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Hydrogeochemical and hydrodynamic features affecting redox processes in groundwater

Aspetti idrogeochimici e idrodinamici che condizionano i processi redox nelle acque sotterranee

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Riassunto: Questo lavoro affronta alcuni aspetti idrogeochimici ed idrodinamici che influenzano i processi redox nelle acque sotterranee, presentando tre casi di studio e tre approcci metodologici diversi. Le informazioni ottenute sono fondamentali nella caratterizzazione dei siti contaminati, nella pianificazione del monitoraggio, nella selezione delle tecniche di bonifica e nella valutazione del rischio per la salute.

Nel caso di studio del sito di San Pedro Sula (Honduras), sono state fornite nuove conoscenze ed un metodo avanzato di zonazione redox degli acquiferi. Il Multi-Collocated Factorial Kriging, una tecnica geostatistica mutuata dall'agricoltura e dalle scienze del suolo, ha permesso di individuare processi redox simultanei, che agiscono a scala diversa: a corto raggio, la dissoluzione riduttiva degli ossi-idrossidi di Mn e la precipitazione degli ossi-idrossidi di Fe; a lungo raggio, la mobilizzazione di Fe. I risultati ottenuti sono supportati dalla Principal Component Analysis e dalla modellazione numerica idrogeochimica.

L'interazione tra diversi eventi di contaminazione nel VR ha permesso di approfondire la competizione per il substrato organico tra diversi processi redox. A tal fine, è stato implementato un modello di trasporto Avvettivo-Reattivo-Dispersivo 1-D e i risultati ottenuti hanno evidenziato che il processo di declorazione riduttiva è inibita dai processi redox inorganici, causando un arricchimento in sottoprodotti fortemente tossici (i.e. Cloruro di Vinile). Infatti, i batteri che utilizzano gli accettori di elettroni inorganici per ossidare il substrato organico risultano più efficienti dei batteri alo-respiratori, che favoriscono la declorazione riduttiva.

Il caso di studio del sito di Bussi Officine ha permesso di chiarire l'effetto che ha l'idrodinamica sulla distribuzione dei processi redox e delle condizioni anossiche. Il confronto tra la distribuzione dei solventi organo-clorurati presenti e quella degli accettori di elettroni inorganici nell'acquifero ha evidenziato che la dispersione inibisce tutte le tipologie di processi redox, in quanto diluisce il contenuto di substrato organico nelle acque sotterranee. Invece, i depositi lacustri ricchi in materia organica (i.e. torba) possono essere considerati come dei veri e propri "reattori chimici", che rilasciano per diffusione sottoprodotti tossici della declorazione riduttiva nelle acque sotterranee.

Abstract: *This research deals with some hydrogeochemical and hydrodynamic features that affect redox processes in groundwater, presenting three different case studies and methodological approaches. This information is vital when characterizing contaminated sites, planning monitoring, selecting remedial techniques, and assessing health risks.*

In the San Pedro Sula site case study (Honduras), new insights and an advanced method for the aquifer redox zonation were provided. The Multi-Collocated Factorial Kriging, a multivariate geostatistical technique borrowed from agriculture and soil science, identified simultaneous redox processes, acting at different scales and mainly due to eutrophicated surface-water/groundwater interaction: at short-range, Mn oxi-hydroxide reductive dissolution and Fe oxi-hydroxide colloidal phase precipitation; at long-range, Fe mobilization. The obtained results are supported by the Principal Component Analysis and hydrogeochemical numerical modeling.

The interaction among different contamination events in the VR site allowed to get a deeper insight into the competition for organic substrate among different redox processes. To this purpose, a 1-D Advective-Reactive-Dispersive transport numerical model was implemented, and its results highlighted that the reductive dechlorination is inhibited by the inorganic Terminal Electron Accepting Processes, enriching groundwater in highly toxic by-products of the reductive dechlorination (i.e. Vinyl Chloride). As a matter of fact, the bacteria using inorganic Terminal Electron Acceptors to oxidize the organic substrate are more efficient than the halo-respiring bacteria, that favor reductive dechlorination.

The contaminated site of Bussi Officine case study allowed to clarify the hydrodynamic effect on the redox processes and the anoxic condition distribution. The comparison between dissolved chlorinated solvents and the inorganic Terminal Electron Acceptors distribution in the aquifer pointed out that dispersion inhibits all the redox processes because it dilutes the organic substrate concentration in groundwater. On the other hand, the lacustrine deposits rich organic matter (i.e. peat) can be considered as "chemical reactors", that releases by back-diffusion toxic by-product of the reductive dechlorination in groundwater.

Keywords: *redox processes, reductive dichlorination, multivariate geostatistics, hydrogeochemical modeling, groundwater.*

Parole chiave: Processi redox; Declorazione riduttiva; Geostatistica multivariata; Modellazione idrogeochimica; Acque sotterranee

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Introduction

In the last few decades, global economic development has led to a rapid increase in population, industrialization, and urbanization, generating an ever-increasing demand for freshwater resources (UN-WWAP 2015). Pollution events decrease the availability of good quality water resources, suitable for drinking purposes. Their accessibility is reduced and the capacity of the ecosystems to adapt to the changes and for the natural water cycle to satisfy the globally growing demand for water is compromised. Groundwater pollution also represents one of the key issues concerning human health, due to the risk of exposure to highly toxic and/or carcinogen compounds (WHO 2011).

In order to face these social and environmental issues, international and national environmental and water-related policies have been implemented (EU 2000; EU 2006; RI 2006; RI 2009). For groundwater pollution, these policies prohibit unsustainable water resource uses and, require the characterization of the polluted site. They also require implementing measures to contain environmental pollution, using groundwater remediation techniques. All the hydrogeochemical processes occurring in the aquifer must be considered to avoid mistakes when characterizing the site, planning groundwater monitoring, selecting remedial techniques, and assessing health risks. Among others, the redox processes, namely Terminal Electron Accepting Processes (TEAPs), are amongst the most important.

TEAPs are triggered by microorganisms oxidizing organic matter that is naturally present or anthropogenically discharged to groundwater (organic substrate; Electron Donor, ED). Bacteria sequentially use electron donor dissolved species during the oxidation process (i.e. O_2, NO_3^-, Mn(IV) and Fe(III) oxi-hydroxides, SO_4^{2-} and inorganic carbon; Terminal Electron Acceptors, TEAs), depending on the available energy and commonly expressed through Gibbs free energy of formation (Appelo and Postma 2005). Different bacteria species present in groundwater will use energy more or less efficiently during the life cycle, depending on which electron acceptor is used. (Jackson and McInerney 2002; Chapelle 2002; Druschel et al. 2008). When an organic substrate is present, there will be an enrichment of reduced species N, Mn, Fe, S and C within groundwater, that will trigger a series of secondary hydrogeochemical reactions (van Breukelen et al. 2004; Greskowiak 2005; Rotiroti et al. 2014, 2015; Caschetto, 2017). Therefore, it becomes of fundamental importance to define the spatial distribution of TEAPs within groundwater (i.e. redox zonation) as these processes affect the mobility, the transport, the degradation and the toxicity of organic and inorganic contaminants (Sracek et al. 2004; Borch et al. 2010; Hedbavna et al. 2016; Filippini 2017). This makes redox zonation a subject of great interest; there are many relevant studies where defining aquifer homogeneous zones has been undertaken at various scales. Different methodologies have been used to define the redox zones. Berner (1981), McMahon and Chapelle (1991), Chapelle et al. (1996), Christensen et al. (2000) and Chapelle et al. (2009a) have identified redox zones by describing the distribution of redox-sensitive substances and the organic substrate within the aquifer. Kloppmann et al. (1996) e Postma and Jakobsen (1996) have instead used a different approach, identifying the prevailing redox process by means of considerations around thermodynamics. McMahon and Chapelle (2008) attempted to standardize redox zonation by proposing thresholds for the TEAs, which identified the prevailing redox process. This approach is widespread (Chapelle et al. 2009b; Landon et al. 2011; Close et al. 2016), as it allows understanding the spatial distribution of a specific TEA. New approaches to redox zonation are multivariate statistical analyses (Hsu et al. 2010; Palmucci et al. 2016), that allows to identify relationships among the considered parameters, and the hydrogeochemical numerical modelling (Hunter et al. 1998; Lønborg et al. 2006; Jakobsen and Cold 2007; Boano et al. 2010). However, in all cases, the spatial relationships between the physico-chemical parameters involved with redox processes (i.e. diagnostic parameters of redox processes) are not considered. Understanding these spatial relationships using multivariate geostatistical techniques borrowed from agriculture and soil science (Sollitto et al. 2010; Castrignanò et al. 2012; Shaddad el al. 2016) would allow overcoming the concept of homogenous zones, considering redox processes as dynamic reactions.

Organic chlorinated solvents are other TEAs of great interest, due to their toxicity and also because they are found in many cases of anthropogenic pollution. (Vogel et al. 1987; Hunkeler et al. 2005, Koenig et al. 2015; Colombo 2017; Dolinova et al. 2017). These solvents are degraded during the oxidation process of the organic substrate, where they lose chloride atoms in favor of hydrogen atoms. In this case, the process is triggered by halo-respiring microbiological species (Grostern et al. 2009; Malaguerra et al. 2011; Chambon et al. 2013). McCarty (1997) verified that bacteria that consume chlorinated solvents during their respiratory activity are less efficient in degrading the organic substrate compared to bacteria that consume inorganic TEAs. This introduces competition among different types of redox processes, which could inhibit reductive dechlorination (Aulenta et al. 2006; Becker and Seagren 2009; Chen et al. 2014). Numerous studies have investigated the competition that takes place between bacteria species for the organic substrate in the presence of chlorinated solvents. Most of these investigations take place by analyzing these biological and chemical processes in laboratory experiments, where attempts are made to replicate conditions that are similar to natural ones (Yang and McCarty, 1998; Nelson et al. 2002; Heimann et al. 2005; Lai et al. 2015; Paul et al. 2016; Cao et al. 2017), sometimes including hydrogeochemical modelling (Fennell and Gossett 1998; Berggren et al. 2013; Mayer-Blackwell et al. 2016). There are relevant studies where the distribution of redox-sensitive compounds present in aquifers has been analyzed (Skubal et al. 2001; Puigserver et al. 2014; Weatherill et al. 2018). Less frequent are those include competition for the organic substrate in reactive transport numerical models aimed to assess natural attenuation (Widdowson. 2004;

Manoli et al. 2012; Viotti et al. 2014). However, modeling reactive transport is an important tool for investigating the competition between different types of redox processes. This modeling is also useful for identifying the species that mostly influence these processes and that determine the spatial-temporal evolution of the reactions involved.

The above hydrogeochemical processes are profoundly dependent on the effects that the hydrodynamics of the aquifer has on the distribution of TEAPs within the aquifer system. In general, hydrodynamic dispersion and molecular diffusion within the aquifer facilitate the mixing of mobile reactants (i.e. NO_3^-, SO_4^{2-}, and chlorinated solvents), thus facilitating biodegradation reactions (Kitanidis et al. 1994; Essaid et al. 2015), while electron acceptors within the aquifer matrix do not require mixing (McNab and Narasimhan 1995; Hacherl et al. 2003; Arora et al. 2013). However, Molins et al. (2012) demonstrated that high fluxes within the aquifer can reduce reaction rates, almost inhibiting them. The different studies within literature are not in agreement with regards to the real effects that hydrodynamic dispersion has on redox processes, especially in highly heterogenous geological contexts (Vessia and Di Curzio 2018; Vessia et al. 2019). Therefore, it is necessary to improve the understanding of these aspects, especially in consideration of the fact that TEAPs in groundwater are mostly a hydrogeological problem, even before they are a chemical or biological one.

The above-mentioned issues led to the identification of the following research objectives, which concern some significant hydrogeochemical and hydrodynamic aspects of aquifers that could affect the occurrence of redox processes in groundwater. Three main aspects were investigated with reference to three case studies:

1. The advanced redox zonation of the San Pedro Sula, Honduras site (SPS site), where multivariate geostatistical techniques were used, supported by multivariate statistical analysis and hydrogeochemical numerical modeling.
2. A contaminated site located in the northern Abruzzo region, Italy (VR site), where the study of the competition between different types of redox processes (i.e. inorganic TEAPs and reductive dechlorination) was undertaken by means of numerical reactive transport modeling of contaminants within the aquifer.
3. The contaminated site of Bussi Officine (PG site), which is a Site of National Interest, is presented, where the role of hydrodynamics on the occurrence of TEAPs was assessed by analyzing the distribution of TEAs (i.e. inorganic TEAs and chlorinated solvents) within the different aquifer bodies.

Materials and methods

For each objective of this research, in the following section, the data related to the corresponding case study and the specific methodological approach are described.

Concerning the advanced redox zonation of aquifers, the used dataset was provided by "Aguas de San Pedro" Spa (ASP), that is the water utility of San Pedro Sula (SPS site). In this case study, the dataset consists of two monitoring surveys consisting in hydraulic head measurements, stream discharges, and chemical analyses of surface-water and groundwater; February (i.e. wet season) and April (i.e. dry season) 2002. All the analyzed samples were pre-treated by 0.45 µm diameter filters. The ASP monitoring network (Fig. 1) consists in wells exploited for drinking purposes, that are characterized by a peculiar well construction: gravel package for the whole borehole length and filters in correspondence of the most productive aquifer layers. Besides proving the well productivity, this peculiar well construction favors mixing of different groundwaters. To explore statistically data, the Principal Component Analysis (PCA) was performed on all the available physico-chemical parameters (i.e. pH, electrical conductivity, turbidity, Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, PO_4^{3-}, Fe, Mn). This statistical method is widely used in hydrogeochemical studies (Di Curzio et al. 2016; Palmucci et al. 2016; Barbagli et al. 2019) and allows identifying relationships among the considered variables. The redox conditions were assessed by the hydrogeochemical numerical modeling by the code PHREEQC ver. 3 (Appelo and Postma 2005). In detail, the Mn and Fe speciation in groundwater was performed, considering the redox-sensitive couple NO_3^-/NH_4^+ to define the actual redox conditions. The advanced redox zonation was performed by the Multi-Collocated Factor Kriging (MCFK) (Wackernagel 2003), considering the physico-chemical parameters that resulted diagnostic of redox processes. This geostatistical technique allows identifying the spatial relationships among the considered parameters, pointing out hydrogeochemical processes. To present the result in the clearest manner, only the wet season results will be presented in the following sections.

In order to study the competition between the inorganic TEAPs and the reductive dechlorination for organic substrate in the VR site, the datasets provided by the Abruzzo Region Environmental Protection Agency (ARTA) and other environmental consultants, related to the 2009-2014 period, were considered. In detail, groundwater chemical analyses related to 9 sampling surveys, soil chemical analyses related to the solid matrix sampling preformed at 3 sites of the study area, and 3 hydraulic head measurement rounds. The whole monitoring network consists of 43 points. Once a consistent hydrogeological and environmental conceptual model was identified, a 1-D Advective-Reactive-Dispersive (ARD) transport numerical modeling was implemented along the main flow path using the PHREEQC ver. 3 code. To simulate the degradation of organic compounds, different equations were selected: the Monod equation for the fuel-related compound fermentation, the first-order equation for the fermentation by-product (i.e. H_2 and Acetate) oxidation, and the modified Monod equation for the reductive dechlorination (Chambon et al. 2013).

Finally, to clarify the effect of hydrodynamics on the redox process occurrence (i.e inorganic TEAPs and reductive dechlorination), a detailed hydro-geological and

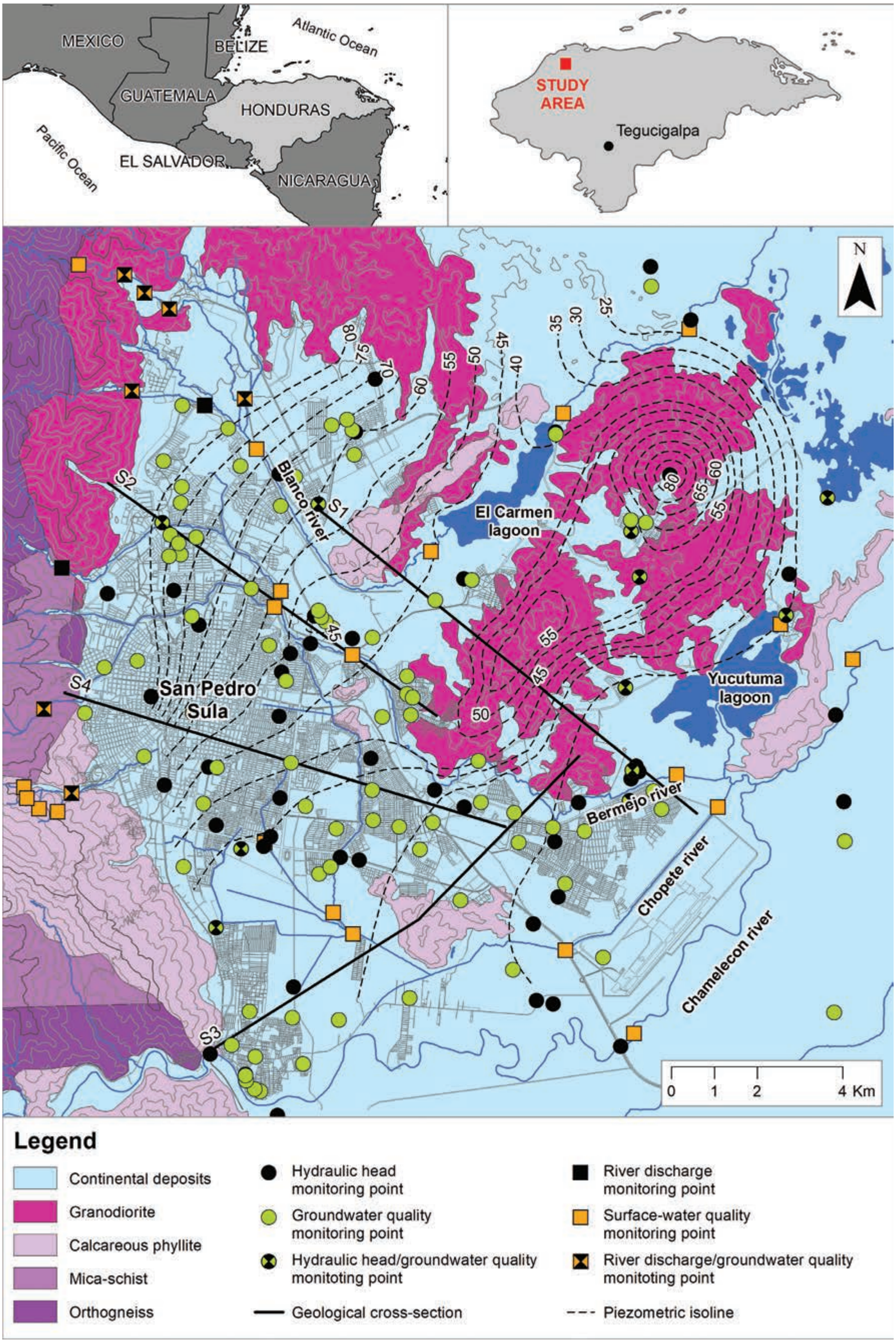


Fig. 1 - Schematic hydrogeological map of the SPS site, with the monitoring network. Reprinted from Di Curzio et al. 2019, with permission from Elsevier.

Fig. 1 - Carta idrogeologica schematica del SPS site, con la rete di monitoraggio. Ristampata da Di Curzio et al. 2019, con l'autorizzazione di Elsevier).

environmental characterization of the PG site was performed. Data are related to hydraulic head measurements (2007-2017 period), daily river level measurements provided by the Hydrographic Service of Abruzzo Region (2007-2013 period), and groundwater chemical analyses and geognostic surveys performed by the Abruzzo Region Environmental Protection Agency (ARTA) and other environmental consultants. In detail, the distribution of TEAs and chlorinated solvent in groundwater was analyzed, taking into account the complex hydro-geological framework and the water flow in the aquifer..

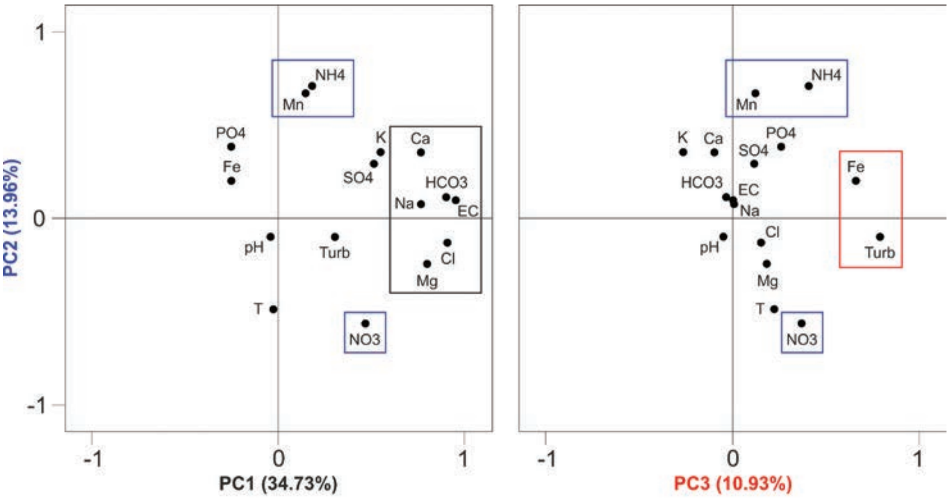
Advanced redox zonation of the SPS site

The San Pedro Sula alluvial plain (Fig. 1) is located in Honduras and represents the northern part of the Sula Valley, that is a tectonic depression related to the strike-slip fault system of the margin between the North America plate and the Caribbean one (Capaccioni et al. 2014). The SPS site hosts an important aquifer made up of heterogeneous continental deposits, that are characterized by complex geometries (e.g. paleo-channels) and are more than 250 m thick (Torrese et al. 2013). The bedrock is made up of high-grade, mid-grade, and low-grade metamorphic rocks; in the eastern part of the study area, also a granodioritic intrusive body is present (Madonna et al. 2007). Groundwater flow takes place mainly within the continental deposits that fill the tectonic depression, and, to a lesser extent, in the shallow weathered portion of the bedrock. Analyzing the water table isoline distribution (Fig. 1), two principal recharge areas can be identified: the first one in the north-western sector, nearby the mountainous massif, and the second one in the eastern sector, in correspondence of the intrusive relief. In addition, clear surface-water/groundwater relationships are present, especially in the eastern part of the urban area.

The groundwater samples highlighted high Mn and Fe concentrations (i.e. above the threshold suggested by WHO 2011), particularly in the wells located nearby the main streams. On the contrary, in the same areas, surface-water is highly enriched in PO_4^{3-}, NH_4^+, BOD_5, and COD, while dissolved oxygen (DO) concentrations are below the detection limit. These conditions indicate heavy surface-water eutrophication, likely due to the large presence of untreated wastewater. In addition, the land use distribution shows wide intensive agricultural and livestock areas, bounding the San Pedro Sula urban area. These activities likely leak additional nutrients in the main streams, contributing to the eutrophication conditions. Further details about the SPS site pollution are provided in Di Curzio et al. (2019).

The PCA results (Fig. 2) show 3 principal components, that are described below:

- PC1 is characterized by a strong correlation with electrical conductivity (EC) and major ions, that suggests water-rock interaction processes.
- PC2 is characterized by a positive correlation with Mn and NH_4^+ and by a negative one with NO_3^-. In this case, anoxic conditions, that are triggered by the oxidation of organic matter leaked from eutrophicated surface-water, are described by PC2.
- PC3 shows a strong positive correlation with Fe and turbidity (Turb). This relation suggests the presence of a Fe oxi-hydroxide colloidal phase, which is likely caused by the peculiar monitoring well construction. As a matter of fact, the well construction favors mixing of different redox conditions and dissolved Fe oxidation and precipitation as a colloidal phase.



	T	pH	EC	Turb	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+	PO_4^{3-}	Fe	Mn	Eig. Val.	Var. %
PC1	-0.03	-0.04	**0.95**	0.30	**0.77**	**0.55**	**0.77**	**0.80**	**0.90**	**0.91**	**0.51**	0.47	0.18	-0.25	-0.25	0.15	5.56	34.73
PC2	-0.49	-0.10	0.10	-0.10	0.08	0.35	0.35	-0.24	0.11	-0.13	0.29	**-0.56**	**0.71**	0.38	0.20	**0.67**	2.23	13.96
PC3	0.22	-0.05	0.00	**0.79**	0.01	-0.26	-0.10	0.18	-0.03	0.15	0.12	0.37	0.41	0.26	**0.66**	0.12	1.75	10.93

Fig. 2 - Projection of the PC loadings obtained by the PCA (wet season) and the corresponding rotated matrix of principal components (below). The significative correlations are represented in underlined bold black. Reprinted from Di Curzio et al. 2019, with permission from Elsevier.

Fig. 2 - Proiezione dei loading delle PC ottenute mediante la PCA (stagione umida) e la relativa matrice ruotata delle componenti principali (in basso) Le correlazioni significative sono rappresentate con carattere nero grassetto sottolineato. Ristampata da Di Curzio et al. 2019, con l'autorizzazione di Elsevier).

The metal speciation (Fig. 3), performed by the hydrogeochemical numerical modeling, confirms the PCA results. In fact, Mn content in groundwater is almost perfectly related to its reduced form activity (log[Mn^{2+}] in Fig. 3a), indicating a close relationship with the anoxic condition. Regarding Fe, it also shows a good relationship with the reduced form activity (log[Fe^{2+}] in Fig. 3b). Nevertheless, some samples, characterized by Turb > 1 NTU, present a higher Fe content with respect to the ones expected in the corresponding redox conditions. For the anomalous samples, the comparison between the modeled Ferrihydrite and the turbidity values (Fig. 3c) confirms the presence of the previously identified Fe oxi-hydroxide colloidal phase.

The use the MCFK as an advanced redox zonation technique allowed to identify a short-range factor (Fig. 4a) and a long-range factor (Fig. 4b). The short-range factor confirms the anoxic conditions nearby the heavily eutrophicated streams, caused by the organic matter oxidation, and the Fe oxi-hydroxide colloidal phase precipitation in some of the monitoring wells. In addition, the long-range factor highlights that the anoxic conditions persist even at a longer distance, especially in the northern area where a pollution event was detected.

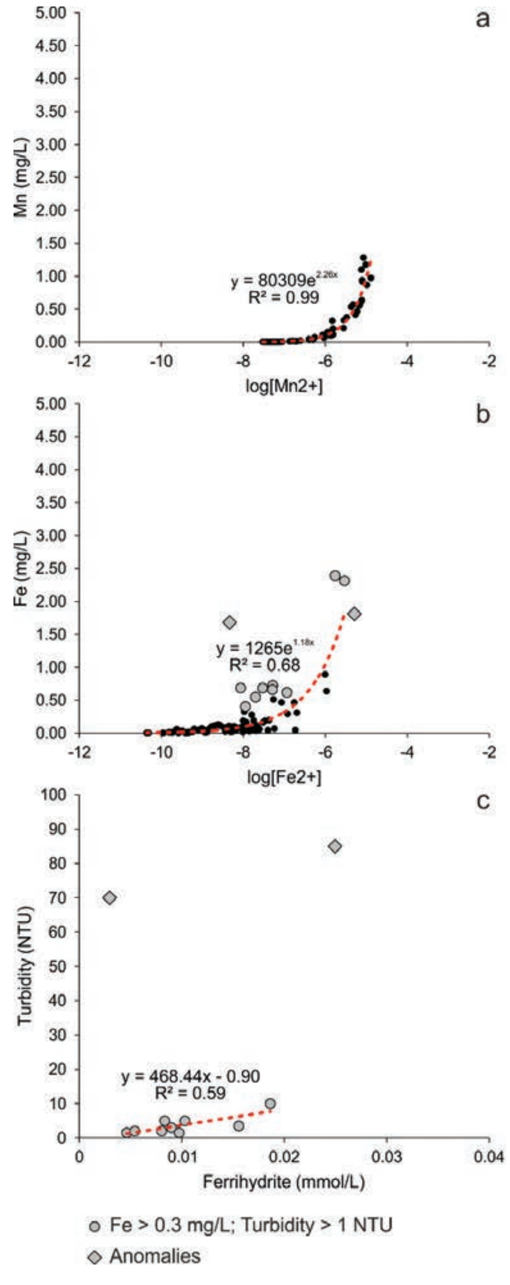


Fig. 3 - Comparison between the activity Mn^{2+} (a) and Fe^{2+} (b) and their total content in groundwater (wet season). For the samples with turbidity greater than 1, the modeled Ferrihydrite amounts have been compared with the corresponding turbidity values (c). Reprinted from Di Curzio et al. 2019, with permission from Elsevier.

Fig. 3 - Confronto tra le attività di Mn^{2+} (a) e Fe^{2+} (b) e il loro contenuto totale nelle acque sotterranee (stagione umida). Per i campioni con torbidità maggiore di 1, i quantitativi di Ferridrite modellata sono stati confrontati con i valori di torbidità corrispondenti (c). Ristampata da Di Curzio et al. 2019, con l'autorizzazione di Elsevier).

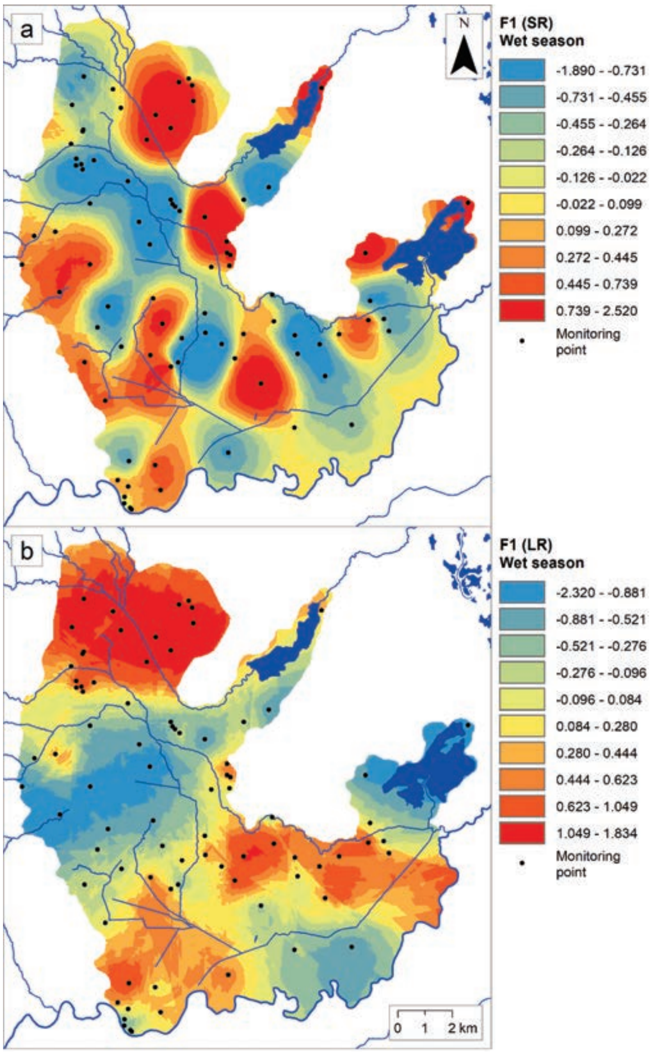


Fig. 4 - Score maps of the regionalized factor scores, at short (a) and long (b) range for the wet season. Reprinted from Di Curzio et al. 2019, with permission from Elsevier.

Fig. 4 - Mappe degli score dei fattori regionalizzati, a corto (a) e lungo (b) raggio per la stagione umida. Ristampata da Di Curzio et al. 2019, con l'autorizzazione di Elsevier).

Competition for substrate assessment in the VR site

The study area of this second case study is located in the mid-Adriatic coastal sector. Here, different contamination events interact each other in the aquifer (Fig. 5): a fuel spill from a gasoline station, at least two areas with buried foundry wastes rich in metals, a chlorinated solvent plume, and fuel-related compound residual phases.

From a geological and hydrogeological point of view, the VR site (Fig. 6) is characterized by mainly sandy and silty sandy marine deposits, that are about 10-15 m thick and constitute the actual aquifer. This porous geological body lies above marly clayey marine deposits, which constitute the aquiclude (Desiderio et al. 2010). Groundwater flows toward the coastline, and the hydraulic gradient is very low and decreases slightly downward. This aquifer is recharged by the local rainfall.

The soil chemical analyses have pointed out that the highest concentrations of metals are present in those areas where the foundry wastes were buried. Since these wastes were used in the eighties and nineties as filling material during the urban expansion, other unknown foundry waste burials could be present in the VR site. In groundwater, the distributions of Methyl tert-butyl ether (i.e. MTBE), Benzene, Toluene, Ethylbenzene, and Xylene (i.e. M-BTEX) are almost the same. These fuel-related compounds form a limited plume that moves along with the main groundwater flow path. Besides the plume, M-BTEX are present also in residual phases

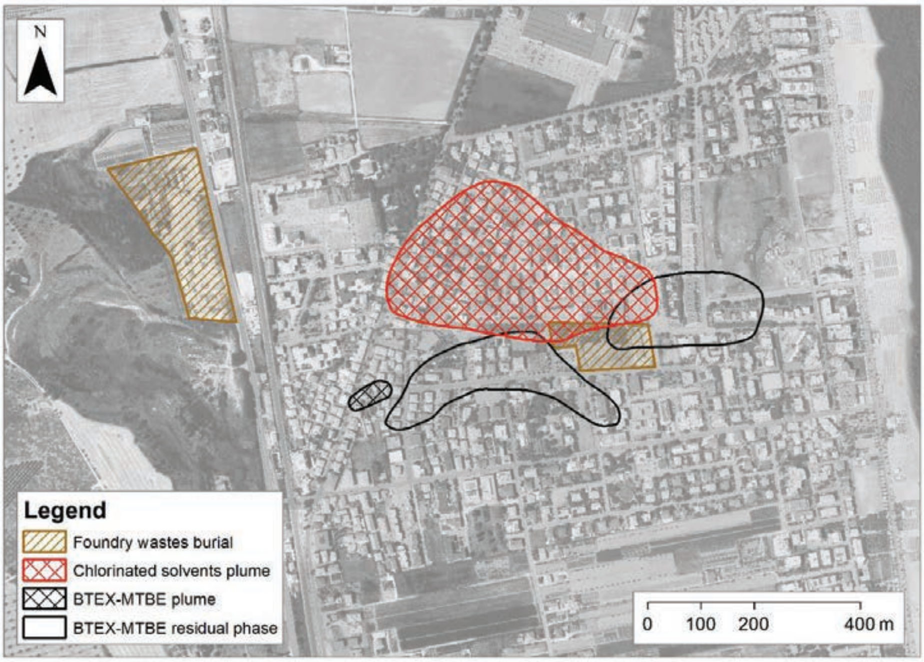


Fig. 5 - Interazione tra eventi di contaminazione diversi nell'area di studio.

Fig. 5 - Interaction among different pollution events in the study area.

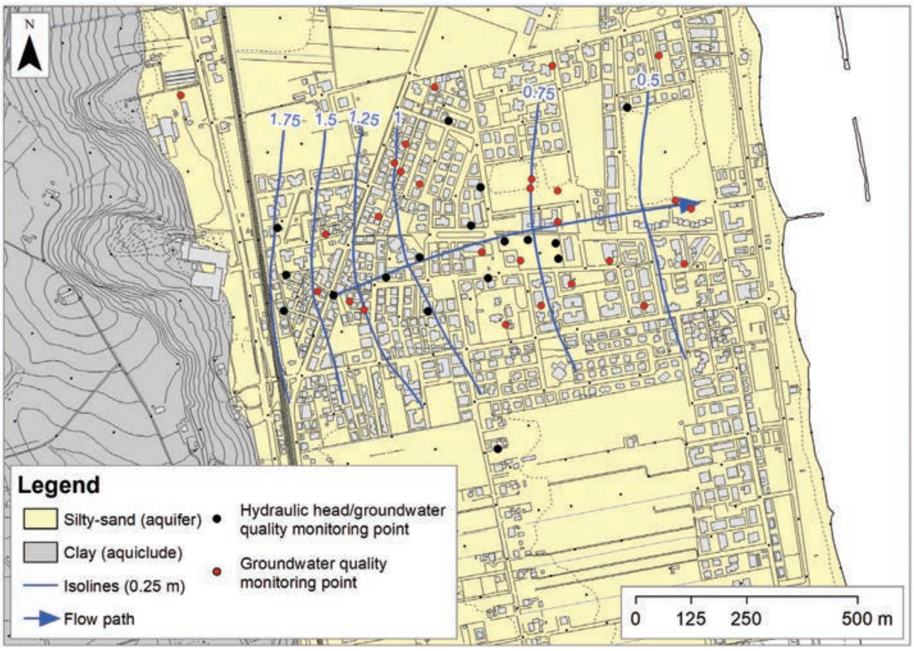


Fig. 6 - Schematic hydrogeological map of the VR site, with the monitoring network.

Fig. 6 - Carta idrogeologica schematica del VR site, con la rete di monitoraggio.

within the aquifer. NO_3^- has an heterogenous distribution, likely related to the presence of several point-sources of nitrate (e.g. vegetable garden fertilization and/or leaking sewers). Contrariwise, Mn and Fe seem to be more homogeneously distributed in groundwater, although Fe is definitively higher than Mn. Concerning the chlorinated solvents, they are present in a well-defined area (Fig. 5). Furthermore, Dichloroethylene (DCEs) and Vinyl Chloride (VC) concentrations are about 2 orders of magnitude higher Perchloroethylene (PCE) and Trichloroethylene (TCE). This peculiar distribution suggests that this is an older contamination event, which evolved by reductive dechlorination.

The 1-D ARD transport modeling results show that the fuel-related compound degradation (i.e. fermentation and oxidation) provokes the Mn and Fe oxi-hydroxide reductive dissolution and the consumption of NO_3^- and SO_4^{2-}. On the other hand, since the inorganic TEAPs are more energetically convenient, the reductive dechlorination is inhibited and delayed, causing enrichment in highly toxic by-products, such as VC (Fig. 7). Among all the inorganic TEAPs, NO_3^- and SO_4^{2-} seem to play a major role, with respect to Mn and Fe, because they are generally more abundant and related bacteria use both H_2 and short-chain fatty acids (e.g. Acetate) as organic substrate.

Evaluation of the hydrodynamic role on the TEAPs in the PG site

The study area (Fig. 8) is located in the Popoli Gorges (PG), whose contamination is strictly related to the industrial activity during the last century. In fact, large volumes of industrial wastes were buried near Pescara River (Fig. 8) and have been leaking contaminants in groundwater for decades (Filippini et al. 2018). Geologically, the PG site is an incised riverine valley within the Morrone massif, subsequently filled with 65-100 m of heterogeneous continental deposits (Desiderio et al. 2012; Petitta et al. 2018; Rusi et al. 2018). In detail, the continental deposits are characterized by different lithologies: (1) coarse head deposits (i.e. breccias, locally cemented) just above the bedrock, (2) different travertine facies (i.e. from solid concretions of travertine with cavities to travertine sands), several fine lacustrine deposits (clayey and/or sandy silts with peats, located especially in A and B in Fig. 9), and (3) shallow sandy gravelly alluvial deposits.

Groundwater flows mainly within the heterogeneous continental deposits (Di Curzio et al. 2018), although these deposits are recharged primarily from the limestone aquifer and subsequently from the local rainfall. Additionally, an important increase in river flow is present in the north-eastern part of the PG site. This increase in river flow is due to the fact that groundwater, in this area, flows through a narrower aquifer section.

The distribution of the different chlorinated solvent groups detected at the PG site points out that the oxidized species concentrations, such as Carbon Tetrachloride (Fig. 9), are higher where the groundwater flow is faster, while decrease abruptly nearby the lacustrine deposits with peats. The reduced by-products, instead, show an inverse trend. Concerning the inorganic TEAs, their content in the lacustrine deposits (i.e. high Mn and Fe, and low NO_3^- and SO_4^{2-}) suggests anoxic conditions, that trigger both the inorganic TEAPs and the

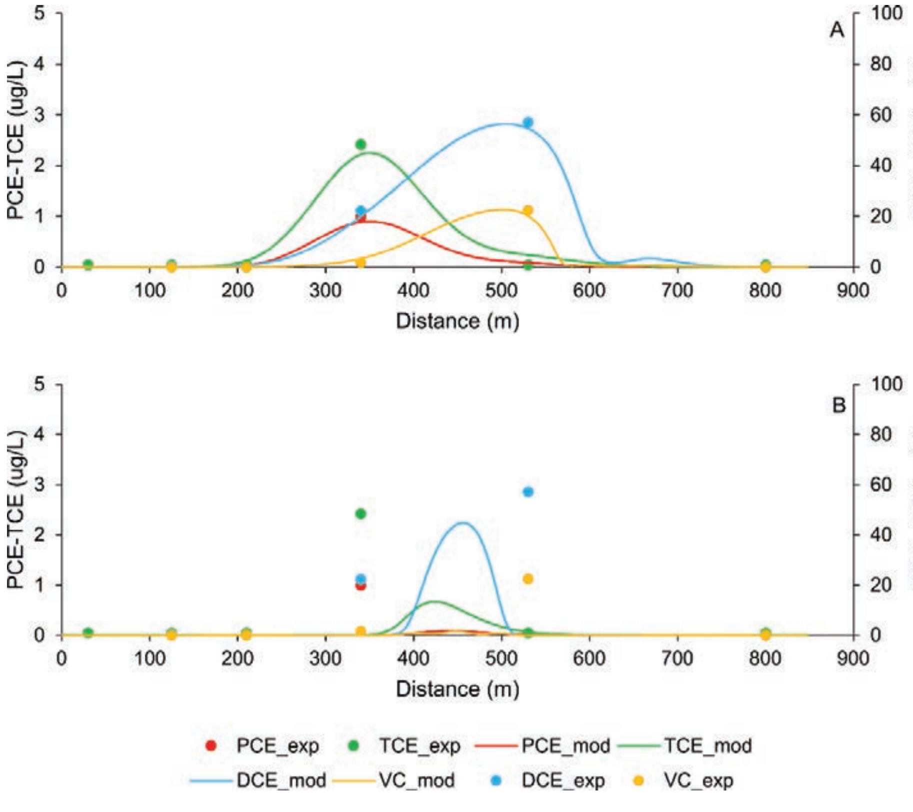


Fig. 7 - Comparison between the ARD transport modeling results performed in the real conditions (A) and not considering the inorganic TEAPs (B). The symbols indicate the experimental data, while the continuous lines the modeling results.

Fig. 7 - Confronto tra I risultati del modello ARD eseguito in condizioni reali (A) e quelli eseguito non considerando i TEAP inorganici (B). I simboli indicano i dati sperimentali, mentre le linee continue i risultati della modellazione.

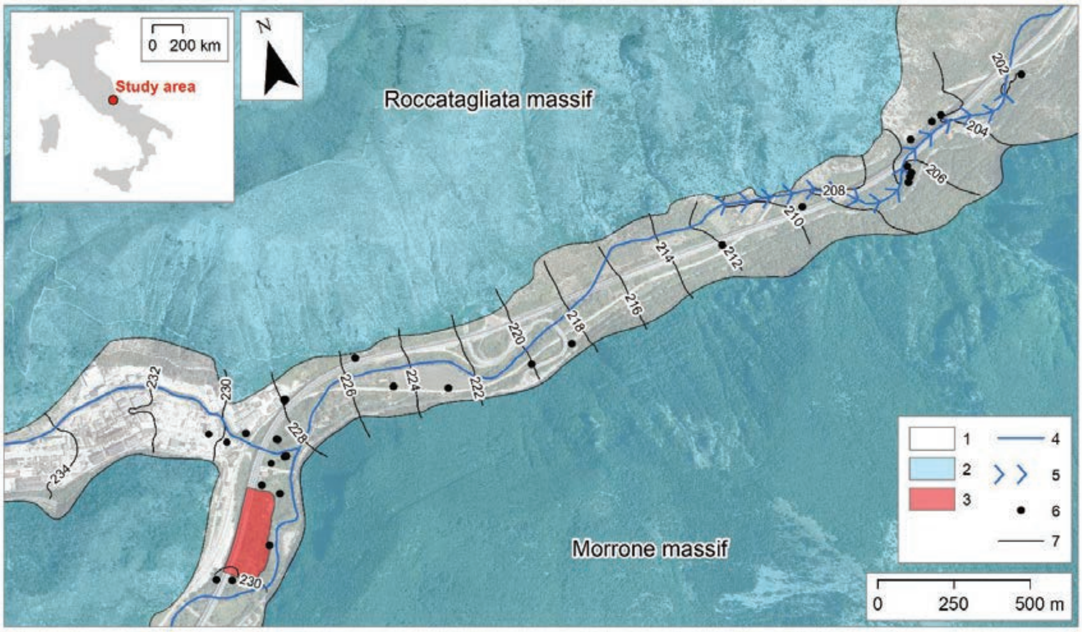


Fig. 8 -Schematic hydrogeological map of PG site (modified after Di Curzio et al. 2018). In legend: 1) continental deposits; 2) limestone; 3) industrial wastes dump; 4) main rivers; 5) increase in river flow; 6) groundwater monitoring network; 7) hydraulic head isolines (every 2 m, numerically simulated in Di Curzio et al. 2018).

Fig. 8 - Carta idrogeologica schematica del PG site (modificata da Di Curzio et al. 2018). In legenda: 1) depositi continentali; 2) calcari; 3) discarica di rifiuti industriali; 4) Corsi d'acqua principali; 5) incremento di portata in alveo; 6) rete di monitoraggio delle acque sotterranee; 7) isopieze (equidistanza 2 m, simulate numericamente in Di Curzio et al. 2018).

reductive dechlorination (even though competition can likely occur). These anoxic conditions are caused by the organic matter (i.e. peat) oxidation and/or by long and deep flow paths, highly depleted in DO. Furthermore, the chlorinated solvents are lipophilic compounds (high koc values), thus they are easily adsorbed on the organic matter present in the lacustrine deposits. Downstream (B in Fig. 9), although the conditions are almost the same, the increase in groundwater flow provokes dilution decreases the organic substrate concentrations and inhibits both the inorganic TEAPs and the reductive dechlorination.

Conclusions

This research addressed issues related to some hydrogeochemical and hydrodynamic features that affect redox processes in groundwater at three case studies.

In the SPS site case study, an advanced redox zonation approach was proposed, borrowing a multivariate geostatistical method from agriculture and soil science. The Multi-Collocated Factorial Kriging, together with the Principal Component Analysis and the hydrogeochemical numerical modeling, allowed to assess the main causes of Mn and Fe mobilization. As a matter of fact, the heavily eutrophicated streams, which are hydraulically connected with the shallower aquifer bodies, transfer organic matter in groundwater, triggering redox processes and causing anoxic conditions. The same thing takes place in the northern area, where an anthropogenic contamination event was identified. However, the peculiar monitoring well construction favors mixing among different redox conditions, which causes Fe oxi-hydroxide colloidal phase precipitation. The methodological approach enabled to identify different simultaneous redox processes, overcoming concepts of predominant TEAPs and homogeneous redox zones, that is not representative of the actual redox conditions in groundwater.

The interaction among different contamination events in the VR site allowed to get a deeper insight into the competition for organic substrate among different redox processes. The 1-D Advective-Reactive-Dispersive transport numerical modeling, selected as an analytical technique to assess competition for organic substrate, highlighted that microbial species that use inorganic TEAs to oxidize the organic substrate (i.e. H_2 and Acetate) produced by the fuel-related compound fermentation (i.e. M-BTEX) are more effective than the halo-respiring bacteria. As a result, the large availability of Mn and Fe oxi-hydroxide, NO_3^-, and SO_4^{2-} inhibits and slows down the reductive dechlorination of the chlorinated solvents present in the VR aquifer. This process enriches groundwater in highly toxic by-products of the reductive dechlorination, such as Vinyl Chloride. The obtained results confirm the effectiveness of the Advective-Reactive-Dispersive transport numerical modeling as a viable tool to investigate in situ competition for organic substrate because all the intrinsic hydrogeochemical and hydrodynamic features of the selected study area can be taken into account, evaluating their actual role in this kind of process.

A deeper insight into the hydrodynamic effect on the redox processes and the anoxic condition distribution was studied in the PG site. The comparison between the hydrogeological complexity of the study area and the distribution

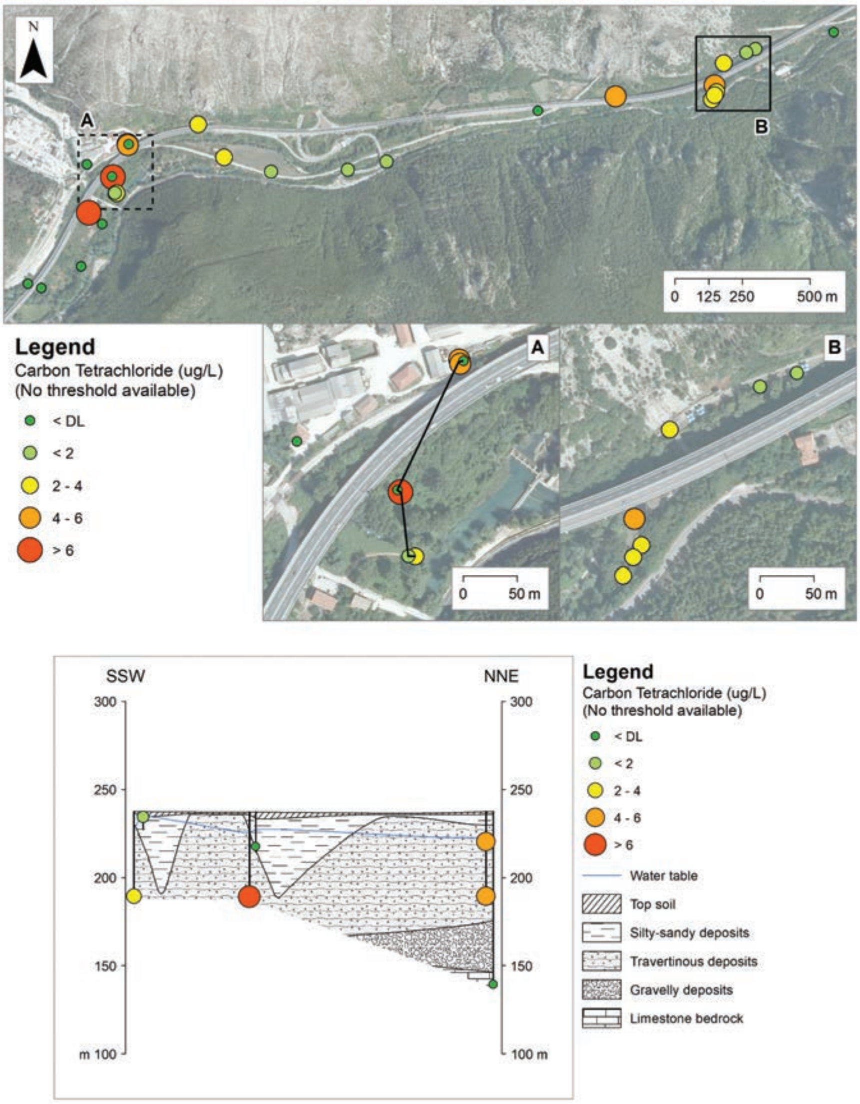


Fig. 9 - Carbon Tetrachloride distribution in the PG site groundwater. The trace of the section shown in the lower part is in box A.

Fig. 9 - Distribuzione del Tetracloruro di Carbonio nelle acque sotterranee del PG site. La traccia della sezione mostrata nella parte bassa è nel riquadro A.

of all the chlorinated solvents and inorganic TEAs in the aquifer pointed out that high dispersivity and dilution inhibit of redox process, as the organic substrate concentrations, related to the peaty lacustrine deposits, are decreased in the aquifer. In aquifer zones where groundwater flow rate is high, these hydrodynamic features, instead of favoring mixing, inhibit redox reactions. On the other hand, the lacustrine deposits with peats can be considered as an actual "chemical reactors", because of the combination of adsorption of chlorinated solvents, low groundwater flow, and oxidizing organic substrate. Although the lacustrine deposits cause retardation in the contaminant transport, these geological bodies back-diffuse mainly toxic by-product of the reductive dechlorination, acting as a secondary contamination source.

In conclusion, the methodological approaches used in the different case studies proved to be able to investigate redox processes in groundwater, in case of contamination events. The results obtained from this research project highlighted the great impact that hydrogeochemical and hydrodynamic features have on the redox processes occurrence and the involved contaminant fate in groundwater. This information must be taken into account when characterizing the contaminated sites, planning groundwater monitoring, selecting the best remedial technique, and assessing the actual health risks.

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