# (PP6) PILOT ACTION REPORT

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# 1 PILOT ACTION TITLE:

MONITORING OF THE AIR QUALITY IN BROWNFIELDS SUBJECT TO REMEDIATION

## 1.1 ACRONYMS

ARPAV: Agenzia Regionale per la Prevenzione e protezione Ambientale (Veneto Region Enviromental Protection Agency)

GC/MS: Gas Cromatography / Mass Spectrography

MLE : Multiple Lines of Evidence

S.I.N.: Sito di Interesse Nazionale di Venezia – Porto Marghera (Venice – Porto Marghera National Interest Megasite)

VOC: Volatile Organic Compound

# 2 AREA OF PA IMPLEMENTATION:

Veneto Region implemented its Pilot action in the site of Porto Marghera (Venice)

One of the main objective of the pilot action is to identify the different sources of chemicals in indoor air and to distinguish the contribution to air pollution related to VOCs migration from the subsurface.

Hence ARPAV conducted field tests based on a multiple line of evidence (MLE) approach within Porto Marghera Megasite to obtain a direct characterization of the VOCs migration process. In the MLE approach the decision making process is based on the investigation of different environmental media and all available results are evaluated to determine whether the vapour migration pathway is likely to be complete. The selected approach should help to distinguish the subsurface sources contribution to air pollution from contributions related to other sources, like anthropogenic background levels or productive cycles.

## 2.1 SELECTION OF FIELD TEST SITES

The criteria reported below guided contaminated sites selection for field test within Venice S.I.N. (Porto Marghera Megasite):

- depth to water table greater than 1 meter, to avoid soil gas probe installation in the vadose zone too close to ground level.
- high concentration of VOC in soil and/or groundwater;
- the owner agree to give the necessary logistic support;

Hence 5 areas were considered eligible for field tests:

- 1 site within “Refineries and Tanks” Macro-island (see deliverable D.T1.1.4-5-6), whose soil and groundwater are contaminated mainly by petroleum hydrocarbons;
- 2 sites within “New Petrochemical Plant” Macro-island, whose soil and groundwater are contaminated mainly by organochlorides;

- 1 site within "Old Petrochemical Plant" Macro-island, whose soil and groundwater are contaminated mainly by organochlorides;

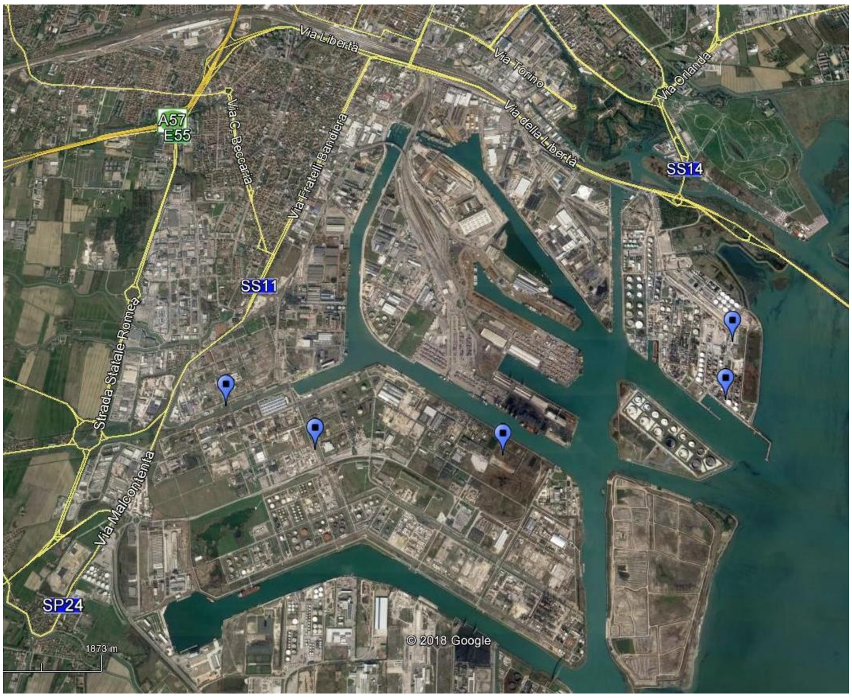

Figure 3: location of sites eligible for field tests

The next chapter describes the lithologic, hydrogeologic and contamination features of the sites selected to carrying out the experimental activities.

## 2.2 Features of Field Test Sites

Preliminary sites investigation were conducted in all eligible sites in order to select the most suitable for experimental activities. The investigation entailed portable instruments measurements as well as collection and subsequent analysis of air and soil gas samples. These preliminary data showed the absence of significant VOC concentrations in all the sites within the New Petrochemical Plant Macro-island. Data gathered in sites within Refineries and Tanks and Old Petrochemical Plant Macro-islands appeared, on the contrary, to be useful for carrying on the Pilot Action.

### 2.2.1 Feature of field test within the Old Petrochemical Plant Macro-island

The field test site is within Old Petrochemical Plant Macro-island, close to the end of the West Industrial Channel that separates the Old from the New Petrochemical Plant Macro-island. Site was selected for experimental activities because previous site assessments indentified the presence of high chlorinated hydrocarbon concentrations in groundwater. Moreover the absence of a pavement makes the area suitable for MLE approach application.

The surface soil consists of a coarse backfill (sand with gravel) up to 3 meters below ground level. The backfill is underlain by a succession of silty clay, clayey peaty silt and fine sand strata. The water table was approximately 1,5 m below ground level during all the monitoring period.

### 2.2.2 Feature of field test within the Refineries and Tanks Macro-island

Data collected by simultaneous monitoring of different gaseous matrices by an oil depot were used to assess COV migration process through vadose zone. The surface soil of the oil depot consists of a coarse backfill (sand with gravel) up to 1 meters below ground level that is underlain by clayey silt. The water table was approximately 1m below ground level during all the monitoring period. Previous site assessments indentified the soil as the matrix more contaminated by the presence of aliphatic and aromatic hydrocarbons.

# 3 DURATION OF PA IMPLEMENTATION:

The pilot action started in June 2017 when a document that collected concrete proposals for the redevelopment (procedures and projects) of Porto Marghera area was drafted and finished in February 2019 with the submission of the Final Report.

# 4 COSTS RELATED TO PA

A Collaboration Agreement was signed on 30 November 2017 by the General Manager on behalf of the ARPAV and the Director of the Environment Department on behalf of Veneto Region, , the latter Public Body will pay the former a total amount of 140,000.00 euros, that includes investment costs. The payment will follow the presentation of a statement of expenses incurred by ARPAV.

# 5 BACKGROUND AND CHALLENGE FACED

## 5.1 Main critical issues related with risk assessment for volatilization pathway.

For Italian law an assessment of risk posed by VOCs presence in the subsurface is necessary to support remedial decision and to calibrate site-specific target concentrations for various environmental media. Risk analysis usually implements transport models that consider soil or groundwater data to estimate indoor/outdoor air concentrations. The most common models are often simplified and not accounting for all fate and transport. An example of widely used transport model, embedded in a lot of risk analysis software, is the Johnson and Ettinger vapor intrusion model. It incorporates one-dimensional diffusion through the unsaturated zone and advection and diffusion through the building slab, but, not including biodegradation, the output may be very “conservative” in particular for aerobically degradable petroleum hydrocarbons.

A lot of guidelines and technical standards (related to risk analysis or gas sampling procedures) consider vapor intrusion models a useful tool to screen out sites that are deemed to require no further investigation. If a simplified and conservative model shows a not acceptable risk level for the volatilization route hence direct monitoring of gaseous matrices, and ambient air in particular, is suggested. Ambient air sampling and analysis provides a direct approach to obtaining concentrations of vapor-forming chemicals in indoor air to which building occupants can be exposed. A potential shortcoming of ambient air testing is that indoor and outdoor sources unrelated to subsurface may contribute to air pollution. Another issue that may affect air monitoring is the high temporal variability.

This report describes the experimental activities planned with the aim to develop a monitoring procedure that could fit risk assessment requirements, overcoming the aforementioned issues. The selected approach entails collecting and weighing multiple lines of evidence to characterize the vapor intrusion pathway. Some kinds of measurement are less influenced by background values (for example soil gas sampling or flux chamber measurement) helping to distinguish the subsurface contribution to air pollution.

## 5.2 Main critical issues related to soil gas and ambient air sampling in Porto Marghera Megasite

The peculiar geologic and hydrologic conditions of Porto Marghera Megasite area may be critical issues for soil gas and ambient air sampling.

The medium-fine superficial and high moisture levels, related to the shallow water bearing unit, may significantly reduce the effective rate of diffusive transport or even impede vapour migration. The gas permeability of unsaturated geologic materials, in fact, is a function of both intrinsic permeability and moisture content.

In the planned activities multiple types samples of environmental media were collected to overcome the aforementioned issues. In particular lines of evidence that do not force extraction of the vapours from the vadose zone and cause minimal disruption of the vapours equilibrium was considered, as for example flux chamber measurement, or passive soil gas sampling.

# 6 PA OBJECTIVES

This report describes the experimental activities realized to achieve the following goals:

- to develop monitoring procedures for gaseous matrices that could fit risk assessment requirements;
- to study the temporal variability of VOCs concentrations and their link with soil-atmosphere dynamics;
- to choose best sampling techniques for Venice – Porto Marghera Megasite i.e. for contaminated sites characterized by superficial water bearing unit and medium-fine soil texture.

# 7 ACTIVITIES CARRIED OUT

ARPAV realized field tests based on a multiple line of evidence (MLE) approach to obtain a direct characterization of the VOCs migration process. In the MLE approach the decision making process is based on the investigation of different environmental media and all available results are evaluated to assess risk related with the vapour migration pathway, if complete. The selected approach helped to distinguish the subsurface sources contribution to air pollution from contributions related to other sources, like anthropogenic background levels or productive cycles. The investigated media (lines of evidence) are reported below.

## 7.1 ACTIVE SOIL GAS SAMPLING

Soil gas sampling generally consists of installing a probe into the ground, drawing gas out of the probe, and collecting the gas for subsequent analysis.

The probes, installed in boreholes, are constructed in a similar fashion to groundwater monitoring wells: a vapour probe is placed inside a borehole, coarse drainage material is placed surrounding the screened portion of the probe, and a bentonite seal is constructed above the screened portion of the probe up to ground level.

Small diameter tubing (3 to 25 mm, i.e. 1/8 to 1 inch) were used to minimize the volume of air needed to purge the probe.

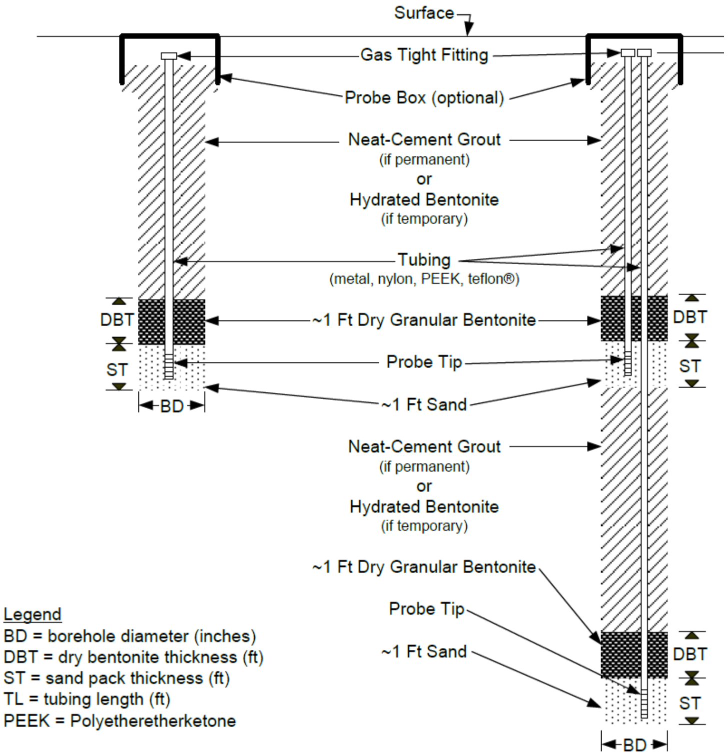

Figure 1: Typical single and multiple soil gas probe design.

In the past the main sampling technique used during ARPAV air and soil gas sampling is direct collection with canister and tedlar bags (the latter for very contaminated gas).

Tedlar bags are filled using vacuum box in order to avoid pumping system contamination.

The use of canisters for soil gas monitoring has many advantages over other methods: first of all the collection of smaller volumes requires less complicated sampling systems and minimize the risk for short-circuiting with atmospheric air through soil surface and risk of stripping from soil.

Holding times are not a critical point for canister, because samples are stable for up to 30 days (ambient conditions); whereas storage time for tedlar bags must be less than 24 hours.

Sample collection using canister allows multiple analysis on the original sample, it is suitable for a wide concentration range and is less influenced by high moisture levels.

Drawbacks of this approach are the cost of the device and the difficult cleaning routine for high contaminated samples. In order to get the best from both techniques, evacuated glass bottles (vacuum bottles) were selected as soil gas samplers: glass bottles are cheaper and can be easily cleaned with ultra pure water when highly contaminated.

The selected analysis method for soil gas are Compendium Method EPA TO-15 (VOCs) and MADEP APH 2009 (Air Phase Petroleum Hydrocarbons).

Concentration of pollutants in soil gas could be affected by sampling variables, such as flow rate, purge and sample volumes. Most of all, flow rate should be maintained as low as possible, in order to prevent ambient air from diluting the soil gas samples and to avoid excessive and unnatural partitioning of volatile organic compounds (VOCs) from soil/pore water to soil gas (induced stripping).

Therefore in study sites a low-flow purging and sampling was conducted. In particular, the purge flow rates were between 100 to 200 ml·min$^{-1}$ (Cal/EPA, 2015). Soil gas was collected connecting the bottles to a valve that contains a filtered orifice restricted sampler. Hence fill rates are constant and equal to 50 $ml \cdot min^{-1}$ until the glass canister reaches one-half atmosphere.

Moreover as general target, purge and sample volumes should also be minimized, in order to reduce the potential for short-circuiting with atmospheric air through soil surface.

In most of cases 2-3 purge volumes will be extracted, where the purge volume is estimated by summation of the internal volume of tubing and the void space of the sand pack around the probe tip (Cal/EPA, 2015).

When using canisters, sample size is known and coincides with the container volume. In the planned activities 1l vacuum bottle was used.

In many of the considered monitoring sites, an oxygen and carbon dioxide measurement was carried out contextually to total VOCs concentration measurement. Such measurements were performed before and after sampling, in order to estimate temporal variability of VOCs concentrations in soil gas samples. Furthermore, temporal variability of $O_2$ and $CO_2$ (and possibly $CH_4$, $H_2S$) concentrations can be considered as an indirect leak test. Volumes of soil gas extracted by field detectors must be considered in the calculation of the purged volume.

During soil gas surveys the following sampling procedure was adopted:

1. low flow purging;
2. taking measurements of total VOCs concentration, using field detectors (e.g. PID);
3. taking measurements of light gases concentration (oxygen, carbon dioxide, methane...), using field detectors (multi-gas detector);
4. sampling;
5. taking measurements of Total VOCs concentration;
6. taking measurements oxygen, carbon dioxide, methane using field detectors.

In some sites a leak test with Helium was conducted after probe installation. This kind of leak test, that entails the use of a shroud and a gaseous tracer compound, allows a quantitative determination of a leak either in the sampling train or from ambient air intrusion down the borehole (Cal/EPA, 2015).

## 7.2 Passive soil gas sampling

Passive sampling can be defined as any sampling technique based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potential of the analyte between the two media.

Passive soil gas sampling consists of burying an hydrophobic adsorbents contained in a chemically inert housing that must facilitate vapor diffusion to the adsorbent. The sampler is subsequently retrieved for analysis. Unlike active soil gas sampling, passive sampling does not force soil gas into the sampling vessel through pumping or vacuum. Instead, as the vapors disperse from a subsurface contaminant source, the sorbent acts as a sink for the VOCs found in soil gas.

Passive samplers are of two general varieties depending on the uptake region in which they operate: kinetic (linear region) and equilibrium samplers (steady-state region); the transitional regime between the two is avoided.

Advantages of the passive soil gas methods are:

- detects compounds with low vapor pressures not easily captured by active methods, such as naphthalene;
- maintains subsurface equilibrium during sampling since there is no forced movement of soil gas into the sampling vessel with passive methods;

- simple to design, install, and retrieve;
- ability to sample soils having low to high permeability and/or low to high soil moistur.

The major obstacle that limits the introduction of passive sampling techniques is that the concentration of the soil vapor depends on many variables (soil particle size, moisture contents, temperature…), leading to difficulties in converting the amount of analyte collected by the sampler to its concentration in the sampled medium.

## 7.3 Flux Chamber

Direct measurement of compound fluxes has been commonly performed in the oceanographic, soil science, and natural resource exploration (i.e., petroleum and minerals) communities for many years. The approach has been recently applied to environmental risk assessment.

The enclosure approach uses an enclosure device, referred to as an emission isolation flux chamber (flux chamber), to sample gaseous emissions from a defined surface area.

Emission flux measurements provide an estimate of the amount of a single species or multiple species being emitted from a given surface area per unit time. These data can then be used to develop emission rates for a given source for purposes of predictive modelling for population exposure assessments.

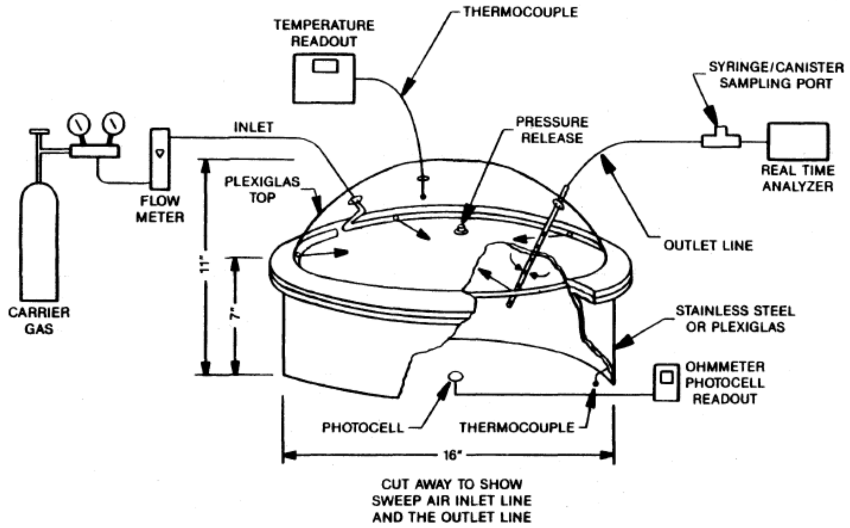

**Figure 2:** *Diagram of a flux chamber and support equipment*.

There are basically two different types of flux-chamber methods: the static chamber and the dynamic-chamber method.

In the dynamic method an inlet gas (sweep gas) is continuously introduced into the chamber during the purge period and an equivalent amount of the chamber gas is allowed to escape.

The system is assumed to reach a steady-state concentration after four or five chamber-residence times, where one residence time equals the chamber volume divided by the sweep-gas flow rate.

At steady state, the contaminant concentration in the outlet gas is equivalent to the concentration in the chamber.

The emission flux is calculated as:

$$J = \frac{C_{in} \cdot Q_{in}}{A}$$

where:

J = emission rate of species

$C_{in}$ = measured concentration into the chamber

$Q_{in}$ = sweep gas flow rate

A = emission surface area.

Air concentration of different VOCs can be estimated using the corresponding flux values.

## 7.4 Indoor/outdoor air

Ambient air sampling results are used to assess the presence of and level of human health risk posed by vapor-forming chemicals in indoor/outdoor air and to determine whether the vapour migration pathway is likely to be complete. A potential shortcoming of indoor air testing is that indoor sources and outdoor sources unrelated to subsurface contamination may contribute to the total exposure. Another issue that may affect air monitoring is the high temporal variability.

# 8 TECHNICAL SPECIFICATIONS AND SOLUTIONS TESTED

There are several categories of air monitoring methodologies, the selection of which is determined by the project quality objective. These methodologies range in sophistication from screening methods which use direct-reading instruments with relatively low precision and accuracy to collection methods which are the most precise and accurate.

There are also analytical field methods which involve aspects of both the direct reading and collection methodologies (all categorized as “analytical methods”). Analytical methods incorporate air sampling as well as on-site detection and quantification of chemical compounds. These methods differ from collection methods, which can typically achieve a more sensitive quantification limit. VOC collection methods involve the concentration or collection of the compound into a container or onto some kind of sorbent material for later analysis. The monitoring techniques selected to carrying out the planned experimental activities are reported below.

## 8.1 ENVIRONMENTAL PARAMETERS RECORDING

As mentioned before, weather and hydrological conditions (temperature, wind, barometric pressure, solar irradiance, rainfall, groundwater level) may influence pollutants concentration. Hence, it’s essential to record weather conditions (in particular: temperature, humidity and barometric pressure) , during the sampling period. This data was directly measured with portable instruments or obtained from the nearest weather station.

## 8.2 Field methods

The field automatic instruments employed during experimental activities are listed below:

- Photo Ionization Detector (PID): the instrument was used for a direct measure of total VOC concentration in air and soil gas. The instrument is characterized by a wide measurement range, detecting gases down to ppb levels up to 20.000 ppm. It can work with high humidity and contamination levels. The PID was used to select the best sampling points.
- Portable light gases analyzer: oxygen, carbon dioxide, methane and hydrogen sulphide concentrations data were collected contextually to total VOCs concentration measurement. Such measurements were performed before and after sampling, in order to estimate temporal variability of soil gas composition. Furthermore, temporal variability of $O_2$ and $CO_2$ concentrations can be used as an indirect leak test.
- Portable instruments with differential pressure sensor: the instruments were used to check the flux chamber sampling procedure. Moreover the differential pressure measurement between soil gas and outdoor air was important to study the influence of soil-atmosphere dynamics on soil gas VOCs concentrations.

## 8.3 Analytical field methods – Portable GC/MS

Further sampling round will be conducted in order to consolidate the dataset collected during the Project. In this occasion soil gas monitoring will be conducted using a portable Gas Chromatography/Mass Spectrometry (GC/MS). This instrument, with low responsive time, allows VOC's quantitative determination directly on field.

Mobile GC/MS is a sensible technique allowing quantitative and nearly instantaneous analysis of many soil gas contaminants and it can be used instead of laboratory analysis. Care needs to be taken in choosing monitoring spots: since only instantaneous sampling is possible it might be necessary to repeat measurements of the same sampling point at different times.

In case of highly contaminated soil gas, the samples should be collected and analyzed in the laboratory, in order to avoid instrument contamination.

## 8.4 Direct-Sampling methods – glass and steel canister

The sample may be collected directly into canisters, without any treatment before. ARPAV employed steel canister to collect air samples and glass canister to collect soil gas samples.

Steel Canisters may be difficult to clean out after sampling highly concentrated soil gas samples. Glass canisters have the same performances as steel canisters but are cheaper and can be easily cleaned with ultra pure water when highly contaminated

## 8.5 Indirect-sampling methods

Indirect sampling methods are based on VOCs and SVOCs capture on absorbent tubes. Since we are dealing with active sampling techniques, a pump pulls the soil gas through the absorbent medium, which is chosen depending on the compounds to be monitored.

On the one hand the advantages of this technique are the low cost of the samplers, easiness of use and a non critical holding time. On the other hand critical points are the risk of breakthrough or surface gas sampling depending on the sampling time and flow, the selectivity on the basis of the absorbent medium, the inconsistency with humid samples.

### 8.5.1 Passive sampling

Passive sampling is suitable for characterization of longer-term duration (up to three weeks) average concentrations of VOCs. These simple sampling devices may be more practical than other methods from a cost and logistical viewpoint for routine, longer-term indoor air sampling.

## 8.6 Analytical methods

Target compounds are chemicals believed to be present, used, or released at the site.

To ensure a more accurate analysis, ARPAV purchased an autosampler for canister analysis by GCMS, equipped with loop injection. The VOC concentration range in soil gas, infact, can be very wide, hence the autosampler ensure a more performing analysis in particular for highly contaminated samples, reducing the need for dilution, that increases analytical error.

Soil gas and air samples were analyzed using EPA TO 15 for organochlorine compounds and MADEP APH 2009 (Air Phase Petroleum Hydrocarbons) for hydrocarbons compounds.

# 9 IMPACT/ RESULTS/ EXPERIENCE (HOW MANY TARGET GROUPS/ STAKEHOLDERS WERE REACHED, PILOT EVENTS)

## 9.1 Temporal variability assessment of VOCs concentration in soil gas and other environmental media

Weather conditions (temperature, wind, barometric pressure, solar irradiance, rainfall) and hydrologic factors (groundwater elevation) may influence vapour migration and attenuation in soil gas concentrations between subsurface vapour sources and the ground level.

In particular conditions ambient air may migrate into the vadose zone influencing the chemical composition of soil gas. The depth of penetration increases as the thickness and permeability of the vadose zone increases.

During the experimental activities high frequency soil gas sampling was conducted to assess how the short-term temporal variability in subsurface vapour migration occurs in response to changes in weather conditions.

## 9.2 Preliminary meteorological data processing

One of the main goals of the performed experiments is to verify the temporal variability of the gaseous matrices' chemical properties; in order to understand the dynamics that affect the soil-air interface. Especially, (see Figures 4-5) this study focuses on the short-term variability of the COV's concentrations (hourly variability) with respect to the meteorological parameters variability.

In order to define the right timing for the sampling, we performed a preliminary retrospective statistical analysis of the time series data of the Ente Zona Industriale's weather stations.

Specifically, we evaluated the daily trend of several parameters: atmospheric pressure, temperature, humidity, solar radiation.

According to the daily trend of the aforementioned parameters for the summer time, and considering the impossibility of acquiring data over night at Petrochemical Plant, we decided to perform the sampling over three different times of the day. In the early morning, when the effect of solar radiation on temperature and humidity, at ground level, is minimal. In the late morning/early afternoon, when those parameters have reached, respectively, their minimum and maximum.

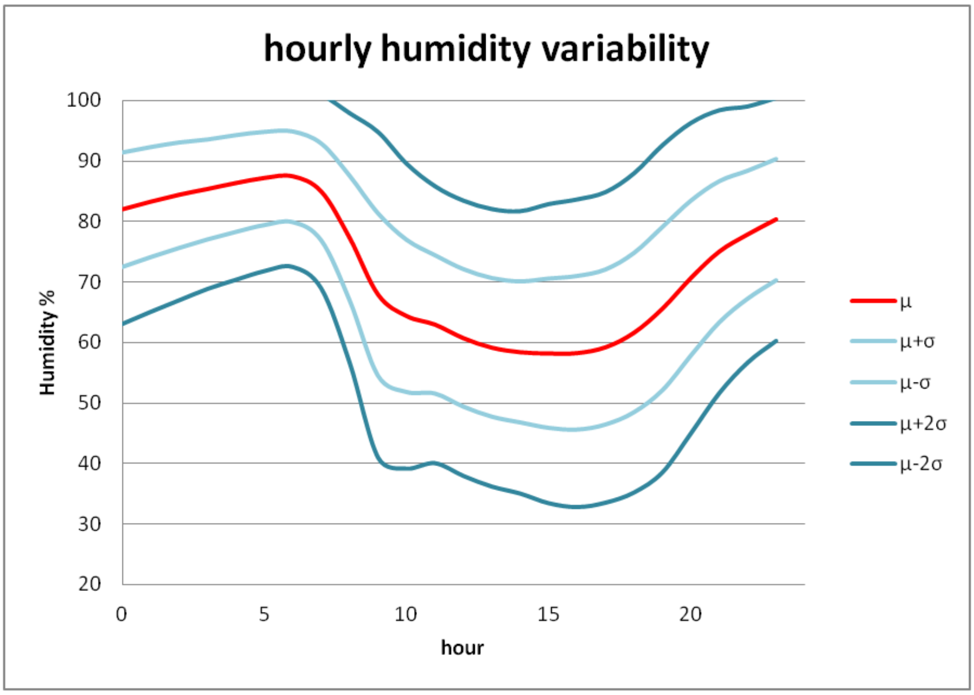

**Figure 4**: *Hourly humidity variation.*

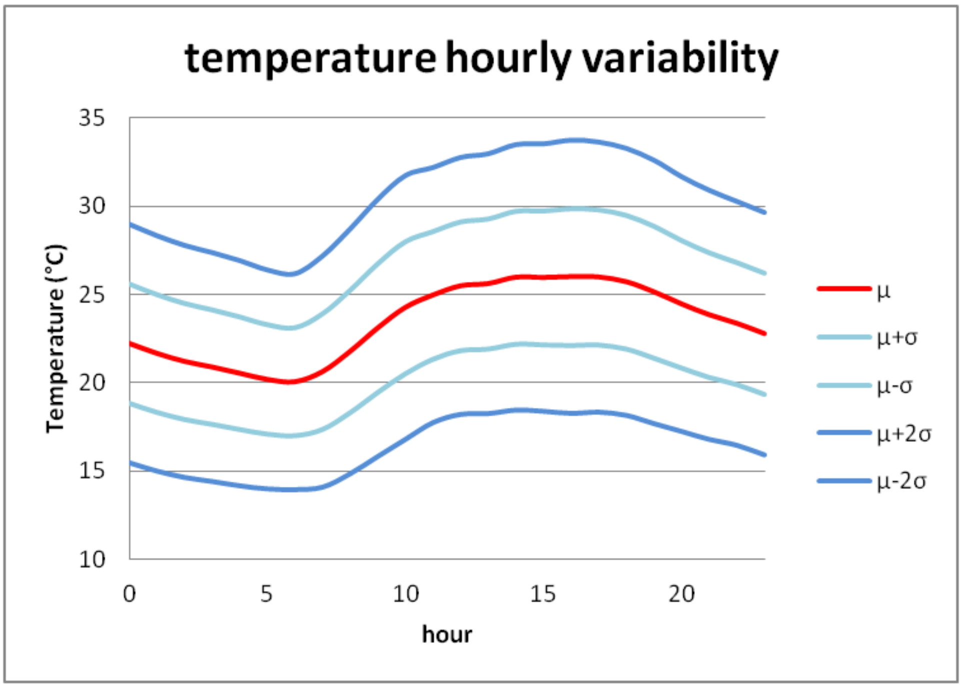

**Figure 5**: *Hourly temperature variation.*

## 9.3 Short-term temporal variability VOC concentrations in gaseous matrices

The daily trends of the COV's concentration in the soil gas, observed in most of the surveys, show similar results with respect to the measurements performed on the 19/07/2018 (see Figure 6).

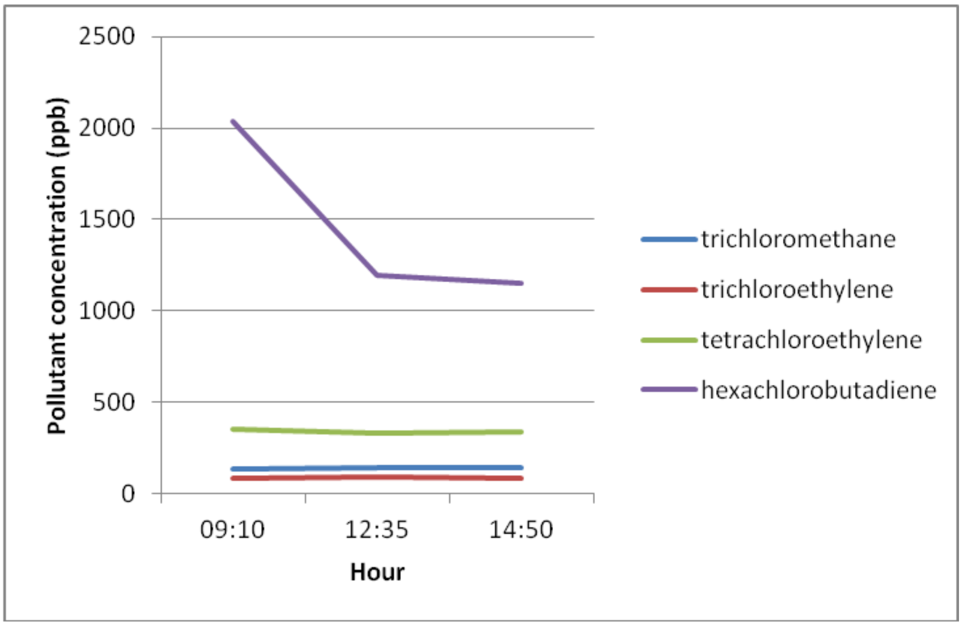

**Figure 6:** *19/07/2018 COV's concentration trend in the soil gas.*

Figure 6 shows a noticeable decrease in hexachlorobutadiene concentration from 9.30 to 12.45, whereas concentrations of trichloromethane, trichloroethylene and tetrachloroethylene remain constant. Analysis of this data may infer that hexachlorobutadiene, presenting higher concentrations the soil gas, accumulates overnight in the proximities of ground level. This effect may be due to a negative pressure differential between soil and atmosphere (over night, air pressure is probably higher than soil gas pressure). The other substances, being present in smaller concentration, show a tendency to distribute in the soil column, with no evident accumulation phenomenon.

In order to provide further means of interpretation for the aforementioned results we present, here, the results for some continuous measurements. These measurements were obtained with automatic instruments, in a site external to SIN, when sites for field tests were not identified yet.

In particular Figure 7 shows the daily trend of differential pressure between soil gas and ambient air.

From the graph, we can infer that the differential pressure between soil gas and air present a cyclical variation. Overnight, the soil gas pressure is lower than the atmospheric pressure, impeding the emission of the COV from the soil and producing an accumulation phenomenon under the ground level (at least, for the most concentrated compounds). When the soil heats-up, thanks to solar radiation, the soil gas pressure increases until it exceeds atmospheric pressure, and therefore finally producing vapour emission.

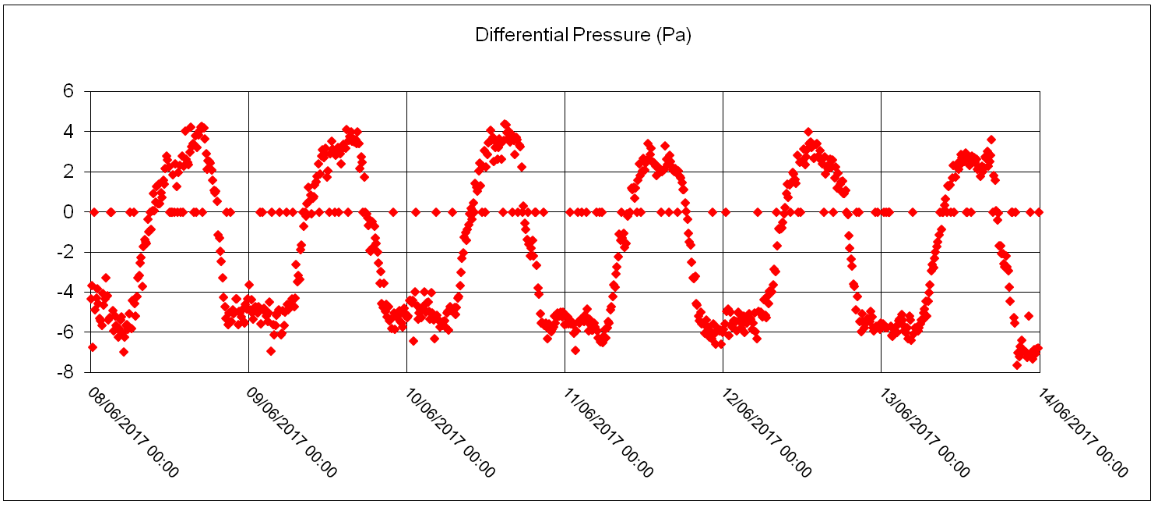

**Figure 7:** *Differential pressure daily trend between soil gas and ambient air*.

Hence, an increase in soil gas concentration does not necessarily correspond to an increase in VOC concentration in air and to an increase in the associated risk. As an example hourly trend of VOC air concentrations is reported below (fig.8).

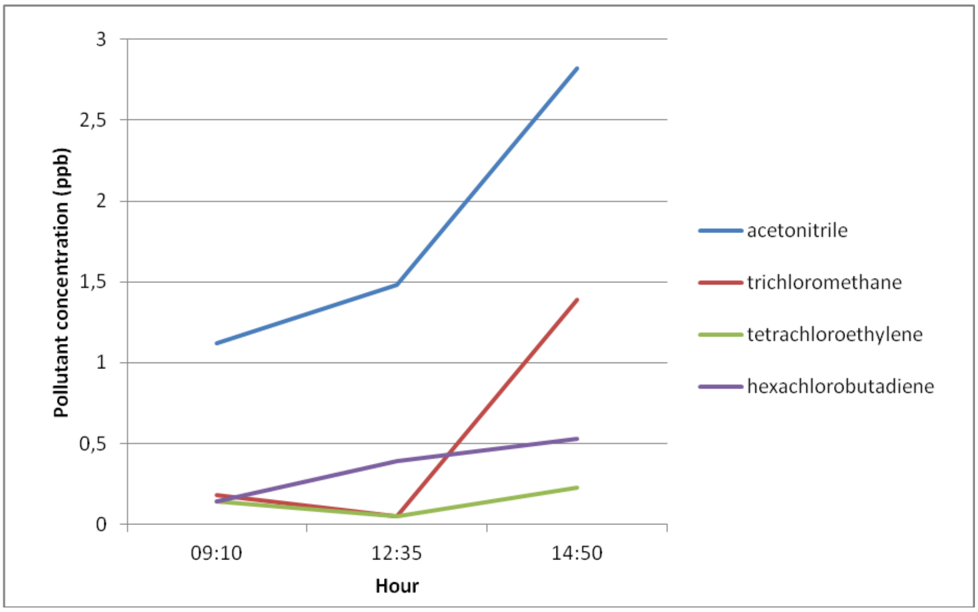

**Figure 8:** *13/09/2018 air pollutions concentrations trend.*

This trend does not follow the trend of the concentrations that were contemporarily measured in soil gas. Overnight and during early morning, the negative pressure differential fosters an accumulation of the COVs under the ground line but, impeding emissions in the atmosphere, does not lead to an air quality deterioration.

The daily trend of concentrations in air does not necessarily follow, therefore, that of concentrations measured simultaneously in soil gas, because during the night and early morning the negative pressure differential fosters an accumulation of VOCs below the ground level but, impeding the emission into atmosphere, does not cause an immediate deterioration of air quality.

## 9.4 Estimating vapour migration process in soil

The assessment of risk posed by VOCs presence in the subsurface is necessary to define remediation goals and to decide upon the possible reuse of a brownfield. Transport models implemented in risk analysis are often simplified and, not accounting for all fate and transport processes, may be very “conservative”. Hence, simultaneous measurements of different gaseous matrices were conducted to directly verify COV migration and attenuation processes through vadose zone. In particular ratio of COV concentrations measured in different matrices were calculated to obtain experimental attenuation factors to be compared with model estimation.

## 9.5 Volatilization pathway simulation using fate and transport models

A risk analysis was performed for volatilization pathway, firstly based on the results of soil and groundwater assessment in the selected sites.

The results of geological, hydrogeological and geothecnical surveys performed during the first site assessment were used to provide the site-specific parameters necessary to implement risk analysis and the transport models.

Risk calculated from soil gas and flux chamber data is usually lower than risk calculated estimating the entire transport process from soil and groundwater to atmosphere.

The estimation of the exposure to the vapours coming from the subsoil using a multiple lines of evidence approach thus leads to a more realistic and less conservative risk assessment, allowing a better calibration of remediation goals.

The next paragraph compares measured and predicted VOC concentrations for each gaseous matrix. In this way it is possible to evaluate which phase of the transport process is correctly simulated by models and which is overestimated. The comparison between model outcomes and monitoring results suggests the presence of further sources of contamination, not identified during the preliminary site assessment and therefore to determine the need for investigative supplements.

Site-specific data, necessary to implement fate and transport models together with risk analysis results are reported in APPENDIX 2 and 3.

## 9.6 Comparison between predicted and measured VOC concentrations for gaseous matrices

The next paragraph describes the monitoring results for sampling rounds in which several parameters were detected in all gaseous matrices. VOC concentrations measured in each matrix are compared with concentrations predicted for the same matrix by transport models.

### 9.6.1 Comparison between model estimation and monitoring results for Petrochemical Plant test site.

In most of the simulations carried out for this project and for other cases, the predicted concentrations in soil gas, in the flow chamber and in ambient air are higher than those actually measured. For example, it is the case of tetrachloroethylene concentrations detected during the autumn campaign within the Old Petrochemical site, compared below with the results of the transport models estimate.

**Table 1:** *Comparison between predicted and measured VOC concentrations for Petrochemical Plant site*

| **Petrochemical Plant 13/09/2018** | **WATER** | **SOIL GAS** | | **CHAMBER** | | **AIR** | |
|---|---|---|---|---|---|---|---|
| UoM | µg/L | µg/m$^3$ | µg/m$^3$ | µg/m$^3$ | µg/m$^3$ | µg/m$^3$ | µg/m$^3$ |
| Parameter | *measured* | *calculated* | *measured* | *calculated* | *measured* | *calculated* | *measured* |
| Tetrachloroethylene | 8.9E+03 | 2.0E+05 | 2.29E+03 | 8.88E+02 | 5.03E+00 | 2.22E+00 | 1.9E-01 |
| Hexachlorobutadiene | 6.0E+01 | 8.8E+02 | 1.30E+04 | 2.60E+00 | 2.87E+02 | 5.16E-03 | 4.2E+00 |
| Trichloromethane | 5.5E-01 | 3.1E+00 | 6.96E+02 | 2.13E-02 | 1.44E+00 | 5.32E-05 | 7.9E-01 |

For hexachlorobutadiene and trichloromethane, on the other hand, despite the known tendency to overestimate of transport models, VOC concentrations measured in soil gas and in the chamber are higher than concentrations calculated estimating the volatilization pathway from groundwater.

The reason for this unusual model underestimate is probably the presence of an unidentified source in the soil. In this case soil gas monitoring techniques, even if less consolidated than those used to collect soil samples, allow a better estimate of VOCs presence in the subsurface, due to a greater spatial representativeness (because it is representative of a greater volume of soil).

In the next table the comparison between estimated and experimental attenuation factors (i.e. the ratio of VOC concentrations measured in two different environmental matrices) corroborates the above reported considerations and at the same time allows to understand which phase of the transport process is correctly simulated by the model and which is overestimated.

**Table 2:** *Predicted and experimental attenuation factors.*

| **Petrochemical Plant - autumn survey** | **WATER/SG** | | **SG/FC** | | **FC/AIR** | |
|---|---|---|---|---|---|---|
| *Parameter* | *calculated* | *measured* | *calculated* | *measured* | *calculated* | *measured* |
| Tetrachloroethylene | 4.5E-02 | 3.9E+00 | 2.2E+02 | 4.5E+02 | 4.0E+02 | 2.7E+01 |
| Hexachlorobutadiene | 6.8E-02 | 4.6E-03 | 3.4E+02 | 4.5E+01 | 5.0E+02 | 6.8E+01 |
| Trichloromethane | 1.8E-01 | 7.9E-04 | 1.5E+02 | 4.8E+02 | 4.0E+02 | 1.8E+00 |

In the case of organo-chlorinated compounds, poorly biodegradable under normal environmental conditions, the overestimate seems to concerns mainly the water/soil gas partition coefficient, usually calculated using the Henry's Law constant, while the migration through the vadose zone is correctly modelled.

## 9.6.2 Comparison between model and monitoring results for Oil Depot test site.

VOC concentrations of aliphatic hydrocarbons measured in soil gas and in the chamber, as for some chlorinated compound, are higher than concentrations calculated estimating the volatilization pathway from soil.

Again, the most reasonable explanation for this anomalous model underestimation is the presence of an unidentified source for these substances in soil.

**Tabel 3:** *Predicted and experimental attenuation factors.*

| **Oil Depot** | **SOIL** | **Soil gas** | | **chamber** | | **Air** | |
|---|---|---|---|---|---|---|---|
| UoM | mg/kg | mg/m$^3$ | mg/m$^3$ | mg/m$^3$ | mg/m$^3$ | mg/m$^3$ | mg/m$^3$ |
| **Parameter** | ***measured*** | ***calculated*** | ***measured*** | ***calculated*** | ***measured*** | ***calculated*** | ***measured*** |
| Aliphatic hydroc. C5-C8 (S1) | 8.1E+01 | 4.1E+01 | 9.30E+02 | 3.03E-02 | 7.90E-02 | 7.00E-05 | 5.7E-01 |
| Aliphatic hydroc. C9-C12 (S1) | 1.2E+03 | 5.6E+02 | 6.20E+02 | 3.65E-01 | 1.10E+00 | 9.10E-04 | 2.1E-01 |
| Aliphatic hydroc. C5-C8 (S2) | 6.6E+01 | 1.2E+03 | 1.36E+04 | 8.54E-01 | | 2.13E-03 | |
| Aliphatic hydroc. C9-C12 (S2) | 1.2E+02 | 1.1E+03 | 2.79E+03 | 7.00E-01 | 1.20E+00 | 1.70E-03 | 2.7E+00 |

Table 3 shows that measured hydrocarbons concentrations in air exceed by different orders of magnitude those estimated for the same matrix. Hydrocarbons overabundance in air, compared to model forecast, is certainly due to the emissions produced by the activities carried out on site. In the case of Oil Depot the overall contribution of emissions from the subsoil to air pollution is, therefore, clearly negligible compared to contribution related to other sources.

**Table 4:** *Predicted and experimental attenuation factors.*

| **Depot** | **SOIL/SG** | | **SG/FC** | | **FC/AIR** | |
|---|---|---|---|---|---|---|
| *Parameter* | *calculated* | *measured* | *calculated* | *measured* | *calculated* | *measured* |
| Aliphatic hydroc. C5-C8 (S1) | 2.0E+00 | 8.7E-02 | 1.3E+03 | 1.2E+04 | 4.3E+02 | 1.4E-01 |
| Aliphatic hydroc. C9-C12 (S1) | 2.2E+00 | 2.0E+00 | 1.5E+03 | 5.6E+02 | 4.0E+02 | 5.2E+00 |
| Aliphatic hydroc C5-C8 (S2) | 2.0E+00 | 4.9E-03 | 1.6E+03 | 2.3E+03 | 4.1E+02 | 4.4E-01 |
| Aliphatic hydroc. C9-C12 (S2) | 2.2E+00 | 2.0E+00 | | | | |

The predicted attenuation factors, reported in Table 4, substantially confirm the considerations reported in this paragraph and in the previous one.

## 9.7 Summary of results

The Pilot Project n. 6 consists of experimental activities planned and realized to achieve the following goals:

1. to develop monitoring procedures for gaseous matrices that could fit risk assessment requirements;

2. to choose best sampling techniques for Venice – Porto Marghera Megasite i.e. for contaminated sites characterized by superficial water bearing unit and medium-fine soil texture;

3. to study the influence of soil-atmosphere dynamics on soil gas VOCs concentrations.

In particular ARPAV conducted field tests based on a multiple line of evidence (MLE) approach to obtain a direct characterization of VOCs migration process. In the MLE approach the decision making process is based on the investigation of different environmental media and all available results are evaluated to determine whether the vapour migration pathway is likely to be complete. The selected approach helped to distinguish the subsurface sources contribution to air pollution from contributions related to other sources, like anthropogenic background levels or productive cycles.

Sampling surveys conducted to pursue the first objective highlight that risk calculated from soil gas and flux chamber data is usually lower than risk calculated simulating the entire transport process from soil and groundwater to atmosphere. Implementation of multiple lines of evidence approach, thus, leads to a more realistic and less conservative risk assessment, allowing a better calibration of remediation goals.

For some substance, however, despite the known tendency to overestimate of transport models, VOC concentrations measured in soil gas and in the flux chamber were higher than concentrations calculated estimating the volatilization pathway from soil and groundwater. The reason for this unusual model underestimate is probably the presence of an unidentified source in the soil. In this case soil gas sampling techniques, even if less consolidated than those used to collect soil samples, allow a better estimate of VOCs presence in the subsurface, due to a greater spatial representativeness.

Referring to the second objective all the monitoring techniques implemented in the Project, active soil gas sampling, flow chamber measurement and, of course, air sampling, proved to be suitable for Porto Marghera Megasite. Further sampling rounds will be conducted in order to consolidate the dataset collected during the Project and to test passive samplers for soil gas.

Measures carried out to pursue the third objective, within the Old Petrochemical site and in other sites outside SIN, showed that the differential pressure between soil gas and air presents a cyclic variation. In particular overnight the soil gas pressure is lower than the atmospheric one, impeding the emission of the COV from soil and producing an accumulation phenomenon in the proximity of ground level (at least, for the most concentrated compounds). When the soil heats-up, thanks to solar radiation, the soil gas pressure increases, until it exceeds the atmospheric pressure, and therefore finally producing vapour emissions. The daily trend of concentrations in air does not necessarily follow, therefore, that of concentrations measured simultaneously in soil gas, because during the night and early morning the negative pressure differential fosters an accumulation of VOCs below the ground level but, impeding the emission into atmosphere, does not cause an immediate deterioration of air quality. The sampling surveys carried out in the field test sites highlight the strong influence of the dynamics at the soil-atmosphere interface on the COVs concentrations in soil gas and air. Moreover, they show the importance of differential pressure measurement between those two matrices for the correct interpretation of the results.

## 9.8 Meetings with stakeholders

A joint meeting was held in 16/02/2018 between the three local partners with interested stakeholders to illustrate the pilot projects of the Porto Marghera area. About 25 technicians and experts from the most relevant institutions and enterprises based in Porto Marghera attended the meeting: City of Venice; North Adriatic Sea Port Authority, ports of Venice and Chioggia; Industrial Zone of Porto Marghera Association; Metropolitan City of Venice; large enterprises in the area. The meeting was aimed at informing on the foreseen activities and expected results and foster their contribution for a more effective implementation of the work. For the Veneto Region, the technical expert in charge for the activity, explained the design and the implementation of the air quality monitoring system in brownfield of Porto Marghera, underlining the need to take into account the level of subsoil contamination as well as the emissions of traffic or other agents during the monitoring process.

As part of the Urbanpromo event, promoted by the INU - National Institute of Urban Planning, ARPAV presented the pilot project in the session dedicated to the presentation and discussion of the results achieved by the European projects GreenerSites and Sustainable land use (21/09/2018). In the frame of this relevant event focused on urban sustainable urban planning and living conditions, a specific session dedicated to the GreenerSites project results was held, representing one of the three Local Pilot events to be organized at a local level.

At the end of the activities, on 14/01/2019, a conclusive event was held, during which the results of the three pilot projects of the FUA of Venice were illustrated to the same interlocutors of the first meeting.

# 10 CONTRIBUTION TO PROJECT OBJECTIVES

The results of Pilot Project 6 will hopefully lead to an update of soil gas and air monitoring procedures for contaminated sites and, therefore, of risk assessment procedures related with volatilization pathway.

These procedures, as better explained in the next chapter, are fundamental to improve brownfields remediation and rehabilitation processes.

# 11 TRANSNATIONAL ADDED VALUE - HOW PA CONTRIBUTED TO OTHER ACTIVITIES IMPLEMENTED BY THE PROJECT & ADDED VALUE FOR PARTNERS

Exposure to chemical vapours released from soil and groundwater is a critical issue in a great number of contaminated sites all around Europe. The assessment of risk posed by volatile compounds presence in the subsurface, hence, is necessary to decide upon the possible reuse of a brownfield. Transport models implemented in risk analysis are often simplified and, not accounting for all fate and transport processes, may be very conservative. On the other hand ambient air monitoring represents a more direct VOCs exposure assessment, that may, however, be uncorrect, because affected by the presence of backround pollutants and by high temporal variability. The monitoring procedures adopted in the PA entails simultaneous measurements of different gaseous matrices (as part of a multiple line of evidence approach), allowing to directly verify COV migration and attenuation processes through vadose zone. The estimation of the exposure to the vapours coming from the subsoil using a multiple lines of evidence approach thus leads to a more realistic risk assessment, allowing a better calibration of remediation goals.

A similar procedure was applied in the area of implementation of PA 3, to assess the effect of capping realized by North Adriatic Sea Port Authority on vapour migration in the subsoil.

The procedure tested in Porto Marghera could be adapted and therefore adopted in other Italian ad European brownfields.

# 12 COMPLIANCE WITH THE SUSTAINABILITY PRINCIPLES

The monitoring surveys carried out, within Porto Marghera Megasite during the PP activities, did not produce any relevant negative impact on the environment.

# 13 MEDIA COVERAGE

The activities were promoted through the project communication channels and the printing of illustrative material, disseminated during the events. No specific articles have been published in the press.

http://www.interreg-central.eu/GreenerSites

twitter.com/GreenerSites

www.facebook.com/GreenerSites

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# APPENDIX 2: OLD PETROCHEMICAL SITE RISK ASSESSMENT

## 3.1 SITE FEATURES

### SITE PARAMETERS: SOURCE GEOMETRY

| Parameter | Symbol | Default | Site-Specific | UM |
|---|---|---|---|---|
| **Source Geometry** | | | | |
| Width of source area parallel to groundwater flow direction | W | 45 | 45 | m |
| Width of source area orthogonal to groundwater flow | Sw | 45 | 45 | m |
| Ambient air mixing zone height | δair | 2 | 2 | m |
| Width of source area parallel to wind direction | W' | 45 | 45 | m |
| Width of source area orthogonal to wind direction | Sw' | 45 | 45 | m |
| **Surface soil** | | | | |
| Depth to surface soil source | Ls,SS | 0 | 0 | m |
| Thickness of unsaturated surface soil source | d | 1 | 1 | m |
| **Subsurface soil** | | | | |
| Depth to subsurface soil source | Ls,SP | 1 | 1 | m |
| Thickness of unsaturated subsurface soil source | ds | 2 | 2 | m |
| **Groundwater** | | | | |
| Depth to groundwater | Lgw | 3 | 1.5 | m |
| **Soil-gas** | | | | |
| Soil-gas depth below ground surface | Lsoilgas | 1 | 1 | m |
| **Flux Chamber** | | | | |
| Flowrate of the carrier gas in the chamber | Qin | 5 | 5 | L/min |
| Chamber surface exposed to soil | Afc | 0.5 | 0.5 | $m^2$ |

### SITE PARAMETERS: VADOSE ZONE

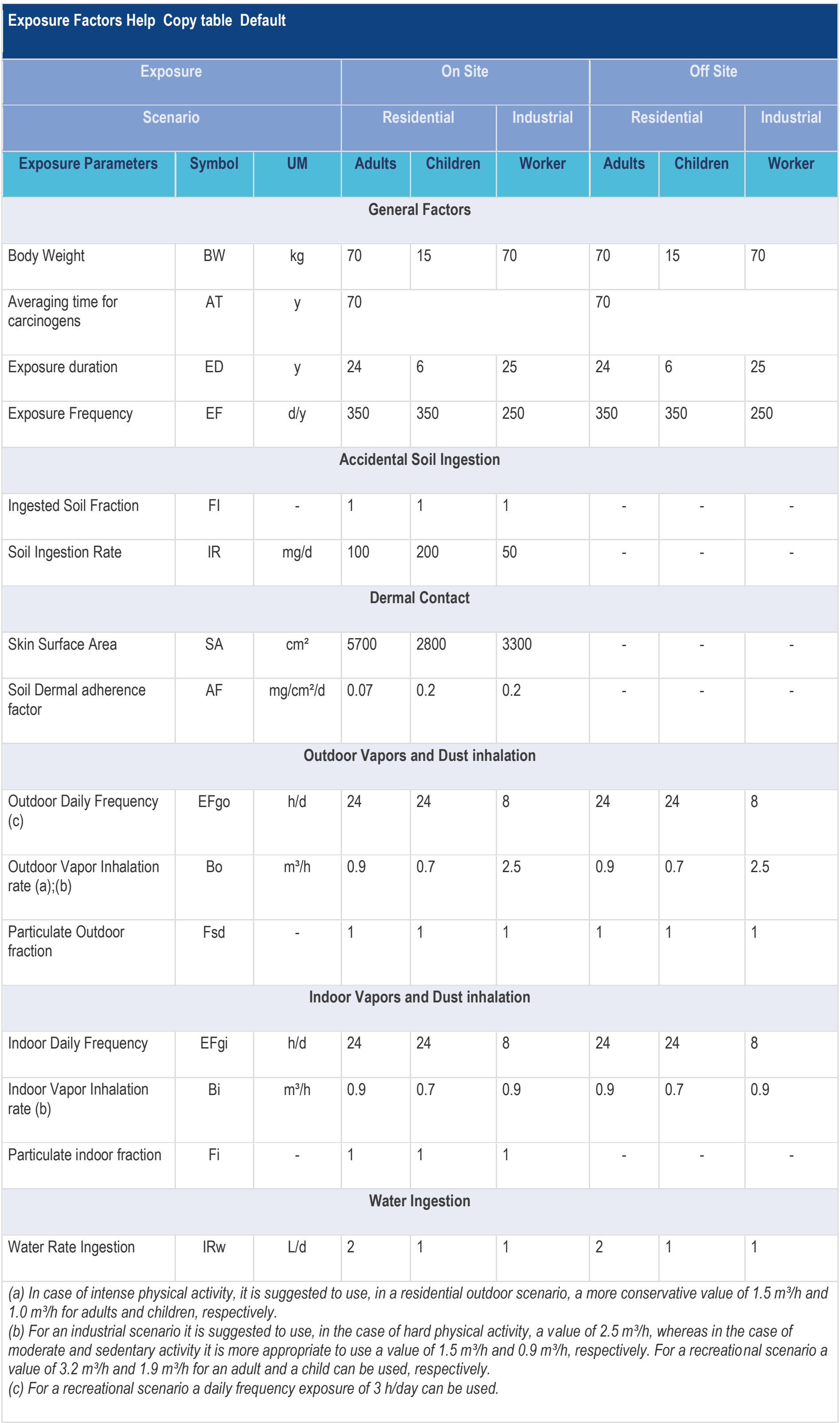
| Parameter | Symbol | Default | Site-Specific | UM |
|---|---|---|---|---|
| **Vadose Zone soil texture** | | | | |
| Effective porosity in the unsaturated zone | θe | Literature | 0.385 | - |
| Volumetric water content in the soil | θw | Literature | 0.068 | - |
| Volumetric air content in the soil | θa | Literature | 0.317 | - |
| Volumetric water content in the capillary fringe | θw,cap | Literature | 0.33 | - |
| Volumetric air content in the capillary fringe | θa,cap | Literature | 0.055 | - |

| | | | | |
|---|---|---|---|---|
| Capillary fringe thickness | hcap | Literature | 0.1 | m |
| Wetting front suction (matric potential) | hcr | Literature | -0.0402 | m |
| Hydraulic conductivity in the vadose zone | Ksat,s | Literature | 8.25e-5 | m/s |
| Ponding depth | Hw | 0.25 | 0.25 | m |
| **Vadose Zone properties** | | | | |
| Soil bulk density | ps | 1.7 | 1.7 | g/cm$^3$ |
| Soil pH | pH | 6.8 | 6.8 | - |
| Organic Carbon Fraction - surface soil | foc,SS | 0.01 | 0.01 | g/g |
| Organic Carbon Fraction - subsurface soil | foc,SP | 0.01 | 0.01 | g/g |
| Residual void fraction in the soil (for Cres) | Sr | 0.04 | 0.04 | m |
| Unsaturated zone thickness | hv | Calculated | 1.400 | m |
| **Infiltration through Vadose Zone** | | | | |
| Annuale Rainfall Rate | P | 129 | 129 | cm/y |
| Outdoor areal fraction of cracks | ηout | 1 | 1 | - |
| Soil Infiltration Rate | Ief | Calculated | 29.95 | cm/y |
| **Other intermediate parameters** | | | | |
| Groundwater mixing zone thickness | δgw | Calculated | 2.00 | m |
| Leachate dilution factor | LDF | Calculated | 4.70 | - |

## SITE PARAMETERS: OUTDOOR

| Parameter | Symbol | Default | Site-Specific | UM |
|---|---|---|---|---|
| **Meteorological data** | | | | |
| Wind speed | Uair | 2.25 | 1.5 | m/s |
| Particulate emission rate | Pe | 6.9e-14 | 6.9e-14 | g/cm/s$^2$ |
| **Atmospheric dispersion** | | | | |
| Distance to outdoor air receptor - ADF | POC ADF | 100 | 100 | m |
| Transversal air dispersion coefficient | σy | Calculated | 5.97 | m |
| Vertical air dispersion coefficient | σz | Calculated | 2.91 | m |
| Aerobic depth below ground surface | La Outdoor | 1 | 1 | m |

## 3.2 EXPOSURE FACTORS

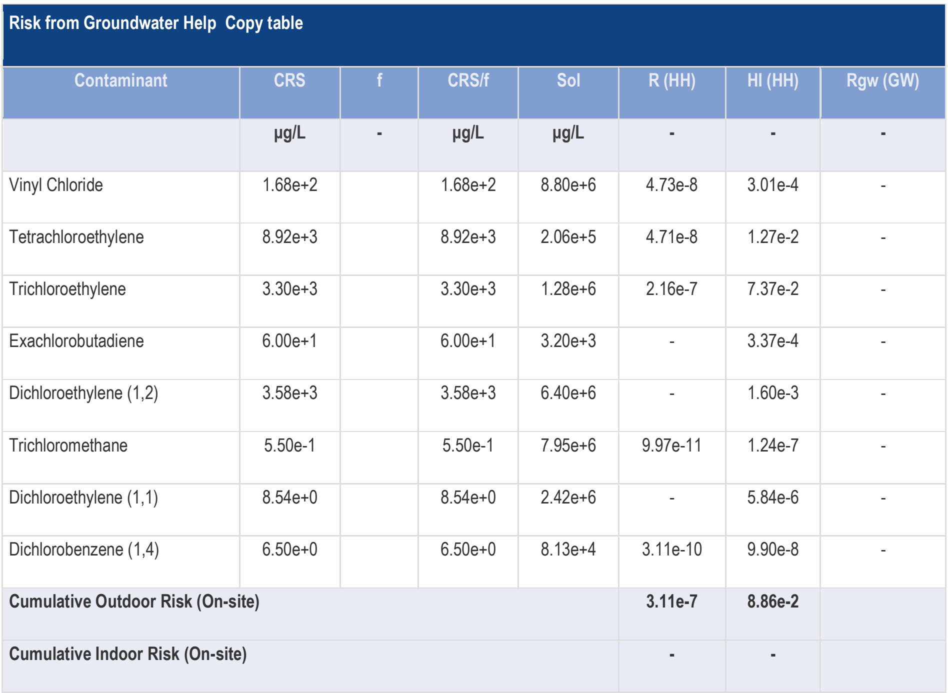


**Exposure Factors Help Copy table Default**

| Exposure | | | On Site | | | Off Site | | |
|---|---|---|---|---|---|---|---|---|
| Scenario | | | Residential | | Industrial | Residential | | Industrial |
| Exposure Parameters | Symbol | UM | Adults | Children | Worker | Adults | Children | Worker |
| **General Factors** | | | | | | | | |
| Body Weight | BW | kg | 70 | 15 | 70 | 70 | 15 | 70 |
| Averaging time for carcinogens | AT | y | 70 | | | 70 | | |
| Exposure duration | ED | y | 24 | 6 | 25 | 24 | 6 | 25 |
| Exposure Frequency | EF | d/y | 350 | 350 | 250 | 350 | 350 | 250 |
| **Accidental Soil Ingestion** | | | | | | | | |
| Ingested Soil Fraction | FI | - | 1 | 1 | 1 | - | - | - |
| Soil Ingestion Rate | IR | mg/d | 100 | 200 | 50 | - | - | - |
| **Dermal Contact** | | | | | | | | |
| Skin Surface Area | SA | cm² | 5700 | 2800 | 3300 | - | - | - |
| Soil Dermal adherence factor | AF | mg/cm²/d | 0.07 | 0.2 | 0.2 | - | - | - |
| **Outdoor Vapors and Dust inhalation** | | | | | | | | |
| Outdoor Daily Frequency (c) | EFgo | h/d | 24 | 24 | 8 | 24 | 24 | 8 |
| Outdoor Vapor Inhalation rate (a);(b) | Bo | m³/h | 0.9 | 0.7 | 2.5 | 0.9 | 0.7 | 2.5 |
| Particulate Outdoor fraction | Fsd | - | 1 | 1 | 1 | 1 | 1 | 1 |
| **Indoor Vapors and Dust inhalation** | | | | | | | | |
| Indoor Daily Frequency | EFgi | h/d | 24 | 24 | 8 | 24 | 24 | 8 |
| Indoor Vapor Inhalation rate (b) | Bi | m³/h | 0.9 | 0.7 | 0.9 | 0.9 | 0.7 | 0.9 |
| Particulate indoor fraction | Fi | - | 1 | 1 | 1 | - | - | - |
| **Water Ingestion** | | | | | | | | |
| Water Rate Ingestion | IRw | L/d | 2 | 1 | 1 | 2 | 1 | 1 |

*(a) In case of intense physical activity, it is suggested to use, in a residential outdoor scenario, a more conservative value of 1.5 m³/h and 1.0 m³/h for adults and children, respectively.*
*(b) For an industrial scenario it is suggested to use, in the case of hard physical activity, a value of 2.5 m³/h, whereas in the case of moderate and sedentary activity it is more appropriate to use a value of 1.5 m³/h and 0.9 m³/h, respectively. For a recreational scenario a value of 3.2 m³/h and 1.9 m³/h for an adult and a child can be used, respectively.*
*(c) For a recreational scenario a daily frequency exposure of 3 h/day can be used.*

## 3.3 RISK BY GROUNDWATER VOLATILIZATION PATHWAY

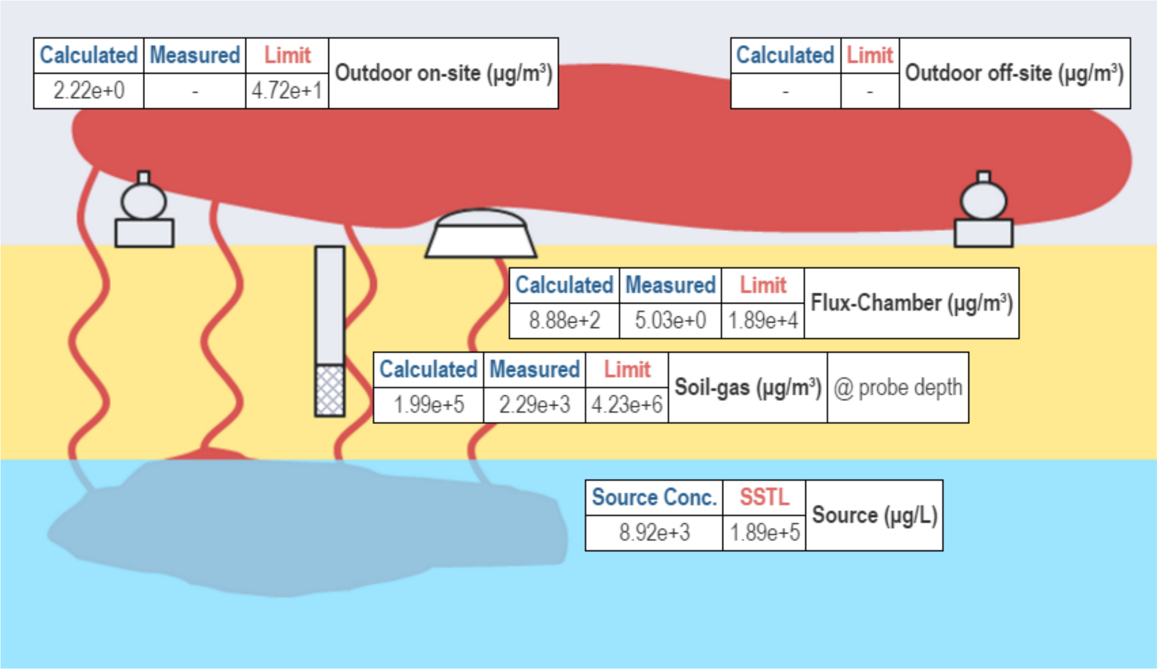


**Risk from Groundwater Help Copy table**

| Contaminant | CRS | f | CRS/f | Sol | R (HH) | HI (HH) | Rgw (GW) |
|---|---|---|---|---|---|---|---|
| | µg/L | - | µg/L | µg/L | - | - | - |
| Vinyl Chloride | 1.68e+2 | | 1.68e+2 | 8.80e+6 | 4.73e-8 | 3.01e-4 | - |
| Tetrachloroethylene | 8.92e+3 | | 8.92e+3 | 2.06e+5 | 4.71e-8 | 1.27e-2 | - |
| Trichloroethylene | 3.30e+3 | | 3.30e+3 | 1.28e+6 | 2.16e-7 | 7.37e-2 | - |
| Exachlorobutadiene | 6.00e+1 | | 6.00e+1 | 3.20e+3 | - | 3.37e-4 | - |
| Dichloroethylene (1,2) | 3.58e+3 | | 3.58e+3 | 6.40e+6 | - | 1.60e-3 | - |
| Trichloromethane | 5.50e-1 | | 5.50e-1 | 7.95e+6 | 9.97e-11 | 1.24e-7 | - |
| Dichloroethylene (1,1) | 8.54e+0 | | 8.54e+0 | 2.42e+6 | - | 5.84e-6 | - |
| Dichlorobenzene (1,4) | 6.50e+0 | | 6.50e+0 | 8.13e+4 | 3.11e-10 | 9.90e-8 | - |
| **Cumulative Outdoor Risk (On-site)** | | | | | **3.11e-7** | **8.86e-2** | |
| **Cumulative Indoor Risk (On-site)** | | | | | **-** | **-** | |

## 3.4 CALCULATED AND MEASURED CONCENTRATIONS COMPARISON

### tetrachloroethylene concetrations comparison



| Calculated | Measured | Limit | Outdoor on-site (µg/m³) |
|---|---|---|---|
| 2.22e+0 | - | 4.72e+1 | |

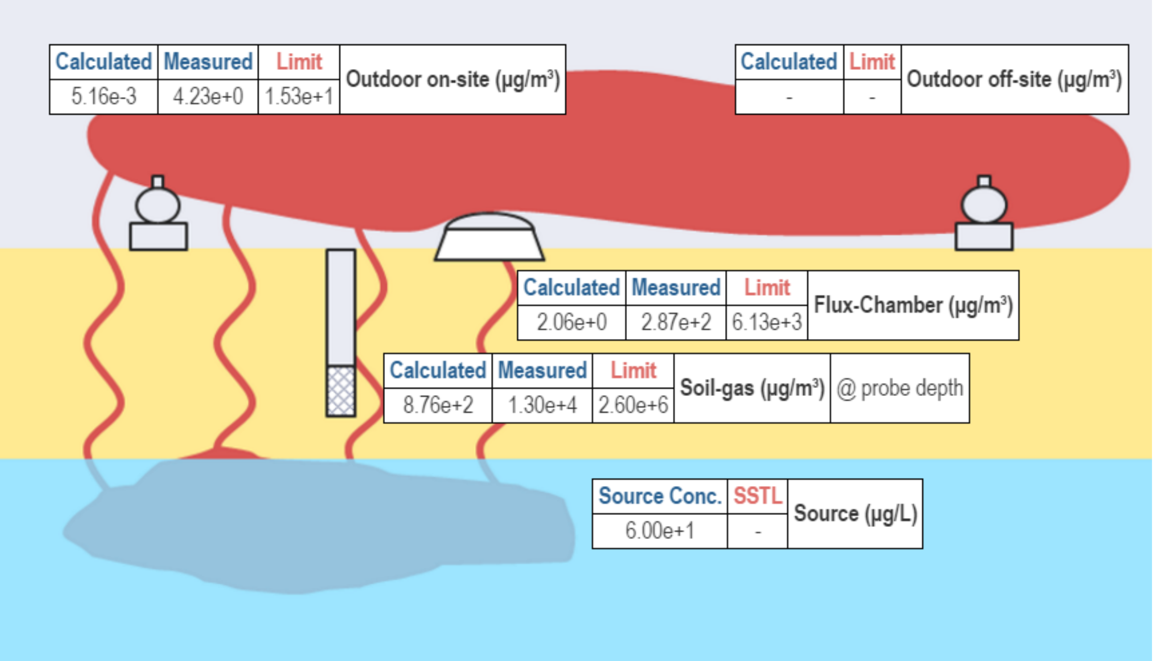
| Calculated | Limit | Outdoor off-site (µg/m³) |
|---|---|---|
| - | - | |

| Calculated | Measured | Limit | Flux-Chamber (µg/m³) |
|---|---|---|---|
| 8.88e+2 | 5.03e+0 | 1.89e+4 | |

| Calculated | Measured | Limit | Soil-gas (µg/m³) | @ probe depth |
|---|---|---|---|---|
| 1.99e+5 | 2.29e+3 | 4.23e+6 | | |

| Source Conc. | SSTL | Source (µg/L) |
|---|---|---|
| 8.92e+3 | 1.89e+5 | |

## Hexachlorobutadiene concetrations comparison



| Calculated | Measured | Limit | Outdoor on-site (µg/m³) |
|---|---|---|---|
| 5.16e-3 | 4.23e+0 | 1.53e+1 | |

| Calculated | Limit | Outdoor off-site (µg/m³) |
|---|---|---|
| - | - | |

| Calculated | Measured | Limit | Flux-Chamber (µg/m³) |
|---|---|---|---|
| 2.06e+0 | 2.87e+2 | 6.13e+3 | |

| Calculated | Measured | Limit | Soil-gas (µg/m³) | @ probe depth |
|---|---|---|---|---|
| 8.76e+2 | 1.30e+4 | 2.60e+6 | | |

| Source Conc. | SSTL | Source (µg/L) |
|---|---|---|
| 6.00e+1 | - | |

# APPENDIX 3: OIL DEPOT RISK ASSESSMENT

## 4.1 SITE FEATURES

### SITE PARAMETERS: SOURCE GEOMETRY

| Parameter | Symbol | Default | Site-Specific | UM |
|---|---|---|---|---|
| **Source Geometry** | | | | |
| Width of source area parallel to groundwater flow direction | W | 45 | 45 | m |
| Width of source area orthogonal to groundwater flow | Sw | 45 | 45 | m |
| Ambient air mixing zone height | δair | 2 | 2 | m |
| Width of source area parallel to wind direction | W' | 45 | 45 | m |
| Width of source area orthogonal to wind direction | Sw' | 45 | 45 | m |
| **Surface soil** | | | | |
| Depth to surface soil source | Ls,SS | 0 | 0 | m |
| Thickness of unsaturated surface soil source | d | 1 | 1 | m |
| **Subsurface soil** | | | | |
| Depth to subsurface soil source | Ls,SP | 1 | 1 | m |
| Thickness of unsaturated subsurface soil source | ds | 2 | 2 | m |
| **Groundwater** | | | | |
| Depth to groundwater | Lgw | 3 | 3 | m |
| **Soil-gas** | | | | |
| Soil-gas depth below ground surface | Lsoilgas | 1 | 1 | m |
| **Flux Chamber** | | | | |
| Flowrate of the carrier gas in the chamber | Qin | 5 | 5 | L/min |
| Chamber surface exposed to soil | Afc | 0.5 | 0.5 | m² |

### SITE PARAMETERS: VADOSE ZONE

| Parameter | Symbol | Default | Site-Specific | UM |
|---|---|---|---|---|
| **Vadose Zone soil texture** | | | | |
| Effective porosity in the unsaturated zone | θe | Literature | 0.345 | - |
| Volumetric water content in the soil | θw | Literature | 0.194 | - |
| Volumetric air content in the soil | θa | Literature | 0.151 | - |
| Volumetric water content in the capillary fringe | θw,cap | Literature | 0.288 | - |
| Volumetric air content in the capillary fringe | θa,cap | Literature | 0.057 | - |

| | | | | |
|---|---|---|---|---|
| Capillary fringe thickness | hcap | Literature | 0.25 | m |
| Wetting front suction (matric potential) | hcr | Literature | -0.0848 | m |
| Hydraulic conductivity in the vadose zone | Ksat,s | Literature | 1.23e-5 | m/s |
| Ponding depth | Hw | 0.25 | 0.25 | m |
| **Vadose Zone properties** | | | | |
| Soil bulk density | ρs | 1.7 | 1.7 | g/cm$^3$ |
| Soil pH | pH | 6.8 | 6.8 | - |
| Organic Carbon Fraction - surface soil | foc,SS | 0.01 | 0.01 | g/g |
| Organic Carbon Fraction - subsurface soil | foc,SP | 0.01 | 0.01 | g/g |
| Residual void fraction in the soil (for Cres) | Sr | 0.04 | 0.04 | m |
| Unsaturated zone thickness | hv | Calculated | 2.750 | m |
| **Infiltration through Vadose Zone** | | | | |
| Annuale Rainfall Rate | P | 129 | 129 | cm/y |
| Outdoor areal fraction of cracks | ηout | 1 | 1 | - |
| Soil Infiltration Rate | Ief | Calculated | 29.95 | cm/y |
| **Other intermediate parameters** | | | | |
| Groundwater mixing zone thickness | δgw | Calculated | 2.00 | m |
| Leachate dilution factor | LDF | Calculated | 4.70 | - |

## SITE PARAMETERS: OUTDOOR

| Parameter | Symbol | Default | Site-Specific | UM |
|---|---|---|---|---|
| **Meteorological data** | | | | |
| Wind speed | Uair | 2.25 | 1.5 | m/s |
| Particulate emission rate | Pe | 6.9e-14 | 6.9e-14 | g/cm/s$^2$ |
| **Atmospheric dispersion** | | | | |
| Distance to outdoor air receptor - ADF | POC ADF | 100 | 100 | m |
| Transversal air dispersion coefficient | σy | 10 | 10 | m |
| Vertical air dispersion coefficient | σz | 10 | 10 | m |
| Aerobic depth below ground surface | La Outdoor | 1 | 1 | m |

# 4.2 EXPOSURE FACTORS

**Exposure Factors Help Copy table Default**

| Exposure | | | On Site | | | Off Site | | |
|---|---|---|---|---|---|---|---|---|
| **Scenario** | | | **Residential** | | **Industrial** | **Residential** | | **Industrial** |
| **Exposure Parameters** | **Symbol** | **UM** | **Adults** | **Children** | **Worker** | **Adults** | **Children** | **Worker** |
| **General Factors** | | | | | | | | |
| Body Weight | BW | kg | 70 | 15 | 70 | 70 | 15 | 70 |
| Averaging time for carcinogens | AT | y | 70 | | | 70 | | |
| Exposure duration | ED | y | 24 | 6 | 25 | 24 | 6 | 25 |
| Exposure Frequency | EF | d/y | 350 | 350 | 250 | 350 | 350 | 250 |
| **Accidental Soil Ingestion** | | | | | | | | |
| Ingested Soil Fraction | FI | - | 1 | 1 | 1 | - | - | - |
| Soil Ingestion Rate | IR | mg/d | 100 | 200 | 50 | - | - | - |
| **Dermal Contact** | | | | | | | | |
| Skin Surface Area | SA | $cm^2$ | 5700 | 2800 | 3300 | - | - | - |
| Soil Dermal adherence factor | AF | $mg/cm^2/d$ | 0.07 | 0.2 | 0.2 | - | - | - |
| **Outdoor Vapors and Dust inhalation** | | | | | | | | |
| Outdoor Daily Frequency (c) | EFgo | h/d | 24 | 24 | 8 | 24 | 24 | 8 |
| Outdoor Vapor Inhalation rate (a);(b) | Bo | $m^3/h$ | 0.9 | 0.7 | 2.5 | 0.9 | 0.7 | 2.5 |
| Particulate Outdoor fraction | Fsd | - | 1 | 1 | 1 | 1 | 1 | 1 |
| **Indoor Vapors and Dust inhalation** | | | | | | | | |
| Indoor Daily Frequency | EFgi | h/d | 24 | 24 | 8 | 24 | 24 | 8 |
| Indoor Vapor Inhalation rate (b) | Bi | $m^3/h$ | 0.9 | 0.7 | 0.9 | 0.9 | 0.7 | 0.9 |
| Particulate indoor fraction | Fi | - | 1 | 1 | 1 | - | - | - |
| **Water Ingestion** | | | | | | | | |
| Water Rate Ingestion | IRw | L/d | 2 | 1 | 1 | 2 | 1 | 1 |

*(a) In case of intense physical activity, it is suggested to use, in a residential outdoor scenario, a more conservative value of 1.5 $m^3/h$ and 1.0 $m^3/h$ for adults and children, respectively.*
*(b) For an industrial scenario it is suggested to use, in the case of hard physical activity, a value of 2.5 $m^3/h$, whereas in the case of moderate and sedentary activity it is more appropriate to use a value of 1.5 $m^3/h$ and 0.9 $m^3/h$, respectively. For a recreational scenario a value of 3.2 $m^3/h$ and 1.9 $m^3/h$ for an adult and a child can be used, respectively.*
*(c) For a recreational scenario a daily frequency exposure of 3 h/day can be used.*

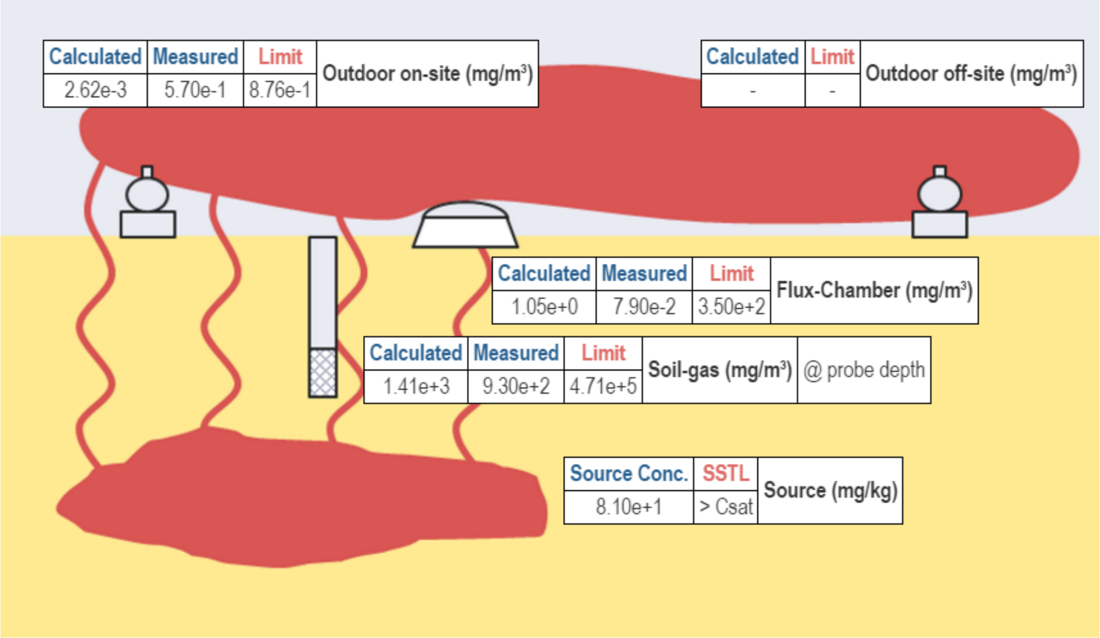
## 4.3 RISK BY SURFACE SOIL VOLATILIZATION PATHWAY

**Risk from Surface Soil Help Copy table**

| Contaminant | CRS | f | CRS/f | Csat | Cres | R (HH) | HI (HH) | Rgw (GW) |
|---|---|---|---|---|---|---|---|---|
| | mg/kg | - | mg/kg | mg/kg | mg/kg | - | - | - |
| Aliphatics C5-C8 | 8.10e+1 | | 8.10e+1 | 3.04e+2 | 2.99e+2 | - | 2.89e-1 | - |
| Aliphatics C9-C12 | 1.21e+3 | | 1.21e+3 | 6.81e+1 | 6.81e+1 | - | 4.16e-2 | - |
| **Cumulative Outdoor Risk (On-site)** | | | | | | **-** | **5.02e-3** | |
| **Cumulative Indoor Risk (On-site)** | | | | | | **-** | **3.31e-1** | |
| **Risk for hydrocarbons in groundwater - MADEP** | | | | | | | | **-** |

## 4.4 CALCULATED AND MEASURED CONCENTRATIONS COMPARISON

### Aliphatics C5-C8 concetrations comparison



| Calculated | Measured | Limit | Outdoor on-site (mg/m³) |
|---|---|---|---|
| 2.62e-3 | 5.70e-1 | 8.76e-1 | |

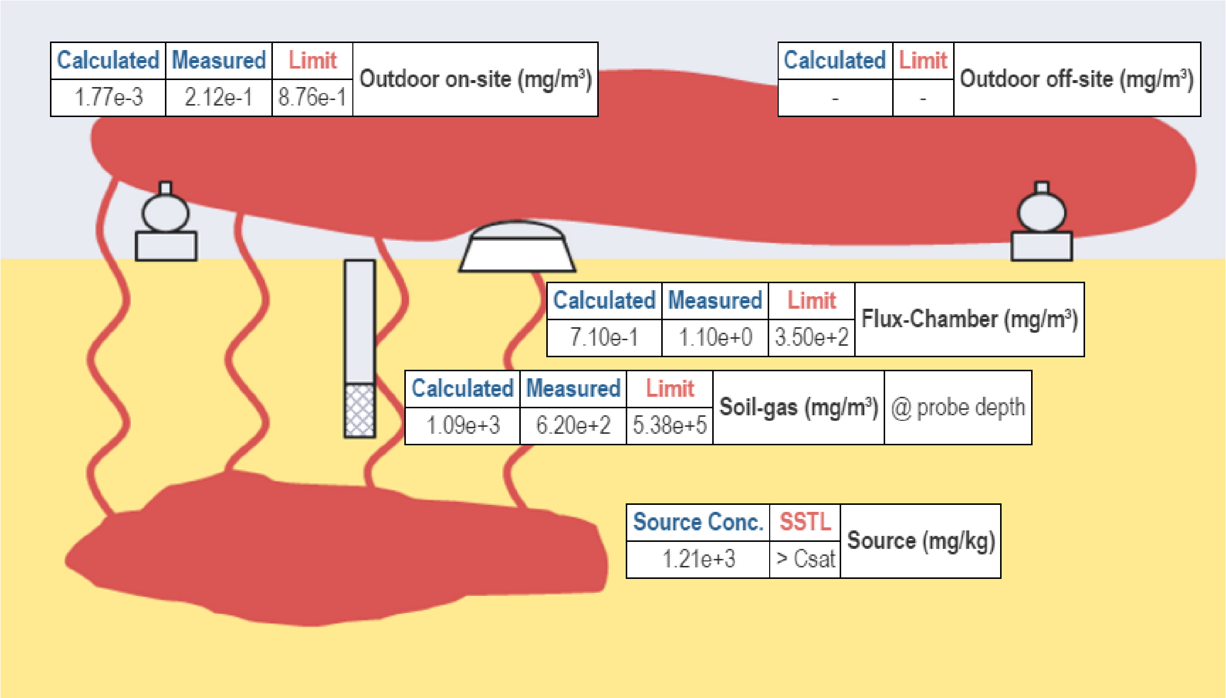
| Calculated | Limit | Outdoor off-site (mg/m³) |
|---|---|---|
| - | - | |

| Calculated | Measured | Limit | Flux-Chamber (mg/m³) |
|---|---|---|---|
| 1.05e+0 | 7.90e-2 | 3.50e+2 | |

| Calculated | Measured | Limit | Soil-gas (mg/m³) | @ probe depth |
|---|---|---|---|---|
| 1.41e+3 | 9.30e+2 | 4.71e+5 | | |

| Source Conc. | SSTL | Source (mg/kg) |
|---|---|---|
| 8.10e+1 | > Csat | |

## Aliphatics C9-C12 concetrations comparison



| Calculated | Measured | Limit | Outdoor on-site (mg/m$^3$) |
|---|---|---|---|
| 1.77e-3 | 2.12e-1 | 8.76e-1 | |

| Calculated | Limit | Outdoor off-site (mg/m$^3$) |
|---|---|---|
| - | - | |

| Calculated | Measured | Limit | Flux-Chamber (mg/m$^3$) |
|---|---|---|---|
| 7.10e-1 | 1.10e+0 | 3.50e+2 | |

| Calculated | Measured | Limit | Soil-gas (mg/m$^3$) | @ probe depth |
|---|---|---|---|---|
| 1.09e+3 | 6.20e+2 | 5.38e+5 | | |

| Source Conc. | SSTL | Source (mg/kg) |
|---|---|---|
| 1.21e+3 | > Csat | |