Multivariate Geostatistical and Natural Attenuation Model Approach for remediation of chlorinated compounds

CASTRIGNANÒ ANNAMARIA, CHERUBINI CLAUDIA, GIASI CONCETTA I., MUSCI
FAUSTA, PASTORE NICOLA
Department of Civil and Environmental Engineering
CRA - SCA - Politecnico of Bari
Via Celso Ulpiani, 5 – Via Orabona, 4 Bari
ITALY
claudia.cherubini@poliba.it

Abstract: - Modelling spatial variability of environmental parameters through the application of modern techniques of geostatistics has permitted to acquire elements apt to evaluate the possibility of using Natural Attenuation as a remediation technique for groundwater contaminated by chlorinated compounds.

Moreover, a precise delineation of hazardous areas in a polluted site is strongly based on accurate predictions of contaminant concentrations, a task that is complicated by the presence of censored data and highly positively skewed distributions.

The present paper proposes a geostatistical approach that includes different methods for the study and the control of the ongoing activity of Natural Attenuation in an abandoned industrial area. The considered variables in this application are the values of concentration in groundwater of some aliphatic chlorinated carcinogenic compounds (PCE and TCE), measured in numerous piezometers, which show highly skewed distributions, characterized by a considerable number of values below the detection limit of the instrument.

Indicator Kriging has been applied and the areas with 90% probability of exceeding the detection limit have been considered, inside which the variables were transformed through Gaussian Anamorphosis. The application of geostatistics has put into evidence the existence of a correlation between them not only from the chemical point of view, but also from the point of view of their spatial distribution: the shared presence of "hot spot" areas might be imputed to the existence of localized hazard sources. In those areas it is possible to detect coherence between the concentrations of the contaminants in study and the distribution of the parameters that control the phenomenon, which might be considered a clue that the degrading chemical activity is in progress.

Successively, some punctual considerations have been done on the basis of the concentration values of contaminants coming from a following sampling plan on the same area, in order to verify this result. At the same time, an analytical model has been implemented to quantify the Natural Attenuation.

Key-Words: - Natural Attenuation, chlorinated compounds, spatial variability, Indicator Kriging, Gaussian anamorphosis, multivariate geostatistics, time of remediation (TOR).

1 Introduction

Up to the eighties, the chlorinated solvents have been considered recalcitrant to the common treatments of remediation and the attempts of remediation were limited to Pump&Treat treatments [1]. Experimental verifications and literature data [2] show that the methodology of Pump&Treat is often not effective, because it requires long periods of treatment and high costs. The reasons are connected to the fact that those compounds are often present as NAPLs in the saturated zone, migrate along preferential pathways and tend to localize in inaccessible zones, so they cannot be removed effectively by means of groundwater extraction [3]; therefore their release as NAPL continues. In this context numerous innovative technologies have been developed and tested in order to enhance the removal of chlorinated ethenes [4]. It has been observed that those compounds go through, in time, a process of Natural Attenuation according to different biodegrading processes; the technologies of Natural Attenuation based on the stimulation of the biological degradation activity prove to be very promising. The other processes involved in Natural Attenuation phenomena of chlorinated solvents are biodegradation, dispersion, sorption and volatilization [5].

In any case, monitoring of Natural Attenuation requires accurate and updated information about spatial distribution of the contaminants and the environmental parameters involved.

Geostatistics, which is based on the theory of regionalized variables [6] [7], is generally preferred to other techniques of space/time interpolation, because it takes into account spatial correlation between neighbouring observations to predict attribute values at unsampled locations.

This analysis has allowed to create maps of concentration of the considered pollutants, in order to visualize the propagation of contamination and therefore to monitor its evolution in time. Because the collection of site characterization data is inevitably limited, knowledge of the real situation is always incomplete and so any estimation will be affected by uncertainty. Therefore, a probabilistic approach is to be preferred because it treats uncertainty explicitly.

Next to it, for an initial analysis, an approach to the mathematical modelling of the chemical and physical processes involved in transport and Natural Attenuation phenomena of contaminants has been implemented. In particular, the Natural Attenuation Software (NAS) has been used, which is based on the analytical solution of the one-dimensional differential equation of the reactive transport phenomena. It allows to define, in a whole, if Natural Attenuation could be an effective remediation strategy.

This kind of methodology requires the knowledge of several site-specific parameters, given that the rate of Natural Attenuation depends on many factors, for example the aquifer geology and its hydrodynamic properties, contaminants chemical properties and hydrogeological parameters.

The first aim of this kind of model is that of demonstrating that the phenomenon of Natural Attenuation is able to reduce the contaminant concentrations to levels lower than the values considered acceptable according to the local legislation. In this study the reference will be the Italian legislation, and in particular the threshold values of contamination (CSC) derived from it.

Secondly, the present study aims at experimenting a methodology of data analysis that would allow to verify, a priori, that in a site contaminated by chlorinated compounds a process of Natural Attenuation is taking place. In the analyzed site the used data are not enough for the application of the technical protocols [4] (RABBIT).

2 Materials and Methods
2.1 Study case
The study area, whose name cannot be explicitly mentioned for privacy reasons, belongs to a wide

industrial district where a diffused groundwater contamination by hydrocarbons and heavy metals has been detected.

In the south eastern area of the district there is massive presence of contamination by chlorinated compounds; this zone, represented in Figure 1, is hydrogeologically delimited by a subterranean watershed and by the Adriatic sea.
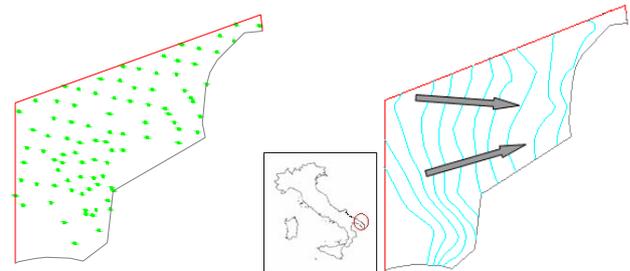
Fig.1 Location of piezometers in the area and map of the piezometry of the site

All the investigations carried out in the past in the various campaigns of characterizations have been finalized to the design of a Pump&Treat system; the applicability of the Monitored Natural Attenuation, object of the present study, has never been taken into account.

A methodology of verification and control of the on-going process has been obtained with the available data and bases itself on the individuation of the possible existing correlation among the various chlorinated species present in the area, that are linked to each other by a "mother- daughter" dechlorination process: Tetrachloroethylene (PCE) → Trichloroethylene (TCE) → cis-1,2-Dichloroetylene (cDCE) → Vinyl Chloride (VC). This analysis has been supported by the verification of the few values of the environmental parameters. Starting from the available data bank, by means of the exploration of them, it is possible to get to the definition of the best method to give reliable estimations on the state of the environmental system. It is important to point out that the precision of estimation depends strongly both on the intrinsic variability within the selected unit of sampling and the number and geometrical configuration of samples. Unfortunately the sampling scheme used in the studied area is incomplete and some areas are not covered, as it can be seen in Figure 1, in which the used piezometers are reported and the irregular polygon that contains them all. Another problem is the considerable presence of samples with no defined concentration values of the chlorinated solvents, that is to say values below the detection limit of the instrument. Due to the impossibility of ignoring those data, because they are numerous and

contain a considerable amount of information, an alternative solution has been used.

2.2 Geological and hydrogeological characters of the area

The examined area is located in Apulia (south-eastern Italy) and coincides with a wide structural depression opened towards the Adriatic coast that interests the strong succession of carbonatic rocks of the Apulian foreland. In this depression sediments of the sedimentary cycle of the Bradanic foredeep and terraced marine deposits have stratified. The succession of the geologic formations can be schematized from the bottom to the top: Altamura limestone (Cretaceous), that extends in depth for thousands of meters; Gravina calcarenites (Upper Pliocene – Lower Pliocene) partially transgressive on the Mesozoic limestones; subapennine blue-grey clays (Lower Pliocene) that constitute the impermeable substrate that sustains the superficial aquifer; terraced marine deposits (middle- upper Pleistocene) where is placed the superficial groundwater sustained by blue-grey clays. These deposits have variable thicknesses between 12-18m; Alluvial and colluvial deposits (Olocene) cover locally the terraced marine deposits with variable thicknesses between 0,5-5,00m. From the hydrogeological point of view it is possible to identify two well distinct hydrogeological systems: a shallow aquifer in the Pleistocenic terraced marine deposits sustained by the plio- pleistocenic clays that has limited discharge, local character and a saturated thickness variable from 10 to 37m; a deep aquifer in the fissured and karstified cretacic carbonatic, as well as in the calcarenites and sands located in continuity on the Cretaceous rocks. In this aquifer groundwater flows towards the coast with pressure head gradient lower than 0,05%.

This study has involved only the shallow aquifer that could be found at a mean depth of 3m below the ground level. In some zones of the examined area the aquifer is delimited in the upper part by low permeability soils that act as aquitard.

2.3 Methodology of analysis

2.3.1 Geostatistical analysis

The analysis has been carried out by means of multivariate geostatistics that uses also the information coming from the relations among the variables in order to improve the precision of the estimates and to separate the different sources of variation in function of the spatial scale at which

they operate [8].

For coregionalized variables it is meant regionalized variables mutually dependent spatially. A measure of the joint variability between two variables is represented by the cross semivariogram, calculated for couples of observed points at a distance $\mathbf{h}$ and defined as half the mean of the product of the increments $\mathbf{h}$ relative to two different attributes Z_i e Z_j:

$$\gamma_{z_i z_j}(h) = \frac{1}{2N(h)} \sum_{\alpha=1}^{N(h)} \{[z_i(x_\alpha) - z_i(x_\alpha + h)][z_j(x_\alpha) - z_j(x_\alpha + h)]\} \quad (1)$$

When one or more variables are estimated, using both the existing spatial dependence and the one among the variables, the technique is called Cokriging and is aimed at reducing the variance of the Kriging.

Differently from Cokriging, Indicator Kriging [9] offers a way to deal with classes or populations of either high values or values below the detection limit. The basic idea is to discretize the range of variation of the environmental attribute by a set of thresholds (e.g. deciles of sample histogram, detection limit, regulatory threshold) and to transform each observation into a vector of L Indicators of exceedence or not of each threshold [10].

The proposed approach is based on a simple binary transformation, whereby each datum is transformed into an Indicator before variography:

$$i(x_a; z_c) = \begin{cases} 1 & if \quad z(x_a) \le z_c \\ 0 & otherwise \end{cases} \quad a = 1,2,...,n \quad (2)$$

Here the threshold z_c for each variable represents the detection limit and $z(x_\alpha)$ each sample datum. Cokriging of binary indicator instead of the raw variable $Z(\mathbf{x})$ provides the conditional expectation of $I(\mathbf{x}_\alpha; z_c)$ which is equal to the conditional cumulative distribution function (ccdf) of $Z(\mathbf{x})$ (F):

$$E\{I(\mathbf{x}; z_c)|(n)\} = \text{Prob}\{Z(\mathbf{x}) \le z_c|(n)\} \equiv F(\mathbf{x}; z_c|(n)) \quad (3)$$

These probabilities can be calculated as linear combinations of the surrounding indicators of the variables $z(\mathbf{x}_\alpha)$ through a cokriging system [11].

Thus, the Cokriging technique for the Indicator variables allows to estimate, in a location where sampling is not carried out, not the value of the variable, but a value between 0 and 1 that represents an estimation of the probability that the value of the variable is not greater than the threshold value [12]. This estimate requires the construction of the linear model of coregionalization (LMC), that considers all the studied variables as the result of the same independent physical processes, acting at different

spatial scales u. The $n(n+1)/2$ simple and cross variograms of the n variables are modelled by a linear combination of N_S standardized variograms at unit sill $g^u(h)$. Using the matrix notation, the LMC can be written as:

$$\Gamma(h) = \sum_{u=1}^{N_S} B^u g^u(h) \qquad (4)$$

where $\Gamma(h) = [\gamma_{ij}(h)]$ is a symmetric matrix of order $n \times n$, whose diagonal and non diagonal elements represent simple and cross variograms for lag h; $B^u = [b_{ij}^u]$ is called coregionalization matrix and it is a symmetric semi-definite matrix of order $n \times n$ with real elements b_{ij}^u at a specific spatial scale u. The model is authorized if the functions $g^u(h)$ are authorized variograms models [8].

The next phase of analysis has concerned the drawing up of concentration maps by using Kriging or Cokriging for the contaminants in those areas in which the probability of exceeding the detection limit proves to be higher than 90%.

Coming back to the original variables to assess estimation uncertainty, because of a shift from normality, the raw variables were preliminarily transformed into a normal distribution and, afterwards, the estimates were back-transformed into the raw distribution.

In fact, even if Cokriging does not require the data to follow a normal distribution, variogram modelling is sensitive to strong departures from normality, because a few exceptionally large values may contribute to many very large squared differences. Moreover, in these conditions Cokriging variance cannot be used as an estimation of local error. With this purpose, in order to produce the map of the four variables we used a prior Gaussian transformation of the initial attribute $\{Z(x), x \in R^2\}$ into a Gaussian-shaped variable $\{Y(x), x \in R^2\}$ with zero mean and unit variance, in such a way as to obtain:

$$Z(x) = \phi[Y(x)] \qquad (5)$$

Such a procedure is known as Gaussian Anamorphosis [13] [2] and it is a mathematical function which transforms a variable Y with a Gaussian distribution in a new variable with any distribution. To transform the raw variable into a Gaussian one, the precedent function has to be inverted (5).

The modelling of the anamorphosis starts with the discrete version of the curve on the true data set; then a model expanded in terms of Hermite polynomials $H_i(Y)$ [2] [14] is fitted to the discretized anamorphosis. This model gives the correspondence

between each one of the sorted raw data and the corresponding frequency quantile in the standardized Gaussian scale. The transformed data are used for interpolation at all unsampled locations using Ordinary Kriging or Cokriging and then back-transformed to the original variables.

2.3.2 Natural Attenuation model approach

The complexity of the studied area does not permit a direct approach to a detailed modelling; therefore it is necessary to carry out different intermediate steps, in order to describe the whole system. In the present study, aimed at evaluating the possibility of using Natural Attenuation as remediation technique, a simple one-dimensional model is proposed. In particular, if the plume is at steady-state conditions $(\partial C / \partial t = 0)$, for boundary conditions of $C = C_0$ at $x = 0$, and $C = 0$ as $x \to \infty$, the solution of the solute transport equation is:

$$C(x) = C_0 \exp - \left[\frac{-v + \sqrt{v^2 + 4Dk}}{2D} \right] x \qquad (6)$$

It describes the exponential decrease in solute concentrations away from a constant source [15] as proportional to groundwater velocity (v), the coefficient of hydrodynamic dispersion (D), and the biodegradation rate constant (k). Thus, knowing hydrogeologic parameters, redox conditions and the contaminant concentration values, it is possible, through a curve-fitting operation, to obtain the first-order kinetic, that describes the single contaminant degradation processes. The knowledge of the site-specific characters, together with the biodegradation parameters, allows to attribute the quantification of Natural Attenuation problem to a time-of-remediation (TOR) problem.

The TOR problem is made up of three interactive components: distance of plume stabilization (DOS) away from a contaminant source of given concentration; time of plume stabilization (TOS) after lowering source-area contaminant concentration; time of NAPL dissolution/dispersion for given mass, composition, and geometry. A combination of analytical solution (DOS and TOS) and numerical solution (NAPL dissolution) to the solute-transport equation can be used to evaluate TOR questions [16].

3 Results and Comments

The elaboration of the four Indicator variables relative to each raw variables, carried out by means

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of the use of the Cokriging technique [12], has allowed to consider both the existing spatial dependence and the one among the variables. Figure 2 displays the direct and cross-variograms (dots) for the four Indicator variables. A linear model of coregionalization was then fitted to the ten variograms, so that the final structure reflected: (a) a general sharp increase of the variograms at short-range, followed by a slower increase at long-range, until a sill is reached at far distances; (b) well spatially structured variograms, except for the direct variogram of Indicator VC, near to a pure nugget effect; (c) the lack of any significant spatial cross-correlation between the Indicator variables, except for the cross-correlation between Indicator TCE and PCE, close to the upper dashed line that represents the perfect positive correlation. The structure includes a nugget effect and an isotropic cubic model with range equal to 650m.
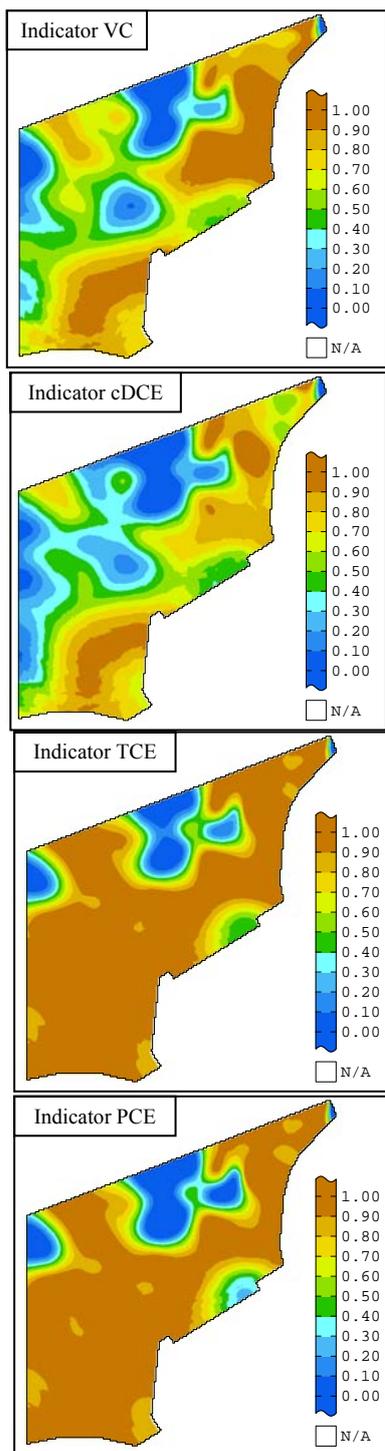
From the analysis of the maps of probability of exceeding the detection limit for the four examined variables (Fig.3) it is possible to make some considerations on the spatial variability of the data:
✓ The Vinyl Chloride concentrates much of the values below the detection limit in the northern part, that proves to be not contaminated;
✓ the cis-Dichloroethylene presents a low number of values below the detection limit, concentrated in a more central area;
✓ the Trichloroetylene and the Tetrachloroetylene show few values below the detection limit, mostly concentrated in a northern area.

These maps show a high similarity in the spatial distributions of the contaminants TCE and PCE. As far as these two substances are concerned, the areas in which the values are higher than the detection limit at 90% probability level prove to be wider than for VC and cDCE.
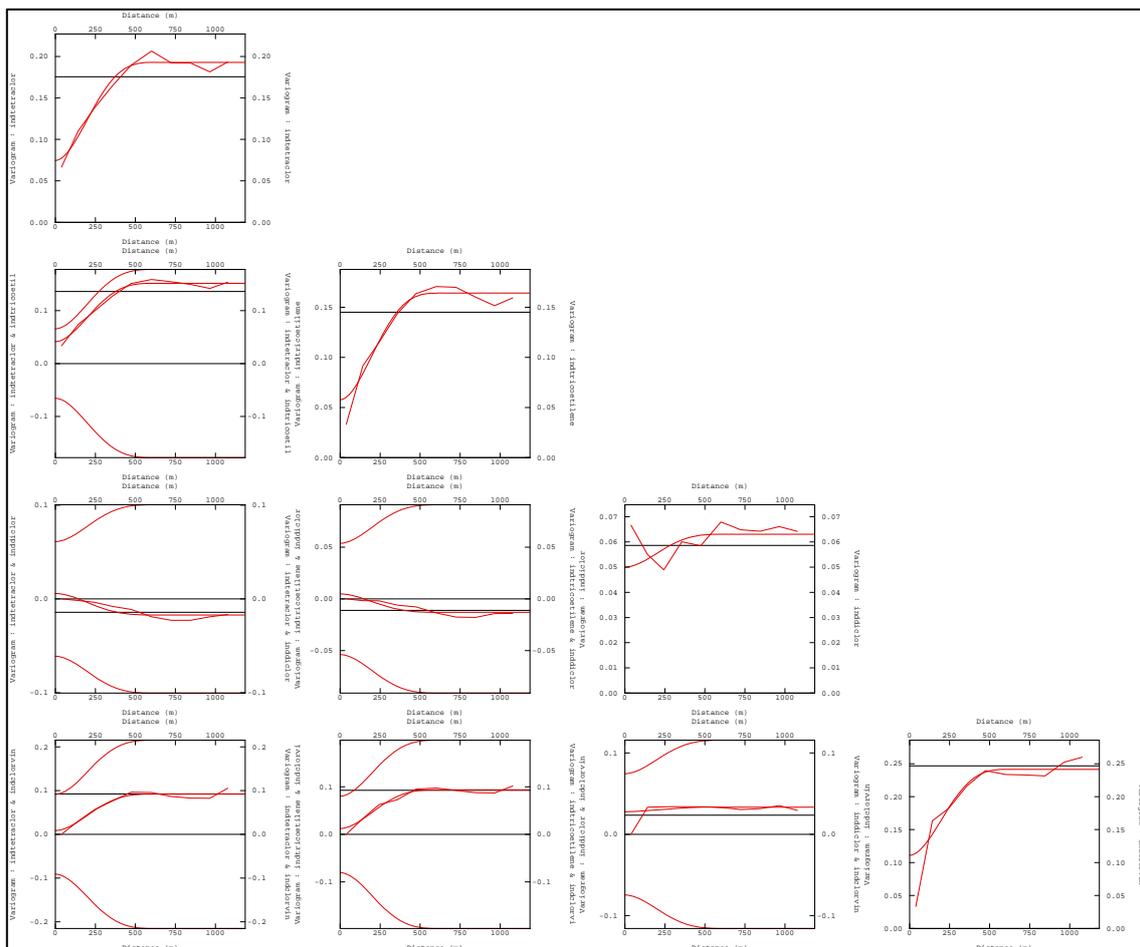
Fig.2 Direct and cross experimental variograms (fine line) and variogram models (thick solid line) for Indicator variables.

Fig.3 Maps of probability of exceeding the detection limits of VC, cDCE, TCE and PCE.

As far as Vinyl Chloride (VC) and cis-Dichloroethylene (cDCE) are concerned, the values found in the area previously delineated from the analyses on groundwater samples vary among the detection limits, equal to 0.05 μg/l and 0.005 μg/l, and the maximum values, equal to 9,184 μg/l and 11,000μg/l, respectively.

The VC's and cDCE's concentration values don't follow the Gaussian distribution, infact their

histograms of the frequencies show concentration of samples with low contamination values and the presence of "outliers". Therefore, it has been necessary to operate normal transformations of the variables by means of a Gaussian Anamorphosis.

In the figure 4 are reported, respectively, the maps of VC and cDCE, with the isolines of the threshold concentration (CSC) for the two pollutants, respectively of 0.5 μg/l and 0.05 μg/l. The concentration maps have been obtained using the isofrequency scale, in such a way as each class represents a decile of the distribution. The area inside the red rectangle can be considered as a spot area, where the highest concentration values were found.
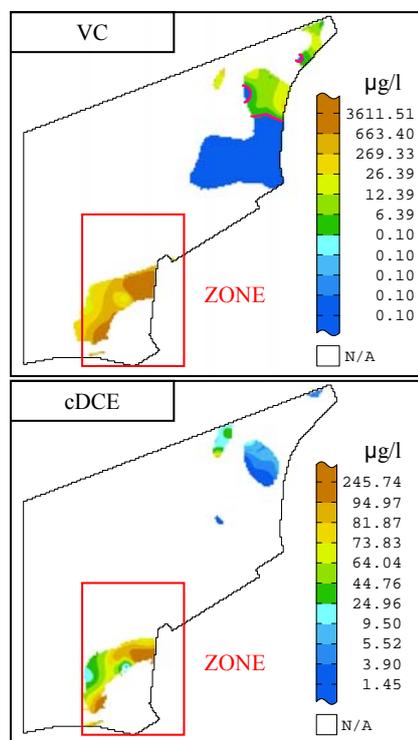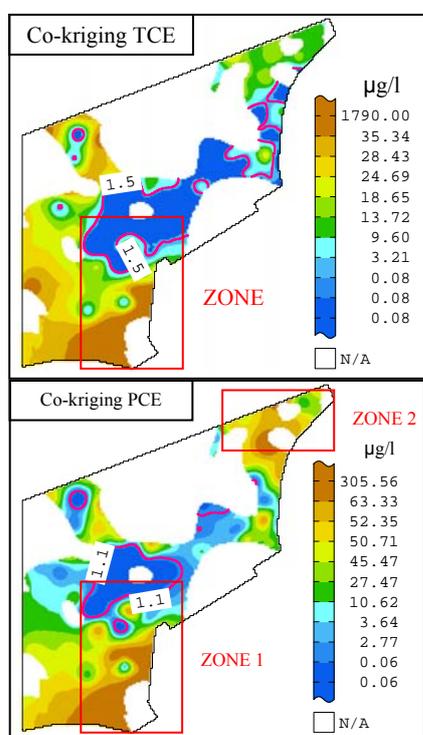

Fig.4 Concentration maps of VC and cDCE, with the area spot highlighted and the isolines (red line) of the threshold concentration.

In the cDCE map the isoline of the threshold concentration is not marked, because the found contamination values exceed in every points the threshold value.

As far as Trichloroetylene (TCE) and Tetrachloroetylene (PCE) are concerned, the values delineated in the area by using the detection limit, vary among the detection limits, equal to 0.02 μg/l and 0.05 μg/l, and the maximum values, equal to 3,400 μg/l and 363 μg/l, respectively.

The distributions of the concentration values for TCE and PCE do not follow the Gaussian distribution. After transforming the two variables by

means of a Gaussian Anamorphosis, the evident correlation between the two variables, as it is shown in figure 3 and in more details in a previous work [17], has suggested to perform an interpolation of them by means of multivariate geostatistics. This analysis has been carried out in the common areas characterized by the 90% probability of exceeding the respective detection limits. The high spatial correlation between the two variables causes their values to be jointly low in some zones and high in others, as it is shown in the maps of figure 5, obtained by using Cokriging. The maps of the estimated values, obtained using the isofrequency scale, were reported in figure 5 together with the isolines of the threshold concentration (CSC) for the two pollutants, respectively of 1.5 μg/l and 1.1 μg/l. Moreover, the spot areas, where the highest concentration values are found, have been identified in the red rectangles.

Fig.5 Concentration maps of TCE and PCE estimated by Cokriging, with the spot area highlighted and the isolines (red lines) of the threshold concentration.

Synthesizing the information obtained from the interpolation of the considered substances, it is possible to conclude saying that two principal spot areas can be identified; one more northern (Zone 2), the other one more southern (Zone 1), which suggests the presence of two centers of hazard.

Starting from the estimation of the least-chlorinated substances, it is possible to detect the presence of cDCE with concentrations higher than the threshold value (CSC) and the presence of VC with maximum values much higher in comparison with cDCE. This can suggest the presence of an on-going chemical degradation process.

A high positive spatial correlation between TCE and PCE has been detected: the two contaminants extend on a wide area, showing common characters. Also in this case, due to the presence of TCE with maximum concentration values much higher than PCE, it is possible to hypothesize the presence of a degradation process.

Making reference to the isopiezometric heads for the examined area (Fig.1), it might be affirmed that the groundwater flow direction appears to be almost coincident with the direction of maximum continuity for the two variables.

In order to verify the hypothesis of Natural Attenuation degradation processes, in a previous study, the conditions of pH, redox potential and dissolved oxygen present in situ, together with few data of the monitoring carried out in 2005, have been analyzed. The distribution of these environmental and contaminant parameters, in particular in the spot area called Zone 1, might confirm the presence of on-going degradation processes [17].

In this work, instead, this control has been carried out through the application of Natural Attenuation Software (NAS) tool [16] that requires detailed site information about hydrogeology, redox conditions, and contaminant concentration. In particular, the required site data, expressed as range of values, are: hydraulic conductivity, measured from pumping tests; hydraulic gradient; total and effective porosity; aquifer thickness, and percentage of organic matter.

Moreover, NAS requires the definition of contaminant plume and the identification of the source with its geometry. From the analysis of the investigations carried out in the area, the source has been located into the southern spot zone and the plume has been hypothesized directed to the subterranean watershed. This choice is due to the presence, in that direction, of some points belonging to the sampling of 2005 that, therefore, may give the possibility to control the obtained results.

To characterize the contaminant plume, NAS requires contaminant concentration and redox chemistry data along the axis of the plume. A data set has been defined, collected in 2004 and constituted by 12 wells. The redox data at the site indicate Fe(III)-reducing conditions in and near the source area grading to oxic redox conditions downgradient. This discontinuity between redox conditions causes a distinct change in biodegradation rates. It can be simulated by means of the multizone

model capability of NAS, as it is shown in figure 6 for PCE.
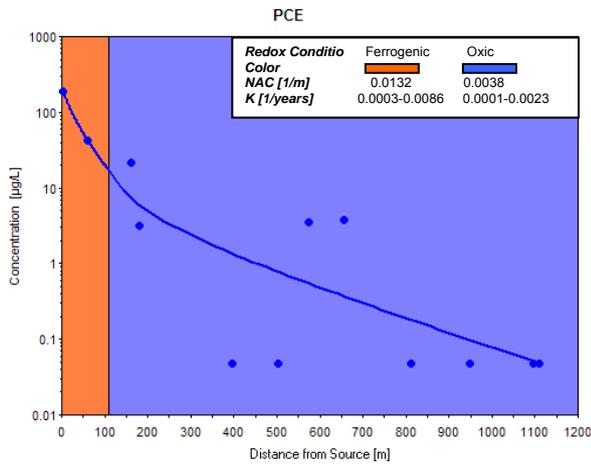
Fig.6 Discontinuity in biodegradation rates between redox zones, for PCE.

Natural Attenuation Capacities (NACs) for each contaminant in each redox zone are calculated and used to determine the maximum plume length, equal to 599 m, longitudinal and transverse dispersivity values, equal to 9.77 m and 0.49 m respectively, and the decay rates for each contaminant in each redox zone.

The maximum source concentration and time-of-stabilization (TOS) calculations performed by NAS should suggest no reduction for PCE, TCE and cDCE; instead it suggests a maximum source-area concentration for VC of 1,486 μg/l, given a point of contact located 1000 m downgradient (roughly corresponding to the subterranean watershed) and a maximum concentration level at the watershed line of 0.5 μg/l (equal to the CSC for VC). The calculated maximum source-area concentration is round about half the concentration at the source area of 2004 (about 2,300 μg/l), suggesting that a reduction in source-area concentrations is needed at this site.

Thus, due to a VC source reduction required, NAS estimates a range of TOS, based on the groundwater contaminant velocities and decay rates previously estimated, from about 6 to 230 years, with a best estimate of 30 years. These estimates suggest that the contaminant plume will persist for the foreseeable future.

Also of interest are TOR estimates for residual NAPL present in the landfill. From the soil samples of the area, the presence of contamination in the unsaturated medium does not emerge; thus, no presence of NAPL mass at the source has been hypothesized. Figure 7 shows TOR analysis at this site for PCE, TCE, cDCE and VC, with no source; in

the graphs the observed data points, also for 2005 sampling, are marked with red points.
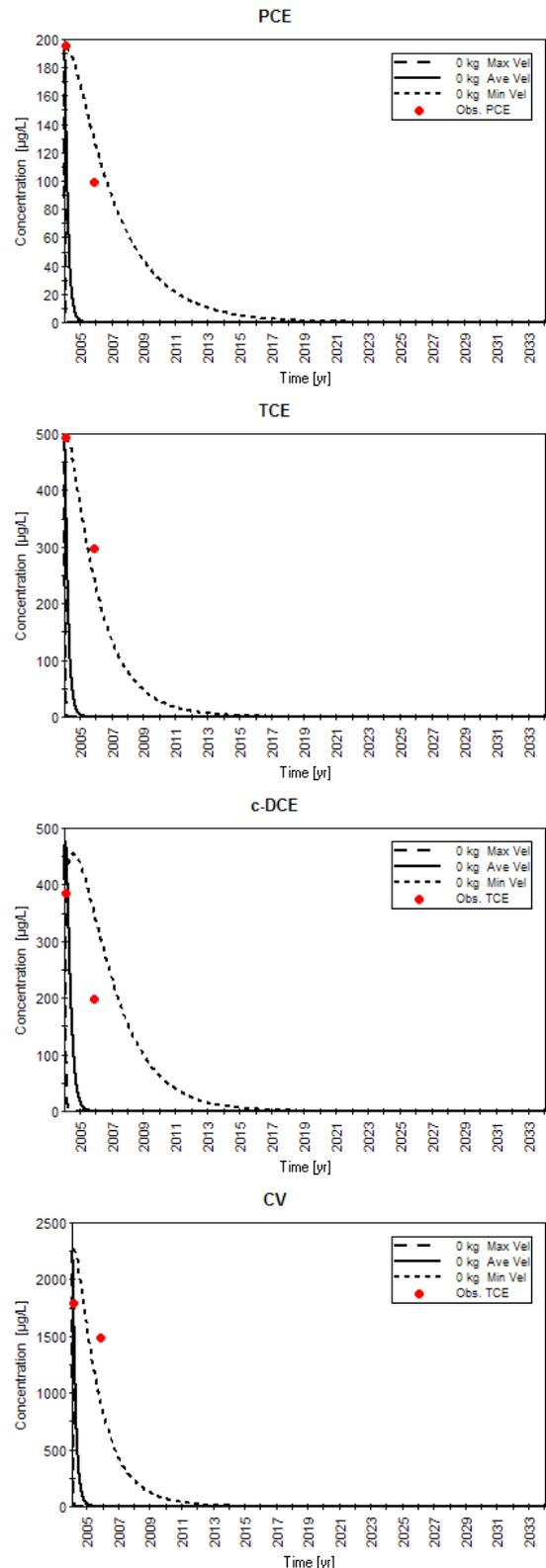
Fig.7 TOR graphical output for PCE, TCE, cDCE and VC.

These graphs show a modeling near to the real values of concentration coming from the successive sampling of 2005, especially with reference to the minimum groundwater velocity. So, this result demonstrates the applicability in the site of the Natural Attenuation processes, with times of lowering the concentration values of analyzed contaminants that vary, in reference to the minimum groundwater velocity, from 12 years (for TCE) to 22 years (for cDCE). Moreover, it confirms the lack of a contaminant source or the presence of completely dissolved contaminants.

4. Conclusions

After that a situation of widespread contamination has been delineated, through geostatistical techniques, the analysis of environmental parameters (pH, dissolved oxygen, redox potential and isopiezometric head) has detected in a roughly way, because of un incomplete sampling mesh, the presence of opportune conditions for the occurrence of Natural Attenuation processes.

The use of a software to confirm the possibility of this scenario, has quantified the required time of remediation for a first analysis. In point of fact, this method could not be considered totally adherent to reality, because the software uses steady-state conditions to calculate TOS, but no source in the TOR calculation has been supposed.

A future development of this study could be the implementation of a more advanced model, able to use more complex and differed kinetics. Moreover, by means of collecting data sets at successive temporal intervals, it would be possible to check and study more accurately the evolution of the situation.

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