

Modelling Efficacy of Soil Vapour Extraction (SVE) in Waste Sites Polluted by Hydrocarbons: A Case Study

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Received May 14, 2008; revised and accepted September 10, 2008

Abstract: The effectiveness of soil vapour extraction (SVE) in the remediation of a site polluted by hydrocarbons located in Southern Italy (Brindisi), has been tested by means of experimental data and a computational code. SVE is one of the most frequent techniques used for the remediation of vadose zones contaminated by hydrocarbons. In the case studied, actual BTEX (Benzene, Toluene, Ethylbenzene and Xylenes) and TPH (Total Petroleum Hydrocarbons) contamination have been considered. The application aimed to examine some technical and economic features of the SVE technique, as well as to point out the very important role of mathematical models in management of contaminated sites. The code simulation predicted both contaminant depletion trends and remediation times at polluted site. The simulation results pointed out different remediation performance for BTEX (more than 150 days) and TPH (more than 600 days) removal. The treatment costs of the simulated SVE “on site” technique resulted competitive with respect to the other “ex site” methods which can be carried out at the same contaminated area and should be encouraged by the local authorities.

Key words: Contaminated sites remediation, unsaturated subsoil, multiphase flow and transport, soil vapour extraction, remediation time and costs.

Introduction

Frequent accidental leakages during petrol or gasoline transport operations from storage tanks usually result in significant migration of hydrocarbons and related problems due to soil and subsoil contamination. After a leakage has been reported, generally, the first step is a delineation of the vertical and horizontal extent of soil contamination. This may include drilling, soil and rock sampling and laboratory concentration analyses, as well as surface and subsurface geophysical measurements. Yet, laboratory analyses are both costly and necessary for monitoring temporal variations. Therefore, mathematical models can integrate monitoring results and can play a

very important role in simulating pollutants migration in subsoils. Simulation models are helpful to locate groundwater plume extension as well, in choosing and designing proper reclamation measures, by providing low cost estimates on technologies performances.

In the case studied the efficacy of soil vapour extraction (SVE) (Unger et al., 1995; Guiguer et al., 1995) in the remediation of a site polluted by hydrocarbons and located near Brindisi (Southern Italy) has been simulated by a mathematical model. As known, SVE is a widely used technology (Figure 1) for the remediation of the unsaturated polluted soils (i.e. vadose zone). In the most commonly practiced method of application, a blower (or vacuum pump) is connected to a well (see Figure 1). The vacuum within the well induces a flow of air from the surrounding soils. The portion of volatile

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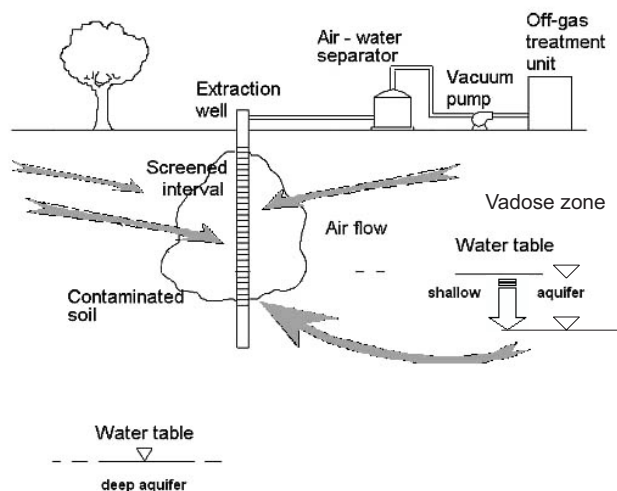


Figure 1: Soil Vapour Extraction (SVE): The extraction well, screened across the contaminated interval of the unsaturated zone, is connected to an air-water separator, a vacuum pump and an off-gas treatment system.

organic compounds (VOC) present as vapour phase into the subsoil voids is removed, along with the air leaving the soil. The portion of VOC still in the soil (adsorbed, dissolved in the soil moisture or present as free-phase liquids) will gradually partition into the surrounding air, due to the concentration gradient, and be extracted from the well. Exhausted air, then, will likely require treatment, to recover or destroy the contaminants, depending on the

specific air discharge regulations. The SVE has been mostly used in order to remove VOC, such as trichloroethane, trichloroethene, BTEX, as well as fuels. The mathematical model applied in this work predicted time and costs required for groundwater remediation for SVE at the test site in order to define the best (low cost) methodology.

The Contaminated Site

The SVE application considers a polluted site located in the industrial area near Brindisi (Southern Italy) (Figure 2). The area was unswerving in the past to the production, storage and distribution of final products like gasoline and diesel-oil.

The geologic and hydrogeologic conditions of the site are well known (AA.VV., 1990) (Figure 3). The substrata of the studied area are upper Cretaceous fractured limestones and dolomites (Calcare di Galatina), overlain by Plio-Pleistocene calcarenite deposits and low permeability clay (Argille azzurre). A shallow phreatic aquifer is present in the Pleistocene-Holocene marine terrace deposits (sand/gravel and silty sand) that outcrop in the considered district, while the regional deep karstic aquifer is present in the carbonate rocks. The two aquifers do not have connections, due to the presence of the thick (10-20 m) clay layer.

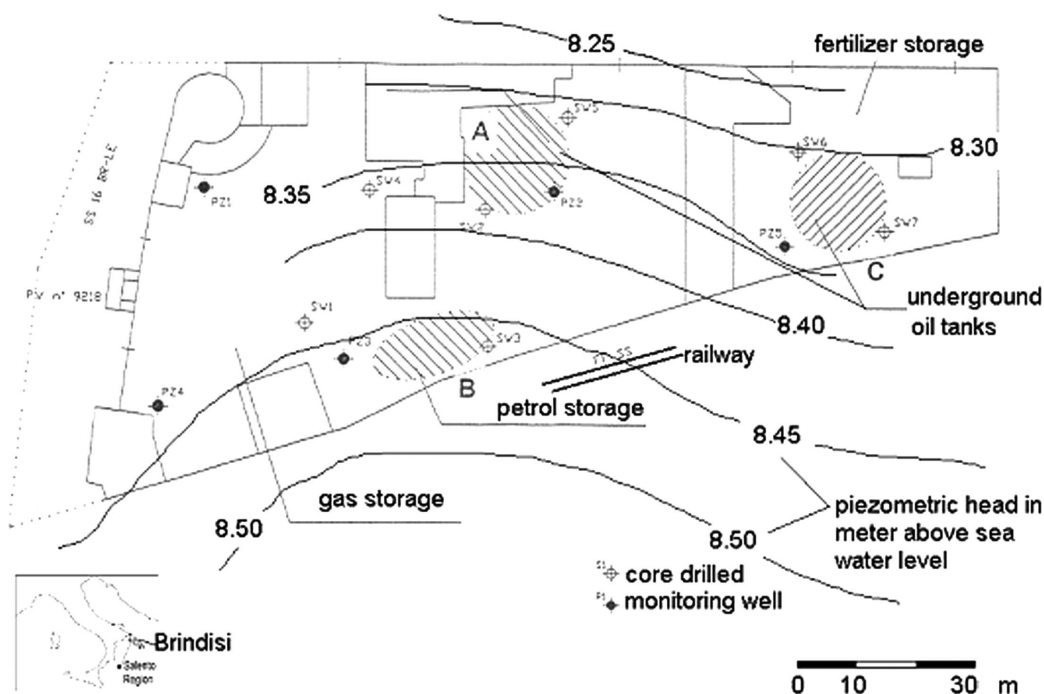


Figure 2: Map of the contaminated area and locations of the soil and water samples.

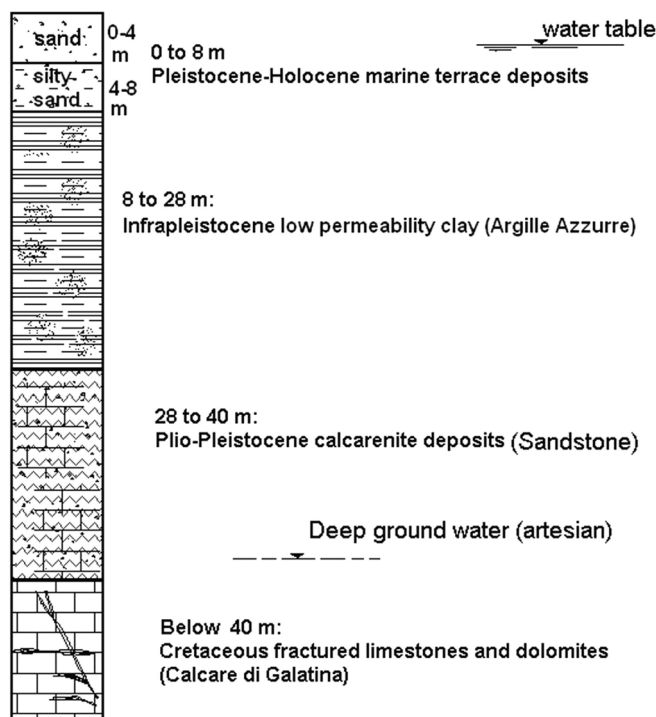


Figure 3: Stratigraphic sequence of the studied area.

Data from recent soil core analyses carried out on the site have pointed out the following upper stratigraphic sequence for marine terrace deposits (see Figure 2):

- 0 to 1.0 m below ground surface (bgs): sandy gravels;
- 1.0 to 4.0 m bgs: sand and cobbles; and
- 4.0 to 8 m bgs: silty sand.

The studied phreatic aquifer has a relatively shallow water table. Recent investigations have given a depth to the water table ranging from 0.8 to 1.3 metres below

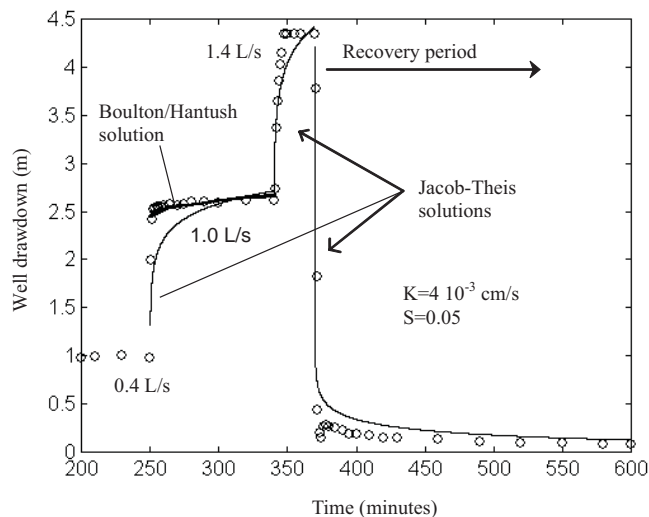


Figure 4: Pumping test data (open circles) (Winter, 2003) fitted by Jacob-Theis and Boulton-Hantush (Bear, 1979) solutions (solid curves) for unsteady radial groundwater flow to a well in a phreatic aquifer.

ground surface. Measurements of the variation of piezometric level in some observation points, owing to a pumping test (Figure 4), pointed out for the upper aquifer a hydraulic conductivity ranging from 2.6×10^{-3} to 5.8×10^{-2} cm/s.

The characterization of the soil contamination was constituted by means of 12 boreholes up to the depth of 8 m bgs, and four monitoring wells that reached a variable depth from 5 m to 8 m. Indeed, due to the presence of subsurface storage tanks it was impossible to investigate the lower zone of the aquifer. Table 1 reports some contaminant concentrations obtained by means of laboratory analyses, referring to the average values

Table 1: Chemical constituents in contaminated soil and groundwater samples (average values)
(the sampling locations reported in Figure 3)

Depth of the sample (below ground surface)	TPH	Benzene	Toluene	Ethylbenzene	Xylenes
Soil cores in the contamination zone A (mg/kg)					
1.0-1.1 m	1270	1	0.5	0.2	0.6
2.7-2.8 m	1100	0.7	<0.1	<0.1	0.2
5.0-5.1 m	8	<0.05	<0.1	<0.1	<0.1
Soil core in the contamination zone B (mg/kg)					
1.0-1.2 m	6200	4.9	3.6	<0.1	17.2
2.1-2.2 m	35	<0.05	<0.1	<0.1	<0.1
3.9-4.1 m	8	<0.05	<0.1	<0.1	<0.1
Average water constituent (µg/L)					
	75	70	17	<1	10

of soil and water samples indicated in the site map (Figure 2) and due to diesel fuel and gasoline contamination sources type. Boldface values indicate soil and water concentrations above the regulatory limits reported by the Italian legislation (D.M. 471/99). These values refer only to BTEX and TPH concentration. Yet, in a multi-component mathematical model, information on every chemical constituent present in the organic phase is required. The simulations, then, were run under the following particular assumptions: (i) besides benzene, toluene and *m*-xylene, the *n*-dodecane has been considered as representative of the persistent hydrocarbons present in the TPH concentration, due to its low volatility; and (ii) *m*-xylene, as well, has been chosen to represent all xylenes, since it is the least volatile one. Contaminant source was petrol and gas storage from tanks settled underground.

Before the SVE modelling a pumping was simulated in the study area in order to remove the contaminated water (water table is at a depth of 0.8 m to 1.3 m) from the upper aquifer and increase the unsaturated thickness to 8 m. The SVE simulation was then applied to a vadose zone 8 m thick.

In order to simulate groundwater depletion due to pumping, the following mathematical formulation similar to that used by Bear (1979) to reproduce the recession period of a spring, was used (see Appendix for details):

$$h(t) = \frac{Q_0}{\alpha_1} \exp \left[-\frac{\alpha_1}{S \times A} (t - t_0) \right] \quad (1)$$

where $h(t)$ (m) stands for the thickness of the saturated zone at time t , Q_0/α_1 (m) is the initial thickness (i.e., at $t = t_0$) of the saturated zone; α_1 (m^2s^{-1}) is a constant which depends on the hydraulic aquifer conductivity (assumed homogeneous and isotropic) and size of the horizontal area A ($=10,000 \text{ m}^2$) of ground water subjected to depletion; Q_0 (L/s) is the initial (i.e., at $t = t_0$) pumping flowrate; B ($=1 \text{ m}$) is the minimum water level necessary for water extraction by pumping and S ($=0.25$) is the aquifer's storativity close to specific yield in sandy phreatic aquifers (Bear, 1979). Obviously the groundwater level recession may be obtained only after the realization of a barrier along the perimeter of contaminated subsoil able to isolate the aquifer in the contaminated area by the natural replenishment. In fact the base of shallow aquifer is confined and isolated from deeper aquifer flux by a very thick (15 m, on average) infra-Pleistocene clay (*Argille Azzurre*). The barrier to ground water inflow may be assembled, for instance, by

means of gypsum injections in micro wells. The ground water contains the pollutant and small polluted zones where the contaminated soil may result confined, so that only the included mobile wastewater will be extracted.

Equation (1) was useful to estimate how much time may be required to extract the water from the saturated zone of the shallow aquifer at the test site. The simulation result established that a period of 300 days can be considered long enough to reduce saturated aquifer thickness from 7 m to 1 m, at an initial pumping flowrate of 1.5 L/s. This last value (1.5 L/s) was defined by pumping test carried out on site. In order to reduce this period more wells can be used, simultaneously.

Model Equations

The simulation in the vertical domain was referred to a cylindrical coordinate system (r, z), where r is the radial and z is the vertical coordinate, with the vacuum extraction well located at the centre of the cylinder. Gas pressure distribution, vapour velocity field and concentrations of volatile compounds were calculated.

As known, the basic mechanisms by which contaminated organic vapours are extracted by vacuum are: pressure-induced advection and molecular diffusion (Guiguer et al., 1995). Indeed the pressure-induced advection caused by minimum barometric pressure fluctuations was neglected. Moreover density-induced advection and aqueous diffusion were also neglected. The gas (containing vapour) flow is governed by generalized Darcy's motion law, under steady state pumping conditions. The phases considered in the model were the following:

- *gaseous phase* (g), in which air (that is actually a mixture of various compounds, but is treated as a unique component with average properties) and volatile NAPLs (non-aqueous phase liquids) are present; the water component is assumed not to be present in the gaseous phase (no water vapour) due to low air temperature (20°C) during SVE operation. Moreover it is also assumed that the transport of vapour cannot affect soil water content;
- *aqueous phase* (w), i.e. the liquid phase comprising ground water (vadose zone) and dissolved NAPLs;
- *non-aqueous organic phase* (o), i.e. the NAPL fraction present around soil particles as free-phase liquid; and
- *adsorbed phase* (s), i.e. the NAPL fraction adsorbed to the soil.

The mathematical formulation of the code used was based on the mass-balance for each component included

in the system and both liquid phases (organic and aqueous phases) were assumed to be stagnant. As the change in mass vapour flux due to organic components mass transfer into the gas can be neglected (Guiguer et al., 1995), the continuity equation for the gas can be written as the following:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{K k_{rg} \rho_g}{\mu_g} \frac{\partial p}{\partial r} \right) + \frac{\partial}{\partial z} \left(\frac{K k_{rg} \rho_g}{\mu_g} \frac{\partial p}{\partial z} \right) = n \frac{\partial (\rho_g s_g)}{\partial t} \quad (2)$$

where p is the gaseous phase pressure (N/m²); K the soil intrinsic permeability (darcy); k_{rg} the relative permeability of the gaseous phase (–); n the soil porosity (–); ρ_g the gas density (kg/m³); ρ_o the NAPL density (kg/m³); and μ_g the dynamic viscosity of the gaseous phase (centipoises).

In Equation (2), according to the Henry's law, the change in mass gas flux vs. time can be written as:

$$\begin{aligned} \frac{\partial \rho_g s_g}{\partial t} &= \rho_g \frac{\partial s_g}{\partial t} + s_g \frac{\partial \rho_g}{\partial t} \\ &= \rho_g \frac{\partial (1 - s_o - s_w)}{\partial t} + (1 - s_o - s_w) \frac{M_a}{RT} \frac{\partial p_g}{\partial t} \end{aligned} \quad (2a)$$

with positions:

$$s_g = 1 - s_o - s_w; \quad \frac{\partial s_w}{\partial t} = 0; \quad \rho_g = \rho_a = \frac{M_a p_g}{RT} \quad (2b)$$

where R is the universal gas constant, T (°K) the vapour absolute temperature and M_a (M/mol) and ρ_a are molar weight and density of the air (=1.2 kg/m³ at 20 °C) whereas s_g (–) is the gas saturation, i.e. fraction of gas volume in the volume of void space; s_w (–) is the wastewater saturation, i.e. fraction of water (and dissolved chemicals) volume in the volume of void space; s_o (–) is the organic free phase saturation, i.e. fraction of NAPL volume in the volume of void space. Equation (2a), can be rewritten as:

$$\frac{\partial \rho_g s_g}{\partial t} = -\frac{\rho_a}{\rho_o} \sum_{i=1}^{N_c} (I_{og}^i + I_{ow}^i) + (1 - s_o - s_w) \frac{M_a}{RT} \frac{\partial p_g}{\partial t} \quad (3)$$

where the mass transfer of the N_c NAPL-gas and NAPL-water components were derived from the following mass balance equation of stagnant organic phase:

$$\begin{aligned} n \frac{\partial \rho_o s_o f_o^i}{\partial t} &= n \rho_o \frac{\partial s_o f_o^i}{\partial t} = I_{og}^i + I_{ow}^i \\ &= n s_g \lambda_{og} (c_g^i - c_{ge}^i) + n s_w \lambda_{ow} (c_w^i - c_{we}^i) \end{aligned} \quad (4)$$

where the NAPL density ρ_o is assumed to be constant and the mass transfer between NAPLs and solid phase is neglected; c_{ge} and c_{we} are saturated vapour concentration and the aqueous solubility of the chemical; λ_{og} and λ_{ow} are mass transfer coefficients from oil/gas and oil/water, respectively. Moreover, as in Equation (3) is $\rho_a < \rho_o$ (≈ 820 kg/m³) and $\partial p_g / \partial t = 0$ due to stationary pumping conditions (i.e., constant vapour extraction pressure), the continuity equation (2) can be rewritten as:

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{K k_{rg} \rho_g}{\mu_g} \frac{\partial p}{\partial r} \right) + \frac{\partial}{\partial z} \left(\frac{K k_{rg} \rho_g}{\mu_g} \frac{\partial p}{\partial z} \right) = 0 \quad (5)$$

The solution of Equation (5) allowed the air pressure and velocity determination in the unsaturated subsoil (or vadose zone) of the test site.

The Transport Equations

The diffusive component of gas transport was determined by Fick's law by neglecting the mechanical dispersion in the gaseous phase.

During SVE operation, the gaseous phase is removed by the vacuum extraction and replaced by atmospheric clean air. This results in the volatilization of the contaminants from the organic and aqueous phase to the gaseous phase, as well as in desorption from the sorbed phase to the aqueous and vapour phases (Gaudet et al., 1977).

When the soil is close to total organic phase saturation, volume of air in the soil pores will be very small and will likely have a very low gas permeability, i.e. there will be very little connected pore spaces for gas flow. In this case the “*local equilibrium assumption*” is implemented. This means an instantaneous equilibrium of the contaminant concentrations between two different phases in contact (i.e., *g/o* or *w/g* or *s/g*). This means that the characteristic timescale of the simulated process (gas flow) is considered relatively large compared with the characteristic timescale of the mass transfer processes of NAPL compounds between phases. The values of the mass transfer rates, then, are infinitely large and the concentration, in the various phases, of each constituent are at the chemical equilibrium. On the contrary in those computational cells (at the boundary, for instance) where no contamination was present, the mass transfer rate was set equal to 0. For intermediate situations, instead, the mass transfer rate was calculated by means of mathematical expression (Guiguer et al., 1995) below reported (see Equation 7).

As the advective and diffusive fluxes in organic and wastewater (i.e., stagnant) phases were ignored, the main

governing equations used in the model for generic mass constituent transport in the vapour was the following:

$$\begin{aligned} n\rho_o \frac{\partial s_o f_i}{\partial t} + n \frac{\partial (R_i s_g c_i^e)}{\partial t} \\ = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{K k_g c_i}{\mu_g} \frac{\partial p}{\partial r} \right) + \frac{\partial}{\partial z} \left(\frac{K k_g c_i}{\mu_g} \frac{\partial p}{\partial z} \right) \\ + \frac{1}{r} \frac{\partial}{\partial r} \left(r n \tau_g s_g D_g \frac{\partial c_i}{\partial r} \right) + \frac{\partial}{\partial z} \left(n s_g \tau_g D_g \frac{\partial c_i}{\partial z} \right) \end{aligned} \quad (6)$$

and

$$n\rho_o \frac{\partial s_o f_i}{\partial t} = -\lambda_i (c_i^e - c_i) \quad (7)$$

with supplementary equations:

$$c_i^e = c_i^p \frac{\frac{f_i}{M_i}}{\sum_{i=1}^{N_C} \frac{f_i}{M_i}}; \quad \sum_{i=1}^{N_C} f_i = 1; \quad s_g + s_o + s_w = 1; \quad (8)$$

In the above equations c_i (kg/m³) is the vapour concentration of generic i component in the gaseous phase; c_i^e (kg/m³) is the “saturated” vapour concentration for the component in the gaseous phase; c_i^p (kg/m³) is the “saturated” vapour concentration for the “pure” component in the gaseous phase; f_i (–) is the mass fraction of the “ i ” compound in the organic phase, i.e. the fraction of the chemical in the total organic mass; M_i (kg/mol) is the molar weight of the single NAPL compound and N_C (–) is the total number of organic compounds. Moreover D_g (m²/s) is the molecular diffusion coefficient in the gaseous phase; λ_i (s^{–1}) is the mass transfer rate coefficient; τ_g (–) is the gaseous phase tortuosity ($=n^{1/3} s_g^{7/3}$) (Millington and Quirk, 1961) and R_i (–) is the retardation factor.

In Equation (6), similar to Equation (5), the component of NAPL volatilization from soil moisture phase was neglected according to Henry’s law (see Equation (3)), due to steady-state pumping conditions (i.e., constant vapour extraction pressure over time).

In the case of horizontal flow and mass transfer towards the gas, in order to determine the mass-transfer coefficient in every computational cell of discretized domain, it is possible to integrate locally the diffusion equation. Thus, the following expression can be obtained (Guiguer et al., 1995), for the mass transfer rate coefficient from the stagnant phase to the gas:

$$\lambda_i = \frac{4n\tau_g s_g D_g}{(\Delta z)^2} \quad (9)$$

The total number of equations (from (5) to (8)) that have to be solved for each component is 3+3 and the number of the variables ($p_g, s_o, s_g, c_i, c_i^e, f_i$) is 3+3, too. This set of equations can be solved numerically by using a computational code similar to the Airflow/SVE (Guiguer et al., 1995), based on the finite difference discretization method. The model domain, then, must be discretized in the vertical and radial directions into a network of finite cells.

A very effective automatic time-step selecting procedure can be based on the estimates of the rates of change of the primary variables—gaseous concentration (c_i), organic phase saturation (s_o), mass fractions of the compounds (f_i)—at the current time.

Model Simulation

Due to radial and symmetrical air flow during the simulation, the modelling domain has consisted of a vertical cross section, bound on the left-hand side by the well and on the right-hand side by the radius of influence of the well, obtained by pumping tests. The computational zone has been set equal to a rectangular region of 8 m × 40 m in the vertical and radial directions, respectively (Figure 5). The extension of the simulation domain was chosen as being large enough to include the contaminated zone. The boundary conditions considered in the case studied were the following:

1. At the water table (at bottom) and along the sealed (because it’s paved) portion of the ground surface (at top), zero vertical vapour pressure gradients have been specified, as well as zero concentration gradients.
2. At the radius of influence of well air pumping ($r = RI$) (i.e., the right boundary of domain), atmospheric pressure and zero concentration values of each compound (in the gaseous phase) have been specified, i.e., $p_g(r, z, t) = p_{atm}$ and $c_i(r, z, t) = 0$.
3. At the well radius ($r = r_w$), along the screened interval, constant vapour vacuum pressure ($p_g = p_w$) has been specified. This screened interval delimited a zone interested by vacuum extraction, where advective fluxes have been assumed to dominate over the diffusive flux. Then the resulting boundary conditions were:

$$p_g(r_w, z, t) = p_w; \quad \frac{\partial c_i}{\partial r} = 0 \quad (9)$$

4. At the well radius ($r = r_w$), along the non-screened interval, zero radial gradients of gaseous pressure and concentration have been specified for each organic compound (i.e., no flow of contaminants).

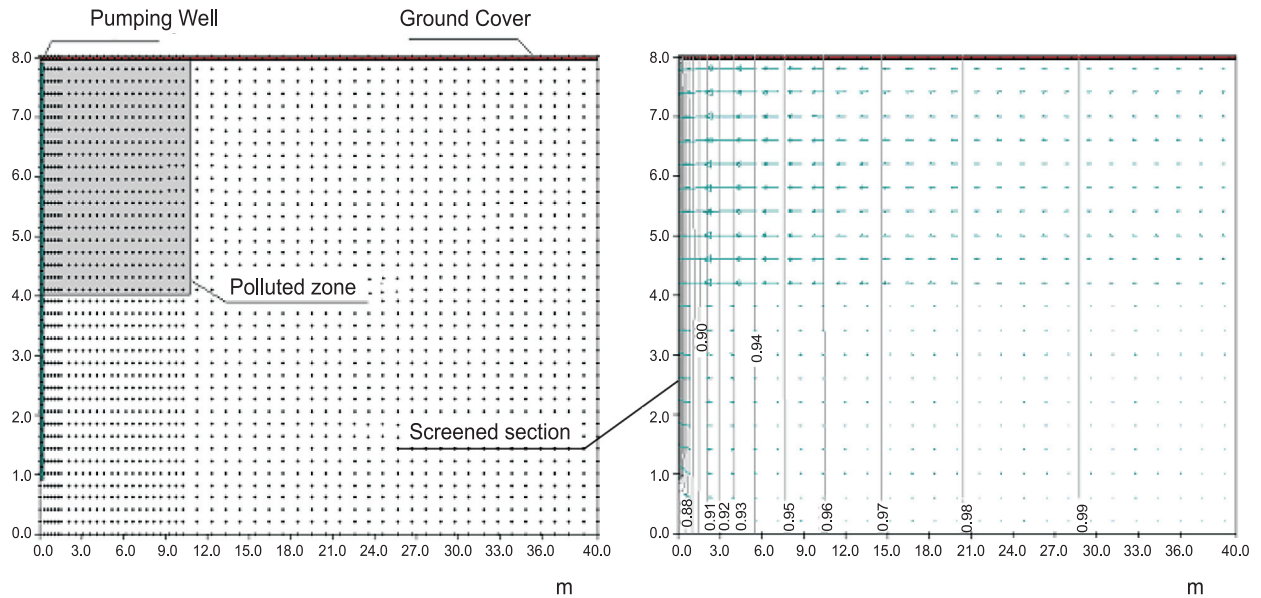


Figure 5: Contaminated zone in the model on the left and air pressure distribution and flow velocity vectors given by model under fixed vacuum extraction well depression of 0.2 bar.

Other assumptions taken into consideration during simulation were the following:

- biological and chemical degradation of the organic compounds have been neglected (this is a limitation of the software that it doesn't take into account the biodegradation of BTEX);
- no movements of the water table have been considered;
- gravity effects and compressibility of the soil (and fluids) have been neglected;
- mass transfer has been assumed to have no impact on the distribution of gas pressure;
- saturated vapour concentrations for each organic compound have been assumed to be governed by Raoult's law;
- variations of density of liquid and solid phases and of viscosity of fluid phases have been neglected;
- capillary forces have been assumed to have no impact on the vapour pressure; and
- mechanical mixing in the gaseous phase is neglected with respect to diffusive and advective processes.

In the unsaturated domain two layered soils have been considered, with saturated permeability values of 20 darcy (for the top layer) and 2 darcy (for the bottom layer). As far as intrinsic permeability is concerned, for both layers the condition of isotropy has been considered, not considering necessary to give different parameters in directions r and z . The saturated permeability value for the top layer was obtained by pumping tests under assumption that the ratio density/viscosity for the extracted fluid flow was constant. The permeability of

the bottom layer was derived from geological study carried out on the same geological formation. Ground cover has been considered over all the surface. The relative permeability-saturation curves are based on the van Genuchten/Parker constitutive relationship (Parker, 1989) has been used to estimate moisture distribution in the unsaturated zone. In the case studied, the relationship coefficients have been chosen in order to obtain a representative curve of the heterogeneous soil. This curve (Figure 6) represents depth (m), measured from the domain bottom, versus saturation. A discontinuity, due to the two different types of soil, is evident and due to silt the lower soil have a capillary saturation zone about 80-100 cm thick. It should be noted that the water content changes in saturation in the subsoil, by changing the volume of gas phase in the voids $s_g = 1 - s_o - s_w$, affect the mass transfer simulation rates defined by means of Equation (9).

As far as soil porosity and water saturation is concerned, the values assigned were resumed from literature on the basis of the granulometric fractions observed in soil cores.

The model parameters defined for the two layered soils, both 4 m thick, have been reported in Table 2; they derive from measurements on the two layered soils or geological studies carried out during the site characterization. The water table was considered as the bottom boundary, while the top boundary was represented by covered ground surface. The extraction well, screened between depths of 3 m and 7 m, was considered with a radius of 0.1 m.

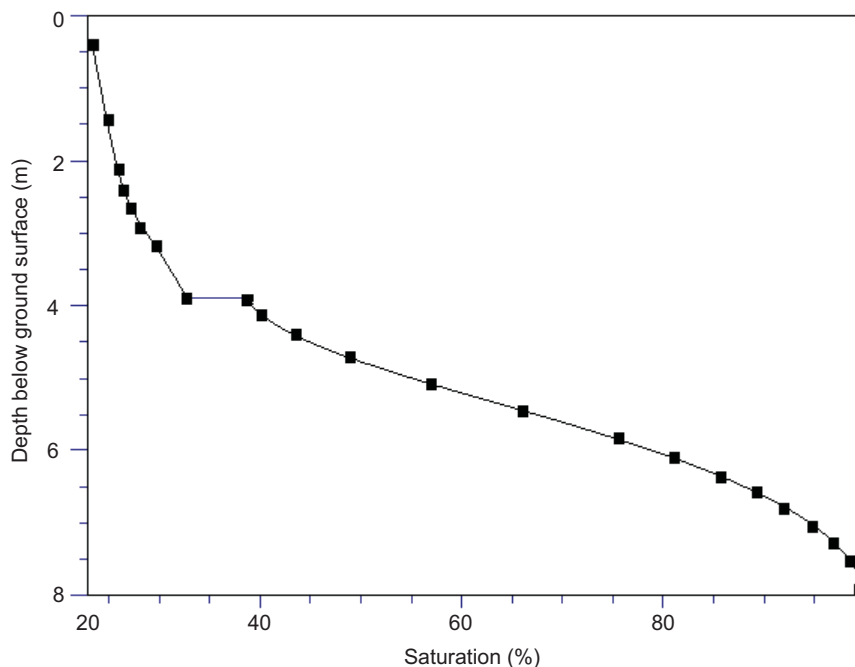


Figure 6: Water saturation vs. elevation for the vadose zone of the subsoil given by van Genuchten/Parker's formula (Parker, 1989).

Table 2: Input data for the two soil layers

Parameter	Upper Layer	Lower Layer
Intrinsic soil permeability in r	20 darcy	2 darcy
Intrinsic soil permeability in z	20 darcy	2 darcy
Porosity	40%	45%
Residual water saturation	12%	20%
Total organic mass fraction	5%	5%
Organic free phase (liquid) at saturation	3%	3%

In this geometric domain, a computational grid was defined: grid spacing was increased close to the extraction well, where maximum pressure gradients were expected, in order to obtain significant reduction of numerical errors.

The soil bulk density (for both layers) was estimated to be 1660 kg/m^3 . The NAPL phase density has been considered with a typical value derived from gasoline for cars, stored in the site, i.e. 820 kg/m^3 , whereas specific molar weights for each component are reported in Table 3.

Isotropic conditions have been considered for both layers. The porosity and saturation values have been estimated from available literature (Bear, 1972) on the basis of the specific granulometric fractions studied. As the mass fraction of organic phase present in the soil in the real situation is not known, a high value (5%) was considered during the simulation as a precautionary measure.

Table 3: Hypothetical composition (i.e., mass-fractions) of the organic phase NAPL (5%) (i.e., car gasoline)

Chemical	Weight %	Molecular weight (g/Mol)
Benzene	1.7%	70.1
Toluene	1.2%	92.1
<i>m</i> -xylene	5.8%	106.2
<i>n</i> -dodecane	91.3%	170.3

The following air parameter values have been used in the simulation:

- Temperature: 20°C ;
- Dynamic viscosity: 0.0181 cp (centipoise);
- Air molar mass: 28 g/mol ;
- Air constant (R): $8.31 \text{ J/mol}^\circ\text{K}$; and
- Gaseous molecular diffusion coefficient: $0.60 \text{ m}^2/\text{d}$.

The contaminated volume (see Figure 5) has been represented, in the simulation, as a cylinder around the well, four metres deep (i.e., as deep as the grained top soil) and with a radius of 10 metres. The organic free phase saturation (i.e., liquid) has been set uniform throughout this cylinder and equal to 3%. This leads to initial concentration of the chemicals (Figure 7) higher than those reported in Table 1: hence, a precautionary longer time in remediation simulation will be obtained with respect to time required for real concentrations removal. The hypothetical composition of the organic phase used is reported in Tables 3 and 4.

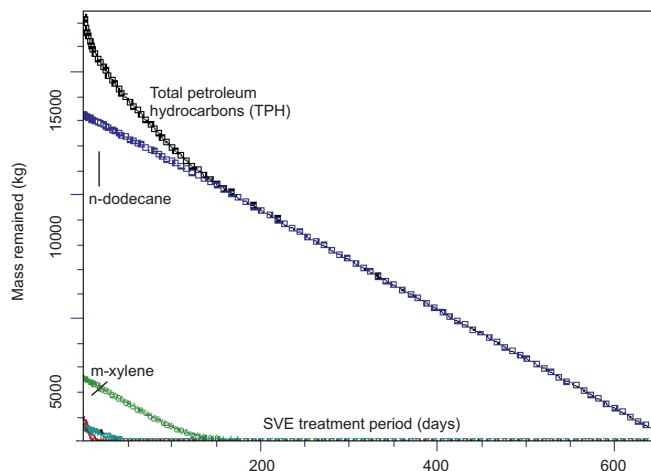


Figure 7: Free NAPL mass still present in the subsoil vs. time under SVE treatment.

Table 4: Hypothetical initial ($t = 0$) concentrations of the chemicals

Chemical	Organic free phase (liquid) and gas (air) concentrations	
	In subsoil (polluted zone) (mg/kg)	In production well (Equation (2b)) (mg/L)
Benzene	368.3	11.0
Toluene	237.5	2.2
<i>m</i> -xylene	1051	3.0
<i>n</i> -dodecane	5413	2.4

Simulation Results

Figure 5 displays gas pressure lines and velocity vector distributions resulting from the code simulation. The pressure curves are almost parallel to the well, due to the radially symmetric boundary conditions with a paved ground surface. Few distortions are present only close by the bottom of the screened zone. The soil discontinuity is not evident, since atmospheric pressure has been specified along with the whole right boundary of the domain. The relative permeability-saturation curves, based on the van Genuchten/Parker constitutive relationship (Parker, 1989), instead, give us very different gas velocity values, which are in the top soil much higher than those in the bottom soil.

Figures 7 and 8 show the efficiency of SVE technique in order to remove the organic compounds from the soil. Benzene, because of its high volatility, is easily removed in few days of operation (about 15 days). Toluene curve decreases quite rapidly, too; *m*-xylene removal requires more time: minimum concentration is reached after 150

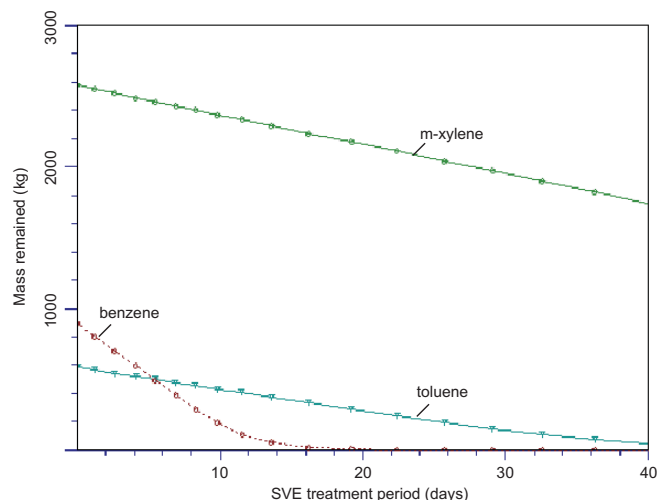


Figure 8: Particular of Figure 7: Behaviour of some aromatic compounds during first 40 days of SVE operations.

days; *n*-dodecane shows a much higher tendency to be retained in the soil: full depletion requires over 600 days. The graph remarks how different the removal times can be for chemicals with different volatility characteristics.

Residual concentration contours can be observed in Figures 9-11, for different compounds, at different times. Gradual depletion can be observed in graphs relating to successive time steps. Figure 10 refers to *m*-xylene concentration contours at the following time steps:

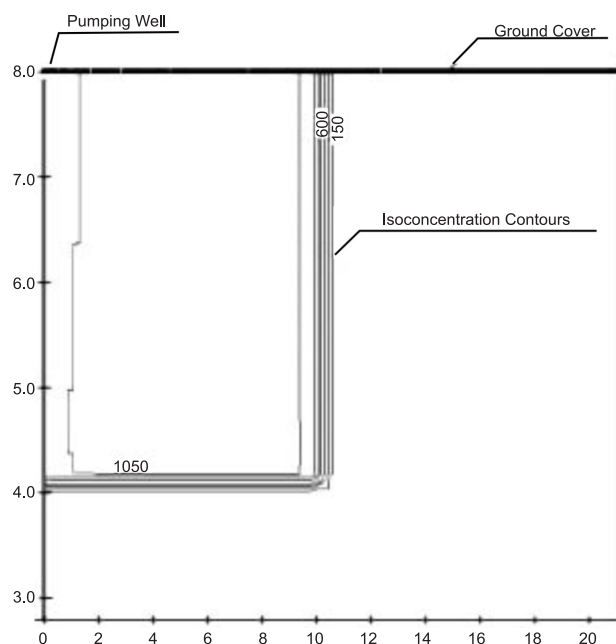


Figure 9: Concentration contours (mg/kg) for *m*-xylene free phase (air), after 0.1 day of SVE operations with respect to an initial ($t = 0$) concentration of 1051 mg/kg.

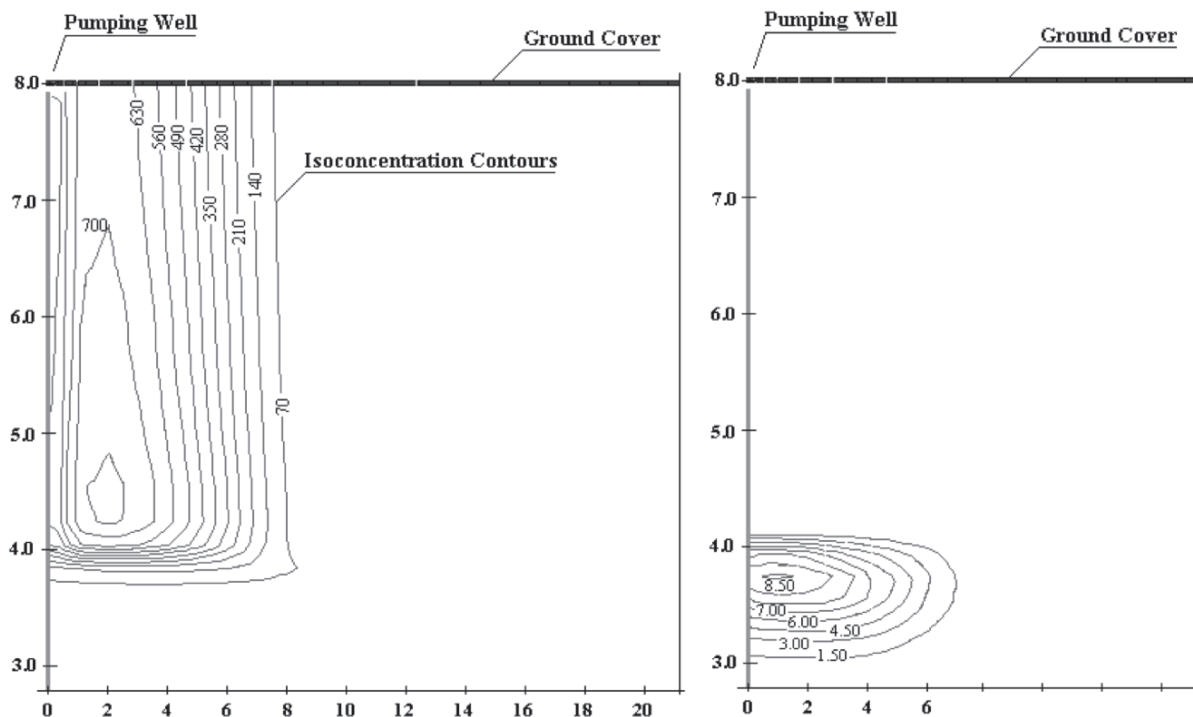


Figure 10: Concentration contours (mg/kg) for *m*-xylene free phase, after 100 days of operation on the left and after 650 days (on the right) of SVE operations.

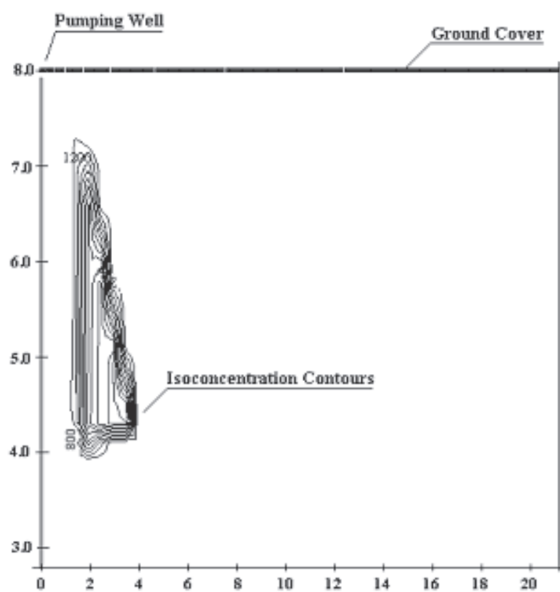


Figure 11: Concentration contours (mg/kg) for *n*-dodecane free phase (air), after 650 days of SVE operations with respect to the initial concentration over 5413 mg/kg.

0.1 d, 100 d and 650 d. Contaminant diffusion throughout the bottom layer can be observed in both the gaseous phase and soil moisture. After 650 days, *m*-xylene can be observed only in the bottom layer. *N*-dodecane, instead

(Figure 11), is nearly absent in the finer bottom soil after the 650th day, because of the minor attitude to mass transfer from the gaseous phase to the stagnant one.

The simulations described so far have been run under isothermal conditions (20°C). Other simulations have been run with different temperature input values (30°C and 40°C). These last results have shown remarkable reductions (up to 50%) in the time necessary for soil remediation. This points out the important contribution of this parameter in removal times.

Final Remarks

Table 5 reports a comparison between the costs of some remediation technologies usually used in Europe. It has been obtained from a recent research carried out by CLARINET (<http://www.clarinet.at> - Contaminated Land Rehabilitation Network for Environmental Technology in Europe) on the 15 European Union countries and also Iceland, Norway and Switzerland. No American cases have been considered in this research, due to the very different economic and environmental conditions (in particular the great extension of polluted areas). No direct comparison could be carried out with these values, because of uncertainty on how they have been obtained. Furthermore, remarkable cost differences can be found

Table 5: Costs (Euro) comparison between different remediation techniques in Europe

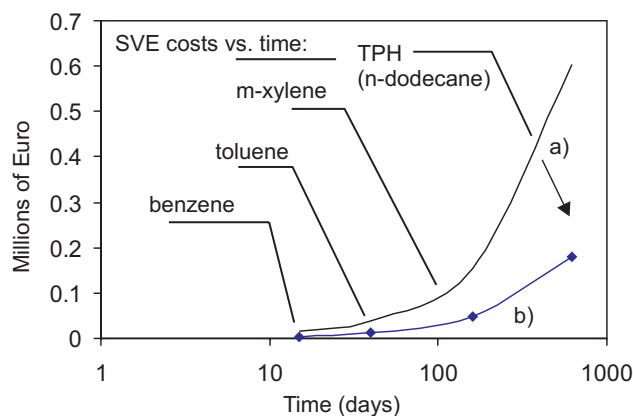
Technology	Cost	
Soil excavation and waste disposal	80	• m ⁻³
Bioremediation	60-75	• t ⁻¹
On site vitrification	65	• t ⁻¹
Soil vapour extraction	65-100	• m ⁻³
Soil washing	50-60	• t ⁻¹
On site oxydation	65-130	• t ⁻¹
Co-solvent flushing and incineration	650	• t ⁻¹
Thermal desorption (including excavation and pretreatment)	60-250	• t ⁻¹

Table 6: Costs (Euro) comparison between two different remediation projects at Brindisi test site

1. SVE treatments			
Site preparation	1	3500	3500
SVE extraction wells (3 × 10 m)	3	1100	3300
SVE observation wells (4 × 10 m)	4	975	3900
Mobil extraction system	1	57600	57600
GAC air scrubber	1	44000	44000
Soil probes (8)	8	600	4800
Specific core sample analyses (VOCs)	24	125	3000
Site restoration	1	3500	3500
Tractability study	1	15000	15000
Soil borings	500	75	37500
Soil sample analyses	40	125	5000
Total project (Euro)			181100
2. Soil transport/treatment/disposal			
Excavation (m ³)	6280	70	439600
Backfill (m ³)	6280	15	94200
Transportation (15 m ³ truck, 135 miles)	419	50	20933
Incineration	2386	0.25	596.5
Soil confirmation/verification samples analyses (10 sidewalls, 3 floors, VOCs)	13	125	1625
Site restoration	1	3500	3500
Soil borings	500	75	37500
Soil Sample Analysis	40	125	5000
Total project (Euro)			602955

waste disposal. Soil excavation and disposal seems to be one of the less expensive and most practised remediation methods in Italy. The small extent of the contaminated area, as well as lack of instrumentation for proper on site treatment, have led to choose this option which seems to be at low cost (80 •/m³). Anyway, disposal of contaminated soil implies the hazard connected to transport and volatile compound release in the environment. In order to obtain a complete soil remediation a final ex situ soil treatment is required by increasing the total cost of about 100 •/tonne. For this, recent Italian regulation suggests in situ method as the best alternative for polluted soils treatment. Actually, a deeper cost-benefit analysis involving also hazard factors and environmental impacts, could lead to prefer in situ techniques like SVE.

By following these costs, a comparative specific analysis was carried out at Brindisi site by considering local costs and SVE efficacy estimated by SVE modelling results. The costs reported in Table 6 lead a total amount of 181,100 US\$ for subsoil clean-up using SVE and 602,955 US\$ for soil excavation, transport, ex site treatment and final allocation in the waste disposal. The final daily trends of SVE and excavation/disposal costs have been summarized in Figure 12.

**Figure 12: Cost comparison between two remediation projects at Brindisi site (Italy): (a) soil excavation and transport to waste disposal after ex-site treatment; (b) SVE in situ treatments.**

Conclusions

in different European countries. In the case studied, the presence of the shallow water table may cause difficulties to excavation, leading to necessity of drilling a pumping well to extract contaminated water, thus causing cost increases.

The only remediation method carried out at the Brindisi site was the soil removal and transport in solid

The simulation results shown in this paper have pointed out SVE effectiveness in achieving aromatic hydrocarbons removal. Indeed few days are required for full benzene and toluene depletion. *M*-xylene requires about 150 days for being almost fully removed. *N*-dodecane depletion, instead, is much slower, because of its low

volatility, taking over 600 days. Treatment costs, as well, seem to be competitive with the method really programmed in the site which consists in the soil subtraction and its confinement in disposal. Indeed this last procedure should also take into account the soil clean up at “external site”. Anyway southern Italy sites are rarely treated with on site techniques, probably due to lack of proper instrumentation and specialists. Due to small extension of contaminated areas, the soil excavation and disposal, instead, is frequently practiced, despite recent legislative suggestions which dissuade from ex-situ soil treatments at higher environmental impacts. On site techniques should be encouraged in polluted areas by local governments. Increasing diffusion of these methods may cause, in the future, further drops of treatment costs. The SVE methods may become a good alternative also for small sites, leading to a reduction in external site remediation technologies and to a more sustainable management of contaminated areas.

Appendix

A mathematical formulation for groundwater volume depletion can be defined by the following continuity equation (Figure A1):

$$Q(t)dt = \alpha_1 h(t)dt = -SA dh \quad (A1)$$

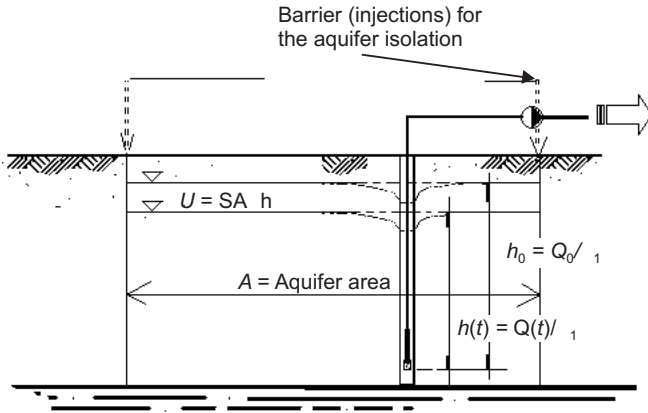


Figure A1: Conceptual scheme for groundwater depletion at Brindisi test site.

where the constant α_1 (m^2s^{-1}) accounts for the hydraulic aquifer conductivity and size of the horizontal area A ($=10000 \text{ m}^2$) of the aquifer subject to the pumping. Equation (A1) can be integrated between the initial height h_0 at $t = t_0$ and generic $h(t)$ at instant t :

$$dt = -\frac{SA}{\alpha_1 h} dh \rightarrow t - t_0 = \frac{SA}{\alpha_1} \log \frac{h}{h_0} \quad (A2)$$

With position $t_0 = 0$, Equation (A2) can be rewritten as the following:

$$-\frac{t\alpha_1}{SA} = \log \frac{h}{h_0} \rightarrow h(t) = h_0 \exp\left(-\frac{t\alpha_1}{SA}\right) \quad (A3)$$

As the initial height ($h_0 = 8 \text{ m}$) and the initial pumping flow rate (1.5 L/s) are known, it was possible to determine α_1 at test site directly by:

$$8 = \frac{1.5 \times 10^{-3}}{\alpha_1} \rightarrow \alpha_1 = 1.9 \times 10^{-4} \text{ m}^2/\text{s} \quad (A4)$$

Equation (A3) reproduces the depletion time reported in Figure A2.

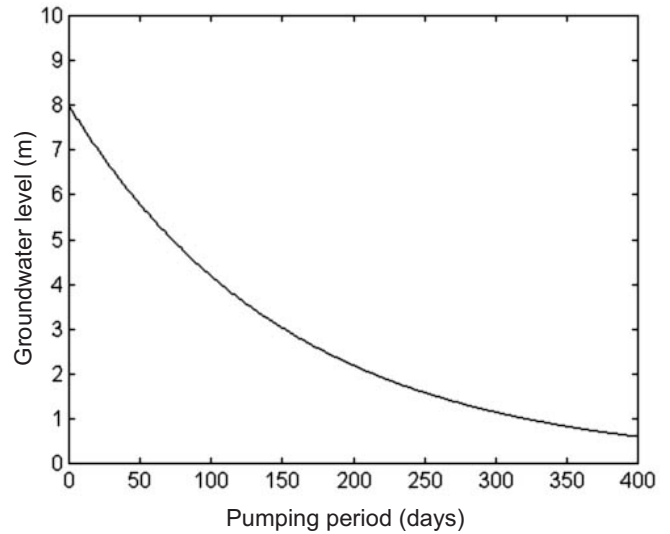


Figure A2: Recession of the groundwater level derived from Equation (1) under the initial pumping flow rate of 1.5 L/s.

List of symbols

- p gaseous phase pressure (n/m^2);
- K soil intrinsic permeability (darcy);
- k_{rg} relative permeability of the gaseous phase (dimensionless);
- ρ_g gas density (kg/m^3);
- ρ_o NAPL density (kg/m^3);
- μ_g dynamic viscosity of the gaseous phase (centipoises);
- n porosity of porous medium (dimensionless);
- τ_g gaseous phase tortuosity (dimensionless);
- D_g molecular diffusion coefficient in the gaseous phase (m^2/s);
- λ_i mass transfer rate coefficient (s^{-1});
- s_g gas saturation, i.e. fraction of gas volume in the volume of void space (dimensionless);

- s_w water saturation, i.e. fraction of water (and dissolved chemicals) volume in the volume of void space (dimensionless);
- s_o organic phase saturation, i.e. fraction of napl volume in the volume of void space (dimensionless);
- R_i retardation factor for generic NAPL component (–);
- c_i vapour concentration of i component in the gaseous phase (mg/L);
- c_i^e saturated vapour concentration for the component in the gaseous phase (mg/L);
- c_i^p saturated vapour concentration for the pure component in the gaseous phase (kg/m³);
- M_i molar weight of the compound (kg/mol);
- N_c total number of organic compounds;
- f_i mass fraction of the “ i ” compound in the organic phase, i.e. the fraction of the chemical in the total organic mass (dimensionless)

Acknowledgement

The authors are grateful to Prof. Ing Concetta I. Giasi, of Politecnico di Bari, for the valuable advice.

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