

The Application of Multivariate Geostatistical Techniques for the Study of Natural Attenuation Processes of Chlorinated Compounds

CASTRIGNANO' ANNAMARIA, CHERUBINI CLAUDIA, DIMA LUCA, GIASI CONCETTA I.,
MUSCI FAUSTA

Department of Civil and Environmental Engineering
CRA Agricultural Research Institute - Politecnico of Bari
Via Celso Ulpiani, 5 – Via Orabona, 4 Bari
ITALY

Abstract: - Modeling 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 work 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 of the parameters that control the phenomenon, which might be considered a clue that the degrading chemical activity is in progress.

In the areas characterized by higher uncertainty for both variables (PCE and TCE), it is possible to presume that the phenomenon of attenuation is in progress, because it is in those areas that the transformations from PCE to TCE may happen in function of the parameters that control the phenomenon.

Key-Words: - Attenuation, chlorinated compounds, spatial variability, indicator kriging, multivariate geostatistics, confidence interval.

1 Introduction

The remediation of soils and groundwater contaminated by chlorinated solvents is object of scientific relevance both at national and international level for the number of researches carried out with the aim of developing adequate technologies of remediation in alternative to the consolidated approach of "Pump and Treat".

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. Experimental verifications and literature data [5] 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 and migrate along preferential pathways and tend to localize in inaccessible zones, so they cannot be removed effectively by means of groundwater extraction [4]; so 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 [7]. 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 rate of natural attenuation depends on many factors, for example the aquifer geology and the hydrodynamic properties of it, chemical contaminant properties and hydrogeological parameters. So it appears to be necessary to carry out a site-specific quantification of the natural attenuation processes at field scale, in order to draw up a model able to simulate the above mentioned processes.

The first aim of this kind of models 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.

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 [7] (RABBIT).

2 Materials and Methods

2.1 Site setting

The study area, whose name cannot be explicitly mentioned, 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 subterranean watershed and by the Adriatic sea.

All the investigations carried out 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.

The available analytic set of investigated parameters consists of the contaminants present in the area and there are only few data related to environmental parameters, such as pH, redox potential, temperature, dissolved oxygen, fundamental indicators of the Natural Attenuation process.

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: $PCE \rightarrow TCE \rightarrow cDCE \rightarrow VC$. 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 variability inside the selected unit of sampling and the variability among the positions themselves.

Unfortunately the sampling distance in the studied area is not completely regular so that some areas are not covered, as it can be seen in Figure 1, in which are reported the used piezometers 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.

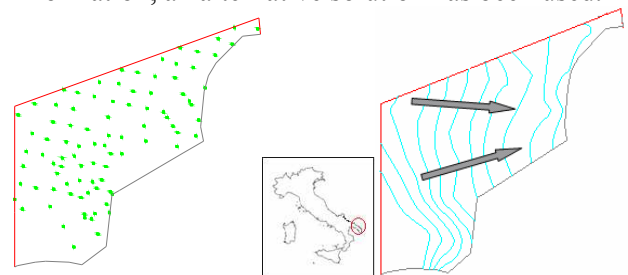


Fig.1 Location of piezometers in the area and map of the piezometry of the site

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 surficial 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 superficial groundwater contained in the Pleistocenic terraced marine deposits and sustained by the plio- pleistocenic clays that has limited discharge, local character and a saturated thickness variable from 10 to 37m; a deep groundwater contained in the fissured and karstified cretacic carbonatic, as well as in the calcarenites and sands located in continuity on the Cretaceous rocks. This groundwater flows towards the coast with pressure head gradient lower than 0,05%.

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

2.3 Methodology of 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 [1].

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, defined as half the mean of the product of the increments relative to two different attributes.

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

The examined variables are the concentration of VC, cDCE, TCE, PCE, expressed in $\mu\text{g/l}$. These variables are characterized by some undefined concentration values, that is to say values below the detection limit of the instrument. In the present study, their elaboration has been carried out by means of the use of indicator variables and the purpose was to draw up for each single pollutant the map of probability of exceeding the detection limit.

The study through indicator variable consists of transforming the concentration of each contaminant

in a two-valued variable that assumes value of 1 if the contamination exceeds the detection limit, and value of 0 otherwise. The elaboration of the four indicator variables has been carried out by means of the use of the cokriging technique [3], that has allowed to consider both the existing spatial dependence and the one among the variables.

The next phase of analysis has concerned the drawing up of concentration maps by using kriging for each contaminant 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. Such a transformation was realised by gaussian anamorphosis, which is a mathematical function transforming a variable with a gaussian distribution into another one with any distribution. This function was written as a polynomial expansion of Hermite Polynomials stopped to a given order.

3 Results and Comments

A coregionalization model has been fitted to the ten (four direct and six cross-) variograms, that includes two structures: a nugget effect and a cubic structure with range equal to 650m.

From the analysis of the maps of probability of exceeding the detection limit for the four examined variables 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 Trichloroethylene and the Tetrachloroethylene show values below the detection limit, mostly concentrated in a central area.

These maps show a high similarity between 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 prove to be wider than for VC and cDCE. The existence of a high correlation between TCE and PCE has allowed to carry out a multivariate analysis on the two variables.

As far as Vinyl Chloride and cis-Dichloroethylene are concerned, the values found in

the area previously delineated from the analyses on groundwater samples vary, respectively, among the detection limits, equal to 0.05 µg/l, and 0.05 µg/l and the maximum values, equal to 9184 µg/l, and 11000µg/l.

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. After this process, the ordinary kriging has been applied and successively the estimated values have been retransformed in the original ones of concentration of Vinyl Chloride and cis-Dichloroethylene through the anamorphosis function previously calculated.

In the figure 2 are reported, respectively, the kriging maps of Vinyl Chloride and cis-Dichloroethylene, obtained using the isofrequency scale, so that each class represents a decile of the distribution.

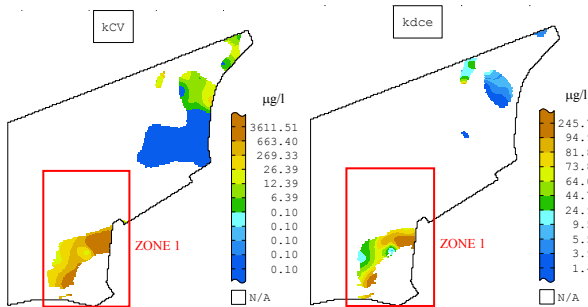


Fig.2 Concentration maps of VC and cDCE, with the area spot highlighted.

In the figures 3 are reported, respectively, the kriging maps of Vinyl Chloride in the best scenario of contamination and in the worst, obtained using confidence interval limits.

The confidence interval maps, that represent the variation range for the contamination values with an error of 5%, show a spot area to the south.

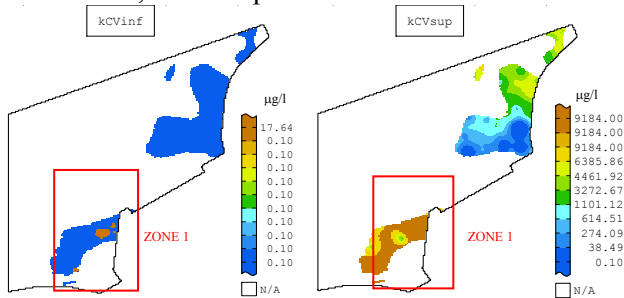


Fig.3 VC's concentration maps, in the best and in the worst scenario of contamination, with the spot area highlighted.

In the figures 4 are reported the same kriging maps of cDCE in the best scenario of contamination

and in the worst one. Again they show, in spite of the high uncertainty variability of the values, a common spot area in the south.

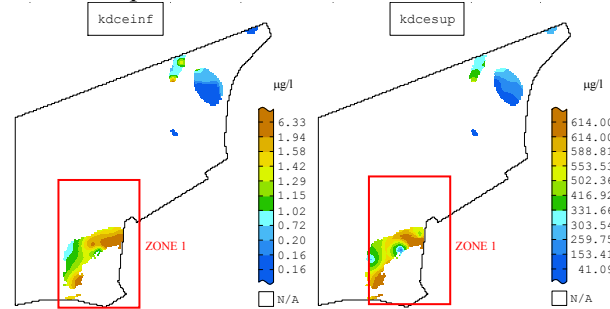


Fig.4 cDCE's concentration maps, in the best and in the worst scenario, with the spot area highlighted.

As far as Trichloroethylene and Tetrachloroethylene are concerned, the values found in the area delineated by using the detection limit, vary among the detection limits, equal to 0.08 µg/l, and 0.02 µg/l and the maximum values, equal to 363 µg/l, and 3400µg/l, respectively.

The distributions of the concentration values for PCE and TCE don't follow the Gaussian distribution, so it has been necessary to normalize the variables.

After transforming the variable by means of a Gaussian Anamorphosis, the multivariate approach has been applied and successively the estimated values have been back transformed in the original ones of concentration of Trichloroethylene and Tetrachloroethylene through the anamorphosis function previously calculated.

The two variables are strongly spatially correlated, as it is shown in the cross-variogram (Fig.5) which is close to the dashed line, corresponding to the maximum spatial correlation [6]. The Linear Model of Coregionalization (LMC) was fitted by using two basic structures: a nugget and a cubic model.

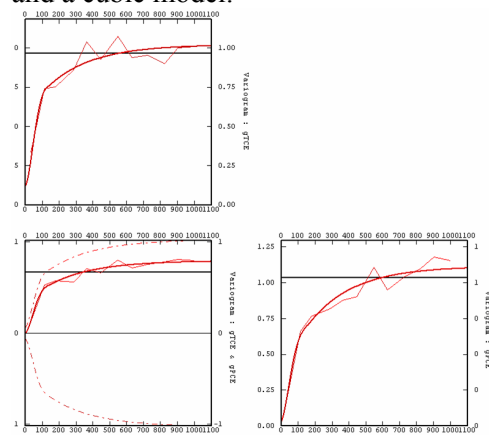


Fig.5 Direct and cross experimental variograms and variogram models for TCE and PCE

The high spatial correlation between the two variables causes their values to be jointly low in

some zones and high in other, as it is shown in the maps of figure 6, obtained by using co-kriging.

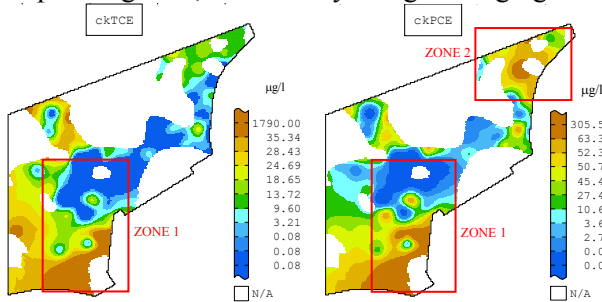


Fig.6 Concentration maps of TCE and PCE estimated by co-kriging, with the spot area highlighted.

The high spatial correlation of the two variables is confirmed by the fact that the same spatial structures are present in the individual maps of the variables, which look to be very similar. In fig.7 are shown the TCE concentration maps, obtained through co-kriging, in the best and the worst scenario of contamination, drawn up by making use of 95% confidence interval limits.

The confidence maps show large differences between the maximum and the minimum values, nevertheless, they identify a spot area of higher values down south.

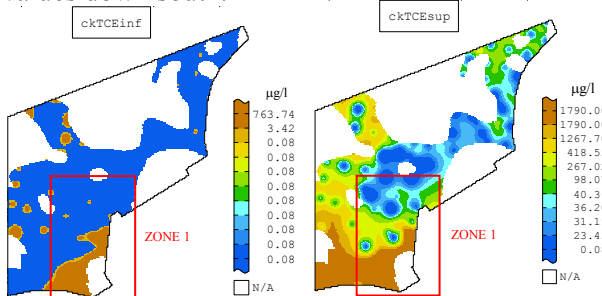


Fig.7 Map of TCE concentration, in the best and in the worst scenario of contamination, with the spot area highlighted.

In fig.8 are shown the same concentration maps obtained for PCE, in the best and the worst scenario of contamination. The two maps show very different PCE values, but they detect two common spot areas, one more southern and the other one more northern, with an error $\leq 5\%$.

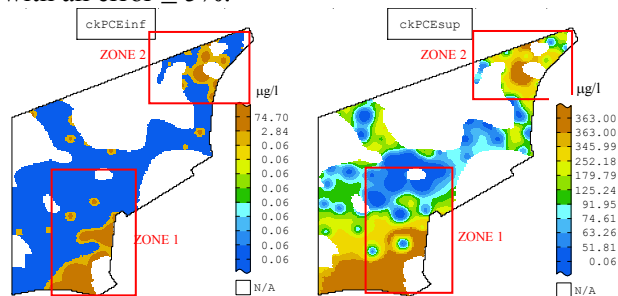


Fig.8 Maps of PCE concentration, in the best and in the worst scenario, with the spot areas highlighted.

In this way it has been possible to obtain three different scenarios for the areas to remediate: the best, the mean and the worst scenario of contamination. The high differences in the absolute values of concentration, shown in the three maps, remark the necessity to follow a stochastic approach (Monte Carlo simulation) or probabilistic approach (confidence interval) in the classification process of the polluted sites, which takes into account the prediction uncertainty.

Synthesizing the information obtained through 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 suggest the presence of two centers at hazard.

Starting from the estimation of the least-chlorinated substances, it is possible to detect the presence of cDCE with concentrations higher than the limit value 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.

As far as the most chlorinated substances are concerned, PCE and TCE, a correlation has been detected, not only chemical, but also from the point of view of the spatial distribution: the two contaminants extend on a wide area, showing common characters. Even in this case, due also to the presence of TCE with maximum concentration values much higher than PCE, it is possible to reveal 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 to the direction of maximum continuity for the two variables. In order to verify the hypothesis of natural attenuation degradation processes, also the conditions of pH, redox potential and dissolved oxygen present in situ have been analyzed. In figure 9 is shown the map of pH distribution, obtained through the application of kriging. This map shows the presence of a more acid situation just where the contamination has been detected, and this might confirm the presence of on-going degradation processes.

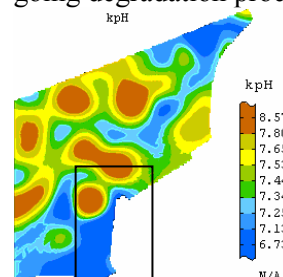


Fig.9 pH distribution and location of samples.

Values of redox potential and dissolved oxygen have been also taken into account, even if, for scarcity of data, they have been obtained from 15 samples, whose location is reported in the plot of Fig.9.

Just because of the scarcity of data, it hasn't been possible to carry out an interpolation by geostatistical techniques, in order to reconstruct the spatial distribution of those environmental parameters. Therefore the analysis is restricted to some considerations on the punctual values.

The redox potential assumes negative values in all the points considered, but the lowest concentration values of dissolved oxygen can be found in the southern part, near the previously detected spot area. These conditions might suggest the presence of degradation processes of the contaminants. Some of the degradation subproducts present a high toxicity: this is the case of the cis-Dichloroethylene and the Vinyl Chloride, that tend to form after the reduction of PCE. In presence of appropriate microorganisms, substrates and conditions, the biological process of decontamination goes up to the complete reduction of chlorinated ethenes, with the formation of the innocuous ethylene. Otherwise it can be possible to eliminate the toxic VC through the Pump&Treat technique or by creating conditions that can help its degradation.

The principal spot areas (Zone 1 and 2), evidenced in the maps of concentration of all variables, are the zones where there might be degradation phenomena of the chlorinated substances. For the southern zone (Zone 1), it has been possible to consider some environmental conditions, as redox potential, dissolved oxygen and pH, that have shown values favorable to the explication of biodegradation processes.

In order to verify the hypothesis of an area potentially subjected to biodegradation in the zone 1, the data of the successive monitoring, carried out in 2005, have been taken into account. The scarcity of data hasn't allowed their elaboration, but a punctual analysis has lead to some considerations.

As far as zone 1 is concerned, the contamination is still detected but the maximum values appear considerably low for all the considered four chlorinated compounds. This confirms the hypothesis, supported by the values of the environmental parameters, of an area potentially

interested by biodegradation processes and allows to exclude the possibility of a still active source of contamination in that area.

As far as zone 2 is concerned, for which no data of the environmental parameters are available, from the later monitoring a decrement has been detected in terms of both extension and concentration of the high chlorinated substances (PCE and TCE) and an increment, instead, of the subproducts of the degradation process (cDCE and VC). It is then possible to hypothesize that in this area a degradation process is ongoing, but the lack of environmental parameters doesn't allow us to investigate further on the situation.

References:

- [1] X1. Castrignano A., Cherubini C., Giasi C.I., Castore M., Di Mucci G., Molinari M., 2005 Using Multivariate Geostatistics for Describing Spatial Relationships Among Some Soil Properties, *ISTRO (International Soil Tillage Research Organization) Soil – agriculture, environment, landscape Proceedings of International Conference Brno 2005*, Czech republic June 29 – July1 2005.
- [2] X2. Goovaerts P., Webster R. and Dubois P., 1996, Assessing the risk of soil contamination in the Swiss Jura using indicator geostatistics, *Environmental and ecological Statistics*.
- [3] X3. U.S.EPA, Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water, *EPA/540/R-97/504*, May 1997.
- [4] X4. Bouwer E.J. 1994, Bioremediation of Chlorinated Solvents Using Alternate Electron Acceptors, *Handbook of Bioremediation*, R.D. Norris, R.E. Hinchee, R. Brown, P.L.
- [5] X5. Wackernagel H. 2003, Multivariate Geostatistics: an introduction with Applications, *Springer-Verlag, Berlin*, 3rd ed., 388 pp.
- [6] X6. Wiedermeier T.H., Rifai H.S., Newell C.J., Wilson J.T., 1999, *Natural attenuation of fuels and chlorinated solvents in the subsurface*, John Willey & Sons, inc. NY
- [7] X7. Innovations in Ground Water and Soil Cleanup: From Concept to Commercialization. *NRC (National Research Council)*, 1997. Washington, DC:National Academy Press.