

ANALYSYS OF CHLORINATED ETHENES BEHAVIOUR IN FRACTURED AND KARSTIC LIMESTONE

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EXTENDED ABSTRACT

Lo studio delle modalità di trasporto e della degradazione dei solventi clorurati negli acquiferi fratturati nonché la valutazione dei tempi di bonifica è un compito difficile.

Nel presente studio è analizzato il caso di studio della contaminazione, principalmente da solventi clorurati, delle acque sotterranee che circolano nell'acquifero carbonatico fratturato e carsico della zona industriale di Bari e Modugno.

Una delle caratteristiche principali dell'acquifero investigato è la sua pronunciata eterogeneità ed anisotropia dovuta al diverso grado di fratturazione ed ai fenomeni carsici che determinano un'alta variabilità in direzione verticale e soprattutto orizzontale della conducibilità idraulica. La contaminazione viene trasportata verso valle a partire dall'area hot-spot in direzione SW-NE. Nell'area hot-spot, il tetracloroetilene rappresenta circa l'80% della concentrazione totale dei solventi clorurati, mentre il tricloroetilene presenta concentrazioni sistematicamente più basse rispetto al tetracloroetilene in tutti i pozzi di monitoraggio. Il 1,2-dicloroetilene si riscontra relativamente a concentrazioni più elevate rispetto al 1,1-dicloroetilene a dimostrare l'evidenza di fenomeni di dechlorazione riduttiva in atto. Il valore del potenziale redox monitorati nell'area di studio, sono consistenti con la presenza di un ambiente ferro riducente. La sorgente di ossido ferrico è principalmente rappresentata dai prodotti residuali della dissoluzione carsica (terra rossa) che rivestono le pareti delle fratture. Ad ogni modo, la concentrazione di ossido ferroso monitorata nelle acque sotterranee è al di sotto dei $20 \mu\text{gL}^{-1}$, mentre i nitrati sono presenti a concentrazioni elevate al di sopra di 1mgL^{-1} , rappresentando il più alto accettore di elettroni dopo l'ossigeno che si rileva a concentrazioni al di sotto di 1mgL^{-1} .

Nel presente studio si riportano i risultati dell'applicazione di un nuovo approccio modellistico per analizzare le dinamiche di trasporto reattivo dei solventi clorurati nell'acquifero fratturato. Un modello di flusso non lineare è accoppiato con un modello di trasporto di tipo Lagrangiano (random-walk particle tracking), includendo lo scambio di particelle tra le zone mobili e stagnanti, i processi di adsorbimento, e i percorsi di dechlorazione riduttiva. La metodologia sviluppata, permette di simulare il moto delle particelle interessate da diverse cinetiche di reazione del primo ordine, cosicché le particelle si muovono secondo il loro stato chimico che si ripercuote sui processi fisici di trasporto (advezione, dispersione, scambio di massa tra le zone mobili e stagnanti).

Si è ottenuta la distribuzione stazionaria della contaminazione da solventi clorurati da una sorgente in corrispondenza dell'area hot-spot sulla base del confronto con lo scenario di contaminazione osservato e quello simulato più ragionevole, con il fine di stimare i processi di trasporto e degradazione nonché la portata di immissione dei contaminanti alla sorgente.

L'analisi condotta ha messo in luce la persistenza dei solventi clorurati all'interno dell'acquifero. Le simulazioni condotte mostrano che il 43% delle particelle associate alla contaminazione risultano intrappolate nelle zone stagnanti. Il confronto tra le simulazioni e i dati di monitoraggio osservati mostrano come il trasporto dei contaminanti risulta influenzato dalle anisotropie dell'acquifero. In particolare, la presenza di una sinclinale in corrispondenza dell'area hot-spot devia il flusso idrico e quindi il trasporto dei contaminanti in direzione E-W.

Lo studio evidenzia una limitata attività di dechlorazione riduttiva in atto, soprattutto dei solventi alto clorurati come il tetracloroetilene che mostrano una maggiore persistenza dell'acquifero percorrendo distanze dalla potenziale sorgente di contaminazione di circa 5000 m. Il tricloroetilene si degrada più velocemente alimentando la formazione del dicloroetilene. Mentre il cloruro di vinile presenta un alto tasso di degradazione. Lo scenario di degradazione è consistente con una dechlorazione riduttiva in ambiente ferro riducente che favorisce la degradazione dei solventi basso clorurati come il cloruro di vinile. La contaminazione da nitrati può essere avvenuta successivamente inibendo i fenomeni di dechlorazione riduttiva. Inoltre, lo scenario è consistente con una dechlorazione riduttiva di tipo abiotico, favorita dalla presenza di minerali come magnetite e pirite presenti nella terra rossa che riveste le pareti delle fratture, favorendo la trasformazione del dicloroetilene direttamente in anidride carbonica e acqua senza la formazione del cloruro di vinile.

Lo studio rappresenta uno strumento prezioso nelle decisioni a riguardo del ruolo rivestito dalla attenuazione naturale nelle opzioni di trattamento, dove la capacità di attenuazione naturale delle acque sotterranee può essere integrata con metodi ingegneristici al fine di ottenere la bonifica del sito.

ABSTRACT

The understanding of the transport and degradation phenomena of chlorinated ethenes in fractured aquifers as well as the assessment of the cleanup times poses an extreme technical challenge. In the present study a method to analyze reactive transport and reductive dechlorination of chlorinated solvents in fractured aquifers is presented. Reductive dechlorination pathway, adsorption processes, mass exchange phenomena between mobile and stagnant zones as well as the non – linear flow behaviour in fractures are considered.

The developed methodology, considering reductive dechlorination processes in a Lagrangian framework, is able to simulate the motion of particles affected by first-order network reactions, so that particles move according to their chemical state affecting physical transport processes (advection, dispersion, mass transfer exchange between mobile and stagnant zone).

The developed model is applied to a case study of groundwater contamination in the industrial area of Modugno – Bari (Italy), where the limestone aquifer has a fractured and karstic nature. The steady state distribution of the contamination by chlorinated ethenes with the source at the hot spot is obtained and compared with the observed scenario of contamination in order to estimate the plausible transport and degradation processes as well as the mass loading at source. The carried out study represents and valuable tool for deciding the role of natural attenuation in a treatment where the natural attenuation capacity of groundwater can be integrated with engineering methods for site remediation.

KEYWORDS: *reductive dichlorination, fractured aquifer, numerical model*

INTRODUCTION

In the industrial area, the most detected contaminants in groundwater are represented by the chlorinated ethenes (CEs). They have been widely used as solvents in manufacturing operations. The fate and transport of CEs as well as the bioremediation clean up techniques for unconsolidated aquifer composed by granular material have been evaluated for several decades. At contrary, there is scarce experiences on the use of bioremediation clean up techniques for in situ treatment of CEs in fractured bedrock.

Several problems affect the remediation in fractured bedrock. As discussed in MUTCH *et alii* (1993), the fractured aquifer remediation could become frustratingly slow at best, and, at worst, an exercise of futility. Dead-end fractures and matrix diffusion represent the primary storage zones for contaminants leading the CEs' persistence after bioremediation activity (VERCE *et alii*, 2015). In fact, dechlorinated microorganisms have been observed into the rock matrix away from the fractures. Therefore, the biodegradation in the matrix block plays an important role and should be taken into account in the natural

attenuation or remediation assessment (LIMA, 2012).

In order to analyze natural attenuation processes in fractured aquifer is crucial the groundwater flow – path characterization (BRADLEY *et alii*, 2009). Moreover, in enhanced natural attenuation clean up strategies, groundwater flow pathways affect the hydraulic connectivity and the travel time between the recirculation wells (VERCE *et alii*, 2015). The homogeneous conceptualization of groundwater flow to design injection remediation wells in less heterogeneous unconsolidated materials fails to reproduce the fracture dominated flow (TIEDEMAN *et alii*, 2018).

Usually, anaerobic condition in presence of iron-reduction, sulfate-reduction and methanogenesis redox conditions promotes natural attenuation process of CEs (LENCZEWSKI *et alii*, 2003). The study of dechlorination of CEs in fractured aquifers have been addressed by several authors through field investigations, laboratory tests and numerical simulations (YAGER, 2000, MANOLI *et alii*, 2012; SIMSIR *et alii*, 2017). Reductive dechlorination leads several chemical reactions between CEs, electron acceptors and donors, organic matter and microorganisms. They can be complex but foreseeable. Pseudo first-order reaction rates equations can be used to predict the transformation rates of the CEs when the contaminant concentration is relatively small (BURNELL *et alii*, 2014).

The set-up of a reactive transport model that incorporate heterogeneity and anisotropy of aquifer properties, diffusion and stagnant zones as well as chemical reaction could become very complex (HENRY & FERNANDEZ-GARCIA, 2015). Under these circumstances, a site-specific transport model is crucial in order to evaluate natural attenuation potential and/or clean up strategies.

Fractured and karstic aquifer can be depicted as multiple – porosity model characterized by a great variation of the hydraulic properties. Matrix pores interact with fractures and conduits in which non-linear flow regime can occur (CHENG & CHEN, 2005). Non – Darcian flow can be disclosed in fracture and conduits governing the flow dynamics and contaminant transport. Deviation from the cubic law was detected by several authors that proposed correction factor and/or velocity dependent functions in order to depict the effect of the roughness of fracture walls and channel tortuosity (ZIMMERMAN & BODVARSSON 1996; WAIT 1998; CHERUBINI *et alii*, 2013a; CHERUBINI *et alii*, 2014).

The contaminants move into connected fractures and they are trapped into the matrix and stagnant zones represented by dead-end channels and irregularities of fracture walls. As a consequence, an anomalous discharge behaviour is observed, characterized by an early arrival and a long tailing (LEE *et alii*, 2017; DOU *et alii*, 2018). Mass diffusion between fracture and matrix (ZHOU *et alii*, 2006), channeling effect due to the variable apertures (TSANG & TSANG, 1987) and stagnation zones

near fracture walls (CARDENAS *et alii*, 2007) represent the main mechanism associated to this non-Fickian behaviour.

Recirculation zones may represent the principal mechanism of non-Fickian transport, especially when matrix porosity is low and non-linear flow regime occurs influencing both advection causing a delay on solute transport with respect to the linear flow assumption and the stagnant zones enhancing the presence of eddies within the fractures (QUIAN *et alii*, 2011; CHERUBINI *et alii*, 2013b, CHERUBINI *et alii*, 2014; LEE *et alii*, 2015). This causes a persistence of contaminant plume in groundwater.

Moreover, biotic and/or abiotic anaerobic reductive dechlorination governs the reaction pathways of CEs and their evolution in the aquifer. Mobile and stagnant zones can be characterized by different reaction rate (CUNNINGHAM & MENDOZA – SANCHEZ, 2006).

The degradation of CEs do not follow a sequential reaction chain. Dechlorination processes produce chloride. For instance, the complete dechlorination of 1 mole of tetrachloroethylene (PCE) leads to 4 moles of chloride (SEMPRINI *et alii*, 1990). In addition, three daughter species: cis-1,2-dichloroethylene (cis-1,2-DCE), trans-1,2-dichloroethylene (trans-1,2-DCE) and 1,1-dichloroethylene (1,1-DCE) derived by the degradation of trichloroethylene (TCE). DCEs species presents different reaction rate and toxicity. In presence of abiotic degradation environment, hydrogenation pathways, α -elimination and β -elimination are promoted (HE, 2015).

Generally, chlorinated solvents and their degradation products such as Chloride and ethylene have different behaviour in sorption processes, affecting advection and the interaction between the mobile and stagnant zones (LU *et alii*, 2011).

Efficient numerical approaches to simulate reactive transport are the particle-based methods (SALOMON *et alii*, 2006; HENRY & FERNANDEZ-GARCIA, 2014). In the literature, different particle-based methods was developed and presented to simulate multispecies transport subjected to first order kinetics (BURNELL *et alii*, 2014; HENRI & FERNANDEZ-GARCIA, 2015) or more complex kinetics (ENGDAHL *et alii*, 2017; SOLE-MARI *et alii*, 2017). These approaches present some limitations about the fact that reaction network and their degradation products is simplified as a sequential reaction chain. For instance, all DCEs represented as single species and the evolution of the daughter species is not predicted well.

In the present work an efficient particle-based method to represent at field scale the transport and reductive dechlorination processes is presented and validated on the case study of the fractured limestone aquifer of industrial area of Bari (Italy). Different conceptual, mathematical and numerical models have been presented to analyze the behaviour of the aquifer of Bari, modeling the fluid flow (CHERUBINI *et alii*, 2013a; CHERUBINI *et alii*, 2018), variable density flow (MASCIOPI

NTO, 2016; MASCIOPI

NTO *et alii*, 2017), conservative transport (CHERUBINI & PASTORE, 2010; MASCIOPI

MATERIAL AND METHODS

Geological and hydrogeological setting

The industrial area of Bari (Italy) is located in the Apulia Region (South-Eastern Italy), overlooking the Adriatic Sea. Morphologically, in the study area, three extended tiered terraces with a height between 10 – 40 m a.s.l. are detectable. They are parallel to the coast sloped down to the sea characterized by paleostream channels (lame) perpendicular to the terraces (Fig. 1).

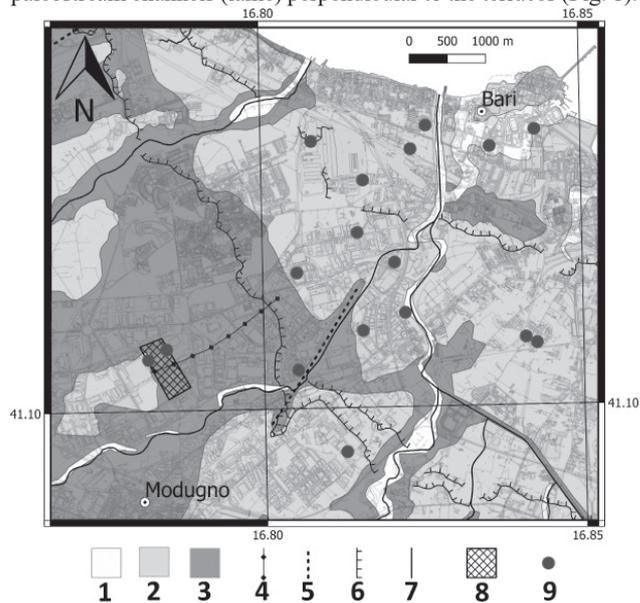


Fig. 1 – Geological map of industrial area of Bari. 1) alluvial and marshy deposits (Holocene); 2) Calcareni di Gravina Formation (Lower Pleistocene); 3) Calcare di Bari formation (Cretaceous); 4) anticlinal axis; 5) fault (uncertain); 6) escarpment; 7) Hydrographic network; 8) potential source area of contamination; 9) monitoring wells

Below the topsoil, the study area is characterized by the presence of alluvial and marshy deposits (Holocene) at the bottom of the “lame” and some depressions in the dune deposits

and by the presence of Calcareni di Gravina formation (lower Pleistocene) with variable thickness from few meters to 20 m. It is a calcarenitic complex, transgressive on the underlying formation, sometimes in angular discordance, constituted by dune bioclastic, detritic and sand-bar deposits constituted by calcarenite with marine fossils, volcanic sands and sandstones, and discontinuous layer of gravel and conglomerates. Below the calcarenitic strata lies the Calcare di Bari formation, represented by a Cretaceous calcareous dolomitic succession extending in depth for hundreds of meters. The succession consists of biopeloidal and peloidal wackestones/packstones alternating with stromatolithic bindstones with frequent intercalations of dolomitic limestones and gray dolostones. This succession appears stratified and fissured and, where it is not intersected by tectonic discontinuities, it shows a subhorizontal or slightly inclined attitude (MAGGIORE, 1993).

The degree of fracturing in the limestone Cretaceous formation is quite variable and mainly depends on the geological and structural evolution of the area, including faulting and folding. Boreholes surveys conducted in the study area highlight the presence of two levels constituted by a carbonate rock sequence intensely fractured and karstified 26 m thick and a lower level represented by a dolomitic sequence >20 m thick, less fractured and karstified.

The study area belongs to the karstic Murgia aquifer, characterised by calcareous lithotypes and having a secondary fissure-type permeability of tectonic origin. BILLI (2005) investigated the geometrical and structural attributes of fractures and fracture networks of the Murgia aquifer, characterised by a succession of carbonate beds separated by sub – horizontal marked mechanical discontinuities and affected by sub – vertical fractures with bed – parting and bed – unparting behaviour, and by rare faults. The authors found that the fracture spacing is directly correlated to beds thickness variable in the range 0.15–1.20 m.

The prolonged karstic dissolution action of water on carbonate rocks has enlarged and interconnected the already existing discontinuities, creating a deep network of subterranean passages. Inside the cavities of variable dimensions created by the complex and relevant karstic phenomena, conspicuous accumulations of red soil “terra rossa” can be detected. The origins of this residual material are not always attributable to its survey site. DELL’ANNA *et alii* (1985) and VINGIANI *et alii* (2018) investigated the geochemical composition of “terra rossa” in the study area and detected silica and calcite (35–45%) kaolinite and illite (25–30%) and iron (10–15%) (hematite, magnetite and goethite) with small quantities of calcium oxides, potassium, titanium, magnesium, sodium, manganese and phosphorus.

Because of karstic phenomena, all the Murgian territory is characterized by scarce surface-water flow, even in the presence

of an extensively developed hydrographic network. The local hydrographic network typical of the Apulian countryside is in fact constituted by the “lame” which act as ephemeral water courses. The high permeability of carbonatic rocks facilitates the infiltration of rainwater into the subsoil so that surface flow occurs only after very intense rain events. This implies the presence of a conspicuous and extended groundwater circulation in the subsoil, floating on underlying seawater of continental invasion.

One of the peculiar hydrogeological characteristics of the Murgia aquifer is the pronounced anisotropy linked to the different degree of fracturing and karst phenomenon of the carbonate rocks that determines a high variability in the vertical and especially horizontal hydraulic conductivity, with values oscillating between 0.2 and 612 m·d⁻¹, whereas rock porosity has values between 1.24 and 5.14% (BORGIA *et alii* 2002).

In the study area, groundwater flows in the limestone Cretaceous formation within fractures and karst channels at variable depths from 40 m below the ground level in the most inland zone of the industrial area, up to about 12–13 m depth at its north-eastern border, with hydraulic head values of about 1–2 m above sea level. Groundwater flows in phreatic or semiconfined conditions mainly in the SW–NE direction perpendicular to the coastline, with hydraulic gradients of 0.1–0.5% (GRASSI *et alii* 1986).

Screening of reductive dechlorination

Chlorinated aliphatic hydrocarbons – PCE, TCE, 1,2-DCE, cis & trans 1,2-DCE and VC – represent the main contaminants that have been detected in the groundwater during the campaign of investigations. According to the flow paths, they are transported downgradient from the potential source area of contamination in the SW-NE direction. In the hot-spot area, PCE is about the 80% of the total CEs, whereas TCE has been found at lower concentration than PCE in all monitoring wells. Evidence of dichlorination processes can be ascribable to the fact that the amount of 1,2-DCE is greater than of the total DCE.

Iron-reducing condition due to the presence of source of ferric iron constituted by the fracture coating composed by red soil is consistent with the redox potential values detected in the groundwater. Anyway, ferrous iron presents concentrations below 20 µgL⁻¹. Besides, nitrate concentrations exceed 1 mgL⁻¹, representing the highest electron acceptor after the dissolved oxygen detected at lower concentration (below 1 mgL⁻¹).

Groundwater flow model

Parallel plate model (MASCIOPIANTO *et alii*, 2010) has been used to represent horizontal flow through the fractured aquifer in the study area. The fractured medium is depicted as a set of a specific number of equivalent horizontal rough-walled

parallel plates with the same aperture distribution variable in space along the horizontal direction. Non-linear flow within the equivalent horizontal rough walled parallel plates is represented by the Darcy – Weisbach equation. Rough-walled parallel plate model has been coupled with inverse modeling and geostatistical analysis in order to infer the value of the equivalent transmissivity distribution. Details on model conceptualization, governing equations, boundary conditions and validation can be found in CHERUBINI *et alii* (2018). MODFLOW numerical code coupled with inverse numerical approach has been used to model groundwater flow. The two-dimensional domain covers an area of 968.7 km² discretised by means of a structured grid of 100 m in size. The flow model has been validated on the basis of the hydraulic head measurements and point dilution tests. Considering a value of effective porosity equal to $\approx 0.3\%$ (MASCIOPIATO & PALMIOTTA, 2016). Simulated specific discharge reaches the observed specific discharge for a number of equivalent conductive parallel plates equal to 20 (Fig. 2). Ground water flow effective velocity varies along the flow paths starting at the potential source area. Water reaches the coast in 220 days traveling about 5600 m.

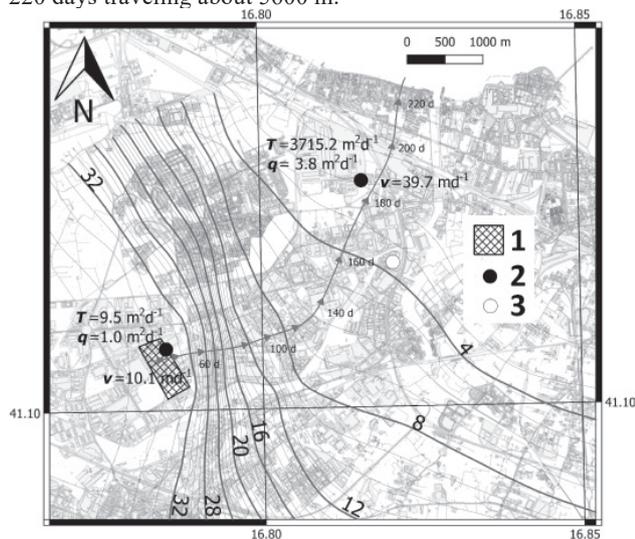


Fig. 2 – Contours of groundwater level (m a.s.l.) and main flow path from the potential source area of contamination with the indication of the evolution of the groundwater travel time along the main flow path. In correspondence of the location of point dilution test is reported the simulated velocity v (md^{-1}), the estimated specific discharge q (m^3d^{-1}) and the estimated equivalent transmissivity T (m^2d^{-1}). LEGEND: 1) potential source area of contamination; 2) location of point dilution test; 3) location of forced gradient test

Transport and reductive dechlorination model

The rough walled horizontal parallel plates are characterized by the presence of a mobile zone (preferential pathways) and stagnant zones. Dual porosity model has been used to model

solute transport dynamics in saturated fractured limestone with first order mass exchange term between the mobile and stagnant zone (GUAN *et alii*, 2008). Mass transfer term varies in space depending by velocity field (CHERUBINI *et alii*, 2013b). The increase of Reynolds number produces eddy growth enhancing the recirculation zones.

Sorption processes of organic compounds occur due to the presence of iron oxides in red soil at fracture walls. Assuming linear isotherm valid, the retardation factor is function of the surface area to volume ratio of the fracture system and the surface distribution coefficient derived as the ratio between the partition coefficient of each species and the internal surface area of the rock as defined by NOVAKOWSKY (1999).

Dechlorination processes are approximated as first-order reactions neglecting the effect of biomass growth and inhibitors. According to biotic reductive dichlorination pathways, PCE reacts to produce TCE, TCE reacts to produce three daughter species, cis-1,2-DCE, trans-1,2-DCE and 1,1-DCE, while the three DCEs further react to produce VC, VC reacts to produce ethylene that react to produce carbon dioxide and water. Furthermore, a result of the biodegradation of CEs is chloride.

Mass transfer, equilibrium adsorption and reductive dechlorination processes has been coupled with random walk particle tracking. Details of used methodology and numerical algorithm can be found in PASTORE *et alii* (2020).

RESULTS AND DISCUSSION

Transport model has been set up in the study area. First, experimental forced gradient breakthrough curve has been used to derive the mass transfer rate and the porosity of the stagnant end recirculation zones. A value of $4.10 \times 10^{-3} \text{ s}$ and 0.16% was estimated for the mass transfer rate and the porosity of stagnant zone assuming a value of the effective porosity equal to 0.3% . The founded values are coherent with the experiments conducted by CHERUBINI *et alii* (2013b, 2014).

CAPURSI (2011) conducted batch experiments on sorption potential of CEs on red soil samples of the study area. The author finds, based on a linear sorption model, a value of apparent organic carbon fraction determined by the ratio between the experimental distribution coefficients and the partition coefficient of each species equal to 0.0681% . The internal specific surface area of the matrix rock is estimated equal to $0.4762 \text{ cm}^2\text{g}^{-1}$, assuming a rock porosity equal to 3% .

Transport and reductive dechlorination simulations start from the condition of no contamination (the number of particles released into the domain at $t = 0$ is zero). A constant mass-loading boundary condition was imposed at the source located in correspondence with the potential source area. At each time step, 20,000 particles were released into mobile domain at potential source area. A time step of 1 day was chosen. The simulation

continues until the quasi-steady state condition has been reached. At the end of simulations, the concentration distribution map of each species was determined and the corresponding distribution along the main flow path. Mass loading rate M ($\text{g}\cdot\text{d}^{-1}$), the percentages of distribution of the CEs at source f_i (%), the first order decay rates λ_i (d^{-1}) and the percentages of distribution ψ_i (%) between the daughters (1,1-DCE, 1,2-DCE cis & trans) of the reduction of TCE were estimated using root mean square error criteria between observed data and simulated data. A value of the constant mass loading rate equal to $M = 35 \text{ g}\cdot\text{d}^{-1}$ has been estimated, whereas the other estimated model parameters are reported in Table 1.

The first order decay rate estimated by the conducted analysis disclosed a limited effect of reductive dechlorination processes. Except for that associated with vinyl chloride, the estimated first-order decay rate of CEs assumes a relatively low

value, although consistent with the literature values (WILSON, 1996; YAGER, 2002).

	f (%)	λ (d^{-1})	ψ (%)
PCE	57	0.001	-
TCE	36	0.008	-
1,1-DCE	0	0.003	10
1,2-DCE cis & trans	7	0.003	90
VC	0	0.03	-

Tab. 1 – Percentage of distribution of the CEs at source f (%), first order decay rates λ (d^{-1}), percentage of distribution between the daughter 1,1-DCE and 1,2-DCE cis & trans of the reduction of TCE ψ (%)

Figure 3 shows the comparison between the observed data and simulated scenarios of contamination along the main flow path. Figure 4 shows the comparison between the steady-state concentration simulated maps and observed concentration of the CEs.

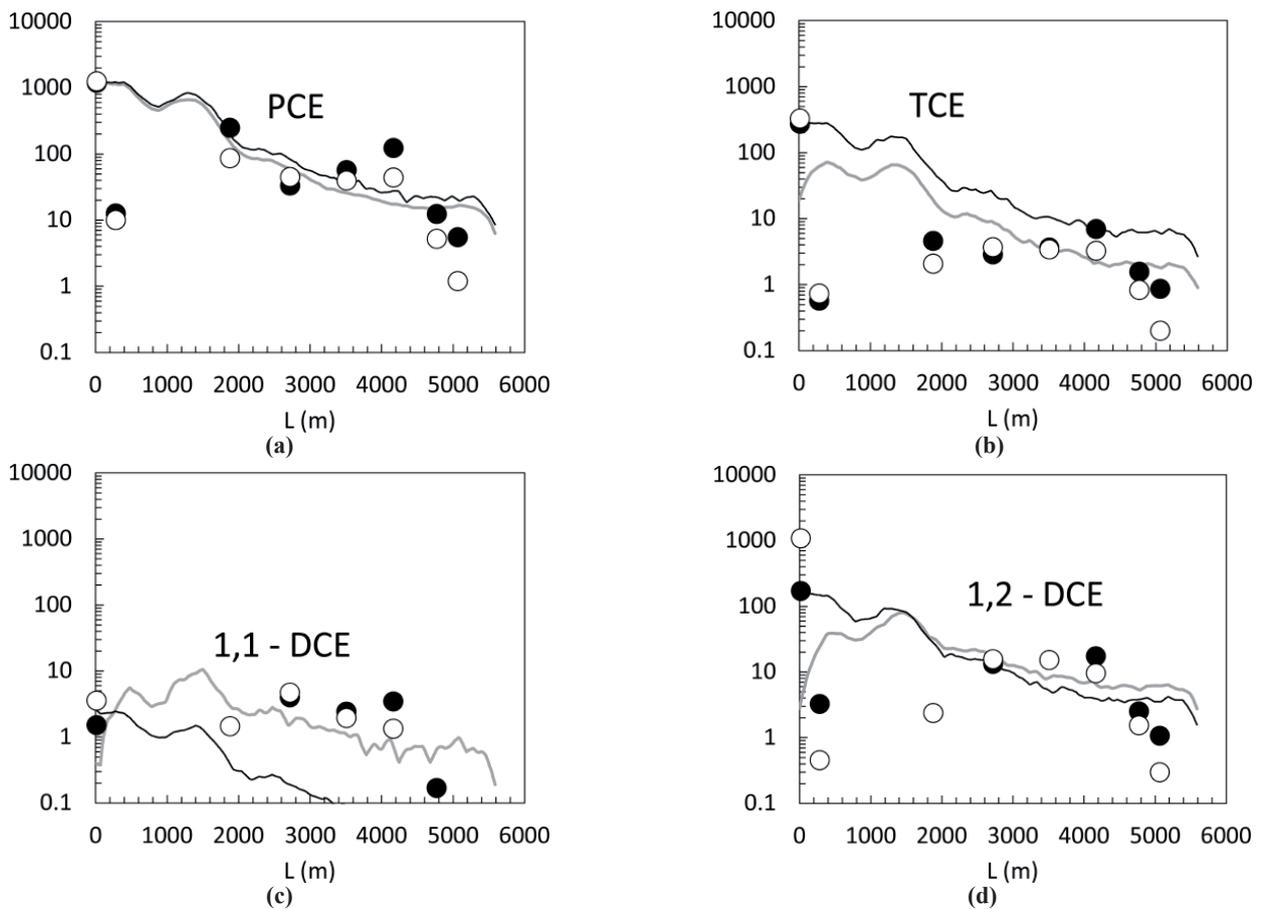


Fig. 3 – Comparisons between the simulated concentration distributions ($\mu\text{g L}^{-1}$) of CEs along the main flow path from the potential source area of contamination (Fig. 2) with reductive dechlorination (bold gray curve), without reductive dechlorination (black curve) and observed concentrations in monitoring wells that cross the main flow path ($\mu\text{g L}^{-1}$), relative to the monitoring periods March– May 2014 (black dot) and October–December 2014 (white dot). a) PCE, b) TCE, c) 1,1–DCE, d) 1,2–DCE cis & trans. The distance along the main flow path associated with the generic monitoring well is measured in correspondence to the intersection between the main flow path and its perpendicular straight line passing through the generic monitoring well

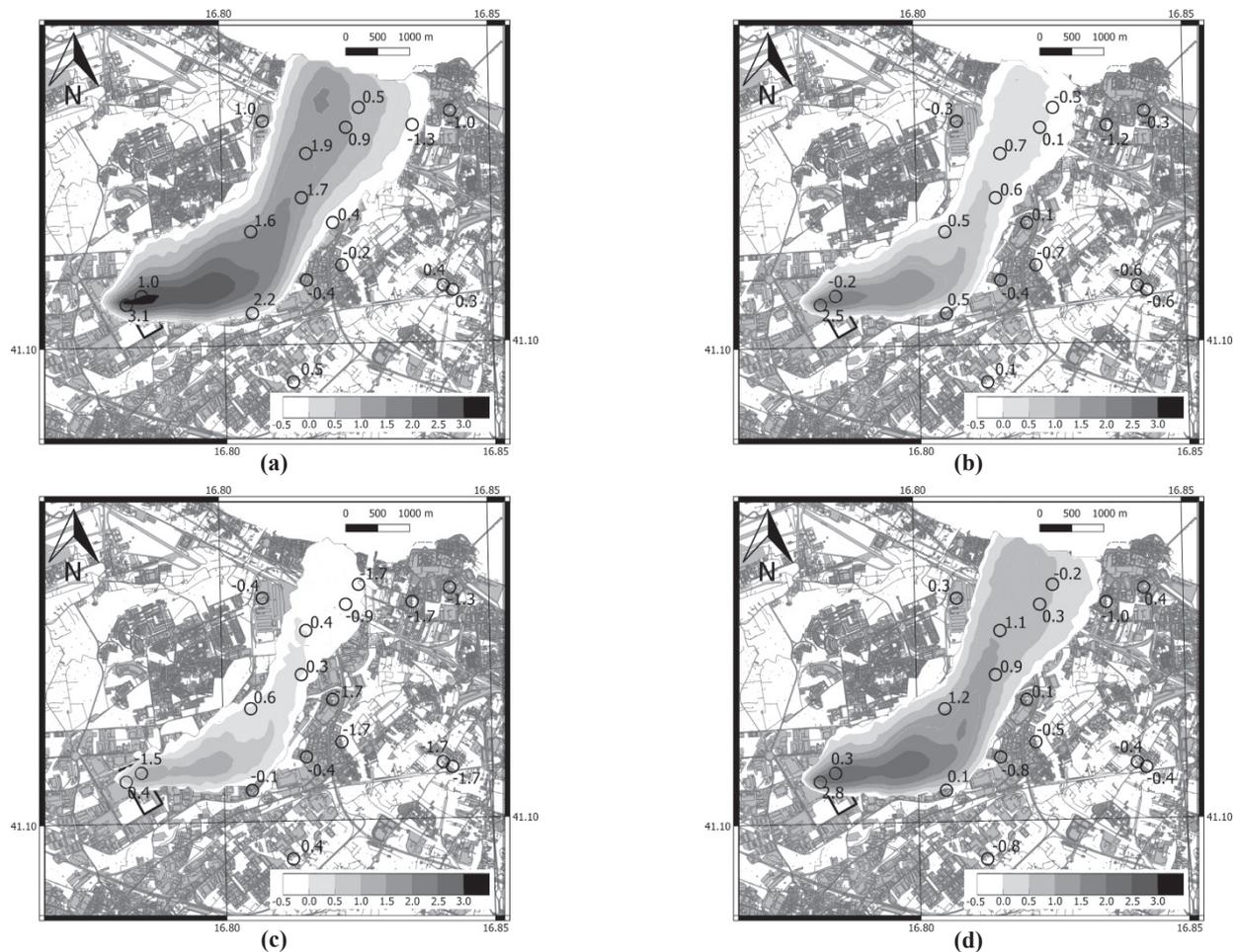


Fig. 4 – Steady-state-simulated concentrations and observed concentrations at monitoring well as $\log_{10}(\mu\text{g L}^{-1})$ relative to transport simulation with reductive dichlorination processes for: a) PCE, b) TCE, c) 1,1-DCE, d) 1,2-DCE cis & trans

PCE shows a relative low value of first order decay rate ($\lambda = 0.001 \text{ d}^{-1}$), coherent with the transport of PCE at long distance. The degradation rate of TCE ($\lambda = 0.008 \text{ d}^{-1}$) appears significant compared to the effect of only physical transport processes which overestimate the concentration distribution; in contrast, the dilution effect underestimates the concentration of 1,2 – DCE ($\lambda = 0.003 \text{ d}^{-1}$) and 1,1 – DCE ($\lambda = 0.003 \text{ d}^{-1}$) and this means that DCE is degraded more slowly than TCE. The model overestimates VC concentration distribution, although with a value of decay rate relatively high ($\lambda = 0.03 \text{ d}^{-1}$). VC was detected only at source and near to the coast at concentrations over the minimum detection limit ($0.25 \mu\text{g L}^{-1}$) and at a concentration much lower than other CEs. The highest VC concentration is $2.1 \mu\text{g L}^{-1}$.

Iron reducing conditions may have favored the oxidation of DCE and VC to carbon dioxide, explaining the lower concentration of VC (BRADLEY *et alii*, 1998). This scenario is also consistent with an abiotic reaction that could involve the process of dehalogenation of CEs

(McCORMICK *et alii*, 2002), explaining the reductive dechlorination scenario under nitrate reducing conditions. Magnetite and pyrite are present in the thin fracture coating (terra rossa), and, as demonstrated in BUTLER & HAYES (1999), LEE & BATCHELOR (2002), these minerals can favor the abiotic degradation of CEs.

Transport simulations depict well the concentration distribution, reflecting the heterogeneity of the aquifer, though the transport simulations are not able to represent the irregular shape of the detected contaminant distribution (Fig. 4). The concentration at the well located immediately downgradient from the hot spot presents a concentration lower than the simulated ones, and the well located more southerly presents a concentration systematically higher than expected especially for the higher-chlorinated CEs. An explanation can be attributable to the presence of a watershed in correspondence to the hot-spot area, as demonstrated by the flow path lines where a change of direction in correspondence of the source is highlighted.

The anticline affecting the Calcare di Bari formation gives rise to

a local anisotropy of the fractured media with the SES – NNW main direction perpendicular to the anticline axis.

The simulated results disclose the persistence of CEs in the aquifer: the 43% of total particles associated to the CEs present in the domain under quasi steady state conditions resulted in a stagnant zone, and 26 % of the particles are associated to PCE. The change of flow field due to pumping wells can be favors the non – equilibrium condition between mobile and stagnant zones changing the behaviour of the contaminant propagation linked to the clean up time of the aquifer.

CONCLUSIONS

The present study is aimed at analyzing the scenario of groundwater contamination by CEs of the industrial area of Bari (Italy) in a fractured, karstic limestone aquifer. Starting from previous studies, the reliability of groundwater flow and transport models has been improved by analyzing literature data concerning experimental breakthrough curves derived by point-dilution and forced-gradient tests conducted in the study area.

The first-order decay rates found are consistent with the mildly reducing conditions detected in the study area, as the result of nitrate

and Ferrous iron reduction. Furthermore, the presence of magnetite and pyrite in the thin fracture coating (terra rossa) may have played a role in abiotic degradation of the CEs.

The main uncertainty in estimating the biodegradation rates and predicting the fate of CEs at the site is represented by the mass of non-aqueous phase liquid (NAPL) and its composition.

A spill of several CEs at source could have occurred, together with the possible geochemical and biological processes influencing the CEs in the NAPL, as demonstrated by the thermal anomalies at the hot-spot area. Furthermore, NAPL release could have occurred at different times and in different modalities, thus the hypothesis of continuous source could be restrictive.

Given the obtained scenario of dechlorination, the use of monitored natural attenuation as a cleanup strategy is not recommended for the study area, as it will not lead to the complete degradation of the CEs and there will be persistence of the contaminant plume in the aquifer. The 43% of the total particles associated to CEs lies in the stagnant zone.

A possible alternative to monitored natural attenuation could be the implementation of enhanced natural attenuation together with reduction in size of the hot-spot area at the source.

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