant maintenance of the control systems (gas analyzers). Lesson learnt:

- Implementation of the vapour treatment system and efficiency enhancement;
- Increase VTU and batch monitoring points;
- Modification of PLC and control systems;
- Hot sampling preliminary to final testing (creation of procedures for soil sampling and analyzing in condition of high temperatures to define, before official testing and cooling, the effectiveness of the treatment and any extension, even in zones, of the heating with vapour extraction.

3) legislative, organizational aspects
The legislative aspects are fundamental: respect for the target values of the reclamation and respect for the legal values for the emission into the atmosphere. This entailed a significant economic commitment in organizational terms (multidisciplinary figures for data and plant management) and analytical control systems. The efficiency of remediation is verified by acceptance tests with the environmental agencies, therefore the improvement of the control systems on the progress of the remediation was important to avoid the repetition of the batch treatment with additional financial charges.

7.2 Additional information

Mainly, as already mentioned in the previous point, the answer is in the most in-depth verification of the actual state of the site and the characteristics of the land, to limit the need for extraordinary maintenance, changes in the execution phase of the treatment systems and evaluate more precisely energy consumption.

7.3 Training need

Regard to the training needs from the technical, procedural, organizational point of view practical experience has allowed to define some fundamental points (some of them are applied in the executive phase):

- Internal periodic technical meetings for sharing activities, critical issues and management data analysis by the various figures (HSE Manager, Environmental Engineer, site manager, project structures, analysis of purchases and management costs, etc.);
- Webinar on ISTD and MPE application, with sharing of activities and presentation of applications in different sites at European level;
- Internal staff competence audits with proposals to improve staff preparation (e-learning from the company headquarters).

7.4 Additional remarks

In this case, the application of MPE technologies was considered in a broader perspective of combined remediation techniques applied on the site and not within a single well. So, an important aspect is that the site approach should consider the strengths and weaknesses of the individual technologies and evaluating their integrated efficiency.

Glossary of Terms

Term (alphabetical order)	**Definition**
C	Carbon (number of atoms)
CoCs	Contaminants of Concern
GAC	Granular Active Carbon
HDPE	High Density Poly Ethylene
ISTD	In Situ Thermal Desorption
LNAPL	Light Non Aqueous Phase Liquid
MPE	Multi-phase extraction
PAH	Polycyclic aromatic hydrocarbons
PLC	Programmable Logic Controller
SVE	Soil Vapor Extraction
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons
VOC	Volatile organic compounds (VOCs) are organic chemicals that have a high vapor pressure at ordinary room temperature
VTU	Vaport Treatment Unit

1. Contact details - CASE STUDY: MPE n.5

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2. Site background

2.1 History of the site

Former automotive production Site in Italy, currently dismissed. In the so-called “Reparto Segmenti” Area, significant impacts due to chlorinated solvents were identified in groundwater.

2.2 Geological setting

The stratigraphy of the Site, up to 20 m from ground level, consists of:

- Local levels of backfill soil (sand or gravel), with thickness generally varying between 1.5 and 2 m;
- A layer of sediments of lacustrine origin (sandy clays and/or silty clays), up to a maximum depth of approximately 20 m from the ground surface.

Groundwater is present in both layers, but extraction rates are limited given the abundance of fine materials. Dept-to-water values are in the order of 1-2 m bgl

2.3 Contaminants of concern

Mainly Trichloroethene (TCE) and daughter products (dichloroethylene and vinyl chloride), with concentrations up to 963,000 µg/l, 9,840 µg/l and 823 µg/ before remediation, respectively.

The greatest mass of halogenated compounds is located at depths between 1 and 6 m from the surface (based on the results of a Membrane Interface Probe survey) in the "Reparto Segmenti" area.

2.4 Regulatory framework

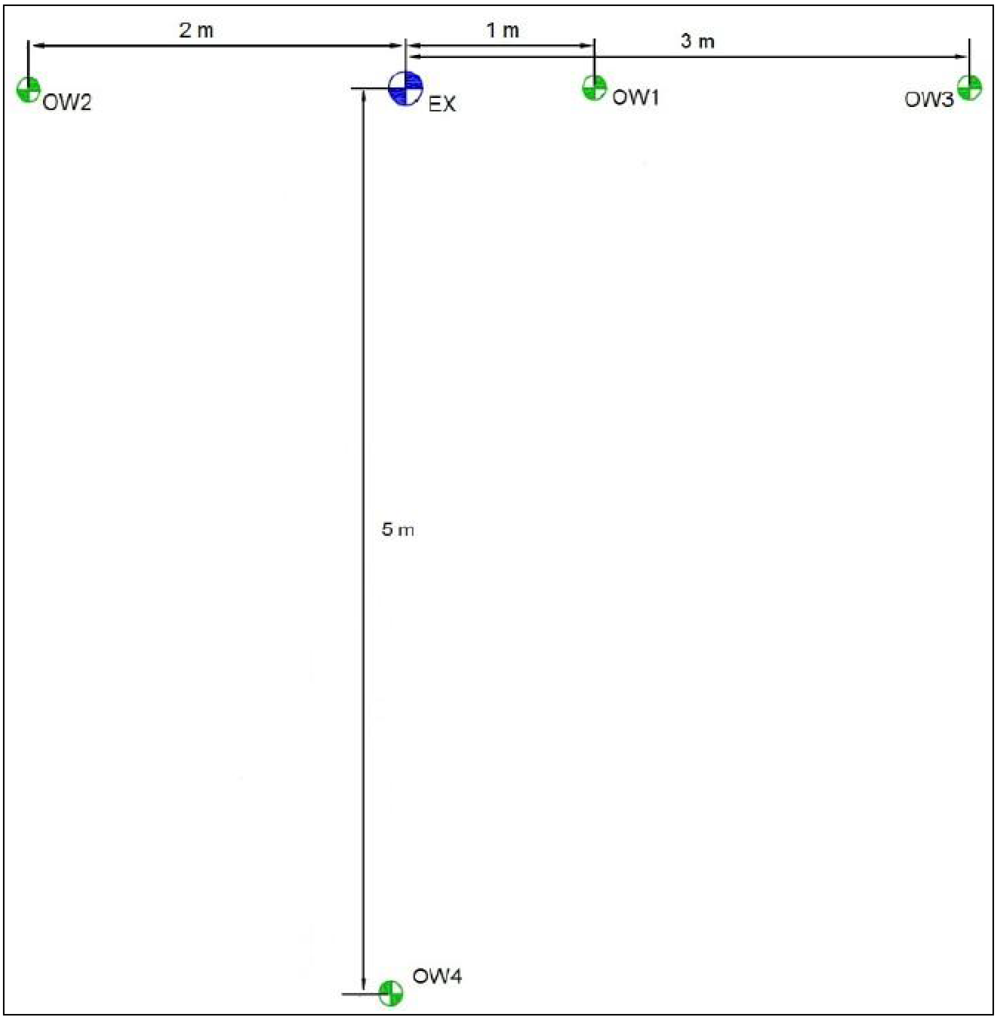
The screening concentrations set by the Italian legislation for groundwater (CSCs, e.g. 1.5 µg/l for trichloroethylene) were exceeded. A site-specific risk assessment was submitted to the Authorities and approved, resulting in less conservative risk-based remediation goals (CSRs, e.g. 1,500 µg/l for trichloroethylene). Since the detected concentrations in groundwater were above the CSRs, a remediation design (based on the application of Multi Phase Extraction technology) was presented to the Authorities and approved.

3. Pilot-scale application in field

3.1 Extraction system

The MPE system used for the pilot test consisted of four main components:

- MPE extraction well (EX, installed within the most impacted area, PVC, 4", 6.05 m deep, screened 1 – 6 m bgl;
- 3 monitoring wells (OW1, OW2, OW3, at distances respectively 1, 2 and 3 m from the extraction well) made of 3" PVC, 6 m deep, screened 1 – 6 m, used to monitor pressure variations in both the saturated and unsaturated zone;
- 1 monitoring well piezometer (OW04), 1" PVC, 1.3 m deep, screened 0.5-1.3 m bgl, used to monitor pressure variations within the unsaturated zone;
- MPE extraction and treatment unit (ECOVAC mobile plant, consisting of a vacuum pump, air/water separator, activated carbons for vapours and a tanker for water);
- -Extraction piping (from the MPE wells to the MPE treatment unit).



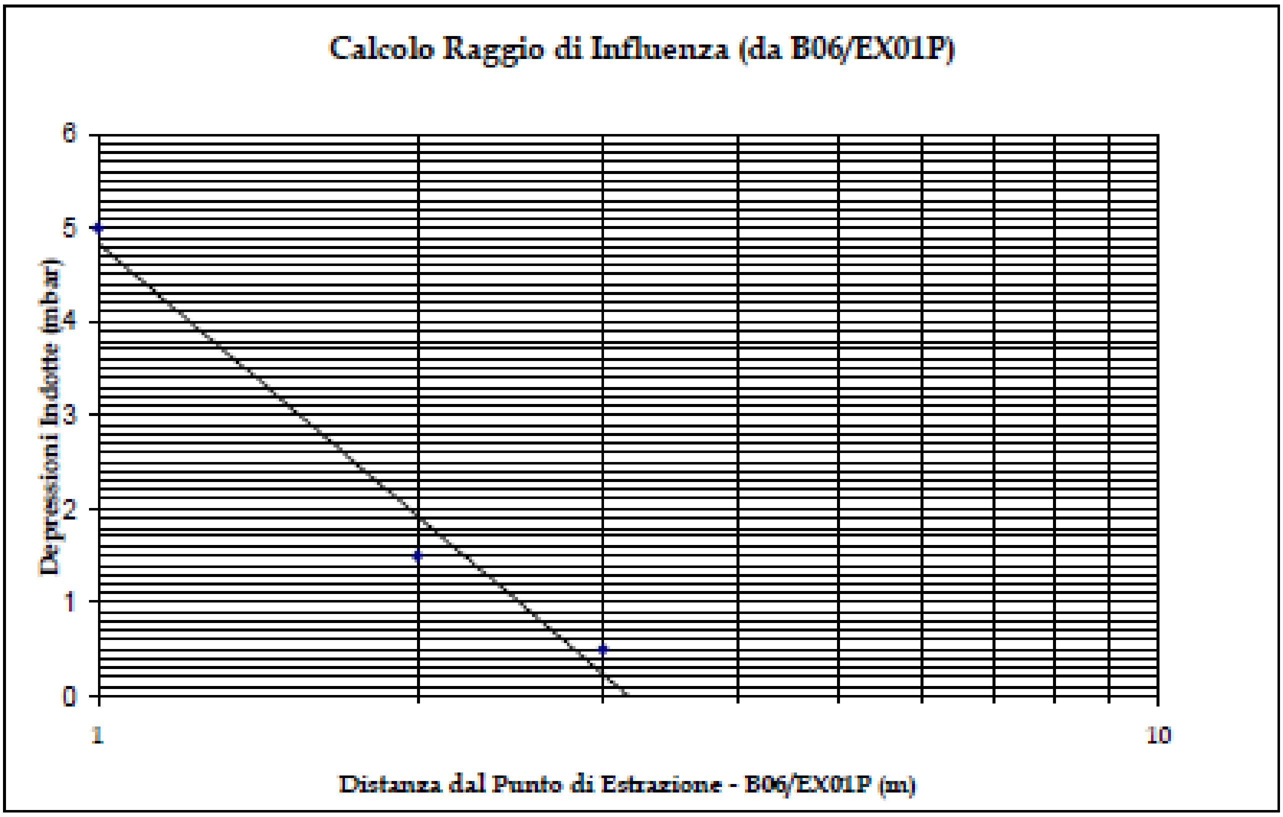
3.2 Feasibility study

During the on-site testing activities, field measurements were carried out for parameters such as: vacuum at the blower, vacuum generated in the unsaturated zone, hydrostatic responses, concentrations of contaminants in the extracted vapors and liquids, vapour and water extraction rates.

3.3 Radius of influence

On the basis of the data from the OW monitoring wells, it was possible to estimate the site-specific radii of influence:

- Hydraulic radius of influence (in the saturated zone) exceeded 3 m;
- Radius of influence for vapour extraction (in the unsaturated zone) was 3 m.



The graph shows that the vacuum induced by the extraction system in the unsaturated zone reaches zero at a distance of about 3 m. Consequently, the radius of influence of the system was set equal to 3 m.

3.4 Off gas Treatment

2 m^3 activated carbon vessel filled with 1200 kg of granular activated carbons. Extracted vapors were treated by means of activated carbons before discharge to the atmosphere. Extracted liquids were stored and disposed of.

3.5 Water Treatment

No water treatment was implemented. Water collected in the air/water separator was stored, properly characterized and disposed of.

3.6 Control parameters

Vacuum at the blower, vacuum generated in the unsaturated zone, hydrostatic responses, concentrations of contaminants in the extracted vapors and liquids, vapour and water extraction rates

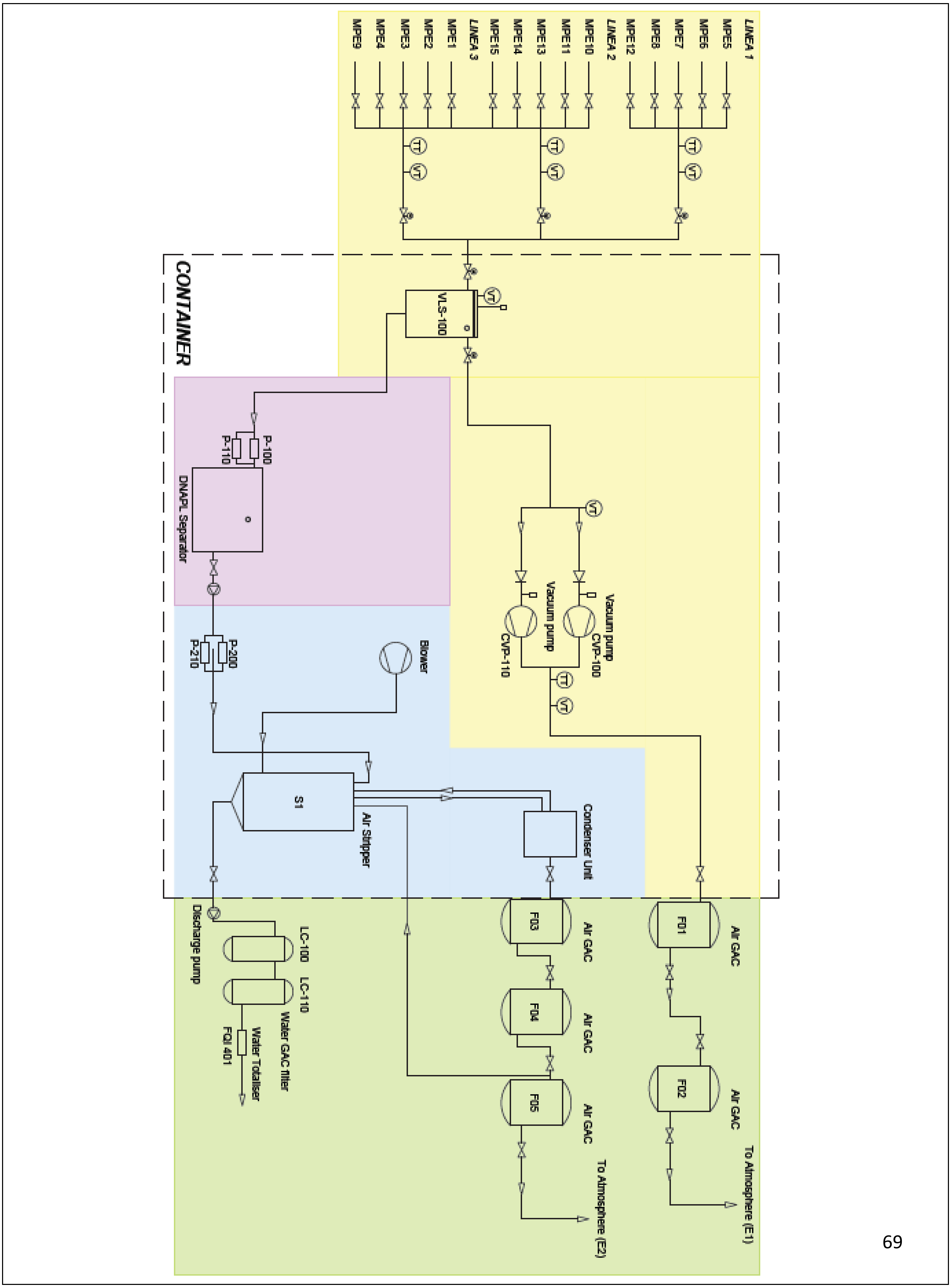
4. Full-scale application

4.1 Full design system

- <u>the number and characteristic of extraction system in the full scale application</u>

The full scale system consisted of 15 6m-deep, 6" diameter extraction wells (screened 2-6 m bgl) connected to two vacuum pumps (max vacuum 750 mbar, max extraction rates 200 Nm^3/h). A slurper was installed in each well. Three extraction lines, each connecting 5 extraction wells, were realized, in order to allow "pulse" extraction from different lines.

A water/vapour separator was installed before the blowers. Water was sent to a DNAPL separator, treated by means of a stripper (for preliminary treatment of extracted GW) and then by means of activated carbons before discharge. Vapors (extracted form subsoil or stripped during water treatment) were treated by means of activated carbons before discharge (or re-use in the water treatment process).


LINEA 1
MPE5
MPE6
MPE7
MPE8
MPE12
LINEA 2
MPE10
MPE11
MPE13
MPE14
MPE15
LINEA 3
MPE1
MPE2
MPE3
MPE4
MPE9
TT
VT
CONTAINER
VLS-100
P-100
P-110
DNAPL Separator
P-200
P-210
Blower
Vacuum pump
CVP-100
Vacuum pump
CVP-110
S1
Air Stripper
Condenser Unit
F01
Air GAC
F02
Air GAC
To Atmosphere (E1)
F03
Air GAC
F04
Air GAC
F05
Air GAC
To Atmosphere (E2)
Discharge pump
LC-100
LC-110
Water GAC filter
Water Totaliser
FQI 401

4.2 Different areas characteristics that affect the project

Not applicable. MPE application was equal throughout the entire treatment area.

4.3 Radius of influence

Not applicable. The radius of influence was not re-estimated during the full scale operations

4.4 Off gas Treatment

A water/vapour separator was installed before the blowers. Vapors (extracted from subsoil or stripped during water treatment) were treated by means of activated carbons before discharge (or re-used in the water treatment process).

4.5 Water Treatment

A water/vapour separator was installed before the blowers. Water was sent to a DNAPL separator, treated by means of a stripper and then by means of activated carbons before discharge.

4.6 Control parameters

Vacuum at the blower, vacuum generated in the unsaturated zone, hydrostatic responses, concentrations of contaminants in the extracted vapors and liquids and after their treatment before discharge, vapor and water extraction rates. These parameters were measured every week (for the first three months) and then every 15 days. Groundwater/soil gas samples at extraction wells were teken every 4 months.

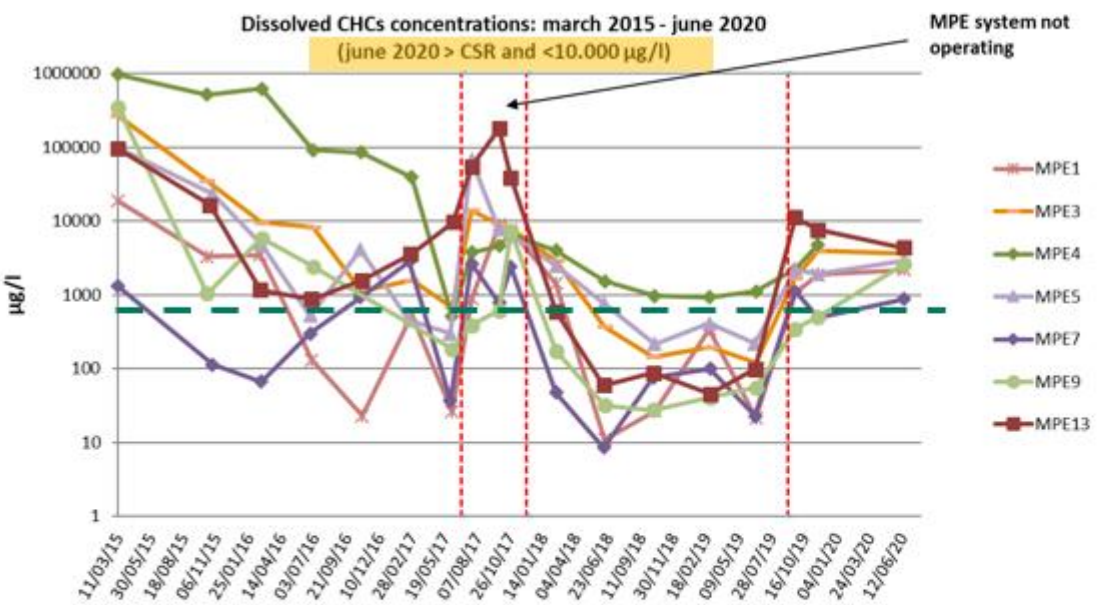
5. Results

5.1 Removal rate

The mass of chlorinated solvents extracted with MPE system after 4 years of operation (2015 – July 2019) was as follows :

- about 6 kg of chlorinated compounds (CHCs) extracted as dissolved phase
- about 278 kg of CHCs extracted as vapors

In 2019 the MPE was shut-off, after achieving its technological limit (the cumulative recovered mass reached an asymptotic trend). Comparing the dissolved concentrations in groundwater before and after the remediation phase, an average decrease of about 70% was registered.



6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring

- After MPE shutdown, two monitoring campaigns were conducted, one at the end of September 2019 and the other in November 2019 to verify concentration rebound (leading to the average remediation performance value of about 70% reported in the previous section);
- Since November 2019, one monitoring campaign has been performed every year.
- Every six months (June and December): sampling and analysis of ambient air.

1. Contact details - CASE STUDY: MPE n.6

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1.7 Phone number	

2. Site background

2.1 History of the site

The site is a former industrial pharmaceutical plant of about 30.000 m2, located in a central area of a small town in Northern Italy. The plant remained active until 1980, and then was used as a warehouse until 1996, when environmental investigations carried out found the presence of contamination in soils and groundwater for compounds such as: Benzene, Toluene, Monochlorobenzene and Trichloromethane.

2.2 Geological setting

The subsoil presents a first superficial layer constituted by soils and backfill materials, in some areas present up to about 2 meters from the ground level, followed by a frequent alternation in vertical and horizontal sense between fine lithotypes (mainly silty) and coarser and more permeable lithotypes (mainly sands and silty sands) up to the first 7-8 meters of depth.
From this depth, a clayey layer is present up to about 32 meters above ground level, which constitutes the basal impermeable level of the surface aquifer.
An exception is the south-western portion of the site where the presence of permeable materials with a sandy-gravel matrix has been detected between 7-8 meters from the surface and about 15 meters from the surface, which implies a subdivision of the surface aquifer into two levels (surface horizon and deep horizon). Below this level there is the clayey layer up to about 32 meters from the surface level detected in the other sectors, which constitutes the basal impermeable level of the surface aquifer also in this sector.
The subjacent level of the surface water table is between -1 and -2 m from ground level.
Beginning at 33 to 42 m from w.g. is the first confined deep aquifer.

2.3 Contaminants of concern

- Benzene (maximum concentration 3.500 µg/l average concentration 550 µg/l)
- Monochlorobenzene (maximum concentration 53.000 µg/l, average concentration 3.300 µg/l)
- Other contaminants: Trichloromethane (average concentration 1,2 µg/l)

2.4 Regulatory framework

Remediation with MPE is a part of the interventions planned for the site, which also includes the use in other areas of different remediation technologies such as Dig&Dump of unsaturated contaminated soil, in situ thermal desorption, on-site soil treatment by SVE, ISCO and Pump&Treat.

With regard to the remediation with MPE system planned for the groundwater in the central area of the site, object of this case study, the approved remediation objectives are the CSR calculated through the site specific risk assessment procedure (benzene 310 µg/l, monochlorobenzene 5.300 µg/l).

3. Pilot-scale application in field

3.1 Extraction system

The test field included an extraction point and 5 monitoring points located at distances between 2 and 9 m from the extraction point. Each point consists of a 4" diameter well with a screened section starting from the groundwater level (2.0 m b.g.s.) to the bottom of the hole (7 m b.g.s.).
The suction of groundwater and vapors was performed using an ATEX vacuum pump that can generate depressions greater than 900 mbar.
A wellhead was attached to the extraction well to which a slurper consisting of 1" HDPE piping was directly connected.
A condensate separator was connected to the pump to allow separation of groundwater and sediment from the extracted vapors.

3.2 Feasibility study

MPE was found to be effective for contaminant removal in areas just outside of source areas, where thermal treatment was not conveniently applicable for economic and logistical reasons. While LNAPL/DNAPL is not present, the technique was deemed suitable for physical removal of contaminants in the saturated soil given their volatility. The low permeability of groundwater (2x10-7 m/s) also allows significant lowering of groundwater levels, thus facilitating vapour extraction in the desaturated section up to a thickness of 3 meters. The assumptions were confirmed by both the pilot test and the full-scale operation of the system, which showed significant gas-phase contaminant recovery rates, especially in conditions of greater groundwater lowering.

3.3 Radius of influence

Radius of influence (ROI) of the system was calculated by performing a pilot test with steps of increasing vacuum. Considering a vacuum of 500 mbar in the extraction well, radius of influence (ROI) was calculated around 5 meters on the basis of induced vacuum. A drawdown of 0,25 mbar was considered as the boundary of the effect of the well. During the pilot test, the induced lowering of the water table was also measured, which was more than 2,5 m at a distance of 2 m from the extraction point and 1,3 m at a distance of 5 m.

3.4 Off gas Treatment

Vapours extracted during the pilot test were treated through a battery of activated carbon filters installed in series.

3.5 Water Treatment

The liquid effluent goes to an existing groundwater treatment plant.

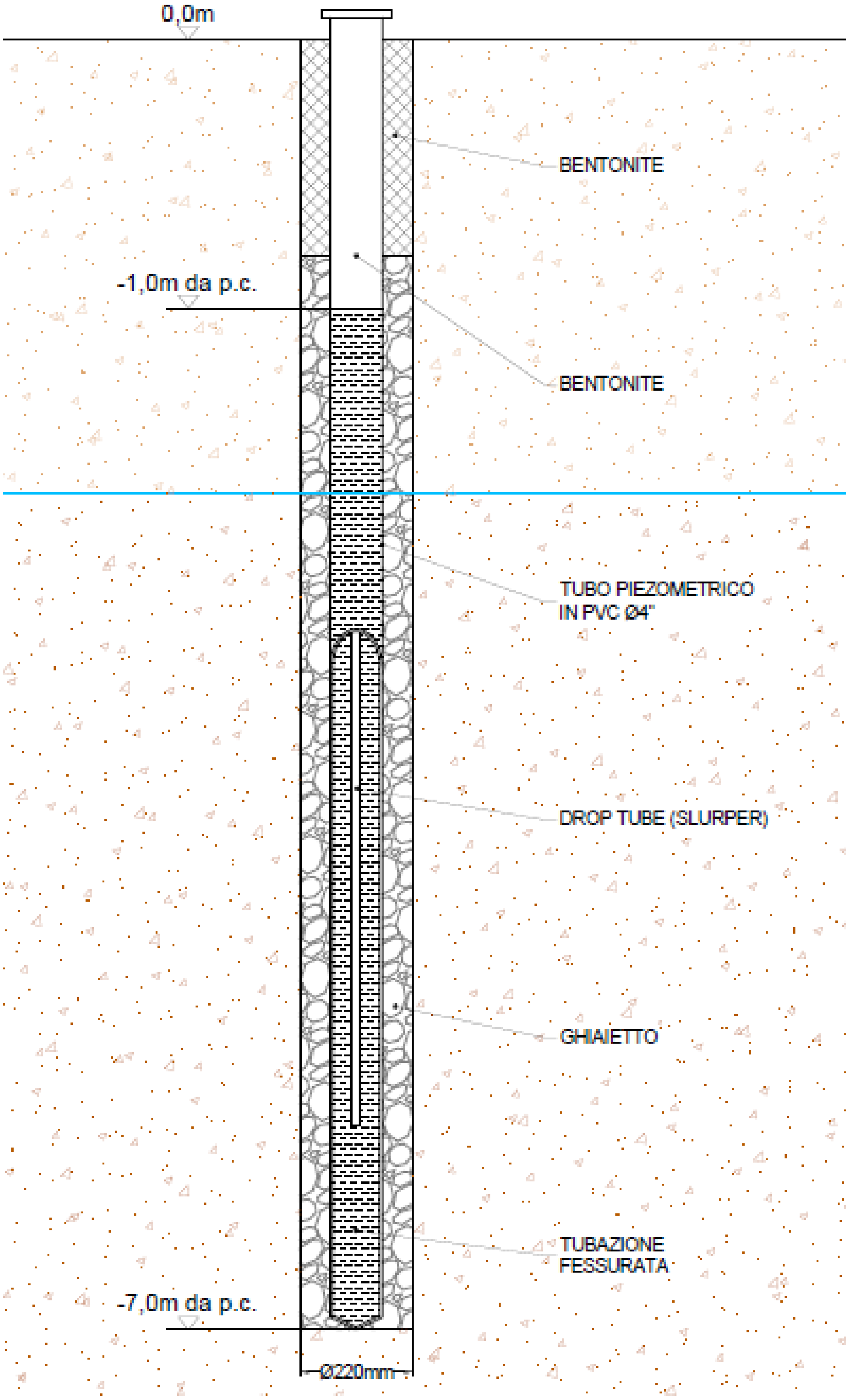
3.6 Control parameters

During the pilot test, the data necessary to design the full-scale system were collected:

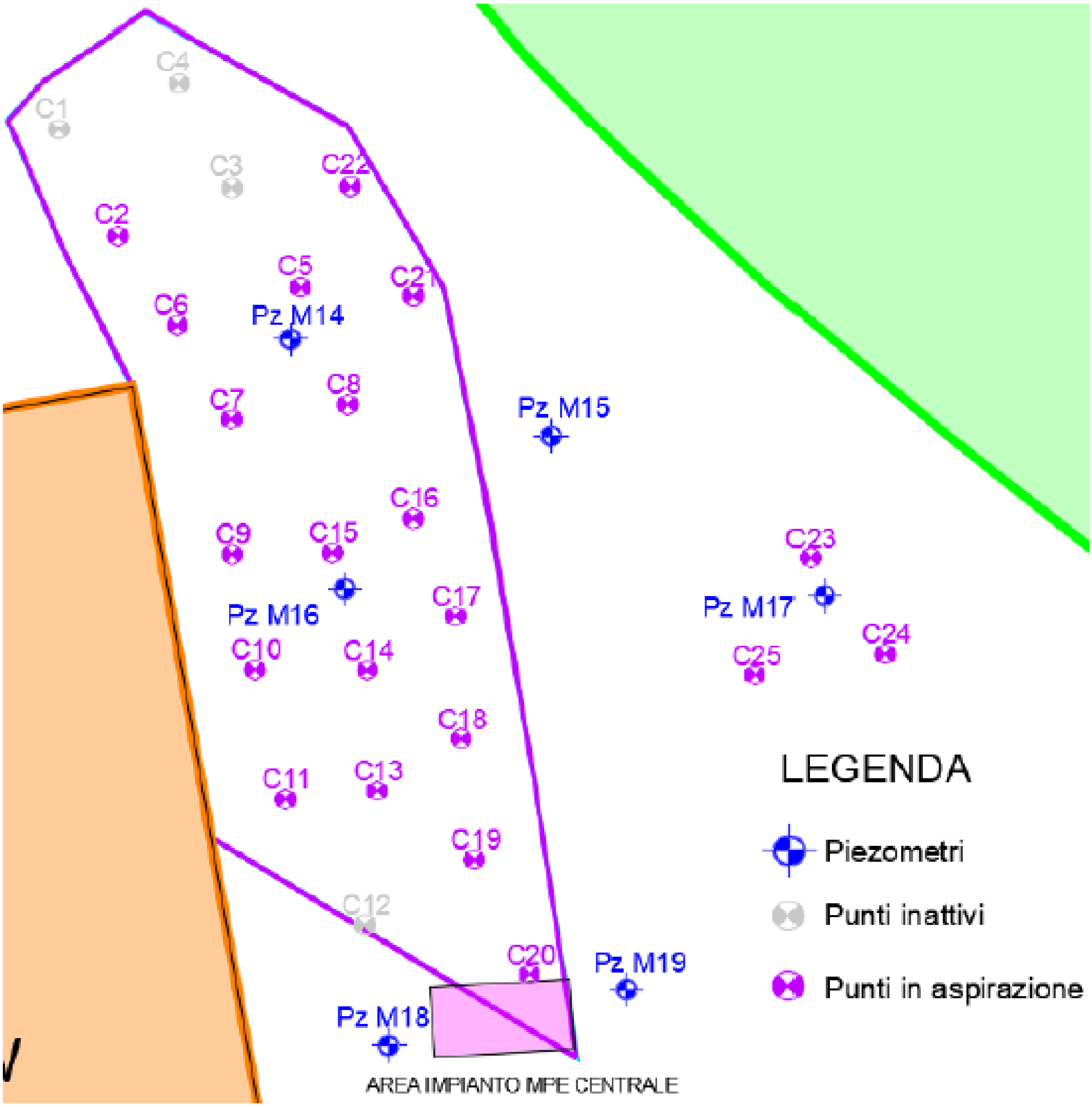
- Vacuum generated at the wellhead and induced at the control points in the different flow steps (to evaluate flow rates and operating vacuum and radius of influence)
- VOCs and percentages of O_2, CO_2, and LEL in the intake gas (to evaluate recovery of contaminants in the gas phase and size the air treatment system).
- Lab analysis of concentrations of contaminants in the inlet gas (to evaluate gas-phase contaminant recovery and to design the air treatment system).
- Extracted liquid flow rates and induced groundwater lowering (to evaluate system effectiveness in groundwater desaturating and to design the water treatment system)
- Possible presence of LNAPL/DNAPL (to size any de-oiling systems and to define the typology of full-scale plant)
- Lab analysis of concentrations of contaminants in groundwater taken from extraction wells (to size the water treatment system and evaluate recovery of dissolved contaminants).

4. Full-scale application

4.1 Full design system



The system consists of two suction units with which the gaseous phase mixed with the liquid phase is extracted from the wells installed through a high vacuum level. Twentytwo PVC extraction wells with a diameter of 4", screened between 1 and 7 m b.g.s, have been installed. Then the intervention areas have been prepared with the installation of a HDPE geomembrane to cover the non-paved areas and to avoid short circuits of air with the surface.



The extracted liquids first pass through a cyclone filter that separates any sand sucked from the MPE wells and then through a check filter to eliminate the finest sediments. Subsequently, the gaseous phase mixed with the liquid phase is appropriately separated in the multiphase separator where gases are separated from liquids by density. The gaseous phase is then sent to the activated carbon treatment section, while the aqueous

phase is sent to the water treatment plant. The DNAPL product eventually present in the aqueous phase is separated by a water/product gravity separator before the water treatment plant.
The inlet line to the cyclone filter is divided into 3 PVC lines of diameter ø 2", each equipped with a valve with pneumatic actuator. The valves are controlled directly by the PLC which allows the opening and closing cycles of each valve to be timed individually, so that they can work alternately or all at the same time.

After the pneumatic valves, the lines divide into a 4 or 5 point comb. Each point, equipped with a ball control valve, is connected by rigid HDPE piping with a diameter ø 1"1/4 to a suction well. The lines, properly labelled with the name of the suction well from which they come, are laid above ground up to the wellhead of competence and then connected, through a flexible pipe equipped with regulation valve, to an HDPE drop tube (slurper) with diameter equal to 1". The drop tube, allows the suction of fluids, water, vapors, and any LNAPL/DNAPL, throughout the contaminated section. The drop tubes are lowered inside the suction wells up to the desired depth, through a sealed well head and their depth can be easily adjusted on the basis of field surveys.



All the well heads, positioned above ground in order to facilitate connections and controls, are equipped with a vacuum gauge to control the depressions induced inside the well and a point of taking samples/measurement with portable instrumentation.

- The system provides a continuous operation (24/24 h) with fully automatic management through a controller with programmable logic.

4.2 Different areas characteristics that affect the project

The MPE plant was chosen for the site area that had the following characteristics:

- Presence of groundwater with maximum base depth of 7 meters from ground level.
- Low permeability
- Volatility of the contaminants (Benzene, MCB).

It should be noted that ISCO technology was preferred in a second area of the site, where the groundwater deepened in an interval with permeability greater than an order of magnitude between 7 and 15 m b.g.s., since the greater depth and permeability characteristics would have made ineffective the application of MPE in this area.

4.3 Radius of influence

ROI was calculated by performing a step test with increasing vacuum based mainly on the induced vacuum.

Considering a vacuum of 500 mbar in the extraction well, ROI was calculated around 5m. However, for the sizing of the full-scale system, a distance of 7 meters between suction wells was considered as a precautionary measure, in order to obtain a good overlap of the areas of influence of each well and thus improve the effectiveness of the system. This spacing also made it possible to constantly lowering groundwater above 3 meters, thus promoting the recovery of contamination in the gaseous phase.

4.4 Off gas Treatment

The fluids extracted from the various suction wells are initially collected in the two filters connected in series to retain the sand sucked and the finer sediments, then conveyed into the multiphase separator.
The collected sand is discharged manually and stored in big bags, to be disposed of in accordance with current regulations.

The separated gaseous phase is sucked by the vacuum pump and then sent to the activated carbon treatment section, consisting of n° 2 carbon filters of 1,0 m^3 each, connected in series.
Each of the vacuum pumps, along the outgoing line, is equipped with digital temperature sensor, digital pressure switch, analogical flow meter and sample tap. In addition, the manifold that conveys the extracted area to the activated carbon filters is equipped with digital thermometer, digital flow meter and sample tap.
Downstream and between the 2 filters there are 2 other sampling points for taking gas samples or making measurements with portable instrumentation.

4.5 Water Treatment

The fluids extracted from the various suction wells are initially collected in the two filters connected in series to retain the sand sucked and the finer sediments, then conveyed into the multiphase separator.
The collected sand is discharged manually and stored in big bags, to be disposed of in accordance with current regulations.

The aqueous phase is conveyed to an oil separator for the separation of any LNAPL/DNAPL. The water coming out from the oil separator is conveyed to an existing groundwater treatment plant through a 2" HDPE rigid pipe. The delivery line is equipped with non-return valve, regulation gate valve, analogical pressure gauge, analogical meter and sample tap.
Any product in free phase is stored in a special double-walled polyethylene tank with a capacity of 0,6 m^3, equipped with an overflow alarm to block the plant.

4.6 Control parameters

The daily monitoring plan foresees the detection of the operating data of the plant in order to verify the correct functioning and optimize the performance.
Specifically, the following measurements are carried out on a daily basis:

- Vacuum upstream of the cyclone filter, bag filter and vacuum pump.
- Flow rates of each vacuum pump and at the stack.
- Temperature at the outlet of each machine and at the stack.
- Ambient temperature inside the container.
- Reading of water meters at the exit of the plant and at the exit of each pump of relaunching multiphase separator.
- Groundwater level of the piezometers.
- PID (Portable Photo Ionizer) measure of the concentrations extracted by each machine, upstream and downstream of the filters and between the 2 active carbon filters.

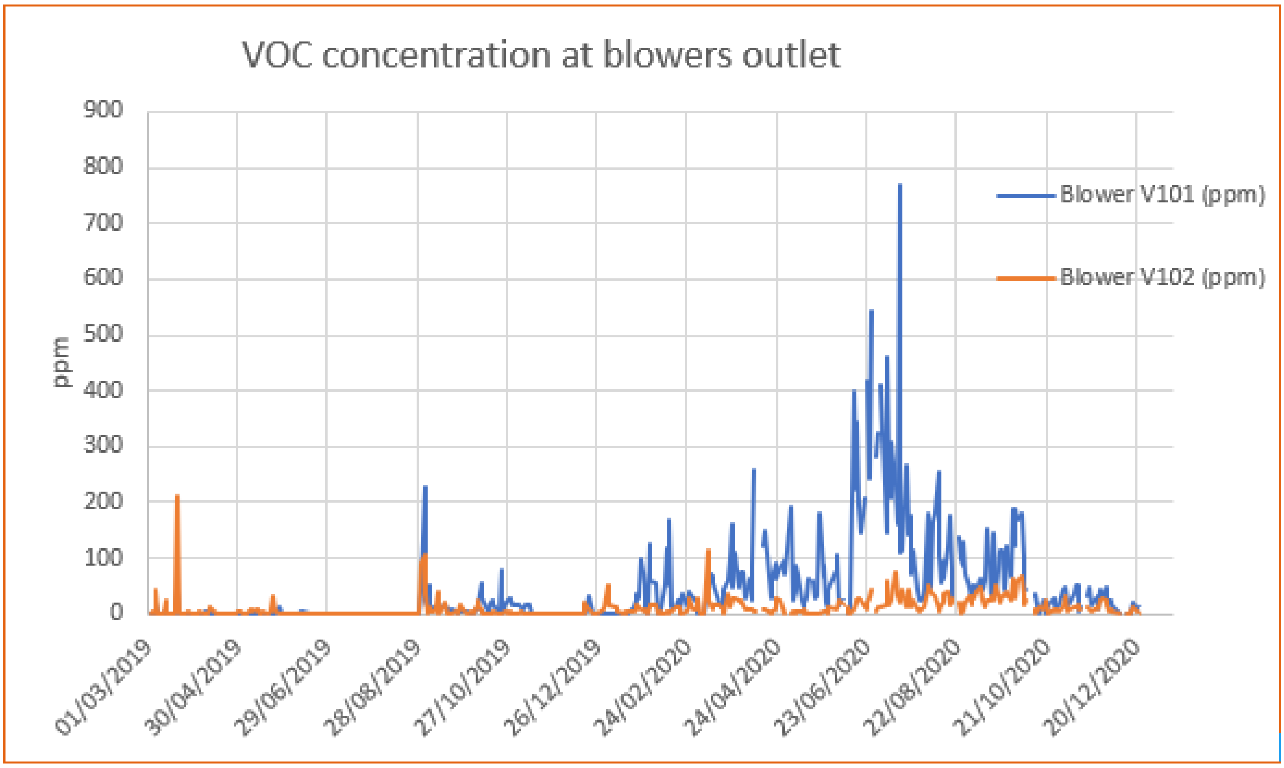
On a weekly basis, it is also detected the possible presence of sand inside the well, in correspondence of each suction point.
All the measurements above made allow in real time to assess any anomalies in the operation of the plant and to intervene in order to optimize the performance.

5. Results

5.1 Removal rate

Evaluations of the rate of contaminant extraction were carried out both through the concentrations of Volatile Organic Compounds (VOCs) detected by PID at the outlet of each vacuum pump and calculating the mass balance of the quantities of contaminants recovered in the aeriform and liquid phases.

The graph below shows the VOCs values measured during the plant's operating period.



The fluctuating trend of the graph is partly linked to variations in vacuum at the wellhead and partly to the variation in the groundwater level.
The variations in vacuum are related to clogging of the cyclone filter and/or the bag filter due to the entrainment of fine material in the extracted fluids. This results in a change in the volume extracted by the vacuum pump.
Groundwater level variations may be due to precipitation or, also, to variations in the suction rate at the wellhead.

The above trend is also repeated in the mass of contaminant recovered in the gas phase, the extraction rate of which was very significant especially in the period between March

and August 2020.
In the period after November 2020, there is a decrease in VOC concentrations indicating that contamination removal is mostly complete.
The quantities of contaminant recovered during the intervention, estimated by mass balance, are as follows:

- 53 Kg of contaminants in the gaseous phase, out of a total of 2.800.000 m^3 of air treated
- 0,64 Kg of contaminants through the pumping of the liquid phase (6.000 m^3 of water treated).

It should be noted that the rate of recovery in the gaseous phase is definitely preponderant with respect to that in the liquid dissolved phase. This situation confirms the existence of a functional desaturation induced by the system in order to promote the recovery of contamination in the gas phase.
The concentrations of contaminants detected in the control piezometers showed a decreasing trend, reaching values significantly lower than the remediation goals even after the temporary shutdown of the plant for the rebound assessment.

6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring

Following the shutdown of the plant, a groundwater monitoring plan was started, valid for the testing of the reclamation and consisting of 4 quarterly groundwater sampling campaigns.
The concentrations of contaminants found in the first three testing campaigns showed a decrease in concentrations with respect to the first phase of remediation respectively of 98% for benzene and 40% for MCB, without showing significant rebound phenomena and being well below the remediation goals.

7. Additional information

7.1 Lesson learnt

A fundamental aspect in the management of the plant has been the constant and frequent maintenance.
In particular, the management of the plant has provided a schedule of daily interventions for:

- adjusting the suction depth of the drope tubes
- the cleaning of the bag filters

These frequent controls have allowed to maintain a full efficiency of operation and to prevent temporary shut-down and clogging of the suction points.

Glossary of Terms

A glossary will help a you to maintain the level of precision necessary for key terms and maintain consistency across the text. We found out that sometimes terms that sounds similar like "contaminated" and "polluted" are used in the same way as synonyms in some country, while in other they have different meanings (due to legislation or for other reasons). So fill in this glossary for your key elements and of course for acronyms.

Term (alphabetical order)	**Definition**
VOC	Volatile organic compounds (VOCs) are organic chemicals that have a high vapor pressure at ordinary room temperature
MPE	Multi Phase Extraction
SVE	Soil Vapour Extraction
ISCO	In Situ Chemical Oxidation
CSR	Threshold risk concentrations (calculated with site-specific risk analysis)
PLC	programmable logic controller
ROI	Radius of influence
MCB	Monochlorobenzene
PID	portable photoionizer

1. Your contact details - CASE STUDY: MPE n.7

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2. Site background

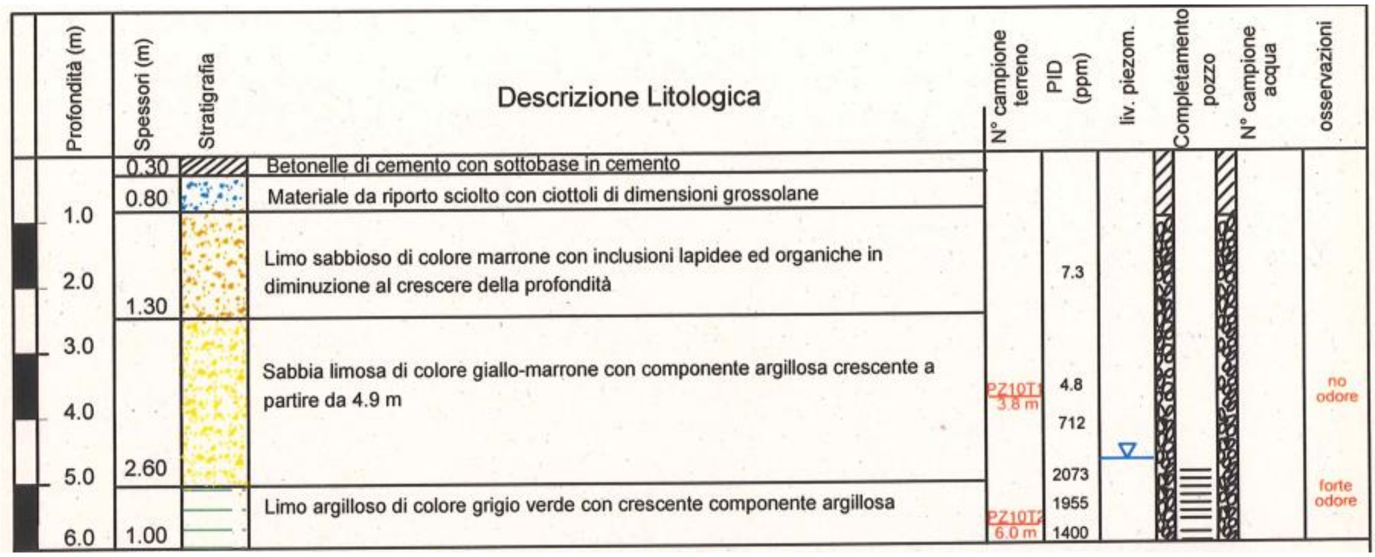
2.1 History of the site

The area in question is used for storage and distribution of petroleum products for transport (gas station).

2.2 Geological setting

The stratigraphic sequence of the subsoil can be summarized in coarse sand, interspersed with slightly silty sand, on the top, followed by clayey silt, tending to slightly sandy, and Clayey silt.

The depth to ground water is approximately maximum 5 meters below ground surface.



2.3 Contaminants of concern

In the soil: light (max 805 mg/kg) and heavy (max 2530 mg/kg) hydrocarbons and aromatic organic compounds:

- Benzene: max 0,28 mg/kg
- Toluene: max 3,3 mg/kg
- Etilbenzene: max 3,51 mg/kg
- Xylenes: max 16,82 mg/kg

For the groundwater (concentrations exceeding CSCs, with the exception of parameters MtBE and EtBE, not regulated but still taken into consideration with a limit of reference equal to 40 µg/l): Total hydrocarbons (6790 µg/l), Benzene (70 µg/l), Toluene (240 µg/l),Ethylbenzene (250 µg/l), p-Xylene (500 µg/l), MTBE (50 µg/l).

2.4 Regulatory framework

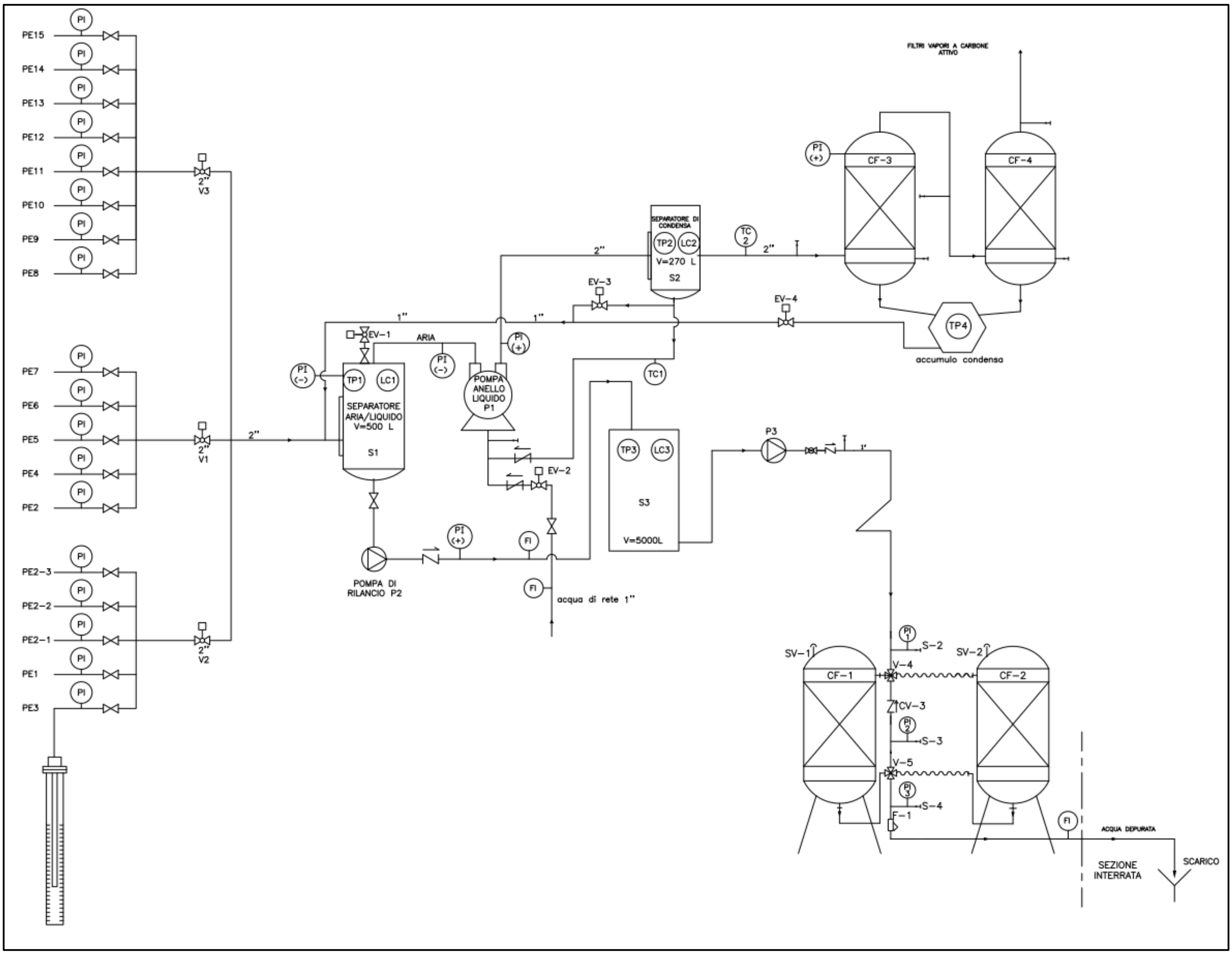
Below is a summary of the technical-administrative process it has is shown concerned the site starting from the event of potential contamination, notified to the EE.PP. in the month of September 2003 pursuant to the D.M. 471/99:

- 19.09.2003: the owner sent to the EE.PP. a communication of potential contamination pursuant to D.M. 471/99 for the detection of contamination in the groundwater, following the execution of a preliminary investigation through the creation of n. 4 monitoring piezometers, PZ1 ÷ PZ4;
- 20.10.2003: Transmission of the document "Descriptive technical report of the Plan of Characterization";
- 17.12.2003: Conference of the Services for the discussion of the elaborate Plan of the Characterization, during which additional investigations were requested;
- 25.03.2004: Transmission of the document "Integration to the Plan of Characterization ";
- 09.04.2004: Release by the Province of the Authorization to discharge into the public sewer;
- 09.04.2004: Start-up of the Groundwater Safety System, through the activation of the P & T system;
- 05.07.2004: Conference of the Services for the discussion of the paper "Integration the Characterization Plan ";
- 21.09.2004: Approval with prescriptions of the Characterization Plan;
- October-November 2004: Execution of the supplementary investigations prescribed in the approval of the Characterization Plan, through the creation of n. 4 monitoring piezometers, PZ5 ÷ PZ8;
- 18.02.2005: Transmission of the document "Preliminary Reclamation Project";
- 20.04.2005: Conference of the Services for the discussion of the "Project Preliminary remediation ";
- 29.04.2005: Approval with prescriptions of the Preliminary Reclamation Project;
- 20-24.06.2005: Preparation of the pilot test field for the execution of the MPE, through the creation of n. 6 monitoring points, Pz9 ÷ Pz14;
- 11-12.07.2005: Execution of the MPE pilot test at the points Pz5 and Pz8;
- July 2005: Transmission of the document "Definitive Reclamation Project";
- 30.09.2005: Conference of the Services for the discussion of the paper "Project Definitive of Reclamation ";
- 05.10.2005: Approval of the Final Reclamation Project;

- 2005-2009: Resolution of a legal controversy between the owner and the neighbors; litigation story delayed the start the installation work of the remediation systems;
- September 2009 – July 2011: Installation of the remediation systems, through the
- realization of the perforations of the MPE points (PE1 ÷ PE15);
- 01.08.2011: Start-up of the remediation systems (MPE) and simultaneous shutdown the P&T plant;
- 20.02.2012: Transmission of the document "Technical report of the launch of the
- reclamation ";
- June 2013: Transmission of the document "Progress report of the Reclamation ";
- October 2013: The drilling activities of the piezometer to be carried out downstream hydrogeological of the site, scheduled for 22.10.2013, have been postponed to following the request for convening, by ARPA, of a Conference of Services for the discussion of the execution of the same, as well as the extension of the reclamation times.
- 10.06.2014: a new "Definitive Reclamation Project" was presented.

3. Pilot-scale application in field

3.1 Extraction system



The plant consists of:

- n. 18 extraction wells (PE1 ÷ PE15), equipped with sealed PVC hermetic wellhead, 1"1/4 PVC pipe with inside a pipe with a diameter of ¾" positioned at the air / liquid interface. The individual wells, connected to the suction system by means of a single PE pipe with a diameter of 25 mm, converge in 3 distinct manifolds:
    - Manifold 1: PE2, PE4, PE5, PE6, PE7
    - Manifold 2: PE1, PE3, PE2-1, PE2-2, PE2-3
    - Manifold 3: PE8, PE9, PE10, PE11, PE12, PE13, PE14, PE15

- a liquid ring pump with a high vacuum degree, housed inside a 10 'marine container, connected to each manifold by PE pipe with a diameter of 63 mm;
- flow rate adjustment valves and measuring points, arranged on each line of aspiration;
- 500 L gas / liquid separation tank;
- 270 L condensate separator;
- system for relaunching the equalization system; by means of a centrifugal pump self-priming;
- 5000 L water storage and equalization tank;
- an air treatment system, consisting of two activated carbon filters in series and containing about 500 kg / each of GAC;
- a water treatment system, consisting of two pairs of activated carbon filters, connected in reversible series (each pair) and containing about 250 kg / each of GAC;
- water recirculation and transfer pumps;
- recirculation water thermostat;
- electrical and hydraulic connections;
- power supply and control panel.

3.2 Feasibility study

The main objectives of the test are summarized below:

- verification of the area of influence through the measurement of different parameters in the points of monitoring;
- estimate of the mass of contaminant that can be removed as a function of time for verification of the achievement of the remediation objectives;
- analysis of the variability of the subsoil parameters / properties that can influence its effectiveness;
- estimate of the process parameters and the concentrations at the discharge of the various units plant engineering for the sizing of the full scale system;
- estimate of the costs of construction, management and monitoring of the basic system.

The pilot test specifically verified:

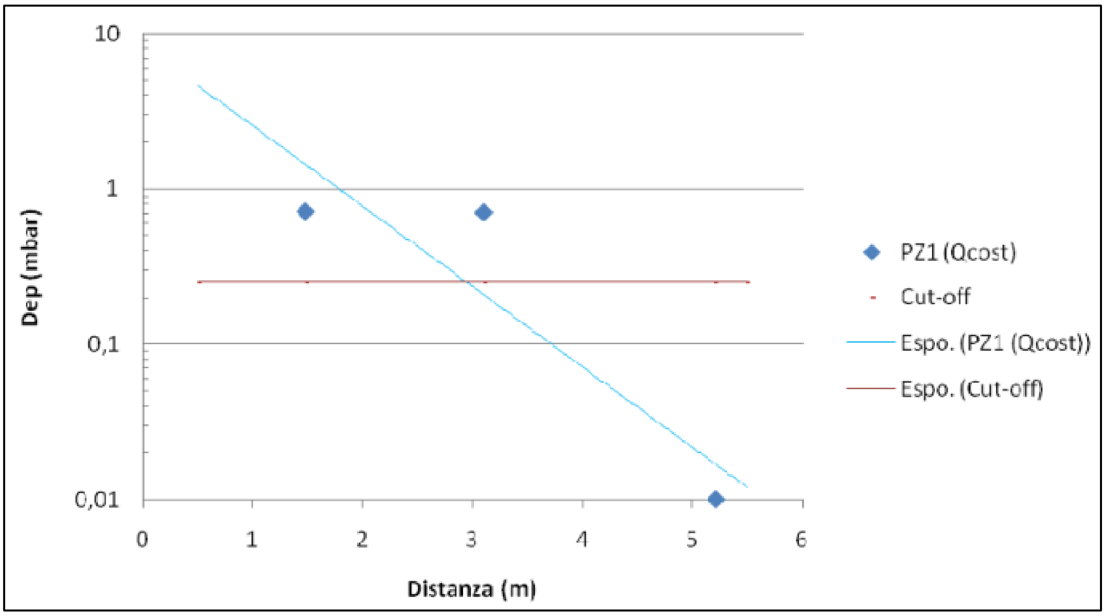
- degree of desaturation of the aquifer at a certain distance from the extraction point (zone of influence in the aquifer) through the measurement over time of the hydraulic levels in the observation points as the liquid flow rate varies / induced depression e of the draft height of the suction tube (slurp tube);

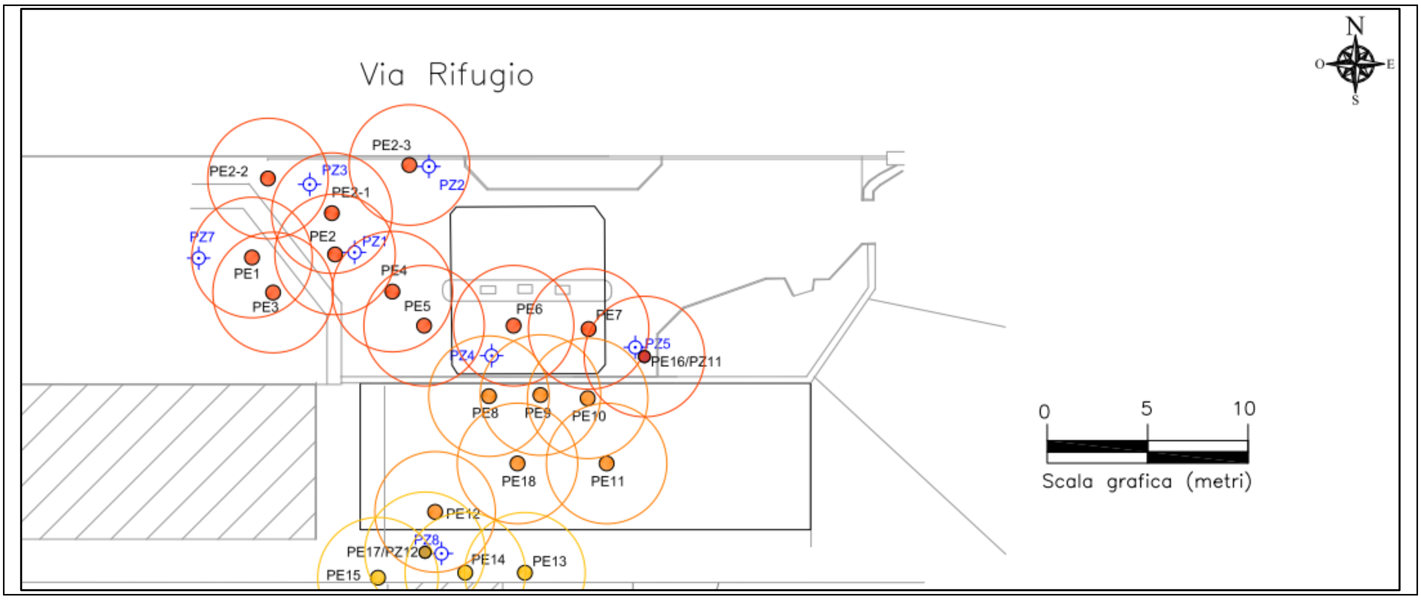
- the optimal air / liquid ratio in order to optimize the extraction of contaminants (maximum concentration) in relation to the efficiency of the system in space (area of influence).

3.3 Radius of influence

By the test, the following data can be extrapolated:

- representative values of induced depression are observed in the monitoring points, of the order of -0.7 mbar, at a distance of 3 m from the extraction point;
- in correspondence with the extraction point, a lowering of the groundwater level of about 70 cm is observed during the, i.e. values significant for the purpose of desaturation of the saturated sector;
- the concentrations of the extracted VOCs show non-zero values;
- the suction flow rate of the discharged water is of the order of 0.3 m3 / day.





3.4 Off gas Treatment

Two activated carbon filters in series and containing about 500 kg / each of GAC.

3.5 Water Treatment

Two couples of activated carbon filters, connected in reversible series (each pair) and containing about 250 kg / each of GAC. The treated waters are discharged into the public sewer.

3.6 Control parameters

Field monitoring and sampling program that will adequately monitor the effectiveness of the treatment in three dimensions.

The execution of the pilot test included:

- n. 1 MPE test from point PE6 at variable flow rate (3 steps with increasing depression / flow rate);
- n. 1 MPE test from point PE7 with variable flow rate (3 steps with increasing depression / flow rate);
- n. 1 MPE test from point PE9 at variable flow rate (3 steps with increasing depression / flow rate);
- n. 1 MPE test from point PZ1 at constant flow rate; for the execution of the test, the equipment was prepared and the point was connected to the gas / water treatment systems already present on site.

The verification of the parameters involved:

- measurement of the gas / liquid flows in correspondence with the extraction points (VOC extracted, volumes of drained water);
- measurement of the parameters in the monitoring points (induced depression, subsidence level, concentration of O_2 and CO_2), located at different distances from the extraction points.

4. Full-scale application

4.1 Full design system

MPE plant consisting of:

- 4 manifolds for a total of 21 lines. Each line (diam = 1 ") equipped with gate valve for regulation, ball valve for sectioning, sampling and measurement point (1/2 "), vacuum gauge
- n.4 vacuum-resistant air / water separators, complete with level switches (LSHH-LSH-LSL), manual dilution valve and automatic dilution valve
- 4 in-line filters for powders
- 4 centrifugal self-priming electric pumps for drainage water from separators (Qmax = 2m^3 / h; H = 20m; 0.55kW), with pressure gauge, non-return valve and ball valve on delivery line
- n.2 dry vacuum pumps (Qmax = approx. 340m^3 / h @ 60Hz; ΔPmax = -800mbar; 6.6kW @ 60Hz), complete with vacuum breaker valve and non-return valve. Pumps implemented by inverter, with manual adjustment
- 2 dry vacuum pumps (Qmax = approx. 450m^3 / h @ 60Hz; ΔPmax = -800mbar; 9kW @ 60Hz), complete with vacuum breaker valve and non-return valve. Pumps implemented by inverter, with manual adjustment
- suction and delivery line of each vacuum pump complete with vacuum gauge, LEL sensor connected to PLC, PLC connected temperature sensor, temperature sensor connected to PLC, shut-off butterfly valves, non-return valve
- n.2 activated carbon filters for air in HDPE (Diam = 1000; H = 1800), with 500kg of virgin carbon for each filter
- water storage tank in HDPE (V = 1000L) complete with level switches (LSHH-LSH-LSL) and valve background download
- 1 centrifugal pump for water recovery (Q_{max} = 50L / min; H = 30m; 0.75kW), with pressure gauge, non-return valve, sample point and ball valve on delivery line
- 1 bag filter, complete with IN / OUT pressure gauges and safety pressure switch
- 2 filters for activated carbon for water, (Diam = 650; H = 1200), complete with pressure gauges, vent valves, sample intakes e inlet pressure switch. Filling with 250kg of virgin carbon for each filter
- liter-counter and siphon at the drain
- switch cabinet and control panel with PLC and GSM modem, for remote control
- 20ft container with lighting and ventilation systems
- safety devices (emergency button, smoke detector, door open signal sensor)

4.2 Different areas characteristics that affect the project

For the site in question, the cognitive conditions and the basic elements used to identify the suitable remediation technology (MPE) are the following:

- the Gas Station is active;
- the subsoil is characterized by the presence of mainly fine-grained materials, with a declaration as the depth increases;
- The aquifer is mainly located in sandy-silty deposits of alluvial origin; the groundwater is placed between 2.8 and 4.8 meters deep from a b.c .;
- the analytical results found in unsaturated soil show a contamination for the parameters Hydrocarbons C≤12 and Hydrocarbons C> 12, Benzene, Toluene, Ethylbenzene , Xylenes;
- the analytical results found in groundwater show a contamination for the compounds Total Hydrocarbons, Benzene, Toluene, Ethylbenzene, p-xylene; the presence of the MtBE parameter is also observed.

4.3 Radius of influence

The estimated operating parameters are shown in the following table.

Parametro	UM	Valore
Portata aria estratta	Nm^3/h	20÷30
	m^3/h	60
Depressione [alla macchina]	mbar g	-700÷-800
Depressione [a testa pozzo]	mbar g	-500
Portata d'acqua	l/min	0,2÷1
Raggio di influenza	m	3

Radius of influence (ROI) was calculated around 3 meters on the basis of induced vacuum.

4.4 Off gas Treatment

N.2 activated carbon filters for air in HDPE (Diam = 1000; H = 1800), with 500kg of virgin carbon for each filter

4.5 Water Treatment

N. 2 filters for activated carbon for water, (Diam = 650; H = 1200), complete with pressure gauges, vent valves, sample intakes e inlet pressure switch. Filling with 250kg of virgin carbon for each filter.

4.6 Control parameters

The monitoring plan provides for the execution of the following findings:

- air flow and liquid flow (if any) in the various extraction points;
- VOC, O_2 and CO_2 concentrations and temperature at all extraction points and monitoring points;
- depressions at the wellheads of the extraction points, on the inlet lines to the manifolds and to the pumps;
- flow of extracted air and total liquid flow (if any) to the MPE system;
- VOC concentration in the total flow at the entrance and exit of the vapor treatment plant;
- subsidence of the groundwater in all piezometers of the monitoring network and eventual monitoring of product formation;
- sampling of groundwater at the entrance and exit of the water treatment plant.

WATER AND LAND

5. Results

5.1 Removal rate

The criteria that will be used to proceed with the testing of the remediation for both the soil and groundwater are illustrated below.
These activities can be undertaken only when concentrations lower than the Reclamation Objectives for the compounds subject to monitoring in groundwater are found for at least n. 3 consecutive campaigns, and if at least one of the following conditions:

- the mass balances will highlight the overall recovery of a mass of contaminant equal to the estimated one;
- achievement of asymptotic concentrations in the interstitial gases extracted from MPE system or in general in the operating parameters;
- absence of rebound effects in the interstitial gas concentrations detected in correspondence of monitoring points before and after system shutdown by MPE.

This testing activity will be conducted in contradiction with the Authorities.

Groundwater testing will be performed as follows:

- shutdown of all systems present on site for a period of no. 2 weeks;
- sampling of all piezometers making up the monitoring network for determination of the parameters Total Hydrocarbons and Benzene, Toluene, Etylbenzene, p-Xylene, Styrene, MtBE, EtBE.

For the testing of the soils, execution of n. 3 surveys. Samples will be taken in the unsaturated zone for these chemical analisis: Hydrocarbons C<12 and C>12, Benzene, Toluene, Etylbenzene, Xylenes.

6. Post treatment and/or Long Term Monitoring

6.1 Post treatment and/or Long Term Monitoring

For post-treatment monitoring, the execution of n. 4 campaigns with a quarterly frequency for a period of 12 months.
Each campaign will include the sampling and analysis of all piezometers making up the monitoring network for the search of the parameters Total Hydrocarbons and Benzene, Toluene, Etylbenzene, p-Xylene, Styrene, MtBE, EtBE.
The monitoring will be considered concluded on condition that all the samples taken are in compliance with the reference Reclamation Objectives.

7. Additional information

7.1 Lesson learnt

In conclusion, the MPE technology was found to be suitable for the specific site situation, however making appropriate changes to the suction system in order to increase its efficiency, such as:

- extraction points equiped with a pipe with a larger diameter (4”);
- connection pipes with larger diameter pipes;
- the use of a dry lobe / hook / cam pump, which is more efficient than the use of the liquid ring pump.

7.3 Training need

Workshops, training on-the job, webinars, e-learning could be an effective training tool