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Geological and hydrogeological features affecting migration, multi-phase partitioning and degradation of chlorinated hydrocarbons through unconsolidated porous media.

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ABSTRACT

Chlorinated solvents are the most ubiquitous organic contaminants found in groundwater since the last five decades. Due to their high degree of carcinogenicity/toxicity and the relatively high mobility and persistence, they represent a serious threat against the human health and the environment. These contaminants generally reach groundwater as Dense Non-Aqueous Phase Liquid (DNAPL), a phase characterized by very different features in respect to water (e.g. higher density and lower viscosity and wettability). This phase can migrate through aquifers, and also through aquitards, in ways that aqueous contaminants cannot. The complex phase partitioning to which chlorinated solvent DNAPLs can undergo (i.e. to the dissolved, vapor or sorbed phase), as well as their transformations (e.g. degradation), depend on the physico-chemical properties of the contaminants themselves and on features of the hydrogeological system in which the contaminants migrate. The peculiar dynamics of chlorinated solvent DNAPLs through geologic media have been investigated during the last three decades (mainly in North America), with a particular focus on hard rock fractured or strongly consolidated porous hydrogeologic systems. Differently, studies relative to the behavior of DNAPLs in loose or poorly consolidated sediments (such as those recently deposited in alluvial plains) are infrequent in literature.

The main goal of the thesis is to provide new knowledge for the future investigations of sites contaminated by DNAPLs in alluvial settings, proposing the application of innovative investigative approaches and emphasizing some of the key issues and main criticalities of this kind of contaminants in such a setting. To achieve this goal, the hydrogeologic setting below the city of Ferrara (Po plain, northern Italy), which is affected by scattered contamination by chlorinated solvents, has been investigated at different scales (regional and site specific), both from an intrinsic (i.e. groundwater flow systems) and specific (i.e. chlorinated solvent DNAPL behavior) point of view. After an initial definition of the regional relationships of groundwater flow systems with sources of recharge and of intrinsic vulnerability of aquifers, by the use of groundwater stable isotopes as natural tracers, a limited-in-space high-resolution investigative approach was employed for the research. Detailed investigations were carried out in particular in one selected test-site, known as “Caretti site”, where high-resolution vertical profiling of different kind of data, including stratigraphic and paleo-environmental analysis, were collected by means of multilevel monitoring systems and other innovative sampling and analytical techniques. This allowed to achieve a deep geological and hydrogeological knowledge of the system and to reconstruct in detail the architecture of contaminants in relationship to the features of the hosting porous medium.

The results achieved in this thesis are useful not only at local scale, e.g. employable to interpret the origin of contamination in other sites of the Ferrara area, but also at global scale, in order to better address future remediation and protection actions of similar hydrogeologic settings.

Contents

Introduction

DNAPLs are among the most challenging contaminants present nowadays in groundwater. Their acronym stays for Denser-than-water Non-Aqueous Phase Liquids and they are ubiquitously present in the hydrogeological systems below many industrialized and urbanized areas throughout the world, since the second half of the last century (Morrison et al., 2010). Even though DNAPLs were spilled in the subsurface environment since the end of the II World War, as the result of accidental leakage or improper/illegal dumping, their criticalities and behavior became known not earlier than a couple of decades ago (Pankow and Cherry, 1996). These contaminants represent a serious hazard towards the human health and the environment and they are very tricky to remediate, as they don't follow some of the main traditional hydrogeological axioms related to groundwater flow. Indeed, DNAPLs don't necessarily migrate in the same directions as groundwater, they tend to accumulate at the bottom of aquifers and are able to migrate through the most part of aquitards. These contaminants occur in the subsoil not only in the shape of DNAPLs (free-mobile or residual-immobile phase), but also in a variety of other phases (dissolved, sorbed or vapor), originated by complex partitioning processes affecting the original DNAPL phase. These partitioning processes are influenced by the physico-chemical features of the contaminants, but also by the geological and hydrogeological features of the system in which the contaminants are hosted. Moreover, DNAPLs (or the descending phases) can undergo complex degradation pathways which, in some cases, lead to the accumulation of compounds even more toxic than the former ones.

From a chemical stand-point, the most part of DNAPLs present in the subsurface are represented by halogenated hydrocarbons. These are organic chemical compounds consisting in aliphatic or aromatic hydrocarbon molecules, with a certain number of hydrogen atoms replaced by halogens (most often chlorine). Among them, the so called "chlorinated solvents" (e.g.: chlorinated ethenes like tetracloroethene – PCE or trichloroethene – TCE; chlorinated ethanes like trichloroethane – TCA; chlorinated methanes like chloroform - CF) represent the most ubiquitous at a global scale.

Contamination by chlorinated solvents in the form of DNAPLs is very diffuse also in Europe and Italy (e.g. Cavellero et al., 1985; CNIC Naval Support Activity Nalpes, 2010; Nijenhuis et al., 2013) and its origin is attributable not only to point-sources related to processing and storage of commercial products but also to the illegal dumping of wastes containing DNAPL phase, such as chlorinated pitches (Nijenhuis et al., 2013). Nevertheless, the European legislation (Ground Water framework Directive, 2006/118/EC) doesn't impose common threshold values relative to the occurrence in groundwater of dissolved PCE and TCE, intended as indicators of chlorinated solvents contamination (Balderacchi et al., 2014). This suggests a missing or at least a partial recognition of the level of criticality related to this type of contamination at European level. Also, in the National Italian

Legislation some discrepancies emerge: according with the Legislative Decree 152/2006, for example, the maximum admissible concentration for PCE and TCE in groundwater is equal, respectively, to 1.1 and 1.5 μg/L; on the other hand, the maximum admissible concentration for drinkable water distributed as public supply is reported in the Legislative Decree 31/2001 and is equal to 10 μg/L (expressed as the sum of PCE and TCE concentration).

The main topic of the present thesis is the analysis and quantification of the effects of geological and hydrogeological features of an unconsolidated alluvial system on the migration, multi-phase partitioning and degradation of DNAPL contaminants. An innovative approach was employed throughout the research, which consists in high-resolution vertical profiling of data, carried out by way of continuous coring and multi-level monitoring, applied at full site scale. The main aim of the thesis is to provide new knowledge for the future investigations of sites contaminated by DNAPLs in alluvial settings, proposing innovative investigative approaches and emphasizing the key issues and main criticalities of this kind of contaminants in this kind of setting.

Selection of the study test-site and scientific collaborations

Notwithstanding uncommon full scale physical model approaches (e.g. the experiments carried out at the scientific test-sites located in Borden -Ontario, Canada- or Cape Cod -Massachusset, U.S.-), the only way to analyze in detail the distribution and natural dynamics of a DNAPL contamination in the subsurface is the investigation of an actual contaminated site, not subjected to remediation or containment measures and located in a convenient hydrogeological setting (in our case represented by an alluvial plain filled with unconsolidated sediments). A certain degree of freedom in choosing the drilling and sampling schemes is also needed for the success of the investigation. Therefore, the main petrochemical plants are excluded from the list of the ideal test-sites, due to the typical numerous limitations of access to spaces and data and also for the probable occurrence of ongoing remediation actions or containment facilities. Eventually, the availability of funding in order to perform the investigations on the field is an obvious but essential obligation to be fulfilled.

Following these directions, a test-site was selected for the present thesis, which is known as the "Caretti site" and is strongly affected by chlorinated solvents contamination in groundwater. The site is located near to the historical city centre of Ferrara (Emilia-Romagna region, northern Italy), 5.5 km to the south of the Po river, in the eastern and more topographically depressed sector of Po river alluvial plain ("Padana" plain). From April 2009 to March 2014 the site has been one of the research test-sites within the framework of an European Union funded project (7th Framework Programme), known as GENESIS (*__G__roundwater and dependent __E__cosystems: __NE__w __S__cientific and technological basis for assessing climate change and land-use __I__mpact__S__ on Groundwater*). The project included the investigation of several sites throughout Europe. In particular, the area of Ferrara was included in this framework as an example of aquifers affected by point-source contamination originated by human pressures such as industrial and dumping activities.

The hydrogeological setting of the area of Ferrara is characterized by the most common features of an alluvial depositional environment and consists of an alternation of several unconsolidated sandy aquifers and silty-clayey aquitards down to a depth of around 200 m b.g.s.

The Caretti site is one of a number of sites, located all around the city of Ferrara, where a severe contamination by chlorinated compounds was found in the three shallower leaky-confined to fully confined aquifers (i.e. down to 60 m b.g.s.). Such a deep diffusion of the contaminants is in strong disagreement with the intrinsic vulnerability of the local aquifers, according to which, at least the quality of the groundwater hosted in the deepest of the three aquifers (totally confined) was strongly guaranteed by the overlaying aquitards.

The contaminated sites found around Ferrara are located not only in industrial zones but also in residential and agricultural areas. The origin of the contaminations is related to accidental spilling or to improper and illegal dumping of chlorinated wastes.

The *Caretti site*, which was named in this way after the name of the main street bordering it to the east, is a recently developed neighborhood (the urbanization started around 1994; Gargini et al., 2011), extended for almost 1 km^2 and located 0.5 km eastward from the historical walls of Ferrara. The strong contamination affecting the aquifers below the site is mainly composed by chlorinated ethenes, in DNAPL and dissolved phase, and took origin from two local old dumps filled, during the ’60 and ‘70, with a highly heterogeneous mixture of urban and industrial wastes (including chlorinated pitches).

The strong scientific interest on this site is related either to the identification of proper tools for the contaminant source apportionment and to the study of the geological and hydrogeological factors affecting the deep migration of DNAPL phase contaminants. An earlier published research concerning the source apportionment of the contaminated sites around Ferrara, allowed to identify dumped chlorinated pitches (residual industrial wastes, by-products of the chloromethanes distillation process) as the main responsible for the contamination at the Caretti site (Nijenhuis et al., 2013).

Differently, the object of this PhD thesis is the detailed multi-level analysis of the distribution of contaminants throughout the three contaminated aquifers, with emphasis on the fact that the dynamics of migration of DNAPLs are completely untied from the intrinsic vulnerability of aquifers, thus needing the application of very specific approaches and assessments.

In the framework of this research, it was possible to benefit from an important scientific collaboration with “*G360*”, a hydrogeology research group at the University of Guelph (Ontario, Canada), focused on DNAPLs and leaded by Prof. Beth L. Parker and Prof. John A. Cherry; the group is probably the most advanced in the world for the experimental on-site study of DNAPLs. The collaboration with this group took to the application of innovative techniques and approaches of investigation, developed between Canada and U.S. during the last two decades and rarely employed in the European and Italian context.

In particular, multilevel monitoring systems (Einarson, 2006) and other high-resolution vertical profiling of data were adopted in our test-site, in order to perform a very detailed geological, hydrogeological and chemical analysis of the local system and to investigate the processes of migration and transformation of contaminants. Other fruitful collaborations were activated with research partners of the GENESIS project. In particular, thanks to the cooperation with Dr. Ivonne Nijenhuis and Prof. Hans Richnow (Department of Isotope Biogeochemistry - Helmholtz Centre for Environmental Research, Leipzig, Germany), a detailed Compound Specific Isotope Analysis (CSIA) was performed on contaminants, from sediment samples collected at high vertical resolution; the collaboration with Dr. Christine Stumpp (Institute of Groundwater Ecology, Helmholtz Zentrum München, Germany) allowed the reconstruction of detailed vertical profiling of environmental stable isotopes, analyzed on the pore-water of sediments.

At the University of Bologna, the present research benefited from the collaboration with the research group of Prof. Alessandro Amorosi, which provided high-resolution stratigraphic reconstructions and depositional facies interpretations, and from the cooperation with Prof. Enrico Dinelli, for what concerns hydrochemical analyses and interpretations.

From an operative stand-point the on-site investigations were performed with the support of the Environmental Service of the Municipality of Ferrara (in the persons of Ivano Graldi and Lorella Dall'Olio).

Short research outline

As already mentioned before, the main goal of the present research is to add new knowledge to the understanding of the complex dynamics driving the DNAPLs migration and transformation in an unconsolidated alluvial setting, where the most part of existing literature about DNAPLs is focused on hard rock fractured systems (featuring the subsoil of many settings in North America where the research on DNAPLs was born).

Specific attention has been devoted within this research to identify the main geological and hydrogeological features driving the complex physical and biochemical processes affecting DNAPLs, including partitioning and degradation. Multilevel monitoring systems were employed in order to obtain detailed vertical profiling of geological and chemical features down to a depth of 60 m b.g.s. As already mentioned above, this kind of approach is very rarely taken into account in the European context and in particular in Italy, where very few cases exist of investigation of sites contaminated by NAPLs by means of -usually rudimentary- multilevel techniques (e.g. Arato et al., 2014; Mastrocicco et al., 2012; Petitta et al., 2013). The infrequent use of the multilevel approach is mainly due to the lack of reliance in limited-in-space detailed investigations rather than traditional areal extensive and less detailed surveys. However, several studies, mainly conducted in North America, extensively demonstrated the need of this kind of limited-in-space high-resolution approach in order to properly define the distribution and dynamics of DNAPLs, and also to address possible consequential remediation actions.

Other innovative methods of analysis, employed in this thesis besides the standardized ones, include the application of high vertical resolution sequential stratigraphy analysis coupled with detailed vertical reconstruction of contaminant concentration (cm scale), obtained from sediment core subsamples. Furthermore, isotopic analyses provided a powerful support in order to interpret the data both at regional and local scale: water stable isotopes were analyzed in groundwater and pore-water of aquifers and aquitards (with an innovative analytical technique) whereas CSIA (Compound Specific Isotope Analysis) was used on organic contaminants to support the local occurrence of biodegradation reactions.

The present thesis is based upon three investigation steps connected in a logical succession; each of these steps can be considered as an independent brick of the whole research wall and has produced a separate paper submitted, or in preparation for submission, to an international ISI-WoS indexed journal.

The three investigation steps are outlined as follows:

1- reconstruction, at regional scale, of the groundwater flow system relative to the three main aquifers involved in the contamination, with a particular focus on the apportionment and quantification of recharge and on the evaluation of the intrinsic vulnerability of the aquifers. The approach is based on water stable isotopic analysis and mixing calculations, performed at two different sampling scales (regional and site specific). The results coming from this investigation represent an essential basis for the interpretation of the different style of migration of DNAPLs in respect to water, which will be analyzed in the two following steps;
2- analysis, at the scale of the Caretti site, of the distribution of the DNAPL multiphase contamination at high vertical resolution, in relation with the geological and physical properties of the unconsolidated porous medium. In this step, the role of aquitards toward the protection of the underlying aquifers is investigated in a DNAPL reading key;
3- development of a conceptual model able to explain the occurrence of peculiar accumulations of vinyl chloride in the subsoil (as product of biodegradation), in relationship to the geological and depositional facies architecture of an unconsolidated alluvial setting. This investigation step is based upon the comparison between the results collected at Caretti site and the ones of other contaminated sites located in the broader Ferrara area.

The results of this research have direct implications not only at the scale of Ferrara, where they can be employed to better address future remediation and protection actions, but also at global scale, for similar hydrogeologic settings. Indeed, the results put in evidence that the behavior of unconsolidated porous aquitards can be drastically different towards DNAPLs in respect to groundwater, thus bringing a series of new threats and new challenges in terms of characterization, data interpretation and risk assessment.

Structure of the thesis

Chapters 1, 2 and 3 contain the main background knowledge on which the research is based. In Chapters 4, 5 and 6 are presented the methods, data and results, organized according to the three forementioned steps of investigation.

In detail:

Chapter 1 contains an overview of the geologic and hydrogeologic setting of the investigated area, with a specific focus on the stratigraphic and hydrostratigraphic architecture, considered as a basic knowledge for the interpretation of the local groundwater flow systems in aquifers and aquitards.

In **Chapter 2** are described the main properties and behaviors of chlorinated solvent DNAPLs and of their main metabolites.

Chapter 3 is focused on the main investigative approaches employed throughout the research (i.e. multilevel monitoring systems and vertical profiling of data). These approaches represent the basement of the data collection carried out in all of the three steps of the investigation.

Chapter 4 illustrates the study carried out at regional scale in the broad area of Ferrara, concerning the evaluation of aquifer recharge and intrinsic vulnerability by means of environmental isotopes. Isotopic results obtained from groundwater sampled at the scale of Ferrara were compared with a high-resolution vertical isotopic distribution obtained at the Caretti site, both from groundwater and sediment samples.

Chapter 5 zooms-in from the broad Ferrara area to the Caretti test-site and deals with the high-resolution vertical analyses carried out along a cross section composed by three vertical profiles, and located on a fringe of the local source of contamination. The overlap between the vertical distribution of stratigraphy, hydraulic heads, hydrochemistry of groundwater and contamination along the cross section allowed to interpret the behavior of the local aquitards towards DNAPLs.

In **Chapter 6** is presented the overlap between the contaminant distribution and a detailed paleo-environmental analyses carried out at the Caretti site. This overlap is focused on the identification of the process responsible for the biodegradation of contaminants and of the most active degradation zones within the local hydrogeologic system. Indeed, the biodegradation of parent contaminants (mainly PCE and TCE) locally caused the accumulation of daughter products (i.e. Vinyl Chloride - VC), even more toxic than the former ones. The results collected at the Caretti site allowed to zoom-out again to the broad area of Ferrara in order to interpret peculiar enrichments in vinyl chloride observed in several other contaminated sites in the area.

CHAPTER 1
The Southern Po plain

1.1 Introduction

The Po river plain is one of the major alluvial plains in Europe and hosts a very dense population (about one third of the whole Italian population) along with important agricultural and industrial activities (Amorosi et al., 2008a). The groundwater hosted in the aquifers below the plain plays a key role in the sustainment of the local human activities and represents the main source of drinkable water of the Lombardy and Emilia-Romagna Regions (Molinari et al., 2007; Regione Emilia-Romagna and ENI-AGIP, 1998; Regione Lombardia and ENI Divisione AGIP, 2002).

The plain has been widely investigated during the last three decades in terms of basin formation and evolution (Dalla et al., 1992; Dondi and D'Andrea, 1986; Muttoni et al., 2003; Ori, 1993; Picotti and Pazzaglia, 2008; Pieri and Groppi, 1981). These early studies showed up the Po Plain as a rapidly subsiding foreland basin bounded by two fold-and-thrust belts, the Alps to the north and the Apennines to the south (Amorosi et al., 2014b) (Fig. 1.1). As a consequence, the Po Basin fill resulted in a syntectonic sedimentary wedge (Ricci Lucchi, 1984; Ricci Lucchi et al., 1982) forming the infill of the Plio-Quaternary Apenninic foredeep. It attains a total thickness in excess of 4000 m, while the Quaternary deposits are about 1000-1500 m thick (Pieri and Groppi, 1981). The Po river, with a mixed contribution from the Alpine and Apenninic chains, acted as the major sediment feeder for the study area during the Late Quaternary. A detailed study concerning the different provenances of the Quaternary Po plain sediments is presented by Amorosi et al. (2002).

Focusing specifically on the southern sector of the Po plain, where the study area of the presented thesis is located, the recent tectonic activity of the Northern Apenninic mountain front affected substantially the sedimentary evolution of the basin filling (Carminati et al., 2003). In particular, buried growing folds and north-verging thrust faults (Pieri and Groppi, 1981; Regione Emilia-Romagna and ENI-AGIP, 1998) (Fig 1.1 and 1.2), that collectively represent the near-surface structural response of the Adria-Europe convergence (Picotti et al., 2009), induced effects on the river network evolution and on the sequence architecture of the Po Basin fill (Dalla et al., 1992; Ori, 1993; Pieri and Groppi, 1981; Regione Emilia-Romagna and ENI-AGIP, 1998; Ricci Lucchi et al., 1982). Tectonic influence, however, seems to decrease progressively moving upward along the stratigraphic sequence, from the strongly deformed Pliocene strata to the relatively undisturbed late Quaternary deposits (Amorosi and Milli, 2001).

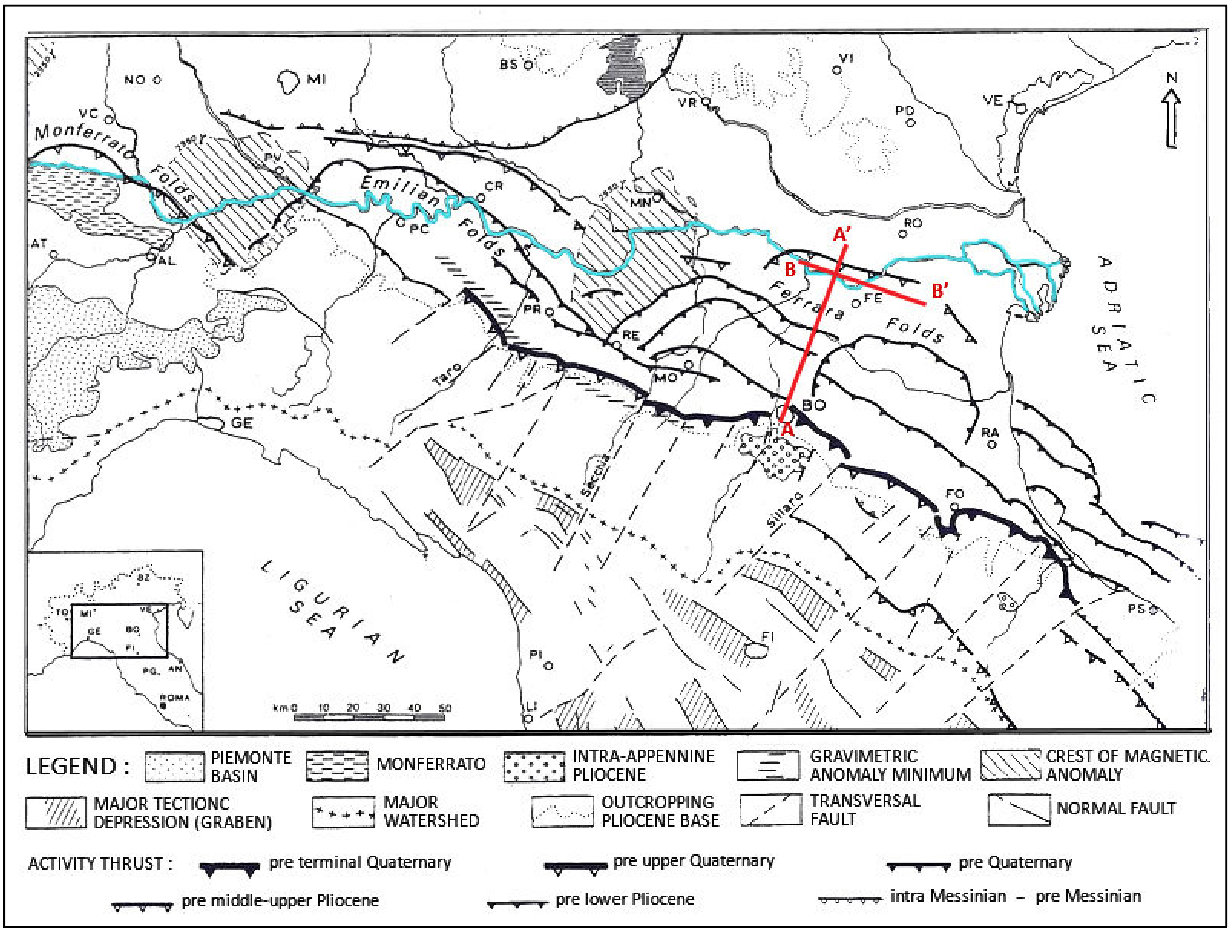


Figure 1.1: Simplified structural map of the Po Plain showing the main tectonic elements (from Castellarin et al., 1985; modified). The current course of the Po river is highlighted in light blue. The structural cross-section A-A' and the hydrostratigraphic cross-section B-B' are depicted in Fig. 1.2 and 1.5, respectively.

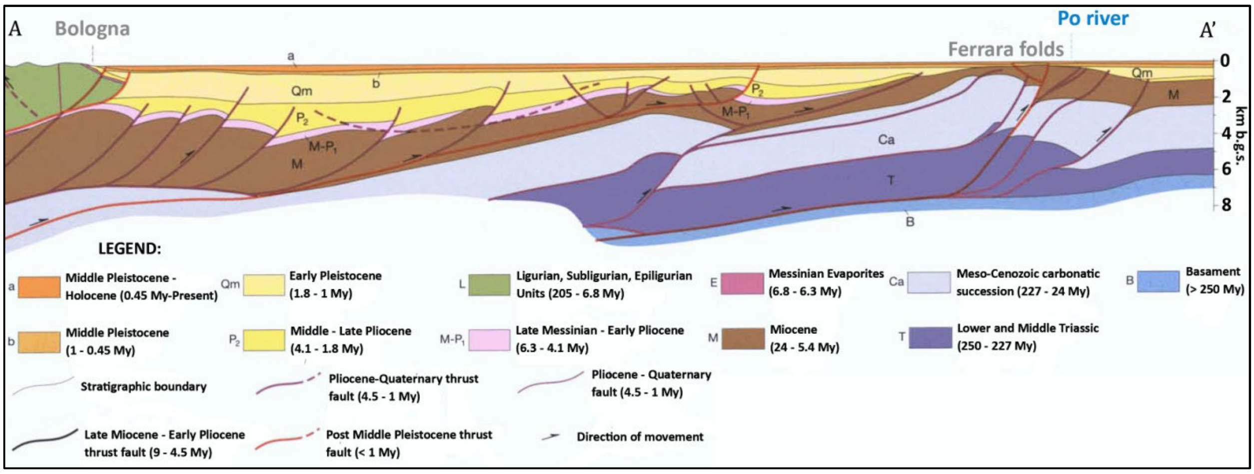


Figure 1.2: Structural cross section of the southeastern Po Plain (between Bologna and the Po river), showing the main buried thrust fronts of the Northern Apennines (from Regione Emilia-Romagna et al., 2004; modified). The location of the cross-section is indicated in Fig. 1.1.

A large body of information from the youngest deposits indicates that pronounced climatic fluctuations and, to a certain extent, eusthatic oscillations played a fundamental role in shaping the stratigraphic architecture of the basin, leading also to remarkable changes in sediment supply and in the type of sediment delivered to the basin (Amorosi et al., 1999a; Amorosi et al., 1999b; Amorosi and Pavesi, 2010). In particular, several studies carried out on the area (Pieri and Groppi, 1981; Regione Emilia-Romagna and ENI-AGIP, 1998) have led to the subdivision of the southern Po Basin fill into a series of unconformity-bounded stratigraphic units (Fig. 1.3). Prominent cyclic facies architecture is the dominant feature of the Quaternary succession, with transgressive-regressive (T-R) cycles representing the building block of subsurface stratigraphy (Amorosi and Colalongo, 2005). The cyclic stratigraphic architecture of the southern basin will be described in detail in Paragraph 1.2.

1.2 Stratigraphy and hydrostratigraphy of the southern Po plain

The following detailed stratigraphic and hydrostratigraphic descriptions respond to the need of fully understanding the hydrogeological architecture of the study area. Indeed, in such complex multilayered system, only the reconstruction of the depositional genesis and evolution of aquifers and aquitards allows to properly interpret the hydrogeological relationships and possible interactions between the different bodies, as well as their peculiar features.

1.2.1 Stratigraphy

Large-scale stratigraphic architecture of the Pliocene-Quaternary basin fill has been reconstructed through multiple-scale input data (from seismic mapping to well-log interpretation; Bersezio et al., 2004; Regione Emilia-Romagna and ENI-AGIP, 1998; Regione Lombardia and ENI Divisione AGIP, 2002). In particular, south of Po River, third-order depositional sequences (sensu Mitchum et al., 1977) were identified on a seismic basis and mapped as unconformity-bounded stratigraphic units (UBSU - Molinari et al., 2007; Regione Emilia-Romagna and ENI-AGIP, 1998). The youngest UBSU, which coincides in outcrop with the well-known Cycle Qc of Ricci Lucchi et al. (1982), is termed the "Emilia-Romagna Supersynthem", and it's further subdivided into two lower-rank units: "Lower Emilia-Romagna Synthem" and "Upper Emilia-Romagna Synthem" (Fig. 1.3). Two stratigraphic unconformities of tectonic origin, identified on a seismic basis and dated to about 450 and 870 kyr, respectively, represent the lower bounding surfaces of the two Emilia-Romagna Synthems (i.e. Upper and Lower Synthem). These unconformities can be tracked and mapped throughout the whole basin.

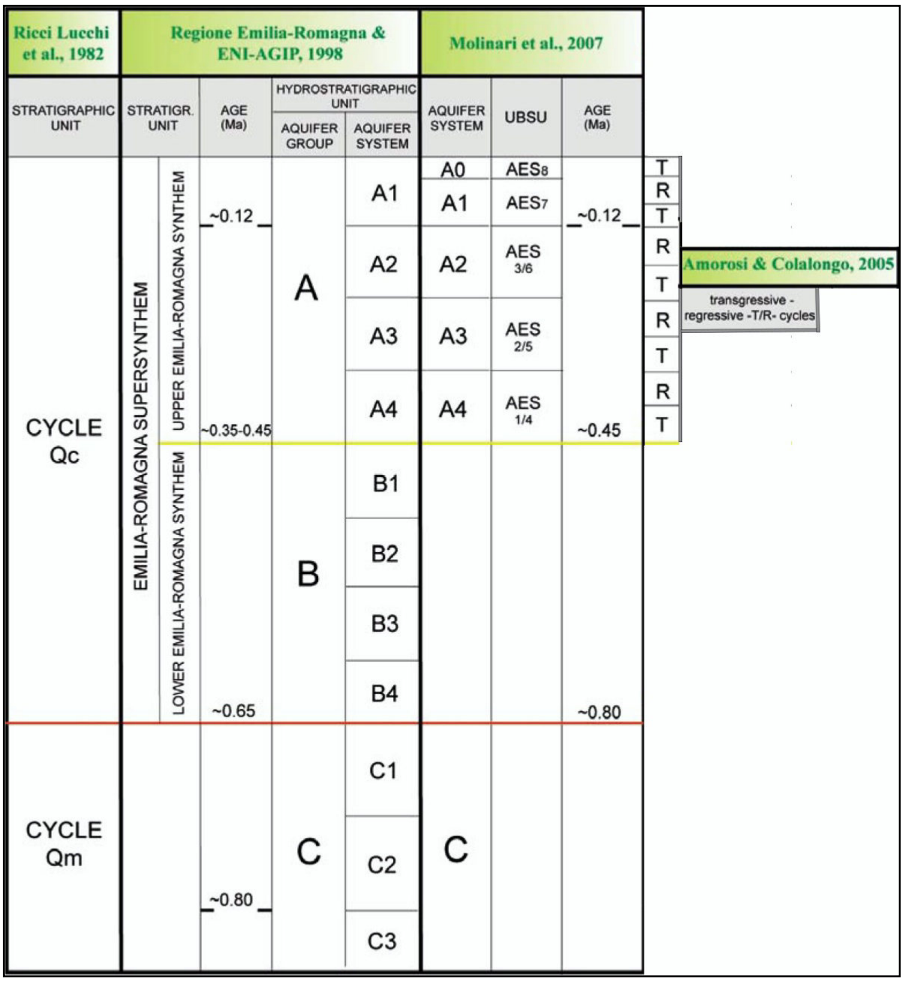


Figure 1.3: Generalized stratigraphic framework for the Quaternary deposits of the southern Po Basin (from Amorosi and Pavesi, 2010; modified)

The Emilia-Romagna Supersynthem displays a maximum thickness of about 650 m in the depocenter, and typically wedges out either toward the basin margins, i.e. the Apenninic and Alpine foothills, or in coincidence of structural highs (e.g. Ferrara buried folds, Pieri and Groppi, 1981; visible in Fig. 1.1 and 1.2). The post-450 kyr unit (Upper Emilia-Romagna Synthem) exhibits a maximum thickness of about 400 m, although over wide areas is less than 250 m thick (Amorosi and Pavesi, 2010). This last unit was further subdivided into a number of subsynthems, indicated as "AES1" to "AES8" by Molinari et al. (2007) and in the Emilia-Romagna geological maps (Amorosi and Pavesi, 2010). From a depositional point of view, these subsynthems correspond to five fourth-order cycles, 50 to 100 m thick, characterized by the alternation of coarse-grained (gravel-sand) and fine-grained (silt-clay) bodies, interpreted as fluvial-channel and floodplain deposits, respectively (Amorosi and Colalongo, 2005). This last stratigraphic architecture have been interpreted to reflect T-R cycles falling in the Milankovitch band (Amorosi et al., 2004; Amorosi et al., 1999a; Amorosi et al., 2001; Amorosi et al., 2008b).

Each cycle represents an interval of approximately 100 kyr and includes basal, silt-clay overbank deposits, with thin and lenticular fluvial-channel sands, showing upward transition to increasingly amalgamated and more laterally extensive fluvial-channel sand bodies (Fig. 1.4).

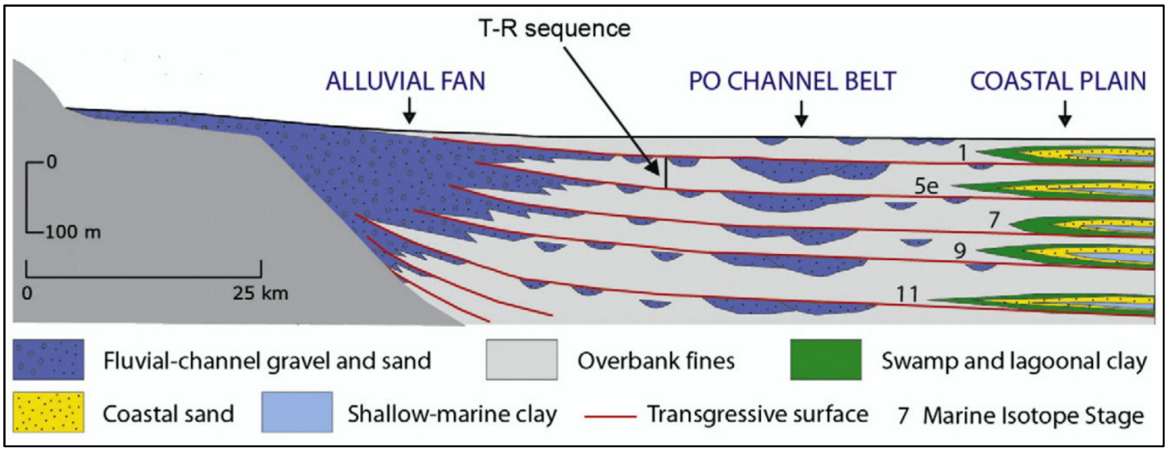


Figure 1.4: Schematic representation of the late Quaternary architecture of the Po River basin. The transgressive–regressive (T–R) cycles, forming the building blocks of the Quaternary succession, are highlighted. An increasing amalgamation between the permeable (gravel and sand) bodies can be observed moving towards the alluvial fans, while swamp and lagoonal deposits are present in the distal zones of the system (from Amorosi et al., 2014b; modified).

Despite this relatively simple picture of facies architecture, several heterogeneities were identified at local scale, with crevasse channels and splays, unconfined and non-channelized sandy units, and laterally continuous organic-rich horizons, which locally complicate the architecture of the single cycles (Amorosi and Pavesi, 2010). Where the shoreline was close to the alluvial fan systems (e.g. in the Ferrara area), channel abandonment due to sea-level rise was followed by widespread swamp development. Thus, very persistent paleo-swamp deposits can be locally tracked at the bottom of some T-R cycles (Fig. 1.4).

Following the hydrostratigraphic sections by Regione Emilia-Romagna and ENI-AGIP (1998) and the conceptual model of Amorosi and Colalongo (2005) and Amorosi et al. (2008b), the surfaces placed at the generally abrupt shift from laterally extensive, amalgamated fluvial-channel bodies to overlying, locally organic-rich, muddy units, were chosen for the stratigraphic subdivisions of the T-R cycles. Indeed, in the case of the Po plain, these abrupt shifts represent almost isochronous, easily mappable surfaces (Amorosi and Pavesi, 2010); on the contrary, the frequently erosive lower boundaries of amalgamated fluvial-channel bodies, which have been taken as bounding surfaces of cycles in many literature instances (Aitken and Flint, 1996; O'Byrne and Flint, 1996; Olsen et al., 1995; Posamentier and Allen, 1999), turned out to be locally characterized by a highly diachronous base.

1.2.2 Hydrostratigraphy

From a hydrostratigraphic viewpoint, there is a correspondence between the three main Aquifer Groups identified by Regione Emilia-Romagna and ENI-AGIP (1998) for the southern Po Plain (i.e. Aquifer Groups A, B, C) and the stratigraphic architecture of the basin described above (Fig. 1.3). In particular, the Upper Emilia-Romagna Synthem coincides with Aquifer Group A and the Lower Emilia-Romagna Synthem with Aquifer Group B. The Aquifer Group C corresponds with older underlying deposits, indicated in outcrop as Cycle Qm by Ricci Lucchi et al. (1982). Further, the five T-R cycles detected within the Upper Emilia-Romagna Synthem (or Aquifer Group A), were inferred to represent distinct regional hydrostratigraphic units (referred to as A0 to A4; Molinari et al., 2007; Regione Emilia-Romagna and ENI-AGIP, 1998). In the central Po Plain, beneath the present Po River course, these distinct hydrostratigraphic units (except for unit A0) are characterized by laterally extensive, stacked channel belts, with excellent continuity (i.e. aquifers), separated by laterally continuous mud-dominated and locally organic-enriched permeability barriers (i.e. aquitards). The aquifer bodies formed during phases of relatively low accommodation (lowstand periods and possibly early phases of transgression), while the permeability barriers were correlated with warm episodes, so marking the onset of transgressive phases. Differently, the A0 unit is generally characterized by scattered and weakly interconnected sandy lenses plunged in a silty-clayey matrix. This shallow architecture was interpreted as the expression of the uppermost incomplete T-R sequence (18 kyr-Present), which lacks almost entirely its upper, regressive portion (Amorosi and Pavesi, 2010).

The different aquifer bodies tend to be amalgamated close to the basin margins, where fluvial sands are replaced by gravels formed in proximal alluvial-fan systems (Fig. 1.4). The shallow aquifer systems A1 and A2 display an impressive lateral continuity and are affected by local tectonic deformation only in the Ferrara area (see Par. 1.2.2.1; Fig. 1.5) and close to the basin margins (Amorosi and Pavesi, 2010).

1.2.2.1 Hydrostratigraphy of the Ferrara area

The area of Ferrara is located in the northeastern sector of the Emilia-Romagna Region, on the right bank of the Po river. Some peculiar features were identified in this sector of the plain in respect to what observed at regional scale. The area is located landward of the maximum Holocenic marine ingression and the T-R cycles composing the Upper Emilia-Romagna Synthem are made up entirely of continental deposits. Above basal, overbank clays and silts including highly lenticular fluvial sand bodies (i.e. A0 aquifer system), each cycle exhibits increasingly amalgamated and laterally extensive channel-belt sand bodies (i.e. A1 to A4; Amorosi et al., 2008b). Tectonic deformation, however, affected significantly the local aquifer architecture. Indeed, due to the presence of the Ferrara buried folds, the lower boundary of Upper Emilia-Romagna Synthem climbs up locally from -320 m to -50 m a.s.l.. A very similar geometry is observable at the base of Emilia-Romagna Supersynthem, which moves from -580 m a.s.l. to -170 m in the Ferrara area (Amorosi and Pavesi, 2010). This causes a general decrease of vertical spacing between the different aquifers and a significant thinning of the single sandy bodies (Fig. 1.5).

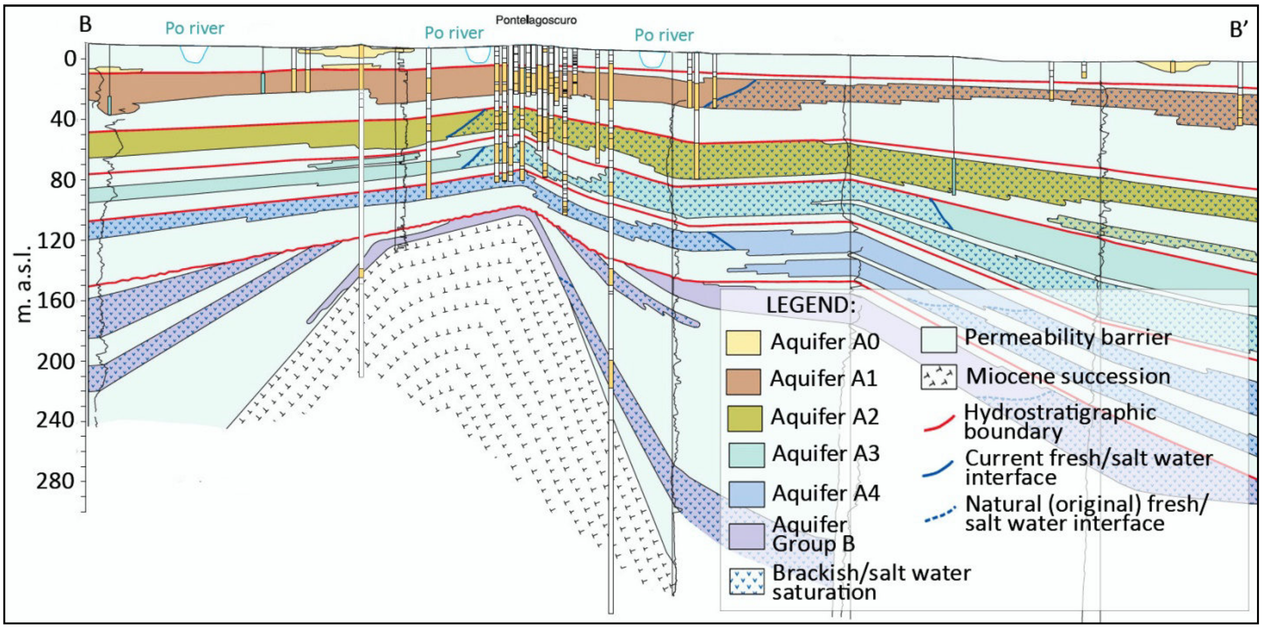


Figure 1.5: Hydrostratigraphic cross-section of the area of Ferrara (from Molinari et al., 2007; modified). The geometry of the aquifer units belonging to Aquifer Group A are shown, together with the main fresh/salt water interfaces. The location of the cross-section is shown in Fig. 1.1.

Another peculiarity identified in the Ferrara area is the massive occurrence of spatially persistent peat-enriched layers. As already stated in Paragraph 2.1.1, the overbank facies associations constituting the bottom of the T-R cycles generally consist of a monotonous succession of massive, locally pedogenized, floodplain silts and clays, with subordinate sand intercalations and faint horizontal lamination. In addition, clays with fine disseminated plant debris, freshwater gastropods, and scattered peat horizons were identified at the bottom of many of the cycles, and interpreted to have formed in freshwater swamps. Differently, a thick (up to 10 m) and persistent interval of transgressive swamp deposits (peats and organic-rich clays), located on top of aquifer A1 and characterized by a very significant spatial continuity, was detected in the area of Ferrara. A more detailed dissertation about these paleo-swamp deposits will be presented in Chapter 6 of this thesis, together with a site-specific description of the main depositional facies present below the territory of Ferrara.

1.3 Hydrogeology of the southern Po plain

From a hydrogeologic point of view, the Po plain can be considered as a multilayered aquifer system (Molinari et al., 2007), where each of the permeable, mainly sandy, hydrostratigraphic units, identified in Paragraph 1.2.2 as aquifers, represent a distinct groundwater reservoirs. Indeed, distinct groundwater flow systems became activated within the aquifers, flowing mainly along sub-horizontal flowpaths. Silty-clayey deposits act as hydraulic barriers.

Actually, the coincidence between hydrostratigraphic and hydrogeological units isn't always rigorous, particularly at local scale. Indeed, a hydrostratigraphic conceptual model is based on a depositional logic, while a hydrogeological one entails the identification of distinct groundwater flow systems. For example, where the sandy bodies originated in different depositional cycles coalesce (i.e. the interposed fine grained material go missing), they must be considered distinct overlapped hydrostratigraphic units but they represent a single groundwater flow system, so constituting a single hydrogeologic unit. On the other hand, when a single hydrostratigraphic sandy unit present local fine grained intercalations with a significant thickness (e.g. metric scale), the sandy layers above and below the fine grained material might be locally considered distinct hydrogeologic units. This potential disagreement needs to be kept in mind whenever up-scaling from the regional, cyclic and regular, architecture of the Po plain, to a local, likely more heterogeneous, site-scale setting.

The silty-clayey aquitards interposed to the Po aquifers are characterized by different degrees of permeability and integrity (Cherry et al., 2006), depending on their genesis and their geological history. Thus, vertical leakage between the different aquifers occurs at a mass flow rate depending on the hydraulic conductivity of aquitards and on the local vertical hydraulic gradients. As a consequence the single aquifers of the multilayered system are characterized by different degrees of vulnerability, depending on their position in the system and on the relationships with the surrounding hydrogeological bodies (i.e. intrinsic vulnerability), but also on the kind of contaminants threatening the system (i.e. specific vulnerability; Vrba and Zaporozec, 1994). As the results presented in Chapter 5 will show, a homogenous clayey-silty layer several meters thick isn't always able to fulfill the role of aquitard in the protection of underlying aquifers from relevant contaminant exchange.

Different sources contribute to the groundwater recharge of the hydrogeologic system of the southern Po plain (Fig. 1.6). In particular, the recharge occurs at 3 levels: 1) vertical recharge from rainfall at ground surface, 2) lateral recharge from Po river, with an active channel eroded about 15 m down into the shallow sedimentary sequence, and 3) deep regional groundwater flow from the distant borders of the Po plain, along the foothill of Alps in the north and Apennines in the south, where macroclastic permeable deposits outcrop as alluvial fans. Concerning direct recharge, the highest contributions occur on average between autumn and spring, while significant rainfall events are scarcer and occasional during the typically dry and hot summer season. Mean annual amounts of precipitation for the study area are around 623 mm/y (average of years 1991-2005). In general, the relative proportion of direct vertical recharge decreases and the contribution of the regional lateral recharge increases from the shallower down to the deeper aquifers (Molinari et al., 2007; Rapti-Caputo and Martinelli, 2009). The different sources of groundwater recharge may be characterized by distinct isotopic signals.

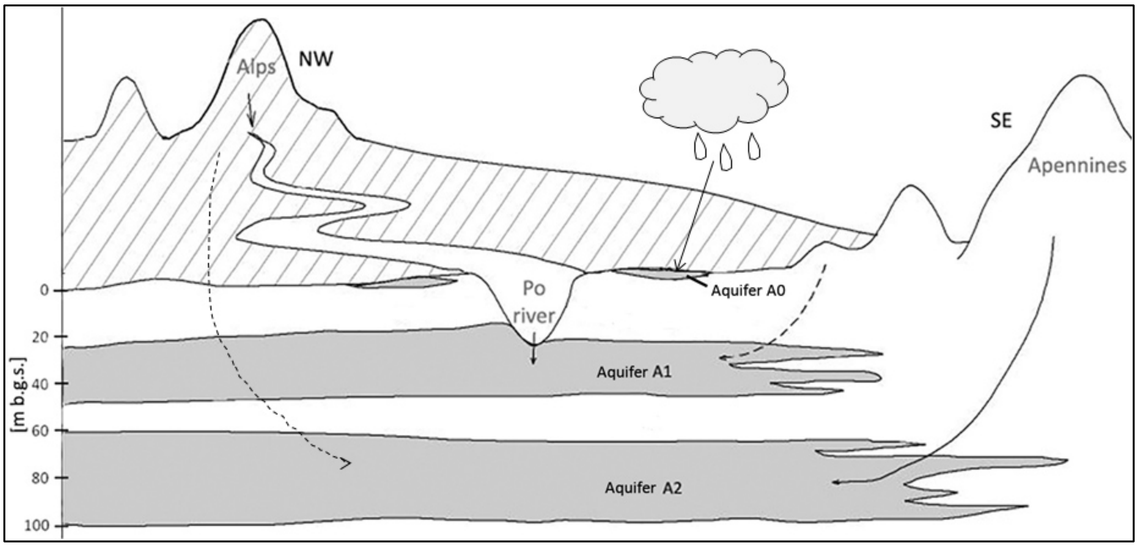


Figure 1.6: Main lateral and vertical groundwater recharge pathways of the shallower 100 m below the southern Po plain (dashed arrows represent supposed pathways while continuous arrows indicate known pathways).

The interest in defining both vulnerability and groundwater recharge is generally circumscribed to the shallower part of the system (coinciding in this case with the Aquifer Group A and the Upper Emilia-Romagna Synthem), since the shallower aquifers are the most exploitable as groundwater resource and they are also the most vulnerable to surface sources of contamination. A method based on environmental isotopes used as tracers to assess at the same time the intrinsic vulnerability of interposed aquifers and the relative importance of the different sources of recharge contributing to the multilayered system, will be presented in Chapter 4.

The hydrochemical and isotopic features of groundwater hosted in the shallower portion of the plain (mainly Aquifer Group A), as well as the hydraulic head distribution of aquifers, are constantly monitored by means of a regional monitoring network, managed by the Regional Environmental Protection Agency (ARPA Emilia-Romagna) and currently composed by 744 wells. The network is active since 1976 for the piezometric monitoring; since 1987 also the monitoring of chemical parameters of groundwater was activated (Regione Emilia-Romagna and ENI-AGIP, 1998). The most part of the wells are screened in the two shallower confined aquifers (i.e. A1 and A2), and only a few of them reach A3 and A4.

Taking into account that the chemical and piezometric features of aquifers are highly variable along the plain, the following Paragraph (1.3.1) will be focused only on the characteristics of the area of Ferrara, which is the area of major interest for the purposes of the thesis.

1.3.1 Hydrogeological features of the Ferrara area

Two detailed head contouring were obtained by Molinari et al. (2007) for aquifers A1 and A2 in the area around Ferrara, by means of the monitoring network described in Paragraph 1.3. In particular, a major drainage line directed NW-SE was detected in A1 aquifer, so denoting a main flow direction in agreement with the Po river course. This suggested a significant local contribution of the river to the recharge of the aquifer. Some diversions from the main flow direction were detected at local scale, mainly caused by significant groundwater extractions related with industrial activities (e.g. the petrochemical activities taking place close to the city since the ’50, and the city public water supply well-field along the right bank of Po river). Concerning A2 aquifer, two main drainage axis were detected in the investigated sector, directed respectively SE and NE. These two flow direction were interpreted as the expression of groundwater recharge occurring from the Alps and Apennines foothills, respectively. The piezometric surface of A2 aquifer turned out to be less influenced by industrial groundwater extraction with respect to A1. The hydraulic gradients observed in both aquifers range between 0.01 and 0.001 (Molinari et al., 2007) and the resulting averaged groundwater flow velocities are around 7E-5 cm/day (2.5E-4 m/year).

Observations of the piezometric distribution in the shallowest A0 aquifer can’t be carried out at kilometric scale due to the pronounced areal discontinuity of the sandy lenses.

Concerning the hydrogeochemistry of the shallow aquifers (i.e. A0, A1 and A2), all of them contain mostly Ca-HCO_3 rich groundwater. The average values of Electric Conductivity (EC, at 25°C) range between 0.4 and 1 mS/cm, for A1 and A2, respectively. The EC values detectable in A0 cover a very wide range of values (around 3 ± 2 mS/cm), depending on local soil composition and human pressures. Local enrichments in chloride and/or sulfate were locally detected in A0 groundwater and were mostly linked to the interference with surface human activities (Rapti-Caputo and Martinelli, 2009). Chloride and sodium enrichments were observed in scattered monitoring points in A1 aquifer, mainly in the eastern portion of the investigated territory: this was interpreted as a likely effect of sea water intrusion, which could have locally influenced the composition of A1 in its seaward portion. On the other hand, the sea water intrusion produced very clear effects on A2 aquifer, causing a systematic chloride-sodium enrichment in the eastward section of the area (see salt water intrusion in Fig. 1.5; Molinari et al., 2007).

The water stable isotope composition of the groundwater hosted in the different aquifers was investigated in some hydrogeological studies carried out in the area of Ferrara (Conti et al., 2000; Molinari et al., 2007; Rapti-Caputo and Martinelli, 2009). The results of these studies showed an isotopic composition of the shallow aquifers ranging from -10 and -7 ‰ for $\delta^{18}O$ and a $\delta^{18}O/\delta^{2}H$ ratio generally around 0.15. The different aquifers show distinct isotopic signatures, so reflecting the composition of different sources contributing to their groundwater recharge. A wide description of the isotopic composition of the shallower aquifers (A0 and A1) will be provided in Chapter 4, together with the results of a new isotopic investigation carried out in the framework of the present thesis.

1.3.2 Hydrogeological features of the Caretti site

The hydrogeologic features of the shallow subsoil below the Caretti test-site (Fig. 1.7) are summarized hereafter. Three sandy aquifers were found at the site, located at a depth between 4-5 and 53 m b.g.s and separated by silty-clayey aquitards with distinct compositional features (Fig. 1.8).

The three aquifers correspond with the units identified at regional scale as A0 and A1. While A0 presents the same features already observed at regional scale (see Par. 1.3), A1 aquifer is characterized by a very peculiar structure at the site, which led to its local subdivision into two distinct hydrogeological units. Indeed, the spatially continuous sandy body identified at regional scale as A1 shows locally a weakening in its upper section, where it turned out to be made up of discontinuous sand lenses, with decametric areal extension and metric thickness (up to 8 m). A continuous sand body with a constant thickness of around 18 m was identified at a deeper position, systematically separated from the upper lenses by a clayey, subordinately silty, layer. This fine grained layer acts locally as an hydrogeologic barrier (i.e. aquitard) between the upper lenses and the basal sandy layer (Gargini et al., 2011; Nijenhuis et al., 2013), bringing significant implications both in terms of local groundwater recharge patterns and contaminant migration. From now on, the two locally separated sections of the regional A1 aquifer will be referred to as “upper A1” and “lower A1” (Fig. 1.8).

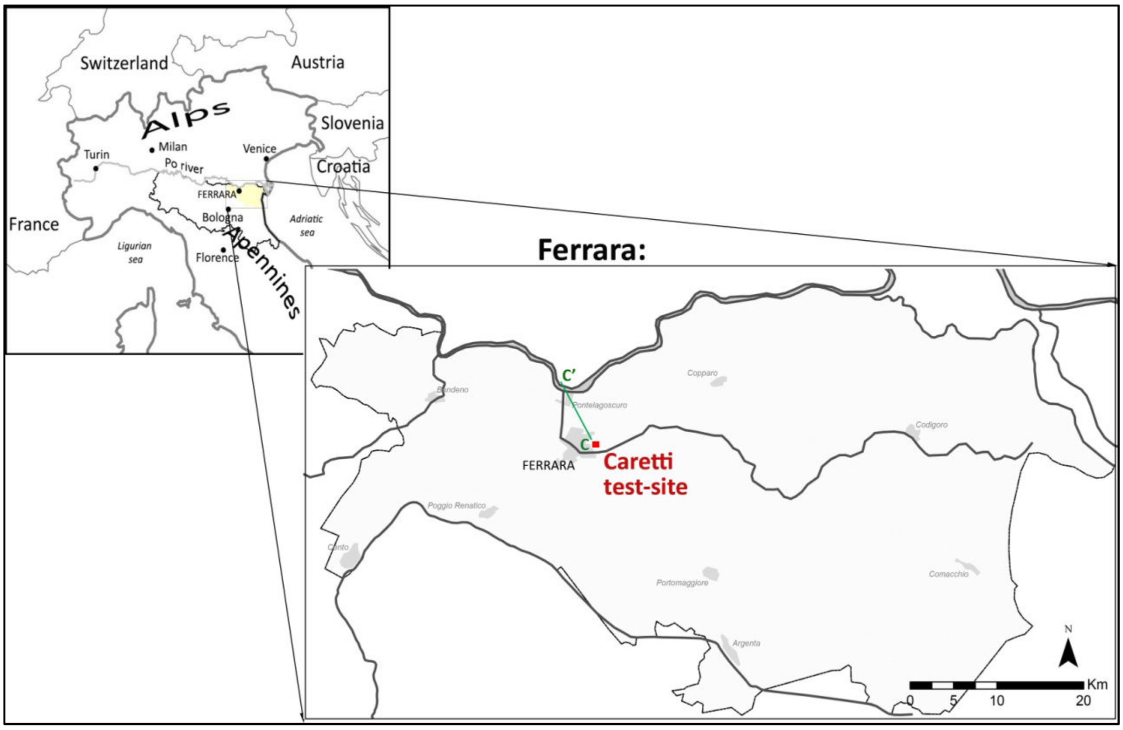


Figure 1.7: Location of the main study areas (regional scale, i.e. Ferrara area, and test-site scale, i.e. Caretti site). The hydrogeological C-C’ cross-section is depicted in Fig. 1.8.

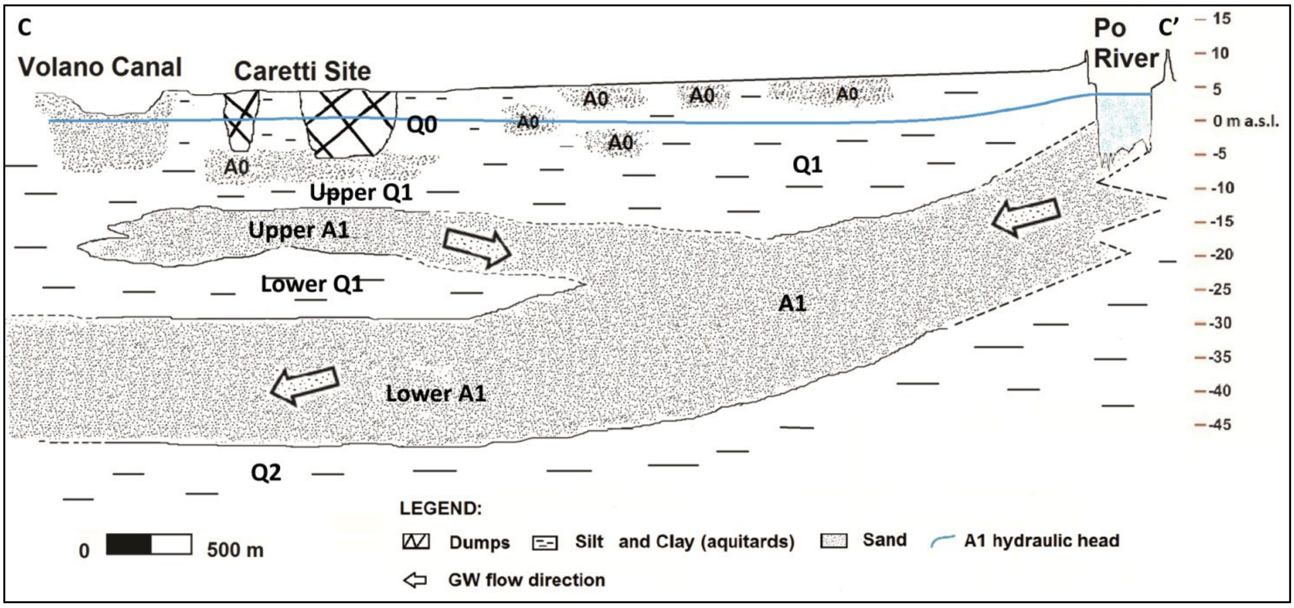


Figure 1.8: Schematic representation of the hydrogeological architecture of aquifers and aquitards below the study area. The regional aquifer A1 is separated in two distinct bodies (i.e. Upper A1 and Lower A1) below the Caretti site (from Nijenhuis et al., 2013; modified). The location of the cross-section is shown in Fig. 1.7.

A0 aquifer is from unconfined to leaky-confined at the site, upper A1 is leaky-confined and lower A1 is fully confined. Local flow directions have been determined at the site, by means of a network of wells and piezometers installed for the preliminary characterization of the contamination (Gargini et al., 2011; Nijenhuis et al., 2013). A main N-NW local flow direction was identified for A0 at the site scale, even though significant diversions from this main direction were found within the area, likely due to markedly lenticular nature of the aquifer. The upper and lower A1 aquifers are characterized by different drainage directions. In particular, the groundwater hosted in lower A1 has been inferred to flow along an E-SE direction, which correspond the main drainage axis observed for A1 at regional scale. Differently, a N-NW to W flow direction was defined for the upper A1, probably constrained by the spatial development of the discontinuous sand bodies (i.e. paleo-river channels) composing the aquifer. A scarce number of monitoring wells reach the depth of lower A1 at the site (three piezometers located a few tens of meters apart from each other and one private well). This scarcity of control points was driven by the need of avoiding cross-contamination from the upper part of the system, as this deeper aquifer was considered uncontaminated until the most recent investigations performed in 2013 (presented in Chapters 5 and 6).

The aquitards interlayered to A0, upper A1 and lower A1 aquifers were deeply investigated within the present thesis (see Chapters 4, 5 and 6), in order to define degree of protection provided to the underlying aquifers and their interactions with the contaminants. They were named after the underlying aquifers, as Q0, upper Q1, lower Q1 and Q2 (Fig. 1.8).

1.4 Conclusions

From a hydrostratigraphic point of view, the Po plain represents a complex multilayered aquifer system, with a regular cyclic architecture at regional scale and several heterogeneities at local scale. This local scale variability often brings significant hydrogeological implications as the flow of groundwater is influenced by the lateral and vertical continuity of the different sand bodies. Thus, it turns out to be important to define the peculiar architecture of each hydrostratigraphic unit at local scale whenever a reliable hydrogeological model is needed.

The aquifers of the Po plain represent an essential groundwater resource for civil, agricultural and industrial activities. On the other hand, the intense human activities taking place on the plain since the beginning of the 20th century strongly deteriorated this resource from both a qualitative and quantitative point of view (Molinari et al., 2007), and the aquifers are still vulnerable to further potential deterioration (mostly qualitative). In this sense, the site-specific hydrogeological models mentioned above represent an essential base in order to interpret properly the local groundwater recharge dynamics as well as the dynamics of contaminant migration.

The territory around the city of Ferrara was subject to a particularly impactful kind of contamination during the last sixty years. The petrochemical activities taking place since the ’50 in the mega-site plant (around 2.5 Km^2 of areal extension) located northwestward from the city, caused, among the rest, the spreading of contamination by chlorinated solvents in the aquifers below the area, inside and outside the industrial plant. These contaminants (widely described in Chap. 2) are currently interacting with the hydrogeological system below the Po plain, at several sites around the city of Ferrara (e.g. at the Caretti site). In this sense, a very detailed site-specific hydrostratigraphic and hydrogeological characterization represents and essential step in order to understand the complex interactions between the chlorinated hydrocarbons and the multilayered aquifer system.

CHAPTER 2
Chlorinated solvents and DNAPL phase in the subsoil

2.1 Introduction

Three general types of contaminant phases can be found in groundwater: (1) aqueous phase (i.e. solute dissolved in water); (2) Non Aqueous Phase Liquid (NAPL), partially immiscible in water; (3) particulate (i.e. colloid size particles - 1 to 1000 μm -, inert or biologically active). The chemical compounds in the NAPL type are also found in the aqueous category because all NAPLs are soluble in water to a certain extent. Considerable variability in contaminant mobility and reactivity exists within a given contaminant type because of major differences in physic and chemical properties. This Chapter will be mainly focused on the properties of NAPLs (and the resulting dissolved contaminants) in the hydrogeological system (i.e. in aquifers and aquitards). Because many NAPLs have density and viscosity much different from groundwater (Mackay et al., 2006), they flow in ways that aqueous contaminants cannot (Cherry et al., 2006). There are two categories of NAPL: Light or less dense than water (LNAPL) and Dense or denser than water (DNAPL). Gasoline, diesel and fuel oil are examples of LNAPLs, whereas chlorinated solvents, creosote and PCB liquids are examples of DNAPLs. Although LNAPLs and DNAPLs are in the same general contaminant category (NAPLs), they exhibit very different subsurface behaviors. In particular, DNAPLs, which represent the contaminants of major interest within this thesis, have the greatest propensity to migrate through fractures in aquitards or through any textural or structural heterogeneity of the fine grained porous media, thus causing impacts on underlying aquifers (Kueper and McWhorter, 1991). Prior to two decades ago, the assumption was commonly accepted that all clayey or silty aquitards would prevent contamination of underlying aquifers from surface sources. In recent years, however, DNAPL contamination was often found in confined aquifers, and its migration through aquitards was attributed to the occurrence preferential pathways such as fractures (even with very small apertures), root holes, small scale heterogeneities or unsealed boreholes (e.g. Hinsby et al., 1996; Jørgensen et al., 1998; Parker et al., 2004; Parker et al., 1994).

DNAPL phase is rarely found inside the liquid column of boreholes and wells. However, it plays an important role in groundwater contamination because it commonly migrates deep in the subsurface, where its slow dissolution results in contaminant plumes typically spread much further than the DNAPL zone. The migration of dissolved plumes is affected by advection, diffusion and mechanical dispersion. The dissolved compounds can also be subject to partitioning (i.e. sorption and volatilization) between the aqueous, solid and vapor phases. Furthermore the solute phase can be affected by natural degradation, either abiotic or biotic.

A group of manufactured commercial products, generally referred to as chlorinated solvents, represent the most ubiquitous compounds present in groundwater in the shape of DNAPLs. Among the most common chlorinated solvents are: tetrachloroethene (PCE), trichloroethene (TCE), trichoroethane (TCA), dichloroethane (DCA), and other reported in Table 2.1. They were first produced in Germany in the nineteenth century; production in the United States began around 1906. Widespread use of chlorinated solvents in manufacturing industries began during World War II, and increased markedly during the next three decades. Contamination of groundwater by these compounds went largely unrecognized until the late 1970s (Morrison et al., 2010; Pankow and Cherry, 1996).

Some of the industrial liquids commercially manufactured as DNAPLs, along with some of their metabolites in the aqueous or in the vapor phase, are highly toxic or carcinogenic (e.g. vinyl chloride - VC, originating from dechlorination of highly chlorinated ethenes like PCE and TCE), and even very low concentrations (ppb) in groundwater or in the indoor air can pose an unacceptable risk towards the human health and the environment (Kueper et al., 2003).

2.2 Properties of the DNAPL phase

In general, a DNAPL is defined as a denser-than-water organic liquid that is only slightly soluble in water. Also, most DNAPLs are less viscous than water, which enhances their propensity for flow in the subsurface (Pankow and Cherry, 1996). The main and most ubiquitous classes of DNAPLs found in the subsoil include chlorinated solvents, creosote, coal tar and PCB oils. Other ones, less frequently encountered, include mercury and certain crude oils.

Unlike petroleum products, the DNAPLs are generally: (1) not noticed by taste or odor at typical groundwater contamination levels; and (2) not stopped at the water table or above the capillary fringe when released in the subsurface in significant quantities. Once in the saturated zone, the DNAPLs tend to sink down to the bottom of permeable layers, thus resulting very difficult to detect. In contrast, when petroleum products are spilled in significant volumes as LNAPLs, they float on the water table where they can be detected more easily (e.g. McKee et al., 1972).

A DNAPL that is composed of only one chemical compound is referred to as a single component DNAPL. Dry cleaning fluid (typically PCE) is an example of this (although, strictly, it also contains low concentrations of stabilizers and preservatives). A DNAPL that is composed of two or more chemical compounds is referred to as a multi-component DNAPL. Whether a single component or a multi-component DNAPL exists at a site depends on past uses of the various compounds at the site and the methods of disposal (Kueper et al., 2003).

All DNAPLs can be characterized by their density, viscosity, interfacial tension, solubility in water, vapor pressure and wettability (McWhorter and Kueper, 1996). The properties of the multi-component DNAPLs depend on the interaction of the different components in the mixture. The effective properties of an individual component in the mixture (i.e. effective solubility or effective saturated vapor concentration) can be estimated using the Raoult's Law (2.1) (Pankow and Cherry, 1996):

$$P_i^e = X_i \times P_i \qquad (2.1)$$

Where P_i^e is the effective property of component i in equilibrium with the multi-component DNAPL, X_i is the mole fraction of i in the mixture, and P_i is the property of the pure component i (at a given pressure and temperature).

2.2.1 Properties of Chlorinated Solvents

Typical uses of chlorinated solvents include dry cleaning, metal degreasing, pharmaceutical production, pesticide formulation and chemical intermediates (Kueper et al., 2003). As already stated by Stroo et al. (2003) and McCarty (2010) chlorinated solvent DNAPLs are the most prevalent organic contaminants found in groundwater. Indeed, the other groups of DNAPLs, including the polychlorinated biphenyls (PCBs), some pesticides, coal tar, and creosote, have not been found in groundwater nearly as frequently as have the chlorinated solvents. There are several reasons for this. Firstly, compared to the chlorinated solvents, these other chemicals have not been used in as many industrial applications, or in quantities that are nearly as large. Secondly, they do not possess a combination of physical and chemical properties that impart a high propensity for widespread groundwater contamination. For example, some of these other DNAPL chemicals are much less soluble than the chlorinated solvents, and so they are much less mobile because they partition strongly to soil materials. As another example, important soluble components of creosote and coal tar are more degradable in the groundwater zone than most chlorinated solvents (Kueper et al., 2003).

Chlorinated solvents are organic compounds generally constructed of a simple hydrocarbon chain (typically one to three carbon atoms in length if aliphatic, or a benzene ring if aromatic) to which at least one chlorine atom is covalently bonded. The most common group of chlorinated solvents is represented by the chlorinated aliphatic hydrocarbons (CAH), which can be further divided into three categories based on the non-halogenated aliphatic hydrocarbon molecule on which they are structured: chlorinated methanes, chlorinated ethanes and chlorinated ethenes (Stroo and Ward, 2010).

The most relevant properties affecting fate and transport of chlorinated solvent compounds (and of their main metabolites) in the subsurface are summarized in Table 2.1. The majority of the properties reported in Table 2.2 were obtained from Mackay et al. (2006), one of the very few sources that contain data for all of the chlorinated methanes, ethanes and ethenes. In general, there is reasonable agreement between these values and several other summary tables available (e.g. Fetter and Fetter Jr, 1999; Pankow and Cherry, 1996; Schwarzenbach et al., 2005).

Table 2.1: Physical and chemical properties of chlorinated solvents and their transformation products at 25°C (from Stroo and Ward, 2010; modified). The last column on the right shows the admissible concentration of contaminants in groundwater ("CSC"), following the Italian legislation (Legislative Decree 152/2006) ("NR" stays for Not Regulated).

Species	Formula weight [g/mol]	Density - ρ [g/mL]	Solubility - S [mg/L]	Vapor pressure - p [torr]	Henry's law constant - K_h [x 10^{-3} atm*m^3/mol]	Log K_{oc}	CSC [mg/L] (DL 152/2006)
Chlorinated Methanes							
CT	153.8	1.59	793	153.8	28.90	209	NR
CF	119.4	1.48	7950	196.8	3.80	43	0.00015
DCM	84.9	1.33	13000	415.0	1.70	12	NR
CM	50.5	0.91	5320	4275.0	9.60	6	0.00150
Chlorinated Ethanes							
1122 TeCA	167.9	1.60	2830	5.9	0.44	94	0.00005
1112 TeCA	167.9	1.54	1070	11.9	2.40	142	NR
111 TCA	133.4	1.34	1290	123.8	14.50	112	NR
112 TCA	133.4	1.44	4590	24.2	0.96	92	0.00020
12 DCA	99.0	1.25	8600	79.0	1.20	18	0.00300
11 DCA	99.0	1.18	5040	227.0	6.20	31	0.81000
CA	64.5	0.89	5320	120.0	1.80	16	0.00150
Chlorinated Ethenes							
PCE	165.8	1.62	206	18.1	26.30	229	0.00110
TCE	131.4	1.46	1280	74.2	11.70	121	0.00150
cDCE	96.9	1.28	6410	203.0	7.40	36	0.06000
tDCE	96.9	1.26	4520	333.0	6.80	40	0.06000
11 DCE	96.9	1.21	2420	604.0	23.00	58	0.00005
VC	62.5	0.91	8800	2660.0	79.20	15	0.00050

2.3 Distribution of DNAPLs in the hydrogeological system

DNAPLs typically enter the subsurface as a result of past disposal directly onto land or in dumps, storage and disposal into unlined evaporation ponds and lagoons, leaking storage tanks, leaking piping and accidental spills during handling and transportation (Kueper et al., 2003).

As already mentioned in Paragraph 2.2, the peculiar physico-chemical properties of the DNAPL phase allow it to migrate to substantial depth below the water table, in both unconsolidated deposits and fractured units. A common situation at contaminated sites is the presence of a DNAPL accumulation zone (i.e. DNAPL pool) at the bottom of unconfined sand or gravel aquifers underlain by clayey aquitards (Feenstra et al., 1996). Further, some DNAPL mass can be "left behind" during the downward migration and come to rest trapped in the solid matrix as disconnected immobile blobs and ganglia of liquid, known as residual DNAPL (Fig 2.1).

The region of the subsurface containing residual and pooled DNAPL is referred to as the source zone (or the secondary source zone, where the primary source is the point of contaminant spilling at the surface). Groundwater flowing through the source zone slowly dissolves the DNAPL, giving rise to aqueous phase plumes of contaminants (Kueper et al., 2003). In particular, when a pool of DNAPL accumulates at the bottom of an aquifer, some of the dissolved mass is transported horizontally along the bottom of the aquifer in the shape of dissolved plume, while some other can diffuse vertically into the underlying aquitard. Aquitards subject to long-term groundwater contamination can in turn become new contaminant sources to aquifers due to reverse diffusion of compounds previously diffused into the top of aquitards (Chapman and Parker, 2005; Freeze and McWhorter, 1997; Geistlinger et al., 1998; Liu and Ball, 1999; Liu and Ball, 2002). When the DNAPL happens to be present as residual phase in the unsaturated zone or in the capillary fringe, the most volatile compounds can volatilize in the dry pores, giving rise to vapor phase contamination.

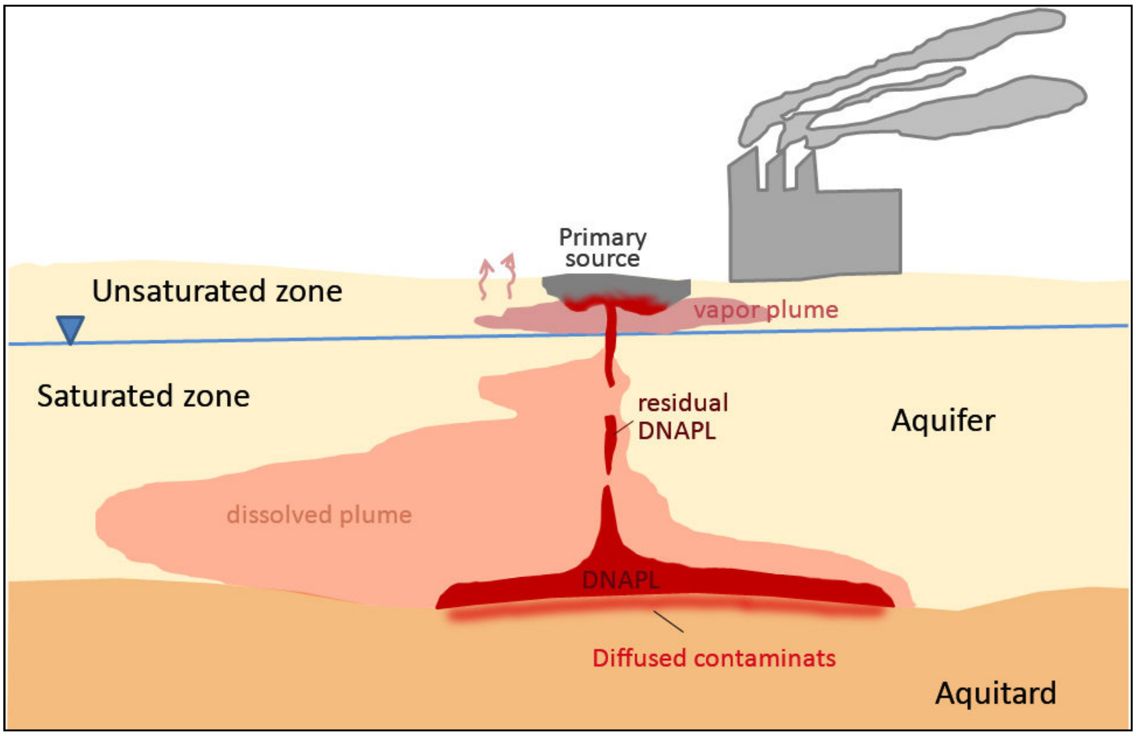


Figure 2.1: Schematic representation of the migration of DNAPLs in the subsoil. A DNAPL phase present in the primary source of contamination migrates downward to the bottom of the permeable layer (i.e. aquifer). A residual trail (i.e. residual phase) is left behind in the porosity of the matrix crossed. A dissolved plume takes origin in the saturated zone, migrating in agreement with the flow direction of the aquifer, and a vapor "plume" originates in the vadose zone, giving origin to potential vapor emission issues. Below the pool of DNAPL accumulated at the bottom of the aquifer (and also below the dissolved plume), contaminants can diffuse into the aquitard, giving origin to potential future back-diffusion issues.

Because the DNAPL phase is only slightly soluble in water, DNAPL source zones can persist for many decades and, in some cases, even hundreds of years. At many sites contaminated by chlorinated solvents the amounts that are present in dissolved form in the groundwater are relatively small, often no more than the equivalent of a few tens of liters of liquid solvent. Since spill volumes have in most cases been much larger than this, significant DNAPL mass still exists in the subsurface at most of these sites (Pankow and Cherry, 1996). Delineating the spatial extent of the DNAPL source zone at a site can be a substantial challenge, requiring at times several years of investigation and significant financial resources (Kueper et al., 2003). Indeed, at most DNAPL sites, the actual DNAPL has never been found (Feenstra and Cherry, 1996) and the field evidence used to designate a site as a DNAPL site is typically indirect (e.g. concentration of contaminats in groundwater close to their solubility limit or large variations in concentration at small spatial scale; U.S. EPA, 1992).

Going into the detail of the DNAPL source zone architecture, this could be actually more complex than the idealized pooled and residual distribution shown in Figure 2.1. For example, Parker et al. (2003) carried out a detailed characterization of five DNAPL source zones in industrial contaminated sites in North America, providing insights about the possible DNAPL distribution styles at the source area and the evolution of the DNAPL source over time. The main results of this study are summarized in Figures 2.2 and 2.3. Concerning the evolution of the source over time (Fig. 2.3), the results of the study suggested that present-day DNAPL in sandy aquifers resides in sporadic thin horizontal layers as a result of a few decades of groundwater flushing. Where DNAPL persisted, slower rates of dissolution were inferred, due to the position of the DNAPL in the less permeable layers or reduction of groundwater flushing due to the relatively higher NAPL saturation.

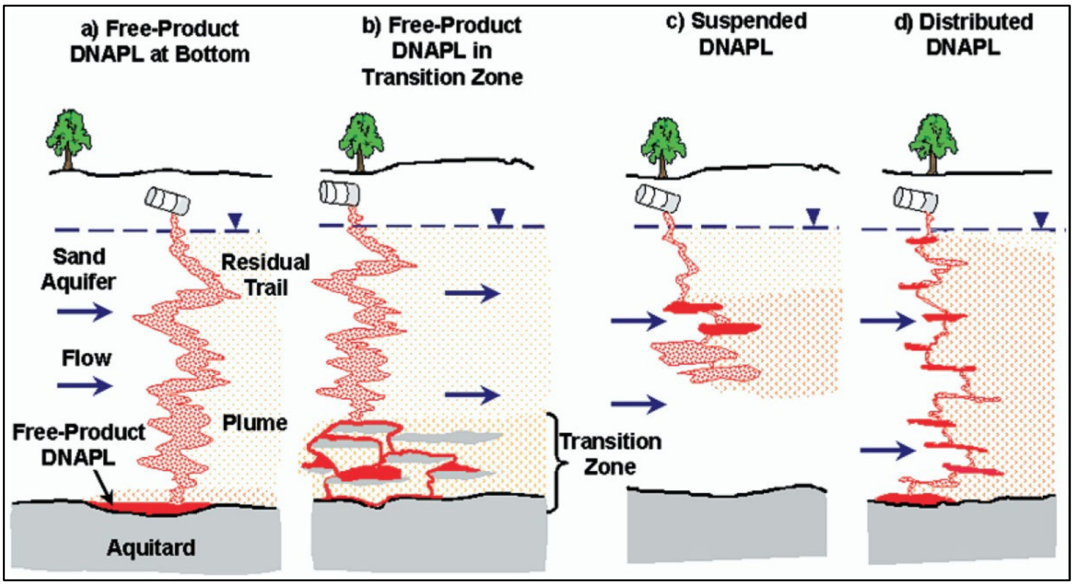


Figure 2.2: Schematic representation of four scenarios for DNAPL source zones in sandy aquifers: (a) DNAPL penetrates to the bottom of an homogeneous sand aquifer to form a bottom pool, (b) DNAPL penetrates through homogeneous sand and accumulates in a layered transition zone, (c, d) DNAPL forms multiple layers distributed throughout the aquifer thickness. Note that all scenarios have residual trails because the source zones are represented at early times (from Parker et al., 2003).

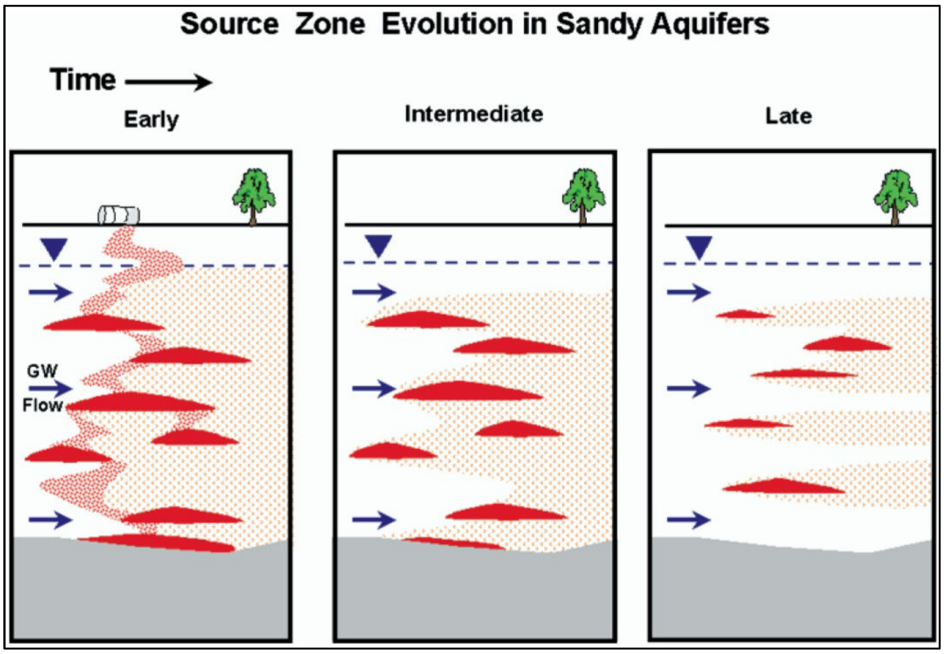


Figure 2.3: Illustration of the evolution of a layered DNAPL source zone showing complete dissolution of residual trails, shrinkage of some layers and complete removal of others due to decades of groundwater flushing (from Parker et al., 2003).

Other published information about the complex nature of DNAPL source zones in sandy deposits came from laboratory and field experiments (e.g. Anderson et al., 1992a; Anderson et al., 1992b; Brewster et al., 1995; Broholm et al., 1999; Illangasekare et al., 1995; Kueper et al., 1989; Kueper et al., 1993).

The literature cited above proved that the DNAPL architecture at an actual contaminated site (as well as its evolution over time) is strongly dependent on site-specific features (e.g. hydrogeological and stratigraphic features and the type of DNAPL present). Thus, a detailed site-specific characterization of the source architecture is needed whenever DNAPLs happen to be in the subsurface. The main methods developed to carry out a detailed characterization of a DNAPL source area will be discussed in Chapter 3.

2.3.1 DNAPL migration through aquitards

Aquitards are expected to protect the underlying aquifers against groundwater contamination (Domenico and Schwartz, 1998; Fetter, 2001; Ponzini et al., 1989). "Aquitard integrity" refers to the degree to which an aquitard is protective of groundwater quality in underlying aquifers, and depends on three factors: (1) state of the hydrologic system (hydraulic head distribution), (2) contaminant characteristics, and (3) geologic and hydrogeologic characteristics (grain size, lithology and thickness; hydraulic conductivity, porosity, etc.). Furthermore, if human disturbances such as quarries or improperly constructed wells are present, they can change aquitard integrity by creating new pathways or short circuits for contaminant migration.

The contaminant type is important because an aquitard can have excellent integrity for one type of contaminant and poor integrity for another. In particular, aquitards with a strong capability to protect underlying aquifers from dissolved contamination should not necessarily be expected to provide strong protection in situations where contaminants moved in the DNAPL state.

The large difference between the propensity of solutes and DNAPL to migrate through aquitards is caused by differences in the relative strength of matrix diffusion effects compared to fluid flux (i.e. advection) in the fractures (or micro-fractures). Indeed, molecular diffusion commonly has a much more important influence on solute transport in aquitards than in aquifers, where advection dominates (Gillham and Cherry, 1982). Differently, because of the higher liquid density, lower viscosity and small interfacial tension of common DNAPLs in respect to water, a substantial accumulation on top of an aquitard causes a strong propensity for the DNAPL to enter very small fractures, even those with apertures smaller than 10 μm (Kueper and McWhorter, 1991; McWhorter and Kueper, 1996). Thus, when contaminants with properties typical of chlorinated solvent DNAPLs enters and then flows into aquitards (though fractures or micro-fractures), matrix diffusion has little or no influence on the flow rate (Kueper and McWhorter, 1991). O'Hara et al. (2000) conducted a laboratory experiment involving 1 meter long cylindrical sample of glacio-lacustrine clay with vertical fractures, in which free-phase TCE DNAPL was pooled on top of the column. The DNAPL entered fractures with apertures in the 5 to 15 μm size range and flowed through the column in less than two weeks. Model simulations indicated dissolved TCE would take years or longer for groundwater transport through this column, in contrast to the rapid DNAPL flow. Although the clay column had fractures allowing rapid DNAPL flow, they were so small that the measured bulk vertical hydraulic conductivity (K_v) of the column did not provide evidence of fractures (i.e. K_v of the column very similar to the one of the matrix, with values of 6.8E-10 and 2.0E-10 m/s, respectively).

In situations where DNAPL rests on top of a low-permeability aquitard where no preferential pathways exist, dissolved contaminants from the DNAPL diffuse into the aquitard (Parker et al., 2003). The most reliable investigative approach for determining whether contaminant migration in a particular aquitard is diffusion-controlled is the analysis of solute profiles. Such analyses are possible if the aquitard already has contamination. Comparisons between the vertical contaminant distribution in the aquitard and simulations of contaminant migration from analytical or numerical models can help determine the importance of diffusion. Goodall and Quigley (1977) were the first to obtain contaminant concentration profiles from a clayey aquitard and to consider diffusion-based transport in the data interpretation. Crooks and Quigley (1984), Liu and Ball (2002), Johnson et al. (1989) and Parker et al. (2004) also provide examples of this approach for clayey aquitards.

2.3.2 Multiphase partitioning

One of the major processes that impacts the fate and transport of DNAPLs in a hydrogeological system is represented by their progressive dissolution in groundwater, followed by the partitioning between the three phases present in the subsurface: solid matrix, water and air (Fig. 2.4; Stroo and Ward, 2010).

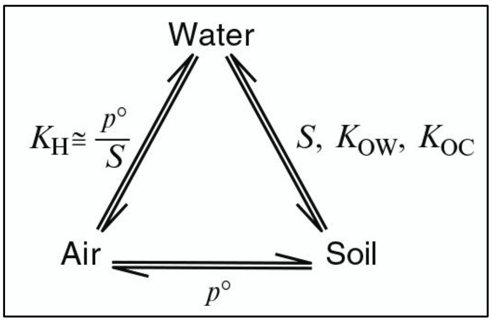


Figure 2.4: The three phases present in the subsurface and the properties of chlorinated solvents that govern the partitioning between these phases (from Stroo and Ward, 2010).

The following discussion will focus mainly on the partitioning processes affecting chlorinated solvents (and their main chlorinated metabolites), which were already identified as the most widespread group of DNAPLs in groundwater (see Par. 2.2.1). At 25°C most chlorinated solvents are colorless liquids with densities (δ) greater than water (i.e. DNAPL). The process through which the organic phase is gradually released into groundwater is referred to as dissolution. For a chlorinated solvent, the extent of dissolution is controlled by the solvent's aqueous solubility (S), defined as the maximum amount of the compound that will partition into water at a given temperature and pressure (Lyman, 1990), and also referred to as saturation concentration (Schwarzenbach et al., 2005). The aqueous solubility of chlorinated solvents decreases as the number of chlorine atoms on a compound increases (Tab. 2.1). This inverse relationship illustrates the influence that molecular size (specifically molar volume; Horvath et al., 1999) exerts on the miscibility of a chlorinated solvent in water. Environmental variables also can influence chlorinated solvent solubility. One such variable is temperature, although changes in the solubility of most chlorinated solvents are relatively minor over environmentally relevant temperature ranges (Horvath, 1982). Another important variable is salinity; an increased concentration of dissolved salts (ionic strength of the solution) results in a moderate decrease in chlorinated solvent solubility (Lyman, 1990). The presence of other organic chemicals (referred to as co-solutes) also can increase the saturation concentration of chlorinated solvents in water.

Concerning partitioning between matrix solids and water, chlorinated solvents can be considered moderately hydrophobic; although they partition (or sorb) onto the solid matrix (i.e. solid surfaces of porous or fractured media), their affinity for such processes is not as great as that for other organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) or polychlorinated biphenyls (PCBs). K_{oc}

represent a measure of a chemical's equilibrium partitioning between water and the organic carbon fraction of aquifer solids (f_{oc}). High K_{oc} values are characteristic of strongly sorbed compounds (e.g. Log K_{oc} ranges between 3 and 6 for the most common PAHs). Such compounds are significantly retarded with respect to groundwater flow. Evidently, another key factor controlling the extent of chlorinated solvent sorption is the organic carbon content of the subsurface material (already referred to as f_{oc}). Organic carbon can be present in the subsoil as particles of organic matter or as organic coating over the surfaces of grains. The general physico-chemical process of sorption includes adsorption to organic matter (the main process affecting chlorinated solvents) but involves also a broader list of processes like: cation exchange, absorption and co-precipitation. Sorption does not result in loss of total chemical mass from the hydrogeologic system but does cause the contaminant front to migrate more slowly than non-reactive contaminants and reduces aqueous phase concentrations in parts of the plume (Cherry et al., 2006).

As chlorinated solvents are relatively volatile compounds, air-water partitioning is expected to take place when contaminated groundwater comes into contact with air (e.g. in the vadose zone). In such instances, the equilibrium partitioning between air and water is typically described by Henry's Law, which is applicable to diluted solutions of a chlorinated solvent in water. The Henry's Law constant, K_H, relates the equilibrium concentration of the chlorinated solvent in air to its equilibrium concentration in water. By definition, large K_H values indicate a chemical's preference to partition from water into air, although additional chemical properties and several environmental factors will also influence the volatility of a species (Thomas, 1990b). In Table 2.1, K_H values are reported with units of atm·m^3/mol, but K_H values are also commonly reported with alternative units (e.g. as a dimensionless value when concentration in air and water is expressed in mol/L). Unlike reported values of S and K_{oc}, the K_H values presented in Table 2.1 do not reveal any significant trends within or across the different classes of chlorinated solvents. Partition to the air phase can occur also directly from the DNAPL phase, but groundwater-air partition can be considered the most common pathway for the accumulation of contaminants in the gas phase.

The last chlorinated solvent partitioning process to consider is that between the phase adsorbed on matrix solids and air. As with volatilization between air and water, several chemical and environmental factors are at play in this partitioning process (Thomas, 1990a). Anyway, our mechanistic understanding of this process is rather limited. One noteworthy variable is the vapor pressure (P or p^0), which represents the maximum attainable concentration of a chlorinated solvent in air (Schwarzenbach et al., 2005). Compounds with high values of P tend to partition more readily between air and sediments (and similarly, between air and water), and empirical relationships have been developed to estimate the rates at which such partitioning processes occur (Thomas, 1990a). The values of P tend to decrease with increasing chlorination, although exceptions to this generalization are frequently observed.

2.3.3 Degradation processes

Together with the multiphase partitioning, another important group of processes that can influence the fate of chlorinated solvents (mostly in dissolved and vapor phase) is represented by the degradation reactions. Chlorinated solvents can be transformed by both abiotic and biotic processes at normal groundwater temperatures, leading to the production of many intermediate compounds that can be also of health concern (Vogel et al., 1987). Degradation processes diminish the total contaminant mass, which causes both attenuation of concentrations and mass along the migration path and retardation of the rate of contaminant front advancement. In some cases, a contaminant is degraded, but the degradation products are also contaminants (Cherry et al., 2006). An example of that is the reductive dechlorination of chlorinated ethenes, that can give origin to accumulations of cis 1,2 dichloroethylene (cDCE) and VC, both of which are more hazardous to human health than the parents PCE and TCE. Hence, degradation is not always a beneficial process.

A detailed dissertation on all the degradation processes to which chlorinated solvents can undergo is presented by Stroo and Ward (2010). Degradation processes affecting chlorinated compounds occur mostly in anaerobic environments. In particular, for chlorinated ethenes, the most important biodegradation process is represented by reductive dechlorination. It was apparent by the early 1980s that reductive dechlorination of chlorinated ethenes is a common occurrence in groundwater systems where dissolved oxygen concentrations are below field-based detection limits for oxic conditions (oxigen 0.1–0.5 mg/L; Stroo and Ward, 2010). The rate and extent of reduction is dependent on the number of chlorine substituents attached to the ethene backbone and on the in situ redox conditions (Bouwer, 1994; Chapelle, 1996; McCarty and Semprini, 1994; Vogel, 1994; Vogel et al., 1987; Wiedemeier et al., 1998). PCE, with its four chlorine atoms and an oxidation state of carbon equal to +2, is a stronger oxidant than the naturally occurring electron accepting species found in groundwater systems, with the exception of oxygen (O_2) (Vogel et al., 1987). Thus, PCE commonly undergoes reductive dechlorination to TCE (oxidation state of carbon +1) in the absence of detectable dissolved oxygen. Reductive dechlorination of TCE to cDCE (oxidation state of carbon 0) can occur under Fe (+3) reducing conditions and even in more strongly reducing environments (Chapelle, 1996). Dechlorination of cDCE to yield VC (oxidation state of carbon -1) appears to be favored under SO_4 reducing and methanogenic conditions (Chapelle, 1996; Vogel et al., 1987). Reductive dechlorination of VC to the non-chlorinated product, ethene (oxidation state of carbon -2), appears to be slow in situ and only associated with highly reducing, methanogenic conditions (Ballapragada et al., 1995; Barrio-Lage et al., 1987; Bouwer, 1994; Carter and Jewell, 1993; De Bruin et al., 1992; Di Stefano et al., 1991; Fennell et al., 1995; Freedman and Gossett, 1989; Maymó-Gatell et al., 1995; Odum et al., 1995; Vogel and McCarty, 1985; Wu et al., 1995).

Thus, in natural conditions in the field, reductive dechlorination of chlorinated ethene contaminants often appears incomplete and leads to the accumulation of cDCE and VC (Haston et al., 1994; Kitanidis et al., 1993; Major et al., 1991; McCarty and Reinhard, 1993; Weaver et al., 1996; Wilson et al., 1995). Subsequent investigations have isolated a number of chlororespiring microbial pure cultures capable of reducing various chlorinated ethene compounds (Cupples et al., 2003; Gerritse et al., 1999; Gerritse et al., 1996; He et al., 2003; Holliger et al., 1993; Krumholz, 1997; Krumholz et al., 1996; Löffler et al., 2000; Löffler et al., 1999; Maymó-Gatell et al., 1999; Maymó-Gatell et al., 1997; Scholz-Muramatsu et al., 1995; Sharma and McCarty, 1996). Notable among these, bacteria belonging to the group *Dehalococcoidia* are able to catalyze the complete reductive dechlorination of PCE to ethene (Hendrickson et al., 2002; Leys et al., 2013; Löffler et al., 2013). The typical fractionation pathway produced by reductive dechlorination on the carbon stable isotopes of chloroethenes was already recognized and described e.g. by Bloom et al. (2000), Hunkeler et al. (2005) and Slater et al. (2001). Thus, the possible occurrence of this kind of biodegradation process in a contaminated site can be easily assessed by means of isotopic analyses on the contaminants (i.e. Compound Specific Isotope Analysis - CSIA; Hayes et al., 1990).

In contrast with the scarce attitude of VC to undergo reductive dechlorination, it is well documented in literature that the compound is readily biodegradable under aerobic conditions (Barbee, 1994; Bradley and Chapelle, 1999; Coleman et al., 2002a; Coleman et al., 2002b; Davis and Carpenter, 1990; Elango et al., 2006; Hartmans, 1995; Hartmans and De Bont, 1992; Hartmans et al., 1985; Verce et al., 2000). Indeed, the tendency of chlorinated ethene compounds to undergo oxidation increases with decreasing number of chlorine substituents (Vogel et al., 1987).

2.4 Chlorinated solvents in Ferrara and at the Caretti site

The aquifers below the city of Ferrara (Emilia-Romagna region, northern Italy) show scattered contamination by chlorinated solvents. The contamination occurs below industrial areas but also beneath residential or agricultural areas with concentrations as high as expected at industrial sites (up to the order of magnitude of 100 mg/L; Gargini et al., 2011). Chlorinated aliphatic hydrocarbons prevail among the contaminants, and in particular VC dominates the composition of the dissolved plumes. This poses a serious threat to the population and the environment, due to the high mobility of the compound both in the aqueous and gaseous phases. Indeed, VC is classified as a known human carcinogen by the International Agency for Research on Cancer and is considered one of the most toxic groundwater contaminants (IARC, 2007).

The origins of these contaminations have to be searched in the history of the industrial development of Ferrara. One of the main Italian petrochemical plants is located northwestward from the city. Inside the huge industrial compound, with an area of about 2.5 km^2, a variety of firms are located and manufacturing of chemicals dates back to the middle of twentieth century; among various compounds, PVC (polyvinylchloride), starting from VC monomer (since 1953 to 1998), chloromethanes (since 1951 to 1984) and 1,2 dichloroethane (1,2-DCA) were produced (Nijenhuis et al., 2013). Notwithstanding toxic and carcinogenic hazards for the on-site workers directly exposed to VC, the PVC manufacturing process did not produce dangerous wastes. Instead, the distillation of halomethanes produced wastes known as "chlorinated pitches" or "heavy ends", composed by a mixture of chlorinated compounds including PCE, TCE and 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA). These wastes, nowadays commonly processed or disposed into special landfills, in the case of Ferrara were improperly dumped in available unlined excavations, pits or dismissed quarries.

According to the available data, groundwater below at least three urban sites around the historical center of Ferrara became contaminated by the residues of heavy ends. One of these is the Caretti test-site (Fig. 2.5). The site is currently affected by a severe contamination of the full chlorinated ethenes and ethanes series, with VC as the dominant compound in the off-source plumes. The contaminant source is represented by old dump sites located inside clay-pits excavated for brick manufacturing activities. When, at the end of the 1950's, the extraction of clay for bricks production stopped, the disused clay-pits were used for urban wastes disposal by the municipality of Ferrara. Industrial wastes were illegally dumped along with municipal and inert wastes during this period. Waste disposal lasted for a decade, till the beginning of the 1970's. At the beginning of the 1990's started the urbanization of the site, with the creation of new residential areas. A decade later the local environmental protection authority (ARPA) detected a severe contamination by chlorinated solvents in shallow groundwater. As a consequence, since 2004 the municipality of Ferrara took over the responsibility of the characterization of the whole area, including both waste dumps and the immediate surroundings. The two dumps will be referred to as Southern Dump and Northern Dump from now on (Fig. 2.5).

The direct relationship between the disposal of chlorinated pitches in the Northern and Southern dumps and the contaminant plumes has been confirmed by means of isotopic fingerprinting (Nijenhuis et al., 2013; Pasini et al., 2008).

The Caretti site was mainly characterized through a direct-push drilling campaign (Gargini et al., 2011; Pasini et al., 2008), concerning both the composition of the sources and the extension and composition of the dissolved plumes. The high concentrations of PCE (up to 62 mg/L) and TCE (up to 70 mg/L) detected in the source leachate provided evidence for a DNAPL phase probably occurring at the bottom of the dumps. Conditions at the source areas are anoxic (Eh -46 to -156 mV) and pH is neutral to slightly acidic (5.7 to 7.4). The presence of methane in all groundwater samples, also outside of the dumps, confirmed the general anoxic conditions of the site and suggested high methanogenic activity (up to about 50 mg/L CH_4). Two plumes, migrating in the A0 and upper A1 aquifers (as defined in Chap. 1), were identified (Fig. 2.5). Both of them are mainly composed by chlorinated ethenes and are developed for a few hundred meters from the sources, in a northward (A0) or northwestward (upper A1) direction. In particular, the upper A1 plume is characterized mainly by VC and cDCE downgradient to the source, showing concentrations up 1730 and 259 µg/L, respectively, at around 800 m NW from the Southern dump. This suggested transformation of PCE and TCE occurring during the plume migration; indeed VC and cDCE are typical degradation compounds (i.e. products of reductive dechlorination of PCE and TCE) in groundwater and not at all supposed as possible parent compounds disposed of at the source.

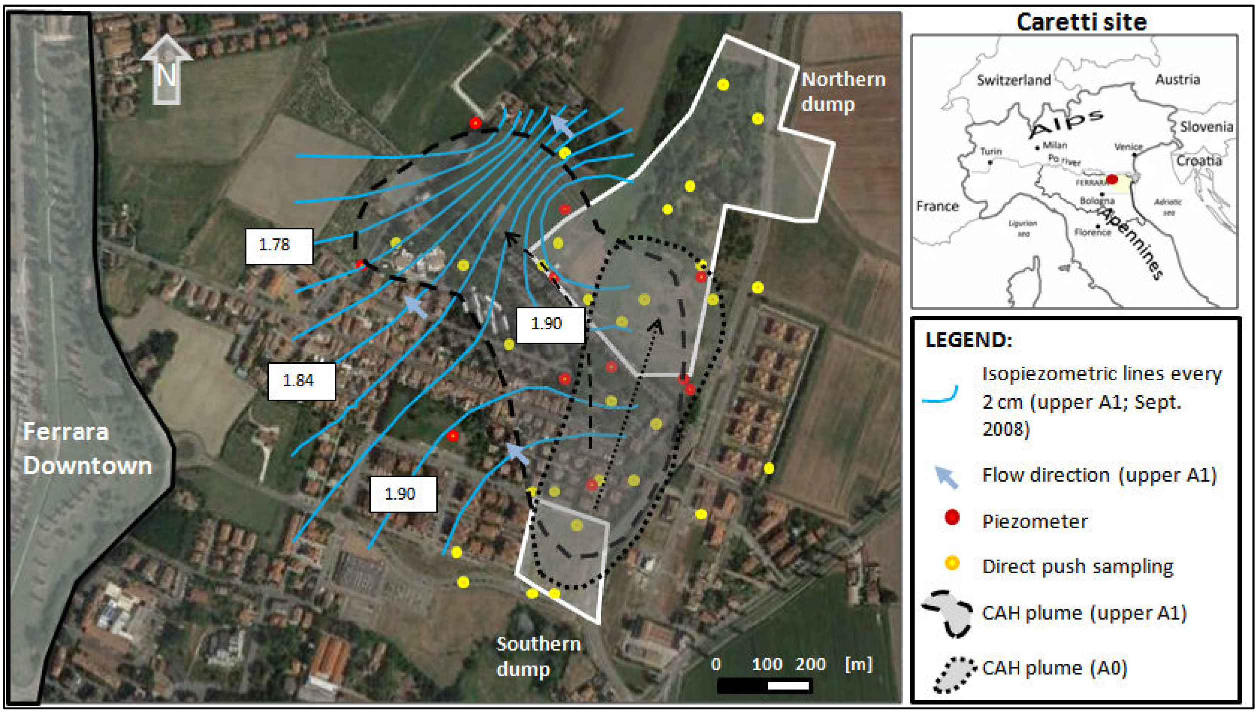


Figure 2.5: Schematic representation of the contamination in the two shallower aquifers at the Caretti site (i.e. A0 and upper A1). "CAH" stays from Chlorinated Aliphatic Hydrocarbons (mainly represented by chloroethenes in the case of the plumes in Caretti site). Only the piezometric surface relative to upper A1 is reported, because the flow direction of A0 is strongly variable at the site-scale and thus difficult to depict (mainly due to the marked discontinuity of the single sandy lenses). The inferred main direction of migration of the CAH plume in A0 aquifer (originated from the southern dump) is indicated with the dotted arrow. (from Gargini et al., 2010; modified).

The investigations carried out at the site during 2013 and 2014 (widely presented in Chapters 5 and 6) allowed to determine that the contamination (at least below the Southern Dump) is extended down to the bottom of lower A1 aquifer. Although the contamination found in the aquifer below the source (up to around 2-3 mg/L of PCE and TCE) strongly suggests the occurrence of a dissolved plume in migration in lower A1, the plume has not been detected yet (no boreholes are currently available in the hydrogeologically meaningful surroundings of the site). The detection and characterization of this plume is included among the objects of future investigations.

Considering that groundwater at the Caretti site is not exploited for drinkable purposes and due to the close proximity of buildings to the shallow contamination (i.e. plume in A0 aquifer), vapor intrusion of VC is the most relevant risk pathway at the site. However, the results of soil gas and indoor air monitoring performed at the site between 2004 and 2007, suggested no significant occurrence of VC in neither of the two environments (Gargini et al., 2011). Further measurements of gas emissions at the ground surface were carried out by means of flux chamber (Saponaro et al., 2011) and the results collected enhanced the hypothesis of an incomplete vapor intrusion pathway at the site. This could be due to the physical separation provided by the clayey cover interposed between the ground surface and the top of the A0 aquifer (i.e. the strongly heterogeneous and discontinuous Q0 aquitard). Alternatively, degradation processes occurring in the unsaturated part of the soil profile could be responsible for preventing vapor emission (this will be further discussed in Chap. 6). In this specific case, the use of Tier II models to assess the risk of VC vapor intrusion (Gargini et al., 2011) was inadequate, as the predictions based on contaminant concentration in groundwater considerably overestimated the risk at the site in respect to actual measurement (i.e. Tier III approach).

2.5 Conclusions

The chapter was focused on the physico-chemical properties of the chlorinated solvents DNAPLs and on their behavior once they are in the subsurface environment. Comments on contaminant remediation approaches and techniques were purposely neglected as they fall outside from the thesis topic. In summary, chlorinated solvents DNAPLs are contaminants able to migrate in a given hydrogeological system with modalities very different than the ones of typical aqueous contaminants. The pure phase DNAPL tends to accumulate in aquifers with a very heterogeneous distribution and can easily cross the most part of aquitards. The dissolved phase can be sorbed by the solid matrix (especially where there are enrichments in organic matter) and be furtherly released by means of back-diffusion. The main volatile compounds (e.g. VC) tend to vaporize in the unsaturated zone, giving origin to potential vapor intrusion issues. The degradation of chlorinated solvents most often lead to the accumulation of products more hazardous and mobile than the original ones (e.g. accumulations of cDCE and VC via reductive dechlorination of PCE and TCE). When spilled in the subsurface in the shape of DNAPLs their remediation is generally extremely challenging, rather impossible in most of the cases.

In the setting of Ferrara, this kind of contamination coexists at several sites with human activities such as residing and farming. A detailed investigation concerning the dynamics of migration and evolution of the chlorinated solvents hosted in the hydrogeological setting of Ferrara was carried out during the last two years and will be presented in the following Chapters. The main approach used for the investigation will be widely described in Chapter 3 and consisted in the reconstruction of high-resolution vertical profiling of several types of data (i.e. stratigraphy, physical properties of the porous medium, hydraulic heads, hydrochemistry of groundwater, contaminant concentrations, stable isotopes). This allowed to identify the peculiarities related with the occurrence of chlorinated solvents in the eastern sector of the multilayered aquifer system of the alluvial Po plain.

CHAPTER 3
Vertical profiling of data

3.1 Introduction

One of the most important discoveries made during the last four decades of contaminant hydrogeology research is that the distribution of dissolved contaminants in the subsurface is spatially complex, especially in the vertical dimension. This is due to a number of factors, including the labyrinthine distribution of residual contamination in most non aqueous phase liquid (NAPL) source zones, geologic heterogeneity, and the relative weakness of mixing mechanisms in groundwater (e.g. mechanical mixing and molecular diffusion) in respect to surface waters systems (National Research Council, 1994). This discovery was made possible by the use of multilevel sampling devices that facilitated the collection of discrete groundwater samples from up to 20 different depths in a single borehole, as well as the depth discrete measurement of hydraulic heads (Cherry et al., 1981; Einarson and Cherry, 2002; MacFarlane et al., 1983; Reinhard et al., 1984; Robertson et al., 1991; Smith et al., 1987; van der Kamp et al., 1994). Indeed, conventional long screened monitoring wells are often ineffective for discerning the details of concentration distribution in plumes and particularly for locating the highest concentration zones because the well screens provide water samples that are a mixture of waters of different composition from various depths (Martin-Hayden et al., 1991; Robbins, 1989; Robbins and Martin-Hayden, 1991). The same is for hydraulic head, which can be much more variable than expected in the vertical direction. Defining the vertical hydraulic head and concentration distribution at a contaminated site is an essential part of the development of a reliable site conceptual model (Einarson, 2006).

The traditional hydrogeological investigation techniques can be adapted in order to obtain vertical distributions of data. For example, nested monitoring wells (i.e. two or more individual wells installed to different depths in the same borehole; Fig. 3.1) can yield depth discrete samples and depth discrete head measurements; however, their use is discouraged because of the difficulty in installing reliable seals between the different well screens (U.S. EPA, 1986). Clusters of conventional monitoring wells (i.e. closely spaced wells installed in individual boreholes but completed to different depths; Fig. 3.1) are an alternative to nested wells but commonly do not monitor more than two or three depth intervals because of the economic limitation in the number of wells used in each cluster (Einarson and Cherry, 2002). Also, it may be possible in some cases to obtain information regarding the vertical distribution of dissolved contamination by carefully collecting depth-discrete samples from within conventional long-screened monitoring wells (Einarson, 2006); however, this last solution can be affected by significant operating biases and there's no way to have control on the reliability of the results.

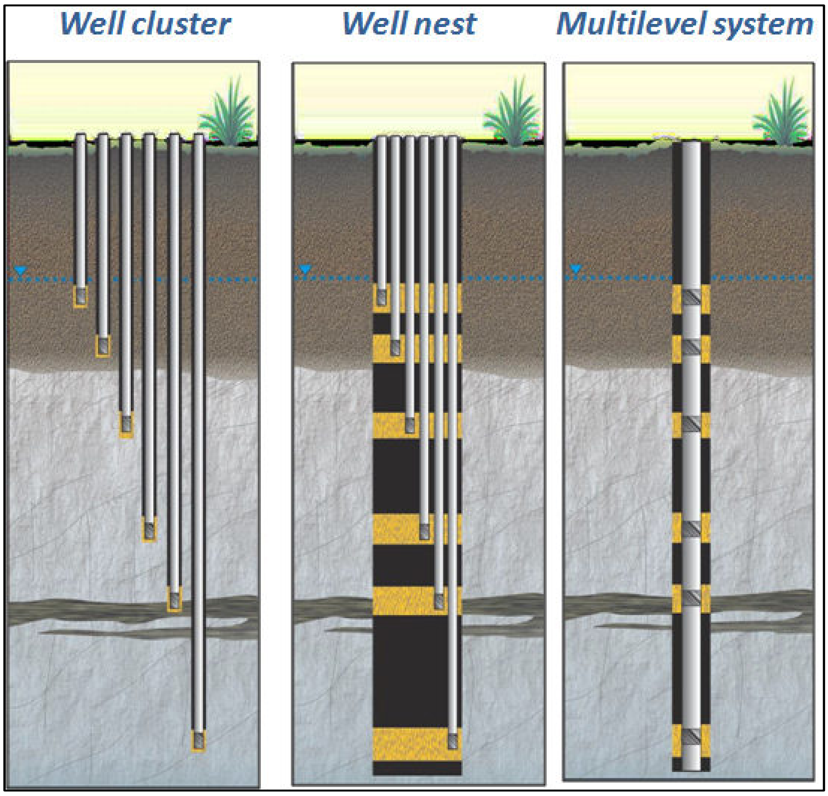


Figure 3.1: Schematic representation of well cluster, nested wells and multilevel system. All of them represent potential solutions for the depth-discrete monitoring of hydraulic heads and sampling of groundwater.

To overcome the limitations presented for the previous techniques, both **multilevel dedicated systems** (Fig. 3.1) or **single shot sampling methods** can be employed. The two approaches are widely described in Paragraphs 3.2 and 3.3, respectively. In particular, the multilevel systems allow to obtain time-series of data, such as hydraulic head or contaminant concentration, with an adequate vertical resolution. On the other hand, the single shot sampling techniques (such as groundwater sampling by means of direct push drilling or sediment core subsampling) allow to collect data at extreme vertical resolution (down to the cm scale) and, in the case of sediment sampling, they provide very useful information that can't be derived from groundwater samples (e.g. vertical distribution of physico-chemical properties of sediment and distribution of NAPL in its different phases). However, these kinds of sampling can't be repeated over time.

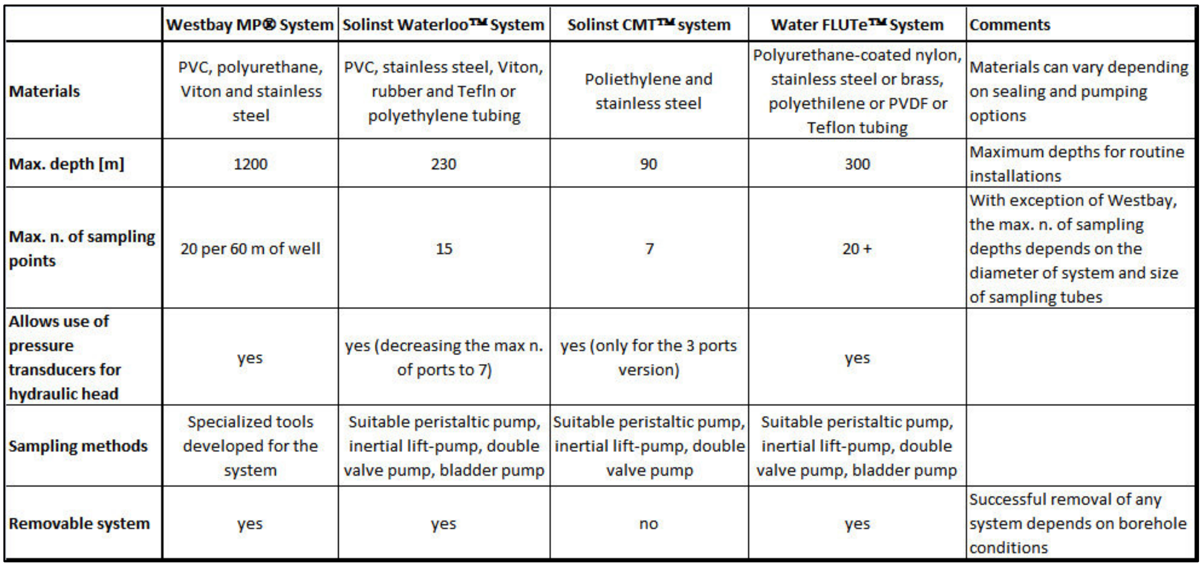
3.2 Multilevel Monitoring Systems

Permanent multilevel groundwater monitoring systems should be installed whenever and wherever it is necessary to determine the vertical distribution of hydraulic heads. Because measuring vertical hydraulic heads is a main pre-requisite in the development of a contaminated site conceptual model, installation of multilevel monitoring wells or piezometers that allow for measurement of hydraulic heads at multiple depths is needed virtually at every contaminated site. Measuring temporal changes in hydraulic heads at a site is particularly important in order to interpret the groundwater flow system, mixing mechanisms and contaminant distribution. Further, these devices should be employed any time that ongoing, long-term multilevel water quality monitoring is needed. Considering that ongoing groundwater qualitative monitoring (i.e. chemistry and contamination) is needed and required at most contaminated sites, once again permanent multilevel monitoring devices should play an important role at most sites. For example, long-term groundwater monitoring is often necessary to verify the effectiveness of active remediation. At other sites, time-series samples may need to be collected to document suspected seasonal fluctuations in the concentration or flux of contaminants emanating from a residual NAPL source zone. And, of course, long-term multilevel monitoring is necessary at sites where monitored natural attenuation (Stroo, 2010) is the selected remediation method (Einarson, 2006).

3.2.1 Typologies

Several specialized multilevel monitoring systems were developed for research purposes and some of them became commercially available. The four main commercial types of multilevel devices are the *Waterloo system* and the *CMT (Continuous Multichannel Tubing) system*, both produced by Solinst® and described by Parker et al. (2006) and Einarson and Cherry (2002), respectively, the *Water FLUTe™ system* described by Cherry et al. (2007), and the *Westbay® MP system* described by Black et al. (1986). In Table 3.1 are reported the main distinctive features of the four systems, each of which is based on a slightly different philosophy of construction.

Table 3.1: Comparison of the four main commercial types of Multilevel Monitoring Systems (from Einarson, 2006; modified).



	Westbay MP® System	Solinst Waterloo™ System	Solinst CMT™ system	Water FLUTe™ System	Comments
Materials	PVC, polyurethane, Viton and stainless steel	PVC, stainless steel, Viton, rubber and Tefln or polyethylene tubing	Poliethylene and stainless steel	Polyurethane-coated nylon, stainless steel or brass, polyethilene or PVDF or Teflon tubing	Materials can vary depending on sealing and pumping options
Max. depth [m]	1200	230	90	300	Maximum depths for routine installations
Max. n. of sampling points	20 per 60 m of well	15	7	20 +	With exception of Westbay, the max. n. of sampling depths depends on the diameter of system and size of sampling tubes
Allows use of pressure transducers for hydraulic head	yes	yes (decreasing the max n. of ports to 7)	yes (only for the 3 ports version)	yes	
Sampling methods	Specialized tools developed for the system	Suitable peristaltic pump, inertial lift-pump, double valve pump, bladder pump	Suitable peristaltic pump, inertial lift-pump, double valve pump	Suitable peristaltic pump, inertial lift-pump, double valve pump, bladder pump	
Removable system	yes	yes	no	yes	Successful removal of any system depends on borehole conditions

The Paragraph will focus on one of these systems, the CMT, which was the one employed for the investigations described in the following Chapters (4, 5, 6).

The Solinst Continuous Multichannel Tubing (CMT) system is a multilevel groundwater monitoring system that uses custom-extruded flexible multichannel High-Density Polyethylene tubing (4 cm OD) to monitor as many as seven discrete zones within a single borehole, in either unconsolidated sedimentary deposits or bedrock (Fig. 3.2). Ports are created along the tubing that allow ground water to enter six outer pie-shaped channels and a central hexagonal center channel at different depths, facilitating the measurement of depth-discrete hydraulic heads and the collection of depth-discrete groundwater samples. The ports are built on site before the CMT tubing is inserted into the borehole. Thus, the multilevel design can be decided directly in the field based on the stratigraphic and hydrogeologic data recovered from coring or other investigation methods (e.g. Cone Penetration Tests or geophysical data). The depth-discrete sampling and measuring points are created by cutting 10 cm long ports through the exterior wall of the tubing, into each of the channels, at the desired depths. The central channel is open to the bottom of the multilevel well. Well screens are constructed by wrapping synthetic or stainless steel fabric mesh completely around the tubing along the intake interval. Draining packs and annular seals between the various monitored zones can be installed by backfilling the borehole with alternating layers of sand/gravel and bentonite.

Hydraulic heads can be measured by means of a small size water level meter (6 mm OD), produced by Solinst® and suitable for small diameter tubing. However, due to the small diameter of the single channels (1.3 cm diameter), the use of the most diffuse types of water level sensors for the time-continuous monitoring of heads is precluded. Groundwater samples can be collected using peristaltic pumps, small diameter bailers, inertial lift pumps or small diameter double-valve pumps.

CMT systems have been installed to depths up to 90 m b.g.s., although most systems have been installed to depths lower than 60 m b.g.s. The systems have been installed in boreholes created in unconsolidated deposits or bedrock using a wide range of drilling equipment including rotasonic, air rotary, diamond-bit coring, and hollow-stem auger.

In addition to the seven-channel CMT version described above, a small diameter three-channel system (2.8 cm OD) has been also developed for installation with direct push sampling equipment.

The CMT multilevel monitoring system is described in detail by Einarson and Cherry (2002). A case study in California where CMT wells were installed to depths of 60 m b.g.s. using sonic drilling equipment is presented by Lewis (2001). An example of use of CMT wells to assess the fate and transport of MTBE in a chalk aquifer in the U.K. is described by Wealthall et al. (2002).

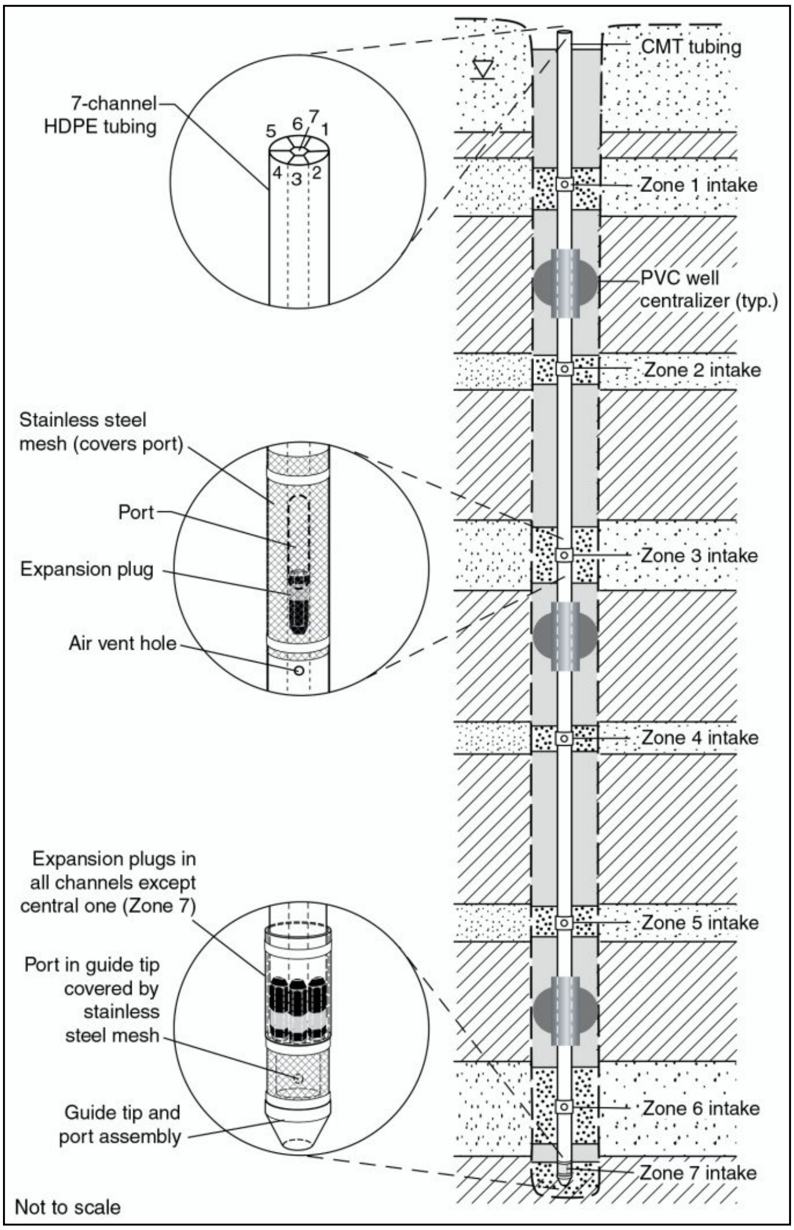


Figure 3.2: The Solinst CMT system (from Einarson, 2006).

3.2.2 Main applications

3.2.2.1 Contaminant concentration

Several field, laboratory, and modeling studies were performed in the last two decades to evaluate whether groundwater samples collected from conventional, long-screened piezometers (i.e. piezometers having a single-screened interval ranging from 3 to 9 m long) accurately reflect the concentration of dissolved contaminants in the portion of the aquifer screened by the wells (e.g. Akindunni et al., 1995; Chiang et al., 1995; Church and Granato, 1996; Conant et al., 1995; Elci et al., 2001; Gibs et al., 1993; Hutchins and Acree, 2000; Martin-Hayden, 2000a; Martin-Hayden, 2000b; Martin-Hayden and Robbins, 1997; Martin-Hayden et al., 1991; Reilly and Gibs, 1993; Reilly and

LeBlanc, 1998; Robbins, 1989). It turned out to be clear from these studies that groundwater samples collected from conventional monitoring piezometers are actually blended or composite samples. If the dissolved contaminants are stratified within the aquifer, which, based on detailed vertical groundwater sampling at several field research sites, appears to be the rule rather than the exception, the results derived from long-screened piezometers likely underestimate the maximum concentrations present in the aquifer.

Defining the true distribution of dissolved contaminants is arguably the most important part of an environmental site assessment (Einarson, 2006). The risk to downgradient receptors is commonly estimated by calculating the forecasted concentration at the receptor's location. The calculations are typically performed by estimating (using analytical or numerical tools) the attenuation of the contaminant from some initial concentration at the source. If this concentration is underestimated, the risk to the downgradient receptor (typically a water-supply well) may be underestimated. Similar arguments can be made for predictions of the risks associated with exposures to vapors emanating from residual contamination near source areas or originating from shallow contaminant plumes. Vapor migration is dominated by molecular diffusion. Because diffusion is driven by concentration gradients, underestimating the peak contaminant concentrations in the subsurface will result in an underestimation of the risk posed to the vapor receptors. However, in other cases, data from long-screened piezometers can overestimate the risk to vapor receptors. For example, groundwater recharge at a site may create a layer of clean water atop a deeper dissolved contaminant plume. The layer of clean water may constitute an effective diffusion barrier that impedes the upward migration of volatile contaminants from the dissolved plume (Rivett, 1995). The layer of clean groundwater overlying the contaminant plume could only be identified if multilevel groundwater monitoring wells or direct-push (DP) samplers (described in Par.3.3) were used. The same layer of clean groundwater would be completely missed by collecting a composite groundwater sample from a single-zone well screened over the same depth interval (Einarson, 2006).

Continued reliance of industry, consultants and regulatory agencies on conventional monitoring wells for site assessment and monitoring has prolonged the misconception that the distribution of dissolved contaminants in the subsurface is more homogeneous than it really is. Among the rest, this misconception can have serious consequences for health risk assessments and the performance of in situ remediation systems (Einarson, 2006).

The biases caused by sampling in conventional or cluster wells in respect to the multilevel approach are shown conceptually in Figure 3.3.

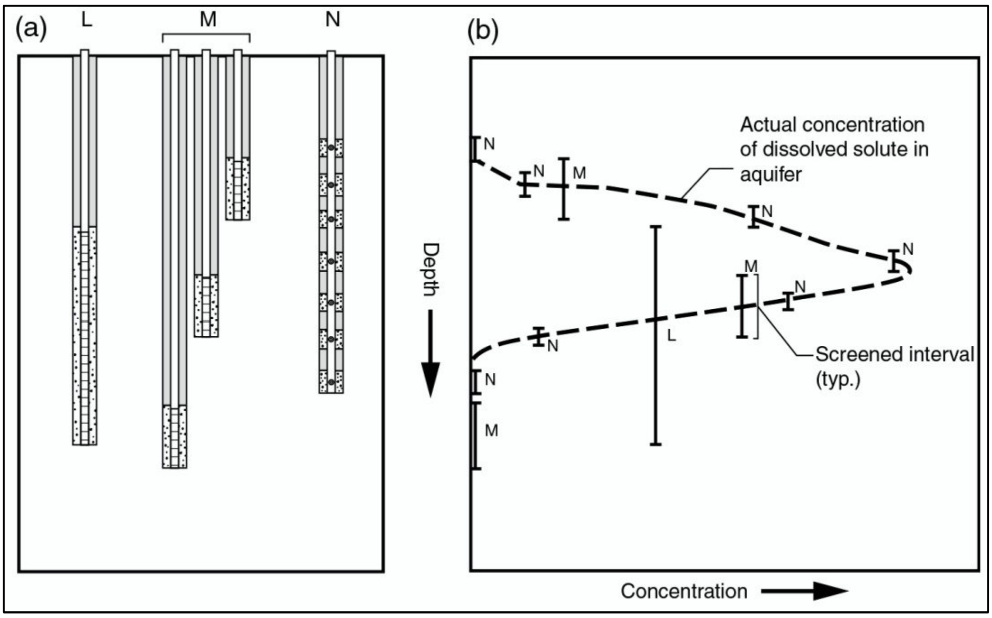


Figure 3.3: Effect of well screen length on sample concentration. (a) Three types of monitoring well completions – long-screen well (“L”); cluster of three wells completed to different depths (“M”); multilevel well (“N”). (b) Heavy dashed line shows actual concentration of a dissolved solute in the aquifer. L yields a sample that is a mixture of high and low concentrations occurring along the screened interval; N yields samples that most closely represent the true distribution of the solute in the aquifer (from Einarson, 2006).

In Figure 3.3a, several monitoring wells are shown. The one labeled “L” is a single-interval long-screened well. Wells labeled “M” make up a cluster of three wells completed at different depths in the aquifer. Well “N” is a multilevel monitoring well system that yields groundwater samples from seven discrete depths. In Figure 3.3b, the concentrations of a hypothetical dissolved contaminant in the aquifer are depicted in a heavy dashed line. Well “L” (the well with a relatively long screen) yields a sample that is a mixture of water containing high concentrations of the contaminant (entering the well from the upper part of the well screen) and water that has lower concentrations of the solute (entering the well from deeper portions of the aquifer). The sample from well “L” is therefore a composite that: (1) understates the peak concentrations in the portion of the aquifer screened by the upper part of the well and (2) overstates the presumed depth of dissolved-phase contamination in the aquifer. The cluster of three wells with shorter well screens (well cluster “M”) yields samples that more closely reflect the actual distribution of the dissolved-phase contaminants in the aquifer than the sample from the single long-screened well. The multilevel well (well “N”) provides samples that most closely resemble the actual distribution of the dissolved-phase contaminants in the aquifer. The conceptualizations presented in Figure 3.3 were extracted from an actual field investigation described by Einarson and Cherry (2002).

3.2.2.2 Hydraulic heads

Depth-discrete measurement of hydraulic head is also a necessary part of environmental site assessments. For example, mapping the hydraulic head distribution in three dimensions allows site investigators to make accurate predictions about the movement and future location of dissolved contaminants (Einarson, 2006). Vertical hydraulic gradients are present at most sites, and the magnitudes of vertical gradients often exceed horizontal hydraulic gradients. The vertical gradients can be directed downward or upward, depending on the recharge-discharge conditions, and they are mostly located inside aquitards (while in aquifers horizontal flow generally prevails). In general, the increase or decrease of hydraulic heads is expected to be homogeneous along the whole thickness of an aquitard, as shown in the conceptualization reported in Figure 3.4.

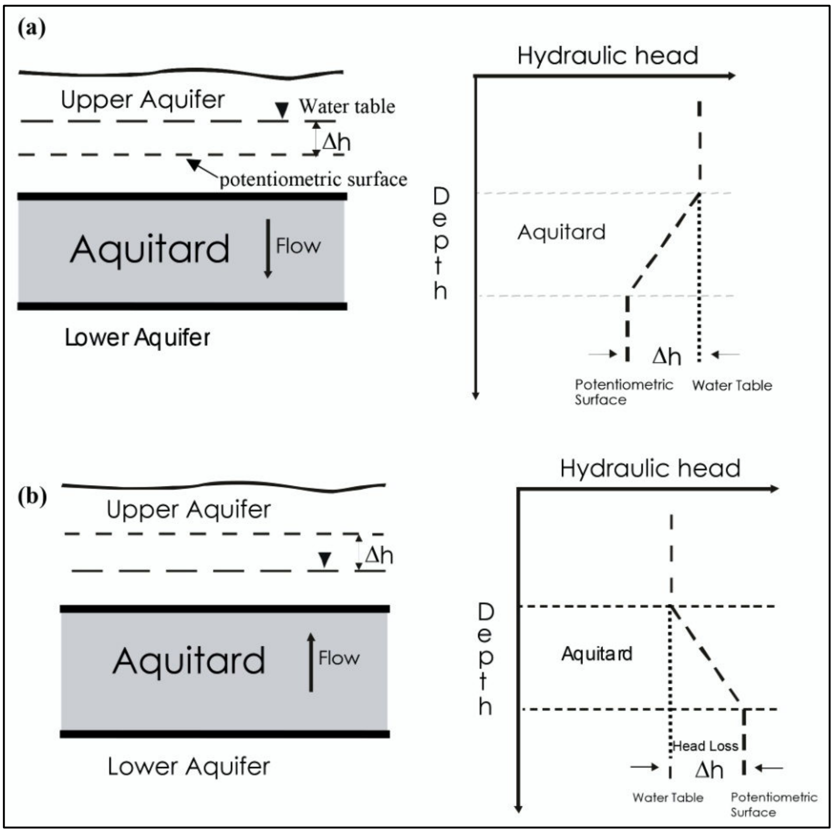


Figure 3.4: schematic example of two cases of vertical flow across homogeneous aquitards: (a) downward flow and (b) upward flow) (from Cherry et al., 2006).

Actually, the straight-line representation of the head profile across an aquitard is appropriate only when aquitard homogeneity can be assumed. However, the most part of the aquitards are strongly heterogeneous (Cherry et al., 2006) and the vertical distribution of heads is expected to respond to the main heterogeneities. The generalized simplification of straight hydraulic gradients within aquitard descends from the approach of using measurements of head external to the aquitard (i.e. collected in the surrounding aquifers) to determine whether groundwater flows upward or downward. However, much more information relevant to aquitard integrity is obtained when head measurements are made inside the aquitard at multiple depths. This can be obtained by means of a piezometer nest or a multilevel monitoring system screened within the aquitard. Actual study cases often show that the hydraulic gradient measured within the aquitard, at any particular elevation, is generally different from the average gradient across the aquitard obtained from external measurements. The internal variability in the vertical gradient distribution in the aquitard is caused by a variability of the hydraulic conductivity in the vertical direction (K_v).

Figure 3.5 a illustrates a situation in which the upper aquitard layer is composed by silt and the lower layer is composed by clay. In Figure 3.5 b, the entire aquitard layer is composed by clay, but has vertical fractures of different lengths and the lower zone of the aquitard is unfractured. In both cases, the large difference in head loss between the upper and lower aquitard zones is indicative of a major difference in the internal distribution of vertical K in the aquitard. The two examples suggest that a hydrogeologic unit, designated as an aquitard based on stratigraphic or lithologic considerations alone, can be much thicker than the zone within the aquitard that actually causes nearly all of the head loss and low groundwater flux (Cherry et al., 2006).

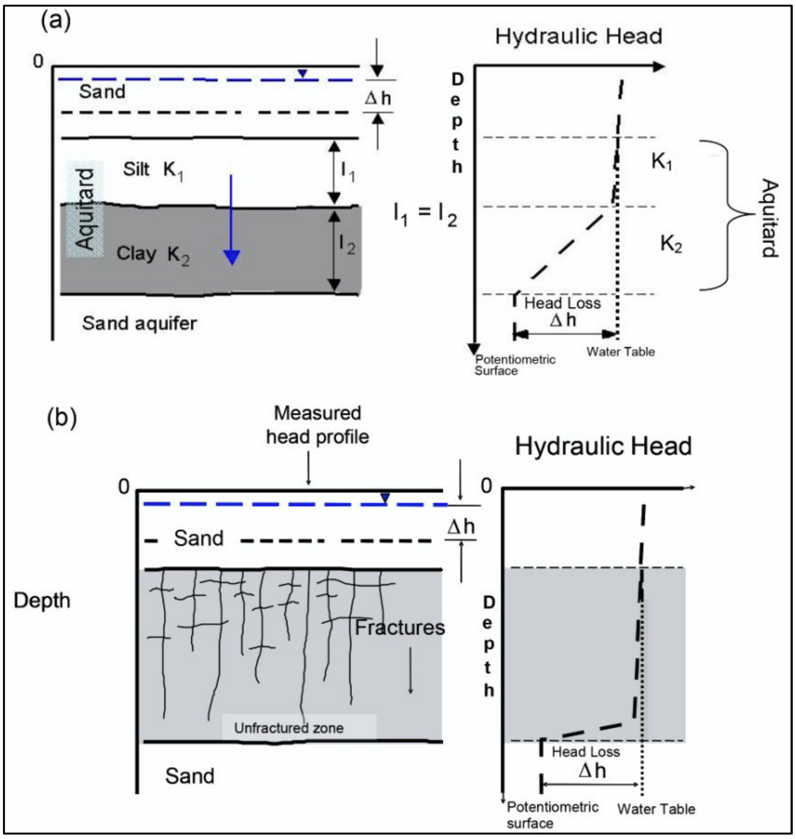


Figure 3.5: Hydraulic head distribution within an aquitard with two zones (K1 >> K2): (a) upper zone is silt and lower zone is clay where nearly all of the head loss occurs; (b) upper zone is fractured clay and the lower zone is unfractured clay where nearly all of the head loss occurs (from Cherry et al., 2006)

Thus, the most direct and reliable approach for identifying the zones with lowest K_v within an aquitard is measurement of the hydraulic head profile. Hydraulic conductivity tests in boreholes using straddle packers provide values for horizontal K that are generally not a reliable representation of vertical K. Laboratory measurements of K_v using borehole core samples do not necessarily indicate the actual bulk vertical K distribution because they generally do not detect fractures. Other lines of evidence need to be assessed to deduce whether or not the K_v values from lab tests on core samples represent the bulk aquitard K_v.

The critical head loss zones within an aquitard can be very thin. Large numbers of ports in each multilevel system provide closest vertical spacing between monitoring points, which in turn provides the best opportunity to determine the presence and the thickness of the critical zones.

An example of investigation where the vertical profiling of hydraulic heads within an aquitard turned out to be useful in order to interpret the distribution of contaminant DNAPLs was presented by Morrison et al. (1998). Their results showed PCE contamination occurring in the local aquitard due to a former experimental release of PCE DNAPL into the shallow sand aquifer (Brewster et al., 1995). The DNAPL penetrated deep into the aquitard via vertical fractures but did not go all the way through to the underlying aquifer. The lack of penetration through the bottom part of the aquifer, where the head profile indicated much lower K_v, was attributed to the presence of less fractures or absence of fractures in this basal zone.

The information presented above for hydraulic heads in aquitards considered only steady state conditions. However, important information can also be obtained from temporal measurements of hydraulic head in aquitards over short- and long-time periods in transient conditions (Cherry et al., 2006).

3.3 Single shot sampling

Single shot sampling techniques are an alternative to permanent multilevel systems. These techniques allow to collect data at higher vertical resolution and they are generally cost-effective in respect to permanent devices. One of the most used methods to collect single-shot groundwater samples is the Direct Push drilling. Direct push technology (DPT, also known as “direct drive,” “drive point,” or “push technology”) refers to a growing family of tools used for performing subsurface investigations by driving, pushing and/or vibrating small-diameter hollow steel rods into the ground. By attaching sampling tools to the end of the steel rods they can be used to collect groundwater samples. The sampling tools typically consist of a short (e.g. 15 to 90 cm) screen nested within a sealed, water-tight tool body. Because the screen is not exposed to the formation as the sampler is advanced into the subsurface, the screen does not become plugged or damaged. In addition, the potential for cross contamination is greatly reduced and a true depth-discrete sample that is representative of the targeted sampling zone can be collected. To collect the sample, the sealed-screen sampler is advanced to the targeted sampling depth and the protective outer rod is retracted, exposing the screen to groundwater. A complete description of the use of the direct push technique for the collection of environmental sampling is provided by U.S. EPA (2005). The groundwater samples collected with this method have the same role of the ones collected from permanent multilevel system, with the difference that DPT sampling can't be repeated over time.

Another type of single shot sampling useful to improve the conceptual model of a contaminated site is the core sub-sampling. It consists in the collection of sediment subsamples from the cores recovered during drilling. The samples can be collected with very short vertical spacing (down to the cm scale) and they can be used for contaminant concentration analyses, to determine the physico-chemical properties of the sediments (water content, fraction of organic carbon, etc.) or for analyses of stable isotopes on water or contaminant molecules. Some of the core subsampling techniques which can be employed in the investigation of sites contaminated by DNAPLs will be presented in the following Paragraph (3.3.1) and described more widely in Chapters 4, 5 and 6.

3.3.1 Sediment core subsampling applications

3.3.1.1 VOC analyses

An effective technique for the detailed reconstruction of the DNAPL architecture along a profile (in pure, dissolved or sorbed phase) is represented by the collection of sediment core subsamples for VOC (Volatile Organic Compounds) analyses. The method was applied in different field investigations (e.g. Chapman and Parker, 2005; Parker et al., 2004; Parker et al., 2003) and provided good results for both DNAPLs zones detection and vertical distribution of dissolved and sorbed phases. The method consists in the collection of small sediment subsamples (e.g. 8-10 g) from the central part of cores, with very short vertical spacing (down to the cm scale). The sampling procedure is optimized in order to minimize the loss of VOCs or sediment moisture from the core. A multi-step decontamination procedure is applied between each sampling step at different depths, due to the propensity typical of VOCs to generate cross-contamination. The laboratory analysis of sediment samples provides the total VOC analyte content per mass of wet sediment, but does not distinguish between the aqueous, sorbed or DNAPL phase, if present. However, a partitioning calculation method described by Feenstra et al. (1991) can be used to infer the presence of DNAPL based on the measured bulk concentration in the sediment. Nevertheless, residual and free-phase DNAPL can be distinguished only qualitatively. Furthermore, the dissolved and sorbed phases can be distinguished with the same partitioning method, when the DNAPL phase is assumed absent. The partitioning calculations are based on the physico-chemical properties of sediment and contaminants, which can be determined specifically for the investigated site (e.g. with the collection of sediment core subsamples along with the VOCs ones) or taken from literature.

Among the rest, the sediment subsampling method optimized for VOCs allows to obtain very detailed information within aquitards, where the collection of reliable groundwater samples can be challenging both for the very low permeability of the matrix and for the uncertain representativeness of the groundwater collected. A reliable and detailed distribution of contaminants in aquitards can provide very useful information about the modality of contaminant transport through the fine grained material (e.g. advection of DNAPL through preferential pathways VS diffusion in dissolved phase).

An example of field results obtained by sediment core subsampling is reported in Figure 3.6. In such a case the core subsampling allowed to detect a TCE-DNAPL zone along the investigated vertical profile.

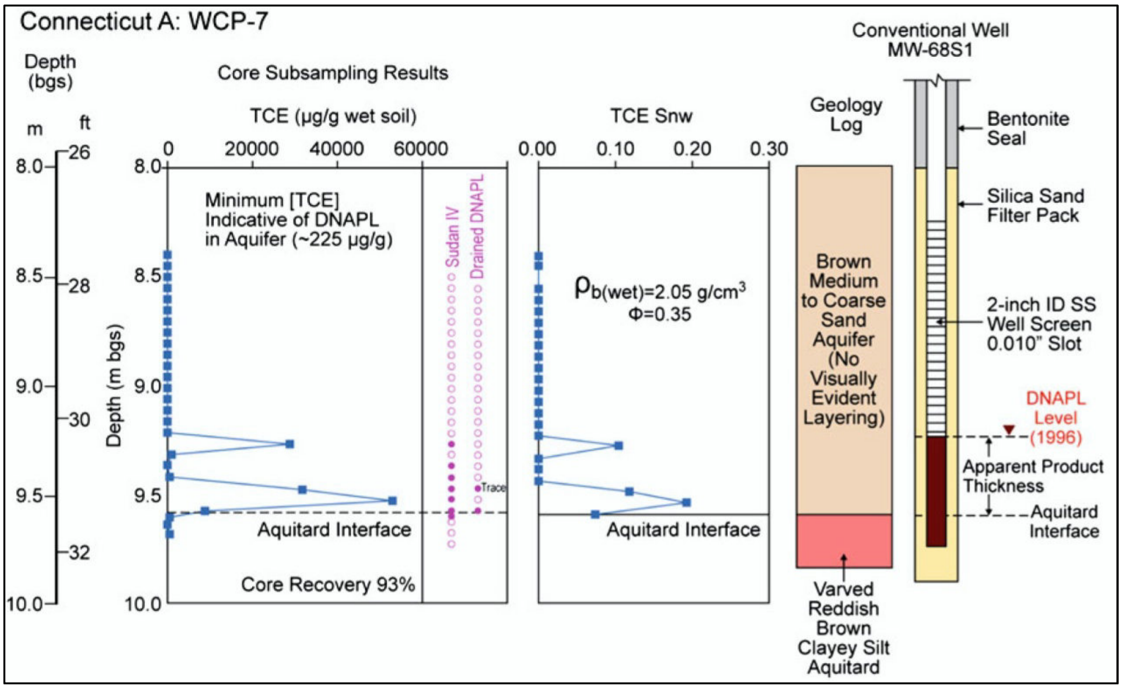


Figure 3.6: Example profile of DNAPL distribution at the source zone obtained via sediment core subsampling for the quantitative analysis of VOCs (results from the "Connecticut site"; Parker et al., 2003).

Sediment samples are generally collected with smaller vertical spacing than the groundwater ones. Indeed, spacing of groundwater samples smaller than some decimeter would produce overlapping of sampling zones because of purge and sample volume requirements. Thus, the core data are more depth-specific than the groundwater data (Parker et al., 2003). Anyway, the comparison between the detailed results obtained by VOC analyses on sediment samples (i.e. estimated concentration in dissolved phase) and the ones obtained by groundwater samples (e.g. collected from multilevel systems or by means of Direct Push Techniques) can be very useful in order to cross-validate the two different groups of results and to extend the detailed vertical interpretations carried out by means of VOC analyses to other profiles where only groundwater samples are collected.

A detailed description of the procedures for the collection and analysis of sediment core subsamples is reported in Chapter 5.

3.3.1.2 Stable isotopes analyses

Sediment core sub-samples can be employed also for stable isotopes analyses on contaminant or water molecules. In particular, in sites contaminated by DNAPLs, a valuable approach is the collection of sediment samples for Compound Specific Isotope Analysis (CSIA) on contaminants (e.g. $\delta^{13}C$) adjacent to the ones used for concentration analyses. This approach allows to detect the general isotopic signatures of the different compounds and to identify the occurrence of processes that cause isotopic fractionation (e.g. degradation processes), even when they occur at very small scale. The main advantages of using sediment samples for isotopic analyses of contaminants instead of groundwater samples are: (1) the achievement of a higher spatial resolution and (2) the collection of higher VOC-DNAPL concentrations (i.e. combination of dissolved, solved and possible pure phase DNAPL). Indeed, the analytical methods for carbon isotopes are often characterized by detection limits which can be easily higher than the typical dissolved concentrations of chlorinated compounds in groundwater. A detailed description of the procedures for the collection and analysis of this kind of samples is reported in Chapter 6.

Sediment core subsamples can also be used for water stable isotopes investigations. The approach allows to gain a high vertical resolution even within aquitards, where it is often difficult to extract groundwater without causing the separation of different water fractions (i.e. groundwater held by gravity, capillary forces and pellicular water). In particular, Wassenaar et al. (2008) proposed an effective method for the determination of $\delta^{18}O$ and $\delta^{2}H$ from core samples. The method consists in the attainment of $H_2O_{(liquid)}$–$H_2O_{(vapor)}$ pore water equilibration and further application of off-axis laser spectroscopy on the vapor phase. This method allows both $\delta^{2}H$ and $\delta^{18}O$ to be measured directly on sediment cores with volumetric water contents >5%, with an accuracy of <2‰ and <0.4‰ for $\delta^{2}H$ and $\delta^{18}O$, respectively. The sediment core subsamples, employed in this type of analysis are generally bigger than the ones described above for VOC and carbon isotope analyses (e.g. sections of 10-20 cm of the whole core). This allows to collect an amount of pore water large enough to perform the analyses without undermining the high vertical sampling resolution. The detailed vertical profiling of water isotopes obtainable by sediment samples is a valuable approach in order to better understand the vulnerability and recharge mechanisms of multilayered aquifer systems. This will be widely discussed in Chapter 4.

3.4 Transect approach

Since the last two decades, groundwater researchers started to utilize high-resolution groundwater sampling networks to characterize dissolved plumes at sites contaminated by DNAPLs. A particularly useful approach is represented by transects of closely spaced multilevel monitoring wells or DP sampling points oriented perpendicular to the plume axes (Borden et al., 1997; Devlin et al., 2001; Einarson and Mackay, 2001; Guilbeault et al., 2005; Kao and Wang, 2001; Newell et al., 2003; Semprini et al., 1995) (Fig. 3.7). The wells or sampling points are often spaced 6-7 m apart (or less) horizontally and facilitate the collection of discrete groundwater samples from multiple depths. The optimal vertical spacing of monitoring points in a sampling transect is a function of many factors (e.g. the purpose of the monitoring, the type of contamination, the nature and geometry of the source zone, subsurface geology, distance from the contaminant source, etc.) and is the subject of ongoing research (e.g. Guilbeault et al., 2005). A minimum of one transect is installed downgradient from the source zone to define the strength and temporal variability of the contaminant source, or to assess the effectiveness of remediation efforts.

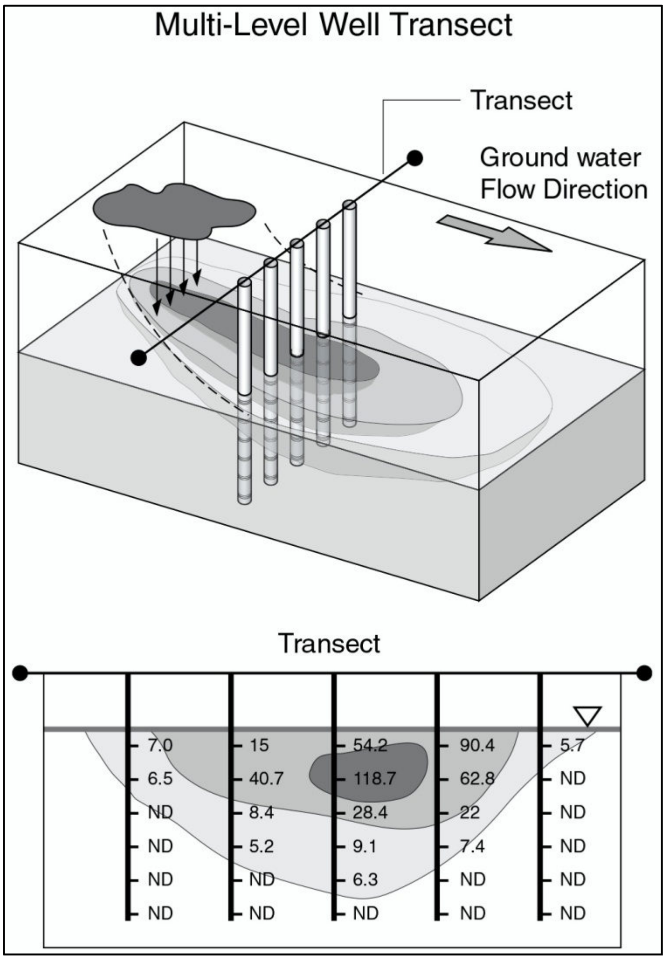


Figure 3.7: Schematic representation of a transect of multilevel wells (from Einarson, 2006).

Transects of multilevel wells (Fig. 3.7) are superior to monitoring networks comprised of spatially distributed conventional monitoring wells for several reasons. First and foremost, the dense grid or "fence" of sampling points makes it far more likely to detect and accurately delineate dissolved-phase plumes of contaminants (especially high-strength zones or “plume cores”) than if sparse networks of conventional monitoring wells were used. Secondly, detailed plume definition may show that plumes that were thought to be co-mingled are actually separated. Thirdly, transects of closely spaced multilevel wells are much less sensitive to slight shifts in the lateral and vertical position of dissolved plumes than sparse networks of conventional wells. For example, in areas where the hydraulic flow systems change over time (e.g. seasonal changes in flow direction), dissolved plumes may shift laterally and vertically in the aquifer. In such a case, samples taken over time from a single well could contain progressively lower concentrations of the target contaminant simply because the well is sampling lower concentration parts of the same dissolved plume over time. A plot of sampling results for the well would show declining concentrations over time. This trend could logically (but incorrectly) be attributed to source depletion or natural biodegradation. If, on the other hand, the same plume was monitored with a dense network of multilevel wells arranged in a transect across the plume, lateral and vertical shifts in the plume location could be easily recognized (Einarson, 2006).

3.5 Vertical profiling at the Caretti site

A transect of CMT systems was installed at the Caretti site during 2013, for the investigation of a chlorinated solvent-DNAPL source area (i.e. Southern Dump). The monitoring cross section is 60 m long and 60 m deep and it is located immediately downgradient to the Southern Dump, perpendicular to the flow directions of the two shallower aquifers (i.e. A0 and upper A1) (Fig. 3.8). The section consists of three vertical profiles, 30 to 60 m deep, located 21 to 25 m apart from each other. The two deeper profiles (MC1/MC2 and MC4/MC5, in Fig. 3.8) are composed by two coupled boreholes, spaced apart 4.5 to 5.8 m. The shallower portions (0 to around 30 m b.g.s.) of MC1/MC2 and MC4/MC5 were sealed by means of permanent casing before advancing the drilling to the bottom. This was done in order to avoid cross-contamination of the deeper investigated aquifer (lower A1), which was erroneously considered uncontaminated based on the results of a previous site characterization (Gargini et al., 2011). All the data collected along the coupled MC1/MC2 and MC4/MC5 profiles were plotted on one single virtual profile located in between the two actual ones. The virtual profiles will be named MC1-2 and MC4-5 from now on.

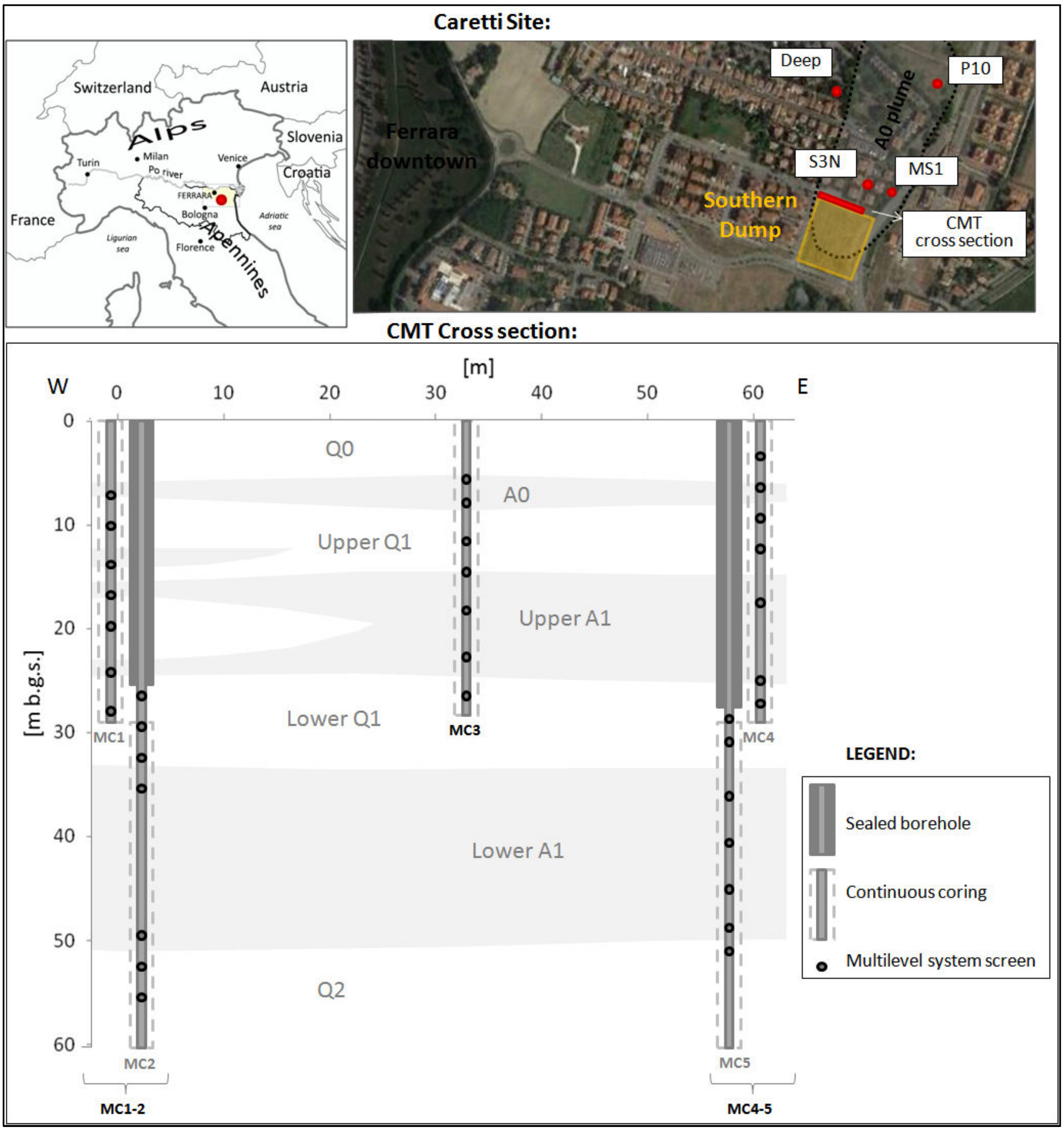


Figure 3.8: Scheme of data collection at the Caretti test-site. In the upper box are shown the locations of the monitoring points exploited at the site throughout the thesis: S3N, P10 and Deep are three long-screen piezometers equipped with pressure transducers for the continuous monitoring of heads; MS1 is an home-made multilevel system 10 m deep installed on the plume in migration in A0 aquifer; the CMT cross section is described in detail in the lower box. The geometry of aquifers and aquitards reported along the cross section is the results of investigations presented in Chap. 5 and 6.

The continuous coring performed along the investigated profiles (see continuous coring intervals in Fig. 3.8) allowed to collect very detailed stratigraphic information and a large number of sediment core subsamples, then utilized to perform different types of physic and chemical analyses (see Chapters 4, 5 and 6 for details). Five CMT systems (7 channels version; Fig. 3.9 a) were installed along the boreholes of the transect in order to collect groundwater samples and monitor hydraulic heads over time. The two coupled MC1-2 and MC4-5 boreholes allowed the installation of two multilevel systems within the total 60 m thickness, so doubling the possible number of monitoring screens on a single profile (i.e. 14 screens from 0 to 60 m b.g.s.). The five CMT systems were installed by means of conventional borehole drilling techniques: alternating lifts of bentonite pellets and calibrated gravel were poured into the anular space between the hole and the CMT system from the surface, according with the output of the stratigraphic log. The permeable packs placed around the screens resulted with an actual averaged length of 1.5 m. An additional groundwater vertical profiling was performed at the site by means of a home-made multilevel system (MS1 in Fig. 3.8). The system was installed 100 m northward from the Southern Dump, on the dissolved plume migrating in A0 aquifer. The multilevel device is extended from 0 to 10 m b.g.s. (ending just below the bottom of A0 aquifer) and equipped with one screen every meter for the collection of groundwater samples. It consist of 10 thin PE tubing (10 mm diameter), bundled around a 2 in PVC central tubing (Fig. 3.9 b). Screens 0.1 m long were realized by wrapping nylon fabric (100 μm aperture) at the bottom of each PE tubing. This system was installed via the collapse technique (Einarson and Cherry, 2002).

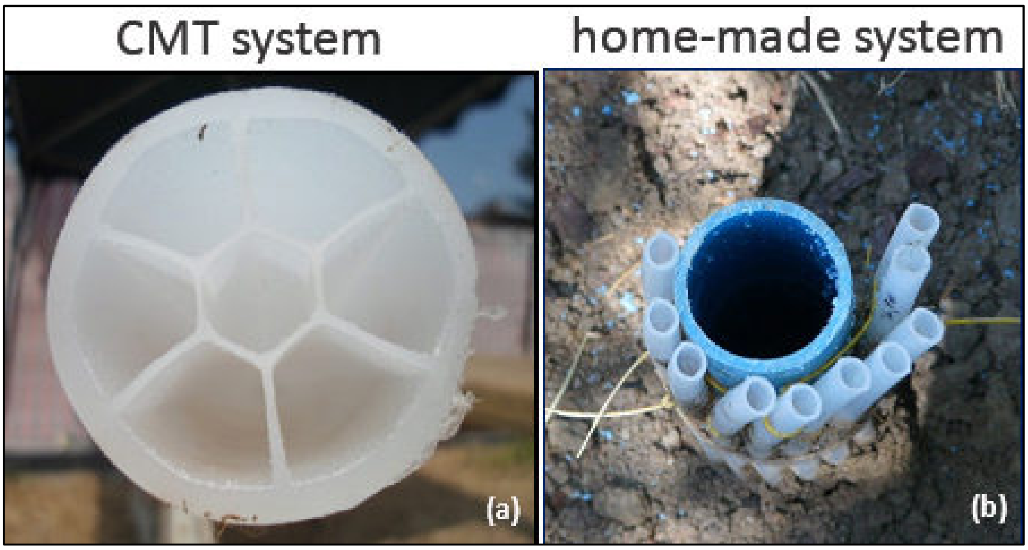


Figure 3.9: “heads” of the multilevel systems installed at the Caretti site: (a) CMT system; (b) home-made bundled system.

The location of the CMT transect and of the MS1 system were selected based on the previous characterization of the contamination at the site, concisely described in Chapter 2 and carried out by Gargini et al. (2011) and Nijenhuis et al. (2013). In Figure 3.8 are shown also the locations of three pre-existing long-screen piezometers (named “P10”, “S3N” and “Deep”) which were used for the continuous monitoring of hydraulic heads of the A0, upper A1 and lower A1 aquifers, during 2013 and 2014 (see results in Chap. 5).

All the detailed vertical investigations carried out at Caretti site (i.e. sediment core subsampling and groundwater sampling from multilevels) were mainly focused on the identification of the role of aquitards both for biodegradation of chlorinated solvents and for the protection provided to aquifers against DNAPL and non-DNAPL surface sources of contamination. Furthermore, the data collected provided some hints about the risk related to the potential VC vapor emission issue (already mentioned in Chap. 2).

3.6 Conclusions

The vertical profiling of data, carried out mainly by means of multilevel permanent wells or single shot sampling, is increasingly recognized as an essential approach in order to obtain a proper characterization of sites contaminated by DNAPLs. The results collected at the Caretti site by means of vertical profiling of data (i.e. contaminants concentration, hydraulic heads, etc.; described in Chapters 4, 5 and 6) represent a further evidence of the inadequacy of traditional hydrogeological approaches (e.g. groundwater samples collected from sparse nets of long-screened wells) in order to get the whole complexity of a multilayered contaminated system. Concerning in particular the multilevel systems, they are widely employed in the characterization of contaminated sites in the U.S. and in Canada, where a significant amount of study cases and evidences were collected during the last decades, in order to test their efficacy in a large number of hydrogeological settings. On the other hand, in Europe and particularly in Italy there is a diffuse skepticism in the employment of such devices rather than traditional solutions (except for few study cases, some of which already cited in the general introduction of the thesis). Among the main reasons for that are: (1) the higher costs of multilevel systems in respect to traditional wells (on a equal number of boreholes); (2) the distrust in the effectiveness of alternate filling on a single borehole; (3) the unawareness of the possible occurrence of complex contaminant architecture in the subsurface.

Eventually, the main missing step towards the widespread of multilevel systems and vertical profiling approaches in the European countries is to become aware that exploiting at the most one single well could provide more useful results than spread resources on sparse networks of traditional wells.

CHAPTER 4

Evaluation of aquifer recharge and vulnerability in an alluvial lowland using environmental tracers[1]

4.1 Introduction

Alluvial plains constitute both the most human affected portion of earth's surface and the main fresh groundwater reservoir of the planet (Jones, 2011; Tockner et al., 2008). Exploitation and protection of alluvial aquifers are two objectives of the sustainable management of groundwater resources that need to be addressed in a strictly coupled way (Aral and Taylor, 2011). At European level, for example, the Water Framework Directive (WFD; 2000/60/EC) emphasizes the role of a parallel and integrated quantitative/qualitative monitoring and evaluation, in order to achieve a good general status of the main European water bodies, including aquifers. Consequently, groundwater budgeting and vulnerability assessment of the main aquifers should be faced together, by means of an integrated approach.

The recharge to groundwater, intended as the quantity of water feeding the aquifer system, can be considered a valuable parameter in order to quantitatively estimate the safe yield and the intrinsic vulnerability of an aquifer at the same time. Indeed, the recharging water represents the main potential carrier of dissolved contaminants. In an alluvial plain setting, recharge is originated partly by rainfall (direct or vertical recharge) and partly by surface water network (lateral recharge from main rivers, irrigation). A permeable hydrologic connection between the aquifer and the ground surface allows a high contribution to the aquifer from direct recharge. However, the same permeable connection with the surface increases the intrinsic vulnerability of aquifers to surface sources of pollution (Vrba and Zaporozec, 1994).

Whereas various techniques are available to quantify recharge, either by experimental tools (Scanlon et al., 2002) or indirect numerical modeling (Mastrocicco et al., 2014), this are rarely combined with intrinsic vulnerability assessments. If the intrinsic vulnerability is considered, mainly subjective index methods are applied rather than objective physically based methods (Gogu and Dassargues, 2000). The drawback of subjective methods is that their results strongly depend on interpretations and

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evaluations, in contrast to objective methods which are based on direct measurement of parameters with a physical value.

Environmental tracers are a valuable tool to assess the intrinsic vulnerability in a physically based way, by identifying time scales and water sources.

Previously, researchers have investigated the stable isotopic ratios of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) as tracers to study groundwater recharge and flow, as they have the potential to trace both source and flow paths in groundwater systems (e.g. de Vries and Simmers, 2002; Gemitzi et al., 2014; Gibson et al., 2005; Liu et al., 2004; Liu and Yamanaka, 2012; Mizota and Kusakabe, 1994; Nakaya et al., 2007; Qin et al., 2011; Rietti-Shati et al., 2000; Weyhenmeyer et al., 2002; Wilcox et al., 2004). Among recharge quantification techniques, the most promising are mixing calculations, capable also to estimate the relative importance of different sources (Tubau et al., 2014; Vázquez-Suñé et al., 2010). Following this direction, End Member Mixing Analysis (EMMA; Christophersen and Hooper, 1992; Christophersen et al., 1990; Hooper et al., 1990; James and Roulet, 2006; Jones et al., 2006; Tubau et al., 2014) is a promising tool to evaluate the contribution ratio of each recharge source of groundwater starting from the stable isotopic composition of the water itself (Liu and Yamanaka, 2012). An end-member for $\delta^{18}O$ and $\delta^{2}H$ represents a groundwater source and, in general, local groundwater at a sample point is formed as a result of multiflow mixing with neighboring flow paths (Nakaya et al., 2007). Stable isotopic compositions of groundwater recharged through direct infiltration of precipitation will reflect that of local precipitation (Clark and Fritz, 1997). If rivers retain the depleted isotopic signature of their headwaters, the difference in stable isotope signatures of rivers and local precipitation can be used to determine the relative contribution of these two sources of groundwater recharge (Kalbus et al., 2006; Lambs, 2004; Scanlon et al., 2002).

In a similar way, hydrochemical data can be used to complement isotopic information. Additionally, the trend of the Electrical Conductivity, which reflects the total dissolved ion concentrations in water bodies, can be indicative of the length of flowpaths and residence times underground (Song et al., 2006), as well as trace possible connections between different hydrogeological bodies.

Therefore, the objective of the work presented in this Chapter is to propose the use of environmental tracers as a tool to quantitatively assess both recharge and intrinsic vulnerability. This tool will be applied to the multilayered aquifer setting of the southern Po river plain, where a quantitative assessment of recharge and vulnerability for the different aquifers is difficult to obtain.

Isotopic and hydrochemical analysis of groundwater and pore water collected from distinct aquifers will be employed as parameters for mixing calculations. Additionally, results from sampling of groundwater and pore water from aquitards will be evaluated, as aquitards are generally neglected in groundwater studies, however playing a key-role for the interpretation of recharge and affecting intrinsic vulnerability.

The results will contribute to close two of the main gaps of classical vulnerability mapping methods: 1) the lack of parameters able to represent the physical processes responsible for the contamination (e.g. groundwater recharge) and 2) the evaluation of vulnerability limited to the shallowest aquifer, although very often (as in the presented case study) the most valuable groundwater reservoir is a deeper confined aquifer.

4.2 Materials and Methods

4.2.1 Extension of the study area and sampling network

This Chapter is focused on the southeastern portion of the Po river plain, which was already described in Chapter 1. In particular, the investigated area extends for about 1400 km^2 along the southern bank of the Po river. The investigated aquifers are the regional A0, A1 and A2. As already mentioned in Chapter 1, the A1 aquifer can be separated in two distinct aquifers in some locations (e.g. at the Caretti site), which were named as upper A1 and lower A1. Where the two separated aquifers are present, upper A1 consists in a spatially discontinuous, confined to leaky-confined body. Differently, lower A1 shows a marked spatial continuity and hydrogeological features very similar to the ones observed for the regional A1. For this reason, the information collected from A1 and lower A1 were grouped together in this Chapter (referred to as "A1/lower A1") and differentiated from the ones relative to upper A1.

Chemical and isotopic data were collected in the study area by means of two different sampling networks, at different scales of investigation. The first sampling network is based on a regional survey approach (boreholes scattered throughout the whole investigated area and screened in different aquifers) and was used to collect groundwater samples. The second network consists in the five multilevel systems present along the monitoring cross section at the Caretti site (described in Chap. 3; Fig. 3.8). This last network was used to collect groundwater and sediment samples (for the analysis of pore water), both from aquifers and aquitards.

Seventy seven groundwater samples were collected from 70 sampling points of the regional network, during spring 2010 and 2011. The samples were taken from preexisting boreholes screened in A0, upper A1, A1/lower A1 or A2 aquifers, consisting in domestic, irrigation and public water supply wells, long screen piezometers, multilevel monitoring systems and direct push drillings. Fourteen samples among the total amount of 77 were collected inside the Po riverbed, 2 to 30 m below the bottom of the river, by means of a direct-push drilling performed from a floating pontoon; 8 of the 14 samples were collected within the shallower 12 m b.g.s. and have been considered representative of the Po riverbed, while the remaining 6 were collected between 12 and 30 m b.g.s. and have been named after aquifer A1/lower A1. In this circumstance, also a surface water sample was collected from the Po river. All the sampling points pertaining to the regional network were sampled once, in 2010 or 2011, except for six of them, which were sampled in both years (Tab. 4.1; Fig. 4.1). The points of the regional survey were selected to obtain a good spatial coverage of the investigated area.

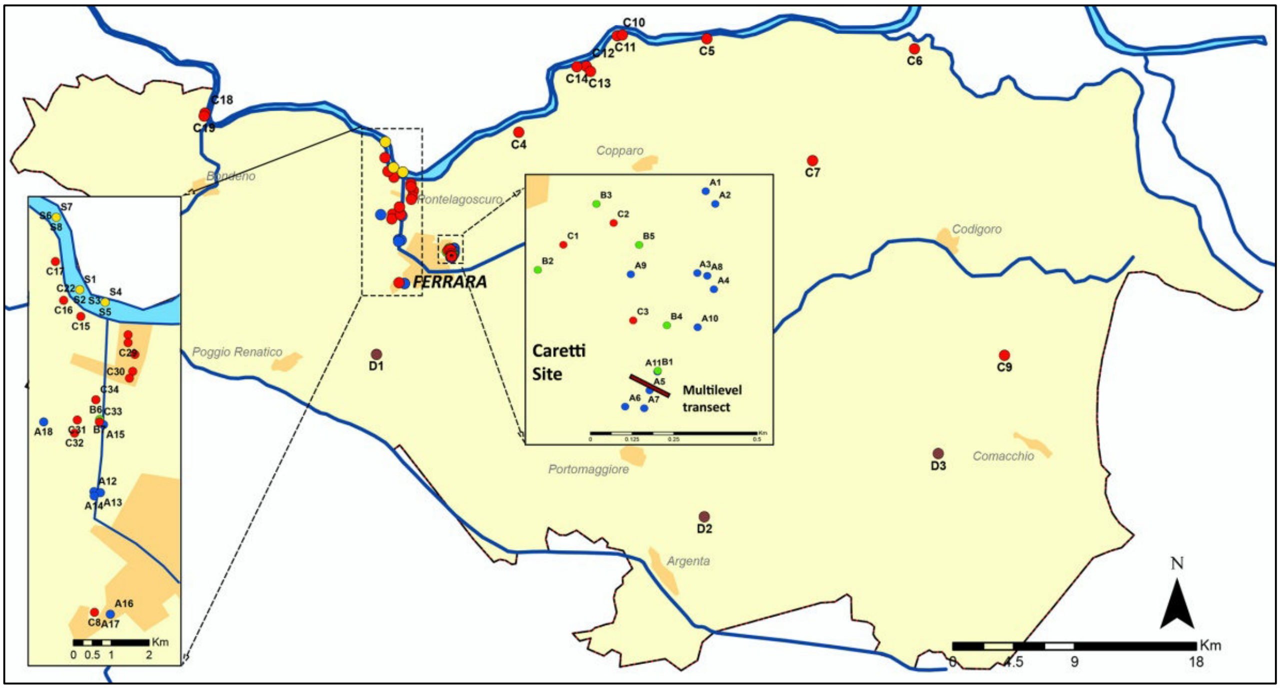

Figure 4.1: Location of the sampling points pertaining to the regional monitoring network, distinguished by screened aquifer (A0 in blue; upper A1 in green; A1/lower A1 in red; A2 in brown; riverbed in yellow).

The three profiles of the cross section at the Caretti site (MC1-2, MC3 and MC4-5; Fig 3.8 - Chap. 3) were sampled during summer and early fall 2013. Thirty four groundwater samples were collected from the CMT systems. Furthermore, 57 sediment samples were collected along one of the profiles (MC1-2), during the installation of the multilevel systems. Subsamples (0.1-0.2 m) of sediment cores were taken with an averaged vertical spacing of 0.8 m, in order to perform isotopic analyses on pore water using $H_2O_{(liquid)}$–$H_2O_{(vapor)}$ pore water equilibration and off-axis laser spectroscopy (Wassenaar et al., 2008).

Table 4.1: Groundwater sampling points selected for the regional monitoring network (Ferrara) and groundwater sampling depths of the multilevel cross section installed at the Caretti site. Under the "sampling depth" column: "?" is reported where the information are missing. Under the "Analyses" column: "I" stands for isotopic analyses performed on that sample, while "H" stands for hydrochemical analyses.

Regional monitoring network - Ferrara					
ID	Aquifer	Sampling system	Sampling depth [m b.g.s.]	Sampling year	Analyses
A1	A0	Direct push	4.80	2011	I
A2	A0	Direct push	6.00	2011	I
A3	A0	Direct push	4.40	2011	I
A4	A0	Direct push	6.00	2011	I
A5	A0	Direct push	6.80	2011	I
A6	A0	Direct push	6.30	2011	I
A7	A0	Direct push	8.00	2011	I
A8	A0	Piezometer	?	2010, 2011	I;H
A9	A0	Piezometer	?	2010	I;H
A10	A0	Piezometer	?	2010	I;H
A11	A0	Piezometer	?	2010, 2011	I;H
A12	A0	Piezometer	10.00	2011	I
A13	A0	Piezometer	10.00	2011	I
A14	A0	Piezometer	10.00	2011	I
A15	A0	Piezometer	?	2011	I;H
A16	A0	Piezometer	4.00	2011	I;H
A17	A0	Piezometer	4.00	2011	I;H
A18	A0	Piezometer	?	2011	I;H
B1	Upp. A1	Piezometer	15.00	2010, 2011	I;H
B2	Upp. A1	Piezometer	19.00	2010, 2011	I;H
B3	Upp. A1	Piezometer	?	2010	I;H
B4	Upp. A1	Piezometer	19.50	2010, 2011	I;H
B5	Upp. A1	Piezometer	16.50	2010, 2011	I;H
B6	Upp. A1	Piezometer	10.00	2011	I;H
B7	Upp. A1	Piezometer	10.50	2011	I;H
C1	A1/Low. A1	Domestic well	?	2010	I;H
C2	A1/Low. A1	Domestic well	?	2010	I;H
C3	A1/Low. A1	Piezometer	?	2010	I;H
C4	A1/Low. A1	Water supply well	?	2010	I;H
C5	A1/Low. A1	Water supply well	?	2010	I;H
C6	A1/Low. A1	Water supply well	?	2010	I;H
C7	A1/Low. A1	Water supply well	?	2010	I
C8	A1/Low. A1	Water supply well	?	2010	I;H
C9	A1/Low. A1	Water supply well	?	2010	I;H
C10	A1/Low. A1	Water supply well	?	2010	I

Regional monitoring network - Ferrara					
ID	Aquifer	Sampling system	Sampling depth [m b.g.s.]	Sampling year	Analyses
C11	A1/Low. A1	Water supply well	?	2010	I;H
C12	A1/Low. A1	Water supply well	?	2010	I
C13	A1/Low. A1	Water supply well	?	2010	I;H
C14	A1/Low. A1	Water supply well	?	2010	I;H
C15	A1/Low. A1	Water supply well	?	2010	I;H
C16	A1/Low. A1	Water supply well	?	2010	I;H
C17	A1/Low. A1	Water supply well	?	2010	I;H
C18	A1/Low. A1	Water supply well	?	2010	I;H
C19	A1/Low. A1	Water supply well	?	2010	I;H
C20	A1/Low. A1	Po river drilling	16.00	2010	I;H
C21	A1/Low. A1	Po river drilling	23.00	2010	I;H
C22	A1/Low. A1	Po river drilling	30.00	2010	I;H
C23	A1/Low. A1	Po river drilling	18.00	2010	I;H
C24	A1/Low. A1	Po river drilling	30.00	2010	I;H
C25	A1/Low. A1	Po river drilling	18.00	2010	I;H
C26	A1/Low. A1	Domestic well	?	2011	I;H
C27	A1/Low. A1	Domestic well	?	2011	I;H
C28	A1/Low. A1	M.L.S.	10.50	2011	I;H
C29	A1/Low. A1	M.L.S.	18.50	2011	I;H
C30	A1/Low. A1	M.L.S.	20.00	2011	I;H
C31	A1/Low. A1	Piezometer	27.50	2011	I;H
C32	A1/Low. A1	Piezometer	20.00	2011	I;H
C33	A1/Low. A1	Piezometer	22.00	2011	I;H
C34	A1/Low. A1	Piezometer	17.00	2011	I;H
S1	Riverbed	Po river drilling	2.00	2010	I;H
S2	Riverbed	Po river drilling	9.00	2010	I;H
S3	Riverbed	Po river drilling	2.00	2010	I;H
S4	Riverbed	Po river drilling	6.00	2010	I;H
S5	Riverbed	Po river drilling	12.00	2010	I;H
S6	Riverbed	Po river drilling	2.00	2010	I;H
S7	Riverbed	Po river drilling	5.00	2010	I;H
S8	Riverbed	Po river drilling	8.00	2010	I;H
D1	A2	Water supply well	?	2010	I;H
D2	A2	Water supply well	?	2010	I;H
D3	A2	Water supply well	?	2010	I

Monitoring cross section - Caretti site					
ID	Aquifer	Sampling system	Sampling depth [m b.g.s.]	Sampling year	Analyses
MC1.1	A0	CMT	7.43	2013	I;H
MC1.2	Upp. Q1	CMT	10.42	2013	I;H
MC1.3	Upp. A1	CMT	13.42	2013	I;H
MC1.4	Upp. A1	CMT	16.42	2013	I;H
MC1.5	Upp. A1	CMT	19.43	2013	I;H
MC1.6	Upp. A1	CMT	24.42	2013	I;H
MC1.7	Low. Q1	CMT	27.35	2013	I;H
MC2.1	Low. Q1	CMT	25.23	2013	I;H
MC2.2	Low. Q1	CMT	28.73	2013	I;H
MC2.3	Low. Q1	CMT	31.73	2013	I;H
MC2.4	Low. A1	CMT	34.73	2013	I;H
MC2.5	Low. A1	CMT	48.73	2013	I;H
MC2.6	Q2	CMT	51.73	2013	I;H
MC2.7	Q2	CMT	54.73	2013	I;H
MC3.1	A0	CMT	5.46	2013	I;H
MC3.2	A0	CMT	7.97	2013	I;H
MC3.3	Upp. Q1	CMT	10.95	2013	I;H
MC3.4	Upp. A1	CMT	14.43	2013	I;H
MC3.5	Upp. A1	CMT	17.92	2013	I;H
MC3.6	Upp. A1	CMT	22.90	2013	I;H
MC3.7	Low. Q1	CMT	26.31	2013	I;H
MC4.1	Q0	CMT	3.28	2013	I;H
MC4.2	A0	CMT	6.23	2013	I;H
MC4.3	Upp. Q1	CMT	9.21	2013	I;H
MC4.4	Upp. Q1	CMT	11.72	2013	I;H
MC4.5	Upp. A1	CMT	17.14	2013	I;H
MC4.6	Upp. A1	CMT	24.64	2013	I;H
MC4.7	Low. Q1	CMT	27.05	2013	I;H
MC5.1	Low. Q1	CMT	27.84	2013	I;H
MC5.2	Low. Q1	CMT	30.84	2013	I;H
MC5.3	Low. A1	CMT	35.84	2013	I;H
MC5.5	Low. A1	CMT	43.84	2013	I;H
MC5.6	Low. A1	CMT	47.84	2013	I;H
MC5.7	Q2	CMT	50.84	2013	I;H

4.2.2 Sampling and Analytical methods

4.2.2.1 Groundwater samples

Before sampling, each borehole was purged in order to collect groundwater representative of the aquifer conditions. The triple of the water volume contained inside the boreholes was purged from the wells of the regional network. Piezometers of the same network were purged by low-flow pumping with a submersible volumetric pump (pumping rate between 0.1 and 1 L/min, according to the aquifer hydraulic transmissivity, in order to maintain a drawdown not higher than 0.1 m; Robbins et al., 2008). From the CMT cross section at the Caretti site, a volume was purged equal to the triple of the water contained in the tubing and in the drains surrounding the screens, using a low flow peristaltic pump suitable for CMT systems (Model 410 Peristaltic Pump, Solinst®).

Groundwater samples were collected with the same pumping systems used for the purging operations, only after the stabilization of physico-chemical parameters of water. Parameters were controlled via flow-cell equipped with electrodes for temperature, specific electrical conductivity (EC at 25°C), pH and redox potential (multi-parameter electrode QuantaD, Hydrolab©).

Groundwater samples from direct-push drilling below the Po riverbed were collected with a peristaltic pump from a 0.8 m long screened interval without any purging.

For the chemical analyses of major ions, groundwater samples were pre-filtered at 45μm in the field and filled into two 250 mL PET bottles, one of which not acidified (anions) and the second one acidified with nitric acid to pH 2 (cations). Alkalinity was directly measured in the field by titration. For the liquid analysis of stable isotopes of water molecules, 100 mL of non filtered and non acidified groundwater were filled into 100 mL PET bottle. All samples were stored cooled (4 to 10 °C) until analyses.

Groundwater samples collected for major ions were analyzed by Ion chromatography for anionic species, using a Metrohm 883 Basic IC Plus chromatographer. Major cations were analyzed by Flame Atomic Absorption Spectrometry with a Perkin Elmer AA100 spectrometer.

Stable isotope ratios (δ^2H and δ^{18}O) in groundwater samples were determined by isotope ratio mass spectrometry. An elemental analyzer (EA1108, CE Instruments, Italy) equipped with a high temperature furnace (Hekatech, Wegberg, Germany) and coupled to a Finnigan MAT 253 Stable Isotope Ratio Mass Spectrometer (Thermo Fisher Scientific, Bremen, Germany) were used. Details about this analytical method are described in Gemitzi et al. (2014), Gehre et al. (2004), Gehre and Strauch (2003) and Kornexl et al. (1999). The hydrogen and the oxygen isotope ratios were reported relative to international standards VSMOW (Vienna Standard Mean Ocean Water) in δ (‰) notation. The analytical precision is ± 1.8‰ for δ^2H and ± 0.26‰ for δ^{18}O.

4.2.2.2 Sediment samples

Continuous sediment cores were collected along MC1-2 profile at the Caretti site, from 0 to 60 m b.g.s. (details about the continuous coring intervals are reported in Fig. 3.8 - Chap. 3). Sediment subsamples were collected on these cores, with an averaged resolution of 2.5 m in aquifers and 0.5 m in aquitards, in order to perform high-resolution δ^2H and $\delta^{18}O$ measurements on pore water. After recovery, cores were immediately cut into 0.1 to 0.2 m long subsamples. The outer 15 mm was immediately removed to minimize contamination of the subsamples by drilling procedures. All core subsamples were placed into two labeled, double sealed, polyethylene bags in the field, in order to minimize vapor loss prior to analyses. The samples were stored in a fridge (3-5°C) before analysis. Details on the core sample collection and analytical methods are presented in Hendry and Wassenaar (2009), Stumpp and Hendry (2012) and Wassenaar et al. (2008). The δ^2H and $\delta^{18}O$ in the subsamples were measured using $H_2O_{(liquid)}$–$H_2O_{(vapor)}$ pore water equilibration and off-axis laser spectroscopy (Wassenaar et al., 2008). Equilibrium between the water in the sediment cores and the gas phase was reached after four days of exposure to dry air. The water vapor was continuously sampled in the headspace using a water vapor analyzer (Picarro L-2120i; at Helmholtz Zentrum München). This method allows both δ^2H and $\delta^{18}O$ to be measured directly on sediment cores with volumetric water contents >5%, with an accuracy of <2‰ and <0.4‰ for δ^2H and $\delta^{18}O$, respectively (Wassenaar et al., 2008). Due to interferences of the water vapor with volatile gases in the spectrum of the analyzer resulting in erroneous measurements (Hendry et al., 2011), only $\delta^{18}O$ contents were used for further data interpretation as relative errors are smaller.

$\delta^{18}O$ contents obtained by means of sediment core sampling will be mentioned as "pore water results" in the further paragraphs, in order to differentiate them from the results obtained by conventional groundwater samples.

4.2.3 End Member Mixing Analysis

End-Member Mixing Analysis (EMMA) was applied to the isotopic compositions obtained from groundwater samples in order to identify and quantify the water sources contributing to the recharge of the different aquifers.

This technique assumes that (Barthold et al., 2011): 1) groundwater is a mixture of source substances with a fixed composition; 2) the mixing process is linear and completely dependent on hydrodynamic mixing; 3) the substances used as tracers are conservative; 4) the source substances have extreme concentrations. Equation (4.1), proposed by Clark and Fritz (1997), was applied to each point, starting from both $\delta^{18}O$ and δ^2H values, in order to distinguish the different percents of recharge delivered by the two sources at the different sampling points:

$$\delta_S = X^* \delta_A + (1-X)^* \delta_B \tag{4.1}$$

where δ represents the isotopic ratio relative to oxygen or hydrogen, S stands for the sample, A and B are the two considered end-members and X is the contribution to the sample S from the end-member A relative to the end-member B. The selection of the end-members will be discussed in Paragraph 4.3.2.

4.2.4 Vulnerability mapping

The intensity of the signal of vertical recharge quantified by EMMA was used as a proxy of the intrinsic vulnerability of aquifers (i.e. A0, upper A1 and A1/lower A1) against surface sources of contamination**.** In order to map the intrinsic vulnerability in the study area, the percentages of recharge were interpolated, considering contributions of 100% and 0% from vertical recharge as the highest and lowest possible degree of vulnerability, respectively. The areal interpolation of percentages was possible where the sampling points showed a good spatial distribution (i.e. A1/lower A1 and A0 aquifers). Concerning upper A1 aquifer, it wasn't possible to obtain a reasonable interpolation of the percentages, due to the inadequate areal distribution of the monitoring points. In this case, general considerations on the values obtained were carried out, irrespective to a spatial interpretation. The results of the interpolation are shown and discussed in Paragraph 4.4.3.

4.3 Results

4.3.1 Chemical composition of groundwater

Chemical analyses were performed on 93 of the total amount of 111 water samples, collected during 2010, 2011, and 2013 surveys and pertaining to aquifers A0, upper A1, A1/lower A1, A2 and to the Po riverbed.

The values of Electrical Conductivity (EC, normalized at 25°C) detected in the aquifers range from 7.09 to 0.30 mS/cm, so denoting an overall high content of ions in the groundwater (Tab. 4.2). The parameter showed a general decreasing trend with depth (in agreement with the trend already observed by Rapti-Caputo and Martinelli, 2009), with the following averaged values in the three shallowest investigated aquifers: 2.98 mS/cm in A0, 1.68 mS/cm in upper A1, 0.77 mS/cm in A1/lower A1. Differently, a sharp increase of EC has been observed in the deeper aquifer A2, with an average value equal to 2.31 mS/cm, similar to the one determined for the shallowest aquifer. One sample (12.38 mS/cm), detected in A0 aquifer, has been considered an anomaly related to local human activities, as it corresponds to a sampling point located on a hot spot of contamination in the local petrochemical plant (Nijenhuis et al., 2013). This value, clearly higher than the rest of the dataset, is in agreement with the range of EC proposed by Sanders (1998) for leachate in contaminated areas.

Table 4.2: Minimum, maximum and averaged values of Electric Conductivity for the different hydrogeological bodies sampled in 2010, 2011 and 2013. The standard deviation (σ) relative to each body is reported as well. “/” stands for missing information.

hydrogeological body	n. of samples	EC max [mS/cm]	EC min [mS/cm]	EC average [mS/cm]	σ
A0	14	7.09	1.40	2.90	1.83
Upper A1	15	4.08	0.30	1.84	1.19
A1/Lower A1	36	1.69	0.37	0.77	0.30
A2	2	3.89	0.73	2.31	2.24
Riverbed	8	0.85	0.30	0.50	0.20
Q0	1	/	/	6.40	/
Upper Q1	4	4.36	1.12	3.22	1.45
Lower Q1	8	1.89	0.69	1.14	0.39
Q2	3	1.63	1.51	1.58	0.06

Major ions composition of different samples has been grouped according to hydrogeological units in the Piper diagrams (Fig. 4.2). Figure 4.2 a shows data collected in 2010 and 2011 from the regional sampling network. Figure 4.2 b contains data obtained in 2013 from the cross section at the Caretti site, when also groundwater samples from aquitards were taken and analyzed.

The samples from A2, A1/lower A1, upper A1 aquifers and the Po riverbed are concentrated on the calcium-bicarbonate pole of the diagram, showing a strong hydrochemical homogeneity (as already observed by Rapti-Caputo and Martinelli, 2009). Few outliers collected in 2013 from upper A1 are characterized by an anomalous enrichment in chloride. Samples pertaining to A0 are clearly distinct from the calcium-bicarbonate pole, showing higher values of magnesium, lower values of alkalis and a relative but not coherent enrichment in sulfate or chloride. Sulfate and chloride enrichments were previously observed in the aquifer A0 beneath the territory of Ferrara (Rapti-Caputo and Martinelli, 2009), and they were attributed to leaching from farming activities, sewers, landfills or clayey and peat-rich superficial soils (Pilla et al., 2006; Sciarra et al., 2013). The samples enriched in chloride or sulfate show systematically higher values of EC than the rest of the dataset.

The results obtained from aquitards in 2013 show hydrochemical trends similar to the overlying and underlying aquifers. In particular, Q0 shows the same enrichment in chloride observed for the shallow aquifer and relatively high values of EC. Upper Q1 aquitard is basically affine to the Q0 aquitard and A0 aquifer, with the exception of one point (corresponding with the deeper sampling point within this body) which shows a Ca-HCO$_3$ rich composition, comparable with the ones of upper A1 and lower A1 aquifers. Lower Q1 and Q2 aquitards are in the range of chemical composition of the deeper aquifers and characterized by relatively low EC. Two points in the lower Q1 aquitard, relatively enriched in sodium and potassium, suggest the presence of markedly clayey sublayers, characterized by very low permeability, at discrete depths within this aquitard.

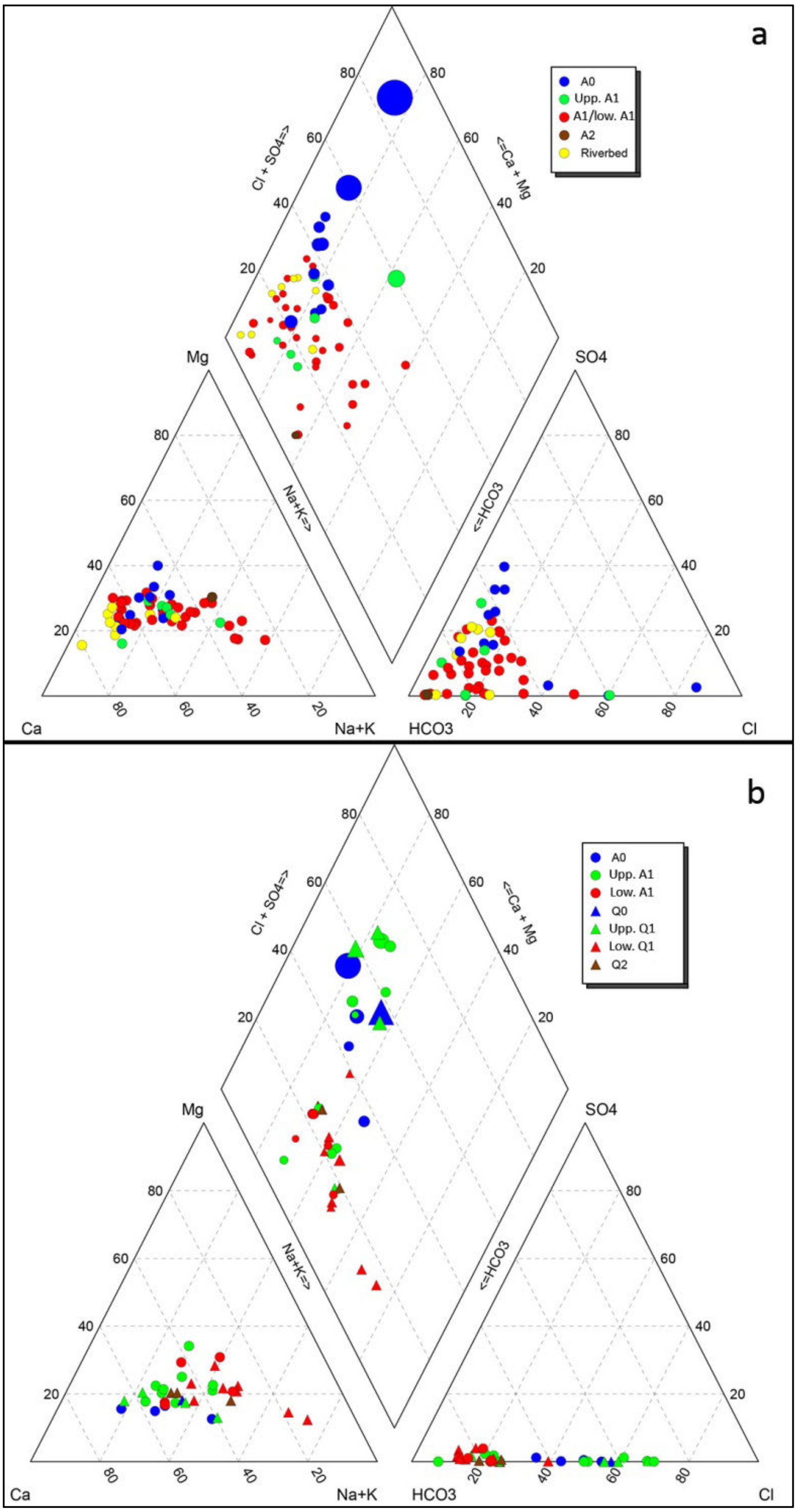

Figure 4.2: (a) Piper diagram containing the groundwater samples collected in 2010 and 2011 from the regional monitoring network of the Ferrara area; (b) Piper diagram showing the hydrochemical composition of the groundwater samples collected in aquifers and aquitards from the multilevel piezometers installed along the transect in Caretti site; the symbols in the main lozenge are sized proportionally to Electric Conductivity.

4.3.2 Groundwater stable isotopes at aquifer scale

The water isotope composition (δ^{18}O and δ^{2}H) for all the 111 groundwater samples collected in 2010, 2011 and 2013, varies between -11.32 to -7.34 ‰ and -73.8 to -42.5 ‰ for δ^{18}O and δ^{2}H, respectively. Average values and standard deviations as well as maxima and minima for each hydrogeological body are reported in Table 4.3.

Table 4.3: Minimum, maximum and averaged values of δ^{18}O and δ^{2}H for the different hydrogeological bodies sampled in 2010, 2011 and 2013, with the corresponding standard deviations (σ). The isotopic composition of the main sources of recharge at regional scale is reported as well. In bold are indicated the values selected as end-members for the mixing calculation. "/" stands for missing information.

(*)Longinelli et al., 2006; Longinelli and Selmo, 2003 (annual averages). (**)Rapti-Caputo and Martinelli, 2009. (***)Bortolami et al., 1983. (****)Martinelli et al. 2014.

hydrogeological body	**n. of samples**	**δ^{18}O min**	**δ^{18}O max**	**δ^{18}O average**	**σ δ^{18}O**	**δ^{2}H min**	**δ^{2}H max**	**δ^{2}H average**	**σ δ^{2}H**
A0	24	-8.74	-7.34	-8.13	0.37	-57.7	-42.5	-52.2	3.9
Upper A1	17	-9.89	-8.46	-9.16	0.37	-65.3	-55.9	-61.0	2.2
A1/Lower A1	43	-10.64	-8.09	-9.49	0.58	-70.1	-53.9	-63.2	4.0
A2	3	-10.46	-9.99	-10.18	0.25	-70.1	-64.2	-67.8	3.1
Riverbed	8	-10.75	-8.39	-9.57	0.81	-65.9	-58.0	-61.6	2.8
Q0	1	/	/	-8.30	/	/	/	-48.9	/
Upper Q1	4	-8.80	-8.62	-8.72	0.08	-61.8	-55.7	-58.0	2.9
Lower Q1	8	-9.74	-8.97	-9.31	0.24	-64.9	-57.9	-61.8	1.9
Q2	3	-8.80	-8.56	-8.67	0.12	-58.4	-57.1	-57.7	0.7
Rainfall END-MEMBER *	/	-8.23	-6.75	**-7.49**	/	-56.0	-42.4	**-49.2**	/
Po river END-MEMBER	1	/	/	**-10.12**	/	/	/	**-70.2**	/
Po river **	/	/	/	-9.90	/	/	/	-71.3	/
Po river ***	/	/	/	-10.00	/	/	/	/	/
Po river ****	/	-10.50	-8.90	-9.9	/	/	/	/	/
Apennines *	/	-8.50	-7.11	-8.02	/	-53.0	-41.4	-49.0	/
Alps *	/	-11.38	-8.75	-9.90	/	-88.1	-58.2	-69.0	/

The individual data fit adequately the local meteoric water line ($\delta^{2}H = 7.7\ \delta^{18}O + 9.4$) determined for northern Italy by Longinelli and Selmo (2003) (Fig. 4.3). Few points pertaining to the contaminated A0 aquifer show enrichment in δ^{2}H relative to the meteoric water line. Such enrichment in δ^{2}H can be caused by exchange of hydrogen from water with hydrogen from hydrocarbons, H_2S or by methanogenesis (Horita, 2005).

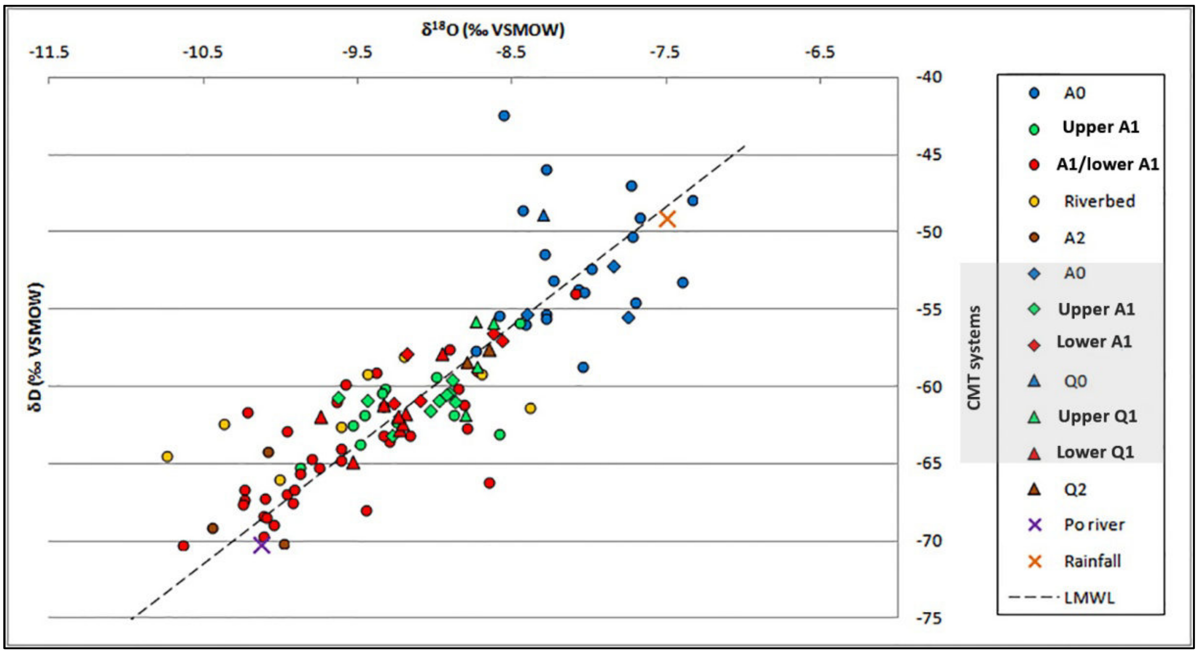

Figure 4.3: Isotopic composition of the groundwater samples collected in 2010, 2011 and 2013 from the regional monitoring network and from the CMT cross section at the Caretti site. The local representative isotopic composition of Po river and rainfall and the local meteoric water line for northern Italy (Longinelli and Selmo, 2003) are reported as well.

Almost all samples range between two end-members, which correspond to the averaged composition of local rainfall and Po river. The isotopic composition obtained from river water samples collected in 2010 was chosen as representative of the Po river end-member (-10.12‰ for $\delta^{18}O$ and -70.2‰ for $\delta^{2}H$). The values of $\delta^{18}O$ and $\delta^{2}H$ chosen as end-member are in agreement with the averaged isotopic composition of the river determined by Rapti-Caputo and Martinelli (2009), Bortolami et al. (1983) and Martinelli et al. (2014), all of which are reported in Table 4.3. The rainfall end-member was taken from the two studies conducted by Longinelli et al. (2006) and Longinelli and Selmo (2003) analyzing the isotopic content in precipitation of northern Italy. For this work, the averaged isotopic content of the station closest to the study area was chosen (Comacchio, -7.49‰ $\delta^{18}O$ and -49.2‰ $\delta^{2}H$).

A0 is clearly distinct from the other hydrogeological bodies, showing isotopic signatures closer to the rainfall end-member. The points pertaining to upper A1 are in between the ones of A0 and A1/lower A1, showing an averaged value slightly more enriched than A1/lower A1. A1/lower A1 and the riverbed are similar between each other and plot close to the Po river end-member. The similarity between these two bodies confirms the strong interconnection of the aquifer A1 with the river Po, already indicated from the chemical composition of groundwater. Few samples belonging to A1/lower A1 and to the riverbed are more depleted than the Po river end-member, relative to $\delta^{18}O$ signature (up to Δ=0.63‰). Nevertheless, taking into account the seasonal variability of the composition of the river, which can decrease to $\delta^{18}O$ values of -10.50‰ in the driest periods (Martinelli et al., 2014), the depleted points can still be considered in the range pertaining to the river. The samples collected in the A2 aquifer showed isotopic signatures as depleted as the ones of Po river (averaged differences from the river: -0.10 and +3.1‰, for $\delta^{18}O$ and $\delta^{2}H$ respectively), which may represent direct contribution from the Po river or reflect the contribution of different sources of recharge (i.e. regional groundwater flow systems originating from areas at high elevation such as Alps and Apennines; Rapti-Caputo and Martinelli, 2009).

The lack of adequate temporal series of data for the individual sampling points did not allow carrying out uncertainty estimations on the time variability of the isotopic composition of water due to seasonal effects or other fractionation processes. Nevertheless, the tracer approach selected for this work can provide recharge estimates integrating long time scale (see Par. 4.3.4), as stated already by Scanlon et al. (2002) for comparable situations.

4.3.3 Stable isotopes vertical profiling

4.3.3.1 Groundwater results

The vertical isotope pattern obtained from the multilevel cross section in Caretti site shows a trend in agreement with the averaged compositions determined at aquifer scale (Fig. 4.4).

In detail, in the upper part of the system (A0 and upper A1 aquifers), the vertical distribution of isotopic compositions matches quite well with the regional averaged values, showing only a slight enrichment at the top of upper A1, relative to $\delta^{18}O$ (Δ = 0.35‰ and 1.4‰, for $\delta^{18}O$ and $\delta^{2}H$ respectively). In the lower A1 aquifer, some differences have been identified between the vertical trend and the mean regional values: (1) correspondence between the vertical distribution and the regional average for both $\delta^{18}O$ and $\delta^{2}H$ at the top of the aquifer (33-35 m b.g.s.; Fig. 4.4); (2) more enriched $\delta^{18}O$ and $\delta^{2}H$ values in the vertical profile compared to regional values in the deeper sections (44-50 m b.g.s.), reaching values in the vertical profile equal to -8.6‰ and -56.5‰ at the bottom of the aquifer.

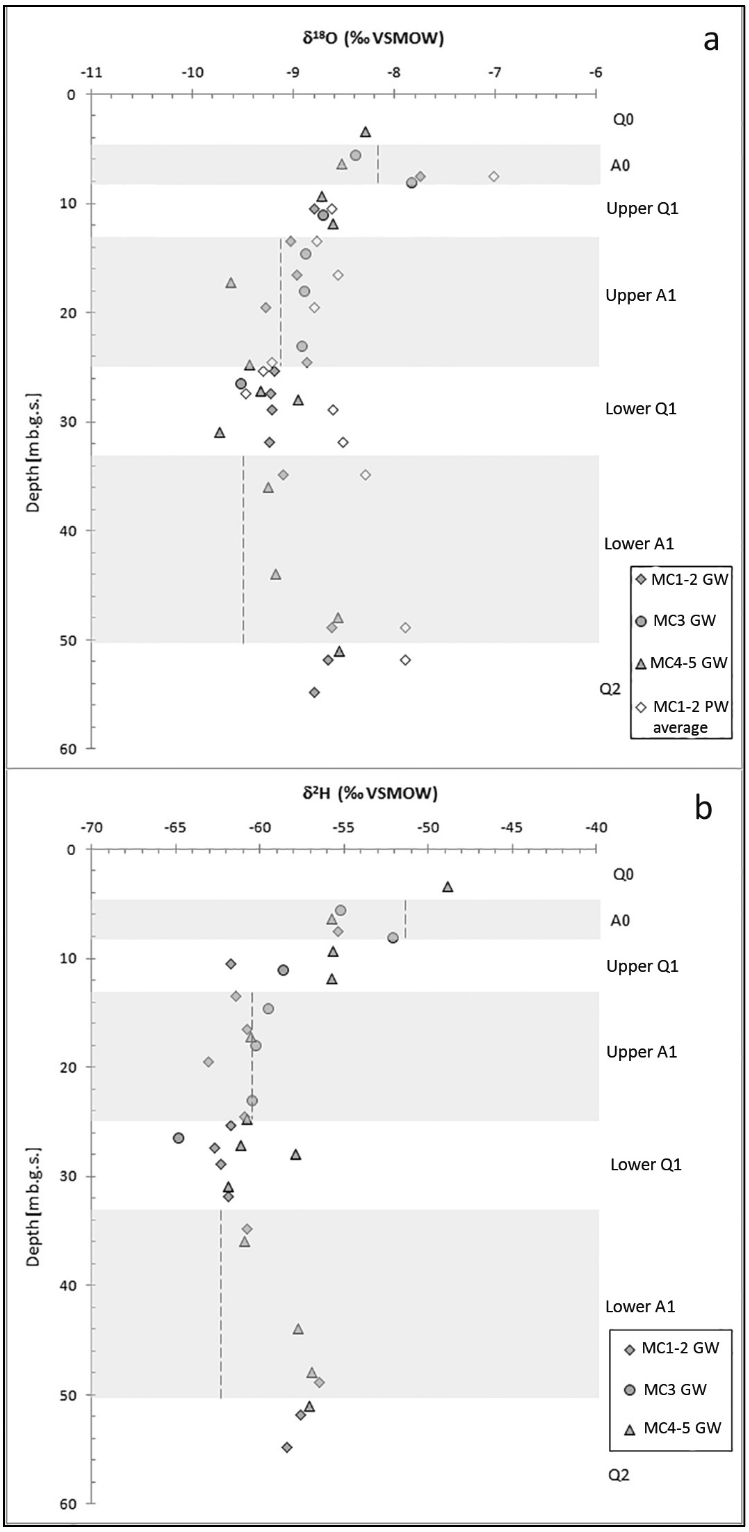

Figure 4.4: Vertical distribution of the isotopic composition of groundwater (GW; $\delta^{18}O$ and $\delta^{2}H$) and averaged pore water (PW; $\delta^{18}O$), along the three profiles of the cross section at the Caretti site. The dashed lines represent the averaged isotopic composition of the different aquifers at regional scale.

4.3.3.2 Pore water results

The general high-resolution isotopic trend obtained by pore water is in agreement with those already described for groundwater (Par. 4.3.3.1). Two main differences have been identified between the two sets of data (compared in Fig. 4.5). First, pore water samples show a sharp and well defined composition gradient within upper Q1 and lower Q1 aquitards; gradients are less pronounced in the groundwater samples. Second, a systematic enrichment of $\delta^{18}O$ can be observed in the pore water values relative to the groundwater ones (averaged Δ =0.38‰). These two differences may be related to the different spatial resolution used in the two sampling methods (i.e. groundwater and pore water sampling), or to other reasons, such as sampling of different water fractions or peculiarities of the analytical methods, which will be discussed in Paragraph 4.4.2.1.

In order to compare results from pore water and groundwater sampling campaigns independent on sampling spatial resolutions, an averaged pore water isotopic signature has been determined within each of the screened thicknesses of the multilevel system MC1-2. The averages were then compared with the groundwater samples collected at the corresponding screens. The new comparison between the two sets of data shows similar trends with depths (Fig. 4.4), so enhancing the suitability of both approaches. Although, a slight enrichment of pore water in comparison to groundwater (+0.2 to 0.7‰) is still observable and will be discussed later (see Par. 4.4.2.1).

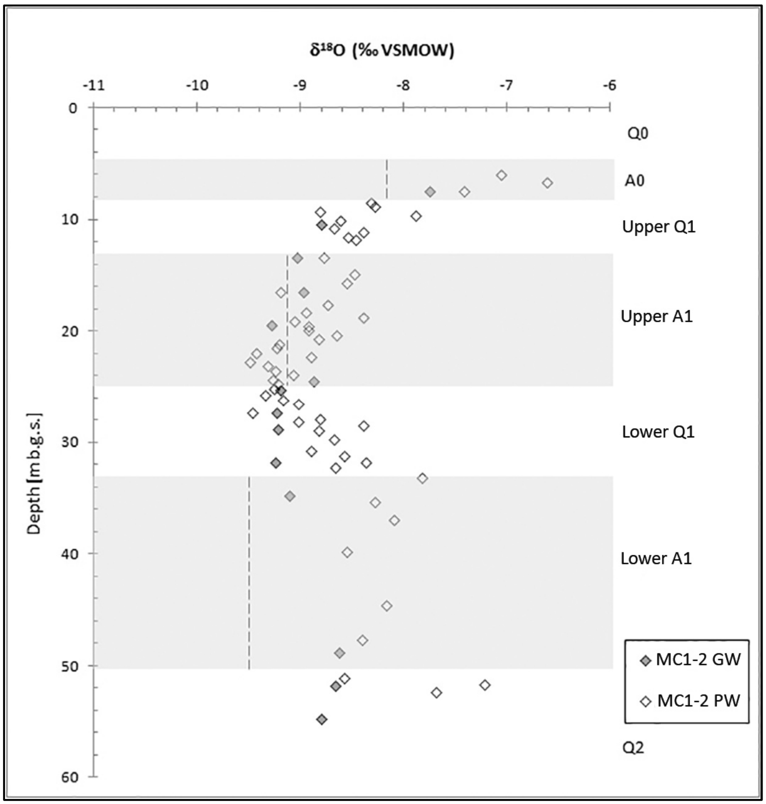

Figure 4.5: High-resolution vertical distribution of the isotopic composition in pore water (PW; $\delta^{18}O$) along the profile MC1-2 of the multilevel cross section; the composition of groundwater samples collected along the same MC1-2 profile is reported for comparison (GW; $\delta^{18}O$). The dashed lines represent the averaged isotopic composition of the different aquifers at regional scale.

4.3.4 Recharge quantification

The isotopic compositions of A0, upper A1, A1/lower A1 aquifers and of the riverbed range between the ones of Po river and local rainfall. Indeed, rainfall and Po river were already recognized in literature as the main sources of recharge for these aquifers (Molinari et al., 2007; Rapti-Caputo and Martinelli, 2009). Thus, the isotope pattern obtained from the samples collected in the Ferrara area has been interpreted as the result of mixing between these two end-members, except for few sampling points with specific conditions, already identified in the previous paragraphs.

The samples collected in the A2 aquifer are relatively more depleted (both for $\delta^{18}O$ and $\delta^{2}H$) than the ones pertaining to the shallower part of the system, even if still included in the range between Po river and rainfall. Nevertheless, based on hydrostratigraphic information (Molinari et al., 2007; Regione Emilia-Romagna and ENI-AGIP, 1998) the aquifer is more likely recharged by Alps and Apennines instead of Po river, due to its deep position in the system and its wide regional extension. Even if a local direct contribution to A2 aquifer from the river Po cannot be definitively excluded, this possible contribution remain affected by strong uncertainties. Therefore, the samples pertaining to A2 aquifer haven't been taken into account for the following elaborations, as they were considered likely unsuitable for the mixing calculation approach.

End-Member Mixing Analysis (EMMA) has been used to evaluate the contribution ratio of the local lateral (Po river) and vertical (rainfall) recharge to the three shallower aquifers of the system.

Concerning vertical recharge, it is important to state that even if the isotopic compositions of precipitation change temporally in response to rainfall history and various seasonal effects (Clark and Fritz, 1997), at the recharge areas, stable isotope composition in the groundwater is generally considered to be equivalent to the average annual weighted isotopic value of recharging water. Any deviation may be attributed to the evaporative enrichment of recharging water, water logging or climate changes (Darling and Bath, 1988; Kumar et al., 2011).

Only the points fitting with a good approximation the local meteoric water line and falling between the two end-members have been used for EMMA, excluding the anomalies already identified in Paragraph 4.3.2. The contributions quantified from $\delta^{18}O$ and $\delta^{2}H$ are consistent between each other for each sampling point (R^2=0.79 in Fig. 4.6), with 85% of the samples showing mismatches lower than 20%.

The percentages of recharge obtained by means of EMMA have been associated to the Electrical Conductivity of each sample, in order to carry out further considerations about the origin of groundwater recharge (Fig. 4.6).

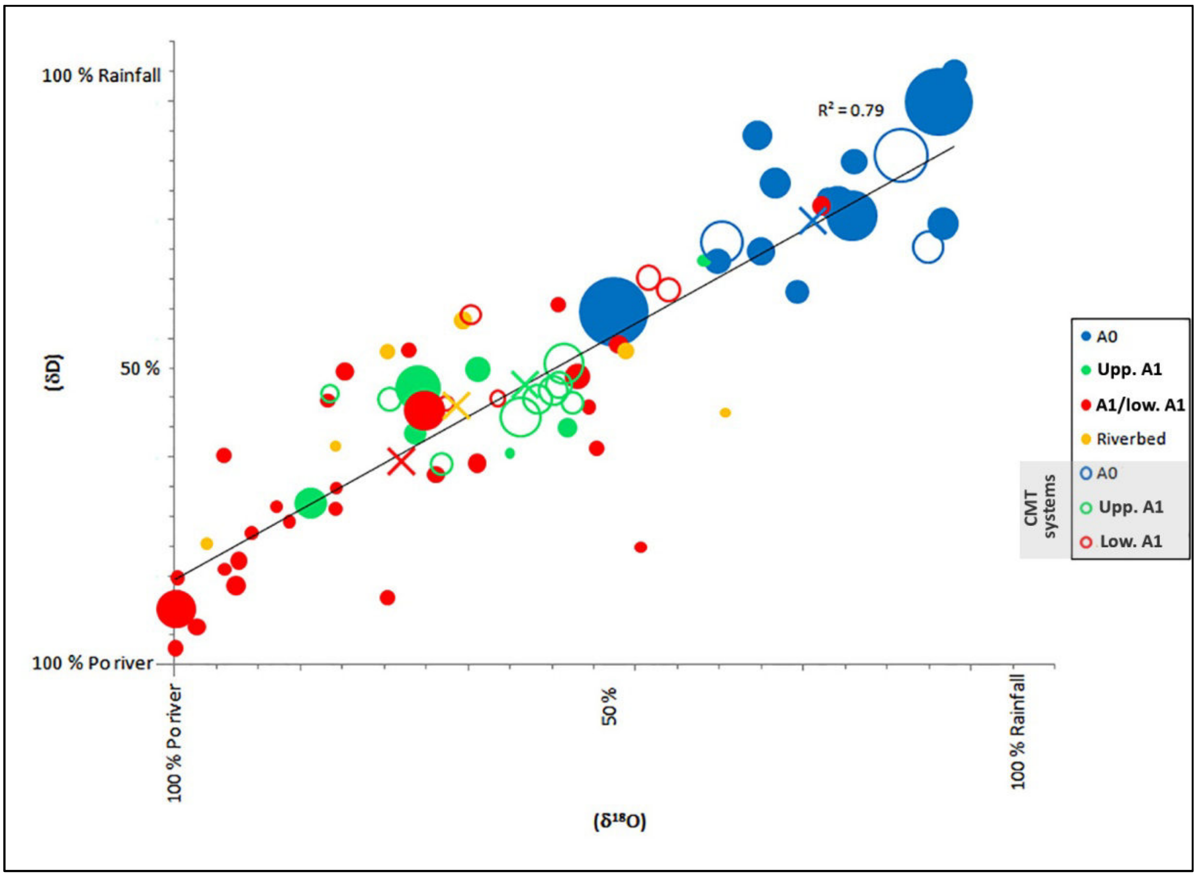

Figure 4.6: Percentages of recharge from Po river and rainfall, determined for groundwater samples collected in A0, upper A1, A1/lower A1 aquifers and in the riverbed (starting from both $\delta^{18}O$ and $\delta^{2}H$). The bubbles are sized proportionally to Electric Conductivity. The crosses represent the averaged percents of recharge for the different hydrogeological bodies.

4.4 Discussion

4.4.1 Evaluation of recharge at regional scale

The regional scale contributions from the two sources of recharge, determined for the different aquifers, meet the purely descriptive hydrogeological conceptual model inferable from literature (Molinari et al., 2007), thus confirming the suitability of the approach. On the other hand, the single samples show a variability which mirrors the local heterogeneities of the system at site scale.

Quantitatively, the application of EMMA shows that A0 aquifer is recharged mostly by local rainfall, with contributions ranging from 93 to 52%, and an averaged percent at regional scale equal to 76%. The rest of the recharge could be supplied by two distinct and more depleted sources: 1) upward leakage from the regional A1 or the local upper A1 aquifer, when these are laterally recharged by high stage events of Po river; 2) irrigation water percolating down from canal ditches networks (supplied by Po river and active only during summer time).

Upper A1 aquifer is characterized by a range of recharge percentages similar to the one determined for A1/lower A1, except for few points which show a marked contribution from direct recharge, in contrast to the averaged trend of the aquifer. This suggests the occurrence of local leakage from A0, through upper Q1. The occurrence of these localized vertical connections agrees with the marked heterogeneous nature of the fine grained cover above upper A1 aquifer (i.e. upper Q1), both in terms of thickness and grain size. The range of recharge from the Po river, determined for upper A1, varies from 84 to 37% and the average at 62% indicates that the river is a major source of recharge for this aquifer.

A1 and lower A1 aquifers are recharged by Po river from 41 to 100% with an averaged regional value of 74%. Our findings are in agreement with published results from numerical modeling estimating that 75% of total recharge comes to the aquifer A1 from Po river (Mastrocicco et al., 2014). This confirms the suitability of the presented environmental isotope approach for recharge estimation.

The samples pertaining to the riverbed show a strong affinity with A1 aquifer, endorsing once more the hypothesis of a significant connection between the aquifer and the Po river.

Some of the regional samples from A1 (C1, C2, C3, C9, C31, C32, C33 in Fig. 4.1) and also from the depth profiles (discussed in detail in Par. 4.4.2) resulted in unexpectedly enriched isotope contents (up to -8.66‰ $\delta^{18}O$ and -57.5‰ $\delta^{2}H$) which excludes the Po river as only source for this deeper aquifer. However, a contribution from vertical recharge is excluded due to the stratigraphy (Molinari et al., 2007; Regione Emilia-Romagna and ENI-AGIP, 1998) and also based on the following hydrochemical evidences: 1) the lower EC values determined for the enriched samples in comparison with the ones of the two shallower aquifers; 2) the lack of hydrochemical affinities between the enriched samples in A1/lower A1 and the ones in aquifer A0 and upper A1 with a similar isotopic composition. Furthermore, the results from the high-resolution depths profiles, discussed in detail Paragraph 4.4.2, provide an additional evidence excluding a contribution of local recharge to the A1/lower A1 aquifer. Therefore, a potential third source of groundwater contributing to the recharge of the A1/lower A1 aquifer has been identified, i.e. the alluvial fans of the Apennines foothills, located about 40 km southward from the study area. This hypothesis is corroborated by the spatial distribution of the samples enriched in $\delta^{18}O$ and $\delta^{2}H$ content, which are concentrated in the southern part of the study area. The rainfall at the alluvial fan areas has an isotopic composition similar to the one of the Ferrara area (values are reported in Tab. 4.3). A mixing between this contribution and the one of the Po river could have resulted in the enriched values detected in A1/lower A1 aquifer. Even if the occurrence of a stratigraphic connection between A1 and the Apennine alluvial fans was never mentioned in previous literature, evidences to this new interpretation are provided by piezometric information (Molinari et al., 2007), which show a northward direction of the groundwater flow in A1 (toward the river) in the southern part of the study area. The northward flow effect is also enhanced by an intense pumping activity which takes place in the north part of the study area and stressed the aquifer since the ‘60, causing modifications on the piezometric surfaces within a 10-20 km radius.

One markedly enriched water sample pertaining to A1/lower A1 aquifer was collected close to the eastern boundary of the study area (only 7.2 km far from the coast). The isotopic composition of this sample (-8.09‰ and -53.9‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively) is likely influenced by the interaction with isotope enriched sea water.

The hydrochemical composition of water confirms the hydrogeological relationships between aquifers observed by means of isotopic data (Fig. 4.2 a and 4.2 b). In particular, A0 shows a markedly differentiated hydrochemical signature, due to an alternated enrichment in chloride or sulfate (already discussed in Par. 4.3.1), always connected with high values of EC, regardless of the occurrence of contamination related to human activities. A1/lower A1 and upper A1 aquifers show a marked hydrochemical affinity, both hosting calcium-bicarbonate rich groundwater, with few anomalies for upper A1, which in some instances is shifted to the sulfate-chloride rich facies, due to the leakage from the above A0 aquifer.

4.4.2 Comparison between recharge at regional and point scale

The vertical isotopic and hydrochemical distributions obtained along the three profiles of the cross section (Fig. 4.7 a) allow to interpret some of the anomalies observed at regional scale. Concerning upper A1 aquifer, there is a correspondence between the enrichment in $\delta^{18}O$ observed in some sections, in the majority located at the top of the aquifer, and the scattered hydrochemical affinities with A0 (see Piper diagram in Fig. 4.2 b). The EC trend determined along the three profiles (Fig. 4.7 b) shows higher values at the top of this aquifer in respect to the bottom (Δ = 2.73 mS/cm), indicating that upper A1 is not well mixed. The hydrochemical composition of upper Q1 aquitard shows a strong affinity with A0 aquifer. All the evidences listed above support the occurrence of a local leakage from A0 to upper A1 aquifer, mostly arising in the upper part of the aquifer, whereas in the middle and bottom part of the body the influence of lateral recharge prevails.

Concerning lower A1 aquifer, a clear vertical trend of recharge can be identified both for $\delta^{18}O$ and $\delta^{2}H$ signatures. At the top of the aquifer the isotopic values reveal a main recharge contribution from the Po river, while an increasing influence from more enriched sources is observed going to the bottom. The EC trend is in agreement with the isotopic data, showing the same regular enrichment from the top to the bottom of lower A1 aquifer. The lack of hydrochemical affinity of lower A1 aquifer and lower Q1 aquitard with A0 aquifer, together with the evidences described above, allow excluding the occurrence of a significant contribution of direct recharge to lower A1. Furthermore, the smooth decrease in EC (Fig. 4.7 b) and the increase in isotope content in aquitard lower Q1, clearly shown by pore water results (Fig. 4.5), indicate diffusion controlled flow conditions (Hendry and Wassenaar, 1999) excluding once more a direct connection between upper A1 and lower A1.

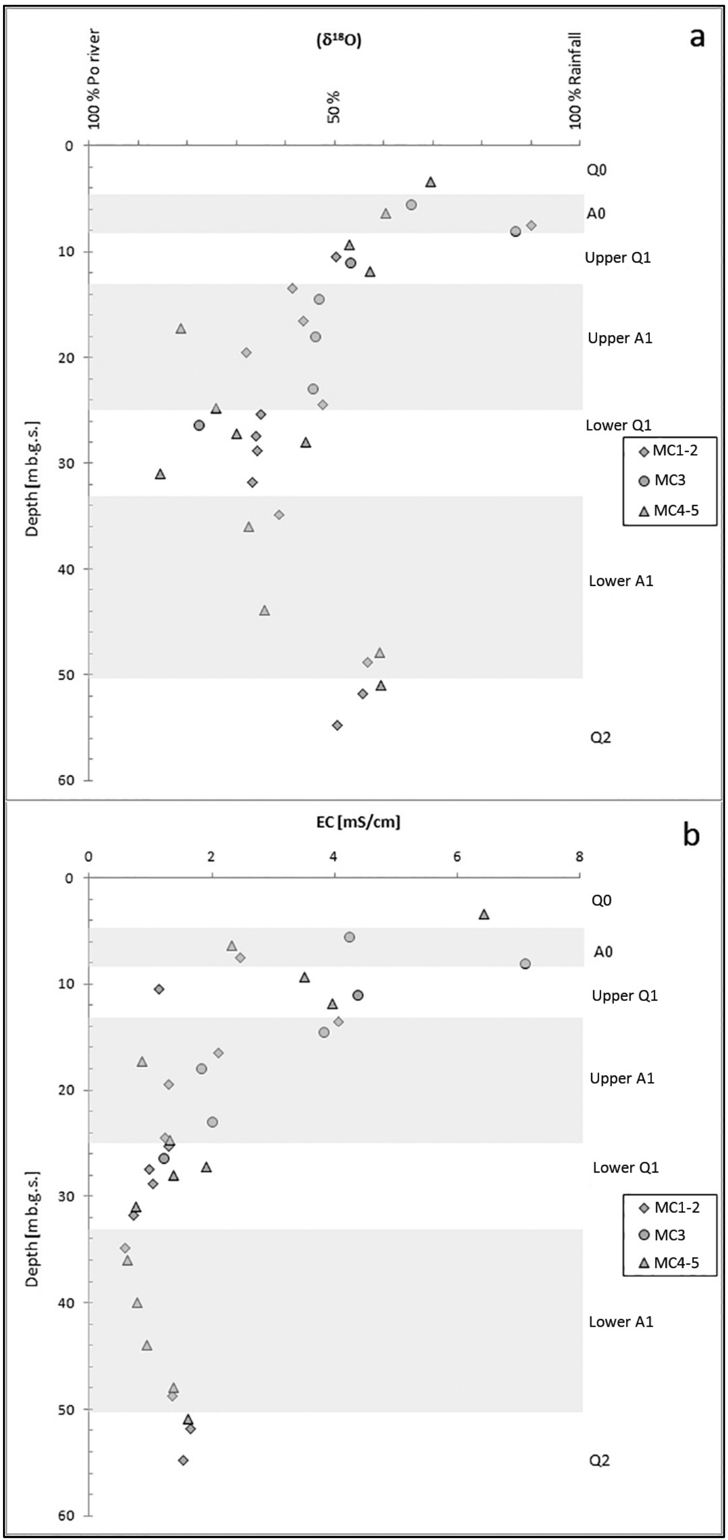

Figure 4.7: Vertical distribution of the percentages of recharge relative to $\delta^{18}O$ (a), and the EC values (b), obtained from groundwater samples collected along the three profiles of the multilevel cross section at the Caretti site.

The vertical isotopic distribution observed in lower A1 suggests the occurrence of a sort of layered delivery of lateral recharge to this aquifer, with a marked contribution of the Po river in the upper part of the aquifer and a supply from a different source in the lower part. This corroborates the hypothesis of a contribution of recharge coming to A1/lower A1 from the Apennines alluvial fans, already discussed in Paragraph 4.4.1.

4.4.2.1 Comparison between groundwater and pore water vertical profiling

The vertical trends of $\delta^{18}O$ obtained from groundwater and pore water show a general congruence, even if a persistent enrichment in $\delta^{18}O$ has been identified for the pore water, with a shift ranging from 0.2 to 0.7 ‰ relative to groundwater samples.

One reason for the discrepancies is that different water fractions were sampled with these two methods: mobile water (groundwater samples) and total water fractions (pore water samples). More specifically, liquid samples pumped from several different sampling screens of the multilevel systems represent the mobile groundwater freely flowing by gravity. As a consequence, water from layers with high hydraulic conductivity is overrepresented compared to low hydraulic conductivity layers in such heterogeneous hydrogeological system. Instead, the pore water analysis of the sediment core samples represents the isotopic composition of the total water (mobile and immobile; i.e. held by gravity, capillary forces and pellicular water) along one profile of the network with high resolution and across the entire hydrogeological system (vadose zone, aquifers, aquitards). The small differences between groundwater and pore water can also be caused by fractionation processes of the novel method itself. Recent findings indicated that the procedure for reaching the water-vapor equilibrium (Gralher and Stumpp, 2014) or bio-physico-chemical activities (Hissler et al., 2014) can result in fractionation processes. Nevertheless, the differences of the absolute values are small not contradicting the main findings, and the relative changes of the depth profile are of main importance for this study, clearly indicating differences in vertical or lateral connectivity within the profile.

4.4.3 Assessment of the intrinsic vulnerability

The percentages of vertical recharge of A1/lower A1 and A0 aquifers have been interpolated in order to use the recharge pattern as an indicator of intrinsic vulnerability to surface sources of contamination (Fig. 4.8). Indeed, the quantification of vertical recharge represents a physically based indicator of the degree of connection of the aquifer with the surface. The map relative to A1/lower A1 aquifer (Fig. 4.8 a) shows a general low degree of vulnerability (1 to 30%), with a slight relative increase toward the southern part (up to 60%). This increase of vulnerability turns out to be illusory, taking into account the hypothesis of recharge contribution from the Apennine alluvial fans in the southern area. Indeed the apparent increase of vulnerability is caused by the contribution from another lateral, and not vertical, source of recharge.

The evaluation of A0 aquifer (Fig. 4.8 b) was affected by a limited coverage of the area, due to the inadequate spatial distribution of sampling points. Nonetheless, the high degree of vulnerability to surface sources of contamination is clearly shown in the area covered by the interpolation.

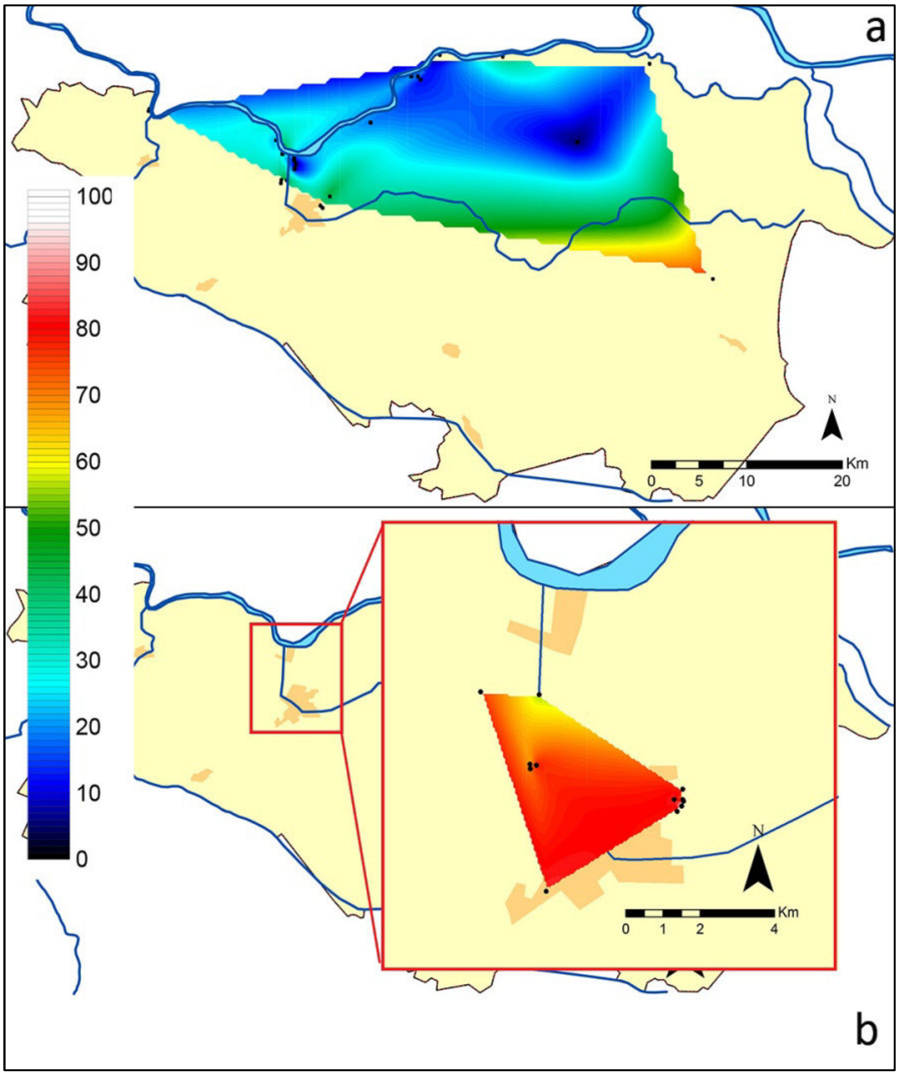

Figure 4.8: Map of the intrinsic vulnerability to surface sources of contamination, relative to the aquifers A1/lower A1 (a) and A0 (b). 100% of vertical recharge indicates 100% of intrinsic vulnerability, while 0% corresponds to 0% vulnerability. The black dots localize the samples used for the interpolation of percentages of recharge, which was carried out using the Natural Neighborhood interpolation algorithm.

Concerning upper A1, only general considerations have been carried out about the information on vulnerability provided by percentages of recharge. The aquifer isn't considered poorly vulnerable to surface contamination, even if the 90% of the points are below the 50% contribution from vertical recharge. Indeed, few enriched anomalies (indicators of high vulnerability) have been identified at regional scale, likely reflecting the occurrence of local connections between upper A1 and A0. Further, the vertical isotopic and hydrochemical patterns obtained via multilevel piezometers prove the possible occurrence of this vertical connection throughout upper Q1 aquitard. The comparison between regional and vertical surveys reveals that the hydrochemical and isotopic results obtained from long-screen piezometers could veil the signal coming to this aquifer from direct recharge, indeed clearly detectable by means of a vertical multi-port sampling.

The determination of intrinsic vulnerability based on the pattern of vertical recharge is an example of physically based and objective assessment method (as defined by National Research Council, 1993), as it takes into account the physical process of flow and transport (Focazio et al., 2002), in this case traced by means of environmental isotopes.

4.5 Summary and Conclusions

A quantitative method to estimate the percentages of recharge delivered to different aquifers from distinct vertical and lateral sources was applied in a multi-aquifer system, characterized by hydrogeological features common to other alluvial settings: the sandy lenticular to tabular aquifers are separated by low permeability silty-clayey aquitards, with a variable amount of leakage occurring between the different hydrogeological bodies. Environmental isotopes were used as tracers in order to quantify recharge, following a dual scale investigation approach, either regional, based on traditional groundwater sampling from preexisting boreholes, and at site scale, based on a detailed vertical profiling of the whole hydrogeological series of aquifers and aquitards.

The approach was validated by the comparison between the results obtained at the two different scales of investigation and hydrochemical information. The method was able to provide valuable information about the averaged behavior of the system on a long time scale, although it did not identify short time scale recharge events.

Moreover, the quantification of recharge via the use of environmental tracers represented a proxy to evaluate the degree of interconnection between the aquifers and the ground surface, expressed as the relative contribution from rainfall to the different aquifers. The vertical recharge pattern was used as a valuable parameter to assess the intrinsic vulnerability to surface sources of contamination. With such a method the vulnerability was expressed and quantified in a physically based way, being independent from the subjectivity of traditional parametric methods.

The site-scale vertical profiling along the whole sequence of aquifers and aquitards turned out to be very effective in order to evaluate the actual hydraulic interconnections between different hydrogeological bodies.

The intense exploitation of groundwater typical of strongly urbanized lowlands, carried on mainly for tap water supply or irrigation purposes, makes such kind of quantification essential both for modeling issues and for considerations related to the vulnerability of the exploited groundwater. Concerning numerical modeling, the approach here presented can provide for the lack of input information about aquifer recharge contributions in complex multilayered systems.

Therefore, the combination of environmental tracers at regional and multi-level high resolution site scale have been proven to be an effective tool for the evaluation of recharge and intrinsic vulnerability in a quantitative physically-based way.

CHAPTER 5

Detailed vertical profiling in order to assess aquitards integrity against migration of chlorinated solvent DNAPLs and solute phase in a complex alluvial setting[2]

5.1 Introduction

Aquitards help protect the quality of groundwater hosted in the underlying aquifers. The degree of this protection depends on many factors, including contaminant type, hydrogeologic setting and flow system dynamics. As already mentioned in Chapter 2, "Aquitard integrity" refers to the capability of an aquitard to provide protection to an underlying aquifer (Cherry et al., 2006). Prior to two decades ago, the assumption was commonly accepted that all clayey or silty aquitards would prevent contamination of underlying aquifers from surface sources. In recent years, however, contamination is often found in confined aquifers, and is attributed to preferential pathways such as open fractures, root holes, stratigraphic windows or unsealed boreholes. These contaminant occurrences often involve chlorinated solvents that entered the subsurface as dense non-aqueous phase liquids (DNAPLs; Parker et al., 2004). Indeed, due to their peculiar physico-chemical properties, DNAPLs (e.g. chlorinated solvents) are inclined to travel much faster through fractured or markedly heterogeneous aquitards than dissolved contaminants, which are strongly retarded due to sorption and mass transfer into the aquitard matrix by diffusion.

Fractures in aquitards can originate through many geologic processes, which may operate when the aquitard material is deposited or after deposition due to weathering effects or stress changes. It is reliable to assume that the most part of clayey deposits developed a certain degree of fracturing during their geological history. However, the presence of open fractures can be extremely difficult to determine during field assessments (e.g. Cherry et al., 1989). Kueper and McWhorter (1991), McWhorter and Kueper (1996) and O'Hara et al. (2000) demonstrated that, differently from dissolved contaminants, DNAPLs have an exceptional propensity to enter very small fractures, even those with apertures smaller than 10 μm (see Chap. 2 for wider discussion). Another factor that can decrease the capability of aquitards to protect the underlying aquifers against DNAPL is the presence of small-scale lithologic heterogeneities. This plays a significant role in unconsolidated fluvial settings, where clay-rich aquitards can locally show cm to mm sand intercalations, depending on the paleo-environmental

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conditions in which the deposition of sediments took place. These conductivity beds and occasional vertical interconnections can create a stair-step pattern of preferential flowpaths for DNAPL flow (Morrison et al., 1998). Therefore, until strong evidence is obtained to the contrary, it is prudent to assume that DNAPLs can penetrate into or through most types of aquitards due to natural preferential pathways, even those with very low bulk hydraulic conductivity (Parker et al., 2004).

An evidence suggesting that DNAPLs have migrated through many aquitards is that volatile organic compounds (VOCs), such as chlorinated aliphatic hydrocarbons, were commonly detected in aquifers formerly believed to be well protected by overlying aquitards. In some of the cases, these VOCs occurred without the presence of other contaminant types, such as chloride or nitrate or atmosphere-derived tritium, originating only in aqueous form and never as DNAPL (McIelwain et al., 1989; PPG Industries, 1995). Although deep penetration of DNAPL in fractured aquitards has been documented at several sites, intensive field studies also showed some aquitards as capable of preventing DNAPL penetration and others allowing partial but not full penetration (Morrison et al., 1998; Parker et al., 2004; Roberts et al., 1982; Schwartz et al., 1982). Thus, some aquitards were proven to have excellent integrity even when DNAPLs were the contaminant source. Nevertheless, the existing literature concerning the migration of DNAPLs through permeability barriers is mainly focused on hard rock aquitards. Differently, very few cases exist which analyze the capability of unconsolidated aquitards to protect the underlying aquifers against DNAPLs (e.g. Parker et al., 2004).

As already mentioned in Chap. 2, in situations where DNAPL phase rests on top of a low-permeability aquitard where no preferential pathways exist, dissolved contaminants from the DNAPL diffuse into the aquitard (Parker et al., 2004). In such cases, the shape of diffusion profiles which originate at the top of the aquitards can provide very useful information in order to reconstruct the evolution of the contamination since its first release in the system.

The most useful information in order to assess aquitard integrity, both against DNAPLs and dissolved contaminants, are usually represented by internal data, such as hydraulic head measurements or water samples collected from piezometers situated inside the aquitard. External measurements, such as hydraulic heads in aquifers above and below an aquitard, provide only indirect evidences of the aquitard performances (Cherry et al., 2006).

While in the case studies cited above the investigated setting is generally limited to a single aquitard expected to protect the shallower (and often the unique) underlying confined aquifer, in this Chapter an unconsolidated alluvial multilayered aquifer system will be investigated (eastern Po plain, northern Italy). The DNAPLs crossed the investigated system down to at least 53 m b.g.s., passing through three aquifers and two silty-clayey aquitards characterized by different physico-chemical features. The investigation has been carried out in a contaminated test-site (the Caretti site) where industrial wastes from the production of chloromethanes were illegally stored in a local dump (known as the Southern Dump), four to five decades ago (see Chap. 2 for details about the origin of the contamination at the site). The contamination at the Southern Dump is mostly composed by chlorinated ethenes, which originally migrated down through the multilayered system in the shape of DNAPLs. Several types of hydrogeologic data have been collected along a cross section disposed on a peripheral fringe of the Southern Dump (see Chap. 3 for the description of the cross section). In particular, concentration profiles obtained from groundwater and sediment core subsampling, hydrochemistry of groundwater, hydraulic head distribution and detailed stratigraphic information have been collected along the sequence of aquifers and aquitards (i.e. from the ground surface down to 60 m b.g.s.).

The specific objectives of the study presented in this Chapter are: (1) to evaluate the integrity of local aquitards against DNAPLs and dissolved contaminants, through the whole hydrogeological sequence interested by the contamination; (2) to deepen the knowledge about the behavior of DNAPLs in unconsolidated alluvial systems; (3) to identify the most useful information, among the ones generally exploited in hydrogeological investigations, in order to predict the fate of DNAPLs in this type of setting.

Many of the geologic features of the investigated system are common to several alluvial lowlands around the world. Thus, the results obtained by this study are potentially relevant for the characterization of many other alluvial plains currently affected by DNAPL contamination.

5.2 Materials and methods

5.2.1 Extension of the study area and scheme of data collected

The investigations presented in this Chapter have been performed at the Caretti site, and in particular along the monitoring cross section disposed on a fringe of the Southern Dump (already described in Chapter 3; Fig. 3.8). The investigated aquifers and aquitards correspond with the ones intercepted by the monitoring cross section (i.e. A0, upper A1 and lower A1 aquifers, and the interposed Q0, upper Q1 and lower Q1 aquitards).

The continuous coring performed on the three profiles of the cross section (MC1-2, MC3 and MC4-5) allowed to collect very detailed stratigraphic information (described in Par. 5.3.1). In particular, the following data have been collected for stratigraphic reconstruction: lithologic description down to the cm scale, grain size analyses on aquifers and aquitards, vertical distribution of estimated total porosity and organic carbon content. Also, pocket penetrometer tests were performed on mainly clayey layers. The results from a piezocone penetration test (CPTU) performed by the municipality of Ferrara in 2010, 30 m deep and located 50 m southeastward from the monitoring cross section, have been used in order to integrate the geotechnical properties of the fine grained layers.

Several core subsamples were collected from the cores, in order to perform contaminant concentration analyses and to determine the physico-chemical properties of sediments.

The Five multilevel monitoring systems (CMT; see Chap. 3) installed along the cross section allowed to collect groundwater samples for the analysis of contaminants and hydrogeochemistry, and to monitor hydraulic heads over time.

5.2.2 Sediment core subsampling

Cores collected along the eastern profile of the cross section (MC4-5; Fig. 3.8 - Chap. 3) were subsampled during July 2013, for quantitative laboratory analysis of VOCs and for the determination of the physico-chemical properties of sediments. The MC4-5 profile was selected to perform the sediment core subsampling for VOC analyses as it was expected to be the most contaminated deep profile (i.e. 60 m b.g.s.) of the cross section, based on the results of previous characterizations of the Caretti site (Gargini et al., 2011; Nijenhuis et al., 2013). The subsampling procedure is described in detail by Parker et al. (2003). Briefly, cores were recovered inside 12 cm diameter PVC tubes 1.5 m long, and placed horizontally in a wooden holder. They were then split in half from end to end, using a circular saw (for the PVC tubing) and a wire (for the core material). The half core chosen for sampling was covered with aluminum foils in order to minimize volatilization of VOCs and moisture losses. The other half was used for stratigraphic reconstruction. Core subsamples were collected by means of small cylindrical stainless-steel samplers (12 mm inner diameter), with an averaged vertical spacing of 20 cm. Possible cross-contamination was minimized by avoiding to advance the sampler down to the core edge and by decontamination of samplers between each sampling depth by using a three-steps wash and rinse sequence with soapy water, methanol and deionized water.

Two subsamples were collected at 297 sampling depths for the purposes of this Chapter, one for VOC analyses and the other one to determine sediment properties (estimated total porosity and organic carbon fraction-f_{oc}). The samples for VOC analysis were extruded into a preweighted 25 mL glass VOA (Volatile Organic Analysis) vial, containing a known volume of HPLC-grade methanol (around 15 mL) for preservation and VOC extraction. The samples for sediment properties were collected in preweighted 20 mL scintillation vials.

All the samples were stored at 2 to 4 °C prior to the shipment to the laboratory.

Bigger sediment samples (around 250 g each) were collected at metric resolution from the cores recovered along profiles MC1-2 and MC3, in order to analyze the grain size distributions of aquifers and aquitards.

5.2.3 Hydraulic heads and groundwater samples from multilevel systems

Hydraulic heads were monitored manually twice a week along the CMT cross section (Fig. 3.8 - Chap. 3), from August 14th 2013 to July 28th 2014, so covering an entire hydrologic year (348 days). At the same time, a continuous monitoring of hydraulic heads was performed in three preexisting long-screen piezometers located in the vicinity of the cross section, during the same 348 days (see the location of the three piezometers in Fig. 3.8 - Chap. 3). The three piezometers, each of which screened along one of the three investigated aquifers, were equipped with Diver water level sensors (Schlumberger©) for the continuous measurement of heads (measurements every 30 min). The results collected with the Diver sensors were used to validate and integrate the manual measurements performed in the CMTs. Furthermore, the monthly trends of the two main local sources of groundwater recharge (i.e. amount of rainfall and Po river hydrometric levels), were obtained from the hydro-climatic monitoring network of ARPA Emilia-Romagna (local regional environmental authority), and compared with the hydraulic head trends.

Groundwater samples were collected from the 35 screens of the CMT cross section, both from aquifers and aquitards, during November 2013, in order to perform contaminant concentration analyses and to determine the hydrogeochemical composition of groundwater (this last being the same already considered in Chap. 4).

The purging and sampling operations on the multilevel systems were the same described in Chapter 4 relative to the CMT systems. In particular, for the collection of groundwater samples dedicated to contaminant concentration analysis, a dedicated Teflon tube was inserted at the bottom of each channel during sampling, in order to minimize the interferences between the contaminants and the HDPE CMT tubing (Einarson and Cherry, 2002).

Samples for hydrogeochemical analyses were collected as already described in Chapter 4.

For samples dedicated to contaminant concentration analyses, 1 L Schott bottles were completely filled with groundwater and sealed with Teflon lined screw caps.

5.2.4 Analytical techniques

Sediment samples collected for grain size distribution from aquifers were analyzed through standard sieving procedures, using sieves 20, 40, 80, 200, 230 (ASTM series); samples collected from fine grained aquitards were also subjected to sedimentation analyses for the determination of silt and clay content.

The sediment moisture content (w) was determined via the gravimetric method. The total porosity was then estimated by means of the relations between void ratio (e), particle density (ρ_s), water content (w) and degree of water saturation (S), assuming S=1 and ρ_s equal to 2.65 g/cm^3.

Organic Carbon content (f_{oc}) on core subsamples was determined via both Combustion/NDIR and Walkley-Black methods (Nelson and Sommers, 1996).

Sediment samples dedicated to VOC analyses were preserved in methanol and analyzed as follows: the VOA vials were shaken on a vortex mixer to break up the sediment. Samples were then stored at 4°C for two weeks to allow adequate time for extraction. The samples were then centrifuged to separate the sediment and methanol in the sample vial, and a small aliquot of methanol extracted from the sample was diluted into pentane (capillary GC grade) containing an internal standard. Further dilutions of samples into methanol were performed as necessary based on initial analysis of the undiluted sample. Standards were laboratory-prepared mixtures of the target analytes (typically PCE, TCE, DCE isomers) in methanol, which were spiked into pentane as described above for the samples. The pentane was then analyzed by direct injection on a gas chromatograph equipped with a micro-electron capture detector and a liquid autosampler. This technique provides the total analyte content per mass of wet sediment, and therefore does not distinguish between concentration present in the aqueous, sorbed and NAPL phase (Parker et al., 2003). The calculation procedures used to distinguish these three phases are presented in Paragraph 5.2.5.

Groundwater samples collected for major ions were analyzed as already described in Chapter 4.

VOC concentrations in groundwater were analyzed by a private certified laboratory, using the analytical methods "EPA 5030 C 2003" and "EPA 8260 C 2006".

5.2.5 Calculation procedure applied to Volatile Organic Compound analyses

The total sediment concentration (C_t) obtained from lab analyses on core subsamples represents the total analyte mass per unit mass of bulk wet sediment, and therefore includes dissolved mass in the pore water (C_w) and sorbed mass on the solids (C_s), as well as any DNAPL phase in the sample. This total analyte concentration can be converted to an equivalent pore water concentration (C_w) assuming equilibrium chemical partitioning between dissolved and solid phases (and no DNAPL present) using:

$$(5.1) \qquad C_w = C_t*(\delta_{bwet}/(R*\phi))$$

where C_t is the total analyte concentration in the bulk sample from lab analyses (μg/g wet sediment), δ_{bwet} is the wet bulk sediment density (g/cm^3), ϕ is the sediment porosity and R is the estimated retardation factor due to sorption that assumes rapid, linear and reversible partitioning between the VOC and the solid-phase organic C in the aquifer sediments. Presence of DNAPL is inferred for samples where the estimated pore water concentration exceeds the aqueous solubility of the contaminant (i.e. relative solubility in the mixture of compounds according Raoult's law and local temperature).

The retardation factor is estimated using the relation:

$$(5.2) \qquad R = 1 + (\delta_b/\phi)*K_d$$

Where K_d is the distribution coefficient and δ_b is the dry bulk sediment density. The distribution coefficient was estimated with the correlation $K_d = K_{oc}*f_{oc}$, using literature values for K_{oc} (e.g. Table A.1 in Pankow and Cherry, 1996), and measured f_{oc} values .

The Raoult's law, as adapted by Banerjee (1984) (5.3), was employed to assess the occurrence of pure phase DNAPL in the samples:

(5.3) $S^e_i = X_i * S_i$

Where S_i is the solubility of the pure compound I and X_i and S^e_i are, respectively, the mole fraction and effective solubility of the compound i in the mixture

Considering that the sum of mole fractions in a mixture should equal 1, the (5.3) becomes:

(5.4) $$\sum_i X_i = \sum_i \frac{S_i^e}{S_i} = 1$$

The substitution of pore water concentration (C_w; estimated by equation 1) for the effective solubility S^e_i provides a check of the occurrence of DNAPL in a sample, where a sum of the ratios (C_w / S_i) lower than 1 means no occurrence of DNAPL.

5.2.6 Analytical modeling of diffusion curves

Diffusion curves were observed for different compounds on top of lower Q1 aquitard, along MC4-5 profile (see Par. 5.3.4.2 for description). The curves were modeled in order to determine the times needed for contaminants to get to the current distribution and to detect possible changes of concentration at the source over time (i.e. aquifer-aquitard interface). An analytical solution of the Fick's Second Law (e.g. Narasimhan, 2004) for 1D vertical (z) diffusion in a homogeneous, semi-infinite porous medium (e.g. Carslaw and Jaeger, 1959) was used to simulate the curves:

(5.5) $$C_w = C_0 \times erfc\frac{z}{2\sqrt{tD_e/R}}$$

where C_w is the aqueous concentration (mg/mL), C_o is the concentration at the source boundary, R is the retardation factor representing linear, equilibrium sorption of contaminant to aquitard solids, D_e is the effective molecular diffusion coefficient (cm^2/s), z is the vertical distance (cm), with z =0 at the aquitard interface, and t is time (s).

The simulation results were expected to be representative of the diffusive aqueous migration of compounds in the aquitard with equilibrium sorption. The portion of the aquitard to be modeled was assumed to be homogeneous and the contaminant source located at the aquifer-aquitard interface. Biodegradation of parent compounds was not included in the simulation as the VOC analyses didn't show the occurrence of daughter compounds in lower Q1 aquitard (see Par. 5.3.4). Aquitard parameters were estimated based on the site-specific measurements described in Paragraph 5.3.1. The effective diffusion coefficient (D_e) was calculated using D_e=$D_o\tau$ (Gillham et al., 1984). The free-solution diffusion coefficient (D_o) was estimated from the modified Wilke-Chang correlation (Geankoplis, 2003) for aqueous compounds at 16°C (average temperature detected in groundwater). The tortuosity factor (τ) was estimated using a correlation relating apparent tortuosity with porosity:

$$\frac{D_e}{D_0} = \tau \cong \varphi^p \qquad (5.6)$$

where the exponent p varies between 1.3 and 5.4, depending on the type of porous geologic medium (Dullien, 1992). A value of 1 was assumed for p in the present study, based on the considerations carried out by Parker et al. (2004) and Parker et al. (1994).

5.3 Results

5.3.1 Stratigraphy of the cross section

The detailed stratigraphic reconstruction performed along the MC1-2, MC3 and MC4-5 geological logs is summarized in Figure 5.1. In particular, grain size distributions have been determined along MC1-2 and MC3 logs while estimated total porosity and organic carbon values are related to MC4-5 log. Pocket penetrometer measurements were performed along MC1-2 log in correspondence of the clayey layers. Regardless to the profile on which they refer, the four groups of data have been considered sufficiently representative of the whole cross section (due to the small spacing between boreholes).

The different hydrogeological units identified along the cross section are described here in sequence from top to bottom, separating aquifers from aquitards:

- A0 aquifer shows a maximum thickness of 4 m, pinching out towards the E and W margins of the section. The lenticular geometry and the limited thickness are in agreement with the A0 framework at regional scale (Molinari et al., 2007; Regione Emilia-Romagna and ENI-AGIP, 1998). Grain size is highly heterogeneous, from coarse to silty and clayey sands. These features suggest a lower degree of transmissivity for A0 in respect to the deeper aquifers;
- upper A1 aquifer displays an averaged thickness of 8 m, and a modal grain size in the range of medium sands. The unit pinches out towards the west margin of the cross section (MC1-2), thus testifying a lower degree of amalgamation between the single sandy lenses (i.e. channel bodies) in respect to lower A1, as already observed at the site scale by Gargini et al. (2011) and Nijenhuis et al. (2013).
- lower A1 aquifer is mostly made up of coarse sands and shows a markedly tabular shape (constant thickness around 18 m). This is in agreement with the geometry observed at regional scale for A1 aquifer (Molinari et al., 2007);

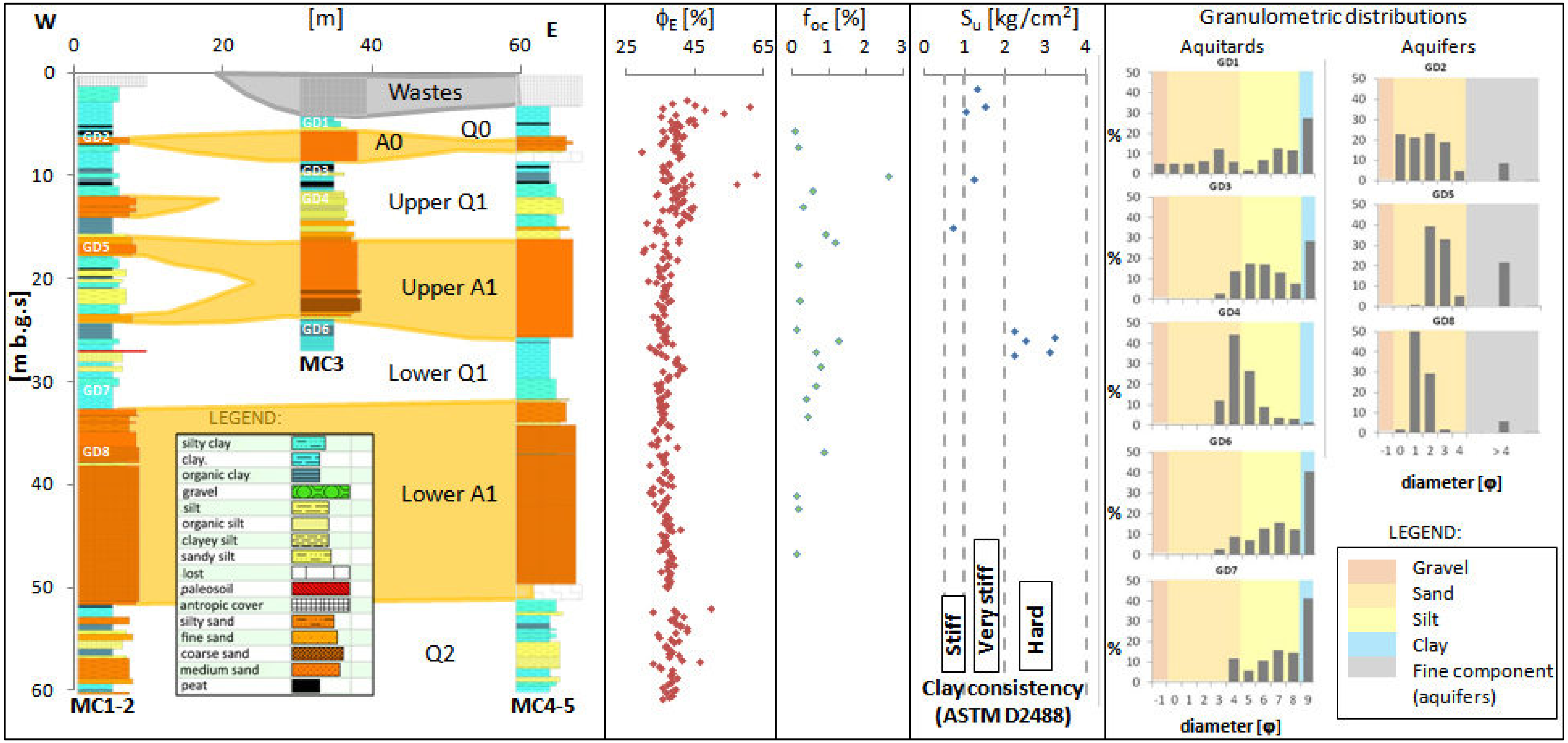


Figure 5.1: Stratigraphic information collected along the monitoring cross section. From the left are shown: the geologic logs obtained along the three profiles and the consequent geometry of aquifers and aquitards; the vertical trend of estimated total porosity (ϕ_E); the vertical trend of organic carbon content (f_{oc}); some estimations of undrained cohesion (S_u) obtained on clayey layers via pocket penetrometer tests; some representative grain size distribution of aquifers and aquitards referred to the depths indicated on the geologic logs.

- Q_0 aquitard shows a thickness of around 3 m along the cross section and the highest grain size heterogeneity, in agreement with what observed by previous investigations at the site (Gargini et al., 2011), when also remarkable local enrichments in silt and sand were identified in the aquitard. The occurrence of thin peaty layers has been observed in the eastern sector of the cross section. In the central (MC3) and eastern (MC4-5) profiles the aquitard is overlaid by a 2-3 m thick blanket of wastes, representing the fringe of the Southern Dump;
- upper Q1 aquitard shows layering at dm scale, with frequent alternation of silt, organic clay and thin (5 to 10 cm) peaty layers. It has an averaged thickness of 7 m along the section. Pocket penetrometer results showed a consistency from "stiff" to "very stiff" (ASTM D-2488 Standard) for the clayey layers located in the shallower 15 m b.g.s.. This is in agreement with the overall local enrichment in organic matter observed within this thickness and with the relatively shallow position in the log; below 15 m b.g.s. the consistency of clays increases up to "hard" (ASTM). Grain size distributions shown in Figure 5.1 well represent the vertical heterogeneity of the body;
- lower Q1 aquitard consists of an homogeneous markedly clayey layer with an averaged thickness of 10 m. Sporadic silt layering has been observed along the western sector of the profile. The pocket penetrometer denoted a "hard consistency" (ASTM) for clays.

The distribution of estimated total porosity (ϕ_E) obtained along the saturated portion of MC4-5 profile shows values in agreement with the ranges reported by Darrell (2006) for equivalent lithologies. The values remain around 36 % for the most part of the profile; slightly higher values (Δ = 4 %) have been observed from the surface down to 15 m b.g.s., reflecting the higher water content of organic-rich layers. The f_{oc} values range from 0.05 % to 2.58 %. The highest peaks have been detected within the shallower 15 m of the profile.

5.3.2 Vertical distribution of Hydraulic heads

The vertical distribution of hydraulic heads along the three profiles of the cross section shows averaged head values in aquifers equal to 2.77 m, 2.84 m and 2.70 m, for A0, upper A1 and lower A1, respectively. These values suggest an averaged upward flow direction within upper Q1 aquitard and a downward flow within lower Q1. Looking at the distribution of heads over time, the three aquifer bodies turn out to be clearly demarcated thanks to hydraulic head drops occurring within the interposed aquitards (Fig. 5.2). In particular, the main vertical head variations are localized in two layers 3 to 3.5 m thick, located within upper and lower Q1 aquitards. The entity of the head drops within the two head loss layers varies over time between 0.01 and 0.65 m. Minor vertical head variations have been detected within A0, upper A1 and lower A1 aquifers, where the main flow directions are expected to be horizontal. Furthermore, the variation of head over time shows that the vertical hydraulic gradient within upper Q1 aquitard was directed downward at the beginning of the monitoring period and inverted to upward in correspondence of days 181-185. The inversion has been interpreted as a response to changes in recharge conditions occurring in the two surrounding aquifers. Differently, lower Q1 aquitard turned out to be characterized by a constant downward gradient (i.e. from upper A1 aquifer toward lower A1).

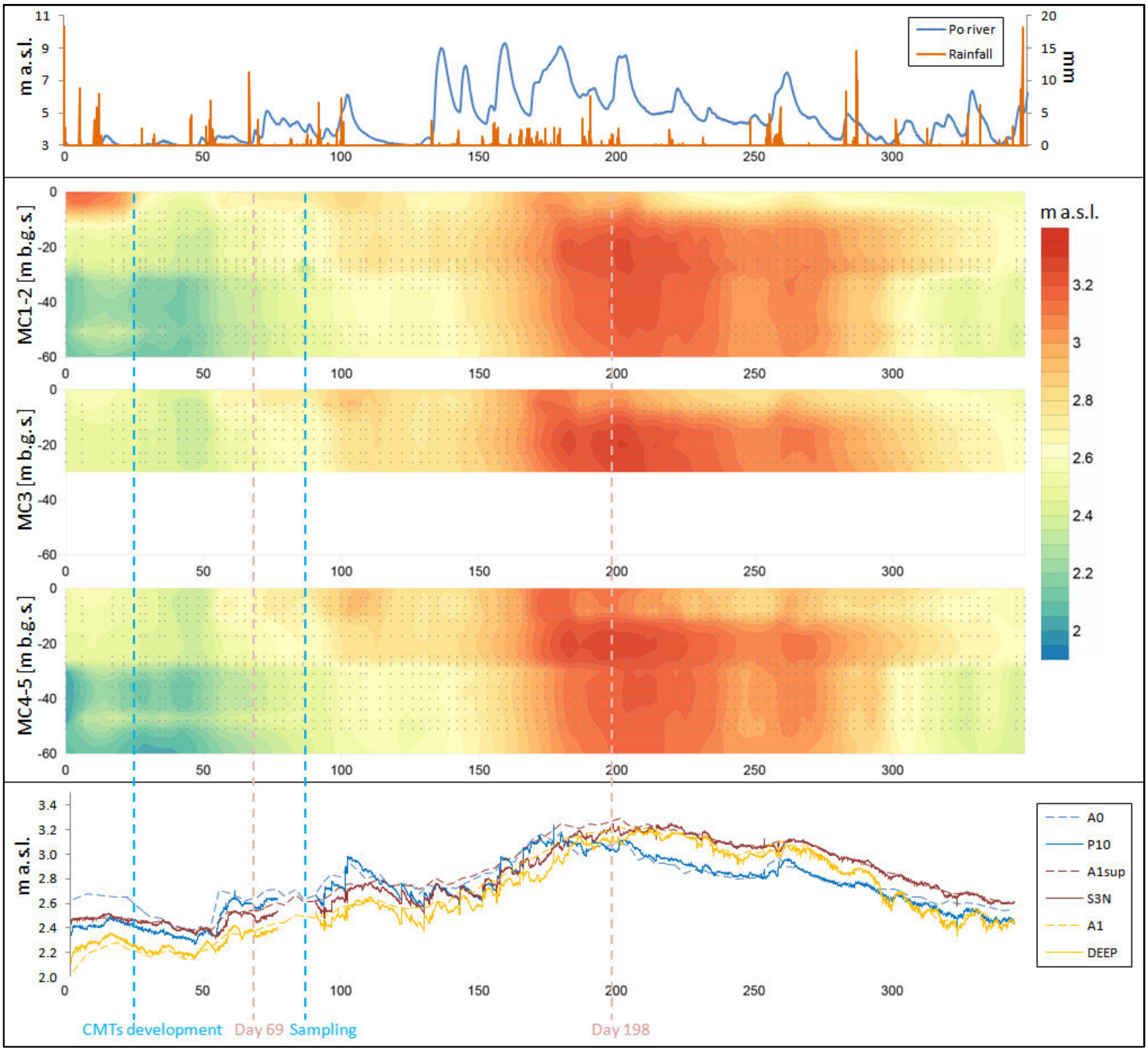


Figure 5.2: Distribution of hydraulic heads over time. From top to bottom are shown: the daily trend of rainfall and Po river stage (the two main local vertical and lateral sources of groundwater recharge); the vertical distribution of heads, measured manually from the three CMT profiles twice a week; the continuous monitoring of heads performed via pressure transducers in the three piezometers shown in Fig. 3.8 (Chap. 3). All the data were collected from 14/08/13 (monitoring day 0) to 28/07/14 (monitoring day 348). The two main hydraulic stresses applied on the CMT systems (development and sampling) are indicated in blue, while in pink are indicated the two monitoring days analyzed in Fig. 5.3.

The two single profiles in Figure 5.3 represent two extreme hydrologic conditions, corresponding with the beginning of the fall rising limb of the hydrograph (day 69) and with the winter peak recharge (day 198). In both the conditions, the main head drops in aquitards are well localized and limited within the head loss layers mentioned above (7.5 to 11 and 27.5 to 30.5 m b.g.s. for upper Q1 and lower Q1, respectively). The good overlap between the three different profiles, both in days 69 and 198, allows to exclude the occurrence of a significant horizontal hydraulic gradient along the transect, thus supporting the assumption of perpendicularity of the transect with the main flow directions in the aquifers. The gradient inversion already mentioned for upper Q1 aquitard is well recognizable from condition (a) to condition (b) (see Par. 5.4.2 for discussion).

The comparison between the vertical distribution of hydraulic heads and the pore pressure (u; kPa) obtained from a CPTU performed 50 m southeastward from the monitoring cross section (Fig. 5.3), highlights a sudden decrease of u at the same depth of the main hydraulic head drops observed in lower Q1 aquitard (see Par. 5.4.2 for discussion).

The continuous hydraulic head trends obtained via Diver water level sensors show a good correspondence with the results from the CMT transect (Fig. 5.2), thus corroborating the reliability of manual measurements. The monthly amounts of rainfall and the monthly averaged Po river stage (both reported in Fig. 5.2 for reference) can explain the inversions of gradients observed within aquitards as well as the hydraulic head pattern over time of the three aquifers. This will be widely discussed in Paragraph 5.4.2.

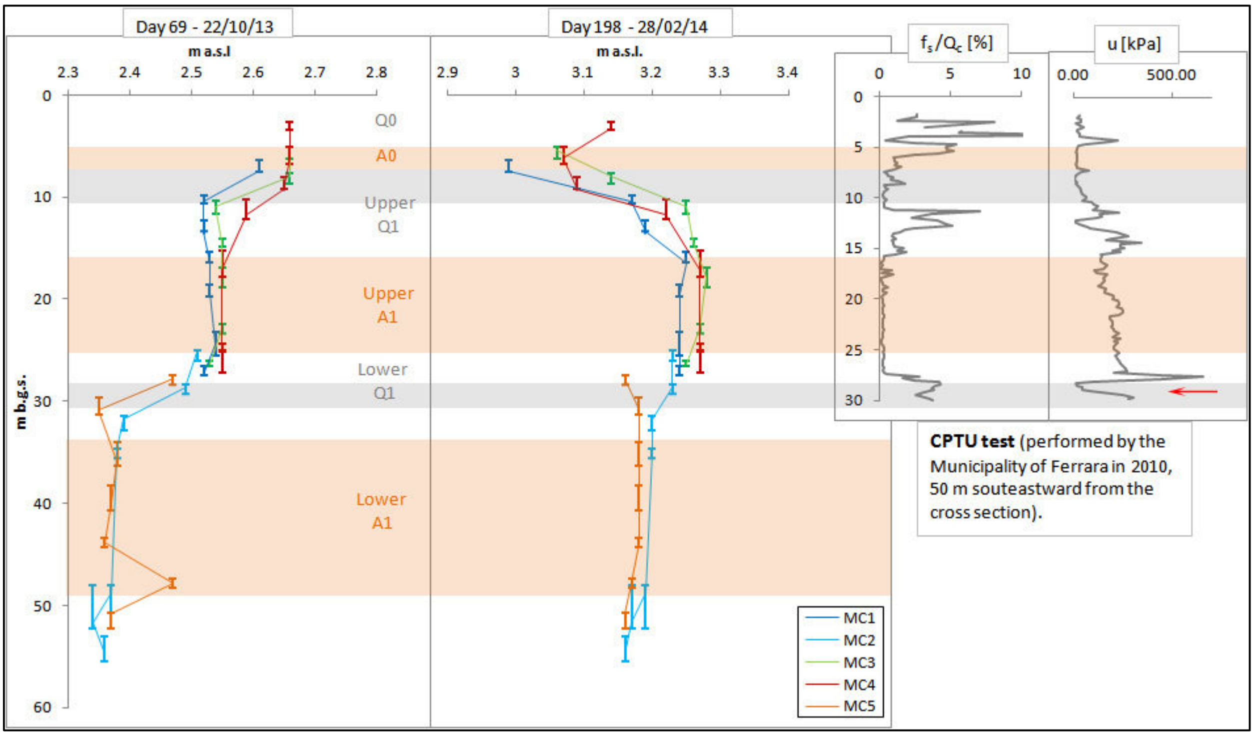


Figure 5.3: Vertical distribution of hydraulic heads along the CMT profiles, in two moments representative of extreme hydrologic conditions: the beginning of the fall rising limb of the hydrograph (day 69) and the winter peak recharge (day 198). The results of a CPTU test performed 50 m southeastward from the cross section are reported on the right. The averaged position of aquifers (as detected along the three profiles of the cross section) is indicated in pink, while in grey are highlighted the two sections of aquitards were the highest vertical hydraulic gradients are localized. It is possible to see a significant decrease of pore pressure (u; see red arrow), in correspondence of the highest hydraulic gradient zone detected in lower Q1 aquitard.

5.3.3 Vertical distribution of Hydrochemistry and parameters

The hydrogeochemistry of the investigated system is influenced at regional scale by the composition of recharge water (i.e. precipitation and Po river) and by further interactions with the stratigraphic setting described in Paragraph 5.3.1. Differently, the hydrogeochemical composition of groundwater along the monitoring cross section is expected to be strongly influenced also by the interaction with the Southern Dump. Indeed, due to its industrial and urban mixed nature, the dump represents a source of contamination for chlorinated compounds but also for potential enrichment of several major ions. In the Piper diagram (Fig. 5.4) the hydrochemical trends of aquifers and aquitards obtained from the CMT systems have been compared with the regional averaged compositions of the three investigated aquifers (i.e. A0, upper A1, lower A1), taken from Molinari et al. (2007) and from the Chapter 4 of the present thesis. In particular, the composition of groundwater collected from lower A1 aquifer falls in the calcium-bicarbonate facies, and is characterized by EC values ranging from 0.56 and 1.34 mS/cm. Groundwater hosted in upper A1 and A0 aquifers shifts gradually towards the chloride facies (sulfate showing very low concentrations), with maximum EC values of 4.01 and 7.10 mS/cm, respectively.

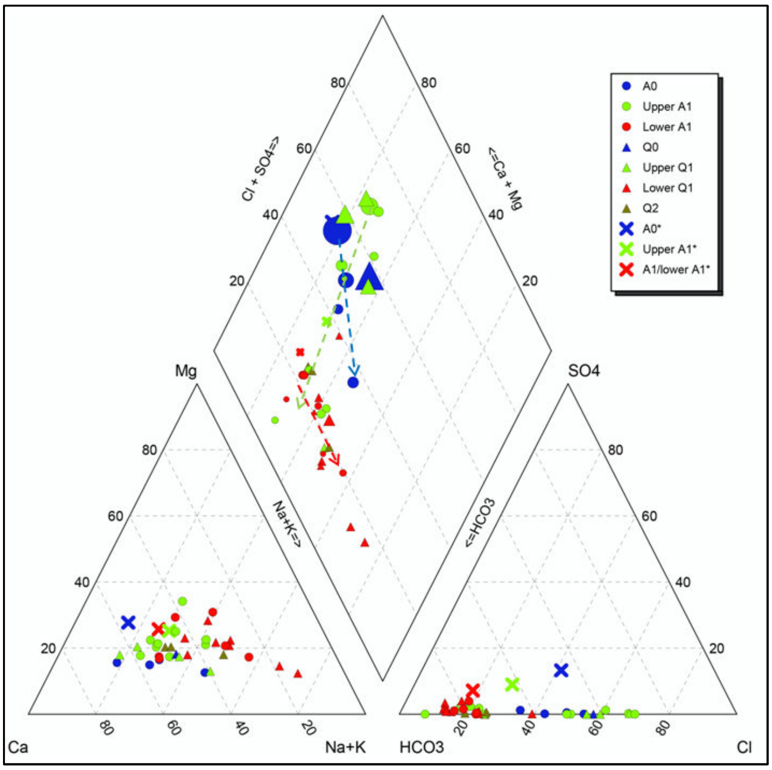


Figure 5.4: Piper diagram showing the hydrochemical composition of groundwater samples collected in the CMT systems (from aquifers and aquitards). The size of the symbols in the main lozenge is proportional to EC. The crosses indicate the regional averaged composition of the investigated aquifers (as determined in Chap 4). The dashed arrows indicate the vertical trends of ion content detected within each aquifer with increasing depth.

The averaged regional compositions of groundwater and the trends observed along the CMT systems show a general agreement in the Piper plot, thus suggesting similar proportions between different ions (as already observed in Chap. 4). However, a significant increase in EC has been observed both in upper A1 and A0, in respect to the regional averages (equal to 1.84 and 2.90 mS/cm, respectively; see Chap. 4). On the other hand, the EC of lower A1 aquifer along the cross section is in agreement with the regional trend (average of 0.77 mS/cm; see Chap. 4)

Vertical hydrochemical trends have been detected within the single aquifers (gradual change in composition with depth; arrows in Fig. 5.4). These trends suggest that groundwater is likely not well mixed within the aquifers, flowing along distinct horizontal pathways. Aquitards show hydrochemical compositions similar to the overlying and underlying aquifers (as already described in Chap. 4).

The vertical distributions of physico-chemical parameters (i.e. EC at 25°C, Eh, pH) and the trends of some of the dissolved ions (Cl, HCO_3, SO_4, F, K, Na, Ca, Mg, NH_4) measured along MC1-2, MC3 and MC4-5 profiles have been used as tracers in order to assess the effect produced by the dump leachate on groundwater (Fig. 5.5).

Concerning ions, all the trends, except for the one of SO_4, show the highest concentrations at the top of the profiles, suggesting a probable enrichment originating from the dump. Further, a common decrease of concentrations from the ground surface to the bottom of upper A1 aquifer has been observed for all the ions. This has been interpreted as the effect of mixing between the groundwater affected by the dump and uncontaminated groundwater recharge, with a downward increasing ratio of uncontaminated water on the altered one. The trends of decreasing concentration with depth are not influenced (except for K and F) by the presence of upper Q1 aquitard. Differently, lower Q1 reveals to be a very effective hydraulic barrier, below which no influence from the dump leachate has been registered on the hydrogeochemistry of groundwater. In agreement with this, the hydrochemical composition of lower A1 aquifer, as well as its electric conductivity, shows a better agreement with the averaged regional values, in comparison with the two shallower aquifers. Also the vertical trends registered for physico-chemical parameters (i.e. EC, Eh, pH) turned out to be influenced by the hydraulic barrier represented by lower Q1 aquitard, in the same way described for ions.

A substantial difference for both EC and ions concentration values has been observed between MC4-5 and MC3 profiles with the western profile MC1-2, within the shallower 30 m. Higher values have been found along MC4-5 and MC3, and they were linked with the presence of the residual thickness of wastes (2 to 3 m thick) found at the top of these two profiles. The wastes are absent above MC1-2, thus explaining the minor effect from the dump observed along this profile. A similar differentiation between the three profiles has been observed in the distribution of contaminants (described in Par. 5.3.4). This allows also to interpret the anomalous distribution of SO_4 in respect to the other ions. Indeed, this compound turned out to be more concentrated in the shallower part of MC1-2 profile, while in the more contaminated MC4-5 and MC3 profiles the ion had been likely depleted by taking part to the degradation of chlorinated compounds (Wiedemeier et al., 1998).

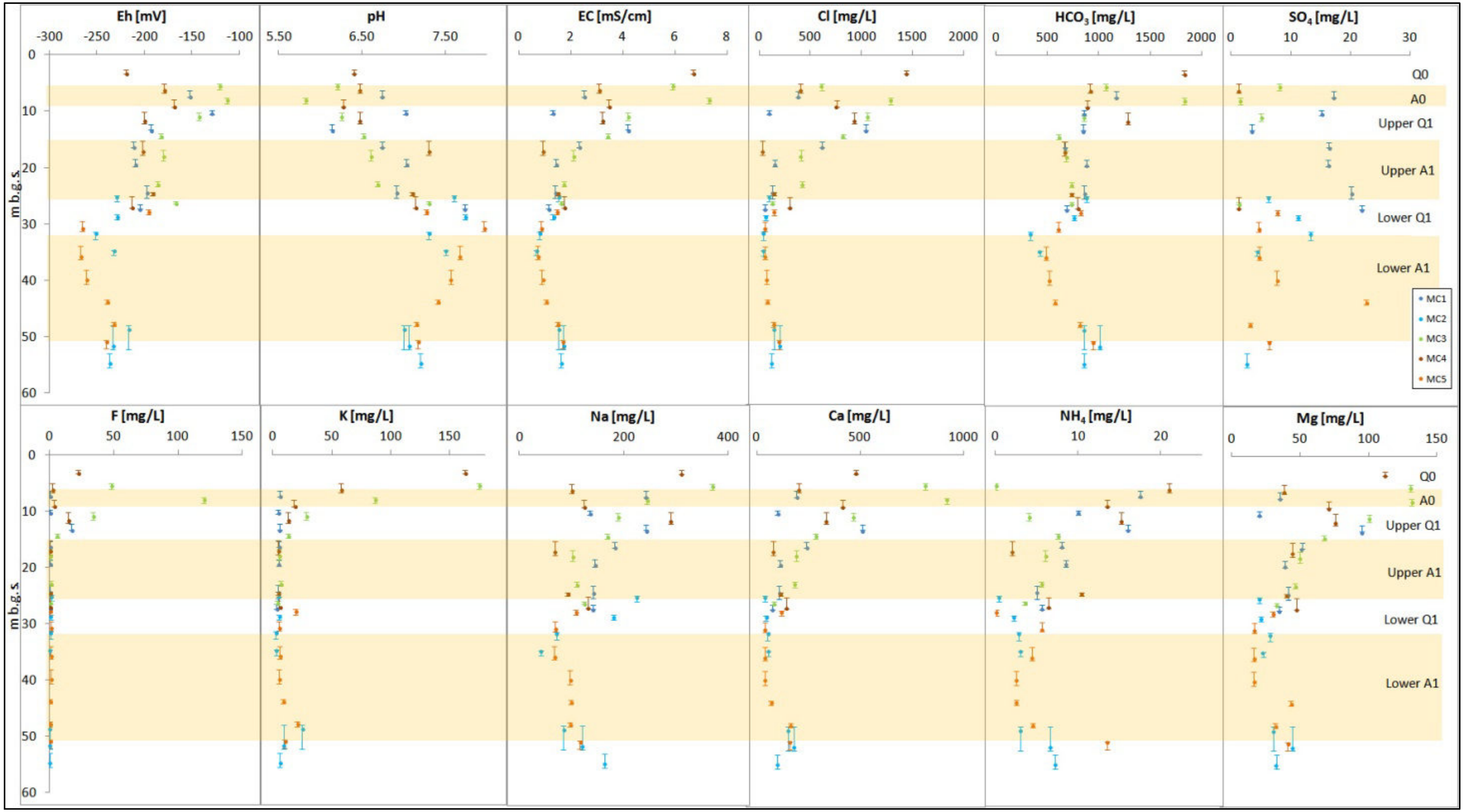


Figure 5.5: Vertical trends of the main physico-chemical parameters of groundwater and dissolved ions, collected along the three profiles of the cross section. The averaged positions of aquifers and aquitards are indicated.

5.3.4 Vertical distribution of Contamination

The total concentration of VOCs (C_t μg/g wet sediment) has been determined from sediment subsamples at decimetric resolution along the MC4-5 profile. C_t values account for all the possible DNAPL phases present in the sediment samples (i.e. pure, dissolved and sorbed phases).

The whole series of chloroethenes, chloroethanes and chloromethanes have been found in the investigated system, with concentrations ranging between 0.001 and 216 μg/g. The highest chlorinated compounds (e.g. TeCA, PCE, TCE, CT) were spilled in the Southern Dump as chlorinated pitches originated by the distillation of chloromethanes (Nijenhuis et al., 2013). The lower chlorinated compounds represent products of biodegradation of the parent contaminants (e.g. cDCE, VC).

The cumulative distribution of VOCs (Fig. 5.6 a) shows sharp concentration gradients at the interfaces between the aquifers (i.e. A0 and upper A1) and the underlying aquitards (i.e. upper Q1 and lower Q1). In particular, preferential accumulations of contaminants have been observed in the shallower part of the profile (down to 11 m) and at the top of lower Q1 aquitard.

Concerning the proportions between the three different series of aliphatic compounds, chlorinated ethenes are the predominant group present along the profile, constituting the 80% of the total VOCs (Fig. 5.6 a). Thus, their vertical distribution will be considered as representative of the general contamination pattern from now on (Fig. 5.6 b,c). The main chloroethenes present along the profile have been labeled as parent compounds (i.e. PCE and TCE, spilled at the source) or daughter compounds (i.e. cDCE and VC, produced by biodegradation).

A very heterogeneous vertical distribution has been detected for each chloroethene, with changes in concentration of over 2 orders of magnitude at dm scale (Fig. 5.6 c). PCE and TCE occur along the whole vertical profile, from the ground surface down to the bottom of lower A1 aquifer (Fig. 5.6 b). Their highest concentrations are located in A0 aquifer (which is in direct contact with the source of contamination) and at the top of upper Q1 and lower Q1 aquitards. VC and cDCE occur almost exclusively in Q0 aquitard (3 to 5.5 m b.g.s.) and in the shallower part of upper Q1 aquitard (8 to 11 m b.g.s.), while they are absent in the deeper part of the profile.

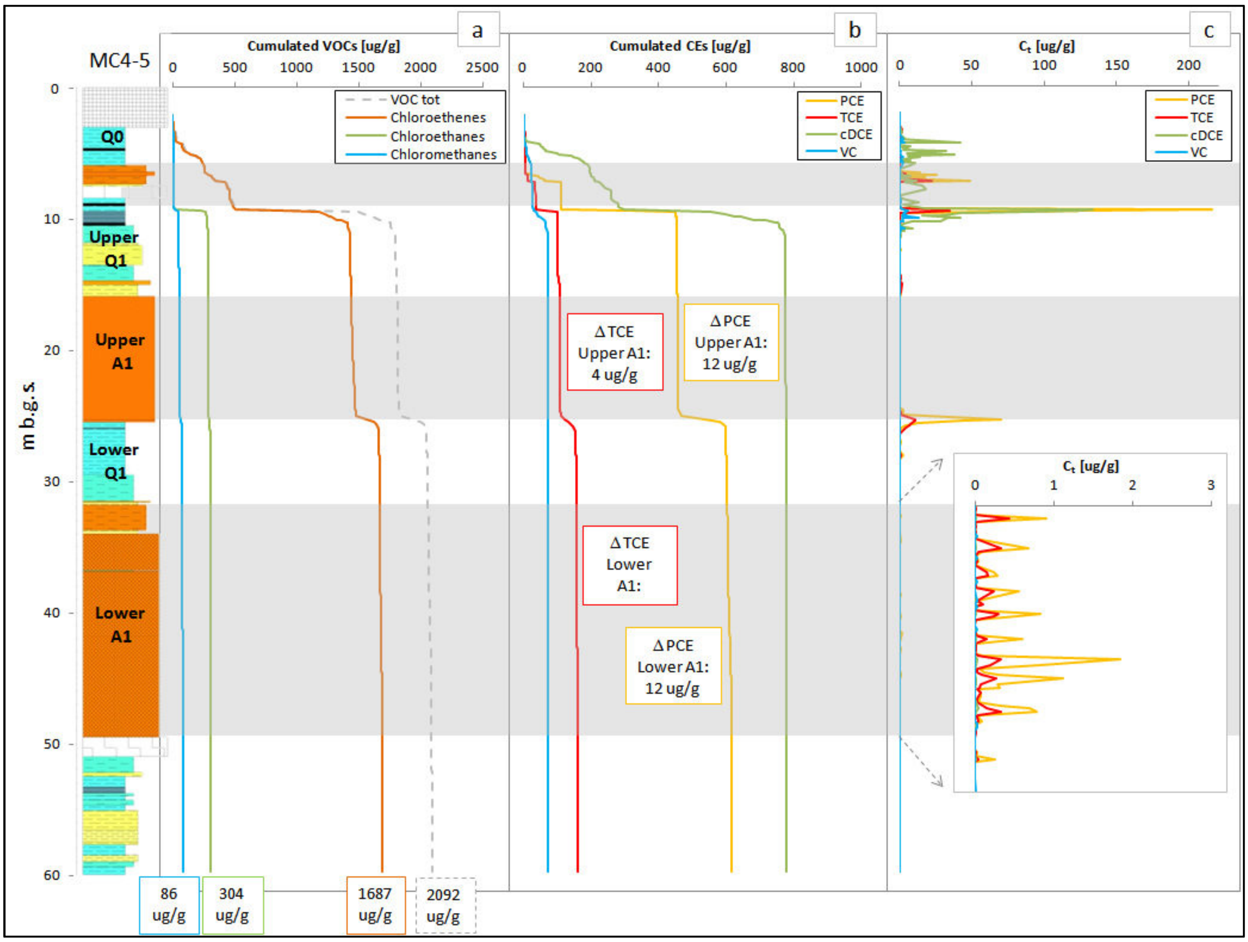


Figure 5.6: Distribution of contaminants (C_t, µg/g) obtained along profile MC4-5 via sediment core subsampling: (a) cumulative concentration curves of total VOCs, chloroethenes, chloroethanes and chloromethanes; (b) cumulative concentration curves of the main chloroethene compounds; (c) vertical distribution of the main chloroethene compounds, with a zoom on lower A1 aquifer, where concentrations of PCE and TCE up to 2 µg/g where detected (notwithstanding the previous characterizations of the site, according to which the aquifer was considered uncontaminated).

5.3.4.1 Phases partitioning

The values of dissolved (C_w) and sorbed (C_s) concentrations have been estimated from total concentrations in wet sediment (C_t). The occurrence of pure phase DNAPL has been excluded along the whole profile, by means of the comparison between C_w and the solubility described in Paragraph 5.2.5. Results obtained from groundwater samples ("GW" from now on) are considered representative of dissolved concentrations and have been compared with the distribution of estimated C_w (taking into account the sampling scale differences described in Chap. 3).

The estimated dissolved phase (C_w; Fig. 5.7) shows an overall distribution very similar to the one observed for C_t. In detail, dissolved ethenes are mostly concentrated in A0 aquifer, and in Q0 and upper Q1 aquitards. cDCE and VC prevail as dissolved compounds in the fine grained material (Q0 and upper Q1 aquitards), with concentrations up to 168 and 49 mg/L, respectively. Differently, dissolved PCE and TCE prevail within A0 (max concentrations equal to 133 and 73 mg/L, respectively), and show also secondary peaks at the top of lower Q1 aquitard (concentrations equal to 45 and 12 mg/L, respectively). In particular, diffusion curves (Parker et al., 2003; Parker et al., 1994) have been recognized from the C_W distribution of PCE and TCE at the top of lower Q1 aquitard (Fig. 5.7) and will be widely described in Paragraph 5.3.4.2.

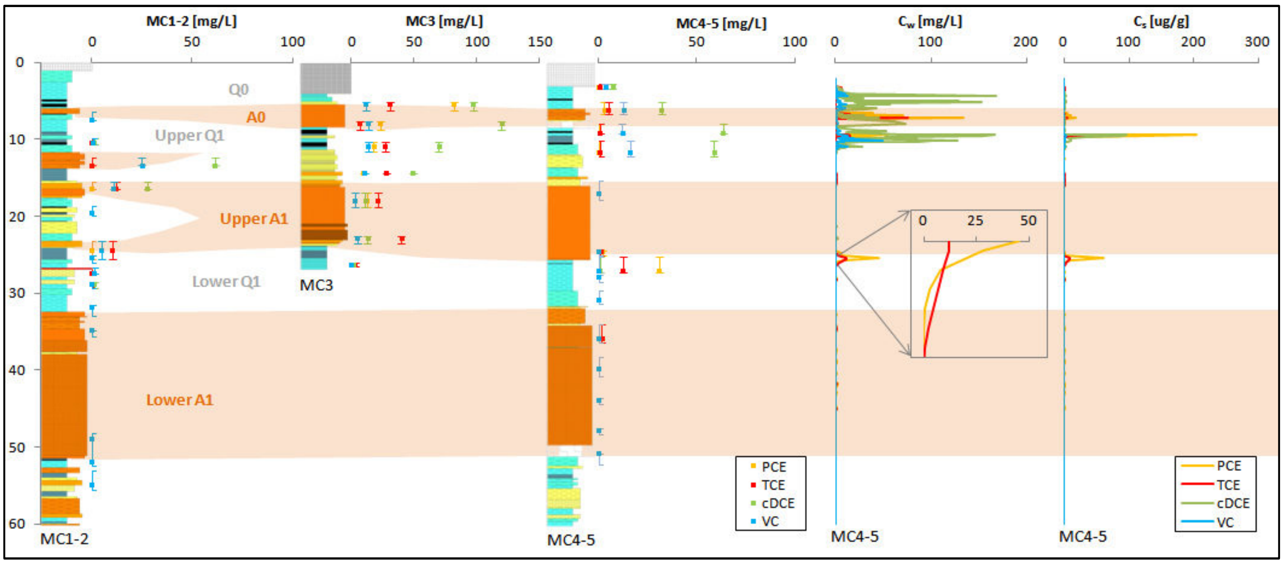


Figure 5.7: Vertical distribution of chloroethenes in dissolved and sorbed phases. From the left are shown: the distribution of dissolved concentrations obtained by groundwater samples collected from all the CMT systems (mg/L); the estimated dissolved (C_w; mg/L) and sorbed (C_s; µg/g) concentrations obtained by phase partitioning calculations along profile MC4-5. A zoom on diffusion profiles detected for PCE and TCE at the top of lower Q1 aquitard is reported with the C_w concentrations.

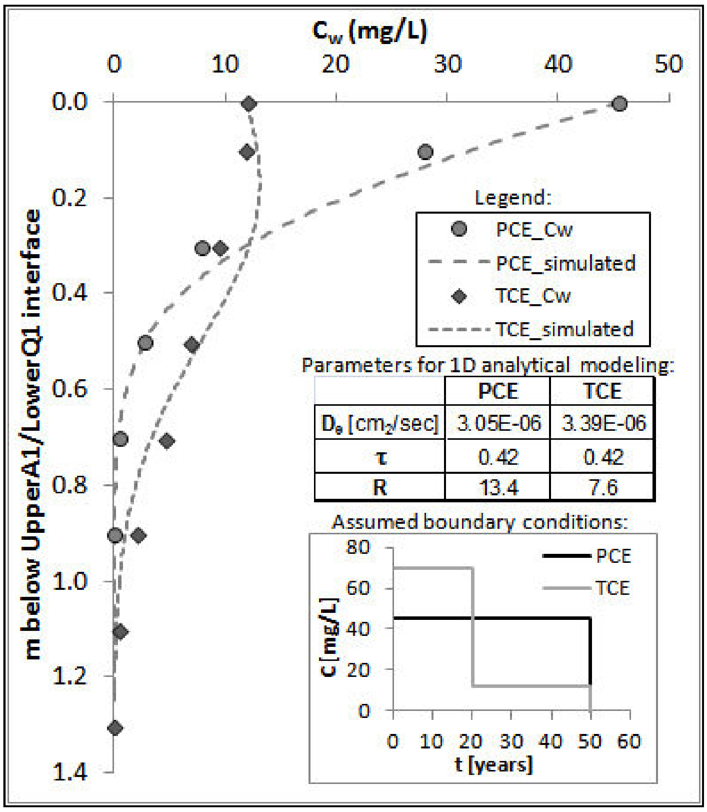
A good match has been observed along the profile MC4-5 between the GW distribution and the estimated C_W (Fig. 5.7). Parent compounds have been detected in groundwater with maximum concentrations of 31 and 13 mg/L, for PCE and TCE, respectively. Daughter compounds show maximum GW values equal to 119.8 mg/L and 25 mg/L for cDCE and VC, respectively. As groundwater samples have been collected also from profiles MC1-2 and MC3, it is possible to observe the GW distribution along the whole cross section (Fig. 5.7). The trends of contaminants observed along MC3 profile are comparable with the one described for MC4-5, with some slight variations in the distribution of the single compounds, attributable to small-scale stratigraphic variability (this will be widely discussed in Chap. 6). Differently, the contamination turned out to be absent in the shallower section of MC1-2 profile, occurring in significant concentrations only in upper A1 aquifer. This difference has been linked with the non-uniform presence of the residual thickness of wastes observed above some of the profiles (already mentioned in Paragraph 5.3.1 and 5.3.3), and will be further discussed in Paragraph 5.4.1.

The contaminants in estimated sorbed phase (MC4-5 profile) are mostly represented by PCE and TCE and are preferentially accumulated at the top of upper Q1 aquitard, within the organic rich layers located between 8 and 11 m b.g.s. (max concentrations equal to 203 and 96 µg/g, respectively; Fig. 5.7).

5.3.4.2 Diffusion curves

Two clear diffusion profiles have been detected at the top of lower Q1 (within the shallower 1 m of the aquitard) from the C_w distribution of PCE and TCE (Fig. 5.7). In general, diffusion is expected to produce smooth aqueous concentration profiles as the ones observed, because the driving force for diffusive transport is the aqueous concentration gradient (Parker et al., 2004). The PCE profile shows a gradual decline from 45.5 mg/L to very low or non-detect values at 0.9 m below the aquifer-aquitard interface. The TCE profile shows a different shape in respect to the one of PCE, suggesting a decline in concentrations at the aquifer-aquitard interface occurred sometime in the past (Parker et al., 2004).

The analytical 1-D solution described in Paragraph 5.2.6 has been used to reproduce the actual PCE and TCE curves. This was useful in order to define the time needed for the profiles to get to their current shape and to infer possible changes of concentration over time at the aquifer-aquitard interface. Averaged retardation factors (R) of 13.4 and 7.6 have been estimated for PCE and TCE, respectively, from the site-specific measurements of porosity and fraction organic carbon (Par. 5.3.1). The effective molecular diffusion coefficient (D_e) was fixed to 3.05E-6 and 3.39E-6 cm^2/s for PCE and TCE, based on the correlations described in Paragraph 5.2.6.



	PCE	TCE
D_e [cm_2/sec]	3.05E-06	3.39E-06
τ	0.42	0.42
R	13.4	7.6

Figure 5.8: Results of 1D analytical simulation of diffusion profiles of PCE and TCE. The simulation was done using a 50-year period and a single-step concentration for PCE (45.5 mg/L), while a two-step concentration was used for TCE (70 mg/L for the first 20 years and decline to 12 mg/L for the remaining 30 years).

The profile of PCE has been modeled first, as the shape of its curve suggested the most stable boundary condition over time (i.e. no variation of concentration at the aquifer-aquitard interface). A time of 50 years has been estimated for this profile to get to its current shape (Fig. 5.8). The timing is in good agreement with the historical knowledge about the contamination at the site (described in detail by Nijenhuis et al., 2013), which happened at sometime between 1960 and 1970.

The diffusion time obtained by PCE has been then applied to the TCE simulation, in order to infer possible concentration steps which could have produced the observed profile. Based on a 50 year diffusion time, two concentration steps have been inferred for TCE, superimposing different analytical solutions (i.e. curves obtained from different values of C_0). The steps correspond to C_0 equal to 70 mg/L for the first 20 years and a later drop to 12 mg/L for the remaining 30 years (Fig. 5.8).

5.4 Discussion

5.4.1 Dynamics of migration of contaminants

The distribution of chlorinated ethenes observed along the cross section agrees with the style of migration of immiscible fluids denser than water (i.e. DNAPLs). In particular, the contamination is spread very deep in the system, at least down to the bottom of lower A1 aquifer (50 m b.g.s.). This is in agreement with the propensity of DNAPLs to migrate downward through aquifers and aquitards, driven by their peculiar physico-chemical properties. Furthermore, a marked vertical variability of concentrations (up to 2 order of magnitude at decimetric scale) has been observed through the whole sequence of aquifers and aquitards along the detailed MC4-5 profile. Preferential accumulations of contaminants have been observed at the main aquifer-aquitard interfaces (Fig. 5.6 b), likely representing the remaining of former pools of pure phase DNAPL lying at the bottom of the aquifers.

What observed in the present days along the cross section are the advective and diffusive pathways resulting from the dissolution of the original DNAPL due to natural groundwater flow. Dispersion, which represents the third term of contaminant transport, is negligible at the scale of investigation. The current absence of DNAPL, verified along MC4-5 profile (see Par. 5.3.4.1) and most likely inferable along the whole cross section, can be explained considering that the cross section is located on a peripheral fringe of the actual source. The evolution of the source over time produced progressive dissolution of DNAPL during the decades elapsed before the investigation, likely causing its total disappearance in the investigated peripheral zone. The 1-D analytical modeling of the diffusion curves located at the top of lower Q1 aquitard (Par. 5.3.4.2) suggests that the concentration of TCE at the bottom of upper A1 aquifer was depleted much faster than the one of PCE (this is in agreement with the higher solubility of TCE in respect with PCE; Mackay et al., 2006). Differently, the shape of the profile of PCE suggests a quite stable boundary condition over time (i.e. concentration at the interface). This would mean that a significant amount of PCE (likely in pure phase) should have been accumulated at the bottom of upper A1 aquifer until a very recent past.

Pure phase DNAPL is probably still present below the source-core, “feeding” the contaminant plumes currently in migration in the aquifers.

Two evidences have been used to infer the occurrence of DNAPL along the cross section, or at least in the vicinity of it, in the past decades: (1) the contamination crossed two aquitards which were expected to provide protection to underlying aquifers against dissolved contaminants, based on hydraulic heads and hydrochemical evidences (discussed in Par. 5.4.2); (2) the contamination reached a depth of at least 25 m b.g.s. (i.e. the bottom of upper A1 aquifer) almost concurrently with the spill of contaminants at the surface (i.e. 50 years ago, as suggested by the simulation of diffusion profiles described in Par. 5.3.4.2). While the migration of dissolved contaminants through aquitards is generally strongly retarded due to sorption and mass transfers into the low permeability matrix (i.e. diffusion), such fast vertical migration could be explained by the occurrence of chlorinated solvent DNAPLs, which are prone to travel much faster through the fine grained layers (e.g. O'Hara et al., 2000).

Two main sharp increases in concentration have been observed from the curves of cumulative concentration of chlorinated ethenes (Fig. 5.6 b). The sharp changes are located at the interfaces between aquifers and aquitards (A0-upper Q1; upper A1-lower Q1) and have been interpreted as preferential accumulations of contaminants occurred in correspondence of the most significant vertical contrasts of hydraulic conductivity (K). Diffusion of contaminants in the fine grained matrix of aquitards occurred below these zones of preferential accumulation. Indeed diffusion profiles have been observed at the top of lower Q1 as well as at the top of upper Q1 aquitards. The profiles observed in lower Q1 are already described in Paragraph 5.3.4.2, together with the results coming from their simulations. The curves observed in upper Q1 aquitard weren’t taken into consideration for analytical modeling, as they are strongly disturbed by the co-occurrence of parents and daughter compounds, indicative of active biodegradation. Further, upper Q1 aquitard is characterized by very dense stratigraphic heterogeneities (centimetric scale), making it difficult to assign representative averaged properties to the aquitard for modeling purposes. Transport of contaminants within the diffusion-dominate zones was mostly vertical and in both cases (i.e. upper Q1 and lower Q1) interested a limited thickness of the aquitard (0.9 to 1.3 m below the interface with the aquifer).

Where the vertical curves of cumulative concentration (Fig. 5.6 b) show a dull and linear increase with depth (e.g. within upper A1 and lower A1 aquifers), advection is assumed to be the main transport mechanism. The distribution of hydraulic heads confirms the predominance of horizontal flow inside aquifers. The horizontal advective transport of contaminants inside aquifer gave origin to different dissolved plumes, which are currently in migration in the aquifers below the Caretti site (described by Nijenhuis et al., 2013).

The distribution of dissolved contaminants obtained along the whole cross section by groundwater samples is described in Paragraph 5.3.4.1 and suggests that the source tends to disappear in the westward direction. Indeed, the absence of contamination in the shallower 13 m of MC1-2 profile confirms that along this profile the contamination should have reached upper A1 and lower A1 aquifers via lateral advective migration, instead of by the direct vertical migration from the source inferred for MC3 and MC4-5 profiles.

5.4.2 Behavior of aquitards

The aquitards interposed to the three investigated aquifers (i.e. upper Q1 and lower Q1) have been investigated in terms of hydraulic head distribution, influence on hydrochemical trends and contaminant distribution, and stratigraphic features. The main behaviors observed are discussed in sequence.

The distribution of hydraulic heads over time along the cross section allows to distinguish two main head loss layers in the system. These layers are located within upper Q1 and lower Q1 aquitard and are 3 to 3.5 m thick. Thus, aquifers A0, upper A1 and lower A1 result to be hydraulically disconnected between each other, thanks to the hydraulic barriers detected within aquitards. The hydraulic gradient within the head loss layers constantly shows a main vertical component, which in some cases was reversed from upward to downward due to changes in groundwater recharge conditions. The main sources of groundwater recharge for the investigated aquifers were already identified in the literature with the local vertical recharge (i.e. rainfall, mainly contributing to A0 aquifer) and the Po river (mainly contributing to the recharge of the lower A1 and upper A1 aquifers; see results of Chap. 4). Indeed, the comparison between hydraulic heads and the monthly trends of the two sources (Fig. 5.2) shows that A0 aquifer responds promptly to the main rainfall events, while upper and lower A1 aquifers respond to the main variations of the river level, with a similar time-lag (estimated at around 45 days). The hydraulic gradient within upper Q1 is directed downward when the contribution from rainfall prevails on the one from Po river, while it reverses upward when the influence of the river overtakes the one of vertical recharge in the system. In both the conditions, the vertical gradient remains enclosed within the same aquitard section. The vertical hydraulic gradient within lower Q1 aquitard is constantly downward, decreasing in magnitude while the contribution from the Po river to the system increases.

The hydrogeochemical composition obtained from groundwater samples (Fig. 5.4) shows clearly independent trends for the three investigated aquifers. This suggests that mixing between groundwater hosted in the different aquifers is unlikely occurring through the aquitards along the transect, so endorsing the hypothesis of hydraulic disjunction between aquifers provided by the head loss layers within the aquitards. All the vertical trends of physico-chemical parameters and ions (Fig. 5.5) hint two very different behaviors for above and below lower Q1 aquitard. In particular, a general inversion of trends and a sudden harmonization between the different vertical profiles can be observed below the deep aquitard. No significant changes in trends have been observed in correspondence of upper Q1 (except for a few ions, i.e. K and F). This information suggests that lower Q1 likely acts as a more effective barrier towards the underlying aquifers in respect to upper Q1.

The two aquitards show very different stratigraphic features. In particular, upper Q1 is characterized by a high number of lithologic heterogeneities (decimetric scale), and merely clayey sublayers have been infrequently found within the aquitard. The head losses detected within this aquitard occur in correspondence of an organic-rich thickness, which was indentified in all of the three investigated profiles (i.e. MC1-2, MC3, MC4-5). Lower Q1 aquitard shows less lithologic variability than upper Q1 and it is for the most part composed by homogeneous hard clay, with sporadic silt intercalations. The head losses occurring within this aquitard are localized in correspondence of a markedly clayey section located around 30 m b.g.s., characterized by "hard consistency" (as estimated from pocket penetrometer tests following the ASTM D-2488 Standard). The drop of pore pressure down to values close to 0 kPa, observed from the CPTU test around 30 m b.g.s. (see Fig. 5.3), indicates a probable high degree of consolidation for the clays (as suggested by Amorosi and Marchi, 1999; Chen and Mayne, 1996; Mayne et al., 1990).

The lithologic heterogeneity of aquitard upper Q1 and its less clayey nature in respect to lower Q1 could represent an explanation to the lesser confining capacity towards the underlying aquifer, in comparison with what observed for the deeper aquitard. Further, the inversions of hydraulic gradient observed within the shallower aquitard over time indicates a lower hydraulic steadiness, which likely contribute to worse the insulation potential of upper Q1.

The detailed vertical distribution of VOCs (Fig. 5.6 and 5.7) shows that the contamination is extended down to the bottom of lower A1 aquifer, so proving that neither of the two aquitards (i.e. upper Q1 and lower Q1) are characterized by an adequate degree of integrity against chlorinated solvents DNAPLs. Both the aquitards partly obstructed the vertical migration of DNAPLs, mainly due to the high contrast of K characterizing the aquifer-aquitard interfaces. Indeed, preferential accumulations of contaminants have been inferred over the top of both aquitards and a general decrease of concentration has been observed moving downward along the whole system. Further, both aquitards affected the evolution of the contamination over time, with different modalities related to their different stratigraphic features. Concerning upper Q1, the curves of cumulative concentration obtained along MC4-5 for chlorinated ethenes (Fig. 5.6 b) show that the products of biodegradation (i.e. VC and cDCE) mostly appear within the organic-rich sublayers. This suggests that biodegradation (i.e. reductive dechlorination; Vogel et al., 1987) is mostly active within the peaty layers, which provide a favorable environment for the process to occur (the relationship between organic layers and the reductive dechlorination of contaminants will be widely discussed in Chap. 6). A preferential sorption of parent compounds (i.e. PCE and TCE) was observed within the same organic-rich sublayers. These two last information suggest that the decline of contaminant concentrations observed from A0 to upper A1 occurred mostly via the combination of biodegradation of parents and sorption within the solid matrix of the aquitard.

Any substantial enrichment in organic matter was observed in the clayey lower Q1 aquitard, and indeed no daughter products were detected within this aquitard. The clear diffusion profiles observed at the top of lower Q1 in MC4-5 profile prove that the vertical migration of contaminants through the aquitard is diffusion-dominated and extended for around 1 m from the aquifer-aquitard interface. Nevertheless, the evidence of contamination spread down to lower A1 aquifer (PCE and TCE in concentrations up to 3 mg/L) clearly indicates that preferential pathways for the migration of contaminants (likely in DNAPL phase) must occur within the aquitard in the vicinity of MC4-5 profile. Based on the site history, man-made interventions which could have affected the system down to lower A1 aquifer causing cross-contamination can be excluded with good confidence. The high level of consolidation already inferred for the thickness of clays acting as hydraulic barrier in lower Q1, hints a prone-to-fracturing behavior ("fragility") for these clays, with consequent probable occurrence of micro-fractures. A macro-fracturing is excluded due to the hydraulic confining capacity observed for the same layer. The inferred micro-fractures represent ideal preferential pathways for the migration of DNAPLs thought the aquitard. In the context of the southeastern Po river plain, the observed high consolidation of clays and the consequent microfracturing can be likely attributed to clay desiccation occurred during the prolonged phase of subaerial exposure that characterized the area during the last glacial maximum and the first stages of transgression (Amorosi and Marchi, 1999; Rizzini, 1974).

The same preferential pathways inferred for DNAPLs are not necessarily effective for the vertical migration of dissolved contaminants. Indeed, hydrogeochemical and hydraulic head information suggest that the same deep aquitard act as an effective barrier in terms of water flowpaths.

5.5 Conclusions

Two silty-clayey aquitards, which turned out to be protective towards underlying aquifers on the basis of hydraulic head data and groundwater exchanges, were crossed by DNAPLs. This happened in an alluvial unconsolidated multi-aquifer system, where the same aquitards were considered able to protect the quality of groundwater hosted in the underlying aquifers in several previous references and technical documents. In the investigated setting, chlorinated solvent DNAPLs (mainly chlorinated ethenes) were able to migrate down to a depth of at least 53 m b.g.s., crossing the two aquitards and contaminating three different aquifers. The groundwater hosted in deepest contaminated aquifer is widely exploited at regional scale (also for drinkable water purposes). Thus, the recognition that this aquifer is overlaid by an aquitard vulnerable to DNAPL contamination is fundamental in order to address the management and protection of the local groundwater resource.

The results of the present study revealed that the aquitards of the investigated setting play a role more complex than simple hydraulic barriers. Indeed, they offer a different degree of protection in respect to different kinds of contaminants and can also work as reactors for biodegradation reactions (as discussed in Chap. 6). The two aquitards crossed by DNAPLs are characterized by different sedimentologic and stratigraphic features. These features allowed to interpret the distribution of contaminants observed at the site and provided insights on their styles of migration and transformation within the investigated system. Differently, the information generally used to investigate the dynamics of contaminants in aqueous phase (e.g. hydraulic head distribution and evaluation of groundwater exchanges between different bodies) suggested very different flowpaths in respect with the ones followed by chlorinated solvents.

Among the rest, the results of the study showed that part of the migration of chlorinated solvents through aquitards occurred via molecular diffusion. However, other evidences (i.e. the depth of migration of contaminants) proved that diffusion can’t be the only mechanism of migration through the investigated aquitards. Indeed, preferential pathways have been proven to exist in the aquitards (sand-beds and microfractures) which allowed the fast migration of contaminants down to 53 m b.g.s. Thus, the occurrence of evidences of diffusion can’t be used to infer the integrity of unconsolidated clayey aquitards against the migration of DNAPLs.

Concerning the Caretti site, this study allowed to add useful elements to the existing hydrogeologic and contaminant conceptual model. In particular, lower A1 aquifer turned out to be contaminated by PCE and TCE in concentrations of up to 3 mg/L; this likely leaded to the formation of a further dissolved plume which will need to be detected and characterized. Also, the modeling of diffusion curves allowed to confirm the hypothesized timing of contaminant spilling, adding an important element for the contaminant source apportionment.

The results presented in this study are useful also at global scale, as they represent an improvement of the knowledge about the behavior of DNAPLs in unconsolidated alluvial systems, providing a valuable base for the characterization of other alluvial plains (where most of the petrochemical and heavy industrial facilities occur).

CHAPTER 6

Naturally enhanced reduction of chlorinated ethenes in peat-rich hydrogeologic settings: opportunities and environmental issues[3]

6.1 Introduction

Chlorinated solvents are the most prevalent organic contaminants found in groundwater (Stroo et al., 2003), and in the dissolved phase they are typically mobile, particularly trichloroethylene (TCE) and tetrachloroethylene (PCE). Their behavior in the subsurface, their potential to be subjected to biodegradation and the threats that can arise, depend to a large extent on the intrinsic characteristics of the contaminants (generally spilled in the subsurface as DNAPLs; Pankow and Cherry, 1996), but also on the geological and hydrogeological features of the system in which they are migrating. These last features are particularly important in the case of unconsolidated porous settings constituted by layered sediments (e.g. alluvial plains), where the contaminants happen to have an intimated and pervasive contact with a very heterogeneous solid matrix, and averaged flow rates lower in respect to a fractured medium. Is such a case, a detailed characterization of depositional environments is a valuable tool in order to identify and group together the geological and hydrogeological features of the system, possibly interacting with the contaminants. For example, the occurrence in the stratigraphic architecture of organic-rich layers (such as peaty layers), could substantially affect the migration and degradation of contaminants, since the organic matter can sorb the contaminants and also act as electron donor in biodegradation reactions. However, this kind of stratigraphic study is commonly neglected in contaminant hydrogeology research. Instead, a robust stratigraphic model, based on the interpolation of distinct depositional facies characterized by well defined petrophysical properties, could help, for instance, to identify the zones of the system where biodegradation of contaminants and potential production of hazardous metabolites (e.g. vinyl chloride) could be enhanced.

Therefore, the main objective of the work presented in this Chapter is to prove the effectiveness of overlapping a detailed reconstruction of the contaminant architecture with sequence stratigraphy and paleo-environmental reconstructions, in order to properly interpret the dynamic of transformation of

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contaminants (e.g. biodegradation) and the possible accumulation of degradation products (e.g. VC), within an heterogeneous stratigraphic system such as an alluvial plain.

To achieve the objective, detailed stratigraphic and hydrogeological investigations were carried out in a complex multilayered aquifer setting, where contamination by chlorinated ethenes occurs at several sites, showing peculiar accumulations of VC. The study area corresponds with the southeastern sector of the Po Plain (Ferrara, northern Italy). The investigations were carried out at two different scales. At both scales, the contaminant architecture was matched against the local distribution of depositional facies in order to interpret the recurring accumulation of the degradation product VC. In particular: (1) detailed facies analysis and high-resolution vertical hydrogeological investigations (i.e. reconstruction of contaminant architecture) were performed in the source area of the Caretti test-site, (in the southeastern sector of the study area; Fig. 6.1). At the same site, also Compound Specific Isotope Analysis (CSIA) was performed on contaminants and the geochemical conditions of groundwater were investigated. The investigation carried out at the Caretti site will be referred to as "source-scale investigation"; (2) The results concerning the transformation of contaminants in relation with depositional environments, obtained at the source area of the Caretti site, were compared with other two contaminated sites, hosted in the same hydrogeological setting. In both of these two sites, "VC-alone" plumes took origin from a source similar to the one investigated at the Caretti site and are currently in migration in the shallower confined local aquifer. The precise location of the source of the two plumes is unknown. The two plumes were named "A" and "B", and are both located in the northwestern portion of the study area (NW setting in Fig. 6.1). The investigation of plumes A and B will be referred to as "plume-scale investigation".

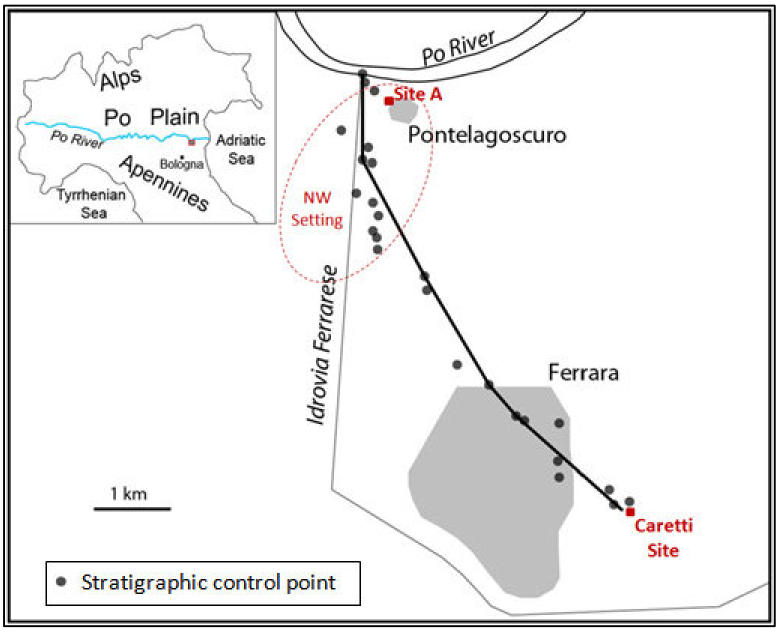

Figure 6.1: Location of the study area. The contaminated sites and the points used for stratigraphic reconstruction are indicated, (except for the location of contaminated site B, which isn't shown on the map for the sake of keeping the privacy about the owners).

The results of this study will be of interest for future contaminant hydrogeology research in other alluvial plains throughout the world, where several sources of contamination similar to the ones investigated here were active during the last five or six decades.

6.2 Theoretical background on the reductive dechlorination of chloroethenes

Organic contaminants can be biodegraded by serving as either an electron donor that becomes oxidized or an electron acceptor that becomes reduced. Because highly chloroethene compounds such as PCE and TCE have relatively high oxidation state, they are biodegraded most easily through reduction reactions under anaerobic conditions (Lorah et al., 2005; Stroo and Ward, 2010; Wiedemeier et al., 1998). As already mentioned in Chapter 2, reductive dechlorination is the most important anaerobic biodegradation process for the highly chlorinated ethenes (PCE, TCE) (Bouwer, 1994; Freedman and Gossett, 1989; Vogel and McCarty, 1985) and proceeds primarily via sequential hydrogenolysis. Thus, PCE degrades sequentially to TCE, cis-1,2 dichloroethene (cDCE), vinyl chloride (VC), and ethene. Several factors were identified in literature, strongly dependent on the physico-chemical features of the system where the contaminants are hosted, which can influence the effectiveness of the dechlorination process: (1) In situ redox environment (Stroo and Ward, 2010): reductive dechlorination of TCE to cDCE can occur under Fe (+3) reducing conditions and in more strongly reducing environments (Chapelle, 1996). Dechlorination of cDCE to yield VC appears to be favored under SO_4 reducing and methanogenic conditions (Chapelle, 1996; Vogel et al., 1987), while reduction of VC to the non-chlorinated product, ethene, appears to be slow in situ, and it is generally associated with highly reducing, methanogenic conditions (Ballapragada et al., 1995; Barrio-Lage et al., 1987; Bouwer, 1994; Carter and Jewell, 1993; De Bruin et al., 1992; Di Stefano et al., 1991; Fennell et al., 1995; Freedman and Gossett, 1989; Maymó-Gatell et al., 1995; Odum et al., 1995; Vogel and McCarty, 1985; Wu et al., 1995); (2) Supply of electron donors: because the contaminants themselves are not an electron donor for the microorganisms (National Research Council, 2000), reductive dechlorination requires an adequate supply of electron donors (Bouwer, 1994; Gibson and Sewell, 1992; Gossett and Zinder, 1996; McCarty, 1996; McCarty and Semprini, 1994; Vogel, 1994; Wiedemeier et al., 1998). The occurrence of abundant natural organic matter in sediments should eliminate electron donor supply as a limiting factor (Lorah et al., 2005). For example, the effectiveness of reductive dechlorination in surface fine-grained and organic-rich environments, such as wetlands, is well documented in literature (Lorah et al., 2005); (3) Hydraulic conductivity (K) distribution: even if the most part of biodegradation reactions are thought to occur in aquifers, low permeability zones (i.e. aquitards) have some features which can favor the occurrence of biodegradation. For example, the long retention times (slow advection rate/no flushing effects) of contaminants in aquitards in respect to aquifers can favor the occurrence of reductive dechlorination (Sale et al., 2013). Differently, the high advective flow rates typical of aquifers could drive the contaminants to bypass the most favorable zones for reductive dechlorination.

A depositional facies typical of alluvial systems, into which the conditions listed above can coexist, is the clayey swamp facies association. Thus, the occurrence of this kind of sediments in the subsoil could represent an ideal environment for the reductive dechlorination of contaminants. However, as already stated in Chapter 2, the efficiency of reductive dechlorination appears to decrease with decreasing chlorine number, such that, even in a favorable environment, the most toxic intermediates (cDCE and VC) may accumulate (Stroo and Ward, 2010). The possible accumulation of VC in the subsurface via reductive dechlorination is considered an element of great concern due to the well known carcinogenic effect of the compound and also due to its higher mobility in comparison with parent compounds. Indeed, vinyl chloride is both highly soluble and volatile (Mackay et al., 2006), having the potential to threat both the groundwater and the subsurface environments. On the other hand, VC tends to be easily biodegraded in aerobic conditions (Bradley and Chapelle, 2010)

6.3 Methods

6.3.1 Study area

As already mentioned in the introduction, the work presented in this Chapter is focused on three contaminated sites located in the surroundings of the city of Ferrara (the Caretti site and the contaminated sites A and B; Fig. 6.1). The contamination at the three sites is mainly composed of chlorinated ethenes and is generally extended from the surface down to the bottom of A1 aquifer (lower A1 in the case of Caretti site). In sites A and B the plumes are composed almost entirely of VC (constituting up to 99% out of the contaminants).

At the Caretti site, a detailed investigation of the local source of contamination (i.e. Southern Dump) was carried out along the monitoring cross section described in Chapter 3 (Fig. 3.8), by means of high resolution vertical profiling of sedimentological information, concentrations analyses and CSIA on contaminants, and determination of the geochemical conditions of groundwater. In sites A and B a the spatial distribution of VC in A1 aquifer has been mapped by means of groundwater samples collected from pre-existing piezometers or using the direct push sampling techniques; also, a km-scale stratigraphic and paleo-environmental reconstruction have been performed along the whole distance between the Caretti site and the northwestern setting, where sites A and B are located.

6.3.2 Stratigraphic data

In order to reconstruct a reliable stratigraphic framework for the study area (both at the scale of Caretti site and at km-scale), the whole stratigraphic database hosted at the Emilia-Romagna Geological Survey (RER) has been considered. From the RER dataset, we selected 24 core descriptions and 1 piezocone penetration (CPTU) test (Fig. 6.1). Stratigraphic descriptions include color, lithology, accessory material and, in a few instances, pocket penetration values.

Cores recovered from the three profiles of the cross section at the Caretti site during summer 2013 (MC1-2, MC3 and MC4-5; Fig. 3.8 - Chap. 3), have been investigated for detailed sedimentological studies. The stratigraphic reconstruction of these cores was already presented in Chapter 5 and has been used here for the identification of depositional facies. The cores are currently stored at the Environmental Service of the Ferrara Municipality.

Facies interpretation from the three reference cores (i.e. MC1-2, MC3 and MC4-5) has been used for calibration of stratigraphic data extracted from the RER dataset. As a result, each stratigraphic description selected from the RER dataset was tentatively converted into facies data. For stratigraphic interpretation of the CPTU test, we used a combination of Q_c values (cone penetration resistance), sleeve friction (f_s) and pore water pressure (u), as suggested by Amorosi and Marchi (1999). Pocket penetration values, where available, have been also used for facies characterization (Amorosi et al., 2014a). Facies analysis has been used as a basis for stratigraphic correlations. This allowed to obtain the reconstruction of depositional facies architecture at both site scale (Caretti site; see Par. 6.4.1.1) and at km-scale (from Caretti site to sites A and B; Par. 6.4.2.2).

6.3.3 Contamination

6.3.3.1 Groundwater sampling and sample preparation

In order to perform analyses on concentration of volatile contaminants (i.e. chlorinated ethenes) and dissolved gases (i.e. ethene and methane), groundwater samples have been collected at the Caretti site and in contaminated sites A and B.

Concerning the Caretti site, 70 groundwater samples have been collected from the 35 screens of the CMT cross section, from both aquifers and aquitards, and used to determine concentration of dissolved volatile contaminants (35 samples; collection and analysis already described in Chap. 5) and concentration of dissolved gases (35 samples). Furthermore, 7 additional groundwater samples have been collected at the Caretti site from a shallow home-made multilevel system located on the dissolved plume in A0 aquifer (MS1; described in Chap. 3). The samples collected in MS1 have been used for contaminant concentration analyses (collection and analysis methods analogous to the CMT systems).

Sampling operations in the multilevel systems were carried out as already described in Chapters 4 and 5. For concentration analysis of dissolved gases (methane and ethene) 220 mL serum bottles were filled to the top, acidified immediately (hydrochloric acid down to pH 2) and closed with butyl rubber stoppers and aluminum crimp seals. Samples were stored at 4 °C, upside down until further investigation.

In contaminated sites A and B several groundwater samples have been collected from the main contaminated aquifer (i.e. A1) during 2004 and 2005, in order to perform volatile contaminant concentration analyses (i.e. chlorinated aliphatic hydrocarbons). In site A, samples have been collected via direct push technique on 17 monitoring points distributed on the plume area. Two to four groundwater samples were collected at each monitoring point, at different depths within the thickness of A1 aquifer (ranging from 12 to 29 m b.g.s.) (Pasini et al., 2008). In site B, samples have been collected from a scattered net of conventional piezometers, located on the dissolved plume and screened on the total thickness or on the shallower 10 m of A1 aquifer. Multi-depth groundwater sampling has been performed from one of the piezometers of the network: samples were collected at five different depths within the contaminated aquifer (from 17.5 to 37.5 m b.g.s.), via low flow groundwater pumping at discrete positions along the screened interval of the piezometer.

6.3.3.2 Sediment Core subsampling

Cores collected along the eastern profile of the cross section of Caretti site (MC4-5, Fig 3.8 - Chap. 3) have been subsampled as already described in Chapter 5. Four subsamples have been collected at each depth for the purposes of this Chapter, one dedicated to contaminant concentration analysis (see Chap. 5 for sampling and analysis methods) and triplicates dedicated to carbon stable isotope analyses on contaminants. The choice of performing isotopic analyses on sediment samples (and not on water samples) was driven by the need to obtain information comparable with the high-resolution contaminant concentrations obtained via core subsampling along the same profile.

Samples for isotopic analyses were extruded into 20 mL headspace (HS) crimp vials, containing 9.5 mL of NaCl water saturated solution (for preservation and salting out of the contaminants). Each subsample corresponds to approximately 9.5 g of sediment. The volume of NaCl saturated solution added in the vials was calculated such that the sediment should be completely covered with the solution (obtaining a ratio g sediment/mL solution of at least 1), as it was recommended before (Pavón et al., 2009). With this sampling procedure the HS volume inside the vial was in all samples ≥ 5 mL.

6.3.3.3 Analytical methods

Concentration analyses in groundwater samples

Concentration analyses of volatile contaminants (i.e. chlorinated ethenes) have been performed by a private certified laboratory, using the analytical method “EPA 5030 C 2003 + EPA 8260 C 2006” (as already mentioned in Chap. 5).

Dissolved gases have been analyzed at the Department of Isotope Biogeochemistry, at the Helmholtz Centre for Environmental Research in Leipzig (Germany). Gas chromatography with flame ionization detection (GC-FID) was applied to analyze methane and ethene (gas chromatograph: Varian Chrompack CP-3800, Middelburg, The Netherlands) equipped with a 30 m 0.53 mm GS-Q column (J&

W Scientific, Waldbronn, Germany). The temperature program used was as follows: 2 min at 50 °C, 50 °C/ min to 225 °C, hold 2.5 min. The FID was operated at 250 °C and helium was used as carrier gas. Air and hydrogen flow were set at 300 and 30 ml/min, respectively. The injection was automated using an HP 7694 headspace autosampler. A 10 mL HS vial was flushed with helium and hermetically closed (aluminum cap with PTFE/butyl septa -3 mm thickness- Th. Geyer, Renningen, Germany), then 1 mL of groundwater sample were introduced through the septum using a Hamilton syringe. 1 mL headspace sample was then injected (split 1:1). Authentic standards were used for identification and all samples were measured in triplicates. The data were recorded using the Varian STAR software.

Concentration analysis of chlorinated ethenes in core subsamples

Sediment subsamples collected for chlorinated ethenes concentration have been analyzed with the techniques already described in Chapter 5 for VOCs. The resulting total concentrations of contaminants in wet soil (C_t, μg/g) were subjected to partitioning calculations, in order to estimate the dissolved concentration of analytes in pore water (C_w, mg/L) (see Chap. 5).

Compound Specific Isotope Analysis (CSIA) of chlorinated ethenes in core subsamples

A selection of 29 sediment subsamples was subjected to carbon stable isotope analysis, in order to obtain a proper characterization of contaminants vertical distribution, with focus on specific depths (e.g. interfaces between different hydrogeological bodies).

The analyses have been performed at the Laboratory of Stable Isotope Analysis at the UFZ in Leipzig (Germany). Gas chromatography combustion isotope ratio mass spectroscopy (GC-C-IRM-MS) was applied to determine the stable carbon isotope composition of the volatile organic contaminants (i.e. chlorinated ethenes) in the sediment samples. An Agilent 7890A GC (Agilent Technologies, Waldbronn, Germany) coupled to an IRMS (MAT 253, Thermo Fisher Scientific, Bremen, Germany) via GC IsoLink (CNH) and ConFlo IV universal interface (Thermo Fisher Scientific, Bremen, Germany) was used. The GC was equipped with a programmed temperature vaporizer (Multimode Inlet (MMI) G3510A/G3511A, Agilent Technologies, Waldbronn, Germany) and a CombiPAL autosampler (CTC Analytics AG, Zwingen, Switzerland). The capillary column was a DB-MTBE (60 m x 0.32 mm ID x 1.80 μm FD; Agilent Technologies, Waldbronn, Germany). The temperature program started at 35 °C and was held for 10 min, then increased at a rate of 4 °C/min to 150 °C and then at 20 °C/min to 260 °C and held for 5 min. A novel pre-concentration technique, consisting on large volume injection of headspace samples into the PTV injector (Elsner et al., 2012), was used for the precise determination of the carbon isotope composition of volatile contaminants present in many of the samples at low concentrations (in μg/g range, see Fig. 6.3). The method was validated for the carbon isotope analysis of volatile organic compounds in water samples, and has been adapted here to the extraction of volatile compounds from sediment samples. The headspace sample was introduced into the injector (deactivated glass liner packed with Tenax-TA®) at 0 °C, with a vent flow of 5.0 mL/min and a vent pressure of 5.00 psi. The split valve was closed 0.5 min after injection, and the liner was heated at a rate of 650 °C/min to 300 °C for desorption of the analytes into the GC column. The cooling of the injector was accomplished by liquid nitrogen, and helium was used as the carrier gas. Different headspace injection volumes (from 250 µL to 5000 µL) were selected depending on the concentration of the target compounds in the samples in order to obtain in all cases peak amplitudes within the linear range of the IRMS system (peaks from 300 to 10000 mV were considered). All samples were analyzed at least in triplicates. A standard solution in Milli-Q water, containing the target compounds with known isotopic composition, was analyzed with the described method every 5 samples, for identification of the target compounds and to ensure accuracy and precision of the GC-C-IRMS system.

6.4 Results and discussion

6.4.1 Source scale results

The detailed investigations carried out at the source of contamination of the Caretti site will be discussed in sequence in Paragraphs 6.4.1.1 (architecture of depositional facies), 6.4.1.2 (contaminant distribution in soil and groundwater) and 6.3.1.3 (dissolved gasses, geochemical conditions of groundwater and CSIA on contaminants). All the information collected have been summarized in a conceptual model of the distribution and transformation of contaminants at the source area of the Caretti site (Par. 6.4.1.4). An issue of potential emission of VC in vapor phase at the site will be outlined eventually (Par. 6.4.1.5).

6.4.1.1 Depositional facies and hydrostratigraphy

Detailed sedimentological analysis of cores MC1-2, MC3 and MC4-5 (Fig. 6.2) enabled the identification of five depositional facies associations on the basis of sediment lithology, lower boundaries, grain size/vertical grain size trends, sediment color, thickness, and accessory materials (fossil content, organic matter, plant debris). Additional data include in situ geotechnical measurements (i.e., pocket penetration tests) from core MC1-2.

The five depositional facies associations are described in sequence.

Fluvial-channel facies association

Description

This facies association consists of well-sorted, generally amalgamated, grey coarse-to-fine sand and locally silty-sand bodies, with thin clay-organic rich intervals, erosional lower boundary and fining-upward (FU) trend. The upper boundary is sharp to slightly gradational. This facies association includes two major distinct sediment bodies, between about 52-34 m core depth and 25-15 m depth, respectively. The lower sand body, corresponding to lower A1 aquifer, is 18 m thick, while the upper one (upper A1 aquifer) has total thickness of 10 m and lower lateral continuity, as documented by its transition to crevasse/levee deposits in core MC1-2. No fossils have been observed.

Interpretation

This facies association has been interpreted as a fluvial-channel deposit, because of the combination of lithology, grain size and FU trend, the latter interpreted to reflect channel abandonment. The erosional lower boundary, total thickness, and the presence of amalgamation surfaces and organic-rich intervals also are consistent with the hypothesis of high-energy fluvial environment. The upper sharp boundary reflects rapid channel abandonment, whereas gradational contacts have been inferred to reflect gradual abandonment.

Levee and crevasse facies association

Description

This facies association has maximum thickness of about 4 m, and locally shows lateral transition to fluvial-channel deposits. It consists of: (i) rhythmical alternations of grey to brownish silty sand, silt and clayey silt organized in few mm- to few cm-thick layers. Silty-sand layers show fining-upward trends, distinctive sharp bases and gradational tops; (ii) very fine to medium sand, silty sand and sandy silt, with FU trend, erosional base and gradational/sharp top, or coarsening-upward (CU) successions, with gradational lower boundary and sharp top.

Interpretation

Because of its stratigraphic relationships with fluvial-channel deposits and grain size trends, this facies association has been inferred to have formed in a variety of depositional sub-environments close to the river axis. In particular, sand-silt alternations were interpreted as (natural) levee deposits, and the mm- to cm-thick interbedded sand/silt layers suggest energy fluctuations from relatively high (traction currents) to low levels (fall-out deposition in proximal overbank deposits). Relatively low sand/silt ratios have been associated to distal deposits, while higher values are typical of more proximal levees. Sand bodies with erosional base and FU trends have been interpreted as crevasse channels. On the other hand, CU silty sand to sand deposits with gradational lower boundary have been argued to represent crevasse splays.

Floodplain facies association

Description

This facies association is composed of massive grey clay and silty clay deposits. Pocket penetrometer values are in the range of 1.8-3.1 kg/cm^2. This monotonous and massive muddy succession may be interbedded with pedogenized levee/crevasse deposits, or softer and grey silty-clay, locally organic-rich. It is laterally continuous, especially between the two main aquifers, where it reaches its maximum thickness of around 7 m. Within this stratigraphic interval a paleosol has been identified in clay deposits, with pocket a penetration value of 3.1 kg/cm^2 (core MC1-2).

Interpretation

This facies association has been interpreted as floodplain deposits: massive clay and silty clay sediments together with relatively high pocket penetrometer values and pedogenetic features (i.e. paleosol) testify to a low-energy depositional environment, where episodes of subaerial exposure under well-drained conditions have been fairly common and quite long, coherently with deposition of overbank fines in an interfluvial setting.

Poorly-drained floodplain facies association

Description

This facies association consists of massive clay and silty clay ranging in color from grey to dark grey. Organic matter may locally form mm- to cm-thick blackish layers. Pocket penetration values fall invariably in the narrow interval of 1.2-1.8 kg/cm^2, with very few exceptions. This facies association characterizes two major stratigraphic intervals: below the lower A1 aquifer and above the upper A1 aquifer, around 3-5 m, where it is laterally connected to more organic deposits (MC 4-5).

Interpretation

This facies association has been interpreted as poorly drained floodplain deposits: lithology and grain size testify to a low-energy depositional environment typical of floodplain deposits. However, the homogeneous grey color combined with relatively low pocket penetration values suggest general development of poorly drained conditions, possibly due to high water level.

Swamp facies association

Description

This facies association is made up of dark grey to blackish organic-rich clay, with abundant mm-sized plant debris and leaf fragments. This unit has maximum thickness of about 3.5 m, and has been typically recorded between about 8.5 and 12 m core depth, where it may include a thin, poorly drained floodplain deposit. A characteristic peat horizon, about 1 m thick, forms a prominent marker bed atop the upper A1 aquifer, in the basal portion of this facies association. In this facies association, the dark clay is commonly very soft, as revealed by its very low pocket penetration values (0.2 to 1.2kg/cm^2). This facies association is also present just below the lower A1 aquifer.

Interpretation

The abundance of clay, organic matter and peat testifies deposition in stagnant, most-likely freshwater environments (swamps). The blackish and dark gray colors indicate an abundance of organic matter. The thinner clay layers are possibly related to occasional river floods and/or water level fluctuations in slightly depressed areas, while the thickest intervals suggest relatively persistent standing bodies of water. The crevasse deposit that interrupts the lateral continuity of this facies association has been interpreted to reflect temporary filling of the paludal environment by fluvial processes.

The depositional facies architecture of the monitoring cross section composed by profiles MC1-2, MC3 and MC4-5 was obtained via the interpolation of the five facies associations described above (Fig. 6.2). As mentioned earlier in this paragraph, the three aquifers crossed by the cross section (A0, upper A1 and lower A1, from the ground surface) correspond to fluvial-channel sand bodies. The aquitards interposed to the aquifers (Q0, upper Q1, lower Q1 and Q2, from the ground surface) consist mainly of floodplain silts and clays, locally replaced by crevasse, levee and swamp facies associations. In particular, the clayey swamp facies association is of main interest for the present study and is located mostly between 3 and 11 m b.g.s. (MC4-5). The residual thickness of wastes (i.e. dump body), already identified at the top of the MC3 and MC4-5 profiles in Chapter 5, is reported in Figure 6.2.

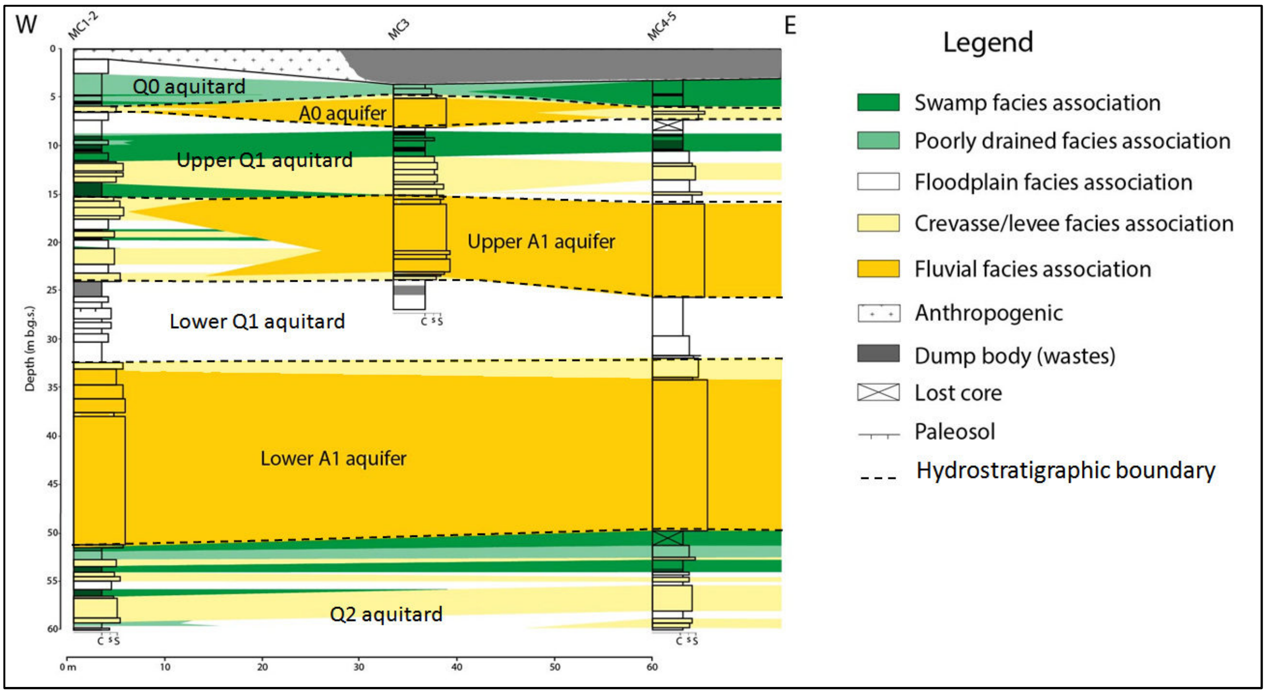

Figure 6.2: Depositional facies architecture along the monitoring cross section (Caretti site). The black dashed lines demarcate different hydrostratigraphic bodies (i.e. aquifers and aquitards).

6.4.1.2 Distribution of contaminants

The very detailed vertical distribution of chlorinated ethenes (C_t; µg/g) obtained by sediment subsamples along the eastern profile of the cross section (MC4-5; Fig. 3.8 - Chap. 3) was already described in Chapter 5. In particular, the distinction between parent (PCE and TCE) and daughter (cDCE and VC) contaminants, already mentioned in Chapter 5, assumes here a key role. This distinction has been carried out based on previous studies concerning the composition of the source of contamination (Nijenhuis et al., 2013) and on evidences of biodegradation observed along the profiles, which will be extensively discussed in Paragraph 6.4.1.3.

As already described in Chapter 5, parent compounds occur along the whole MC4-5 profile (0 to 60 m b.g.s.), with the highest concentrations located in A0 aquifer and at the top of upper Q1 and lower Q1 aquitards (Fig. 6.3). Differently, daughter products are present exclusively within the uppermost 11 m of the MC4-5 profile. They show the highest concentrations at the bottom of Q0 aquitard (3 to 5.5 m b.g.s.) and at the top of upper Q1 (8 to 11 m b.g.s.). In A0 aquifer, cDCE and VC are present in concentrations respectively 50% and 90% lower than in the surrounding aquitards (Fig. 6.3).

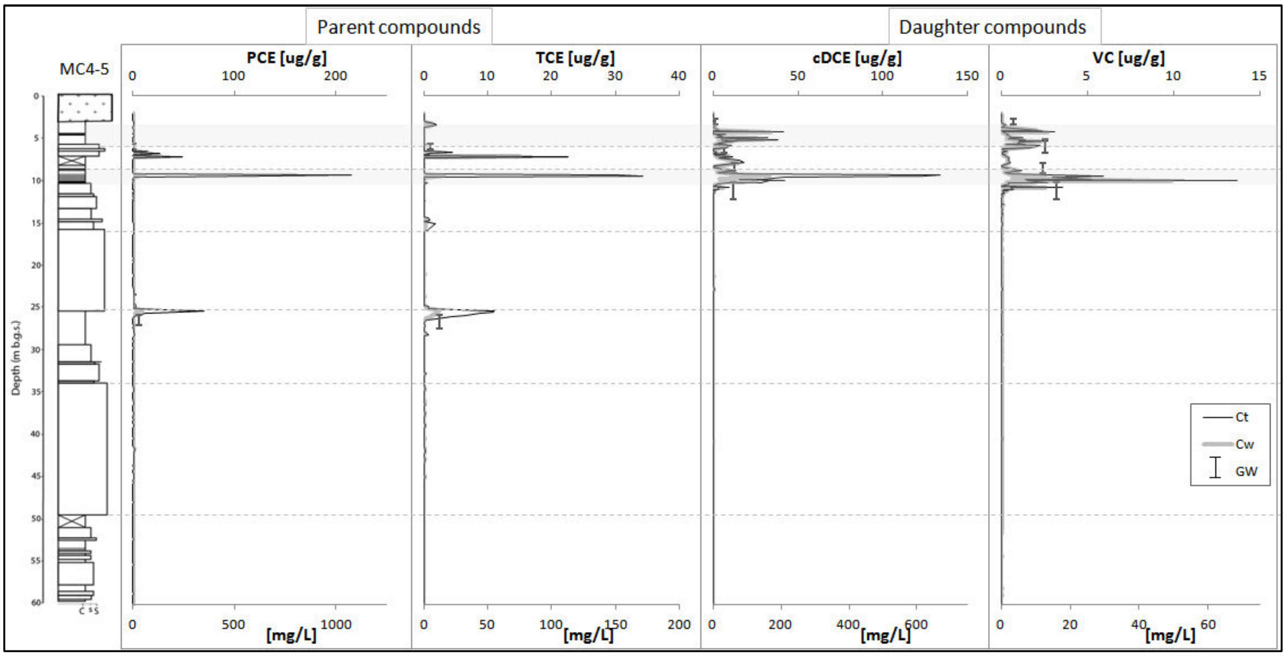

Figure 6.3: Vertical distribution of chlorinated ethenes obtained by core subsamples and groundwater samples collected along profile MC4-5. The total concentrations of the main analytes (C_t; ug/g wet soil) are reported together with estimated dissolved concentrations (C_w; mg/L). Dissolved concentrations obtained by groundwater samples are referred to as GW, and expressed in mg/L. The location of swamp deposits is highlighted in light grey, while the interfaces between aquifers and aquitards are identified with dotted lines.

The trend of estimated dissolved concentrations (C_w; mg/L), obtained via the phase-partitioning suggested in Chapter 5, turned out to be very similar to the one already observed for C_t. The comparison between stratigraphic architecture along the cross section (Par. 6.4.1.1) and the distribution of C_t and C_w of daughter compounds shows that the peak concentrations of VC and cDCE occur within the shallow, peat-rich swamp deposits. This suggests a cause-effect relationship between the presence of organic swamp sediments and the biodegradation of parent compounds, likely occurring via reductive dechlorination (Vogel et al., 1987), as discussed in Paragraph 6.4.1.3.

As already described in Chapter 5, it was possible to use the contaminant concentration results obtained from groundwater samples collected along M1-2 and MC3 profiles, in order to extend the observations carried out on profile MC4-5 to the rest of the cross section. This allowed to identify substantial variations in the vertical distribution of parents and daughter compounds along the three profiles (Fig. 6.4). In detail, differently from MC4-5, the compounds identified as dechlorination products (i.e. cDCE and VC) are spread in upper A1 both along MC1-2 and MC3 profiles, maximum concentrations in groundwater being equal to 61.4 mg/L (cDCE) and 25 mg/L (VC). In the western profile (MC1-2) both parent and daughter compounds show remarkable concentrations in upper A1 aquifer, being almost absent in the shallower portion of the profile. Also, PCE, which is the highest chlorinated compound, show relatively low concentrations along the whole MC1-2 profile (max concentration equal to 0.4 mg/L). These variations have been interpreted as a response to the slightly different distribution of depositional facies along the three profiles, which likely influenced the possible vertical flow connections between different hydrogeological bodies; also, the non-uniform presence of a marginal fringe of the source of contamination (i.e. dump body) above the profiles (already mentioned in Chap.5) likely contributed to the variability of contaminant distribution (see the conceptual model in Par. 6.4.1.4).

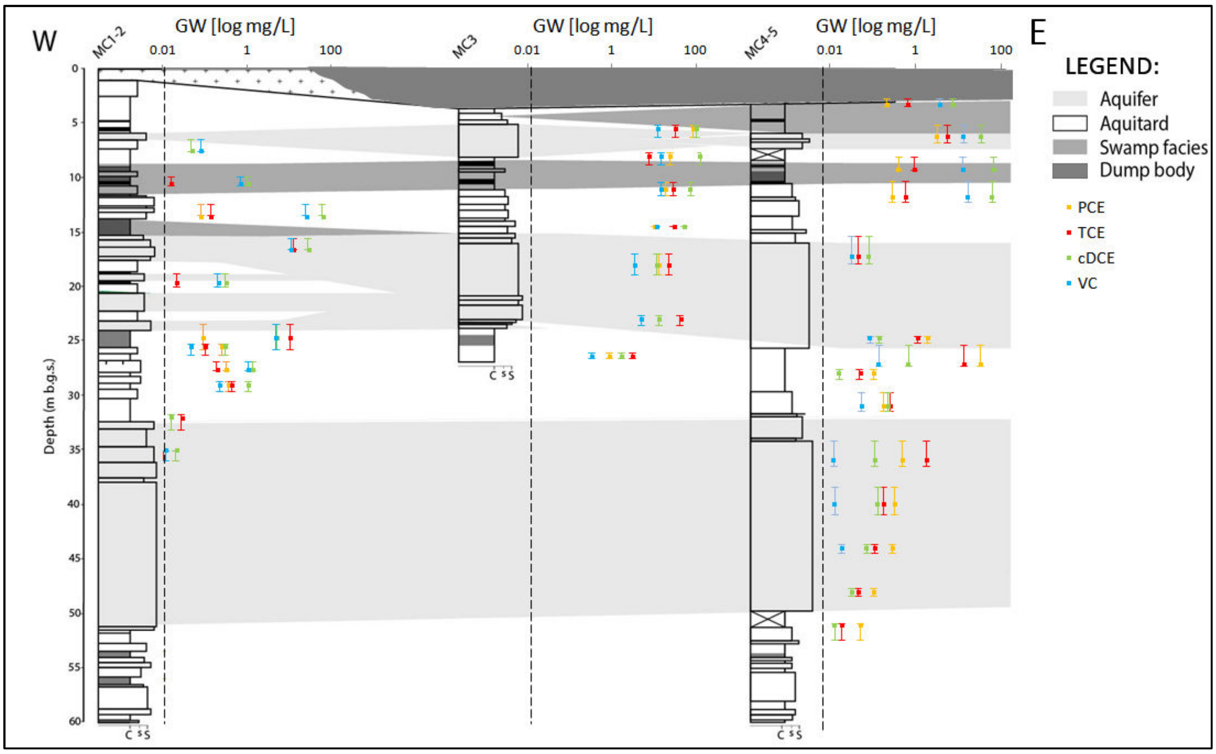

Figure 6.4: Distribution of parent and daughter contaminants obtained by groundwater samples collected along the whole monitoring cross section (profiles MC1-2, MC3 and MC4-5). The concentrations are expressed in mg/L and shown in logarithmic scale.

6.4.1.3 Vinyl Chloride origin

The overlap between different physico-chemical information collected along the monitoring cross section (mainly along profile MC4-5) allowed to interpret the genesis of accumulation of daughter contaminants (e.g. VC) and its relations with the architecture of depositional environments. The different information collected are described, as follows.

Redox conditions

Markedly negative values of Eh have been detected in groundwater along the whole cross section (-278 to -100 mV; Fig. 6.5). Dissolved methane has been found in all the groundwater samples analyzed, with concentrations ranging from 30.65 to 1296.22 mg/L (Fig. 6.5). In particular, the averaged concentration of methane within the shallower 11 m of the system is 223.62 mg/L, around two orders of magnitude higher than the averaged background value at regional scale (6.63 mg/L; Sciarra et al., 2013). This massive occurrence of dissolved methane and the markedly negative Eh confirm the occurrence of methanogenic conditions along the whole system. The methanogenic condition represents the most favorable groundwater geochemical condition for reductive dechlorination down to VC (Stroo and Ward, 2010).

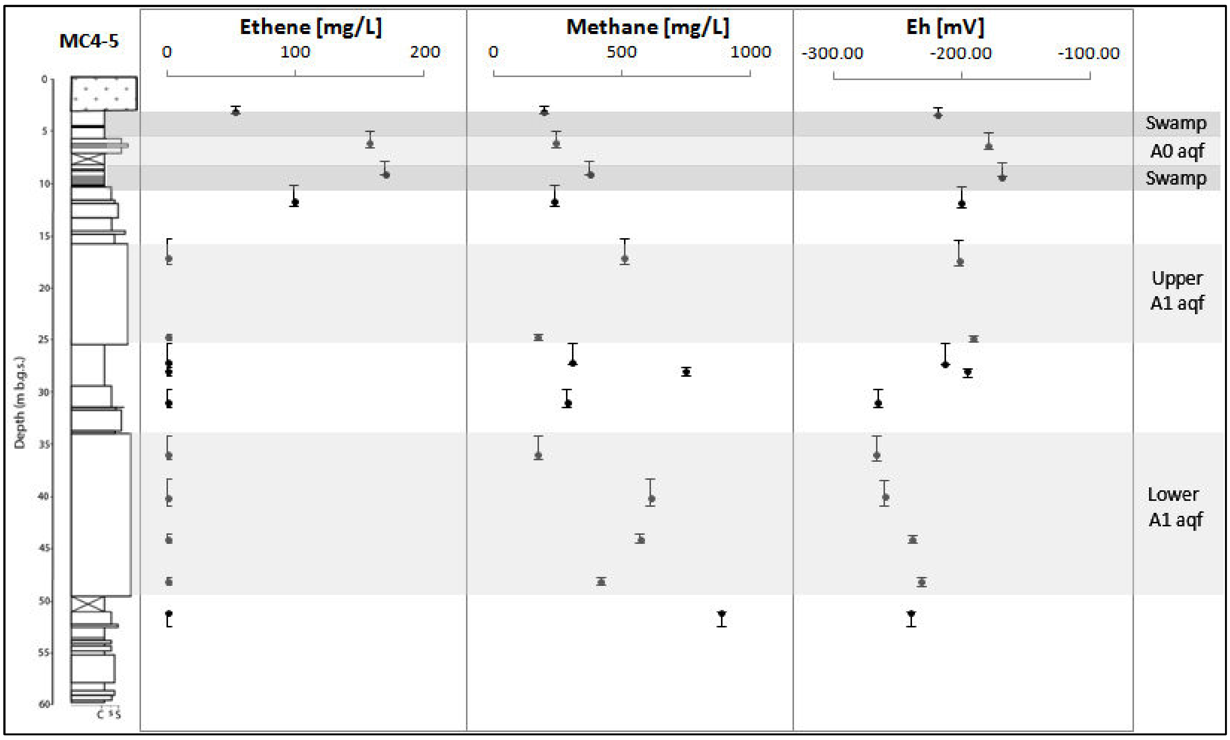

Figure 6.5: Distribution of dissolved gases (ethene and methane) and Eh along profile MC4-5.

Vertical distribution of parent and daughter contaminants

The detailed vertical distribution of contaminants (MC4-5; see Par. 6.4.1.2) shows alternated peaks of concentrations of parent compounds (i.e. PCE and TCE) or dechlorination products (i.e. cDCE and VC). The two groups of compounds rarely coexist along the profile. In particular, cDCE and VC peaks occur within the shallow organic-rich swamp sediments, where the concentrations of parent compounds PCE and TCE in dissolved phase are significantly lowered. No accumulation (or very low concentrations) of daughter compounds is detectable in correspondence of the concentration peaks of PCE and TCE observed in A0 aquifer and at the interface between the upper A1 and the lower Q1 aquitard (this last body being mostly composed of inorganic to slightly organic clay and silt; i.e. floodplain facies association). The distribution of dissolved gases along the MC4-5 profile shows significant concentrations of ethene occurring exclusively within the swamp deposits (Fig. 6.5), as already observed for VC and cDCE. These distributions suggest the occurrence of reductive dechlorination, and subsequent accumulation of degradation products, occurring in correspondence of the swamp layers. The presence of ethene also testifies that the dechlorination process was completed for a portion of the contaminant mass.

CSIA of chlorinated ethenes

The general depleted $\delta^{13}C$ values obtained for chlorinated ethenes in the study area ($-76‰ < \delta^{13}C < -51$ ‰), in comparison with the one of common commercial products (-37‰ < δ13C < -23‰; Hunkeler et al., 2005; Sherwood Lollar et al., 2000; Shouakar-Stash et al., 2003), are related to the characteristics of the primary source of contamination, described by Nijenhuis et al. (2013) (Fig. 6.6).

The detailed vertical trend of carbon stable isotopes obtained along MC4-5 profile is very heterogeneous for all the compounds (Fig. 6.6 b). Such variability probably reflects the high lithologic heterogeneity of the local stratigraphy and the complex architecture of contaminants. In order to try to simplify the profile and thus identify possible isotope fractionation patterns, the isotopic signatures corresponding to the main peaks of concentration of contaminants have been isolated (Fig. 6.6 c). This allowed to identify two main isotopic conditions, named as A and B: in condition A only parent contaminants are present, with relatively depleted signatures (-75‰ < δ13C < -68‰). This corresponds with the peak concentrations of PCE and TCE; in condition B both parent and daughter compounds are present, parents showing relatively enriched signatures (-56‰ < δ13C < -50‰) and daughters being relatively depleted (-76‰ < δ13C < -61‰). This corresponds with the peak concentrations of daughter compounds (i.e. peaty swamp layers). Conditions A and B have been related with two different steps of the isotopic dechlorination pathway (Bloom et al., 2000; Hunkeler et al., 2005; Slater et al., 2001). In particular condition A would correspond with the beginning of the dechlorination, when no (or very few) products are present; condition B would correspond with the end of the dechlorination pathway, when the most part of parent compounds are converted into products, and products reach an isotopic signature similar to the one of the original parents. This interpretation supports the occurrence of a strong biodegradation activity, via reductive dechlorination, within the organic-rich swamp layers. Differently, no dechlorination activity can be inferred in the layers not enriched in organic matter.

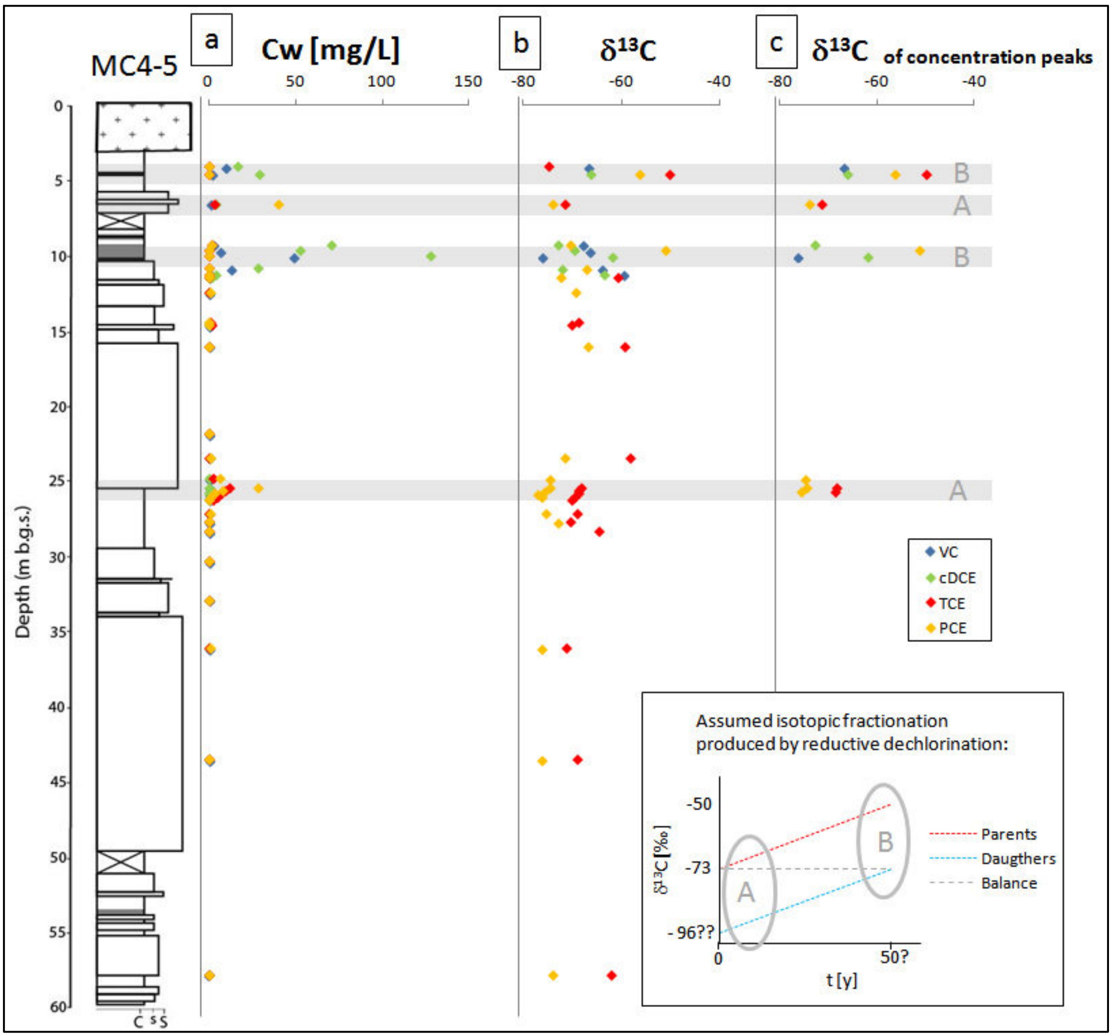

Figure 6.6: $\delta^{13}C$ of chlorinated ethenes obtained from core subsamples collected along profile MC4-5. The estimated dissolved contaminant concentration (C_w) obtained at the sampling depths of isotopic analyses are reported for reference (a). The grey stripes highlight the contaminant concentration peaks (parent or daughter compounds). A and B refer to two distinct steps of the isotope fractionation pathway produced by reductive dechlorination.

All the data presented above support the occurrence reductive dechlorination of chloroethenes at the site, mostly occurring within the shallow organic-rich swamp deposits. This produced local accumulation of products characterized by a higher degree of toxicity and carcinogenicity than the parent contaminants (i.e. VC).

The accumulation of VC in a shallow position in the system favors both the migration in dissolved phase within adjacent hydrogeological bodies (upper A1 aquifer; see Par. 6.4.1.2) and the emission in vapor phase in the surface environment (see discussion in Par. 6.4.1.5).

6.4.1.4 Contamination conceptual model

The following conceptual model (Fig. 6.7) has been developed in order to match together the information presented in Paragraphs 6.4.1.1, 6.4.1.2, 6.4.1.3 and the detailed distribution of contaminants already described in Chapter 5:

a pure phase DNAPL, mainly composed by PCE and TCE, took origin from the local source of contamination (i.e. old dumps filled with urban and industrial wastes during '70; Nijenhuis et al., 2013), and easily migrated into the A0 aquifer, which at some locations is in direct contact with the dump body. DNAPL was then able to migrate downward trough the upper Q1 aquitard, where some mass was left behind as residual phase, while the remaining contaminant mass reached the upper A1 aquifer. Contaminants stored in the organic-rich swamp layers within the Q0 and upper Q1 aquitards (as DNAPL residual phase) were subject to dissolution and further reductive dechlorination, with consecutive accumulation of cDCE and VC (mostly in dissolved phase). The vertical migration of DNAPL proceeded down to the A1 aquifer, crossing the whole thickness of Q1 aquitard, likely through micro heterogeneities and discontinuities (see discussion in Chap. 5).

Only parent compounds are present in the portions of the system where no enrichment in organic matter was observed, thus testifying that in the absence of organic-rich layers (i.e. swamp facies association) dechlorination of high chlorinated compounds did not take place.

Concerning the occurrence of daughter compounds in the upper A1 aquifer along the MC3 profile (Fig. 6.4), this can be attributable to slight changes in stratigraphic architecture along this profile with respect to MC4-5. Indeed, while in MC4-5 profile the upper Q1 aquitard consists of swamp deposits overlying floodplain clays and silts (about 4 m thick), these latter are replaced by more permeable crevasse and levee deposits in MC3. The occurrence of this sandier horizon between the swamp deposits and the upper A1 aquifer likely allowed the migration of daughter products in dissolved phase from the organic-rich layer down into the aquifer.

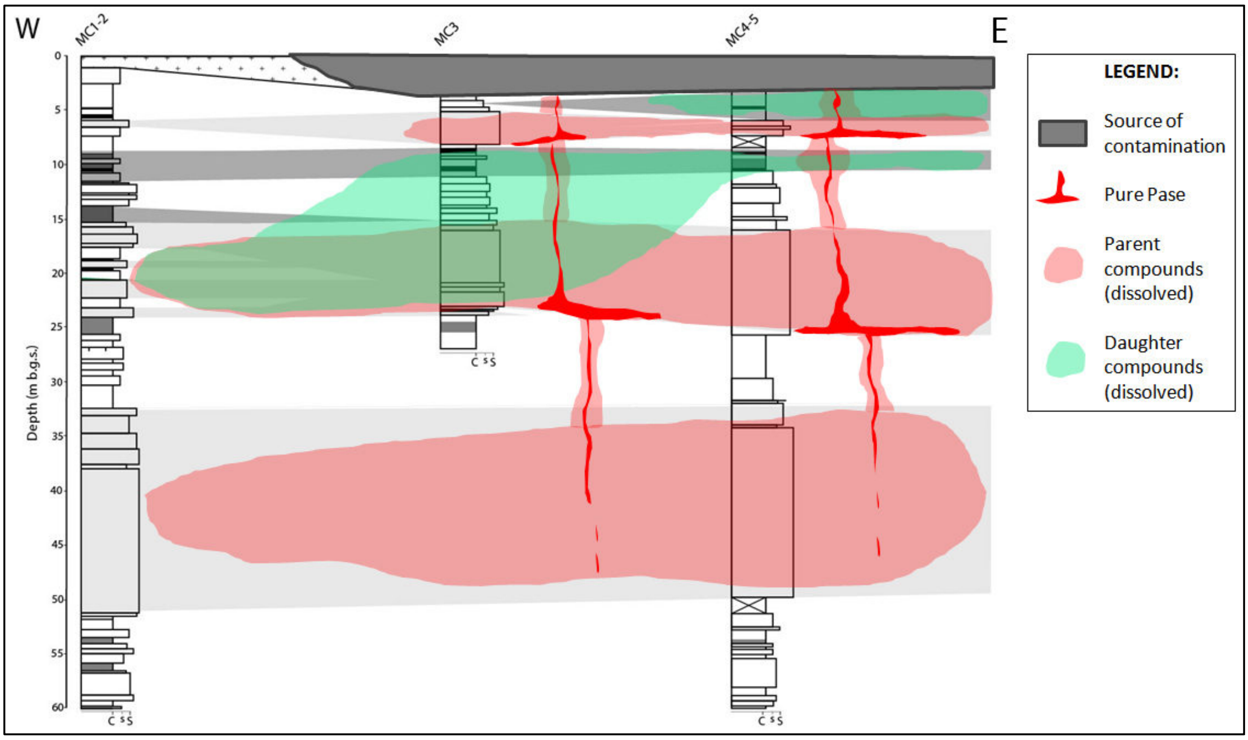

Figure 6.7: Conceptual model of the distribution and transformation of contaminants along the monitoring cross section.

Concerning the MC1-2 profile, the contaminants found in the upper A1 aquifer likely represent a plume originated upgradient, as already inferred in Chapter 5. The relatively low concentrations of PCE detected in MC1-2 suggest that the contamination along this profile was subjected to a higher degree of degradation than in the rest of the cross section. This likely reflects a further natural attenuation of contaminants occurred along the plume during its migration (Wiedemeier et al., 1998).

6.4.1.5 Vinyl Chloride vapor emission issue

As a group, the dense chlorinated solvents are quite volatile, and can thus partition into the gas phase and migrate great distances as vapors in the unsaturated zone (Pankow and Cherry, 1996). In particular, VC is characterized by the highest Henry constant (Kh, equal to 7.92 E-2 atm m3/mol at 25 °C; Mackay et al., 2006) among chlorinated ethenes, and by the lower density (0.91 g/cm3 at 20°C; Mackay et al., 2006). These characteristics make the compound strongly inclined to volatilize in the unsaturated domain, under purely diffusive or convective flux, with possible release in the surface environment.

As described in Paragraph 6.4.1.2, VC has been observed at shallow depth in the source area of Caretti site. This gave origin to contaminant plumes in upper A1 and A0 aquifers, mainly composed of VC (Gargini et al., 2011; Nijenhuis et al., 2013). These plumes are currently in migration below a newly developed neighborhood (Fig. 2.5 – Chap. 2).

The plume in the A0 aquifer is very shallow (4 to 10 m b.g.s.) and the soil cover above A0 is strongly heterogeneous (poor lateral extension, very variable thickness, local enrichments in silt or fine sand). Therefore, a potential risk for human health arises, which consists in the possible emission of VC in vapor phase at the ground surface through the unsaturated zone, with further inhalation by residents (Gargini et al., 2011; Saponaro et al., 2011).

The detailed vertical distribution (metric resolution) of dissolved chlorinated ethenes in the A0 aquifer and in the saturated part of the soil cover have been determined in order to assess the possibility of a VC partition to gas phase within the unsaturated zone. The contaminant profiling has been performed from groundwater samples collected from the shallow bundled multilevel system described in Paragraph 6.3.3.1 (MS1 in Fig. 3.8 - Chap. 3), located on the plume, around 80 m north of the source area.

The maximum concentrations of chlorinated ethenes detected along the profile (Fig. 6.8 a) are 4 orders of magnitude lower than in the source area. All main parents and daughter compounds detected at the source are also present in the plume. A general decrease in concentrations occurs from the aquifer towards the soil cover. In particular, a regular decrease of VC concentration can be observed from the bottom of A0 aquifer to the ground surface (from 0.055 mg/L at A0 bottom to 0.003 mg/L at 2 m b.g.s.). This decreasing trend has been interpreted as possible result of aerobic biodegradation of VC while moving toward the surface oxygenated environment. Indeed, is well documented in literature that VC is readily biodegradable under aerobic conditions (Barbee, 1994; Bradley and Chapelle, 1999; Coleman et al., 2002a; Coleman et al., 2002b; Davis and Carpenter, 1990; Elango et al., 2006; Hartmans, 1995; Hartmans and De Bont, 1992; Hartmans et al., 1985; Verce et al., 2000). Thus, the occurrence of and significant aerobic degradation of VC, while migrating through the vadose zone, represents a reliable hypothesis. This hypothesis is corroborated by the trend of Eh observed along MS1 (Fig. 6.8 b), which shows a sharp increase from the top of A0 toward the ground surface. However, in order to verify the effectiveness of aerobic degradation of VC within the vadose zone further investigations should be carried out at the study site.

Regardless of possible aerobic degradation, the distribution of VC along the MS1 profile proves that the contaminant is not reaching the ground surface in gas phase within the plume area. The possible partition of VC to gas phase is disfavored by the vertical distribution of dissolved VC, which is accumulated at the bottom of A0 aquifer, around 7 m below the interface between the saturated and unsaturated domains.

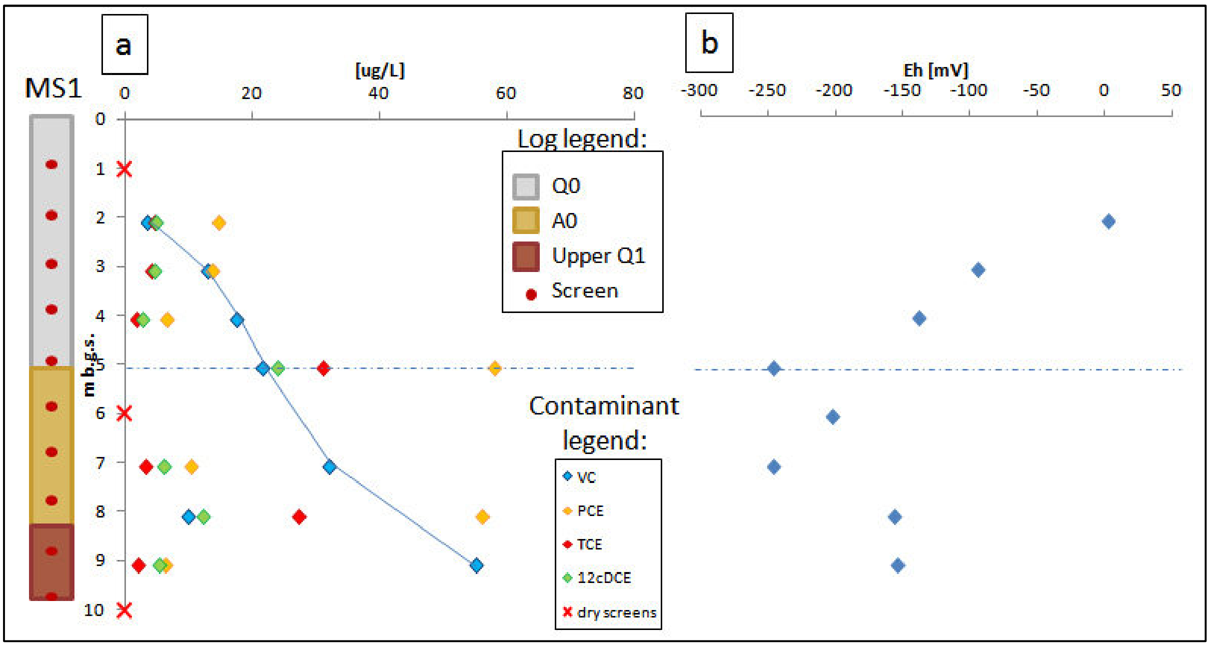

Figure 6.8: Distribution of chlorinated ethenes (a) and Eh (b) from water samples collected in system MS1. The dashed line highlights the interface between Q0 aquitard and A0 aquifer. The blue line in (a) highlights the decreasing trend of VC towards the ground surface.

The evidence provided by the MS1 profile is in agreement with recent studies from the study area (Gargini et al., 2011; Saponaro et al., 2011) concerning measurements of gas fluxes by means of dynamic flux chamber and indoor air monitoring. According to these studies, no significant concentrations of VC were detected neither in indoor environment nor at the ground surface.

Thus, the potential emission of VC vapor at the surface and the connected risk of human health is unlikely affecting the study site.

6.4.2 Plume scale results

The evidences of biodegradation of contaminants and accumulation of daughter compounds collected at the Caretti site have been employed for the interpretation of the genesis of the VC-alone plumes A and B, where there is no exact knowledge about the location and composition of the source. The architecture of plumes A and B is discussed in Paragraph 6.4.2.1. A comparison between the plumes and the architecture of depositional facies is discussed in Paragraph 6.4.2.2.

6.4.2.1 Contaminant areal distribution

Two plumes almost entirely composed of VC are present at the contaminated sites A and B, in the northwestern portion of the study area. Both sites are located 1.5 to 3 km NW from the historical city of Ferrara ("NW setting" in Fig. 6.1), within the multilayered hydrogeological system presented in Chapter 1. The location of site A is indicated in Figure 6.1, while the precise position of site B will remain unknown for the sake of keeping the privacy about the owners. In both cases the plumes are hosted in A1 aquifer (Fig. 6.11), and are markedly developed along the main flow direction (up to around 1.2 km), while they are characterized by a limited transversal extension (up to 300 m in the case of plume A, the largest one). Plume B is characterized by a higher longitudinal to transversal extension ratio, in comparison with A (4.6, versus 2.7 of plume A). This can be implied to an important pumping activity occurring immediately downgradient to site B, which stressed the piezometric distribution during the last decades, locally increasing the hydraulic gradient along the main flow direction.

It is known that the origin of the contamination at both sites is related to local sources directly or indirectly linked with industrial activities (Nijenhuis et al., 2013). Highly chlorinated compounds were spilled in the environment as industrial wastes, while VC must represent a product of degradation of former compounds. However, for neither of the two sites it was possible to identify the exact location and composition of the primary source of contamination.

Concerning plume A, in Fig. 6.9 a,b,c are shown three areal distributions of the main compound VC, which are representative of three different depth intervals within the A1 aquifer (a: 12 to 17 m; b: 19 to 23 m; c: 24 to 28.7 m). The depth discrete characterization of the plume has been obtained by means of direct push groundwater sampling, as already mentioned in Paragraph 6.3.3.1. The shallower distribution (Fig. 6.9 a) shows the highest concentrations of VC, localized in particular in the upgradient portion of the plume, and a limited longitudinal extension in comparison with the deeper sections. Distributions of VC in Figures 6.9 b and 6.9 c show a progressive decrease in concentration with depth and a slight increasing longitudinal extension. The whole architecture of the plume suggests the occurrence of an active source of VC located above the top of the aquifer.

Concerning plume B (Fig. 6.10 a), the only multi-depth groundwater sampling performed in one piezometer of the local monitoring network shows that the maximum concentrations of VC occur within the shallower 10 m of the aquifer (Fig 6.10 b), suggesting also in this case a supply of the compound from above the top of the aquifer.

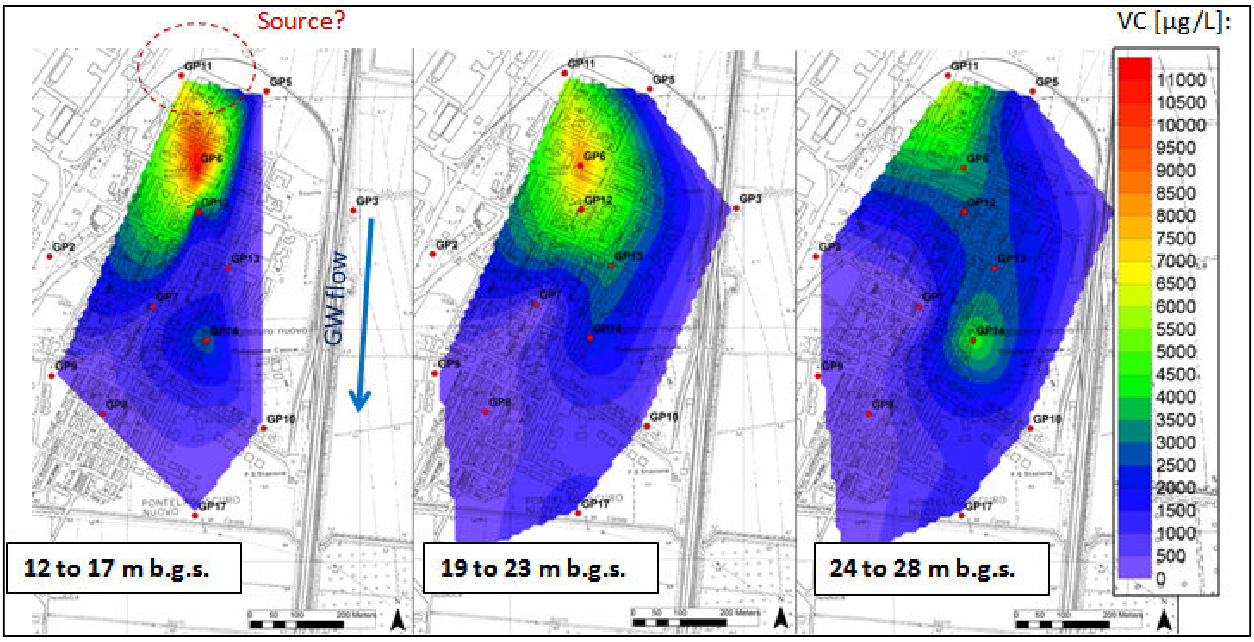

Figure 6.9: Distribution of vinyl chloride in plume A obtained by direct push groundwater sampling. The three maps refer to different depth intervals within A1 aquifer.

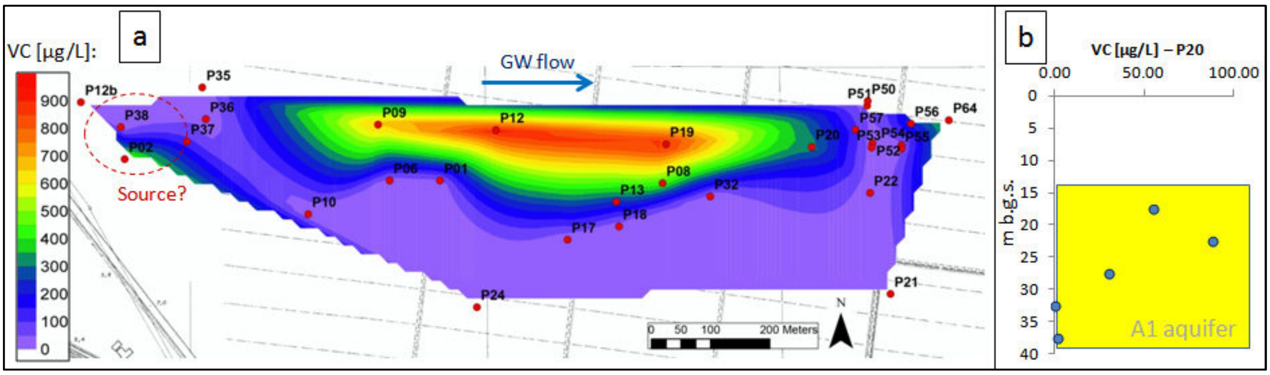

Figure 6.10: (a) Distribution of vinyl chloride in plume B; (b) results from multi-level groundwater sampling performed on piezometer P20.

6.4.2.2 Stratigraphic architecture and Vinyl Chloride alone plumes

A stratigraphic transect, 6 km long, between the Caretti site and the northwestern setting (where sites A and B are located) depicts the stratigraphic architecture of the five depositional facies illustrated in Paragraph 6.4.1.1 (Fig. 6.11). Concerning the fluvial channel facies association, the spatial distribution of which controls the geometry of aquifers, it is clear from the cross section that the aquifer A1 forms a single hydrostratigraphic body in the northwestern part of the transect, while it is split into two distinct confined aquifers (i.e. lower A1 and upper A1 in Fig. 6.11) at the Caretti site. At this location, two fluvial bodies are separated, between about 20 and 30 m b.g.s., by a thick stratigraphic interval made up of poorly drained floodplain deposits. The stratigraphic transect also shows the ubiquitous presence of swamp deposits across the whole study area. This unit invariably overlies aquifer A1 (upper A1, at the Caretti site), and shows an increasing volume of peat-rich deposits toward distal locations (i.e., NE-ward).

The overlap between depositional facies architecture and the architecture of plumes A and B suggests that the dynamics of biodegradation and accumulation of VC observed at the Caretti site can also be applied to the interpretation of the VC-enriched contamination at sites A and B. Specifically, based on the evidence from the Caretti site, the organic-rich swamp deposits are very likely to represent an efficient "reactor" for the degradation of high chlorinated aliphatic compounds. The local hydrogeological interconnection between swamp deposits and the underlying aquifer favors the migration of daughter products in the groundwater flow of the aquifer, with further formation of dissolved plumes enriched in low chlorinated compounds. In support of this interpretation, the distribution of VC observed in plumes A and B (Fig. 6.9 and 6.10; Par. 6.4.2.1), suggests that the supply of contaminant occurs mostly at the interface between the contaminated aquifer and the overlying aquitard. Therefore, the same conceptual model inferred at the source area in Caretti site can be used to interpret the genesis of plumes A and B: a pure phase DNAPL composed by high chlorinated compounds migrated vertically from a surface source area through the peat-rich swamp deposits. Reductive dechlorination occurred in this zone with further release of daughter compounds in the underlying aquifer. The greater thickness and higher persistence of organic-rich layers in the northern part of the stratigraphic transect could have exacerbate the dechlorination process, causing the disappearance of parent compounds in site A and B. Moreover, the natural attenuation of the plumes during their migration in the aquifer could have produced a further relative increase of VC concentration (Wiedemeier et al., 1998). Indeed, also the plumes developed in the Caretti site show a relative enrichment in VC, as the distance from the source increases (as shown from data described by Gargini et al., 2011).

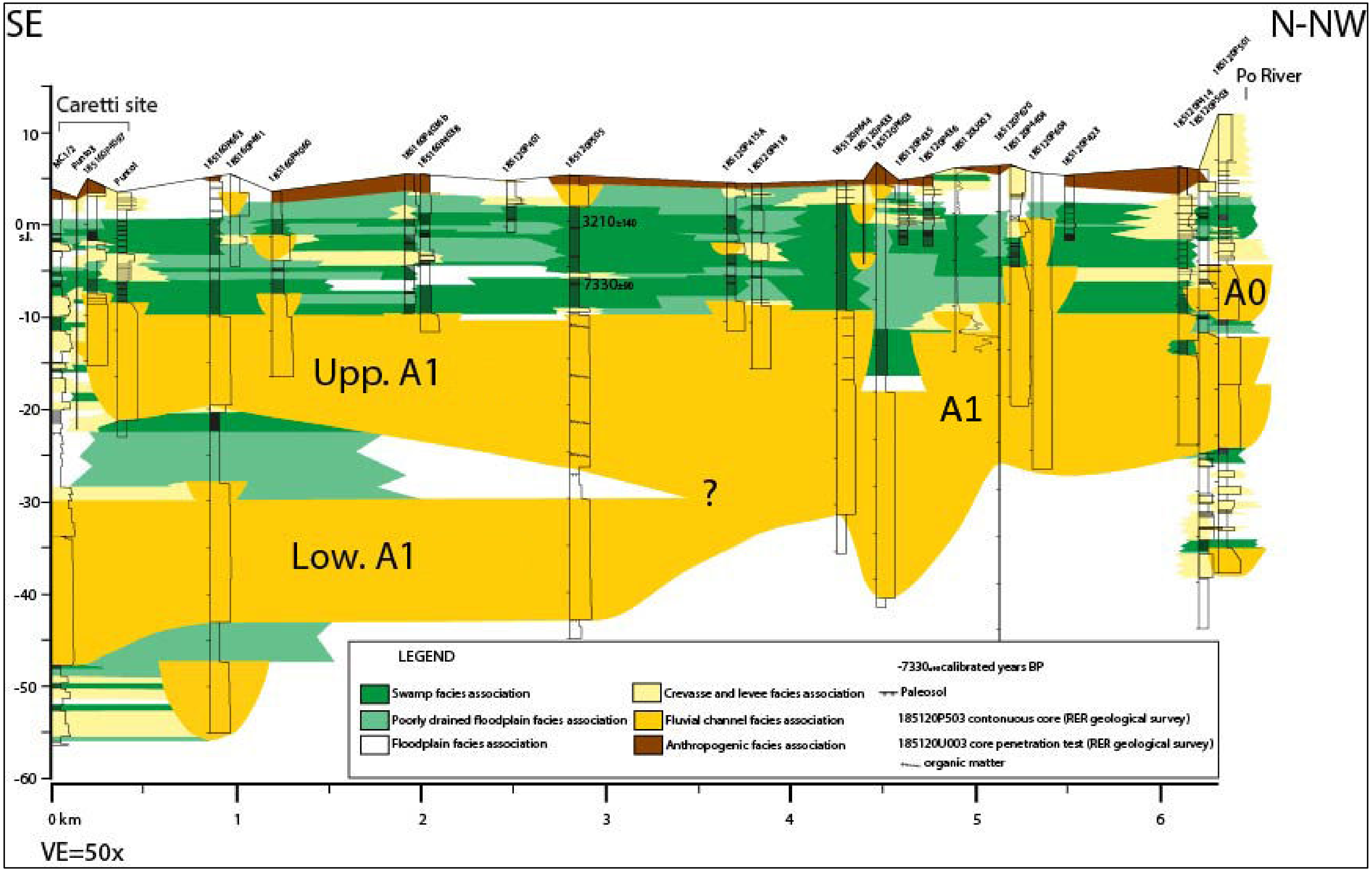

Figure 6.11: Depositional facies and hydrostratigraphic architecture from the Caretti site to the Northwestern setting (contaminated sites A and B). The locations of the profiles used to realize the transect are indicated in Fig. 6.1.

6.5 Summary and conclusions

The hydrogeological system below the territory of Ferrara is characterized by recurring accumulations of VC in groundwater. In particular, two very peculiar VC alone plumes are developed for more than 1 km from the source, within the shallower confined aquifer of the area. Also, significant accumulations of VC were found 3 to 11 m b.g.s. in urbanized areas (concentration up to 70 mg/L in Caretti site), giving origin to potential vapor intrusion issues.

A detailed stratigraphic and hydrogeological investigation carried out at different scales (i.e. source- and plume-scale) allowed to interpret the complex contaminant distribution and to identify the biodegradation processes responsible for the accumulation of low chlorinated compounds, as well as the most active biodegradation zones. In particular, the co-occurrence of peat-rich deposits (corresponding to Holocene swamp sediments) and scattered primary sources of chlorinated solvents were identified as the cause of the massive occurrence of VC in the local hydrogeologic system. Following the conceptual model developed for the area of Ferrara, reductive dechlorination of high chlorinated compounds (PCE and TCE), down to VC, took place subsequently to the migration of a DNAPL phase through the fine peat-rich swamp deposits, which represent a local "reactor" for biodegradation.

Thus, the co-occurrence of organic-rich sediments and chlorinated solvent contamination represents both an opportunity for the natural attenuation of contaminants and an environmental and human-health issue. Indeed, if the biodegradation of high chlorinated compound get suck to VC, as in the case of Ferrara, the threats related to the contamination arise exponentially, due to the extreme mobility (both in dissolved and vapor phase) and high carcinogenicity of the compound. In this respect, the location in the system of the swamp deposits, "reactor" of biodegradation, plays a key role in the definition of the possible risks arising by the accumulation of VC. For example, an accumulation of VC in a shallow portion of the system favors the emission in vapor phase in the surface environment.

The results of this study proved the usefulness of combined paleo-environmental and hydrogeological investigations as a tool to interpret the subsurface distribution of contaminants and foresee their fate. In particular, the analysis of depositional facies in a hydrogeological reading key highlighted dynamics peculiar of alluvial systems contaminated by chlorinated solvents. Taking into account that contaminations by chlorinated solvents are very diffused in all the industrialized parts of the world, thus affecting several other alluvial plains with hydrogeological features likely similar to the Ferrara area, these results represent also a valuable basis for the interpretation of anomalous accumulations of daughter products of biodegradation, possibly occurring in this type of depositional systems.

Summary and final remarks

A test-site located in an alluvial plain and strongly contaminated by chlorinated solvents DNAPL (source still active) was investigated in detail throughout this thesis. From a methodological viewpoint, a limited-in-space high-resolution investigative approach was favored in this research, consisting in the analysis of a cross section disposed on the fringe of the local test-site source of contamination, and composed by three vertical profiles 30 to 60 m deep. Detailed distributions of data were collected from these three profiles, concerning both aquifers and aquitards, by means of high resolution techniques based on multi-level and multi-port vertical profiling.

The selected investigative approach gave us the chance to go deep into the processes of migration and degradation of contaminants and to verify their strict relationships with the geologic and stratigraphic features of the local hydrogeological system.

The research was conducted following a three-steps investigation, each of them connected to the others in a logical and multi-scale succession; multi-level vertical profiling provided data for each of the three steps.

In the first step (Chap. 4), the hydrogeological system was investigated at regional scale, adopting a quantitative evaluation approach based on water stable isotopes ($\delta^{18}O$, $\delta^{2}H$). The isotopic signatures of water were employed as conservative natural tracers of groundwater flow from the recharge areas to the sampling points. This allowed to quantify the relative amounts of recharge contributing to the different aquifers from the different local sources, by means of relatively simple mixing calculations. In such a manner, considering the amount of vertical recharge (i.e. rainfall) contributing to the different aquifers as a proxy of the degree of interconnection with a possible surface source of contamination, the intrinsic vulnerability of the distinct aquifers was evaluated. The use of mixing calculations applied on environmental isotopes turned out to be a valuable tool both to allocate different sources of recharge (direct or lateral) and to assess the intrinsic vulnerability of aquifers in a multilayered hydrogeological setting. A link from the regional to the local scale of investigation was provided by a multi-level vertical reconstruction of the stable isotope composition of pore-water, obtained by means of a detailed vertical sampling of sediments performed throughout aquifers and aquitards. These last site-scale results allowed to integrate and validate the regional model of quantification of recharge and assessment of intrinsic vulnerability. Also, strong isotopic gradients were detected across aquitards at the site scale, thus confirming that the fine grained layers behave as hydraulic barriers for the surrounding aquifers.

The second investigation step (Chap. 5) was conducted exclusively at the test-site scale. The contamination event and the associated dynamics were observed and analyzed as a “natural process” occurring in a natural porous medium, where fluids with very different properties in respect to water migrated for the last four decades. The pattern of migration and transformation (i.e. phase-partition and biodegradation) of DNAPLs and associated dissolved chlorinated compounds was defined in detail inside the multilayered aquifer-aquitard system and was compared with the stratigraphic, hydrological and chemical properties of the same system, investigated at the same high spatial resolution.

In particular, the behavior of DNAPLs was tracked back starting from the actual distribution of the contaminants themselves, which can be considered as a very sensitive artificial tracer incidentally put in the system a certain time ago (about four decades ago in the investigated case). This kind of tracer allowed also to deepen the knowledge about the hydrogeologic system (e.g. it highlighted the main contrasts of permeability, the occurrence of heterogeneities and microfractures, the zones with higher horizontal flow).

A comparison between the vertical profiling of contaminants and the ones relative to hydraulic heads and major inorganic ions dissolved in groundwater, provided an evidence of the strong vertical migration capability of DNAPLs in respect to groundwater flow. Indeed, thin layers inside aquitards, which showed the capacity of maintain high vertical hydraulic gradient and to act as barriers towards the vertical migration of inorganic dissolved ions, were easily crossed by DNAPLs. This process caused the contamination of the deepest confined aquifer, which represents the main local fresh water reservoir for drinkable and irrigation purposes. This deep migration of contaminants was in strong disagreement with the intrinsic vulnerability of the system, as determined on the basis of groundwater flow dynamics during the first step of the investigation. The migration of DNAPLs through the portions of aquitards apparently behaving as hydraulic barriers was enhanced by the occurrence of sandy seams or local heterogeneities (particularly in the case of the shallower investigated aquitard) or by the presence of microfractures (in the case of the deeper investigated aquitard). The microfracturing wasn’t directly detected during the field investigation but was inferred based on the geological and depositional history and physical features (e.g. consistence of clays and CPTU pore-water pressure drops), suggesting a marked consolidation and a prone-to-facturing behavior for head loss layer detected in the deep aquitard.

The 1D analytical modeling of diffusion profiles detected for PCE and TCE at the top of one aquitard, allowed to date back the contamination event to 50 years ago. This was in good agreement with what inferable from the known historical activities at the source of contamination.

The third step of investigation (Chap. 6) leaded to important conclusions about the possible origin of accumulations of vinyl chloride, observed in many of the contaminated sites around the area of Ferrara. Starting from the observation of the biodegradation processes at the test-site scale, it was possible to infer that the local accumulation of vinyl chloride is related with reductive dechlorination of chlorinated ethenes occurring within organic-rich swamp layers, present at shallow depth (i.e. 3 to

11 m b.g.s.) in the local system. The hypothesis advanced at the test-site scale was supported by the comparison with information collected on two other plumes mostly composed of vinyl chloride, present in other contaminated sites of the broad Ferrara area. In this investigation step, Compound Specific Isotope Analysis (CSIA) was performed on the contaminant molecules (the $\delta^{13}C$ was determined on chlorinated ethenes) in order to verify the occurrence of biodegradation reactions (i.e. reductive dechlorination). Following the conceptual model developed during the investigation step, the occurrence of clayey peat-rich swamp deposits a few meters b.g.s. in the local, fully saturated and strongly reducing system, induced a strong reductive dechlorination of the highest chlorinated compounds (like tetrachloroethene and trichloroethene) with the production of dichloroethene and vinyl chloride (where the reaction seems to get stuck). This gives origin to two main effects: (1) the formation of rather stable vinyl chloride alone plumes in the saturated zone, which can migrate more than 1 km downgradient to the source, thus representing a big challenge in term of remediation actions; (2) the occurrence of potential vapor intrusion issues from the unsaturated zone, which can represent a significant criticality in urbanized areas. The co-occurrence of peaty layers in a stratigraphic succession and local accumulations of VC in the aquifers should then represent a warning for planners and protection agencies in order to address specific vulnerability evaluations and risk management.

The results achieved in the three investigation steps are useful not only for the obvious implications at local scale (e.g. for the management of the contamination around the area of Ferrara), but also for the interpretation of contaminant migration and transformation in the many alluvial plains contaminated by DNAPLs which are present around the world.

Eventually, two methodological remarks of global usefulness, already reclaimed throughout the whole thesis, are renewed as follows:

- the use of a limited-in-space high-resolution investigation approach is needed whenever the dynamics related to contaminants (DNAPLs and others) must be understood in their whole complexity. A significant level of high-resolution can be achieved only with the employment of effective depth-discrete sampling techniques;
- the investigation of aquitards must be considered as important as the one on aquifers, or even more, in the most part of the contaminant hydrogeology research. Indeed, aquitards constitute an integral part of the hydrogeological system, often playing very complex roles in the distribution and transformation of contaminants, not derivable from the mere and “classical” investigation of aquifers

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