







# Multi Phase Extraction (MPE) report

Final Report

Date of report: 21 November 2022 Report number: 2021/08 WG6 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

| Title of the report:                              | Number report: 2021/08     |
|---|----------------------------|
| Multi phase extraction (MPE) report               | WG6 MPE EN                 |
|   |                            |
| Report adopted at IMPEL General Assembly Meeting: | Total number of pages: 122 |
| 29-30 November 2022, Prague (Czech Republic)      |                            |
|   | Report: 36 pages           |
|   | Annexes: 86 pages          |

**Project Managers:** 

Marco Falconi (IT) IMPEL ISPRA

Dietmar Müller-Grabherr (AT) Common Forum Unweltbundesamt AT

Frank Swartjes (NL) EIONET WG Contamination RIVM Wouter Gevaerts (NL) NICOLE Arcadis

**Authors:** 

Wouter Gevaerts (NL) NICOLE ARCADIS
Pavlos Tyrologou (GR) EFG, CERTH
Nazare Couto (PT) NOVA FCT, CENSE

Francesca Benedetti (IT) IMPEL MITE

Iustina Boaja (RO)

Romanian Geological Survey

Matteo Cozzani (IT) RAMBOLL
Marco Falconi (IT) IMPEL ISPRA

Marco Falconi (IT) IMPEL ISPRA Federico Fuin (IT) IMPEL ARPAV

Güray Hatipoğlu (TK)

Farmlabs Agriculture Technologies

Antonio Laganà (IT) IMPEL ARPAV
Jussi Reinikainen (FI) Common Forum SYKE

## **Contributors to Annex 1 ISCO:**

Andro Barabesi (IT)

Tommaso Brinati(IT)

SIMAM

JACOBS

Simone Biemmi (IT)

Federico Caldera (IT)

Rodolfo Costa (IT)

Claudia Costanzo (IT)

SIMAM

ARCADIS

ARCADIS

WSP GOLDER

Luca Ferioli (IT) ERM

Nicola Pozzi (IT) ARCADIS

Gianpiero Zaccone (IT) WSP GOLDER

#### **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.

Marco Falconi – IMPEL
Dietmar Müller Grabherr – COMMON FORUM on Contaminated Land in Europe
Frank Swartjes – EEA EIONET WG Contamination
Wouter Gevaerts – NICOLE

## Glossary

| TERM   | VI DEFINITION  |              | 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<br>performance<br>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' <sup>1</sup>                     | substance(s) or agent(s) present in the soil as a result of human activity   | ISO EN 11074 | 3.4.6      |  |
| 'contaminated<br>site' <sup>2</sup>            | 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' <sup>3</sup>                   | <remediation method=""> measure of the ability of a remediation method to achieve a required performance</remediation>   | 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<br>quality standard'            |  |              | Art. 3 (6) |  |
| 'Henry's<br>coefficient'                       | partition coefficient between soil air and soil water  | ISO EN 11074 | 3.3.12     |  |
| <i>'in-situ</i> treatment method' <sup>4</sup> | 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     |  |

\_

 $<sup>^{1}\,\</sup>mbox{There}$  is no assumption in this definition that harms results from the presence of contamination

<sup>&</sup>lt;sup>2</sup> There is no assumption in this definition that harms results from the presence of contamination.]

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

A 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<br>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<br>strategy' <sup>5</sup> | 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 sitespecific constraints  | ISO EN 11074 | 6.1.20      |
| 'remediation target<br>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<br>the bedrock and the surface. Soil is composed of<br>mineral particles, organic matter, water, air and<br>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       |

-

<sup>&</sup>lt;sup>5</sup> The choice of methods might be constrained by a variety of site-specific factors such as topography, geology, hydrogeology, propensity to flood, and climate

## TABLE OF CONTENTS

| 1 INTRODUCTION   | 9  |
|--|----|
| 2 DESCRIPTION OF THE TECHNIQUE   | 11 |
| 2.1 General process description  | 11 |
| 2.2 Two-phase extraction (TPE)   | 11 |
| 2.3 "Dual-phase extraction" (DPE)  | 12 |
| 2.4 Bioslurping  | 14 |
| 2.5 MPE selection and implementation                                     | 16 |
| 3 SITE CHARACTERICS, CONTAMINANTS AND LABORATORY INVESTIGATION           | 19 |
| 3.1 Site Conditions and Site Conceptual Model                            | 19 |
| 3.2 Liquid and Gas Phase Movements                                       | 20 |
| 3.2.1 Hydraulic Conductivity & Transmissivity                            | 20 |
| 3.2.2 Vadose Zone Soil Permeability to Air                               | 20 |
| 3.2.3 Geologic Setting   | 20 |
| 3.2.4 Formation Characteristics  | 21 |
| 3.2.5 Drawdown/Recovery Rate   | 21 |
| 3.2.6 Contaminant Location   | 21 |
| 3.2.7 Contaminant Characteristics  | 21 |
| 3.3 Note on Laboratory/Bench/Column scale Testing in MPE Remedial Design | 22 |
| 3.4 MPE Feasibility Consideration / Overview                             | 22 |
| 4 IN FIELD/LABORATORY TEST   | 23 |
| 4.1 Pilot test systems and conventional equipment for pilot tests        | 23 |
| 4.2 Effluent treatment technology  | 27 |
| 4.3 Control parameters   | 28 |
| 5 MONITORING OF THE PERFORMANCE  | 29 |
| 5.1.1 Chemical parameters  | 29 |
| 5.1.2 Physical parameters  | 29 |
| 5.1.3 Meteorological   | 30 |
| 6 CONCLUSIONS  | 33 |
| REFERENCES   | 34 |

#### 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].

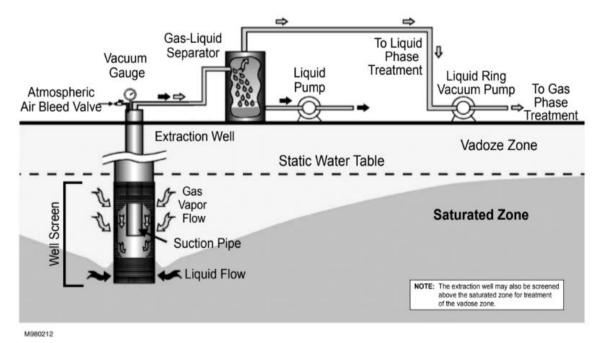


Figure 2.1.: Schematic of TPE System [1]



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.

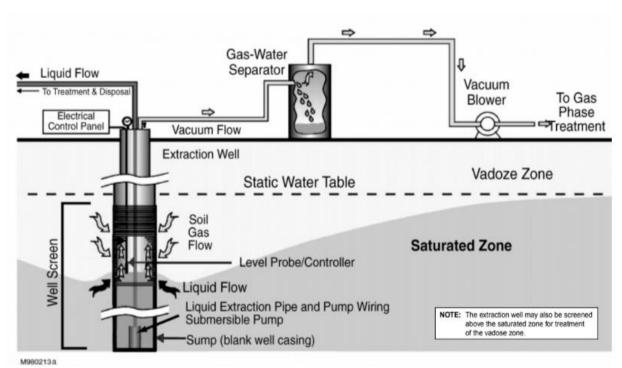


Figure 2.3.: Schematic of DPE System [1]

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.

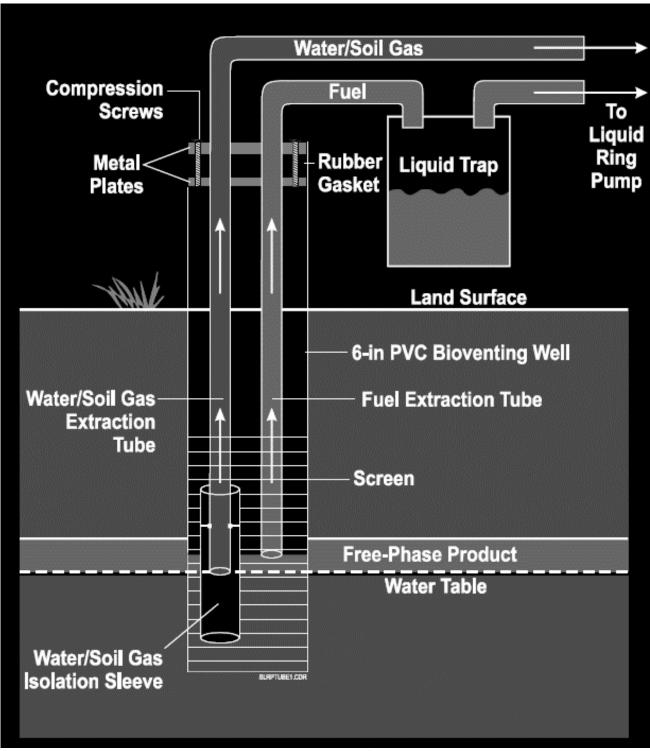


Figure 2.4.: Schematic in-well water/oil separation [2]

## 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].

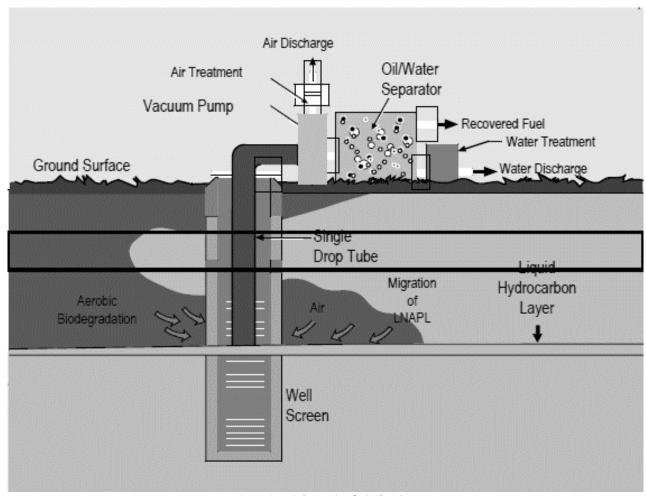


Figure 2.5.: Schematic of Bioslurping



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]

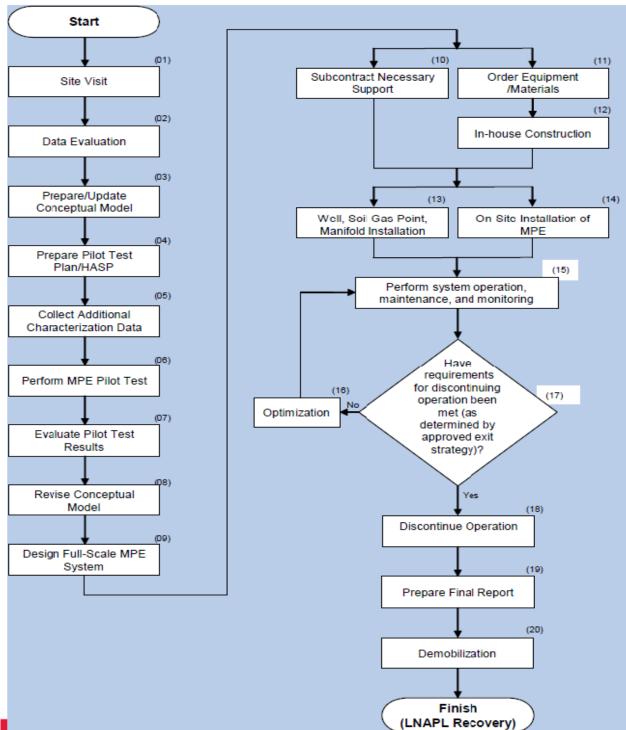


Figure 2.7.: MPE implementation scheme

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).

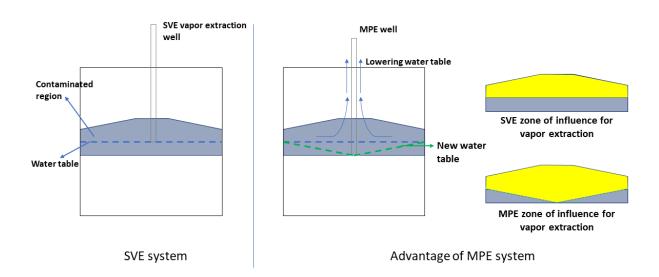


Figure 3.1.: The advantage of MPE system over SVE in removing volatile contaminants

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 subsections 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  | Halogenated VOCs                            |  |  |  |  |
|  | 2. Non-halogenated VOCs and/or Total        |  |  |  |  |
|  | Petroleum Hydrocarbons (TPH)                |  |  |  |  |
| Contamination location                               | Below groundwater table                     |  |  |  |  |
|  | 2. Both above and below groundwater table   |  |  |  |  |
| Henry's Law Constant of majority of contaminants     | >0.01 at 20° C (dimensionless) <sup>a</sup> |  |  |  |  |
| Vapor pressure majority of contaminants              | >1.0 mm Hg at 20° C                         |  |  |  |  |
| Geology below groundwater table                      | Sands to Clays                              |  |  |  |  |
| MPE application above the groundwater table          |   |  |  |  |  |
| Air permeability of soil above the groundwater table | ole Moderate and low permeability (k) soils |  |  |  |  |

<sup>&</sup>lt;sup>a</sup> Dimenssionless Henry's Law Constant in the form (concentration in gas phase) / (concentration in liquid phase)

## 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  $7.18 \times 10^{-5}$  m<sup>2</sup>/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<sup>2</sup> 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<sup>2</sup>. As a remark, SVE is estimated to be infeasible in air permeabilities lower than  $10^{-14}$  m<sup>2</sup> 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  $3\times10^{-4}$  m<sup>3</sup>/s groundwater

<sup>&</sup>lt;sup>b</sup> Soil gas permeability (k): =  $10^{-14}$  m<sup>2</sup> [8]

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  $3.33\times10^{-4}$  m<sup>3</sup>/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   | ٧٧                   | <b>VV</b> | ٧          | ٧     | -          | √√    | -     |
| Low Vac DPE   | ٧٧                   | <b>VV</b> | √√         | ۷۷    | -          | ٧٧    | ٧     |
| High Vac DPE  | ٧٧                   | ٧٧        | <b>V</b> V | ۷۷    | -          | √√    | ٧     |
| Bioslurping** | ٧                    | ٧         | ٧٧         | √√    | -          | ٧٧    | -     |

<sup>\*</sup>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

## 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).

As ISCO is a very versatile remediation technology, the application must be tailored to each specific site. Projecting sustainable remediation also means that environmental, social and economic aspects must be combined to reach the best solution possible for the site. So, it is crucial to compare more feasible solutions and identify the more sustainable one.

To acquire the necessary information, the following steps must be performed:

- definition of the objectives of the ISCO in the remediation project;
- applicability of ISCO treatment by:
  - initial screening;
  - detailed screening.

<sup>\*\*</sup>Mostly single pump configuration that is applied directly between or very near to the air-water intersection Legend: V - limited effectiveness; VV - demonstrated effectiveness

## 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 <u>DPE</u> 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<sup>3</sup>/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.

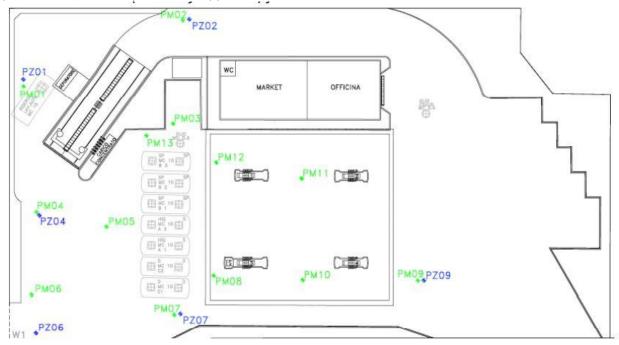


Figure 4.1.: Site map and monitoring points (courtesy of Ing. Caldera F., Mares Italia)

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).

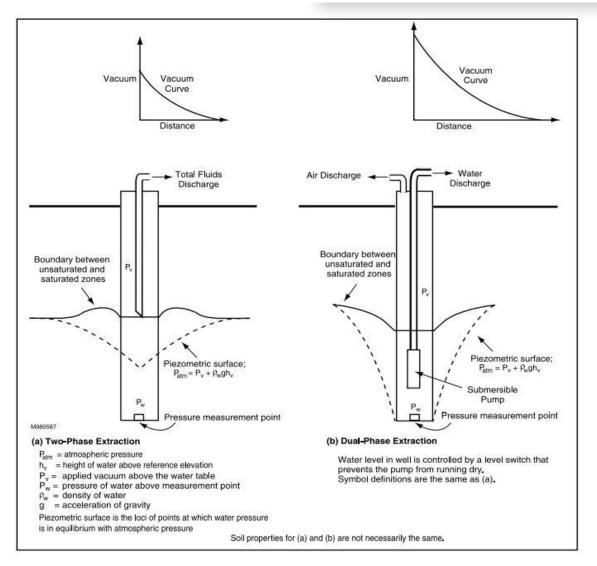


Figure 4.2.: Scheme of groundwater depression and vadose zone effect in a TPE vs. DPE system [25]

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;
- <u>groundwater extraction</u> data collected during extraction will be useful for calculating hydrostatic responses, specific yield, extraction rate and permeability;
- <u>soil gas extraction</u> 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<sup>3</sup> /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.

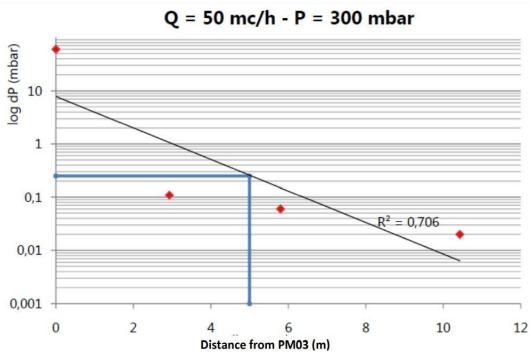


Figure 4.3.: Graph of ROI test (courtesy of Ing. Caldera F., Mares Italia)

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.

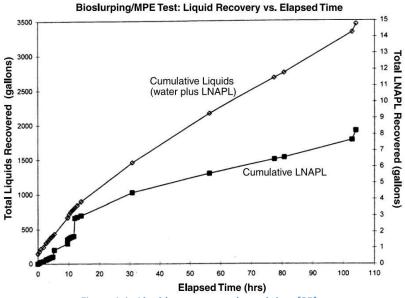


Figure 4.4.: Liquid recovery vs elapsed time [25]

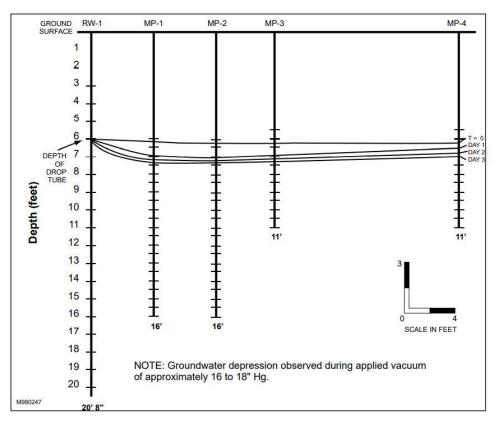


Figure 4.5.: Groundwater depression during bioslurping pilot test [25]

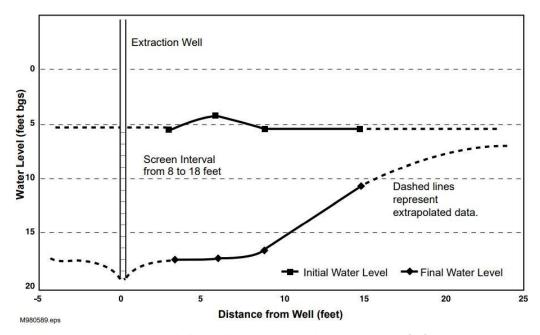


Figure 4.6.: Shallow well Pilot test groundwater depression [25]

## 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<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub> 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]

| Table 4.1 Data to be con      | TWO-PHASE EXTRACTION DUAL PHASE EXTRACTION |              |                | CTION          |             |                |   |  |
|-------------------------------|--|--------------|----------------|----------------|-------------|----------------|---|--|
| GOAL PARAMETERS               | LNAPL recovery                             | SVE/BV       | GW<br>recovery | LNAPL recovery | SVE/BV      | GW<br>recovery | Comments  |  |
| Extracted LNAPL/water ratio   | x  |              |                | x              |             |                | Increasing level of applied vacuum favours the effect   |  |
| Groundwater extraction rate   | (X)  | (X)          | x              | (X)            | (X)         | х              | an increase in flow rates could increase the vacuum effect  |  |
| Drop tube depth setting       | х  | х            | х              |                |             |                | Check the extraction rate according to the depth reached  |  |
| Water table elevation changes | х  |              | х              | х              |             | х              | The changes are an indicator of the influence of pumping, greater depression, greater the recall of LNAPL |  |
| Vadose zone pressure changes  |  | х            |                |                | х           |                | The changes are an indicator of the influence of vacum  |  |
| Groundwater mass removal      | х  |              | х              | х              |             | х              | an increase in the rate may mean<br>that we are recalling the mass from<br>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        |  | х            |                |                | х           |                | Increasing level of applied vacuum favours the removal effect   |  |
| ·                             |  | <b>X</b> - p | arameters      | (X) - optiona  | al paramete | rs             | ·   |  |

## 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 aguifer 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.

#### **REFERENCES**

Documents are quoted in alphabetical order as: [Author/s, Year, Title, #]

- [1] AFCEE, 2001. United States Air Force Environmental Restoration Program: Guidance on Soil Vapour Extraction Optimization. Air Force Centre for Environmental Excellence, Brooks Air Force Base, Texas. Last accessed July 17, 2012, at http://www.dtic.mil/docs/citations/ADA392205;
- [2] <u>Berglund</u> S., <u>Cvetkovic</u> V.,1995: "Pump-and-Treat Remediation of Heterogeneous Aquifers: Effects of Rate-Limited Mass Transfer", groundwater vol. 33 - n.4
- [3] Cal/EPA, 2015: California Environmental Protection Agency, *Advisory Active Soil Gas Investigations*, Department of Toxic Substances Control.
- [4] Kuang et al., 2013 Review on airflow in unsaturated zones induced by natural forcings. Water Resour. Res., 49 (2013), pp. 6137-6165
- [5] EPA. 2001. Development of Recommendations and Methods to Support Assessment of Soil Venting Performance and Closure. EPA/600/R-01/070, U.S. Environmental Protection Agency, Washington, D.C.
- [6] Newell, C. J., S. D. Acree, R R. Ross, AND S G. Huling, 1995. "Light Nonaqueous Phase Liquids". U.S. Environmental Protection Agency, Washington, DC, EPA/540/S-95/500 (NTIS 95-267738), 1995.
- [7] RAE System, 2013 The PID handbook. Theory and Applications of Direct-Reading Photoionization Detectors,ISBN: 0-9768162-1-0
- [8] USACE. 2002. Engineering and Design: Soil Vapour Extraction and Bioventing. EM 1110-1-4001, U.S. Army Corps of Engineers, Washington, D.C. Last accessed July 17, 2012, at http://publications.usace.army.mil/publications/eng-manuals/EM\_1110-1-4001\_sec/toc.htm
- [9] USACE, 1999. Engineering and Design Multi-Phase Extraction, Engineer Manual 1110-1-4010, June 1999. from: <a href="https://www.publications.usace.army.mil/Portals/76/Publications/EngineerManuals/EM\_1110-1-4010.pdf">https://www.publications.usace.army.mil/Portals/76/Publications/EngineerManuals/EM\_1110-1-4010.pdf</a>
- [10] USEPA, 2008. A Systematic Approach for Evaluation of Capture Zones at Pump and Treat Systems Final Project Report, January 2008, EPA 600/R-08/003.
- [11] Truex, M. J., D. J. Becker, M. A. Simon, M. Oostrom, A. K. Rice, AND C. D. Johnson. "Soil Vapour Extraction System Optimization, Transition, and Closure Guidance", PNNL-21843. U.S. Department of Energy, Washington, DC, 2013.
- [12] USEPA. (1999). Multi-Phase Extraction: State-of-the-Practice. Retrieved in June 15, 2022 from: <a href="https://www.epa.gov/remedytech/multi-phase-extraction-state-practice">https://www.epa.gov/remedytech/multi-phase-extraction-state-practice</a>
- [13] USEPA. (1993). Presumptive Remedies Site Characterisation and Technology Selection for CERCLA Sites with VOCs in Soils. EPA/540/F-93/048. Retrieved in June 15, 2022 from: <a href="https://semspub.epa.gov/work/02/65012.pdf">https://semspub.epa.gov/work/02/65012.pdf</a>
- [14] Baker, R., Groher, D., Becker, D. (1999). Minimal desaturation found during multi-phase extraction of low permeability soils. *Ground Water Currents.* 33. Retrieved in June 19, 2022 from: <a href="https://cluin.org/products/newsltrs/gwc/gwc0999.htm#minimal">https://cluin.org/products/newsltrs/gwc/gwc0999.htm#minimal</a>
- [15] USEPA. (1997). Presumptive Remedy: Supplemental Bulletin Multiphase Extraction (MPE) Technology for VOCs in Soil and Groundwater. Retrieved in June 15, 2022 from: <a href="https://nepis.epa.gov/Exe/ZyPDF.cgi/2000L29B.PDF?Dockey=2000L29B.PDF">https://nepis.epa.gov/Exe/ZyPDF.cgi/2000L29B.PDF?Dockey=2000L29B.PDF</a>
- [16] FRTR. (2020). FRTR technology screening matrix: multi-phase extraction. Retrieved In June 21, 2022 from: <a href="https://frtr.gov/matrix/pdf/Multi-Phase Extraction.pdf">https://frtr.gov/matrix/pdf/Multi-Phase Extraction.pdf</a>

- [17] USEPA. (1997b). Analysis of Selected Enhancements for Soil Vapor Extraction. EPA-542-R-97-007. Retrieved in June 16, 2022 from: <a href="https://clu-in.org/download/remed/sveenhmt.pdf">https://clu-in.org/download/remed/sveenhmt.pdf</a>
- [18] Peyton, Leeson, and Gibbs. (1996). Bioslurping/Bioventing Demonstration in Tight Soils at Tinker AFB Southwest Tanks Site. Report No. AL/EQ-TR-1996-0046. Retrieved in June 19, 2022 from: <a href="https://apps.dtic.mil/sti/pdfs/ADA332738.pdf">https://apps.dtic.mil/sti/pdfs/ADA332738.pdf</a>
- [19] USEPA. (n.d.). MULTI-PHASE EXTRACTION AND PRODUCT RECOVERY. Air-Based Remediation Technologies. Retrieved in June 21, 2022 from: <a href="https://clu-in.org/download/techfocus/mpe/abr09-5-mpe.pdf">https://clu-in.org/download/techfocus/mpe/abr09-5-mpe.pdf</a>
- [20] ITRC. (2009). Evaluating LNAPL Remedial Technologies for Achieving Project Goals. Retrieved in June 21, 2022 from: <a href="https://frtr.gov/matrix/documents/Multiphase-Extraction/2009-Evaluating-LNAPL-Recovery-Technologies-for-Achieving-Project-Goals.pdf">https://frtr.gov/matrix/documents/Multiphase-Extraction/2009-Evaluating-LNAPL-Recovery-Technologies-for-Achieving-Project-Goals.pdf</a>
- [21] FRTR. (2020). Table 3-2. Treatment Technology Screening Matrix. Retrieved in June 26, 2022 from: https://frtr.gov/matrix2/section3/table3 2.pdf
- [22] Ji, W., Dahmani, A., Ahlfeld, D. P., Lin, J. D., and Hill, E., III (1993). Laboratory study of air sparging: air flow visualisation. *Ground Water Monitoring Rev.*, 13(4), 115–126.
- [23] Baker, R.S., Groher, D.M. (1998). Does multi-phase extraction require soil desaturation to remediate chlorinated sites? In: Wickramanayake, G.B., and Hinchee, R.B. (Eds.) Physical, Chemical and Thermal Technologies: Remediation of Chlorinated and Recalcitrant Compounds. pp. 175-180. Battelle Press, Columbus, OH.
- [24] Fact sheet presumptive remedy: supplemental bulletin multi-phase extraction (mpe) technology for vocs in soil and groundwater EPA, April 1997 directive No. 9355.0-68FS, EPA 540-F-97-004 PB97-963501, freely downloadable at <a href="https://semspub.epa.gov/work/HQ/174624.pdf">https://semspub.epa.gov/work/HQ/174624.pdf</a>
- [25] Multi-phase extraction Engineer Manual 1110-1-4010, Department of the Army U.S. Army Corps of Engineers Washington, DC 20314-1000Engineer Manual 1110-1-4010, July 1999, freely downloadable at https://www.publications.usace.army.mil/Portals/76/Publications/EngineerManuals/EM\_1110-1-4010.pdf?ver=2013-09-04-161049-977
- [26] USACE. 2002. Engineering and Design: Soil Vapour Extraction and Bioventing. EM 1110-1-4001, U.S. Army Corps of Engineers, Washington, D.C. Last accessed July 17, 2012, at <a href="http://publications.usace.army.mil/publications/eng-manuals/EM">http://publications.usace.army.mil/publications/eng-manuals/EM</a> 1110-1-4001 sec/toc.htm
- [27] EPA. 2001. Development of Recommendations and Methods to Support Assessment of Soil Venting Performance and Closure. EPA/600/R-01/070, U.S. Environmental Protection Agency, Washington, D.C.
- [28] RAE System, 2013 *The PID handbook. Theory and Applications of Direct-Reading Photoionization Detectors*,ISBN: 0-9768162-1-0
- [29] [30] USEPA, 2008. A Systematic Approach for Evaluation of Capture Zones at Pump and Treat Systems Final Project Report, January 2008, EPA 600/R-08/003.
- [31] Truex, M. J., D. J. Becker, M. A. Simon, M. Oostrom, A. K. Rice, AND C. D. Johnson. "Soil Vapour Extraction System Optimization, Transition, and Closure Guidance", PNNL-21843. U.S. Department of Energy, Washington, DC, 2013.
- [32] Cal/EPA, 2015: California Environmental Protection Agency, *Advisory Active Soil Gas Investigations*, Department of Toxic Substances Control.
- [33] Kuang et al., 2013 Review on airflow in unsaturated zones induced by natural forcings. Water Resour. Res., 49 (2013), pp. 6137-6165
- [35] EPA. 2001. Development of Recommendations and Methods to Support Assessment of Soil Venting Performance and Closure. EPA/600/R-01/070, U.S. Environmental Protection Agency, Washington, D.C.

- [35] Newell, C. J., S. D. Acree, R R. Ross, AND S G. Huling, 1995. "Light Nonaqueous Phase Liquids". U.S. Environmental Protection Agency, Washington, DC, EPA/540/S-95/500 (NTIS 95-267738), 1995.
- [36] Berglund S., Cvetkovic V.,1995: "Pump-and-Treat Remediation of Heterogeneous Aquifers: Effects of Rate-Limited Mass Transfer", groundwater vol. 33 - n.4