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“Integrated Multidisciplinary Modeling to Support the Remediation of Contaminated Sites”

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Abstract

Hydrogeological uniqueness and chemical-physical peculiarities guide the contamination dynamics and decontamination mechanisms in the environmental arena. The experimental work carried out in 3 polluted sites in Italy, exhibiting different geological and contamination contexts, emphasized the contribution of the multitemporal and multidisciplinary geodatabase, which was created for the integrated management, representation, and analysis of different data, to reach a high-resolution characterization of underground geological heterogeneities, aquifers, and contaminated areas. The research aims to demonstrate the contributions of multiple lines of evidence approach to leading to refinement of conceptual site models, assessment of contamination, and successful remediation of contaminated sites. A multiscale approach was followed for the creation of a 3D hydrogeophysical model which acts as an effective "near real time" decision support system able to manage and release data during the different remediation phases from the site characterization up to the proper remediation intervention, all by allowing the user to view, query, and process data in 3D space. The construction of a multi-source conceptual model along with LIF (Laser Induced Fluorescence), ERT (Electrical Resistivity Tomography), and multilevel piezometers, capture the information related to the hydrogeochemical sphere in all its dimensions. The assemblage and the integration of data from the different cited sources has proven to be indispensable in the: characterization and construction of thematic and numeric models, evaluation of intervention techniques, identification of suitable sites to perform the pilot testing, implementation of tests, control and evaluation of the operating conditions at the field scale, design and implementation of full-scale interventions. 3D modeling tools, hydro-geochemical data, and high-resolution detailed site characterization strengthen the conceptual site model. The data-driven model comprises, collects, and establishes a connection between the environmental variables, to optimize the contribution of each aspect supporting the design, implementation, and validation of the remediation techniques. The multi-source geodatabase harmonizes the fusion of data, by generating a digital conceptual model that can be defined as hybrid. The spatial accuracy and dimensionality are preserved, making it a practical reality. The model does not exist within a user interface, the model is the interface supporting the decision-making processes. The hydrogeophysical model and the thematic database act as integrated and continuously updated tools, able to optimize the investigations during the

characterization phase, to support the choice of the strategies in planning phase, manage and calibrate in progress the intervention modalities according to innovative approaches during the remediation phase. The research highlights the need for a large amount of multi-source data to build a reliable and high-resolution conceptual model, and to design effective remediation strategies.

1. INTRODUCTION AND STATE OF THE ART

The national legislation on the remediation of contaminated sites was introduced with the Ministerial Decree 471/99 and profoundly modified by Legislative Decree 152/06 and subsequent amendments. The "Environmental regulations", in Part IV, Title V, "Remediation of contaminated sites", regulate the remediation and environmental restoration of contaminated sites. They define the procedures, criteria, and methods for accomplishing the necessary operations for the elimination of pollution sources and for the reduction of contaminant concentrations, in harmony with the principles and community norms, with particular reference to the "polluter pays" principle. The term “contaminated site” refers to all those areas in which, following previous or ongoing human activities, an alteration of the qualitative characteristics of the environmental matrices soil, subsoil, and groundwater was ascertained. The impairment of the environmental quality status represents a risk for human health. Legislative Decree 152/06, in Title V Part IV, which guides the remediation of polluted sites, considers the drafting of the Characterization Plan (PC) and the Conceptual Model of the Site (CSM). The PC and the CSM cannot prescind from the integration of the geological-hydrogeological and chemical data, as they describe the geological-technical characteristics of the subsoil, the hydraulic properties of the aquifers, possible pathways of the contamination, and the potential pollution of the environmental matrices. These peculiar aspects are influenced by the local geological architecture and represent unique site-specific elements, according to which it is possible to select a targeted, effective, and sustainable intervention for the remediation of contaminated sites. The Characterization Plan represents only the first phase of an environmental characterization. It constitutes the set of activities that allow to reconstruct the contamination phenomena, the geological characteristics, the chemical-physical parameters that condition the transport and the mobility between the phases of the pollutants. The Characterization Plan should provide basic information to support feasible and sustainable decisions for eventual definitive remediation. A Conceptual Site Model (CSM) is a comprehensive graphical and written summary of what is known or hypothesized about environmental contamination at a site and the relationships among key site information that are pertinent to decision-making. A CSM is a representation that evolves over the site investigation and cleanup efforts. It provides a platform for evaluating the data gaps and uncertainty associated with site history and operations. The site-specific uniqueness of geology, hydrogeology, hydrology, contaminant sources, release mechanisms, fate and transport, potential receptors, and exposure pathways guide the contamination dynamics and decontamination mechanisms in the environmental arena. The development of an accurate CSM, through the integration of geothematic data (stratigraphic, hydrogeological, geophysical, and chemical) plays a key role in the decision-making process, to achieve the planning of targeted, effective, and economically sustainable remediation interventions.

This research is inscribed within the framework of activities held by a multidisciplinary group of researchers (GEO / 05, ING-IND / 25, GEO / 11, ICAR / 03) that work together to bring innovative solutions for remediation strategies. At first the team has expressed the need to harmonize and manage the various types of information requested in a single cockpit able to store multi-source data. Whilst it may seem of common practice, the management of the different data remains a complex task. Often the contributions of the different skills are examined in their whole only ex-post while the standardization of best practices should lead to integrated data management processes in order to design in a targeted and ergonomic way, any integrative investigations and/or (re)calibrate the modalities of intervention during the test phase. The challenge to be faced is that of bridging this gap which, although of a methodological nature, has important implications on the efficiency of the selection, planning and control of remediation operations. The joint management of heterogeneous data and the contributions of the various competences lead to the standardization of an operational and conceptual protocol, for integrated data coordination processes. The development of a multidisciplinary conceptual model requires by definition the integrated analysis of data of different nature, in order to dynamically harmonize the different elements and return in near real time useful information for design purposes. The objective of the research is to provide a contribution to the optimization, management, and monitoring of polluted site remediation interventions with innovative techniques. The acquisition and the construction of multidisciplinary data storage models, is able to harmonize the different elements and to return in "near real time" pre-processed information, useful for the analysis, management, and optimization in pilot test and / or full site of innovative solutions for remediation.

This highlights the importance of bridging the methodological gap regarding the joint management of ex-post data, which has important implications on the efficiency of the selection, planning, and control of remediation interventions. At the current state of knowledge, there are no specific operational protocols for the integrated management of the various data sources. The research project aims to develop a methodology in this sense, with particular reference not only to the characterization phase, but also to experimentation and monitoring of adopted interventions at a site-specific scale.

The experimental research considers some sites that exhibit different geological configurations, contamination contexts, and pollution mechanism. Ascertained contamination scenarios show the presence of hydrocarbons and chlorinated solvents in soil and groundwater. These classes of contaminants are the most common in anthropic environments, due to their wide use in the industrial context. The presence of petroleum fuels in the subsurface is a hazard in almost every town and city in the modern world (Wu et al., 2014). Leaking underground storage tanks and the resulting contamination and hazards have proven to be a challenge to investigate and remediate (Ghosh et al., 2019). Petroleum fuels can consist of thousands of compounds constituting the light non-aqueous phase liquid (LNAPL) (Vasudevan et al., 2016). LNAPL spills are a widespread source of contamination in shallow aquifers (Teramoto et al., 2019). One issue is adequately characterizing the presence and spatial extent of LNAPLs in the subsurface (Lari et al., 2018). The accuracy of characterization phase affect the efficiency of remediation operations. On the other hand, groundwater contamination by dense non-aqueous phase liquids (DNAPLs), such as chlorinated solvents, has been increasingly recognized as a serious environmental problem (Kueper et al., 2014). Chlorinated solvents, including trichloroethylene (TCE) and tetrachloroethylene (PCE) are the most important sub-class of DNAPLs (McCarty, 2010) due to their wide-spread use in the electronics, chemical, dry-cleaning, and metal fabrication industries (Ajo-Franklin et al., 2006). The physical and chemical properties of DNAPLs, aside from their relatively low solubility (Luciano et al., 2010), high specific gravity (Lee and Chrysikopoulos, 2006), and tendency to remain adsorbed to organic and fine-grained materials (Abdel-Moghny et al., 2012), make DNAPLs difficult to locate and characterize in the subsurface (Fjordbøge et al., 2017), and this can impact the effectiveness of conventional remedial technologies (Rao et al., 2000).

The proposed research activity is applied to real cases such as the Decimomannu military airport, the Bologna high speed station, and an industrial site operating in northern Italy.

At the NATO Military Base of Decimomannu, which is now the subject of MISE (emergency safety measure), significant spills of aviation fuel occurred in the groundwater. The spills interested an area used for the storage of fuel tanks (Figure 1).

Figure 1. Area used for the storage of fuel tanks inside the Decimomannu airbase.

The remediation intervention adopted at the site consists of pumping wells arranged to form a sort of hydraulic barrier (Brusseau, 2019). Pumped water is sent to a treatment plant according to pump and treat technology (Naidu, 2013; Trulli et al., 2016). The pump and treat intervention (still operational) over time allowed both the reduction of the contaminant mass and a narrowing of the contaminant plume, that progressively reached an asymptotic trend. The data resulting from characterizations carried out many years prior do not take into account the natural "aging" of potential secondary sources of contamination (Tran et al., 2018) but are used as an informational basis for the design of the interventions. This aspect is particularly relevant in the case of fuel contamination, complex mixtures of hydrocarbons that contain categories of substances with significantly different chemical / physical and biodegradable properties (Vozka et al., 2019). In the initial phase of the spill (when the primary source is active), the most soluble components (i.e., BTEX) could be mobilized in the groundwater and aerobic biodegradation processes are active on the more readily degradable fractions (linear hydrocarbons with shorter chain) (Koshlaf and Ball, 2017). The progressive aging of the contamination sources corresponds to an impoverishment of the more mobile and degradable fractions with the accumulation of fractions characterized by higher molecular weight (Tran et al., 2018). Therefore, the accurate characterization of the residual phase's real characteristics allows the definition of the best remediation strategy. The data used for the construction of a georeferenced database, were enriched by field hydraulic tests and detailed speciation, through Gas Chromatography - Mass Spectrometry (GC-MS) (Vozka et al., 2019), of supernatant that was occasionally detected over the years in the piezometric monitoring network. A campaign was conducted on the site with the LIF (Laser Induced Fluorescence) technology, the first in our country, which intended to delimit the subsoil volumes previously impacted by primary spills. The performed laboratory and field investigations had for purpose the identification of contaminants in the residual phase (Teramoto et al., 2019). The integrated approach aims at filling the lack of knowledge of the actual source zone extent, the complexity of its distribution due to geological heterogeneity, the sequestration of hydrophobic compounds because of the aging of contaminants, and entrapment caused by water table fluctuations. Surely, the coordinated investigation path optimizes the effectiveness of the contribution of each sensor data and overcomes the limit of their singular applicability, making an experimental workflow effective from a global viewpoint. An in situ enhanced chemical desorption strategy was implemented to increase the desorption of hydrocarbons adsorbed to saturated soils or at the capillary fringe and to increase the product recoverability in a separate phase. The use of the Regenesis PetroCleanze™ product aimed to increase the desorption of hydrocarbons adsorbed to saturated soils or at the capillary fringe. The hydrocarbons are made available in the dissolved phase or in a separate phase with lower viscosity, to enhance the recoverability of the product in a separate phase, allowing a subsequent rapid and effective physical recovery. The possibility for scaling up the process was evaluated using a pilot test. The pilot test, appropriately coordinated through the multidisciplinary and multitemporal data management model, was checked in the implementation phase in terms of yield, through Electrical Resistivity Tomography (ERT) and groundwater sampling. Geophysical surveys and groundwater sampling were accomplished to control the effectiveness of the intervention, both in terms of product diffusion capacity and in terms of effective reduction of pollutant concentrations. The study of the pilot test provided the elements for the verification of the efficiency, for the optimization of the intervention layout and for a preliminary design of an optimized full-scale intervention. The case study is considered to be of interest as it illustrates an example of how it is possible to optimize the removal of LNAPL contaminants when these are substantially unrecoverable using traditional technologies.

The Bologna railway station (Figure 2) was characterized by the presence of chlorinated solvents at low concentration in the groundwater.

Figure 2. Aerial photo of the new high speed railway station of Bologna.

The selected remediation strategy implied the creation of "reactive" zones capable of reducing the concentration of chlorinated solvents in groundwater through the combined action of adsorption on micrometric activated carbon, which is injectable into the aquifer and degradation of organic contaminants, stimulating the dechlorinating biological activity by addition of an electron donor (Ciampi et al., 2019$_b$). The possibility to use a new dispersed colloidal activated carbon (Plumestop™, Regenesis) was experimentally investigated as a site-specific remediation approach (Georgi et al., 2015). The micrometric carbon can be easily injected in the contaminated aquifer, creating an in-situ adsorption zone able to reduce chlorinated aliphatic hydrocarbons (CAHs) concentration and to raise the kinetics of the biological reduction by increasing the concentration of bioavailable CAHs at the carbon surface (Fan et al., 2017). The colloidal activatated carbon was co-injected with an electron donor (HRC™), to provide initial biostimulation of the treatment (Wood et al., 2006). Over the last decade, in situ application of activated carbon-based amendments has emerged as a promising remedial technology for the cleanup of subsurface organic contaminants such as chlorinated solvents (Simon, 2015; Fan et al., 2017). The technology involves the combination of adsorption, which has been extensively characterized and well understood, and degradation (Georgi et al., 2015; Simon, 2015; Fan et al., 2017). The combination of these two processes is proposed to be more effective than the conventional in situ remedial technologies that solely rely on degradation (Fan et al., 2017). Despite the rapidly increasing number of field-scale applications, questions remain to be answered regarding the effectiveness and persistence of contaminant degradation, especially biodegradation (Fan et al., 2017). The performance of in situ application of activated carbon-based amendments is heavily affected by the subsurface heterogeneity and the resulting uncertainty in the delivery and distribution of reagents (Fan et al., 2017). The selected remediation technology was verified through a pilot test, to obtain technical and operational information for the optimization of the intervention procedures on a larger scale. Based on the satisfactory results of the laboratory investigations (microbiological and microcosm tests) (Aulenta et al., 2005; Aulenta et al., 2007; Matturro et al., 2007), the design and implementation of a field test was performed as the final step of the evaluation process that led to the selection of an appropriate remediation technology according to the hydrogeochemical peculiarities of the site (Suthersan et al., 2016). The pilot test had to be representative of the process at full scale. The pilot test implementation provides useful information about the process efficiency and the actual extent of treatment, which may vary depending on the site's subsurface characteristics. Analytical monitoring and integration of geophysical data during pilot test implementation facilitated the assessment of the remediation technology performance and the evaluation of possible modifications and integrations of the intervention strategy (configuration of injection points and quantity of product to be injected). The overall goals are to furnish a demonstration of the biodegradation processes in conjunction with contaminant adsorption for in situ subsurface remediation of chlorinated solvents with activated carbons and to illustrate how geological heterogeneity affects reagent distribution. The research illustrates the remediation measures adopted and the full-scale results of post-treatment monitoring for a period of 2 years. The results that led to the achievement of the objectives and to the project closure derive from the integration of multidisciplinary data, using a multiscale approach. This research represents the first completed example in European territory for the remediation of an aquifer contaminated with chlorinated solvents by a combination of adsorption and biodegradation.

The industrial site operating in northern Italy (Figure 3) is characterized by the presence of active secondary sources in the low permeability layers and high concentrations of chlorinated solvents in soil and groundwater.

Figure 3. Industrial plant operating in north Italy.

This study investigates a new technology for the remediation of a dense non-aqueous phase liquid (DNAPL) aged source zone, with the aim of enhancing in situ bioremediation by coupling groundwater circulation wells with a continuous production system of electron donor. The technology was verified through a pilot test performed in a portion of the site highly contaminated by chlorinated aliphatic hydrocarbons. The multidisciplinary conceptual model confirmed a complex hydrogeological situation, with the occurrence of active residual sources in low permeability layers (Ciampi et al., 2019_a). A new technology was used for the progressive remediation of DNAPL secondary sources—coupling groundwater circulation wells (GCWs), with a production system of electron donor for the stimulation of in situ biological reductive dechlorination (Pierro et al., 2016). In this case, because of the geochemistry and hydrogeology of the site, the conventional addition methods are not suitable; traditional injection approaches are often limited by the preferential migration of injected fluids through better permeable zones, while delivery through less permeable and contaminated layers is usually limited (Petrangeli et al., 2016). On the other hand, Groundwater Circulation Wells (GCWs) could be considered a strategy for the progressive remediation of the source zone. This remediation technology is designed to create in situ vertical groundwater circulation cells, by drawing groundwater from an aquifer through one screened section of a multi-screened well, and discharging it through another screened section (Tatti et al., 2019). The pressure gradient between the two hydraulically-separated screen sections in the well induces a circulation flow in the aquifer, forcing water to move through a less permeable layer where residual sources of chlorinated aliphatic hydrocarbons (CAHs) are usually located (Petrangeli et al., 2016). In situ bioremediation involves the stimulation of microorganisms to metabolize or destroy contaminants through the addition of various amendments (biostimulation) to the subsurface environment (Aulenta et al., 2005). The combined technology is verified through a pilot test (the first of its kind) carried out in an operative industrial site located in the Po plain, which is heavily contaminated by CAHs. Based on the satisfactory results of the laboratory investigations (microbiological and microcosm tests), which indicated that reductive dechlorination might be successfully enhanced at the considered site (Aulenta et al., 2007; Matturro et al., 2013; Petrangeli et al., 2016; Pierro et al., 2017), the design and execution of a field test was performed as the final step of the evaluation process (Petrangeli et al., 2016; Pierro et al., 2016; Pierro et al., 2017). The pilot test intended to verify the possible mobilization of contaminants trapped in horizons with very low permeability, and the effective distribution of electron donor to stimulate the in situ processes of natural attenuation (Pierro et al., 2017). The pilot test was designed to optimize the layout and to calibrate the implementation of an optimized full-scale intervention, in order to check its efficiency. The application in the field during the pilot test determined the process efficiency and extent of treatment, which may vary depending upon the site's subsurface characteristics. The pilot test results clearly demonstrate a significant mobilization of contaminants from the low permeability zone, and the possibility of favoring the in situ natural attenuation mechanisms based upon biological reductive dechlorination. The results obtained during the experimentation supported a definitive design choice for the full-scale intervention. The implementation of the strategy in full scale will verify the effectiveness of the adopted technology for the persistent, low permeability contaminant source zones.

The selection and deployment of appropriate technologies for the remediation strategy rely on initial characterization activities (Brusseau, 2019). In environmental issues, geology-related factors control the migration of contaminant plumes and affect the performance of remediation technologies (Harris et al., 2004). Delineation and understanding of the geology and the hydrogeology of a contaminated site, considering its chemical-physical and biological aspects, are fundamental requirements for successful environmental remediation. The high-resolution characterization of underground geological heterogeneities, and the integration of different information, represent a key element for a remediation design, the optimization of interventions, and performance monitoring (Suthersan et al., 2016). The creation of a four-dimensional (4D) geographical database, (which also considers the time factor), enables the integrated management, representation, and analysis of different data (geological, hydrogeological, hydrogeochemical, and geophysical) (Artimo et al., 2008). Notably, the integration of geological, hydrogeological, and chemical data describes the geological–technical characteristics of the subsoil, the hydraulic properties of aquifers and also the potential pollution of environmental matrices (Raiber et al., 2012). These peculiar aspects, influenced by the local geological architecture, are unique site-specific elements, according to which it is possible to implement a targeted intervention for a remediation purpose (Suthersan et al., 2016). Georeferenced databases, GIS applications, and the new 3D modeling frontiers are an indispensable tool for the management of the complex set of data resulting from the characterization. They are equipped with tools for spatial analysis, integration of different methods of investigation, and graphic restitution of the results to visualize the environmental features (Wycisk et al., 2007). The representation of the geological structure through a 3D model facilitates its understanding and depicts the hydrogeological setting (Raiber et al., 2012). The dynamics linked to the groundwater flow play a fundamental role in the transport of contaminants (Seyedpour et al., 2019). Seifert et al. (2012) underline the importance of the conceptual geological model for calibrating variables and conditions in hydraulic modeling. Before presenting a conceptual model for the behavior and transport of pollutants, the hydrogeology and the physical structure of the soil must be understood (Adamsky et al., 2005). The numerical modeling of groundwater flow and transport, combined with a multiscale approach, finds application in the geological-hydrogeological characterization of polluted sites and represents a valuable tool for assessing the relevance of minimal lithological-stratigraphic variations in the correct formulation of a hydrogeological model and in the subsequent adoption of a reclamation project (Bozzano et al., 2007). The geolocalization of the concentration data of chemical species provides a complete picture on the trend in time and space of contaminant concentrations. Detailed knowledge of all the aspects mentioned above optimizes the planned remediation and safety measures.

Furthermore, a 3D hydrogeochemical model represents the decision support system, which increases the effectiveness of the analysis, as it provides support to all those who must make strategic decisions (Wycisk et al., 2007). In the context of remediation of contaminated sites, the challenge to be faced is to simultaneously integrate the information relating to the hydrogeochemical sphere in all its dimensions (Harris et al., 2004). The construction of a multidisciplinary geodatabase and the realization of an integrated model achieve this objective. The multi-source geodatabase and the data-driven model represent the tools for the integrated management of heterogeneus and geo-referenced elements. This ensures the interchangeability of information in the multidisciplinary nature of the elements involved, contributing to the continuous convergence of different types of geomodeling. Their interaction and the high-resolution characterization of environmental variability support the design of a targeted and effective remediation strategy (Harris et al., 2004; Suthersan et al., 2016). Holding a significant amount of data, the integrated geodatabase allows useful information for decision-making processes to be extracted in a short time and in a versatile way (Suthersan et al., 2016). The presented research focuses on the essential role of the proper collection, storage, representation, and integration of geothematic data from different sources in defining reliable remediation strategies for a contaminated site. The aim of this thesis is to provide some evidence about the effectiveness of a single composite geodatabase, which integrates hydrogeochemical data, to act as a “cockpit” in the different phases of remediation strategy development-the definition of a conceptual model, the design of a remediation strategy, and the implementation, monitoring and validation of pilot tests, and full-scale interventions.

Application of data fusion to the characterization of contaminated sites incorporates geologic knowledge, geophysical data, geochemical analysis, direct sensing investigations, hydraulic test data, and observation of head to reduce uncertainly associated with subsurface interpretation (Prasanna et al., 2008; Arato et al., 2014; Sauer and Dietrich, 2016; Kurup et al., 2017; Abbas et al., 2018; Gatsios et al., 2018). In this context, the challenge to be faced is to simultaneously integrate the information relating to the hydrogeophysical sphere in all its dimensions (Harris et al., 2004). The construction of a multidisciplinary geodatabase and the realization an integrated model represent the tools for the management and analysis of multi-source data. The information exchange, the overlapping of knowledge, and the high-resolution characterization of environmental variability capture the hydrogeological uniqueness, the geophysical peculiarity and the contamination dynamics. A real-time, immersive, interactive software, based on a ''3D geospatial'' graphical user interface (GUI), allows complex geological architectures to be depicted, and is more inherently intuitive than software based on a standard ''desktop'' GUI (Kingdon et al., 2016; Chiabrando et al., 2019). Many different hydrogeological and geophysical data sources can be combined into a single model. The spatial accuracy and dimensionality are preserved, making the multi-source model a practical reality. The possibility for the user to view, query and process data in 3D space is a significant extension of the standard desktop-based GUI, for human-computer interaction. In short, the model does not exist within a user interface, the model is the interface (Jones et al., 2009; Harvey et al., 2017) supporting the characterization and the decision-making processes. The presented research focuses on the essential role of the proper collection, storage, representation, and integration of geothematic data from different sources to reach the high-resolution characterization of underground geological heterogeneity, aquifer, and polluted areas, by providing an image of the subsoil at a level of detail rarely attainable. The high resolution of the multi-source characterization harmonizes the high accuracy, the density of information, the fusion of data, by generating a digital model that can be defined as a hybrid. The multitemporal and multidisciplinary geodatabase assumes the role of an effective "near real time" decision support system (DSS) (Huysegoms and Cappuyns, 2017) able to manage and release data from the characterization to the implementation of technique.

Experience has shown that conventional soil coring methods and groundwater monitoring methods are fraught with limitations that can lead to significant errors in the estimation of the amount and spatial distribution of NAPLs in the subsurface (Algreen et al., 2015). This leads to the development of inaccurate conceptual site models (CSM) and costly errors in remedial actions (McCall et al., 2018). Investigations on the origin and fate of hydrocarbons in the subsurface heavily rely on information related to the geological and hydrogeological characteristics (Hunkeler, 2016). The CSM can't prescind from the integration of the geological-hydrogeological and chemical-physical data, considering the geological-technical characteristics of the subsoil, the hydraulic properties of the aquifers, which are possible pathways of the contamination, and the potential pollution of the environmental matrices (Harris et al., 2004). Adequate characterization of this peculiar aspect and unique site-specific elements, which are influenced by the local geological architecture, is critically important for the sustainable use, protection, and remediation of groundwater resources (Suthersan et al. 2016). The investigation of contaminated sites is usually a long and expensive process. It is therefore desirable to use a combination of methodologies in an integrative approach that can reduce redundant information gathering (Abbaspour et al., 2000). The combined use of hydrological and geophysical measurements is arguably the most effective means of achieving this objective (Atekwana and Atekwana, 2010). Traditionally, the hydrological characterization of aquifers has been based on evidence from drill cores, hydraulic borehole logs, and tracer and pumping experiments (Leray et al., 2012; Hunkeler, 2016). Core- and borehole-based measurements can provide detailed local information, but such information is inherently 1D and spatially sparse in nature (Deiana et al., 2007), while tracer and pumping experiments tend to capture only the gross average properties of the probed subsurface region (Tronicke et al., 2004). Correspondingly, there is a large gap in terms of spatial coverage and resolution between these conventional hydrological techniques and hence they are, without complementary information, often inadequate for characterizing heterogeneous aquifers (Ruggeri et al., 2014). Geophysical methods have the potential of bridging this gap in resolution and coverage associated with traditional hydrological measurements, by capturing the data spatialization (Crook et al., 2008). The combination of different prospection technique adds additional and precious information, by capturing the complexity of geological heterogeneity and providing the data spatialization (Samouelian et al., 2005). Contaminant transport in groundwater is strongly controlled by geological heterogeneity, which plays a key role in a variety of scales. This implies the need to combine traditional and non-replaceable investigations that allow to acquire punctual information, with other linear prospects that facilitate the spatialization of data and are therefore able to capture the variability and complexity of transport processes. Different scenarios and configurations can then be appropriately simulated through the use of hydrogeological numerical models, based on the hydraulic parameters acquired with site and laboratory tests (Monego et al., 2010). The use of geophysical data from tracer monitoring can be used to calibrate the hydrogeological model (Cassiani et al., 2006; Camporese et al., 2011). Combining the traditional and irreplaceable techniques of punctual prospecting (geological surveys and hydrogeological tests) with the linear survey techniques (geophysics) it is possible to capture in detail the underground geological variability and the complexity of the transport processes. Geophysical methods have emerged as valuable tools for supporting investigation of the shallow subsurface and for monitoring the dynamics of hydrological and biogeochemical processes that occur within it (Binley et al., 2010; Binley et al., 2015). Geophysical techniques have the advantages of reducing the need for intrusive investigations (Chambers et al., 2010), and can provide spatially continuous information regarding subsurface structure (Samouelian et al., 2005). A comprehensive site characterization and remediation design and testing can strongly benefit from the combination of indirect (GPR, ERT, EMI, EC) and direct (chemical) investigations that can lead to understanding the distribution of contamination (Cassiani et al., 2014). ERT, GPR, and EM profiles, associated with survey data, were used to study the electrical properties of a contamination plume (Atekwana et al., 2000). Some geophysical techniques can focus with adequate resolution onto possible links exist between the relevant measured physical quantities and the hydrological and environmental quantities of interest for contaminated site characterization (Cassiani et al., 2014). Constitutive relationships that link measured geophysical parameters to hydrological properties are essential for reliable hydrological interpretation of geophysical data. This allows upgrading a model easily by acquiring and adding new data or reinterpreting and validating existing information.

Most studies to date on contaminant-geophysical behavior have been purely empirical and an overarching physicochemical model that explains observed geophysical signals is currently lacking. Given the complexity of physicochemical processes within contaminated porous media, the search for universal models that link geophysical signals to contaminant characteristics is likely to be futile (Binley et al., 2015). The emergence of the laser-induced fluorescence (LIF) technique overcomes this limitation, providing direct information on the LNAPL migration and distribution (Teramoto et al., 2019). LIF is a direct sensing method for the screening, in real time and in situ, of the contaminants present in the subsoil. LIF technique uses ultraviolet (UV) laser light delivered via direct push boring tools to excite (put energy into) polycyclic aromatic hydrocarbons (PAHs) molecules present in LNAPLs and logging florescence with depth thereby allowing the distribution of LNAPL to be characterized semi-quantitatively within the subsurface. PAHs are particularly efficient at being fluorescent when exited by UV light (Lu et al., 2014). LIF technology efficiently delineates petroleum, oil, and lubricant (POL) contaminants in the subsurface. All the usual forms of POLs, including; gasoline, diesel fuel, jet fuel, and hydraulic fluids, can be detected via the fluorescence response of their PAH constituents. Because this technology can be delivered using direct push equipment, it provides an efficient tool when used in conjunction with traditional core logging and sampling to more comprehensively characterize contaminant distribution (Gruiz et al., 2017). LIF measurements combined with cone penetrometer testing (CPT) were successfully used for time- and cost-effective in situ detection of fuels and petroleum products and proved to be effective in obtaining geophysical properties of subsurface environments (Pepper et al., 2002). The complete characterization of the site and the design of remediation tests can greatly benefit from the combination of indirect (geophysical) and direct (LIF-CPT, geological surveys, chemical water analysis, hydrogeological tests) investigations that can lead to understand the distribution of the contamination with high resolution detail. Surely, the integrated approach optimizes the effectiveness of the contribution of each sensor data and overcomes the limit of their singular applicability, making an experimental workflow effective from a global viewpoint.

The purpose of this research is to provide some evidence about the effectiveness of a single composite geodatabase, which integrates geological/hydrological, geophysical, and chemical data, to act as a "cockpit" in the different phases of definition of a conceptual model, selection/design of a remediation strategy, implementation, near real-time monitoring, and validation/revision of a pilot tests and full-scale interventions. The integrated data cockpit (Artimo et al., 2008) reflects the interdisciplinary action that involves the contribution and collaboration of the different scientific spheres to guarantee valid results in qualitative terms. The geodatabase favors the dynamic interchangeability of information in the multidisciplinary nature of the elements involved in the hydrogeochemical environment. The central system to organize / return even heterogeneous data (Huysegoms and Cappuyns, 2017) is a support tool for the evaluation and design of targeted, effective, and economically sustainable remediation interventions (Suthersan et al., 2016). Contaminated site remediation can't disregard from the integration of different information related to the hydrogeochemical sphere in all its dimensions (McCarty, 2010). Geological uniqueness and chemical peculiarities guide the contamination dynamics and decontamination mechanisms in the environmental scene (Harris et al., 2004; Kueper et al., 2014). Their knowledge and the high-resolution characterization of environmental variability support an effective remediation strategy. The multidisciplinary approach unites all the strengths of the different branches and considers the contamination phenomenon in all its dimensions, to obtain a high-resolution characterization (Harris et al., 2004). Geology can represent the link between the various disciplines (Figure 4), favoring the information interchangeability in the multidisciplinary nature of the elements involved (Suthersan et al., 2016). The holistic approach supports the design of targeted, effective, and economically sustainable remediation interventions.

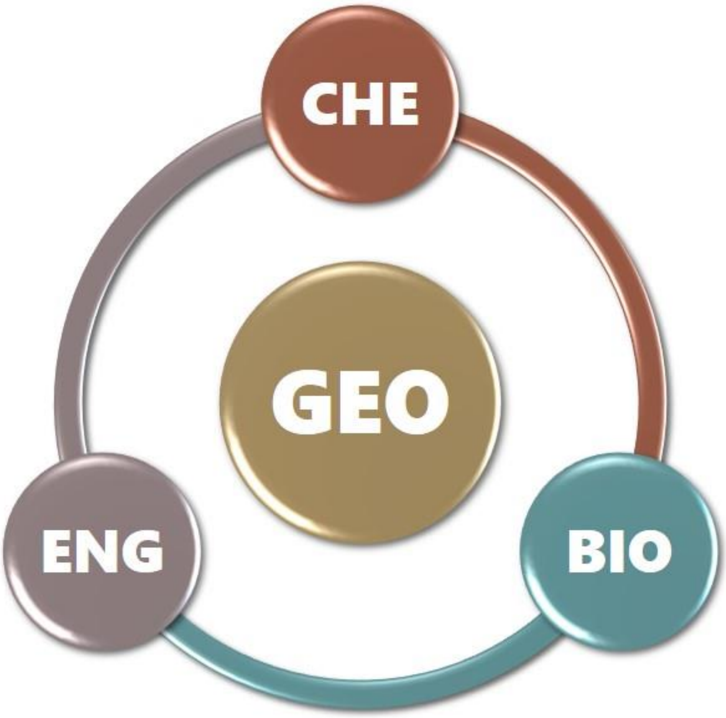


Figure 4. Schematic illustration showing how geology represents the link between different disciplines in the remediation of contaminated sites.

2. MATERIALS AND METHODS

2.2 An Integrated Geodatabase for the Management of Contaminated Sites

This research highlights the role and the potential of integrated geodatabases for the management of remediation processes, based on the design and implementation of innovative remediation strategies in 3 polluted sites in Italy: the Decimomannu military airport, the Bologna high-speed railway station, and an industrial site operating in north Italy. The management of a large amount of heterogeneous data supported the entire remediation projects, from the characterization phases up to the application of the interventions (Suthersan et al., 2016). A large amount of multithematic data was stored and centralized in an integrated information management and analysis platform. The multidisciplinary geodatabase contains information related to geological, geotechnical, geophysical, hydrological, and chemical spheres (Figure 5).

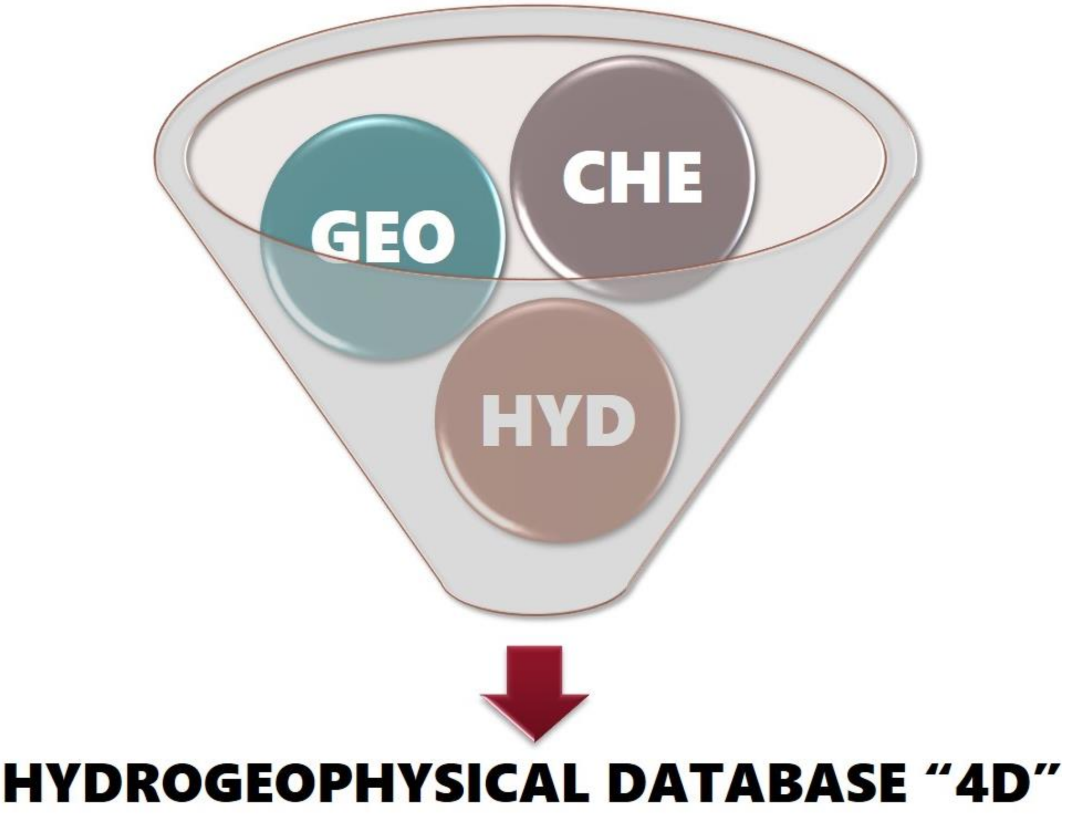


Figure 5. Representation of the multidisciplinary dataset used for the management and the storage of heterogeneous data.

The geodatabase also contains information related to variuos tests performed in the different sites and in laboratory (more than 50 particle-size analyses, 32 LIF investigations, 15 ERT lines, 15 triaxial cell permeability tests, slug and pumping tests, Lefranc tests, determinations of Atterberg limits, and assessments of water content). Most of the field and laboratory activities were carried out as part of my research activity. 7 particle size tests and Lefranc tests were inherited from previous studies. The data cockpit assumed the role of an effective "near real time" decision support system (DSS), able to manage and release data from the characterization to the technique implementation (Huysegoms and Cappuyns, 2017). The collection of hydrogeochemical data was rendered in digital format through the creation of a 4D geodatabase that considered the time factor. The thematic database represented a georeferenced data storage model used for processing and editing (Artimo et al., 2008).

2.3 Contextual Data Collection and Activities

2.3.1 The Military Site

During the site characterization phases, many geological surveys, permeability tests, geophysical prospectings, soil and groundwater samplings were executed at the military site. The advanced geological modeling followed the archiving of stratigraphic data in the geodatabase. It contains stratigraphic data referring to 85 geological surveys realized inside the base area (Figure 6).

Figure 6. Stratigraphic log realized inside the Decimomannu military base.

Stratigraphic logs were carried out from 2007 to 2016. They reach depths ranging from 10 m to 26 m and cover an investigation area of about 265000 m^2. During the drilling activities soil samples were collected to perform laboratory analysis. Ten granulometric tests (ASTM International, 2011) provided the geotechnical description of the soils constituting the shallow aquifer. As known, it is possible to associate to the lithotype grain size a typical range of hydraulic conductivity coefficient (Lambe and Whitman, 1979). Geological surveys and laboratory analyses identified the lithotechnical units and evaluated the permeability of the stratigraphic horizons present in the subsoil (Safarbeiranvnd et al., 2018). Fifteen Lefranc field tests (Zhang et al., 2018), two permeability tests in traixial cell, two pumping tests (Gatsios et al., 2018), and ten slug tests (Maliva, 2016) supplied hydrodynamic parametrization of a strongly heterogeneous and anisotropic aquifer (Figure 7).

Figure 7. Instrumentation used for pumping tests (a, b) and slug tests (c).

The pumping tests were implemented by pumping a constant flow rate for a sufficiently long time (24 hours) in a well and measuring the drawdowns in one or more monitoring points (well / piezometer). Hydrogeological tests provided the hydraulic boundary definition of the subsoil portion close to the fuel storage area.

The evaluation of hydrodynamic parameters furnished the elements to evaluate the velocity of groundwater flow (Chidichimo et al., 2015). The hydrogeological and hydrochemical setting was assembled based on a piezometric network consisting of 62 measurement points. The reconstruction of the evolution of the groundwater contamination status was reproduced based on the chemical analyses of waters sampled in the monitoring network, in the period 2011-2018. To visualize the evolution of the groundwater contamination status, contour maps were created for the parameter considered representative of the contamination. Several thematic maps were produced by considering the total petroleum hydrocarbons (TPH), which are correlated with the state of contamination that was previously ascertained. The concentration values (in µg/L) were compared to the Italian threshold limits (CSC)—the limits between each class corresponded to multiples of the CSC value for each contaminant. A detailed speciation, through GC-MS, of supernatant that has been occasionally detected over the years in the piezometric monitoring network provided interesting indication about the contamination dynamics and the "aging" of potential secondary sources of contamination. The integration of analytical data within the geodatabase had for purpose the development of a conceptual model that considers extension and degree of contamination, characteristics, and chemical-physical parameters that condition the mobility and the division between the phases of the pollutants.

To strength and refine the geological model, which arises from the interpolation of punctual data, geophysical investigations were carried out by performing fifteen electrical resistivity tomography (ERT) profiles (Binley and Kemna, 2005). The realization of 15 prospecting lines using ERT aimed to provide the evaluation of the variation of the electrical properties of the subsoil in a horizontal and vertical direction, furnishing the spatialization of data in two dimensions (Crook et al., 2008). Note that the ERT line geometry determines the maximum depth of investigation, that can be estimated to reach 1/4 to 1/5 of the line length (Cassiani et al., 2006). In the case here considered, generally lines of 94 electrodes with a 0,5 m spacing were deployed, and thus we could only reach a depth of about 10 m. This implies that the ERT investigation can image reliably only the shallow aquifer. The electrode configuration type employed in electrical prospecting was the dipole-dipole array, and more precisely a skip-4 dipole-dipole (i.e., the dipole size is equal to 5 times the electrode spacing, in total 2,5 m). The acquisition was conducted using a Syscal Pro 72 produced by Iris Instruments. For the data inversion, and thus the production of the imaging results, we used the open software ProfileR provided by A. Binley (Cultrera et al., 2018). While geophysics may differentiate low-permeability and high-permeability units, is extremely challenging to search for universal models that link geophysical signals to contaminant characteristics (Binley et al., 2015). On the other hand, the LIF technique opens the possibility of a more precise estimation of the LNAPL migration and extent in a complex distribution scenario (Teramoto et al., 2019). LIF investigation were implemented for the continuous detection of pollutants along a vertical profile with a high spatial resolution (Figure 8).

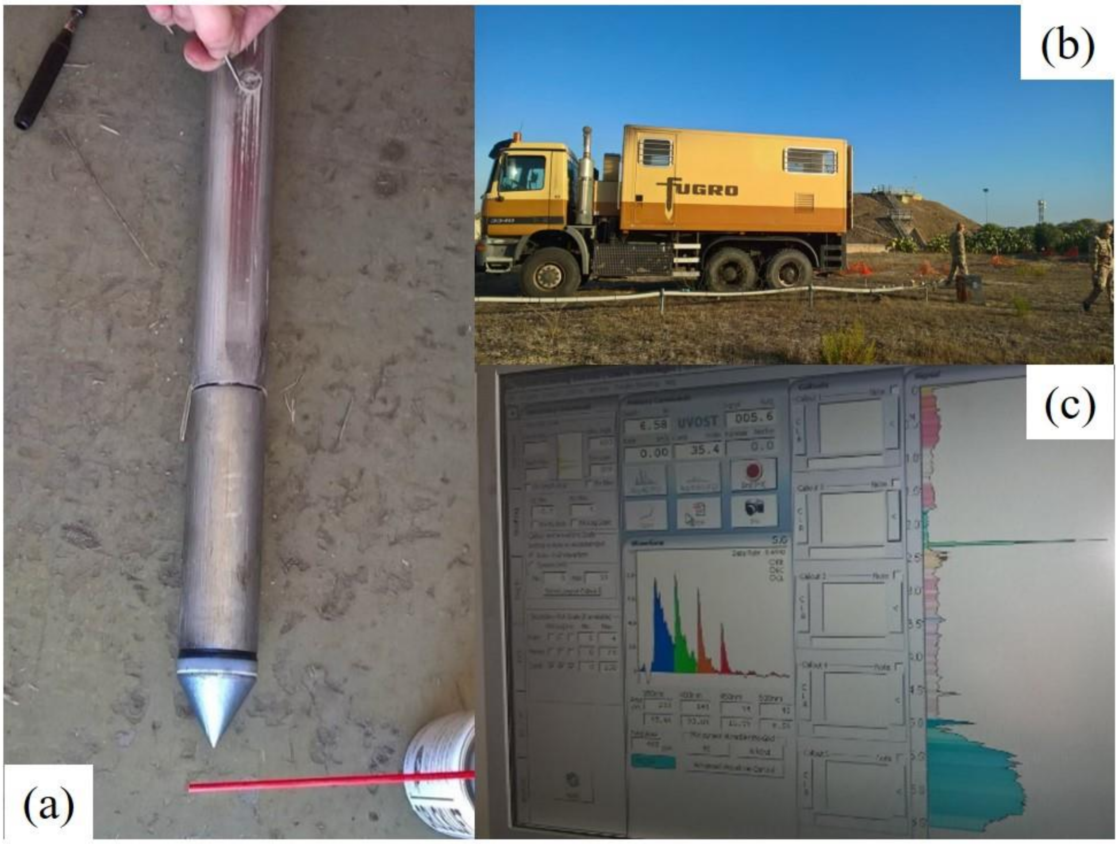


Figure 8. Conical tip adopted to realize the LIF profiles (a), truck used to transport the equipment inside the air base, fluorescence signal acquired in real time.

Currently available LIF equipment is not designed to detect dissolved-phase contaminants (Fedotov et al., 2019). The realization of 30 survey points using the LIF- ultra violet optical screening tool (UVOST) technology intended to add precious indication on pollutant characteristics and contamination dynamics. The combination of the above-mentioned direct sensing techniques with CPT measurements envisaged to capture the high-resolution characterization of the geological structure and the contamination state of the saturated and unsaturated subsoil. The data thus acquired were organized, georeferenced, and stored in a geodatabase, also useful for the purposes of visualization and data processing.

2.3.2 Bologna

At the contaminated site of the new high-speed railway station of Bologna, a large amount of slightly contaminated soil (~1.000.000 m^3) was excavated to create the new underground train station. The excavation activities for the construction of the structure that houses the station involved the removal of land attributable to shallow and intermediate aquifers. In correspondence of the excavation, a bypass system made of activated carbons for the treatment of groundwater was realized prior to our intervention. In the study area, 47 stratigraphic logs from boreholes drilled between 2005 and 2014 were available. A further 17 boreholes were drilled within the characterization activity, for refining the geological model and taking soil samples useful for laboratory tests. Geological surveys and laboratory analyses identified the lithotechnical units and evaluated the permeability of the stratigraphic horizons present in the station subsoil (Cheong et al., 2008). The stratigraphic data were re-interpreted and homogenized for a hydrogeological perspective, i.e., the various stratigraphic levels were merged or differentiated according to grain size and, therefore, permeability (Mirus, 2015). The subsoil geological structure was subdivided with reference to the elaborate groundwater circulation scheme. Permeability was evaluated via small-scale in situ tests (5 Lefranc tests), as a function of the particle size, and through permeability tests in triaxial cells. Twenty-one soil samples were collected to perform particle size tests (ASTM International, 2011), determination of Atterberg limits (ASTM International, 2010[a]), and assessments of water content (ASTM International, 2010[b]) (Figure 9).

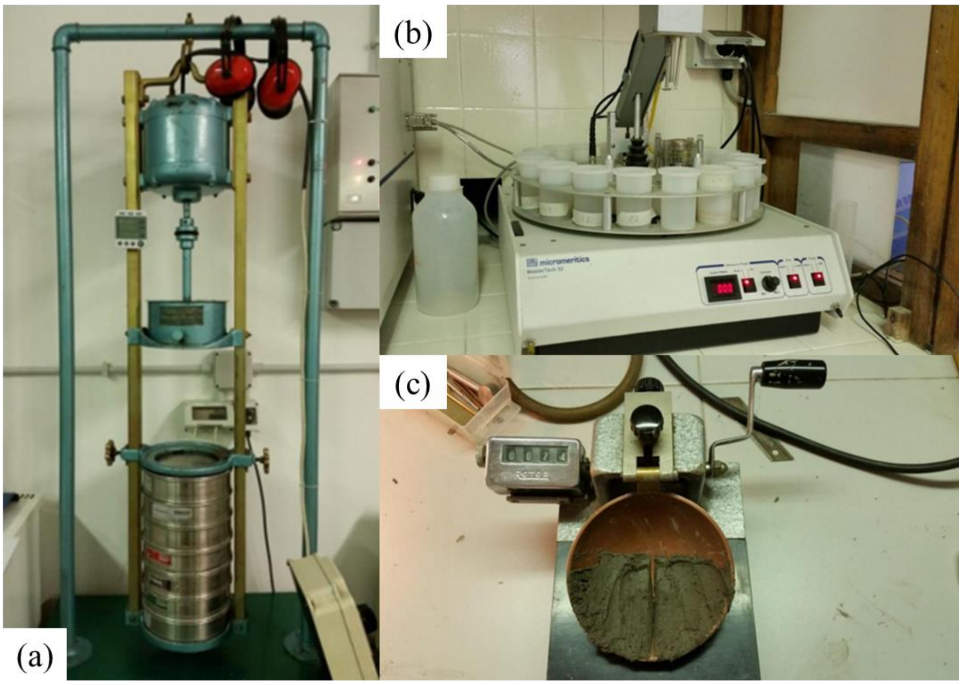


Figure 9. Instrumentation employed for laboratory tests: mechanical shaker and X-ray sedifer for granulometric analysis (a, b), Casagrande’s spoon used for the determination of the liquid limit (c).

These analyzes were realized at the Applied Geology Laboratory of the University of Rome - "La Sapienza". The data thus acquired were organized according to a hydrostratigraphic criterion (Mirus, 2015), georeferenced, and stored in a geodatabase, also useful for the purposes of visualization and data processing.

At the Bologna railway station, the geo-referencing of previous data and new periodic measurements allowed the realization of the hydrogeological structure modeling and the reconstruction of the groundwater circulation scheme. The evaluation of hydrodynamic parameters quantified the velocity of groundwater flow (Chidichimo et al., 2016). The hydrogeological setting was assembled based on a piezometric network consisting of 61 measurement points. Twenty-nine e thirty-two piezometers that intercept respectively the shallow and the intermediate aquifer were considered. The reconstruction of the evolution of the groundwater contamination status was reproduced based on the chemical analyses of waters sampled in the monitoring network. A total of 180 monitoring campaigns were conducted in the period 2005-2019. Several thematic maps were produced by considering some key contaminants, which are correlated with the state of contamination that was previously ascertained. The concentration values were compared to the Italian threshold limits (CSC)—the limits between each class corresponded to multiples of the CSC value for each contaminant. Thematic maps were created for the most relevant parameters, i.e., TCE and PCE concentration values, to visualize the evolution of groundwater pollution and to identify intervention areas. To investigate the contamination dynamics, we grouped the data considering the different phases of construction of the train station. These correspond to the different phases of aquifer response to possible sources of contamination. For each of the parameters and for each considered aquifer formation, contour maps for the following phases were produced:

1) Pre-operative (Oct 2004 - May 2006);
2) Preliminary excavations (May 2006 - Oct 2009);
3) Excavation (Oct 2009 - Aug 2011);
4) Post-excavation (Aug 2011 - Jan 2013);
5) Post-operative (Jan 2013 - Dec 2014).

In the industrial plant area, 83 stratigraphic logs from boreholes drilled between 2001 and 2014 were available. A further four boreholes were drilled within my activity (2017) for refining the geological model and taking soil samples useful for laboratory tests. Forty-eight particle-size analyses (ASTM International, 2011), 12 triaxial cell permeability tests, determinations of Atterberg limits (ASTM International, 2010[a]) and assessments of water content (ASTM International, 2010[b]), offered the analytical evaluation of the textural and permeability characteristics. The particle-size tests, Atterberg limits determination and permeability definition through the triaxial cells (Figure 10), were performed at the Applied Geology Laboratory of the University of Rome—"La Sapienza".

Figure 10. Instrumentation used for the determination of permeability in a triaxial cell.

The data thus acquired were organized according to a lithotechnical criterion, i.e., considering the granulometric and hydraulic conductivity characteristics which are the most influential on groundwater circulation (Cheong et al., 2008).

2.3.3 Industrial Plant

The geo-referencing of previous data and new periodic measurements in 95 piezometers installed inside the industrial plant allowed the realization of the hydrogeological structure modeling and the reconstruction of the groundwater circulation scheme (Xiao et al., 2016; Adhikary and Dash, 2017; Safarbeiranvnd et al., 2018). The storage, processing and representation of data monitoring in a geographic information system (GIS) environment reconstructed the evolution of the groundwater contamination status over time (Kourgialas and Karatzas, 2015; Mirzaei and Sakizadeh, 2016; Safarbeiranvnd et al., 2018). Thematic maps, representing the groundwater contamination status evolution, were produced based on the chemical analyses of waters sampled in the monitoring network in the period of 2008–2017. This type of representation permitted the visualization of the evolution status of groundwater pollution, the identification of the areas impacted by contamination, and the individuation of the intervention areas. The spatial overlay of the geological and hydrochemical models provided important indications on the contamination dynamics (Harris et al., 2004). The geological sections, extracted from the 3D solid model, were enriched by the hydrochemical data relating to the concentrations of contaminants detected in the multilevel piezometers (Mayo, 2010), which were located in the pilot test area. A multilevel system is a groundwater monitoring device which allows the monitoring of a number of discrete groundwater zones within the subsurface. Installation multilevel systems can provide three-dimensional data regarding a site for more accurate source and plume delineation. The hydrochemical profiles were extrapolated from contamination models which were generated for data referred to monitoring campaigns carried out from 2014 to 2016.

2.4 A Multidisciplinary and Multiscale Approach Supporting the Remediation Strategy

The hydrogeophysical model analysis and the remediation technology selection have been achieved previously using multiscale and multiphase approaches (Bozzano et al., 2007). In the first phase, the main hydrogeophysical and hydrogeochemical characteristics, surrounding the different sites at full scale, were detected. In the second phase, starting from the multidisciplinary conceptual model obtained from the first one, the analysis focused on the pilot test areas, increasing the observation scale to analyze in detail the effects of geological heterogeneity and chemical peculiarity in the first intervention area. The advanced geological modeling at both scales followed the reworking of stratigraphic data and their archiving in the geodatabase.

The hydrogeological 3D models were reconstructed by means of RockWorks 17 software (Lekula et al., 2008). This software enabled the acquisition, analysis, visualization and integration of information from geo-referenced data. The data integration and analysis phase involved the interpolation and processing of the geological, geophysical, and hydrochemical parameters (Kalirai et al., 2015, Safarbeiranvnd et al., 2018). The parameters include the characteristics of stratigraphic horizons, groundwater levels, LIF data, geophysical information, and the chemical analysis of water sampled. Data belonging to different scientific spheres were elaborated with the inverse distance weighted geostatistical method (Mirzaei and Sakizadeh, 2016; Adhikary and Dash, 2017; Safarbeiranvnd et al., 2018) to obtain an integrated multidisciplinary model. The interpolation of punctual data, performed using appropriate algorithm, generated three-dimensional models, which illustrate the spatial distribution of the parameters obtained from all the investigations. The 3D georeferenced model allows useful information for the decision-making process to be extracted in a short time and in a versatile way (Lekula et al., 2008). The 3D voxel-based solid model (Wang et al., 2012) is able to overlap information related to the different scientific spheres. Three-dimensional digital models are a powerful way of visualization, analysis, integration, and interpretation of multi-source information. The combination of these highly complementary data types – geology, hydrogeology, geophysics, direct sensing, geochemistry – enables the production of value-added photorealistic outcrop models, adding new information that can be used for capturing the geological uniqueness and the contamination peculiarity.

Following an accurate reconstruction of the geochemical peculiarities, the realization of laboratory tests (microbiological and microcosm tests) evaluated the possibility to implement particular remediation strategies. The comparative evaluation of potentially applicable interventions was also accomplished based on laboratory experience. Based on the results obtained from the site characterization, microbiological (Matturro et al., 2013), and microcosm (Aulenta et al., 2005; Aulenta et al., 2007) studies, pilot tests were designed to optimize the operating conditions at the field scale. The application in the field during the pilot test determined the process efficiency and extent of treatment, which may vary depending on the site's subsurface characteristics. Based on the results of the laboratory investigations (microbiological and microcosm tests), the design and execution of a field test was then performed as the final step of the evaluation process (Petrangeli et al., 2016; Pierro et al., 2017).

The remediation technology selection was achieved moving from the laboratory to the pilot to select/optimize an appropriate strategy to be implemented in full scale. The analysis of the hydrogeochemical model and the selection of the remediation strategy followed a step by step process, considering all the aspects involved in the environmental arena (geology, hydrogeology, geochemistry, geophysics). The pilot test was designed to optimize the layout of the intervention, to check its efficiency, and to calibrate the full-scale intervention. The realization of a pilot test was aimed to verify the feasibility of proposed remediation solutions. The field test is an expression of the holistic approach employed. It promotes an interdisciplinary action and an integrated intervention, combining all the strengths of the various disciplines and considering the contamination phenomenon in all its dimensions (Harris et al., 2004; Suthersan et al., 2016). The results of the experimentation, from the laboratory to the field pilot test, supported a definitive design choice that implies, for the full-scale intervention, the implementation of an innovative remediation strategy, determining the remediation of the entire identified contamination source.

During the pilot testing some investigations were realized, to evaluate the effectiveness of adopted remediation interventions. Some surveys were executed in the pilot test area using direct push (Geoprobe) penetrometers (Hunkeler, 2016) and a passive groundwater sampling system was installed (Figure 11).

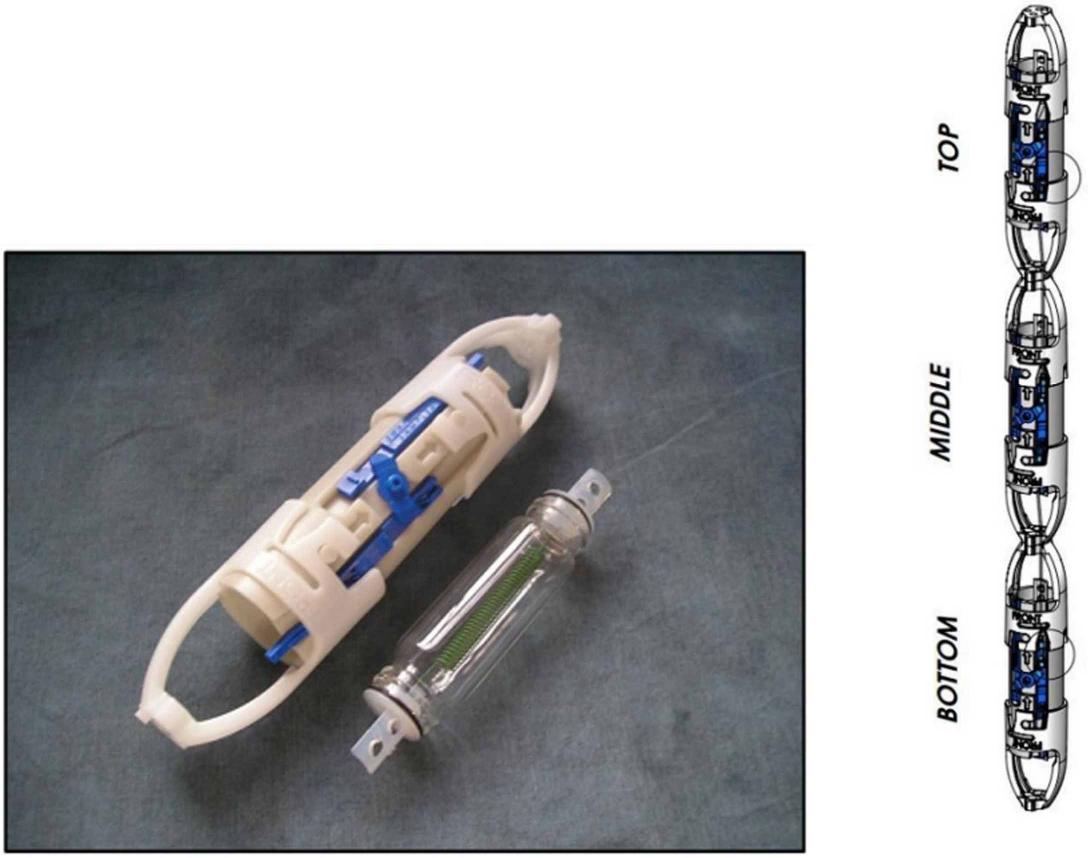


Figure 11. Passive groundwater sampling system.

Among the monitoring activities, a specific role was played by time-lapse geophysical investigations. The use of repeated geophysical measurements to highlight changes in the system state is state-of-the-art for several hydrological applications (Cassiani et al., 2006; Deiana et al., 2008; Perri et al., 2012; Haaken al., 2017) but it is of relatively scarce use at contaminated sites, particularly during remediation activities. These methods can provide nevertheless potentially critical information, especially in terms of where and how in situ remediation actions affect different portion of the subsurface, as an effect of subsoil hydraulic heterogeneity (Vereecken et al., 2006). In fact, the physical variable of interest, i.e., electrical resistivity, is strongly related to state variables of key environmental interest (Lesmes and Friedman, 2005). Geophysical surveys and groundwater sampling were realized to control the effectiveness of the intervention, both in terms of product diffusion capacity and in terms of effective reduction of pollutant concentrations (Figure 12).

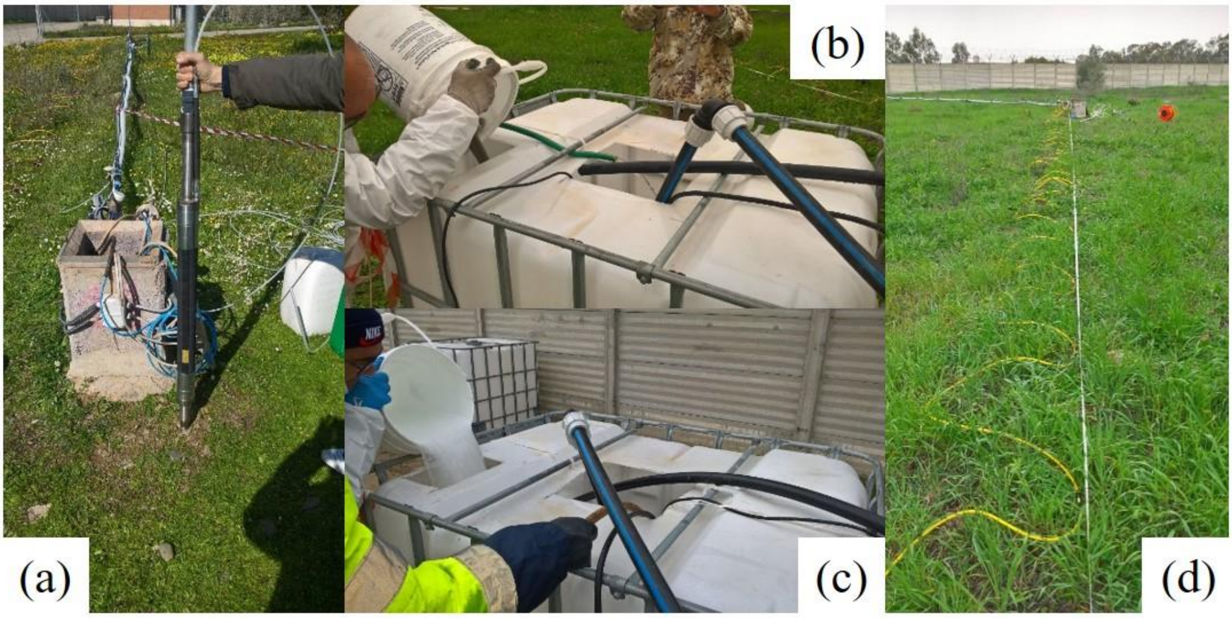


Figure 12. Pump used for the injection of different reagents in groundwater (a, b, c), ERT line realized in conjunction with the injection of amendments.

The study of the pilot test provided the elements for the verification of the efficiency, for the optimization of the intervention layout, and for the design of an optimized full-scale intervention.

The analytical monitoring of the piezometric network allowed to weigh the yield of the remediation technology used, thus indirectly assessing the performance and contribution of the methodology developed to design the intervention. To verify the effectiveness of the interventions implemented in full-scale as a result of the previous activities, the work carried out consisted in i) monitoring of the piezometric network, ii) sampling and repositioning of passive samplers (Snap Sampler) in some monitoring piezometers. Monitoring the effects resulting from the full-scale interventions played a fundamental role, since the innovative remediation technologies used must be validated at a performance level. The thematic database act as an integrated and continuously updated tool, able to optimize the investigations during the characterization phase, support the choice of the strategies in planning phase, managing and calibrating in progress the intervention modalities according to innovative approaches during the remediation phase (Figure 13).

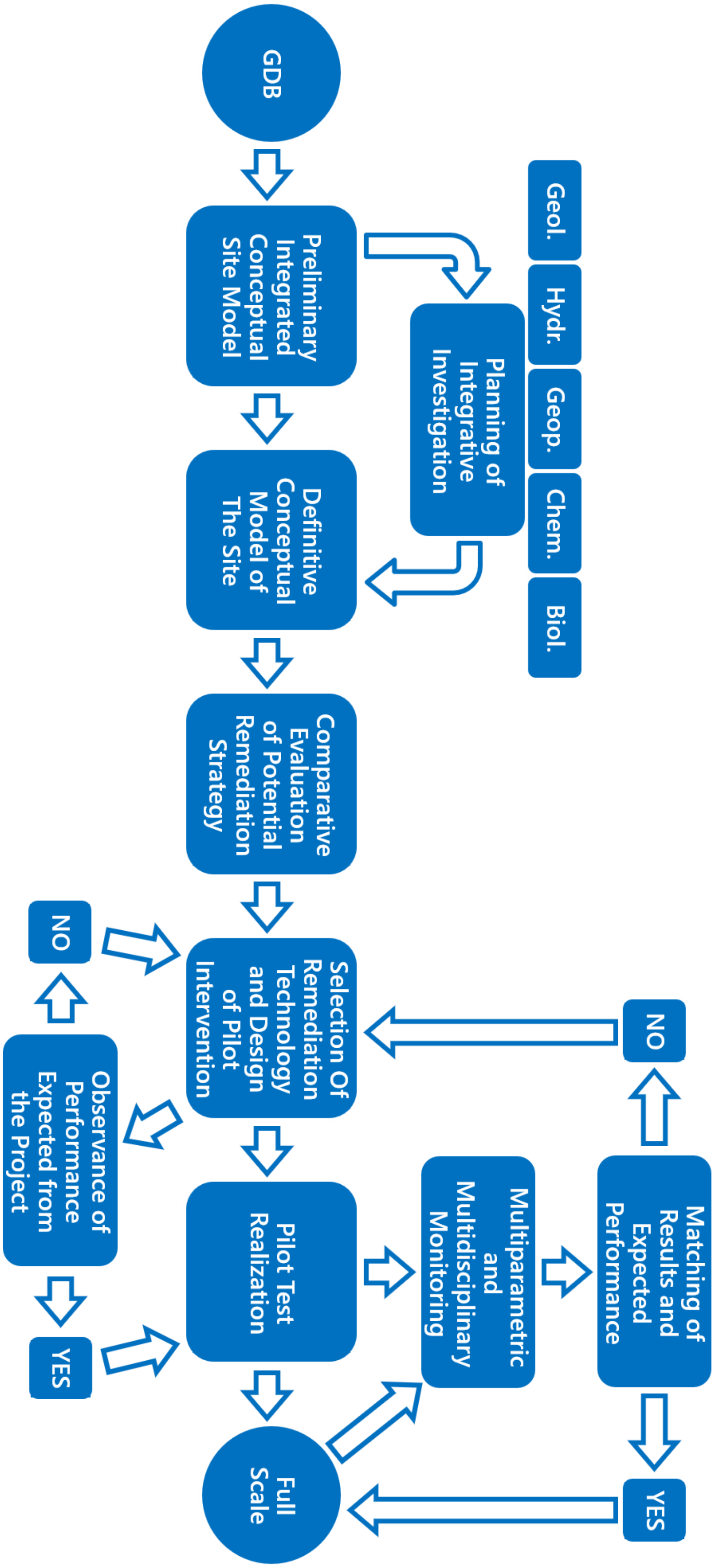


Figure 13. Flow chart illustrating the methodological approach followed in the various phases of work.

3. RESULTS

The experimental research is applied on sites that exhibit different geological and contamination scenarios. A single composite geodatabase integrates geological/hydrological, geophysical, and chemical data and acts as a "cockpit" in the different phases of definition of a conceptual model, design of a remediation strategy, implementation, near real-time monitoring, and validation/revision of a pilot test, monitoring of full-scale interventions. The integration and combined analysis of geognostic, hydrogeological, geophysical, and chemical data within the geodatabase facilitates the development of conceptual models that consider extension and degree of contamination, geological, hydrogeological, and chemical-physical parameters that condition the mobility and distribution between the phases of pollutants. The optimization of databases reduced the processing times and encouraged/coordinated the exchange of information between the various disciplines for the purpose of identifying gaps to be filled or to confirm what emerged during the characterization phase, laboratory and / or field experimentation, and adoption of innovative remediation technologies. The 3D hydrogeophysical model represents an effective "near real time" decision support system (DSS) able to manage and to release data during the different remediation phases, from the characterization to the technique implementation. The tridimensional model increases the effectiveness of the analysis as it provides support to all those who must make strategic decisions. The main function of a 3D georeferenced model is to extract in a short time and in a versatile way the information useful for decision-making processes, coming from a significant amount of data. The representation of the geological structure through a 3D model facilitates its understanding and depicts the hydrogeological setting with a high-resolution detail. Geophysical prospecting strengthens and refines the stratigraphic model, increasing the degree of detail in terms of spatial resolution. The ERT data, acquired along a line, bring to data spatialization and geological model refinement. The storage, processing and representation of monitoring data in a geographic information system (GIS) environment allowed to reconstruct the groundwater circulation scheme and the status evolution of groundwater quality over time. Laboratory tests capture the geotechnical paramerization of different stratigraphic horizons. Pumping tests and the slug tests provide the hydraulic parameters of the aquifer. LIF-CPT surveys delimit the presence of contaminant along a vertical profile with high resolution and provide a high resolution "lithotechnical" log. The

4D geodatabase enables integrated management, representation, and analysis of different data types (geological, hydrological, chemical, and physical) to reach a high resolution characterization of underground geological heterogeneities, aquifers, preferential flow paths, and contaminated areas. The complete multidisciplinary and multitemporal characterization supports the choice, the sizing, and the configuration of the remediation technology to be implemented. Considering the experimental characterization approaches, the assemblage and the integration of data from different sources proved to be an indispensable tool in the characterization and construction of thematic and numeric models, evaluation of intervention techniques, identification of suitable sites to perform the pilot testing, implementation of tests, control and evaluation of results to calibrate the design and implementation of full-scale interventions. Based on the results obtained from the site characterization, microbiological (Matturro et al., 2013; Pierro et al., 2017), and microcosm (Aulenta et al., 2005; Aulenta et al., 2007) studies (not shown here), pilots tests were designed to optimize the operating conditions at the field scale. The pilot test is an integrated system designed to optimize the layout of the intervention, to check the efficiency, and to calibrate/adjust the implementation of full-scale intervention (to optimize performance in full scale). The results obtained during the experimentation, from the laboratory to the field pilot test, support a definitive design choice for the full-scale intervention, determining the remediation of the entire identified contamination source. Depending on geological uniqueness, contaminant characteristics, and chemical-physical peculiarities, the applicability of the intervention options was evaluated in an efficient way from the economic point of view, the timing, and the invasiveness of the survey. Pilot testing is properly coordinated through the multidisciplinary and multitemporal data management model and controlled in the execution phase in terms of yield. The integrated data cockpit reflects the interdisciplinary action that involves the contribution and collaboration of the different scientific spheres to guarantee valid results in qualitative terms. The multidisciplinary geodatabase, the integrated hydrogeophysical model, and the field test are an expression of the holistic approach followed from the characterization phases up to the adoption of remediation strategy. Supporting a holistic, multidisciplinary and integrated approach means working in the direction of a renewed and necessary "contamination of knowledge". “Contamination” is realized by promoting an interdisciplinary action that involves the dynamic interchangeability of the different scientific spheres to evaluate and design targeted, effective, and economically sustainable remediation interventions.

3.1 Geological and Hydrogeological Settings

3.1.1 The Military Base

The first illustrative case history concerns the military airport of Decimomannu (Cagliari, Italy) (Figure 14).

Figure 14. Location of the Decimomannu military airport in southern Sardinia.

The investigated area is located in the Southern Campidano Plain, within the vast tectonic depression known as “Campidano graben”. Many Authors proposed a tectono-sedimentary scenario for the Southern Sardinia (Italy) using field observations and the interpretation of onshore and offshore seismic profiles (Casula et al., 2001; Carmignani et al., 2004, Arragoni et al., 2016). The major structural events are tied to the general geodynamic evolution of the Western Central Mediterranean. Thus, the extensional late Oligocene–Aquitanian event is a consequence of an ‘Apenninic’ westward subduction process associated with a volcanic arc

(29–30 to 15–16 My) which is particularly well exposed in Sardinia. Deposition of Sub-aerial clastics, was followed by transgression of the rift depression at the beginning of the Aquitanian (Casula et al., 2001). Subduction terminated at the opening of the oceanic Provençal Basin and the rotation of Sardinia–Corsica during Burdigalian time (20–21 to 15–16 My) (Arragoni et al., 2016). The Messinian compressional event (NE–SW oriented) strongly affected the Oligo-Miocene basin. The superimposed Plio-Quaternary Campidano Graben, which is probably related to the formation of the Tyrrhenian Basin, contains more than 600 m of syntectonic deposits (Carmignani et al., 2004). From a structural point of view, the Campidano Graben is a narrow deep graben, extending approximately in a NW–SE direction, limited by two Palaeozoic granitic–metamorphic horsts, bounded by regional faults. The above-mentioned geological and geophysical data suggest that the central depression is about 3000–5000 m deep, 100 km long, and 30 km wide (Angelone et al., 2005). This tectonic depression originates in a system of faults with directions North West - South East and is filled by a heterogeneous syntectonical succession of tertiary and quaternary sediments for some thousands of meters (Casula et al., 2001; Bini et al., 2013; Reuter et al., 2017) (Figure 15).

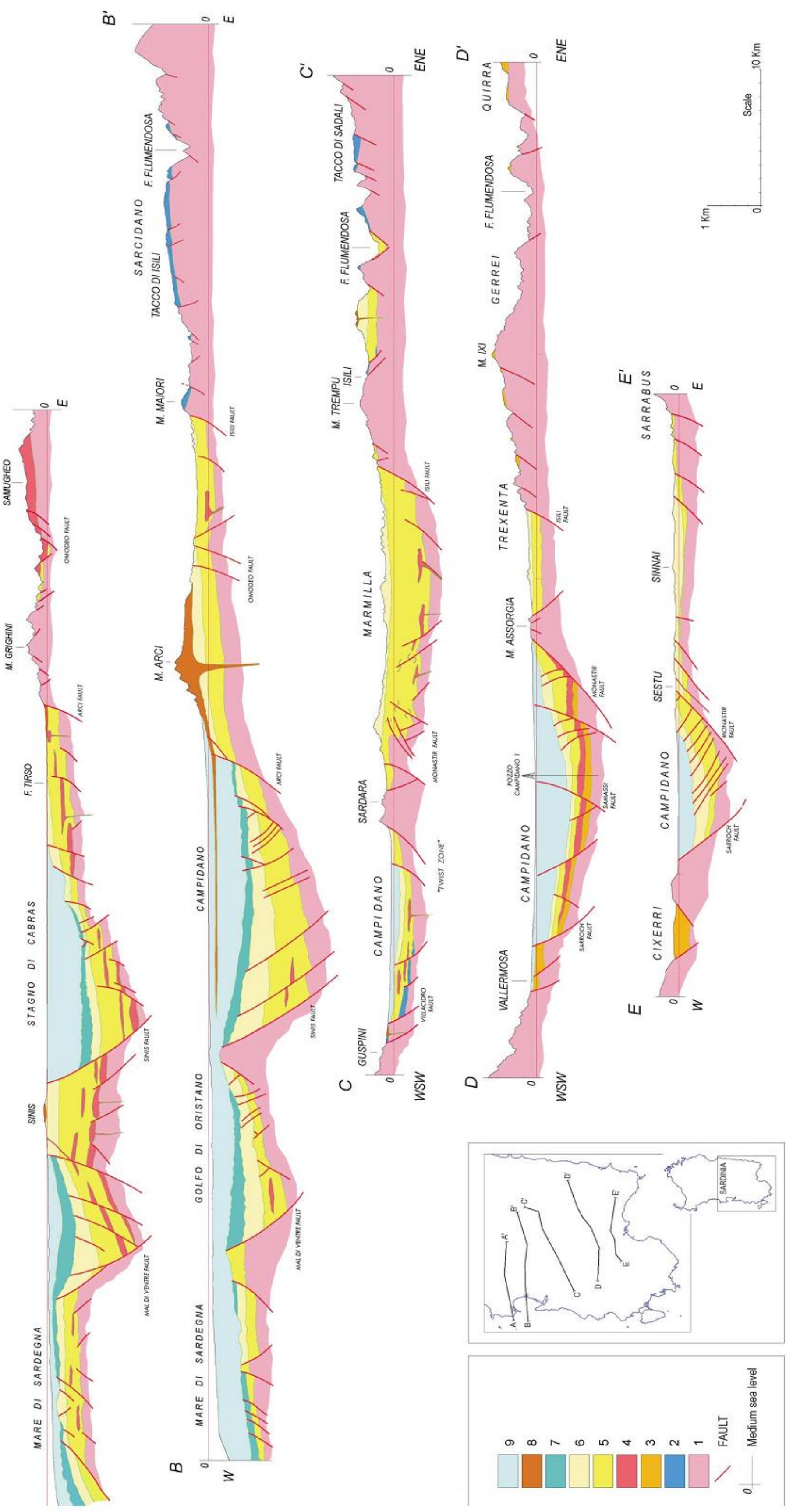


Figure 15. Geological cross-section in the South Sardinia Oligo-Miocene rift: (1) Palaeozoic basement; (2) Permian to Mesozoic; (3) Palaeocenze-Eocene; (4) Oligo-Miocene volcanics;

(5) Oligo-Miocene syn-rift deposits; (7) Lower Pliocene marine deposits; (8) Plio-Quaternary volcanics; (9) Middle-Upper Pliocene-Quaternary continental deposits (Casula et al., 2001).

The Quaternary is largely represented by deposits in continental facies. The depositional sequence of Quaternary alluvial sediments, which characterize the subsoil of the military base, has been identified through the study of stratigraphy. Beyond the backfill material, the latest deposits that outcrop in the study area represent the so-called "ancient floods" and "recent floods". They are formed by alluvial debris accumulations (Carmignani et al., 2001). The recent floods are characterized by gravels and sands with presence of fine fraction. They are found at a depth ranging from 1,5 m to 6 m below the ground with an average thickness of 3,5 m. The “ancient floods” are featured by gravel and sand in a silty-clay matrix. This lithotype has very variable thickness, varying from a minimum of 4,0 m to a maximum of 8,0 m. A lens of “hazelnut clay” separates the two alluvial horizons; it is formed by sandy-gravelly clays with hazelnut color. This depositional variation is distinguishable on the whole area and shows non-uniform thickness variations. The Quaternary covers are characterized by local heterogeneity, consequent to the variations of water flow regime. The stream energy assumes variations in a way to allow the sedimentation of both fine-grained (lower energy phases) and coarse-grained (higher energy pulses) deposits (Funedda et al., 2009). A base layer (“base clays”) is composed by clays and silty clays; it is the impermeable substrate of the study area. The thickness of this lithotype was measured in the deep surveys and was equivalent to an average of 13 m. The top of this layer has an inclination direction about SE. Below the base clays layer a horizon made up of gravels and sands (“base gravels”) immersed in a silty-clayey matrix with decametric cobbles follows in the stratigraphic sequence. The irregularity of the stratigraphic contacts and the peculiar structures that characterize the different horizons are evident in the three-dimensional lithostratigraphic model—a vertical exaggeration factor was used to mark the lithological steps (Figure 16).

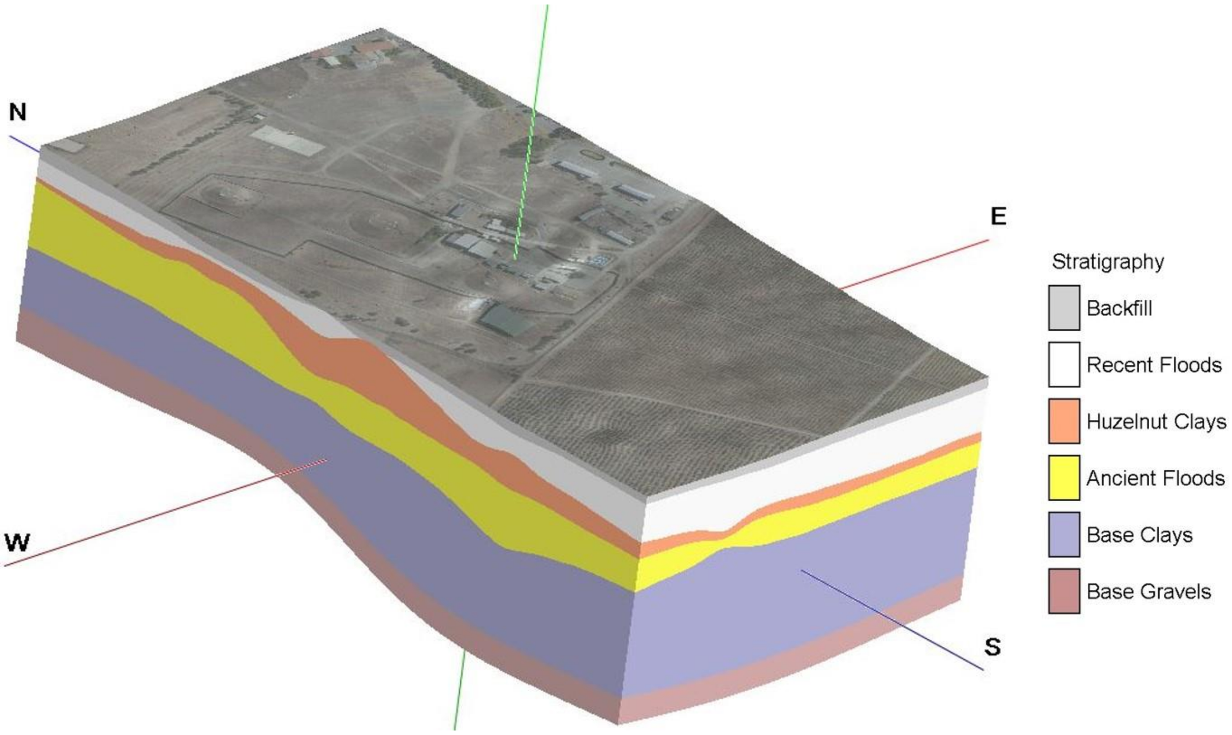


Figure 16. Three-dimensional geological model of the Decimomannu military airbase.

The model clearly shows how the hazelnut clays reach greater thickness in the western sector. Particle size and permeability tests estimated the permeability of the above distinct lithotypes. The valuation of the permeability coefficient from particle size tests showed values between 1,8x10^{-4} and 6,5x10^{-6} m/s for the “recent floods”. The evaluated permeability of “hazelnut clays” ranges from 3,4x10^{-9} to 6,1x10^{-9} m/s. The assessment of hydraulic conductivity relative to the “ancient floods” varies from 1,7x10^{-6} to 1,9x10^{-8} m/s. Tests in the triaxial cell performed on the "base clays" gave respectively the following permeability values: 9,7x10^{-11} m/s and 5,8 x10^{-10} m/s. The ubiquitous presence of an impermeable clay’s substrate delimits the groundwater circulation in the overlying gravelly-sandy alluvial sediments. The shallow aquifer is relevant for the contamination issue. The piezometric surface has an average depth of 4,5 meters from the ground level. Note that the shallow aquifer changes its state from phreatic in some areas to partially confined elsewhere. Groundwater circulation in the shallow aquifer is complex in terms of flow directions. The groundwater flow is oriented mainly from NE to SW (Figure 17).

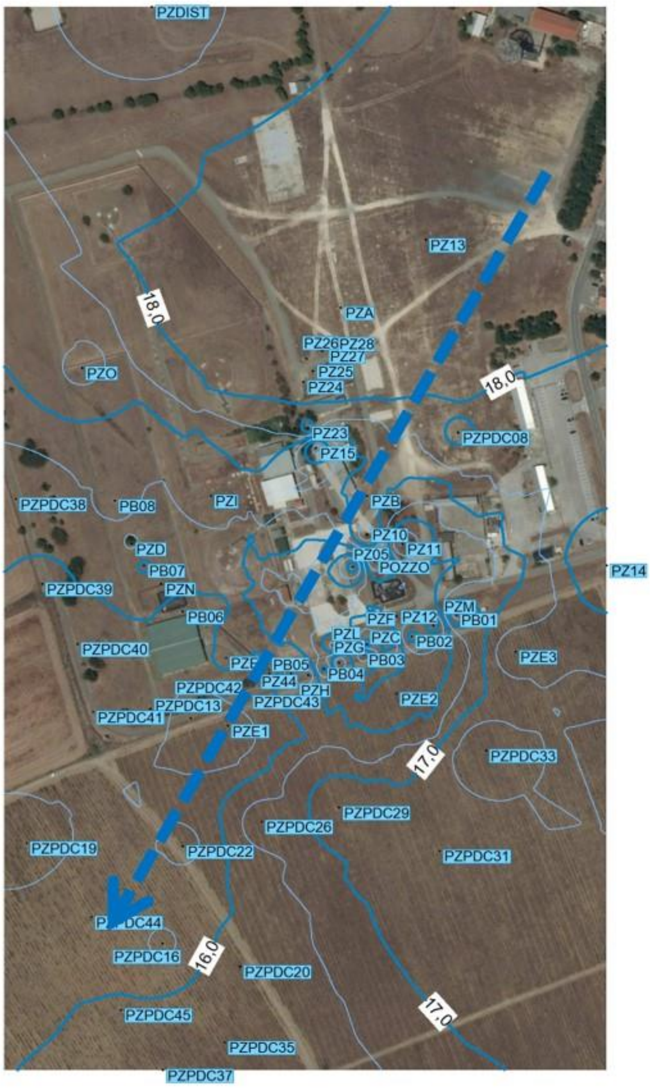


Figure 17. Piezometric level (meters above sea level) of the shallow aquifer in the investigation area.

The isopiezic map reveals the local disturbance of the piezometric surface and the pumping effects, due to the presence of the hydraulic barrier wells. The hydraulic characteristics of the shallow aquifer reflect the heterogeneity and the anisotropy of the depositional system. The hydrogeological investigations defined in more detail the hydrogeological characteristics of the site, with particular reference to a better and more reliable definition of the hydraulic conductivity values of the aquifer. The aquifer permeability obtained with Lefranc tests is variable between $1{,}4 \times 10^{-5}$ m/s and $2{,}2 \times 10^{-7}$ m/s. The interpretation of the data acquired during the slug test determined values of hydraulic conductivity between $2{,}78 \times 10^{-4}$ and $6{,}66 \times 10^{-6}$ m/s. The aquifer transmissivity, obtained through pumping tests, was included in the interval between 1,45x10^{-3} and 3,19x10^{-3} m^2/s; the resulting permeability is between 1,19x10^{-4} and 8,61x10^{-4} m/s. Considering a hydraulic conductivity around 10^{-5} m/s and a hydraulic gradient of 0,9 %, it is possible to estimate the velocity of groundwater flow in the shallow aquifer around 20 m/year. The hydrogeological model capture the high-resolution characterization of geological uniqueness, the detailed parametrization of aquifer deposit, and the peculiar configuration of groundwater circulation scheme (Chidichimo et al., 2015).

3.1.2 The New High-Speed Railway Station of Bologna and the Industial Plant

The contaminated sites of the new high-speed railway station of Bologna and the industrial plant are located in the Po Plain (Figure 18).

Figure 18. Location of the the new high-speed railway station of Bologna and the industrial plant.

The evolution of the Po basin is characterized by the transition from Pliocene open marine deposits to Quaternary marginal marine sediments, which are followed by alluvial deposits (Lugli et al., 2004). The Po Basin fill is a syntectonic sedimentary wedge forming the infill of the Pliocene-Pleistocene Apenninic foredeep (Barchi et al., 2006), a basin that was bounded by two main belts (Apennines to the south, Alps to the north) showing opposite polarity of tectonic transport. It attains a total thickness in excess of 4000 m; the Quaternary deposits are about 1000-1500 m thick (Fantoni and Franciosi, 2010). A major structural boundary between uplifting and subsiding crust occurs along the southern margin of the Po Basin, the Pede-Apenninic Thrust Front (PTF of Boccaletti et al., 2011). The analysis of the Apennines–Po Plain margin evidences the presence of two distinct sectors with different morphostructural characters, extending north-west and southeast of Bologna. The north-western sector (Emilia Apennines) is marked by presence of the major pede Apenninic thrust front, characterised by a prominent morphotectonic signature (Figure 19); the southeastern sector (Romagna Apennines) is featured by a monoclinal setting with north-east immersion, which determines the development of tilted surfaces connecting the plain with the Apenninic relieves. The tilting affects Quaternary deposits and is connected with movement along blind back thrusts (Bocaletti et al., 2011).

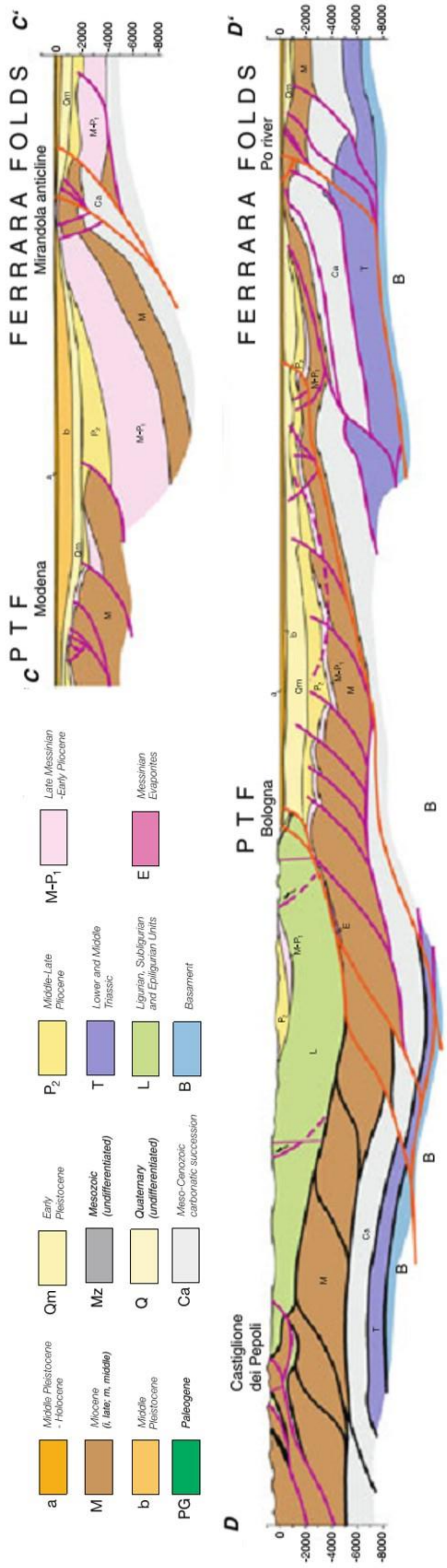


Figure 19. Transversal geological cross sections (oriented approximately North-South) of the external Northern Apennines (Bocaletti et al., 2011).

This major structural element was also repeatedly active during the Pleistocene, as documented by a 600-700 m vertical offset of the Quaternary marine succession. The effects of Quaternary tectonic activity decrease from the Apennines toward the Po Plain, where the Quaternary deposits display an overall lenticular shape and represent the filling of large, flat depressions almost unaffected by compressional deformation (Amorosi et al., 1996). The sedimentary evolution of the Po Basin exhibits an overall 'regressive' trend, punctuated by minor fluctuations, from Pliocene open marine facies to Quaternary marginal marine and then alluvial deposits. On the basis of an accurate study of seismic profiles by AGIP, the Quaternary alluvial units have been interpreted as the topset portion of an offlap sequence, encompassing both paralic and shallow marine deposits. Throughout the area, seismic profiles of the subsoil confirm that Middle Pleistocene sediments are folded and faulted (Bocaletti et al., 2011) (Figure 20).

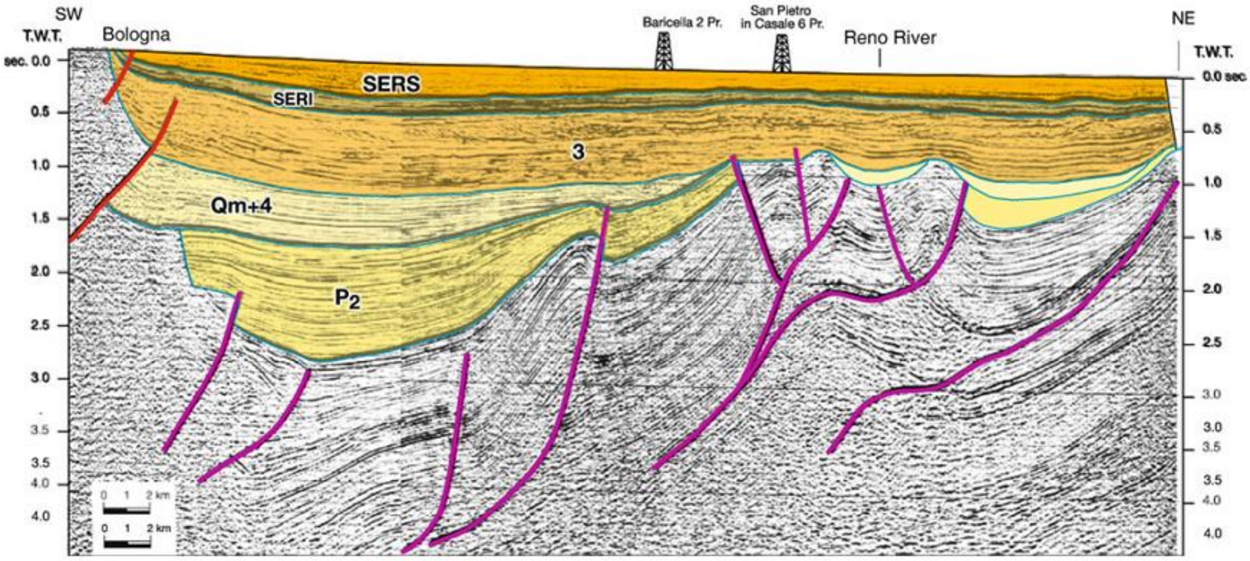


Figure 20. Example of interpreted seismic line. Note that Middle Pleistocene and Late Pleistocene units (3: Imola Sands; SERI: Lower Emilia-Romagna Synthem; SERS: Upper Emilia-Romagna Synthem) are folded and faulted. P2: Late Pliocene; Qm: Lower Pleistocene marine sediments; 4: Yellow Sands (1–0.8 M year) (Bocaletti et al., 2011).

The studies confirm that the filling of the basin and the passage from marine to continental sedimentation are the result of tectonic-sedimentary events, separated over time by periods of strong subsidence. The numerous surfaces of discontinuities observable on the seismic lines are the result of the various phases of structuring of the basin (Regione Emilia-Romagna et al., 1998). The deposition of gravelly sediments is associated with the proximity to the hills. Moving away from the foothill area, sediments with finer grain size increase. The Quaternary alluvial sequence in the study areas shows a periodic alternation of coarse-grained and fine-grained deposits; their repeated alternation represents the main feature of the depositional system (Regione Emilia-Romagna and Eni-Agip, 1998).

The outcropping deposits in the Bologna area are represented by the Quaternary alluvial succession of the Po River Basin, exceeding 300 m in thickness. A subdivision of the Quaternary alluvial succession of the Po River Basin in the Bologna area was proposed by Lugli et al., 2004 and Regione Emilia-Romagna and Eni-Agip, 1998. The Quaternary alluvial sequence shows a periodic alternation of coarse-grained (gravel and sand) and fine-grained (silt and clay) deposits (Lugli et al., 2004; Regione Emilia-Romagna and Eni-Agip, 1998). In the study area, this arrangement is clearly recognizable—predominantly gravelly-sandy levels (characterized by a variable thickness) are separated by silty-clay deposits. Beyond the backfill material, it is possible to distinguish a first level with a fine granulometry, consisting of silty clays and clayey silts with thin laminations of very fine sand. A horizon composed of sands, fine sands with silt, and sandy silts follows in stratigraphic succession. A layer of plastic clays and silty clays underlies the previous ones and covers a stratum of medium sands with heterometric gravels. Below consistent clays overlap sandy gravels. The lateral and vertical lithological heterogeneity has important implications on the variability of the subsoil permeability. This alternate structure of high and low permeability zones can create preferential pathways for groundwater flow and solute transport (Harris et al., 2004; Bozzano et al., 2007, Ciampi et al., 2019$_b$). For this reason, the geological structure of the subsoil was subdivided based on permeability characteristics, as follows:

1) Backfill (anthropogenic) materials;
2) Shallow clays and silts, a low permeability level of separation between the backfill materials and the shallow aquifer deposits;
3) The shallow aquifer;
4) Aquiclude 1, a low permeability level of separation between the shallow aquifer and the intermediate aquifer;
5) The intermediate aquifer;
6) Aquiclude 2, a low permeability level of separation between the intermediate aquifer and the deep aquifer;

7) The deep aquifer.

The sub-parallel structures that characterize the different horizons are very evident in the three-dimensional lithostratigraphic model (Figure 21)—a vertical exaggeration factor was used to identify the stratigraphical transictions.

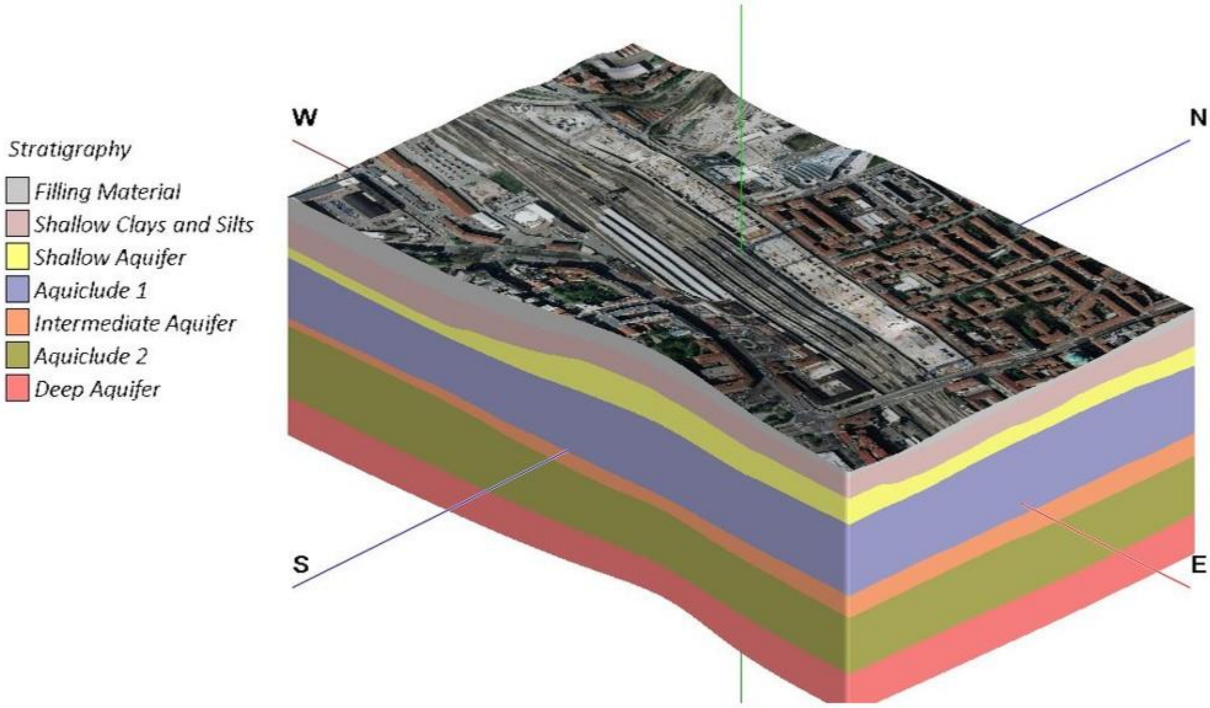


Figure 21. Three-dimensional geological model of the new high-speed railway station of Bologna (Ciampi et al., 2019b).

The hydrogeological conceptual model shows the presence of three aquifers separated by low permeability layers. The shallow and the intermediate aquifers are relevant for the contamination issue. The shallow aquifer is composed of deposits with predominantly sandy and sandy-silty grain size. The intermediate aquifer is composed predominantly of gravelly and gravelly-sandy deposits. The shallow aquifer is characterized by a variable thickness. The morphology of the limits of the intermediate aquifer is less articulated. The piezometric data collected during different campaigns allowed the producuction of interpolated piezometric maps for the shallow and intermediate aquifers. The contour maps (Figure 22) illustrate the position of the excavation that involved the removal of land attributable to shallow and intermediate aquifers for the construction of the station and the installation of the by-pass system.

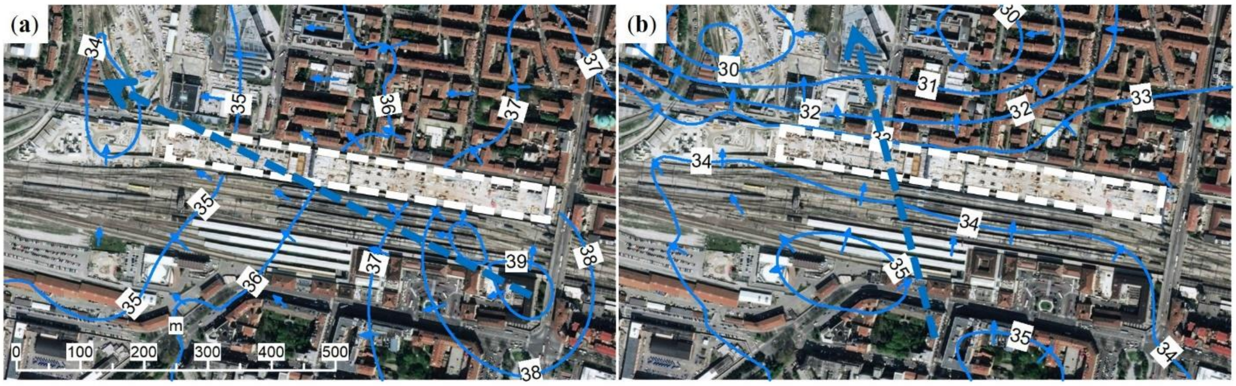


Figure 22. Representation of the piezometric surface (meters above sea level) for the shallow (a) and the intermediate aquifer (b); the white dashed rectangle represents the excavation hosting the station structure (Ciampi et al., 2019_b).

Groundwater circulation in the shallow aquifer is complex in terms of flow directions (Figure 22a). The groundwater flow is oriented mainly from SE to NW. Considering a hydraulic conductivity around 10^{-7} m/s, it is possible to evaluate the velocity of groundwater flow in the shallow aquifer around 1-5 m/year. Note that the shallow aquifer changes its state from phreatic in some areas to fully confined elsewhere. The intermediate aquifer, which is constantly confined, shows a prevailing direction of groundwater flow from S to N (Figure 22b). Considering an average hydraulic conductivity in the order of 10^{-4} m/s, it results a groundwater flow velocity around 50-100 m/year. The comparison between the piezometric levels after (2014) and before (2005) the excavation hosting the underground structure, highlights the piezometric recovery and the restoration of the pre-operation flow configuration for both aquifers (not shown here). This demonstrates the hydraulic efficiency of the bypass system. To provide useful information for design purposes, in terms of sizing and configuration of the remediation (Suthersan et al., 2016), attention was focused on the subsoil in the pilot test area. The high-resolution geological model was constructed based on data from 17 boreholes; it covers an area of about 350 m^2. The stratigraphic relationships are those mentioned above (Figure 23).

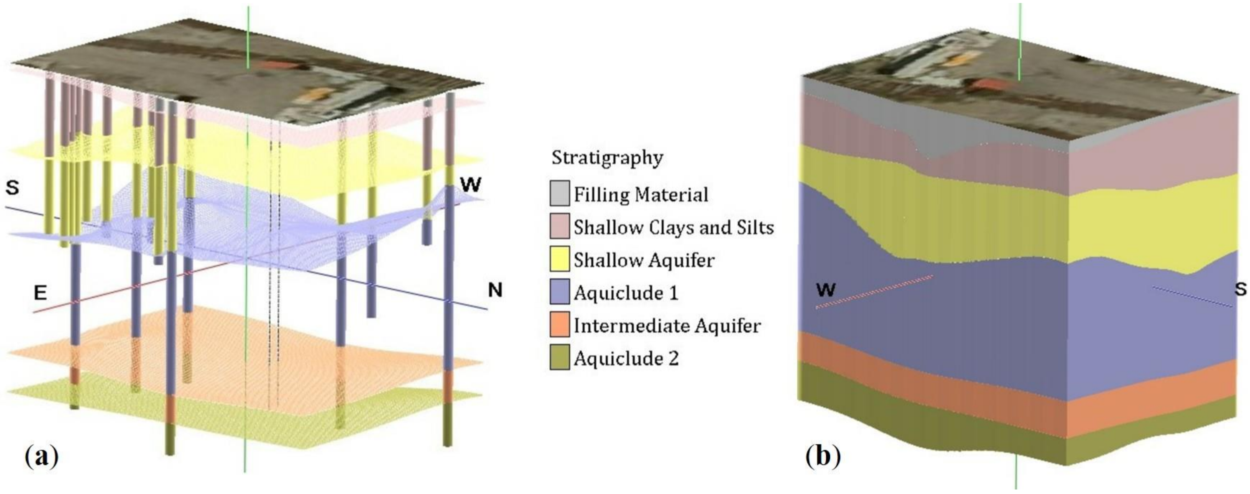


Figure 23. Boreholes, stratigraphic contacts (a) and geological model of pilot test area (b) in 3D (Ciampi et al., 2019b).

The high density of information in the pilot test area produces a stratigraphic model which identifies lateral and vertical heterogeneity. The presence of lenses with low permeability and the occurrence of preferential outflow pathways influences greatly the diffusion of contaminants, reagents, and the choice/design of the remediation strategy (Harris et al., 2004, Ciampi et al., 2019b). The spatial sampling that can be achieved via direct borehole investigations is of course limited and is not able to capture the complexity of small-scale preferential pathways (Pharr and Humphreys, 2004). On the other hand, the refinement of the geological model thus represents a key element for the choice and the designing of a technical intervention (Suthersan et al., 2016).

In the industrial plant area, the periodic interchange of predominantly gravelly-sandy levels and silty-clay deposits is clearly recognizable. The stratigraphic data highlight a very complex geological and hydrogeological situation, which is featured by a marked variability of the subsoil composition, as the different layers are arranged with lenticular geometries. These lithological variations are reflected in the modes of groundwater circulation, resulting in groundwater being divided into aquifer levels with different permeabilities that variously communicate with each other. For this work, the already available stratigraphic data were re-interpreted and homogenized for a hydrogeological perspective, i.e., the various stratigraphic levels were merged or differentiated according to grain size, and therefore, for permeability (Heinz and Aigner, 2003). The geological structure of the subsoil of the area in question was subdivided with reference to the elaborate underground water circulation scheme. It is possible to recognize several levels in stratigraphic succession from top to bottom as follows:

1) Backfill, up to 5 m in depth;
2) Silty clays and clayey silts (and sometimes weakly-structured sand) with an average thickness of 8,5 m;
3) Sandy silts and clayey silts arranged in a discontinuous level;
4) Silty sands and fine-to-medium sands with hydraulic conductivity values between 10^{-5} and 10^{-8} m/sec, forming a shallow aquifer with variable thickness—sometimes in continuity with the underlying layer of gravels, and sometimes separated by a low lens permeability;
5) A discontinuous level at an average depth of about 20 m, represented by fine-grained, low-permeable silts and clayey silts soils, that acts—where present—as an aquitard;
6) A layer of gravels and sands characterized by permeability values in the order of 10^{-4} m/s and lateral continuity, forming a deep aquifer with a thickness of about 4 m over the entire area;
7) A clayey-silty horizon at a depth of about 25 m below the ground level, characterized by lateral continuity and by permeability values in the order of 10^{-11} m/s, that acts as a basal aquiclude.

The overall structure of the subsoil is typical of alluvial plains close to the foothill sectors, where the stream energy assumes variations in a way to allow the sedimentation of both fine-grained (lower energy phases) and coarse-grained (higher energy pulses) deposits (Regione Emilia-Romagna and Eni-Agip, 1998). The irregularity of the stratigraphic contacts and the lenticular structures that characterize the different horizons are evident in the three-dimensional lithostratigraphic model (Figure 24)—a vertical exaggeration factor was used to mark the lithological steps.

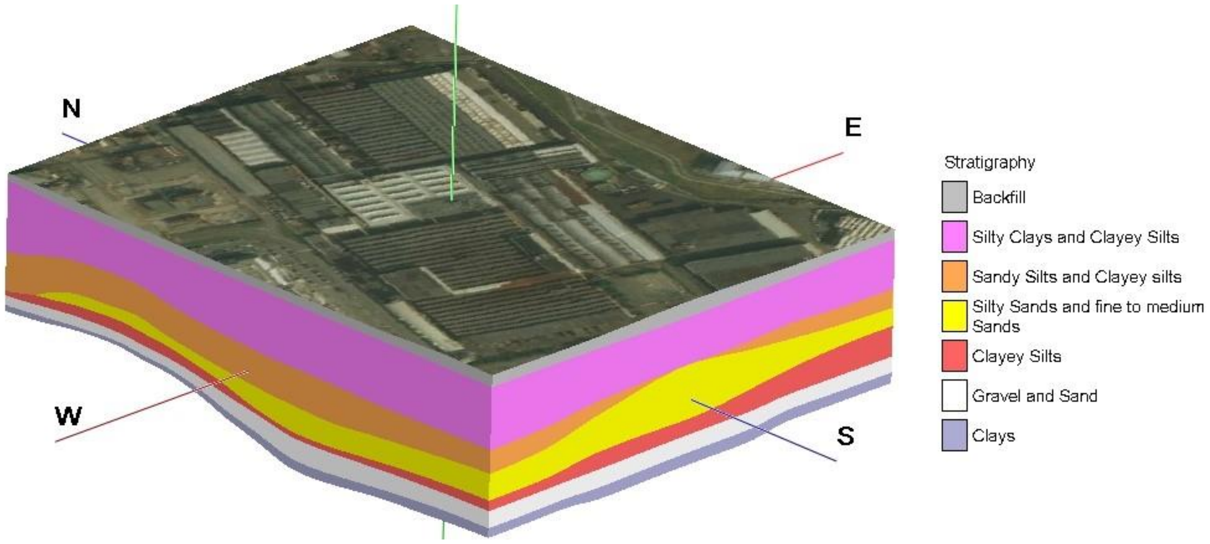


Figure 24. 3D geological model of the industrial plant area (Ciampi et al., 2019$_a$).

The basal aquifer (deep aquifer) hosted in the gravel and sand layer at a depth of 22 m is the only one with spatial continuity. The water circulation in the shallow aquifer is fragmented in several layers due to the alternation of sandy/sandy-gravelly and clayey-silty horizons. For this reason, the piezometric surface shows local anomalies and relevant differences of piezometric levels referred to piezometers placed at a short distance. Another disturbance factor, which could explain the uneven variations in piezometric levels, is represented by the existence of active wells inside the plant, which—beyond locally induced depressions—may have put the two aquifer levels into communication with each other (Mayo, 2010). In general terms, the shallow aquifer, which has an average depth of 2 m below ground level, is confined due to the presence of the overlying fine layers. From the interpolation of the data coming from the piezometric surveys carried out in the historical monitoring wells, it was possible to produce an isopiezic map (Figure 25).

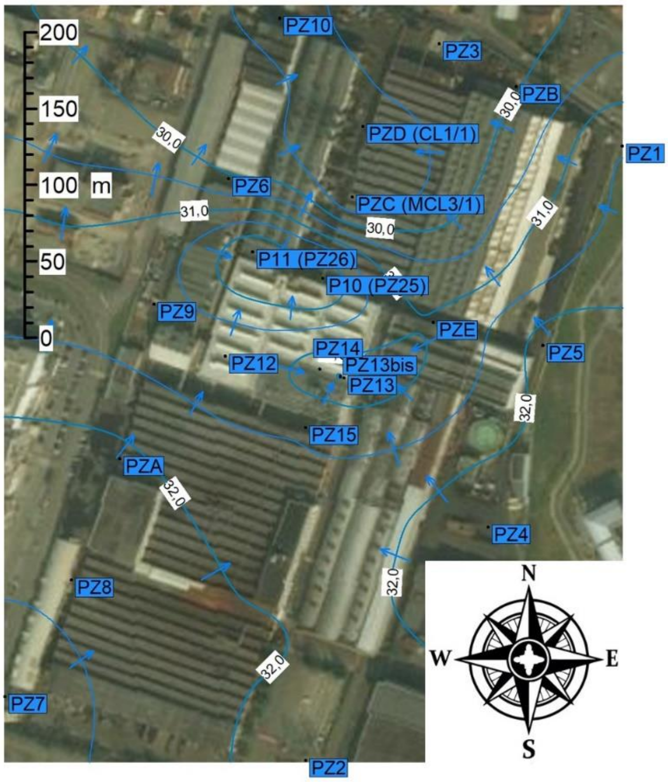


Figure 25. Representation of the piezometric surface (meters above sea level) of the shallow aquifer (Ciampi et al., 2019_a).

Groundwater showed a prevailing flow direction from S to N, locally disturbed by the presence of pumping wells. The hydraulic gradient is between 1.0% and 1.2%. The velocity of the water flow is approximately 10 m/year. To provide useful information for design purposes, in terms of the sizing and configuration of the remediation intervention (Suthersan et al., 2016), attention was focused on the subsoil in the pilot test area. The morphology of the aquifer limits is very articulated, in agreement with what is expected for this depositional environment (Figures 26 and 27). The high-resolution geotechnical parameterization of the different lithostratigraphic horizons captures the geological heterogeneity, which exerts a decisive action on the contaminant transport and adsorption processes (Harris et al., 2004; Kram et al., 2001).

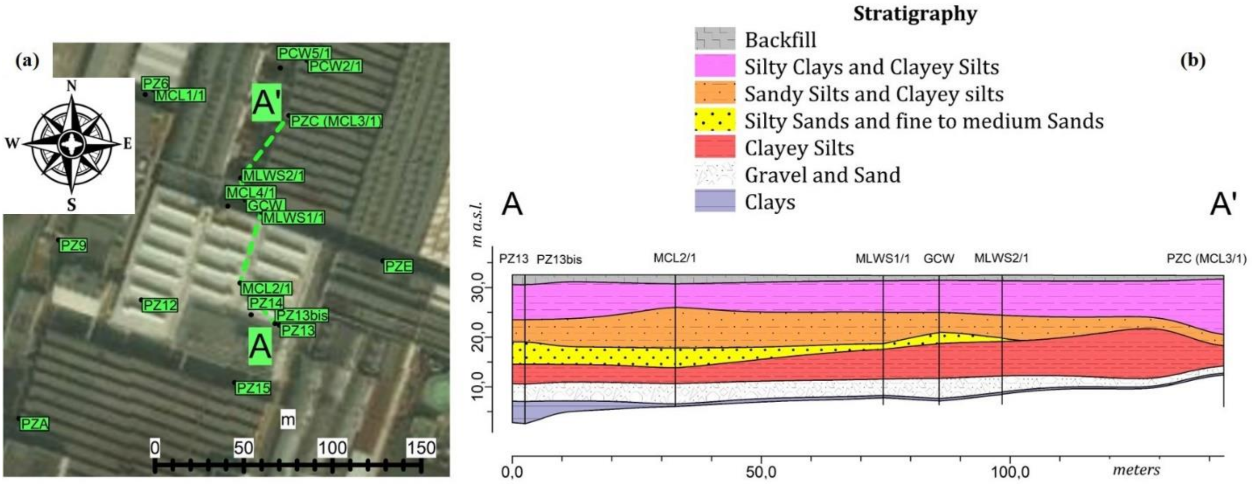


Figure 26. Tracking map (a) and stratigraphic section across the pilot test area (b) (Ciampi et al., 2019a).

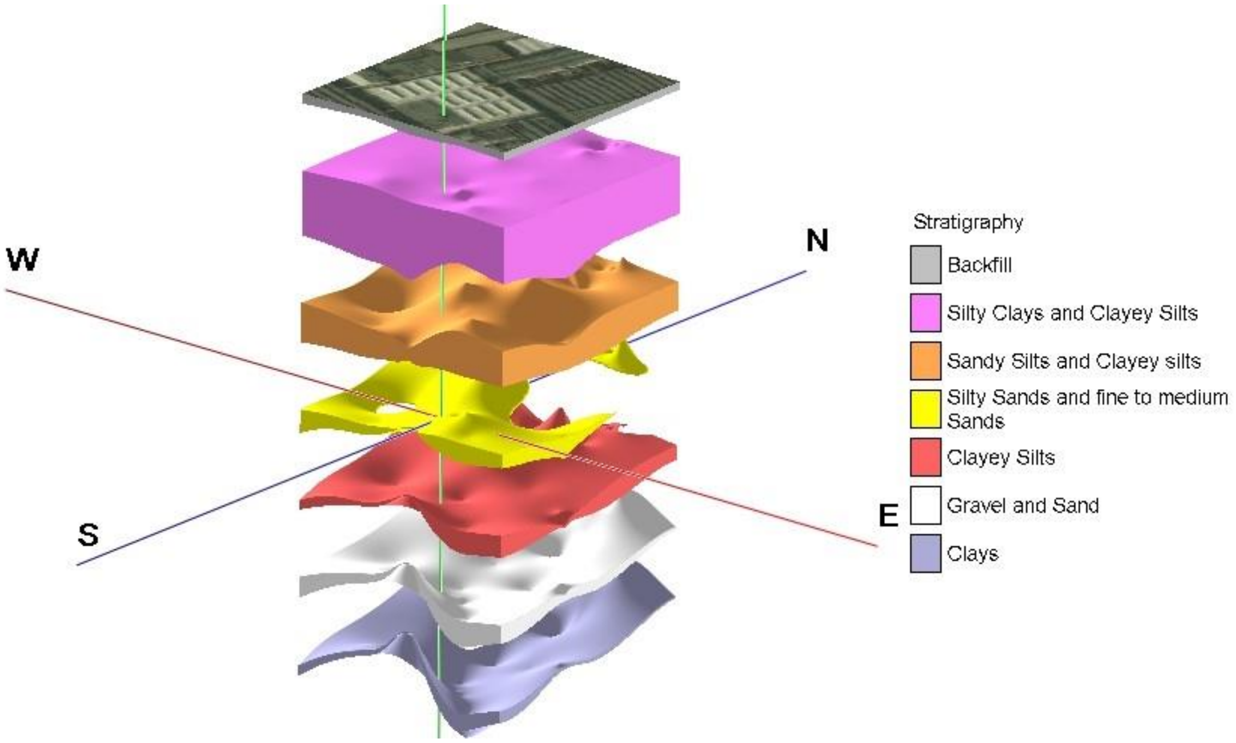


Figure 27. Pilot test 3D “exploded” lithostratigraphic model (Ciampi et al., 2019a).

3.2 Geophysical Model

Geophysical techniques reduced the need for intrusive investigations (Chambers at al., 2004) and provided spatially continuous information regarding the subsurface structure (Samouelian et al., 2005). Geophysical investigations focused with adequate resolution down to a depth of 20/30 meters. In addition, they linked the relevant measured physical quantities with the hydrological and environmental quantities of interest for contaminated site characterization (Cassiani et al., 2014). The technique considered in this study is electrical resistivity tomography (ERT). Electrical resistivity tomography measurements have indicated that the geological site structure (Crook et al., 2008), the hydrogeology (Binley et al., 2015), the injected (Ciampi et al., 2019$_b$) and the contaminated materials may be discriminated based on altered electrical properties. In the case we present, the 3D geological models, produced based on stratigraphic surveys, were refined and strengthened by integrating the geophysical evidence. The combination of ERT mesurements added additional and precious information, by capturing the complexity of geological heterogeneity and providing the data spatialization (Samouelian et al., 2005). The high-resolution characterization of underground geological heterogeneities and the integration of different information represent a key element for the characterization refinement, the remediation design, the optimization of intervention, and performance monitoring (Suthersan et al., 2016). ERT investigations were not carried out at the industrial site due to reduced accessibility and logistical limitations (presence of flooring).

3.2.1 Decimomannu

At the Decimomannu Nato airbase, the realization of 15 ERT prospecting lines differentiated low-permeability and high-permeability units during the characterization phase. The geophysical model reinforced and enriched stratigraphic data. Several resistivity sections represent the results acquired along the tracks (Crook et al., 2008). The fusion of linear prospecting techniques, which facilitate the spatialization of data, with the traditional and non-replaceable techniques of punctual prospecting, captures the variability of geological heterogeneity, which influences transport processes (Binley et al., 2015). The variations of the investigated parameters, such as the resistivity of the materials, schematize with great precision the anisotropy of the subsoil. The processing and the analysis of geophysical data revealed a good correlation between the low resistivity layers and the clay levels ascribable to the hazelnut clays, characterized by a greater relative electrical conductivity (Figure 28).

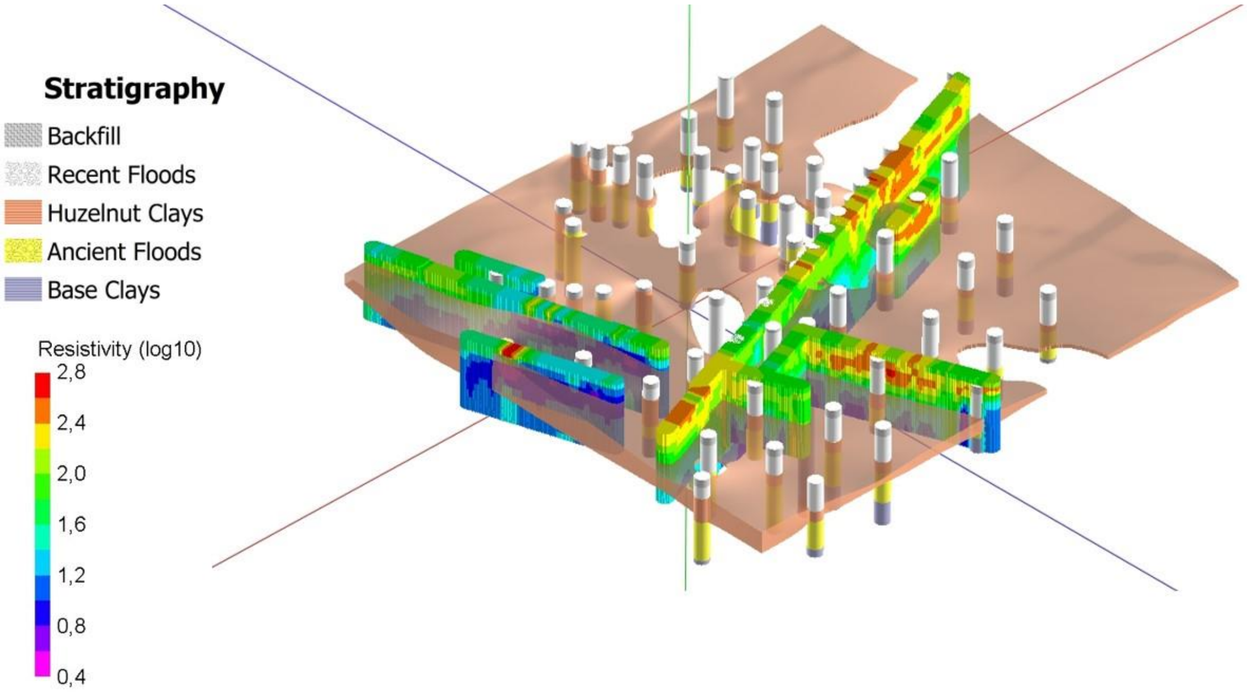


Figure 28. 3D model that illustrates the results of the geophysical surveys, the layer of hazelnut clays and stratigraphic logs.

In the west sector, where the hazelnut clays show a greater thickening, the layers with low resistivity correspond to the clayey horizons, whereas the levels with higher resistivity coincide with the sandy layers of the shallow aquifer. In the east sector, otherwise, the ERT profiles acquired along the traces show higher relative resistivity values. In this portion of the airbase the clayey hazelnut lens is almost or totally absent, while the recent floods are preponderant. This affects the electrical properties of the subsoil, resulting in higher resistivity values. The realization of 15 ERT prospecting lines differentiated low-permeability and high-permeability units during the characterization phase. The integration of geophysical prospecting represents a useful tool in the phase of characterization of contaminated sites, providing the high-resolution characterization of underground geological heterogeneities, aquifer and preferential flow pathways (Ruggeri et al., 2014).

3.2.2 Bologna

To strength the geological model, which arises from the interpolation of punctual data, geophysical investigations were carried out by performing three electrical resistivity tomography (ERT) (Binley and Kemna, 2005) profiles that cover the pilot test area of the Bologna railway station. The 3D geological/hydrogeological model was refined and strengthened by integrating the geophysical evidence (Crook et al., 2008). The three resulting ERT sections are presented in Figure 29. A resistivity model in 3D (Figure 30) was produced by interpolation across the three ERT lines.

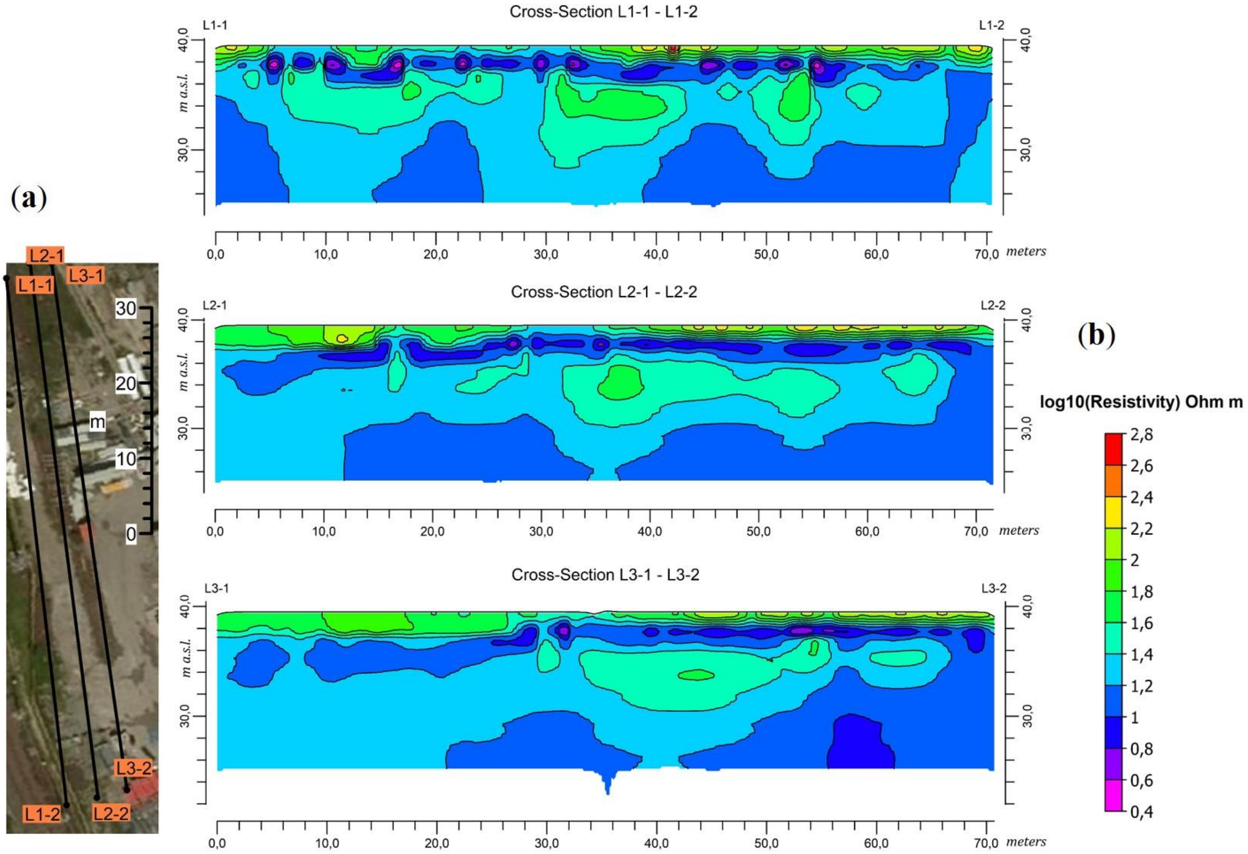


Figure 29. Arrangement of the electrodes on the soil in the pilot test area (a) and resulting ERT profiles (b) (Ciampi et al., 2019b).

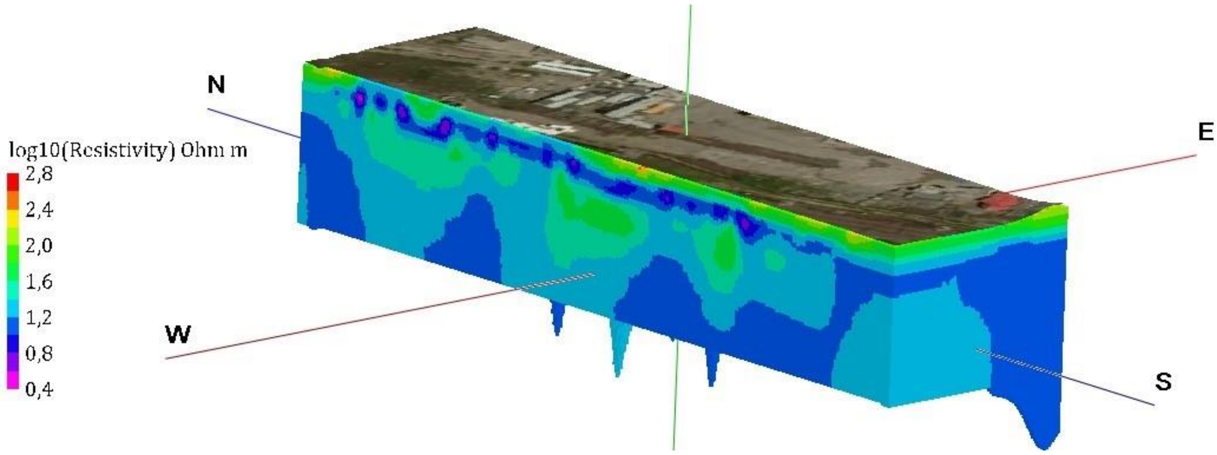


Figure 30. 3D resistivity model that covers the pilot test area (Ciampi et al., 2019b).

The spatial continuity of the geo-electrical data correlates the high resistivity zones with sandy deposits of the shallow aquifer, which are characterized by a good hydraulic permeability. These represent preferential flow pathways and transport routes, while the layers with lower resistivity correspond to the clayey horizons, which are featured by low permeability. The use of closely spaced 2D ERT data facilitates spatialization of data (Crook et al., 2008). The combination of non-invasive methods with traditional and non-replaceable punctual prospecting techniques captures the variability of geological heterogeneities and the complexity of transport processes (Binley et al., 2015). The high-resolution characterization and the integration of geophysical models represent key elements for the remediation designing and the optimization of intervention configuration (Suthersan et al., 2016; Ciampi et al., 2019b).

3.3 Contamination Status Evolution

The analytical data, which refer to the monitoring campaigns carried out in the three contaminated sites, were used for the construction of contour maps. The thematic maps represent the concentrations of the contaminants detected in the historical piezometric networks over time. They were produced by considering some key contaminants, which are correlated with the state of contamination that was previously ascertained. The concentration values were compared to the Italian threshold limits (CSC)—the limits between each class corresponded to multiples of the CSC value for each contaminant. The analysis of contamination status evolution provides impressive indication about contamination dynamics and decontamination mechanisms. The integration of analytical data within the geodatabase favors the development of a conceptual model that considers extension and degree of contamination, characteristics and chemical-physical parameters that condition the mobility and the division between the phases of the pollutants.

3.3.1 The Military Airbase

The reconstruction of the evolution of the groundwater contamination status at the Decimomannu military base was reproduced based on the chemical analyses of waters sampled in the monitoring network, in the period 2011-2018. Several thematic maps were produced by considering the total petroleum hydrocarbons (TPH). The detected contamination, despite being mainly caused by some spills, was quite extensive and has been the subject of years of a Pump & Treat intervention (still operational) that over time has allowed both the reduction of the contaminant mass and a narrowing of the contaminant plume, that progressively has reached an asymptotic trend. The thematic maps show the decrease in the concentrations of pollutants detected, illustrating evolutionary trends of the substances considered (Figure 31).

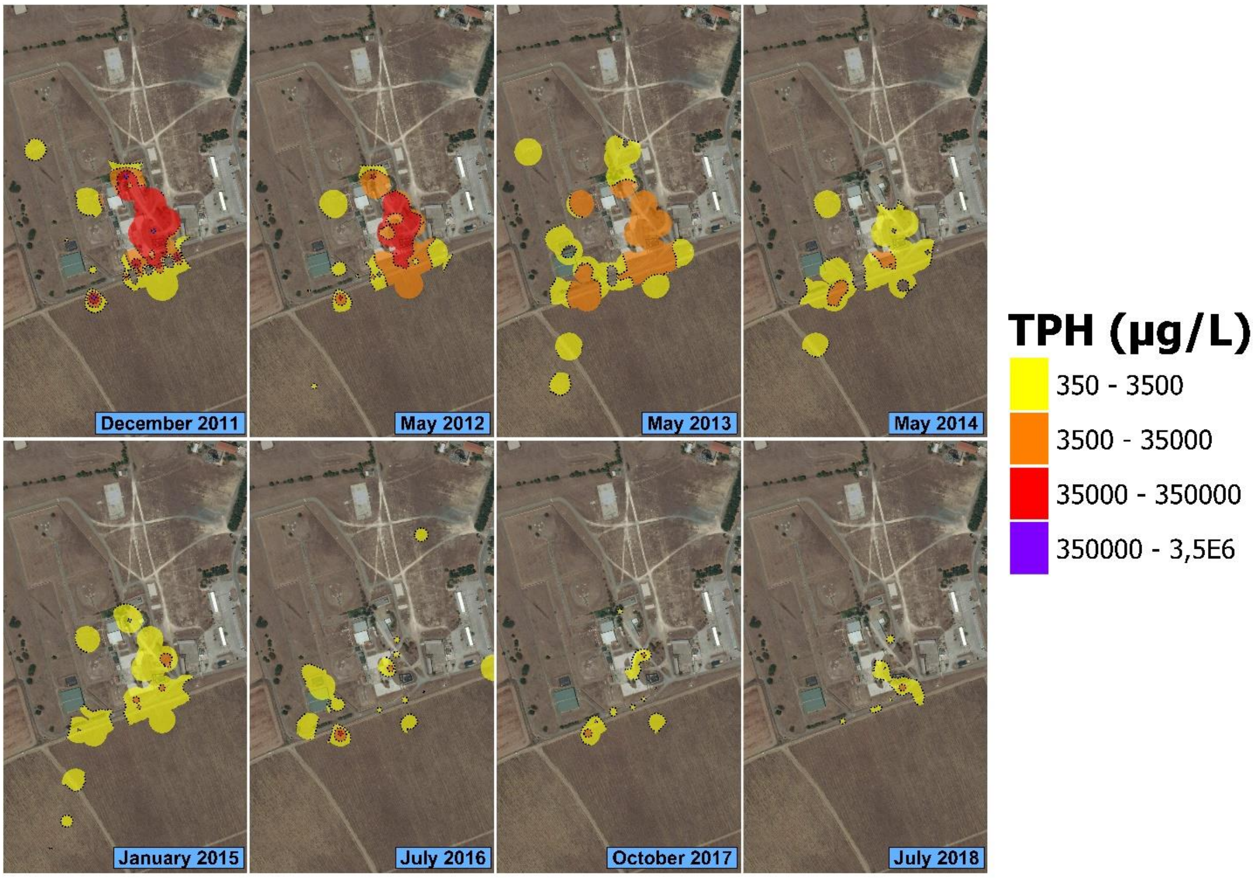


Figure 31. Contour maps of total hydrocarbon concentrations (in µg/L) detected in groundwater from 2011 to 2018.

Through the maps, the most critical areas can be easily identified, and it is possible to imagine an intervention hypothesis to reduce the level of contamination. This type of representation defines in a more objective way the possible areas of intervention. The analysis of the monitoring data totality confirms the progressive improvement of the site contamination status and the decreasing trend of total hydrocarbon concentrations detected in the piezometric network. In the last year, limited "critical issues" are sporadically found at some piezometers located within the tank storage area and around the hydraulic barrier zone. The collected data confirm the decidedly decreasing trend of contamination factors.

The data used for the construction of a georeferenced database, were enriched by detailed speciation, through GC-MS (Vozka et al., 2019), of supernatant that has been occasionally detected over the years in the piezometric monitoring network. The chromatograms of jet fuel and supernatant samples show a significant difference in the chromatografic fingerprint regarding the peaks of more volatile fractions, less present in the supernatant, coherently with the aging of the product (Figure 32).

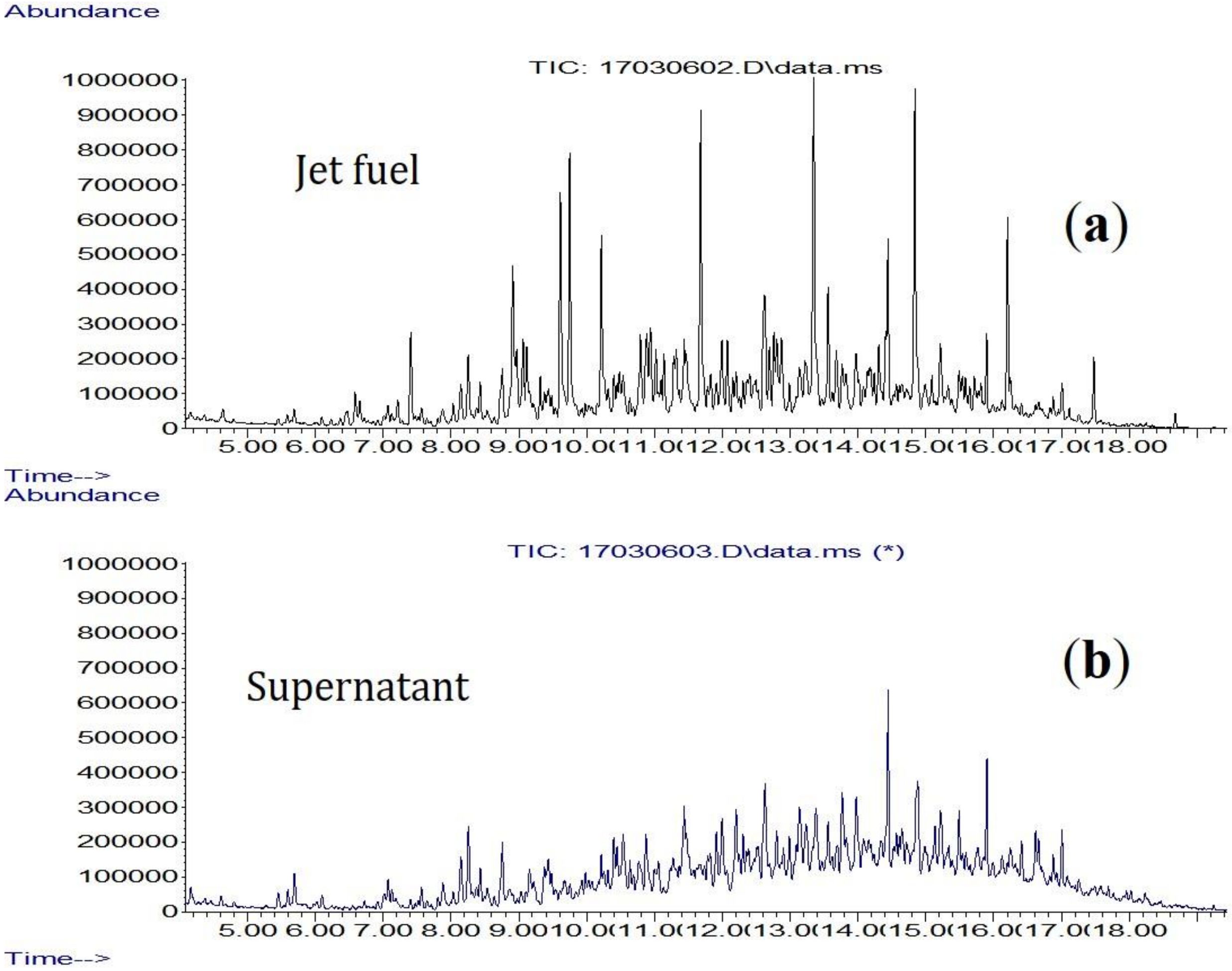


Figure 32. GC/MS chromatographic fingerprint (total ion) related to jet fuel (a) and supernatant (b) that was occasionally collected in the piezometric monitoring network.

Comparing the GC/MS chromatographic fingerprint of jet fuel and supernatant samples, a clear difference is noted for all linear components that are drastically reduced in the supernatant, since these fractions are more bioavailable to biodegradation (Tran et al., 2018) (Figure 33).

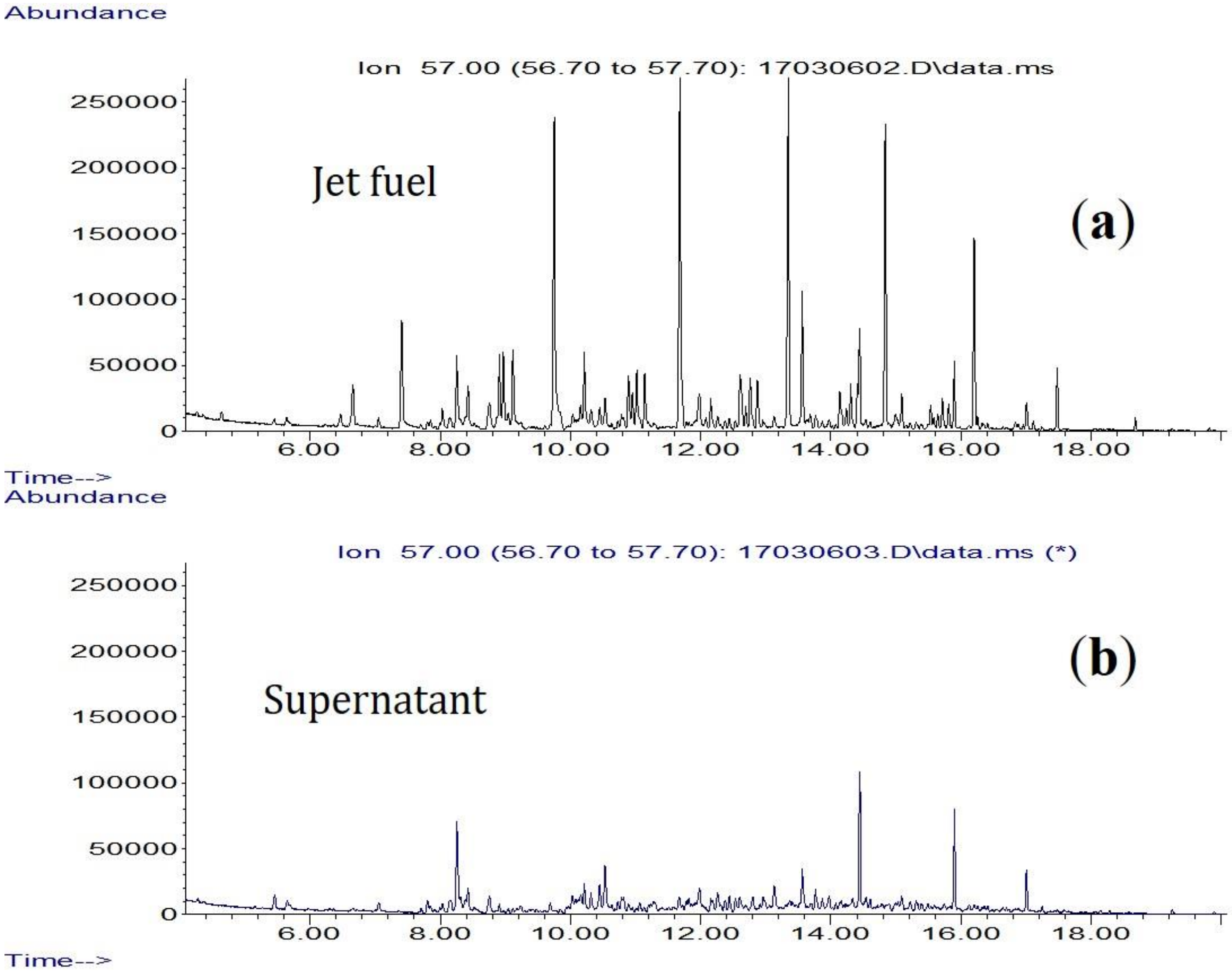


Figure 33. GC/MS chromatographic fingerprint relative to linear aliphatics (C6 – C16) measured in the fresh product (a) and in the supernatant (b).

The photo-ionization dectetor analysis demonstrates that the medium-light aromatic fractions (C8-es. toluene, xylene, etc.) are almost completely absent in the supernatant sample (Tran et al., 2018). For medium heavy compounds (C10-es. butylbenzene, tetramethylbenzene) the phenomenon is much less marked (Figure 34).

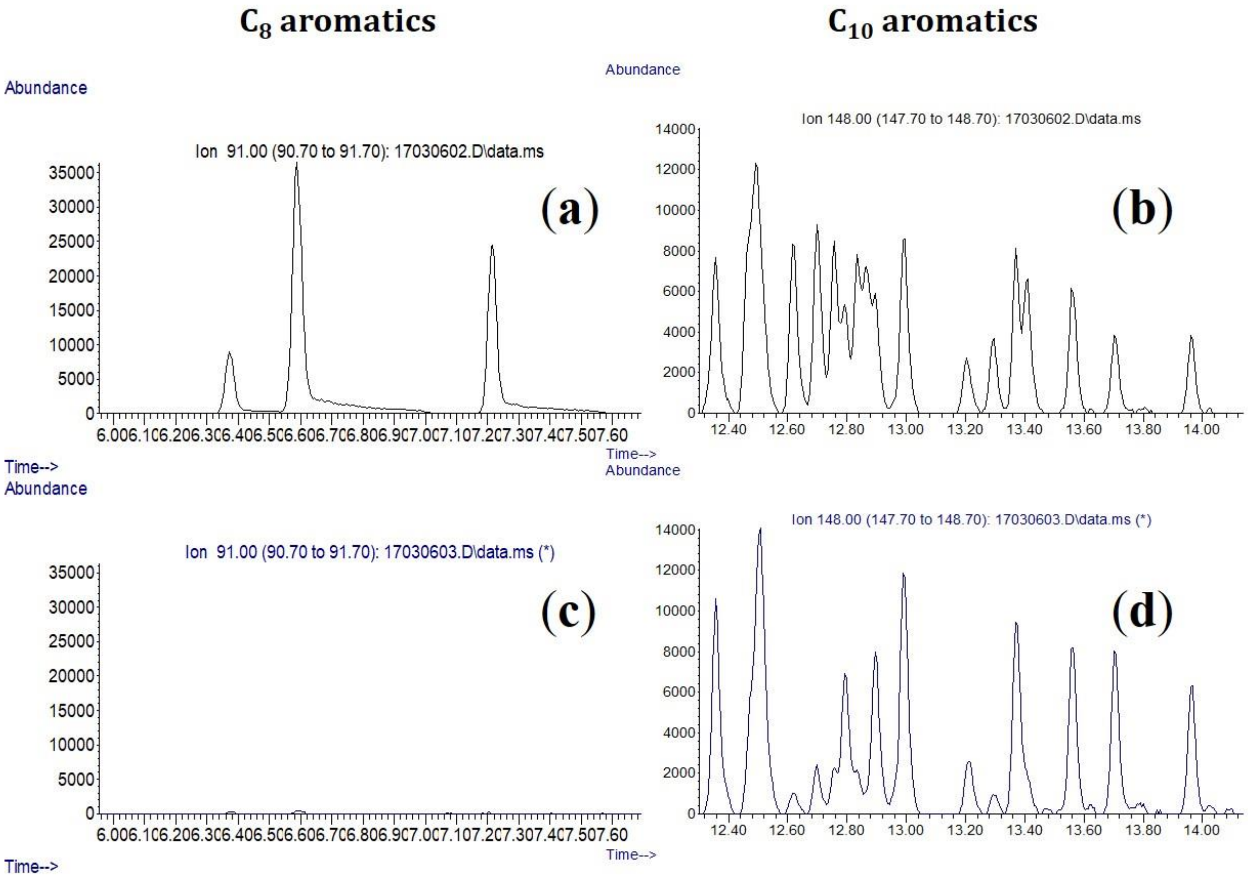


Figure 34. Photo-ionization detector analysis of medium-light (a, c) and medium-heavy (b, d) aromatic fractions measured in jet fuel (a, b) and in the separate phase (c, d).

The solubilization analysis of the components in water confirms the aging of the LNAPL phase. These laboratory tests were performed on a sample of water in contact with the fresh product and on a sample of water in contact with the supernatant (Figure 35).

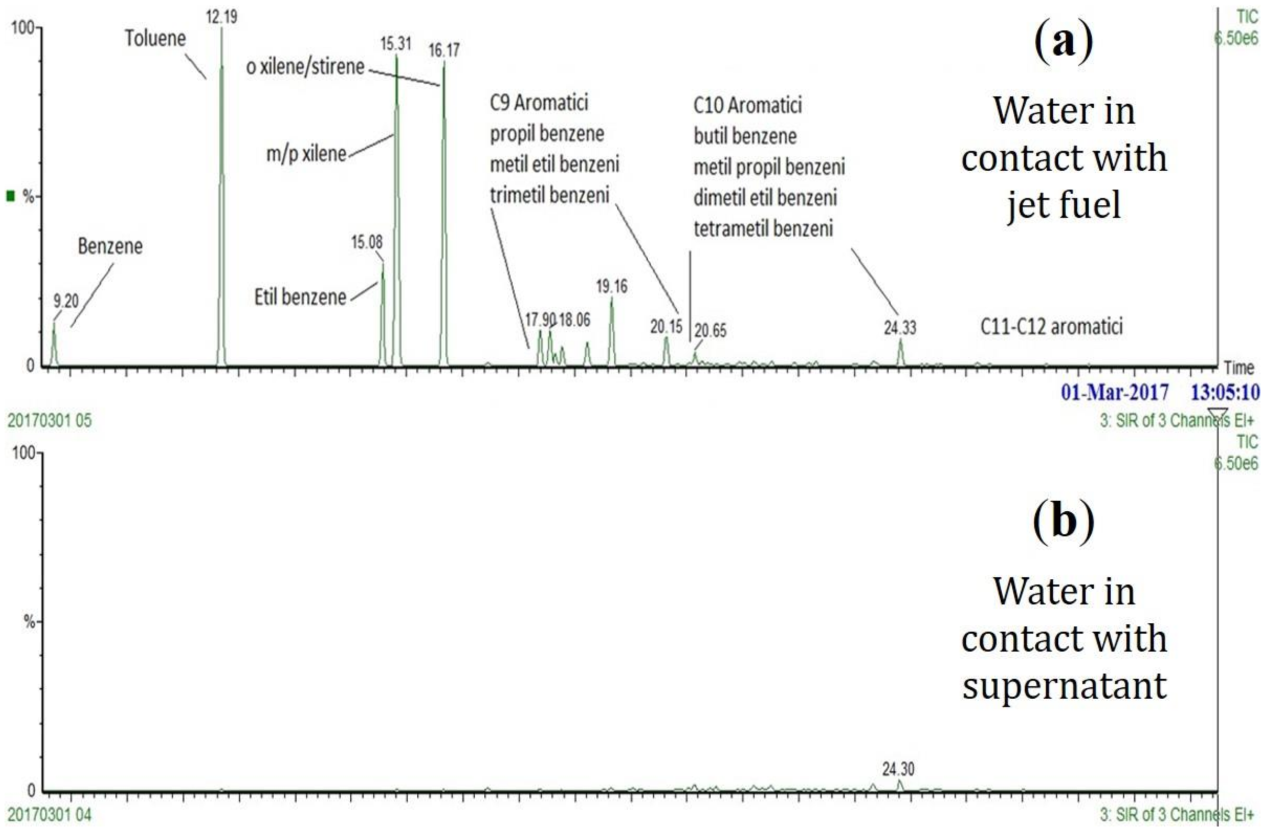


Figure 35. Solubilization of components in water for the jet fuel (a) and the supernatant (b).

The analytical investigations for water samples in contact with the supernatant and the jet fuel exhibite the very low presence of light aromatic fractions in the water in contact with the supernatant. The comparative analyzes carried out on fresh product (jet fuel) and supernatant recovered during the monitoring campaigns showed the presence of residual product (Lekmine et al., 2017). The analyzes revealed how the soluble component of the residual fraction is actually exhausted. The laboratory investigations identified the presence of contaminants in the residual phase. The resulting data prove the natural "aging" of potential secondary sources of contamination. This aspect is particularly relevant in the case of fuel contamination, complex mixtures of hydrocarbons that contain categories of substances with significantly different chemical / physical and biodegradable properties (Vozka et al., 2019). In the initial phase of the spill (when the primary source is active), the most soluble components (i.e., BTEX) could be mobilized in the groundwater and aerobic biodegradation processes are active on the more readily degradable fractions (linear hydrocarbons with shorter chain). The progressive aging of the contamination sources corresponds to an impoverishment of the more mobile and degradable fractions with the accumulation of fractions characterized by higher molecular weight (Lekmine et al., 2017). The comparative analyzes conducted both on the fresh product and on the supernatant, occasionally recovered during the monitoring campaigns, confirm that the soluble component of the residual product fraction is, in fact, depleted. This residual fraction, therefore, although still present in the environmental matrices, is not able to release significant quantities of soluble substances into the groundwater (this is confirmed by the total absence of the aromatic fraction throughout the monitored piezometric network).

3.3.2 The Contaminated Site of Bologna

At the contaminated site of Bologna, the contour maps consider some of the different phases of construction of the train station. Figures 36 and 37 show the maps more relevant for the reconstruction of the contamination status of groundwater (PCE and TCE). PCE and TCE were certainly used in the past as degreasing solvents and constitute the primary contaminants. Each figure shows the values of concentrations at three different time instant. The contour maps illustrate some of the different phases of construction of the train station. These are compatible with the different phases of aquifer response to possible sources of contamination. Concentration values are compared to the Italian threshold limits (CSC): the limits between each class correspond to multiples of the CSC value for each contaminant.

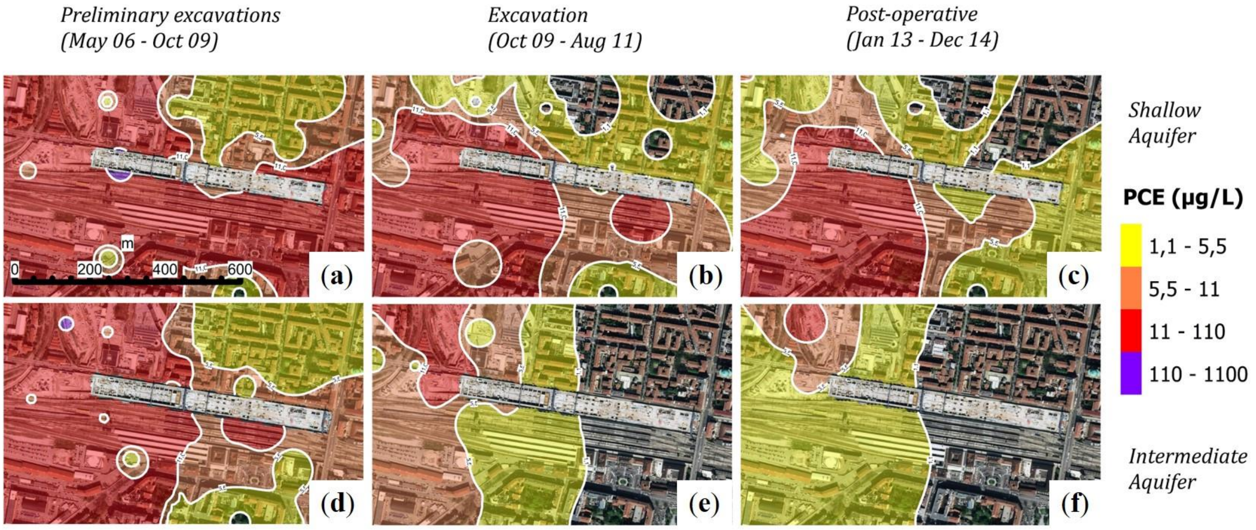


Figure 36. Contour maps that represent the values of PCE concentrations in the shallow (a, b, c) and intermediate (d, e, f) aquifers, at three-time instants (Ciampi et al., 2019_b).

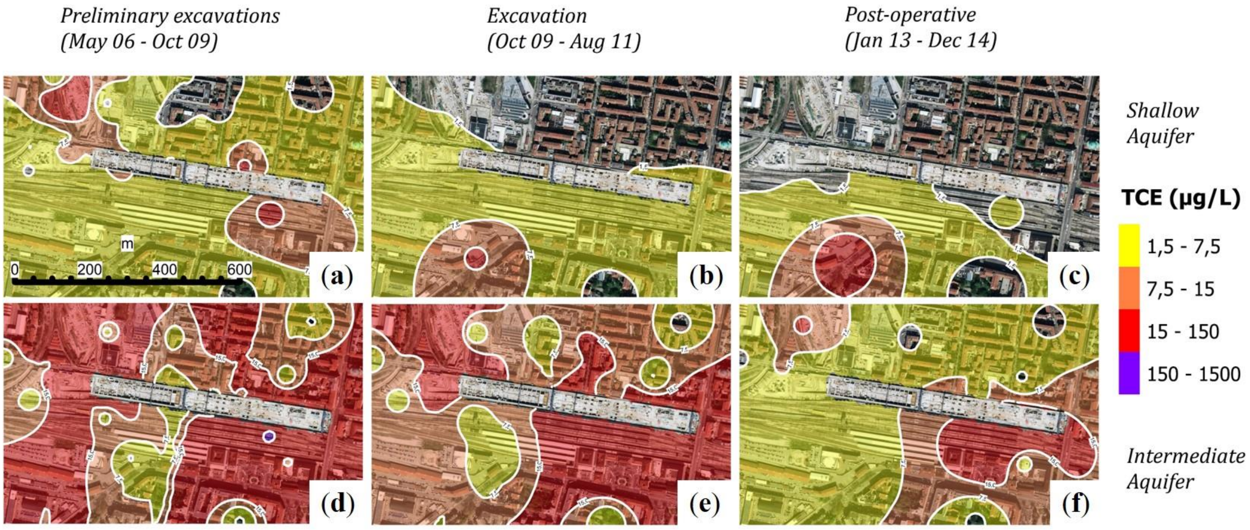


Figure 37. Contour maps that represent the values of TCE concentrations in the shallow (a, b, c) and intermediate (d, e, f) aquifers, at three-time instants (Ciampi et al., 2019_b).

The CSC exceedances are concentrated during the working activities, in phases “preliminary excavation” and “excavation”. Afterwards the contamination levels decrease in terms both of areal extension and concentrations. The general evolution shows how station processing activities have clearly influenced the quality of groundwater. In fact, as soon as the "preliminary excavation" phase ends, there is a constant improvement of groundwater quality. Moreover, during the "post-operative" period there is an improved qualitative state and it is possible to identify the areas affected by significant residual contamination (Leharne, 2019). The increase of chlorinated solvents concentration during the excavation phases could be related to the remobilization of the contaminants adsorbed on the solid soil matrix, or partly present as trapped non-aqueous phase (Tatti et al., 2016).

3.3.3 The Industrial Site

The analytical data, which refer to the monitoring campaigns carried out from 2008 to 2017 in the industial plant, were used for the construction of some contour maps, which represent the concentrations of the contaminants detected in the historical piezometric network. The thematic maps were produced by considering some key contaminants (vinyl chloride (VC) and 1,2-dicloroethylene (1,2-DCE)), which are correlated with the state of contamination that was previously ascertained (Petrangeli et al., 2016; Pierro et al., 2017). Each subfigure shows the concentration value at three different time instants (Figure 38).

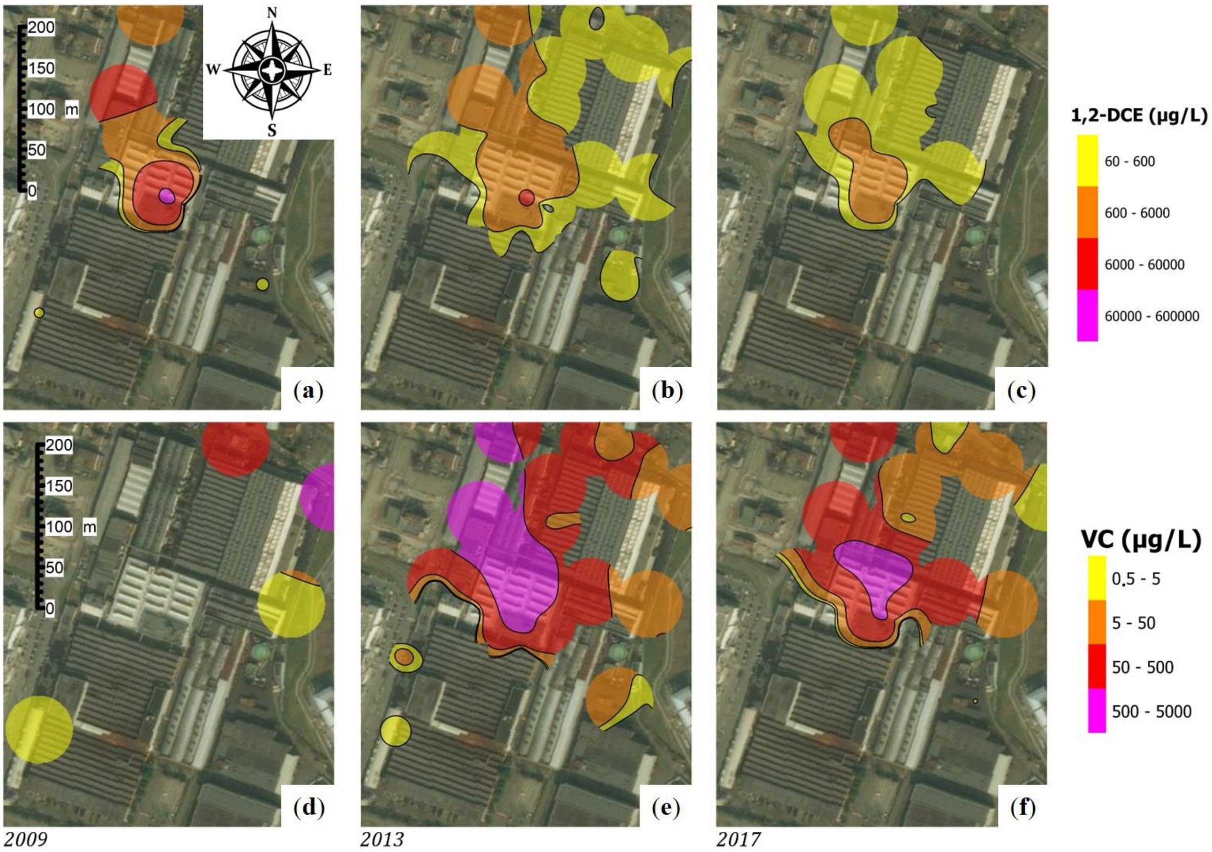


Figure 38. Contour maps that represent the 1,2-dicloroethylene (1,2-DCE) (a, b, c) and vinyl chloride (VC) (d, e, f) concentrations detected in groundwater in 2009, 2013, and 2017 (Ciampi et al., 2019_a).

The reduction of 1,2-DCE and the increase of VC over time indicate that natural attenuation is underway at the site. The presence of compounds with a lower degree of chlorination indicates an intense but incomplete microbial dichlorination activity (Aulenta et al., 2005; Petrangeli et al., 2016; Pierro et al., 2016). The areas most affected by these classes of contaminants are located at the central portion of the plant, at a building that in the past housed two washing machines for the degreasing of mechanical parts. Industrial washing machines, which used organochlorine solvents, potentially represent historical contamination sources. For the reasons set out above, the pilot test was carried out at the central sector of the industrial plant. The extraction of hydrogeochemical data from the geodatabase and their spatial overlap reveals valuable information on the contamination dynamics (Ciampi et al., 2019a). The high-resolution hydrogeochemical characterization identifies in detail the subsoil horizons affected by residual phase contamination (Leharne, 2019). The integration of the geological section and the hydrochemical profiles clearly shows that the highest concentrations of contaminants are detected in the low permeability layers (Figures 39 and 40).

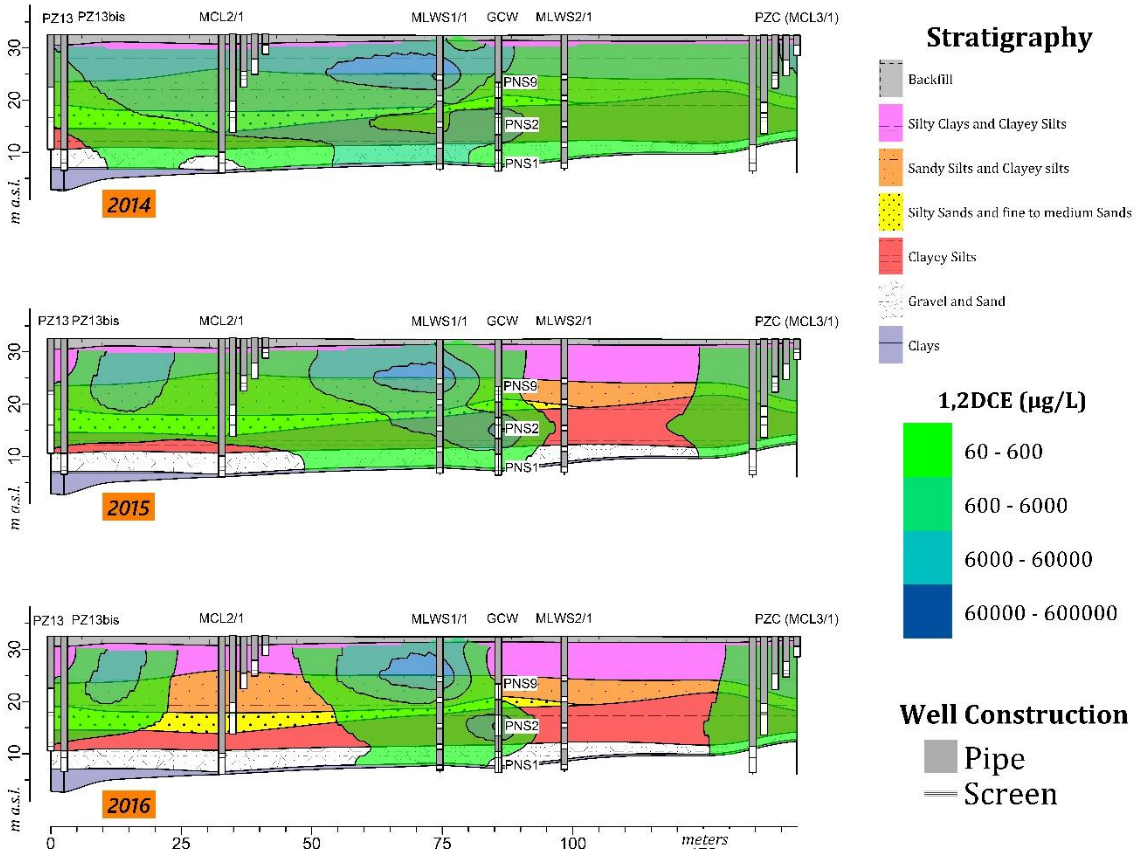


Figure 39. Hydrogeochemical sections relating to concentrations of 1,2-DCE detected in multilevel piezometers within the pilot area (Ciampi et al., 2019a).

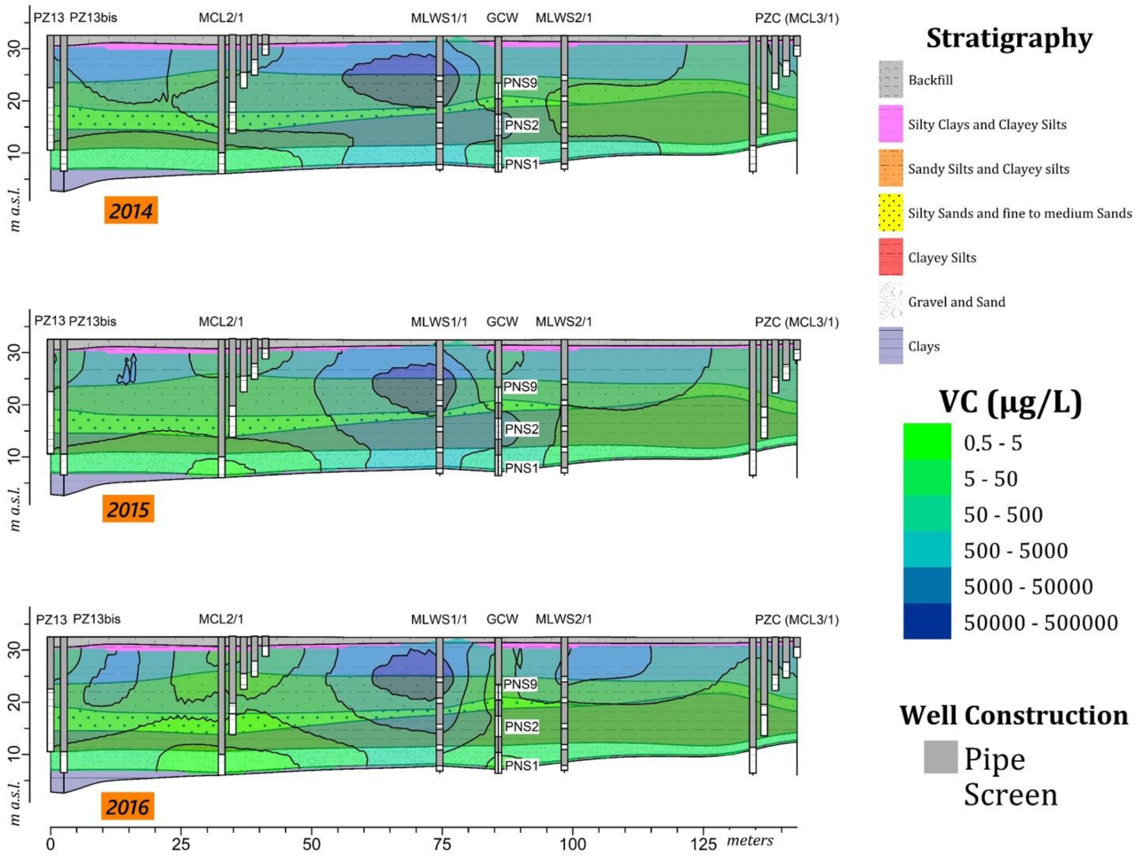


Figure 40. Hydrogeochemical sections relating to concentrations of VC detected in multilevel piezometers within the pilot area (Ciampi et al., 2019$_a$).

The high-resolution characterization, in geological and chemical terms, displays the association of a significant mass of contaminants with lenses of fine materials (Ciampi et al., 2019$_a$). These very low permeability layers, in the saturated zone, act as slow-release sources of contaminants (Petrangeli et al., 2016; Pierro et al., 2017). 1,2-DCE and VC were the main pollutants of the groundwater. They were detected in concentrations up to 100 mg L−1, and indicate the presence of residual areas of DNAPL, acting as persistent secondary sources. The residual source releases contaminants into the most permeable areas through a slow back-diffusion mechanism (Lapworth et al., 2018). Compounds with a higher chlorination degree were certainly used in the past as industrial solvents, and therefore constitute the primary contaminants (Aulenta et al., 2002). They were detected at significantly lower concentrations, highlighting an intense biological dechlorizing (Aulenta et al., 2005) activity (Figure 41).

Figure 41. Contour maps representing the contamination state evolution of trichloroethylene (TCE) in the historical piezometric network (Ciampi et al., 2019a).

3.4 Laser Induced Fluorescence Investigations

The LIF technology is used to evaluate the presence and distribution of LNAPL in the subsurface. For this reason Laser Induced Fluorescence investigation were carried out at the Decimomannu airbase. At the Decimomannu Nato base, the identification of product in residual phase suggested the realization of an integrative survey campaign using the LIF technique; to better determine the presence of the residual fraction of spilled fuel (Fedotov et al., 2019). An investigation campaign was conducted on the site with the UVOST-LIF technology, for the first time in our country, which allowed to delimit the subsoil volumes previously impacted by primary spills (Teramoto et al., 2019). The LIF was implemented in combination with CPT to detect the pollutants along a vertical profile and to determine the geotechnical proprieties of the different stratigraphic horizons. LIF-CPT surveys delimit the presence of residual phase along a vertical profile, by characterizing accurately the vertical distribution of LNAPL mass, and provide a high resolution "lithotechnical" log (Pepper et al., 2002). The execution of 30 survey verticals using LIF-UVOST technology (Annex 1) identified with high spatial resolution the presence of contaminants adsorbed on the solid matrix, delineating the areas impacted by residual contamination (Algreen et al., 2015). The results of the investigation, which allowed to map the distribution of the residual contamination present, are shown below.

The profiles illustrared in the following figure refer to the penetration resistance of a mechanical tip and the fluorescence emitted by the particles present, at certain depths, along a vertical profile (Figure 42). The first fluorescence profile is set on a natural scale, the second on a logarithmic scale.

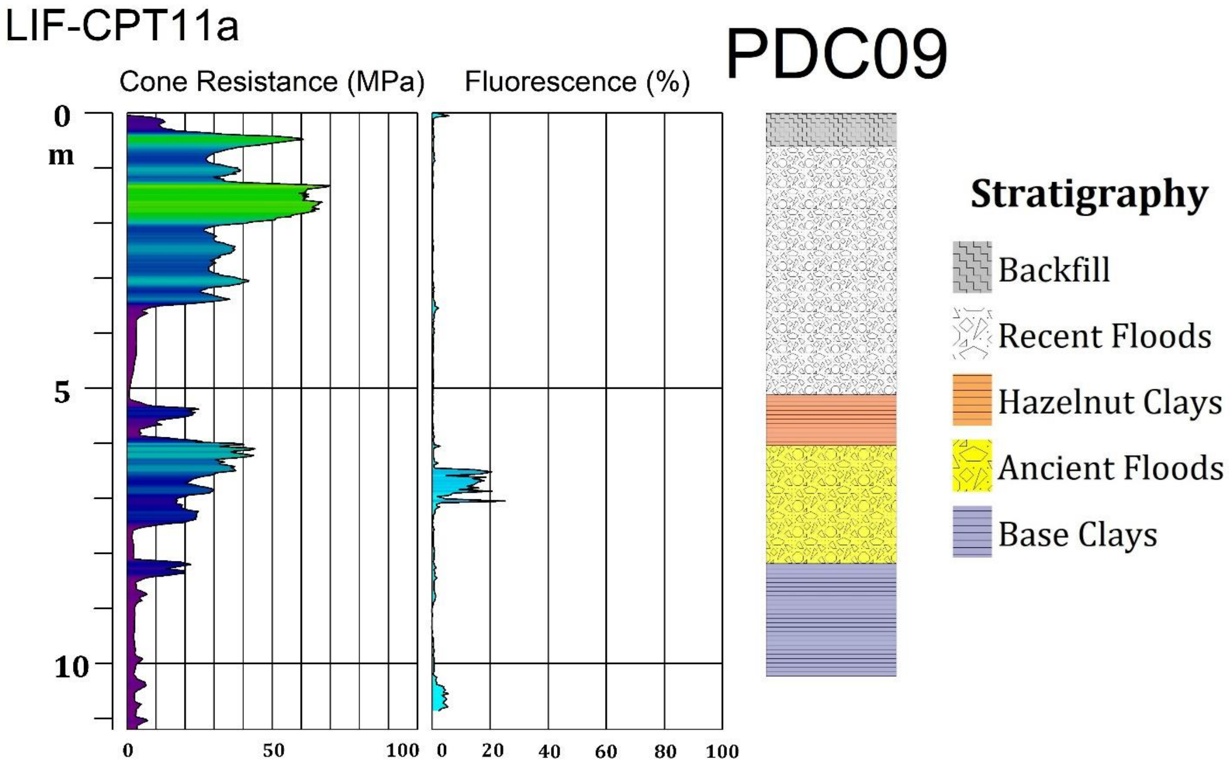


Figure 42. Vertical profiles related to cone resistance (MPa), fluorescence (%), obtained at the LIF-CPT survey point and stratigraphic log closer to the LIF investigation point.

The Figure 42 displays different response of above distinct lithologies to cone penetration, showing a major separation in terms of cone resistance values between coarse-grained (recent and ancient floods) and fine-grained (hazelnut and base clays) deposits. Coarse-grained horizons display high cone resistance, whereas fine-grained levels have low cone resistance. The correct lithotechnical determination is ensured by calibration with cores and stratigraphic position (Gruiz et al., 2017). The survey campaign using LIF-UVOST technology delimited the distribution of residual contamination present in the area. Fluorescence peaks, found along the vertical profiles and highlighted by a blue chromatic band, clearly indicate the presence of residual product at particular depths (Teramoto et al., 2019).

The combination of geotechnical aspects and geological interpretation provides a high resolution of stratigraphy insights. The continuous recording of parameters that highlight stratigraphic peculiarities, make the CPT tests ideal for the identification of lithological variations and the reconstruction of the geotechnical profile (Pepper et al., 2002; Einarson et al., 2018). The following representation refers to the penetration resistance (MPa) of a standard-sized conical tip (Pepper et al., 2002) and confirms what emerged from geological and geophysical prospecting, refining and reinforcing the integrated multidisciplinary model. The following voxel-based model exhibits an excellent correlation between the low cone resistance layers and the levels ascribable to the hazelnut clays in the W sector. Differently, in E portion, cone tip resistance increase is due to the presence of the gravel levels belonging to the ancient and recent floods (Fig. 43).

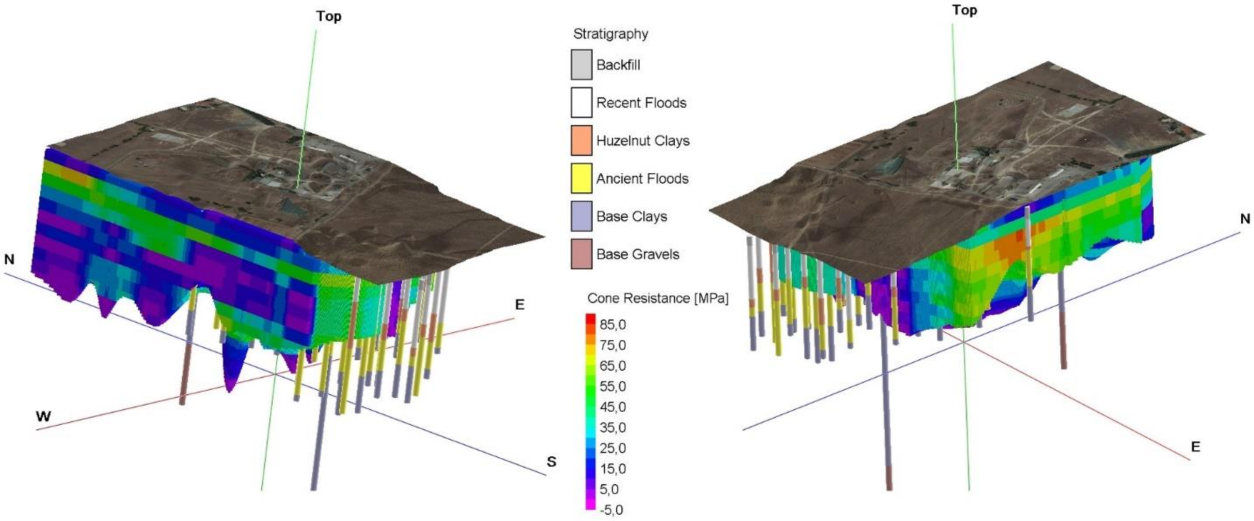


Figure 43. 3D models illustrating the penetration resistance (MPa) of the CPT tip.

The following models, obtained by interpolating the fluorescence profiles, illustrate, in the three dimensions, the location of the residual phase inside the military air base (Figure 44).

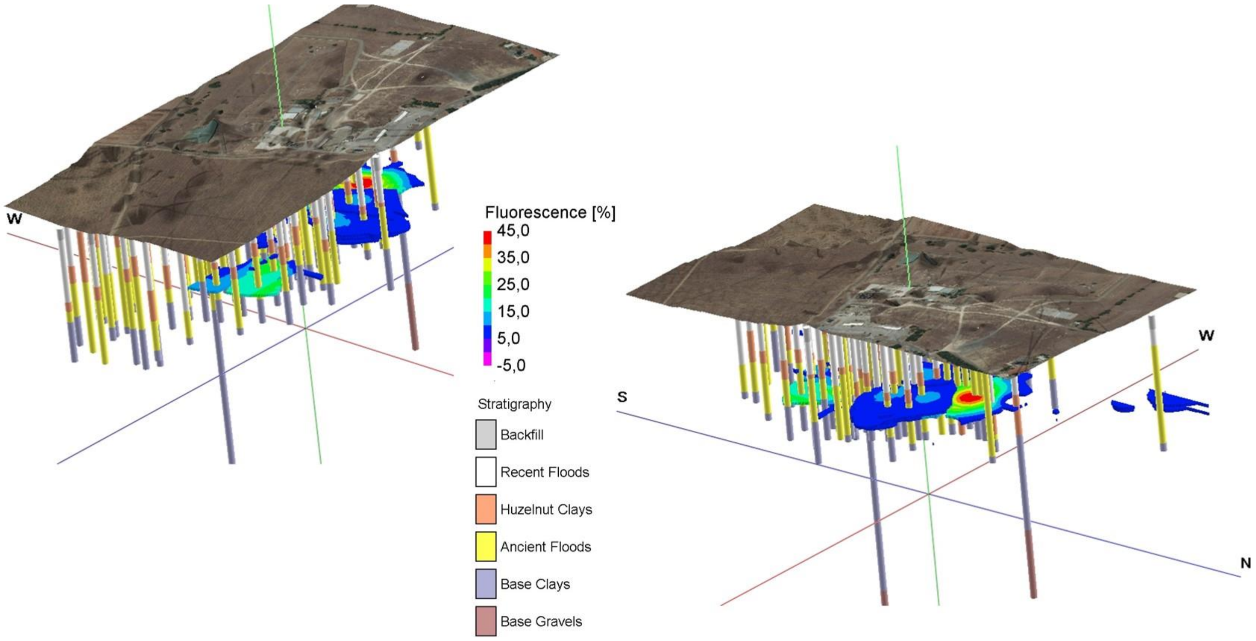


Figure 44. Fluorescence model obtained by interpolation of LIF - UVOST profiles.

Starting from the solid three-dimensional model, 2D thematic maps were extrapolated. They illustrate the maximum fluorescence peaks measured in the study area, the qualitative distribution of kerosene in the military base, and the subsoil thickness affected by the presence of residual product (Figure 45).

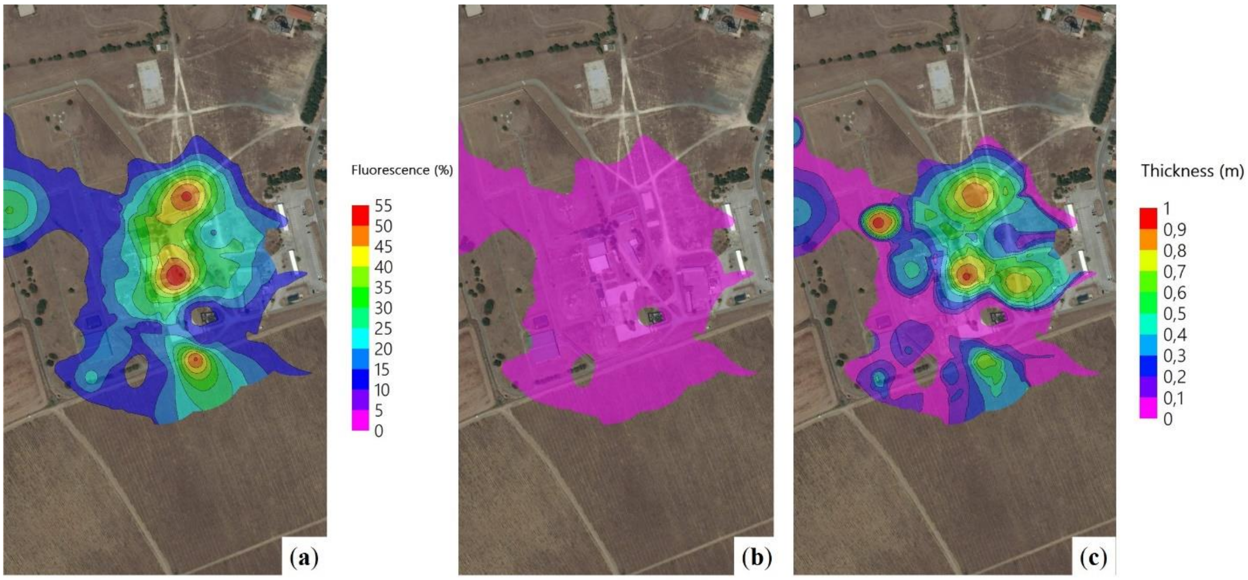


Figure 45. Maximum fluorescence peaks measured in the study area (a), distribution of kerosene (b) and subsoil thickness affected by the presence of residual product (c).

Investigations using LIF-UVOST technology identify the secondary contamination source with great resolution detail (Fedotov et al., 2019; Teramoto et al., 2019). The figure 46 demonstrate that contaminants, adsorbed in the residual phase on the solid matrixm (Trulli et al., 2016), are distributed along the smear zone. This represents an effect due to the oscillation of the water table, which has redistributed the contaminants along the piezometric level fluctuation band.

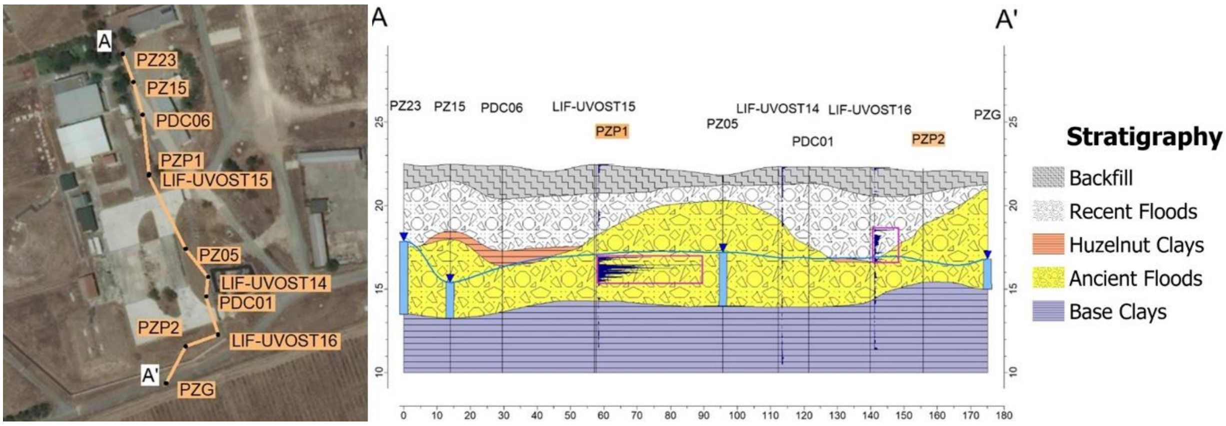


Figure 46. Stratigraphic section, piezometric level and LIF surveys executed along the track reported in the map.

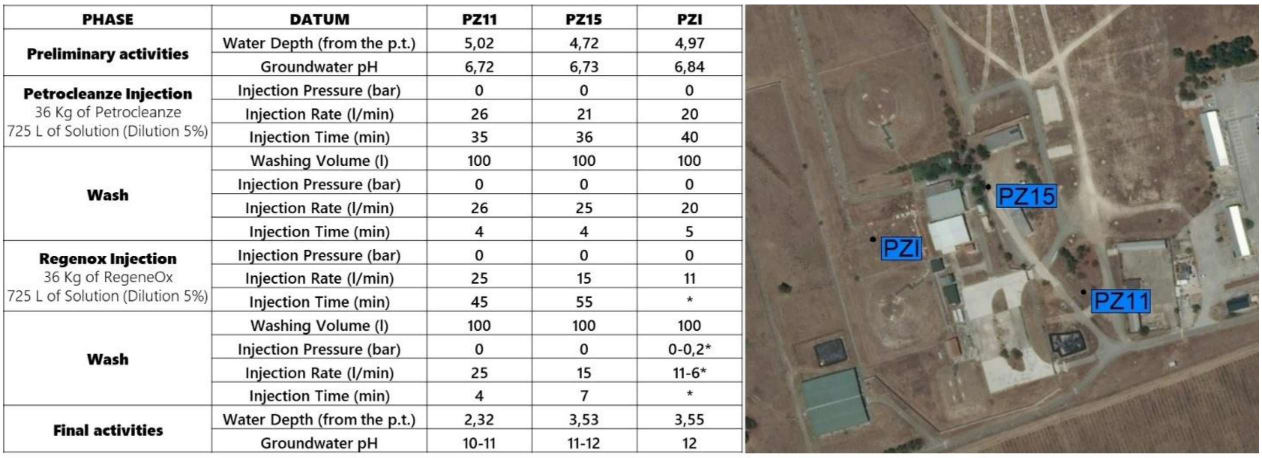
The fluorescence peaks clearly show the presence of residual product along the oscillation band of the piezometric surface. The profile also highlights the effects of pumping at the extraction wells. The pumping action carried out by the hydraulic barrier wells and the seasonal oscillation of the water table have favored the redistribution of the product in the residual phase along the smear zone (Trulli et al., 2016). This multi-source image reveal not only where LNAPLs are present, but also information not previously available about the behavior of LNAPLs in the formation matrix. This information help the understanding of LNAPL behavior in the subsurface (McCall et al., 2018) in the context of a fluctuating water table.

3.5 Remediation Strategy Design and Pilot Testing

The integrated geodatabase represents an effective “near real time” DSS (Decision Support System) able to manage and to release data during the different remediation phases, from the characterization to the technique implementation in the test area (Huysegoms and Cappuyns, 2017). The field test is an expression of the holistic approach employed. It promotes an interdisciplinary action and an integrated intervention, combining all the strengths of the various disciplines, harmonizing different information, and considering the contamination phenomenon in all its dimensions (Harris et al., 2004; Suthersan et al., 2016). The pilot test is an integrated system designed to optimize the layout of the intervention, to check the efficiency, and to provide eventual corrections that enable the implementation of full-scale intervention (to optimize performance in full-scale). Based on the results obtained from the site characterization, microbiological (Matturro et al., 2013, Pierro et al., 2017), and microcosm (Aulenta et al., 2002; Aulenta et al., 2005; Aulenta et al., 2007) studies (not shown here), the pilot test is the last step of the evaluation process and is designed to calibrate, adjust, and optimize the operating conditions at the field scale.

3.5.1 The Decimomannu Airbase

The complete multi-temporal and multidisciplinary characterization pointed to the selection of a remediation technology at the military base. An in situ enhanced chemical desorption strategy was implemented to increase the desorption of hydrocarbons adsorbed to saturated soils or at the capillary fringe and to raise the product recoverability in a separate phase. The hydrocarbons are made available in the dissolved phase or in a separate phase with lower viscosity, allowing a subsequent rapid and effective physical recovery. The intervention was carried out during the pilot phase in 2 different areas, by a direct application in the existing wells and reactivating the Pump & Treat system a few days later. The joint management of geological and hydrochemical data within the geodatabase oriented the location of the interventions at the field scale. The pilot test was realized in correspondence of areas characterized by two geological scenarios that are representative of the site. The two zones differ in the presence / absence of the hazelnut clay lens, which influences the hydraulic characteristics of the sediments of the air base. In addiction, the selected zones recorded the highest concentrations of contaminants in the groundwater during the historical monitoring campaigns. The remediation strategy involves the injection of reagents into the aquifer through piezometers. Performing the test in areas affected by an important historical contamination and a different geological setting provided valuable information to evaluate the efficiency of the implemented technology, to optimize the removal of pollutants, to improve the diffusion of reagents, and to plan the configuration of the intervention at full scale. The reagents consist of two parts: a desorbent part (PetroCleanze®, Regenesis) and an oxidising part (Regenox®, Regenesis). The desorbed fractions are partially oxidized, but mainly physically removed by pumping. Partial oxidation "breaks" the longest chains, rendering the hydrophobic contaminants (slightly degradable) more soluble and easily degradable. The pilot test assessed the potential mobilization of product present in the residual phase. The pilot test was conducted on three points of the piezometric network. ERT monitoring and groundwater sampling followed the three phases of the pilot test execution. ERT method was applied both to assist in site characterization and to monitor remediation processes (Chambers et al., 2010). Figure 47 presents the configuration of the pilot test; in terms of quantity of product to be injected and injection pressure/rate of the different reagents.



PHASE	DATUM	PZ11	PZ15	PZI
Preliminary activities	Water Depth (from the p.t.)	5,02	4,72	4,97
	Groundwater pH	6,72	6,73	6,84
Petrocleanze Injection 36 Kg of Petrocleanze 725 L of Solution (Dilution 5%)	Injection Pressure (bar)	0	0	0
	Injection Rate (l/min)	26	21	20
	Injection Time (min)	35	36	40
Wash	Washing Volume (l)	100	100	100
	Injection Pressure (bar)	0	0	0
	Injection Rate (l/min)	26	25	20
	Injection Time (min)	4	4	5
Regenox Injection 36 Kg of RegeneOx 725 L of Solution (Dilution 5%)	Injection Pressure (bar)	0	0	0
	Injection Rate (l/min)	25	15	11
	Injection Time (min)	45	55	*
Wash	Washing Volume (l)	100	100	100
	Injection Pressure (bar)	0	0	0-0,2*
	Injection Rate (l/min)	25	15	11-6*
	Injection Time (min)	4	7	*
Final activities	Water Depth (from the p.t.)	2,32	3,53	3,55
	Groundwater pH	10-11	11-12	12

Figure 47. Configuration of pilot test and location of injection piezometers.

During the reagent injection activities, the product ascent along the PZI was observed (* in Figure 47). The results of geophysical investigation reveal interisting aspects about the reagent diffusion and the decontamination dynamics. The results of ERT lines carried out in time lapse are expressed as resistivity in % with regard to the background. The sections in correspondence of the LTP1 line (permeable zone) show a good diffusion of the second reagent in the aquifer (tested by the blue band) (Figure 48).

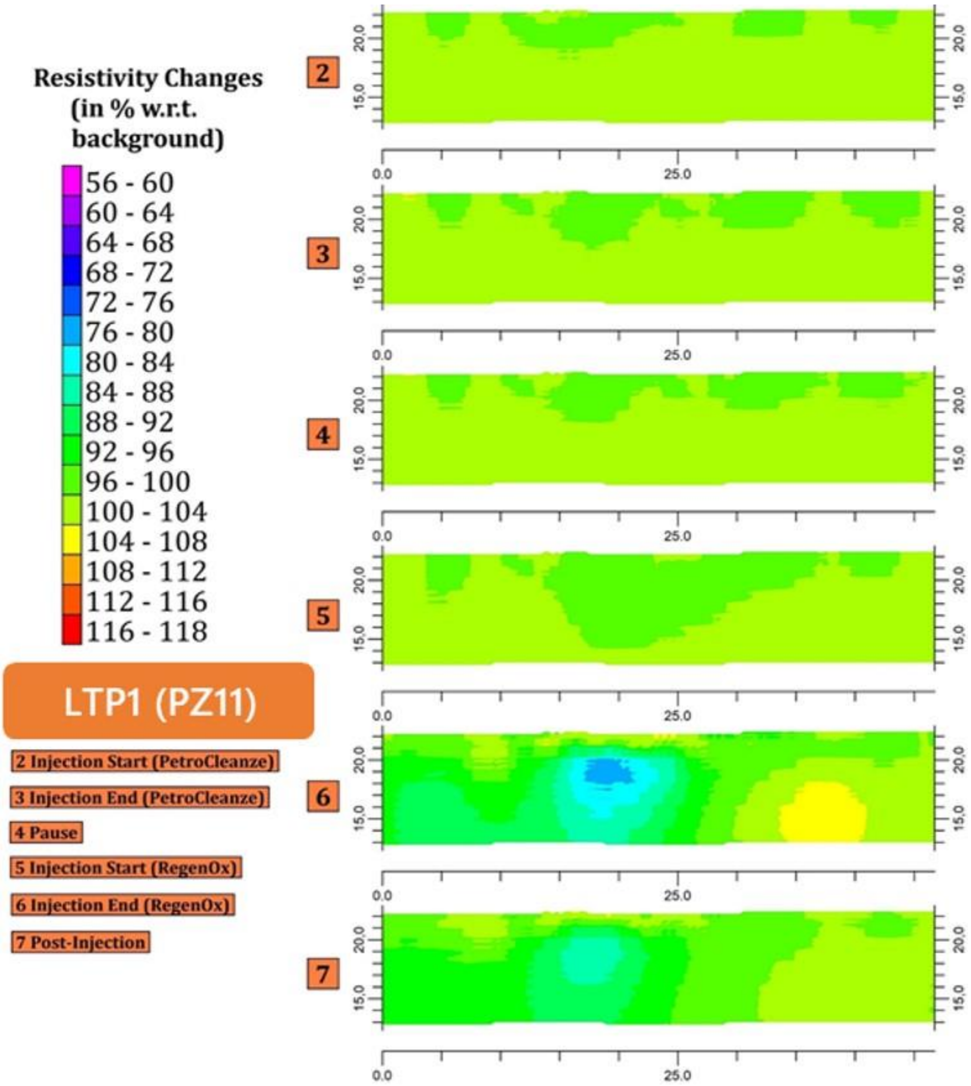


Figure 48. ERT section realized in corrispondence of LTP1 line.

The blue shallow band of the sections created at the LTP3 line (low permeability) displays the ascent of the second reagent along the piezometric tube (as evidenced by the photo) (Figure 49).

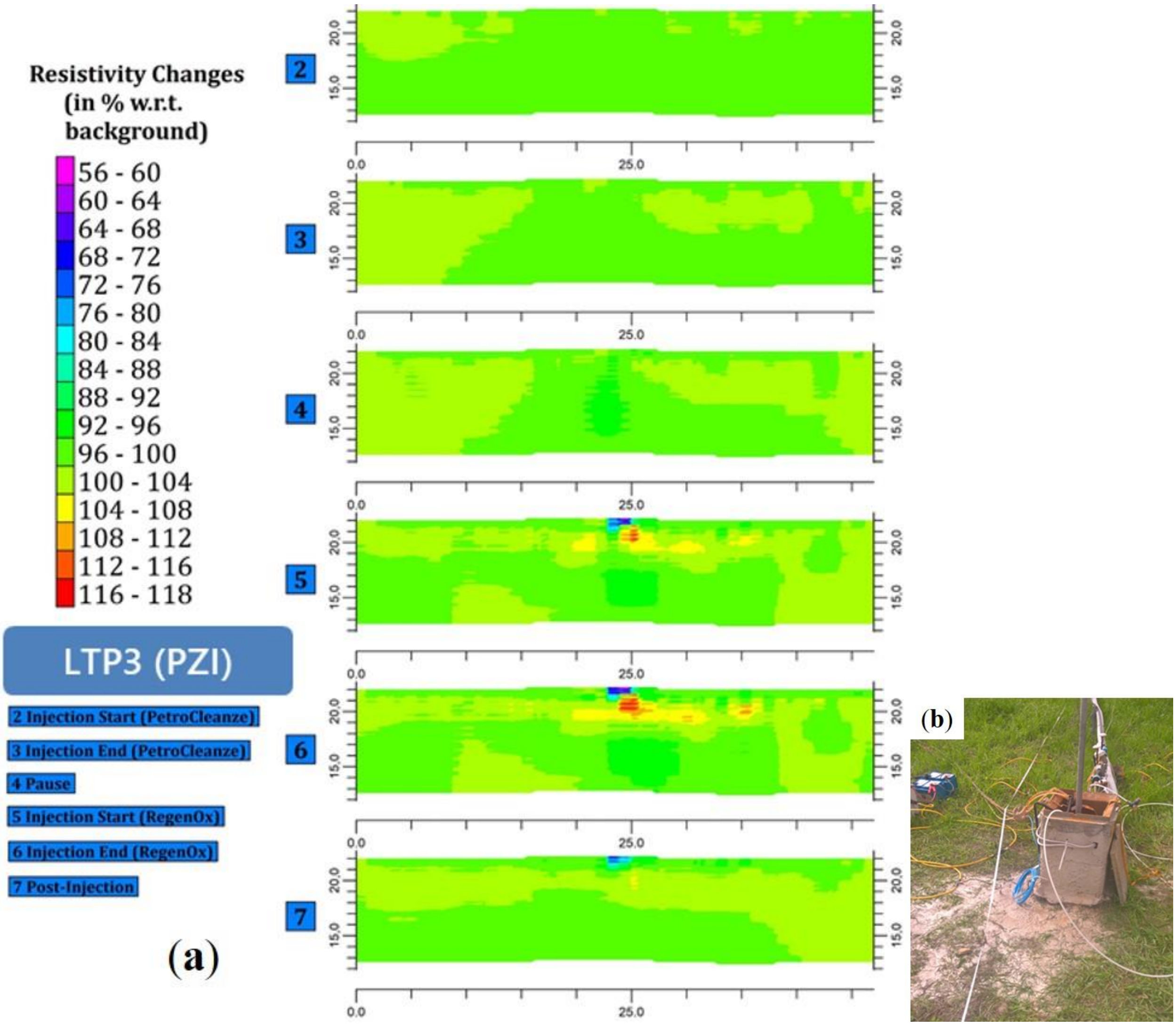


Figure 49. ERT section realized in corrispondence of LTP3 line (a), ascent of the product along the piezometric tube (b).

The red band in figure 49 represents the mobilization of the contaminants desorbed by the solid matrix. This claim is confirmed by the chemical analysis executed on the water samples collected during the implementation of the field test. Monitoring performed on water samples in the three phases of the pilot test implementation exhibits a substantial increase in post application dissolved concentrations, with a subsequent decrease following the pumping activities. The data demostrate how a considerable mass of contaminants was recovered and how the polluting load was reduced in the area of interest (Figure 50).

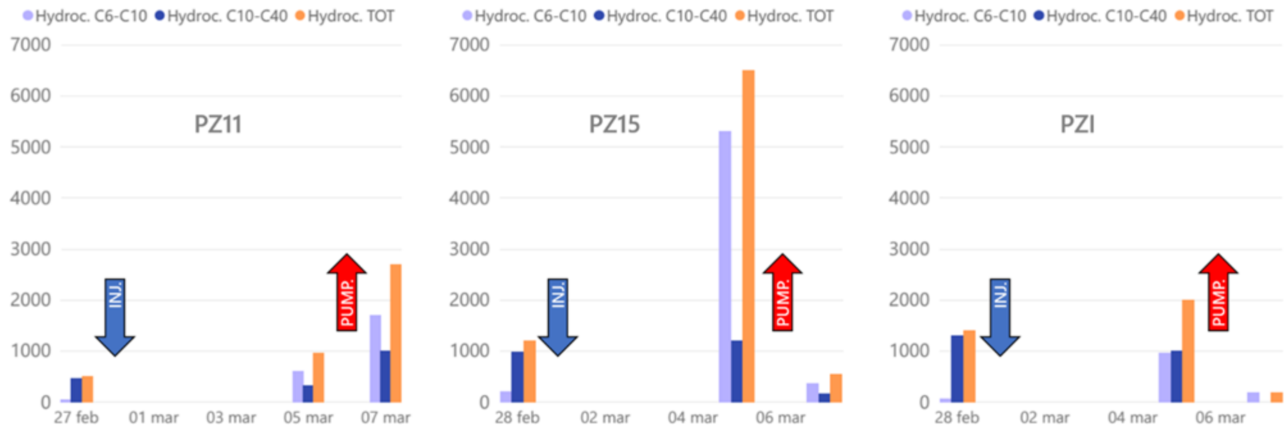


Figure 50. Analysis of water samples recovered during the three phases of the pilot test implementation.

Speciation analysis revealed an increase especially in the shorter hydrocarbons chains, probably indicating that the prevailing effect of the treatment is oxidative, with partial rupture of longer chains (Figure 51).

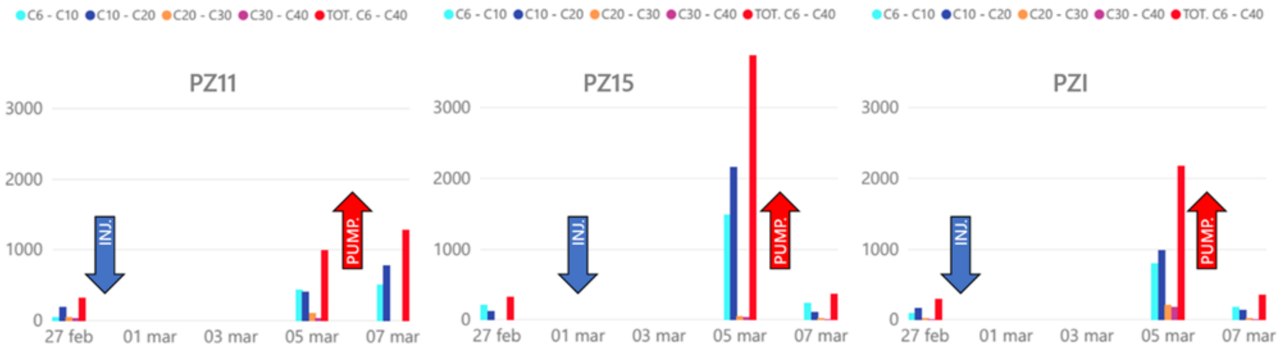


Figure 51. Mass Spectrometry and Gas Chromatography characterization of water samples recovered during the implementation of the experiment at the field scale.

The treatment carried out with the pilot test clearly shows the mobilization of the petroleum product which constitutes the secondary contamination source. The results obtained at the PZ11 reveal the occurrence of desorption and oxidation processes even after pumping activities. This evidence provides valuable information on site-specific reaction times and will optimize the full scale intervention configuration.

The low flow velocity of the groundwater and the presence of the hydraulic barrier do not involve problems concerning the possible migration of mobilized contaminants. The monitoring data obtained during and after the test activities showed that a significant mass of contaminants was recovered (significantly increasing the efficiency of the system present on the site) and highlighted a reduction of the pollutant mass in the area of interest. In addition to the groundwater monitoring activities, geophysical tests were performed during the pilot test. They provided interesting information about the distribution of the reagents in the saturated subsoil, furnishing an estimation of the injection radius for each reagent. ERT measurements represent a tool for intervention optimizing and performance monitoring. The case study is considered of interest as it illustrates an example of how it is possible to optimize the removal of LNAPL contaminants when they are substantially no recoverable by conventional technologies.

3.5.2 The Railway Station of Bologna

At the Bologna railway station, the remediation strategy consider the specificity of the contaminated site, that can be summarized as follows:

1) A relatively large area is affected by low concentration of contaminants;
2) Small masses of chlorinated solvents to be treated;
3) The presence of a thin and slow groundwater circulation in the shallow aquifer;
4) The presence of channelized coarse-grained sediments that can act as drains for fluids to be injected into the aquifers.

The technological approaches suitable to face a situation of widespread contamination with the presence of well-identified higher contamination spots were considered. The potentially applicable technologies fall under the range of in situ interventions, both physical-chemical and biological. The applicability of technologies such as monitored natural attenuation (MNA) and enhanced natural attenuation ENA (Declercq et al., 2012) was experimentally verified. Experimentation (not shown here) revealed that the natural attenuation phenomena do not allow the significant reduction of the contaminants in the groundwater. However, the experiments revealed the possibility to accelerate the reductive dechlorination biological processes by addition of an electron donors (Aulenta et al., 2007). Based on these results, biological reductive dechlorination was recognized as a potential approach for the site remediation but the extremely low CAHs concentration and the consequent kinetic limitation made it unfeasible for the site.

The possibility to use a new dispersed colloidal activated carbon (Plumestop®, Regenesis) was investigated as a site-specific remediation approach (Fan et al., 2017). The micrometric carbon is marked by a proprietary surface-charge modification to enable dispersion and can be easily injected in the contaminated aquifer. It creates an in-situ adsorption zone potentially able to quickly reduce CAHs concentration. Furthermore, it raises the kinetics of the biological reduction, by locally increasing the bioavailable CAHs concentration at the carbon surface (Georgi et al., 2015). The technology was co-injected with an electron donor (HRC®, Regenesis), to provide initial biostimulation of the treatment (Wood et al., 2006). The intervention consists of creating an injection front in correspondence of some contaminated piezometers. Based on contamination evolution, the different areas for the application of PlumeStop® and the HRC® were selected. The complete multidisciplinary, multiscale, and multitemporal characterization identified the intervention areas and supported the choice of remediation technology to be deployed. The realization of a pilot test aimed to verify the feasibility of proposed remediation solution. It was designed in one of the four intervention areas to optimize the layout and to calibrate the implementation of an optimized full-scale intervention in order to check its efficiency (Figure 52).

Figure 52. Identification of pilot test and other interventions areas.

For each area, the characteristics of the aquifers to be treated and the quantities of product to be injected were identified. A multiple injection system was developed for the generation of reactive zones (Fan et al., 2017) (Figure 53).

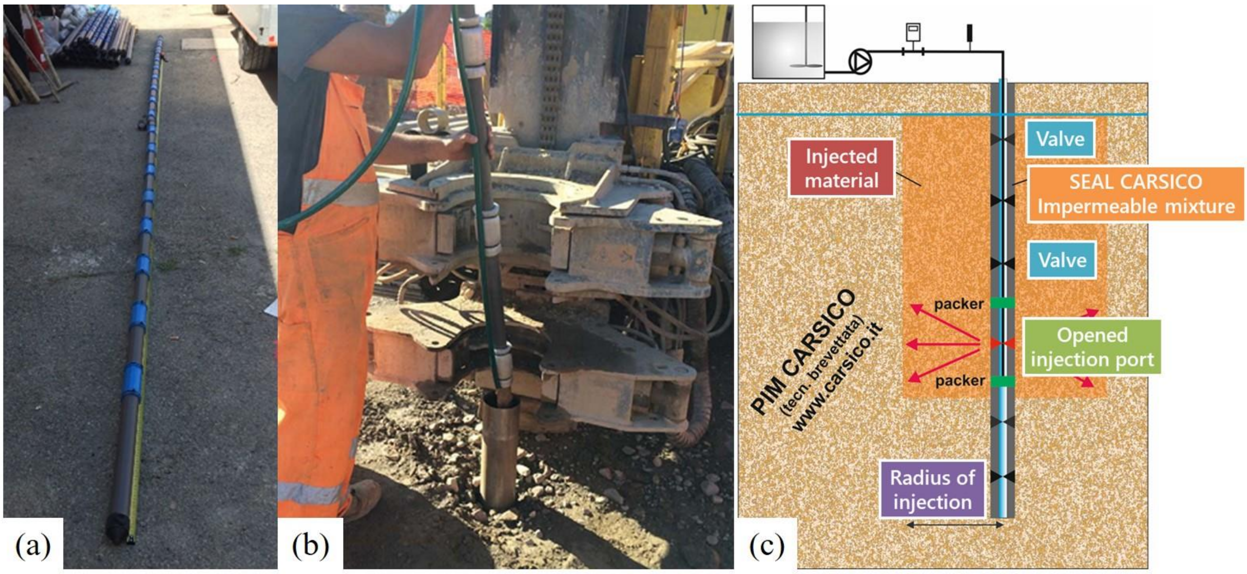


Figure 53. Multiple injection system (a, c) used to inject PlumeStop® inside piezometers (b).

Fixed stations allowed the injection of reagents at high pressure, repeated over time and at different depths along the vertical, to use a selective dosing in correspondence of the most contaminated zones. The treatment stations were customized depending on the type of contamination, the geological sequence, and permeability characteristics. Injections were performed at regular depth intervals, by starting from the deeper portions and gradually moving towards the shallower ones, to affect the more permeable layers of the intermediate aquifer ("isolated" by an impermeable septum) first, and then the less permeable shallow aquifer. High pressure injections highlighted the product's rise along fractures and preferential flow pathways. Thus, low pressure injections were performed, to facilitate a good distribution of the product into the more permeable layers. The multiple injection system was customized depending on the local characteristics. For this reason, the pilot test area was characterized in detail.

During the pilot testing some investigations were realized, to evaluate the effective distribution of the product within the two aquifers affected by injection. After the PlumeStop® injection activities, some surveys were executed in the pilot test area using direct push (Geoprobe) penetrometers (Hunkeler, 2016). These investigations aimed to check visually the sediment color after injection and collect soil samples for various analyses and tests. A total of 7 penetrometric surveys were performed to investigate the subsurface to a depth of 10 m. The sediments subjected to a treatment with PlumeStop® undergoes a slight color variation, due to the covering of soil particles with activated carbon. The visual comparison showed a good distribution of the product, a homogeneous coating of soil particles, and evidence perceptible up to 3 meters away from the injection point. The most permeable aquifer portions (9 - 9,5 m from ground level) have a more evident change in color, probably due to a greater quantity of product that was able to permeate this zone. During the monitoring activity, a passive groundwater sampling system was installed in some piezometers intercepting the intermediate aquifer. The Snap Samplers® (ProHydro, Inc.) minimize the impact of sampling process on groundwater chemistry (Britt et al., 2010). Groundwater samples were collected using this method after PlumeStop™ injection. The vials demonstrated a good distribution of the amendment in the intermediate aquifer (Figure 54).

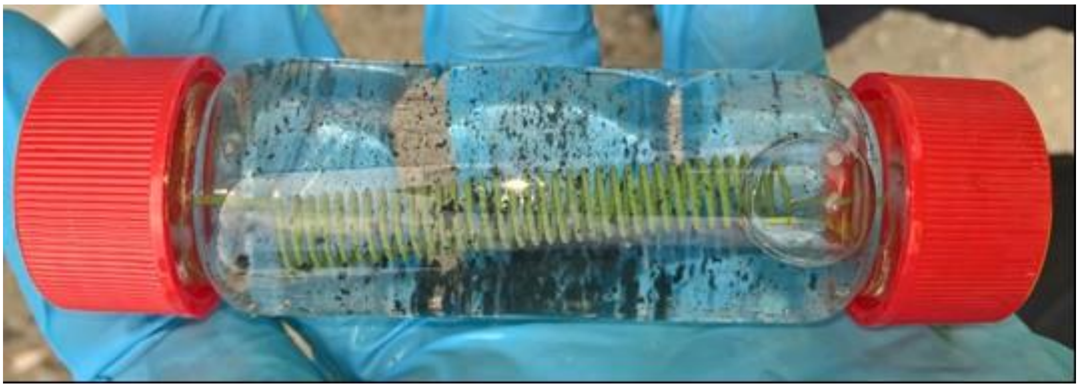


Figure 54. Evidence of the PlumeStop® distribution inside the intermediate aquifer.

Among the monitoring activities, a specific role was played by time-lapse geophysical investigations. The use of repeated geophysical measurements to highlight changes in the system state is state-of-the-art for several hydrological applications (Cassiani et al., 2006; Deiana et al., 2008; Perri et al., 2012; Haaken et al., 2017) but it is of relatively scarce use at contaminated sites, particularly during remediation activities. These methods can provide nevertheless potentially critical information, especially in terms of where and how in situ remediation actions affect different portion of the subsurface, as an effect of subsoil hydraulic heterogeneity (Vereecken et al., 2006; Ciampi et al., 2019$_b$). In fact, the physical variable of interest, i.e., electrical resistivity, is strongly related to state variables of key environmental interest (Lesmes and Friedman, 2005). In the case considered here, the injected solutes (Plumestop® and HRC®) raise the electrical conductivity of natural groundwater, as shown also by laboratory tests (not shown here). Thus, it is relatively easy to track the injected plumes by using time-lapse ERT. Figure 55 shows the results of a preliminary Plumestop™ injection and monitored using an ERT line corresponding to the direction of line L1 (see Fig. 29a) but slightly shifted to the North. Note how the low electrical resistivity manifests itself, because of Plumestop® injection, in correspondence of the sandy bodies also identified in Figure 30. The resistivity changes are not symmetrical with respect to the injection point (blue arrow in Figure 55) because of the strong heterogeneity of the shallow aquifer. The red zones in Figure 55 indicate no resistivity changes: these zones mainly correspond to aquiclude 1, where the product could not penetrate because of the lower permeability of this formation.

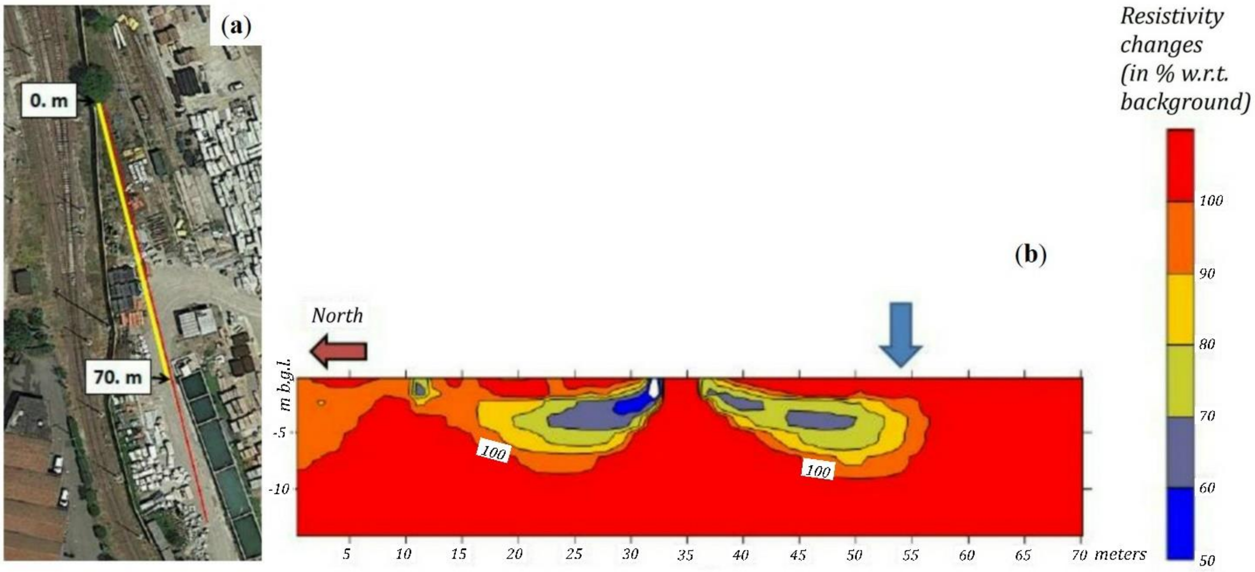


Figure 55. Trace of the ERT line (a) and section illustrating the resistivity changes (in % w.r.t. background) caused by Plumestop® injection (b). The injection point corresponds to the blue vertical arrow (Ciampi et al., 2019$_b$).

The geophysical prospecting was able to detect the resistivity changes, following reagent injection. Figure 55 highlights the distribution of the product in the shallow aquifer and the strong influence of geological heterogeneity on Plumestop® diffusion. These evidences furnished relevant informations about the capacity of reagent distribution in the site specific geological configuration. The pilot test had to be representative of the process at full scale. Its implementation provided useful information about the process efficiency and the actual extent of treatment, which varied depending on the site's subsurface characteristics. Analytical monitoring and integration of geophysical data during pilot test implementation facilitated the assessment of the remediation technology performance and the evaluation of possible modifications and integrations of the intervention strategy (the configuration of injection points and quantity of product to be injected).

Based on literature, uncertainties reside in how subsurface heterogeneity may affect the design, implementation, and monitoring of this technology (Fan et al., 2017). The remedial investigation phase primarily focuses on the characterization of subsurface geology and contaminant distribution (Kueper et al., 2014). From the implementation perspective, field applications should continuously stress on adequate site characterizations for remedial design. The verification of the amendment distribution should be part of the performance monitoring (Ciampi et al., 2019$_b$). The distribution of activated carbon-based amendments is one of the key factors that determine the success of the remedy (Fan et al., 2017). The multidisciplinary geodatabase and the integrated data modeling supported the design, the sizing, and the configuration of the intervention strategy. In fact, the injection mode strongly depends on geological, hydrogeological, and operational characteristics, and particularly critical is the possible presence of preferential flow pathways. The geophysical model, obtained from the three ERT profiles, strengthened the geological model and provided the necessary high-resolution details. Electrical resistivity tomography measurements indicated that the geological site structure, the hydrogeology and the injected product may be discriminated based on altered electrical properties (Crook et al., 2008; Atekwana and Atekwana, 2010; Binley et al., 2015). The realization of the injection stations and the injection of the PlumeStop™ were made on the base of the most suitable configuration. The pilot test, appropriately coordinated through the multidisciplinary and multitemporal data management model, was checked in the implementation phase in terms of yield, through ERT, soil and groundwater sampling. Geophysical surveys and monitoring activities were realized in near real time to control the effectiveness of the intervention, in terms of capacity of product diffusion. The field test provided an impressive picture, illustrating how in situ remediation actions affected different portion of the subsurface, as an effect of subsoil hydraulic heterogeneity (Ciampi et al., 2019$_b$). The study of the pilot test provided the elements for the verification of the efficiency, for the optimization of the intervention layout, and for the design of an optimized full-scale intervention. The indications obtained during the operations of pilot test conduction optimized the configuration of the intervention to be realized in full scale.

3.5.3 The Industrial Plant

At the industrial site, hydrogeochemical modeling and contamination evolution highlighted the presence of active secondary sources in the low permeability layers (Petrangeli et al., 2016, Pierro et al., 2017). Microcosm tests (conducted both in natural conditions and in addition to electrons) showed the possibility of stimulating the biological reductive dechlorination processes up to ethylene (Aulenta et al., 2005). The results of the microcosm experiments provide interesting information on the natural attenuation processes in the contaminated aquifer, and on the possibility of accelerating bioremediation processes, i.e., the biological degradation reaction of the chlorinated solvents by the addition of electron donor amendments (Aulenta et al., 2008).

A groundwater circulation well (GCW) (Johnson and Simon, 2007) was designed and installed at the site to create in situ vertical groundwater circulation cells. The GCW (internal diameter of about 390 mm and external diameter of 400 mm) is at a depth of 26 m from the ground level, and has three fenestrated sections at depths of 8–12 m, 15–19 m, and 22–26 m, separated by packers (Pierro et al., 2016). The pilot test was carried out in an area characterized by the presence of numerous soil lenses with different textures and permeabilities (between 5 and 20 m below the ground level) and a clayey-silty impermeable horizon (at a depth of 26 m from the ground level), which is characterized by lateral continuity (Petrangeli et al., 2016). The GCW was equipped with a pumping system that extracted the groundwater from the filtering sections located between 22–26 m (permeable zone) and 15–19 m from the ground level (low permeability zone). The flow rate of the pump connected to the filtering section located in the permeable area (PNS1) was set to approximately 2 m^3h^{-1}, while the flow rate of the pump which recalled the water from the low permeability part of the aquifer (PNS2) was adjusted to around 0,35 m^3h^{-1} (Pierro et al., 2016). The extracted water was re-introduced through the upper filtering section between 8 and 12 m by using a third pump, after passing through an external treatment unit (Petrangeli et al., 2016).

The installed GCW operated in the "standard flow" configuration, (groundwater is recirculated from top to bottom), generating, in this specific case, two overlapping ellipsoidal recirculation cells (Pierro et al., 2017):

1) A first circulation zone between the lower fenestration (22–26 m from ground level—suction) and the upper one (8–12 m from ground level—re-introduction);
2) A second and smaller circulation zone between the middle fenestration (15–19 m from ground level—suction) and the upper one (8–12 m from ground level—re-introduction).

Figure 56 shows the configuration of the recirculation system in the specific lithostratigraphic situation.

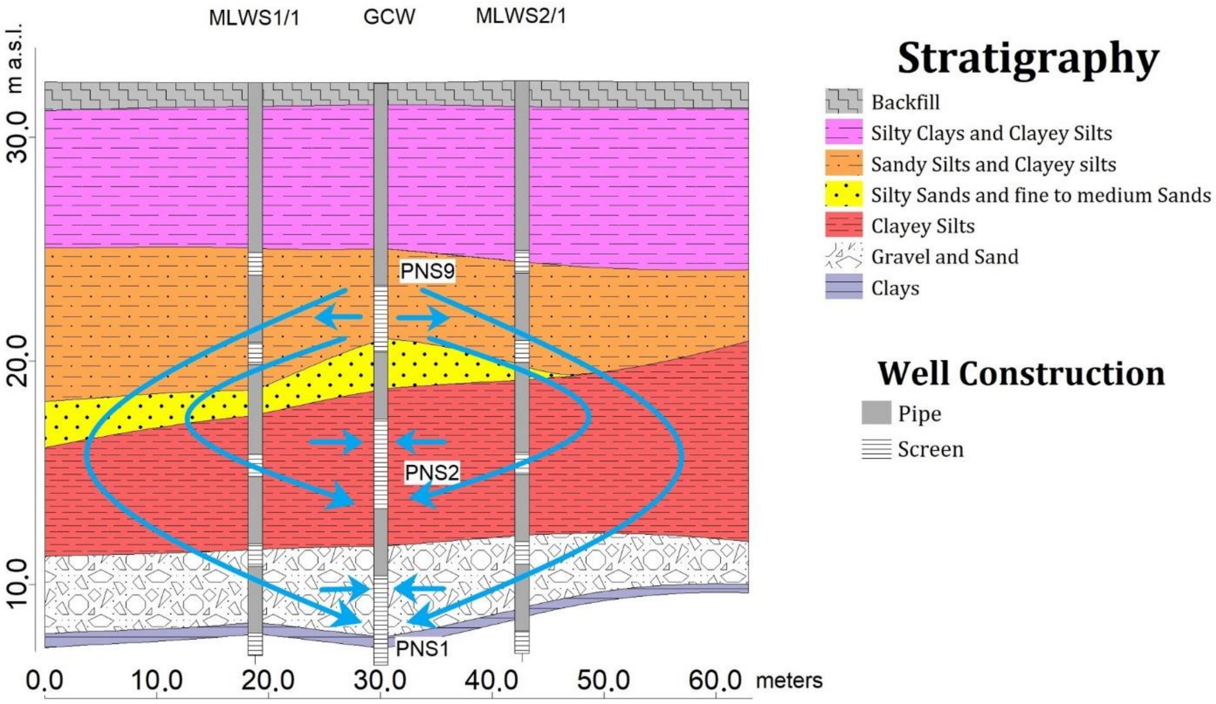


Figure 56. Pilot plant configuration (Ciampi et al., 2019_a).

The water coming from the pumping system passes through an external "treatment" module (Petrangeli et al., 2016) before being re-introduced, to stimulate in situ biological reductive dechlorination processes and to significantly reduce the chlorinated solvent concentration present in the pumped groundwater. The external treatment unit consists of:

1) A sand filter for the removal of suspended solids in the groundwater stream pumped before their passage through the successive stages of the treatment;

2) A reactor containing poly-3-hydroxybutyrate (PHB) for the continuous production of electron donors (Aulenta et al., 2008) dissolved in the recirculated water stream;
3) A reactor containing zero-valent iron. Zero-valent iron (ZVI/Fe) is a well-known reactive material widely used to perform the abiotic reductive dechlorination of chlorinated solvents (Dries et al., 2001);
4) Relaunch tank, where the treated water is collected and re-injected into the most superficial part of the aquifer (8–12 m from the ground level), thus closing the circulation circuit, and generating the circulation cells described above.

The use of this technology has underlined the potential of continuously removing the chlorinated solvents mobilized by the recirculation of water, and above all, through the zones with low permeability—the site of the residual source of contamination (Petrangeli et al., 2016). This allows the re-introduction of groundwater with a concentration of solvents significantly lower than the pumped ones (Pierro et al., 2017). To visualize the pilot test results, the cis-dichloroethene (cis-DCE) and VC trends in the extracted water have been reported. The data analysis showed how the concentration of chlorinated solvents in the groundwater extracted by the low permeability layer was considerably higher than that measured at the PNS1 monitoring point.

The concentrations of VC and cis-DCE did not exceed 200 μg L−1 in the water pumped from the transmissive portion, while the concentrations of the chlorinated substances detected in the water extracted by the low permeability layer reached tens of thousands of μg L−1 (about 20,000 and 6000 μg L−1 for cis-DCE and VC, respectively) (Pierro et al., 2016). This evidence obviously confirms how the low permeability horizons represent the areas where the contaminants are mostly adsorbed and/or trapped as a residual phase (Petrangeli et al., 2016) (Figure 57).

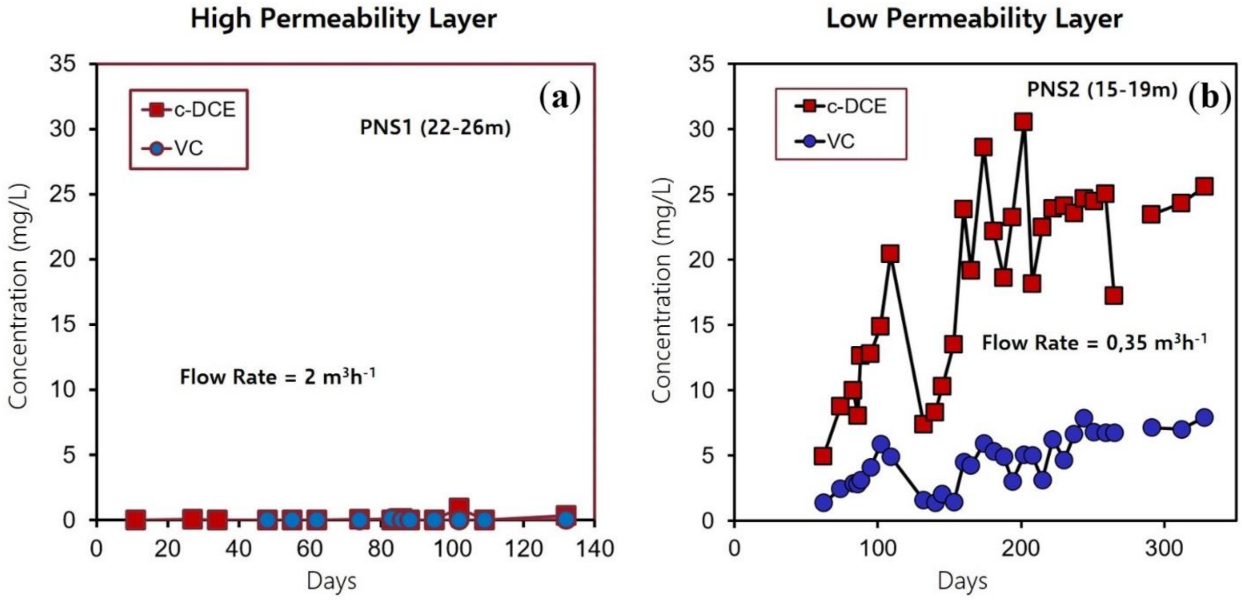


Figure 57. Trend of VC and cis-DCE concentrations in groundwater extracted from the permeable area (PNS1) (a) and the low permeability area (PNS2) (b) monitoring points (Pierro et al., 2016).

It is noteworthy to underline how the realized recirculation system allows both areas to pump water from the sections with permeability, which is certainly prohibitive for traditional pumping systems, and to mobilize very high quantities of contaminated substances (Pierro et al., 2016). The designed and installed pilot test verified the increasing mobilization of the contaminants and their removal, as well as the effective distribution of electron donors in the groundwater (Aulenta et al., 2008). The GCW, unlike traditional injection/pumping systems, allowed the extraction of water from the very low permeability layers by mobilizing the contaminants (residual DNAPL) trapped/adsorbed in these areas (Petrangeli et al., 2016).

3.6 Full-Scale Intervention

Considering the experimental characterization approaches, the assemblage and the integration of data from different sources proved to be an indispensable tool in the characterization and construction of thematic and numeric models, evaluation of intervention techniques, identification of suitable sites to perform the pilot testing, realization of tests, control and evaluation of results to calibrate the design and implementation of full-scale interventions. The 3D geodatabase represents an integrated system able to manage and to release data during the different remediation phases, supporting the selection, the location and the configuration of the intervention in full-scale.

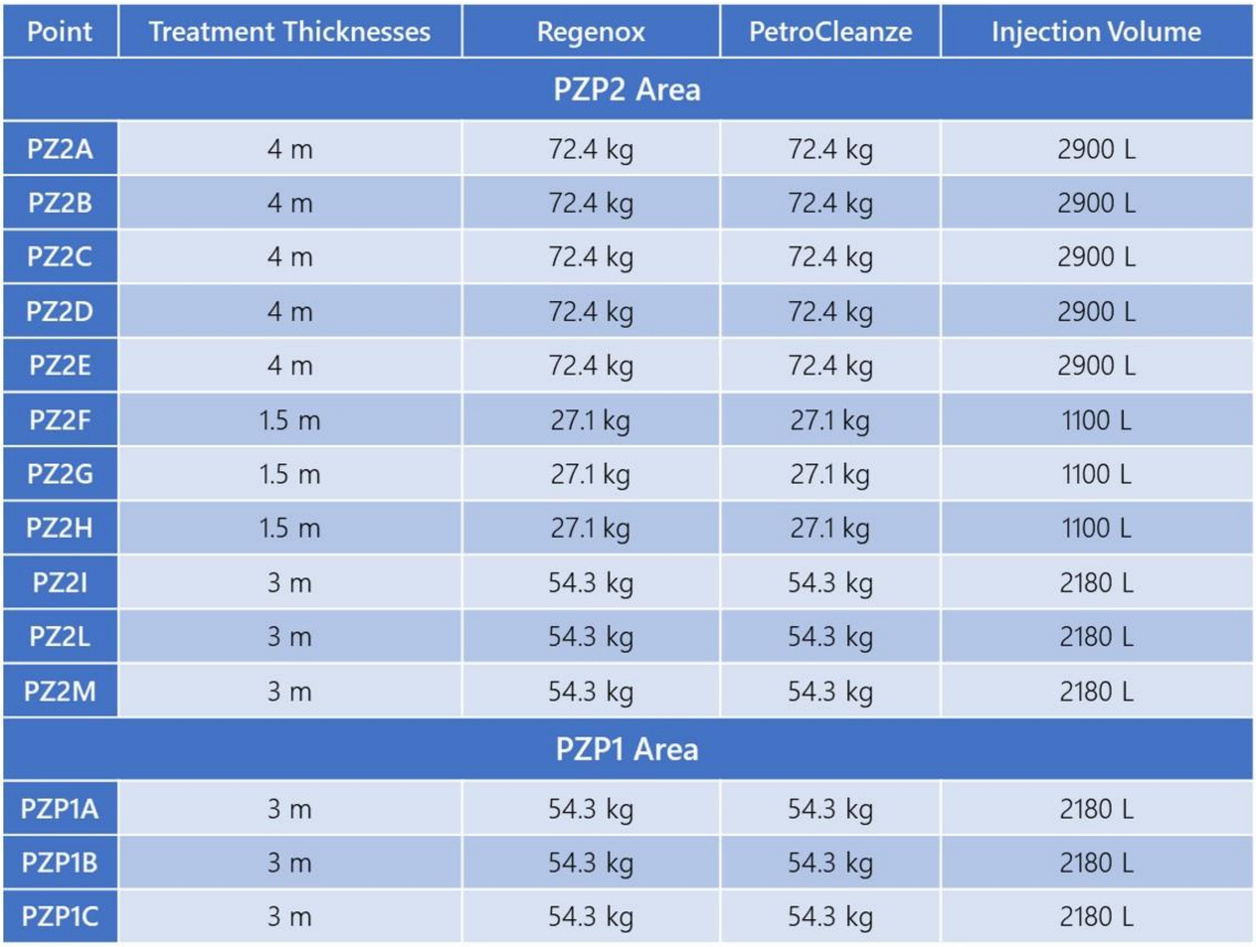
3.6.1 Decimomannu

The treatment carried out with the pilot test at the Decimomannu military base clearly showed the mobilization of the petroleum product which constitutes the secondary contamination source. The experience gained with the pilot test supported the configuration and the design of interventions in full scale, in terms of injection point number and quantities of products to be used. Pilot testing was properly coordinated through the multidisciplinary and multitemporal data management model and controlled in the execution phase in terms of yield. The results obtained during the experimentation, from the laboratory to the field pilot test, support a definitive design choice for the full-scale intervention. Experimentation at the field scale aims at obtaining information and indications for the purpose of optimizing the selected strategy on a full scale. The identified intervention technique consists in inducing the mobilization of the residual phase through the introduction of specific reagents in correspondence of wells made ad hoc for the intervention in full-scale. The subsequent forwarding to the existing groundwater treatment plant follows the pumping of water (in which the mobilization of the residual phase was provoked). The possibility of using ad hoc injection wells (with specific fenestrations for injections) adapts their construction on the basis of field evidence. This ensures more effective recovery of desorbed contaminants and guarantees efficiency in terms of quality.

The reconstruction of the evolution of the qualitative state of water over time clearly highlighted the persistence of exceedances of CSCs, only in the south-east sector of the storage tank area (near to the hydraulic barrier). The LIF-UVOST surveys delimited the potential presence of a residual fraction in the central portion of the same sector and in the area close to the hydraulic barrier. The complete multitemporal, multidisciplinary and integrated characterization supported the localization of the interventions to be performed at full scale and identified the subsurface thicknesses that must be affected by the treatment. The remediation strategy involves the implementation of an active intervention to mobilize the potential residual hydrocarbon fraction present within the site in well-defined positions. Fourteen points were identified for the injection of reagents. They are located around the PZP1 and in the area that extends around the PZP2, for a length of about 100 m, upstream of the hydraulic barrier (Figure 58).

Figure 58. Location of injection points for the full-scale intervention.

The spacing of 10 m between the different injection points present in the PZP2 area was established in order to ensure the diffusion of reagents along the intervention band parallel to the hydraulic barrier. The distance between the different injection points takes into account the results deriving from the ERT surveys, performed in conjunction with the realization of the test at the field scale. The configuration of intervention and the treatment thicknesses are strongly affected by the areas interested by residual contamination, which were identified with a high resolution of characterization, through the LIF surveys. The hypotheses on the quantities of products to be used for each single point are shown below (Figure 59).



Point	Treatment Thicknesses	Regenox	PetroCleanze	Injection Volume
PZP2 Area				
PZ2A	4 m	72.4 kg	72.4 kg	2900 L
PZ2B	4 m	72.4 kg	72.4 kg	2900 L
PZ2C	4 m	72.4 kg	72.4 kg	2900 L
PZ2D	4 m	72.4 kg	72.4 kg	2900 L
PZ2E	4 m	72.4 kg	72.4 kg	2900 L
PZ2F	1.5 m	27.1 kg	27.1 kg	1100 L
PZ2G	1.5 m	27.1 kg	27.1 kg	1100 L
PZ2H	1.5 m	27.1 kg	27.1 kg	1100 L
PZ2I	3 m	54.3 kg	54.3 kg	2180 L
PZ2L	3 m	54.3 kg	54.3 kg	2180 L
PZ2M	3 m	54.3 kg	54.3 kg	2180 L
PZP1 Area				
PZP1A	3 m	54.3 kg	54.3 kg	2180 L
PZP1B	3 m	54.3 kg	54.3 kg	2180 L
PZP1C	3 m	54.3 kg	54.3 kg	2180 L

Figure 59. Quantity of products to be injected in the two areas identified for full-scale intervention.

3.6.2 Bologna

At the Bologna railway station, the results obtained during the experimentation supported a definitive design choice for the full-scale intervention, determining the remediation of the entire identified contamination areas, the achievement of the objectives, and the project closure. Full-scale results provide information on the long-term trend of the groundwater treatment onsite. This thesis illustrates the remediation measures adopted and the results of post-treatment monitoring for a period of 2 years. The results that led to the project closure derive from the integration of multidisciplinary data, using a multiscale approach. This research represents the first completed example in European territory for the remediation of an aquifer contaminated with chlorinated solvents by a combination of adsorption and biodegradation. The following graphs illustrate the results of post-treatment monitoring in some piezometers installed in the 4 intervention areas, for a period of 2 years. The first series of graphs refers to the Pilot Test area. The graphs show a reduction in chlorinated solvents detected after full scale intervention in shallow aquifer below the threshold limits (CSC) established by Italian legislation (Figure 60).

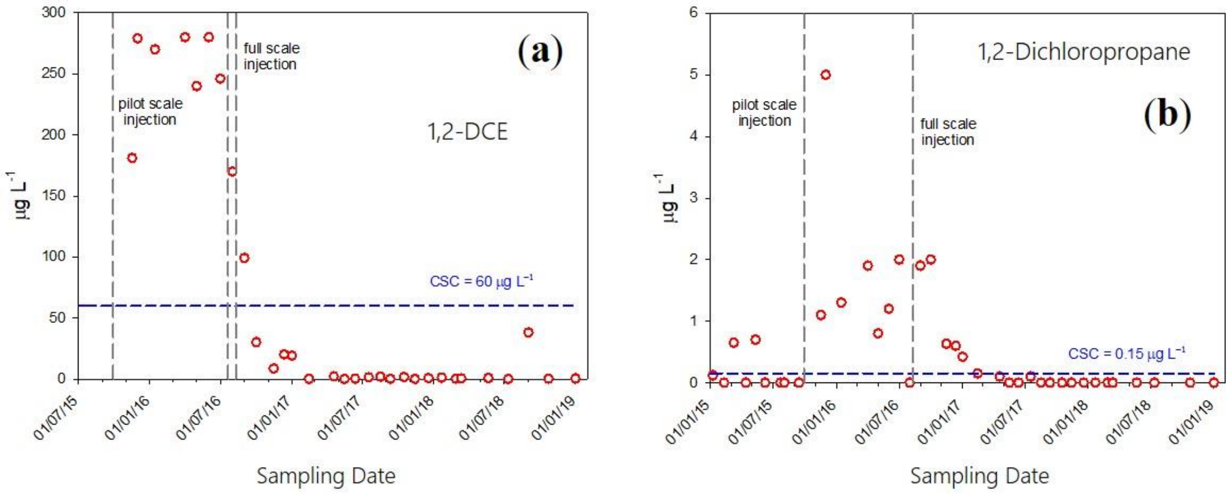


Figure 60. Concentrations of 1,2-DCE (a) and 1,2-Dichloropropane (b) detected in a piezometer installed in the pilot test area (Ciampi et al., 2019b).

The tendencies of the CAH concentrations revealed a reduction to non-detectable level within only few weeks from the application. The evolution of the concentrations of chlorinated solvents measured in some piezometers that intercept the intermediate aquifer in the intervention areas 2 and 3 (see Figure 52 for the identification of intervention areas) are shown below (Figure 61).

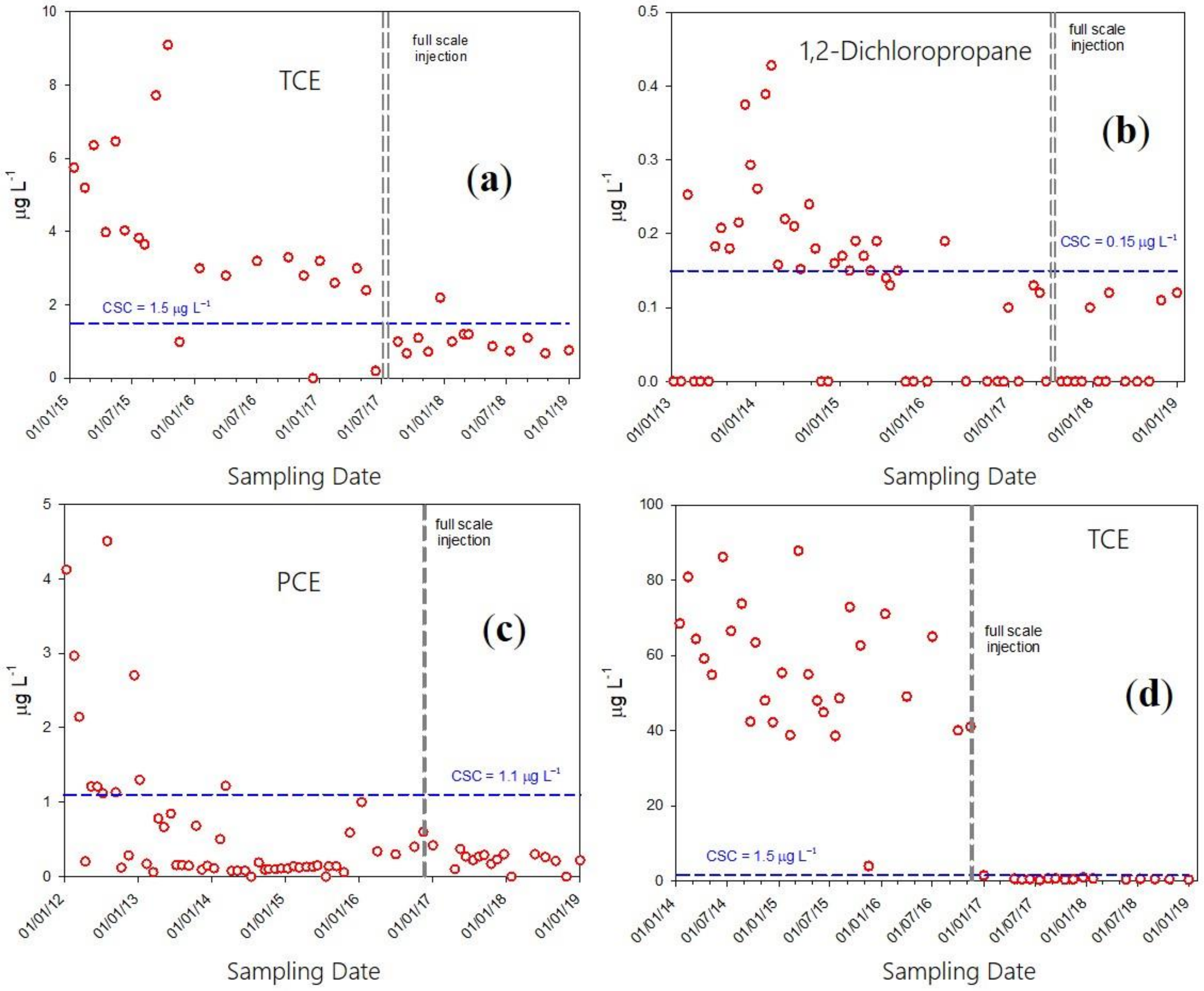


Figure 61. Concentration trends of chlorinated solvents measured in the intervention area 2 (a, b) and 3 (c, d) (Ciampi et al., 2019$_b$).

The post-intervention scenario shows a clear improvement in the status of water contamination. The concentrations detected across the piezometric network after the full-scale intervention are clearly below the remediation objectives. The parent compounds (PCE and TCE) and daughter compound DCE (Aulenta et al., 2005; Aulenta et al., 2007) exhibited reductions of one order of magnitude within the first month. With regards to the concentration detected in the shallow aquifer in the last area of intervention (area 4-see Figure 52), a sequential increase of DCE and vinyl chloride has been observed in subsequent monitoring data (Figure 62).

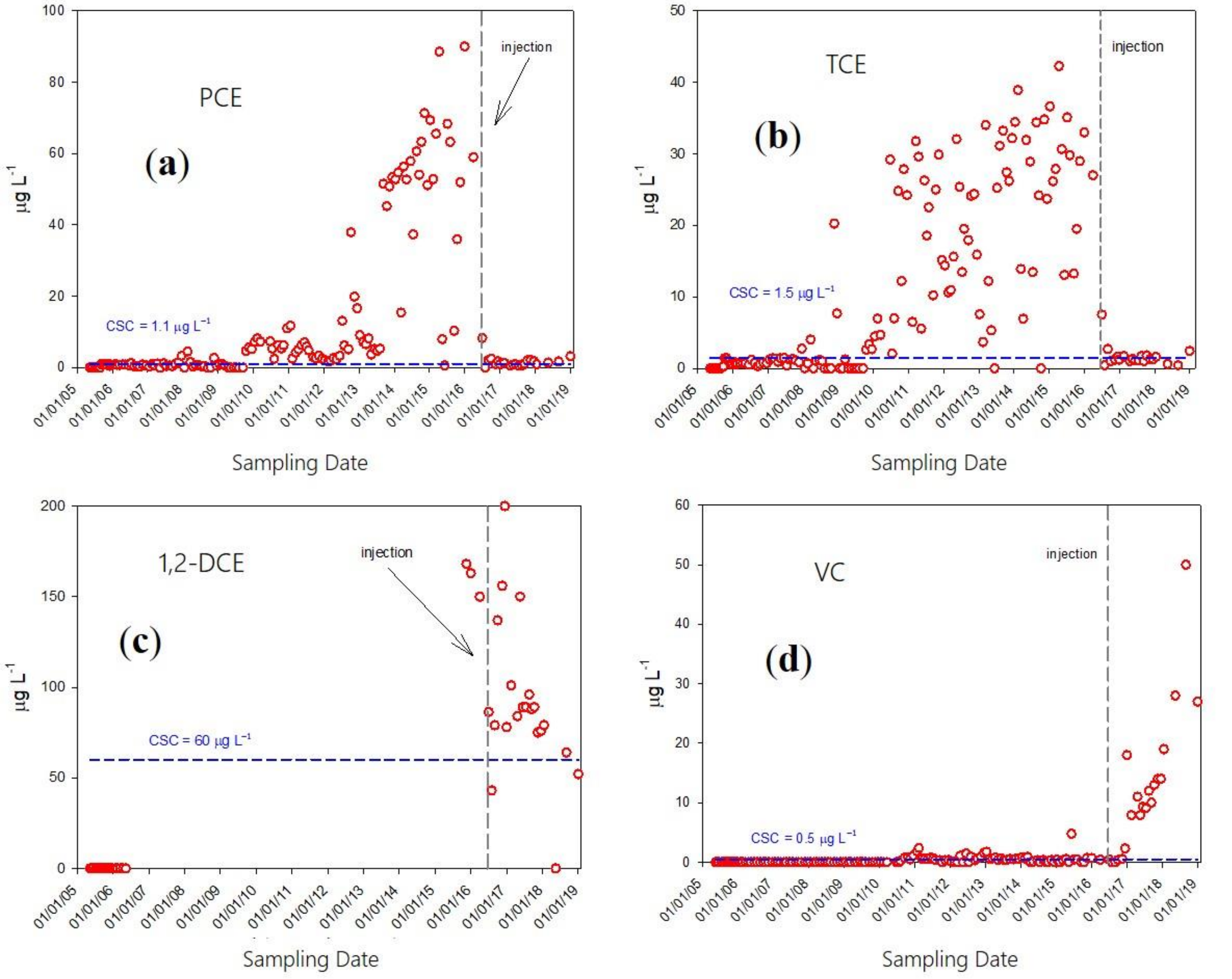


Figure 62. CAHs concentrations detected in the shallow aquifers in the last intervention area (a, b, c, d) (Ciampi et al., 2019$_b$).

The last intervention area is located upstream of the railway station from a hydrogeological point of view. The increment of PCE and TCE concentrations in the post-excavation phases testifies the entry of chlorinated solvents from areas outside the site. The injection of reagents reduced the concentration of compounds with a higher number of chlorine atoms. The increase of DCE and VC after the injection indicates that solvent degradation is proceeding without limitation despite the significant reduction of parent compounds in aqueous phase (Aulenta et al., 2005; Aulenta et al., 2007). Under anaerobic conditions, an accumulation of cis-DCE or VC is often observed at CAH contaminated sites (Tiehm and Schmidt, 2011). The hydrogen atoms replace the chlorine atoms one after the other, resulting in the typical dechlorination sequence from PCE, via TCE, cis-DCE and VC down to ethane.

The rate of reductive dechlorination decreases with the decreasing number of chloroatoms, causing an accumulation of cis-DCE or VC (Tiehm and Schmidt, 2011). Compounds with a higher degree of chlorination, like PCE and TCE, have been detected at lower concentrations, presenting an intense biological dechlorizing activity after the injections. The results of full-scale intervention provide information on the long-term trend of the groundwater treatment onsite. The post-application image clearly indicates an improvement in the qualitative state of groundwater, which led to achieve the site-specific remediation targets. The results that led to the project closure derive from the integration of multidisciplinary data, using a multiscale approach (Bozzano et al., 2007).

3.6.3 The Industrial Site

At the contaminated industrial site, the pilot testing was properly coordinated through the multidisciplinary and multitemporal data management model and controlled in the execution phase in terms of yield. Results from the field test demonstrated the important mobilization of contaminants from the low permeability zone and the possibility of distributing electron donors to enhance in situ the natural attenuation mechanisms based on biological reductive dichlorination. The GCW allowed the extraction of water from the very low permeability layers by mobilizing the contaminants (residual DNAPL) trapped/adsorbed in these areas.

The results obtained during the experimentation supported a definitive design choice for the full-scale intervention, with the purpose of determing the remediation of the entire identified contamination source. The operational remediation project in full-scale involved the construction of three GCWs. The GCWs are positioned around the industrial warehouse, where industrial washing machines were located. The integrated 4D characterization supported the localization and configuration of the interventions from an engineering point of view. The recirculation wells are located in the area where secondary contamination source were clearly identified in corrispondence with fine grained layers. The screened section of GCWs are positioned so that recirculation influences portions of low permeability that are not affected by traditional extraction systems. The GCW can also be operated in the "reverse flow" configuration (groundwater is recirculated from the bottom to the top). Changing the recirculation configuration could prove beneficial, by enhancing the mobilization of pollutants from less accessible zones. The implementation of the strategy in full scale will verify the effectiveness of the adopted technology for the persistent, low permeability contaminant source zones.

4. DISCUSSION

At the military base of Decimomannu, the planning of the interventions in full scale is strongly affected by the site-specific geological and chemical-physical peculiarities. The multi-source model has undoubtedly identified the presence of residual hydrocarbon fractions below the storage tank area and close to the hydraulic barrier (Figure 63).

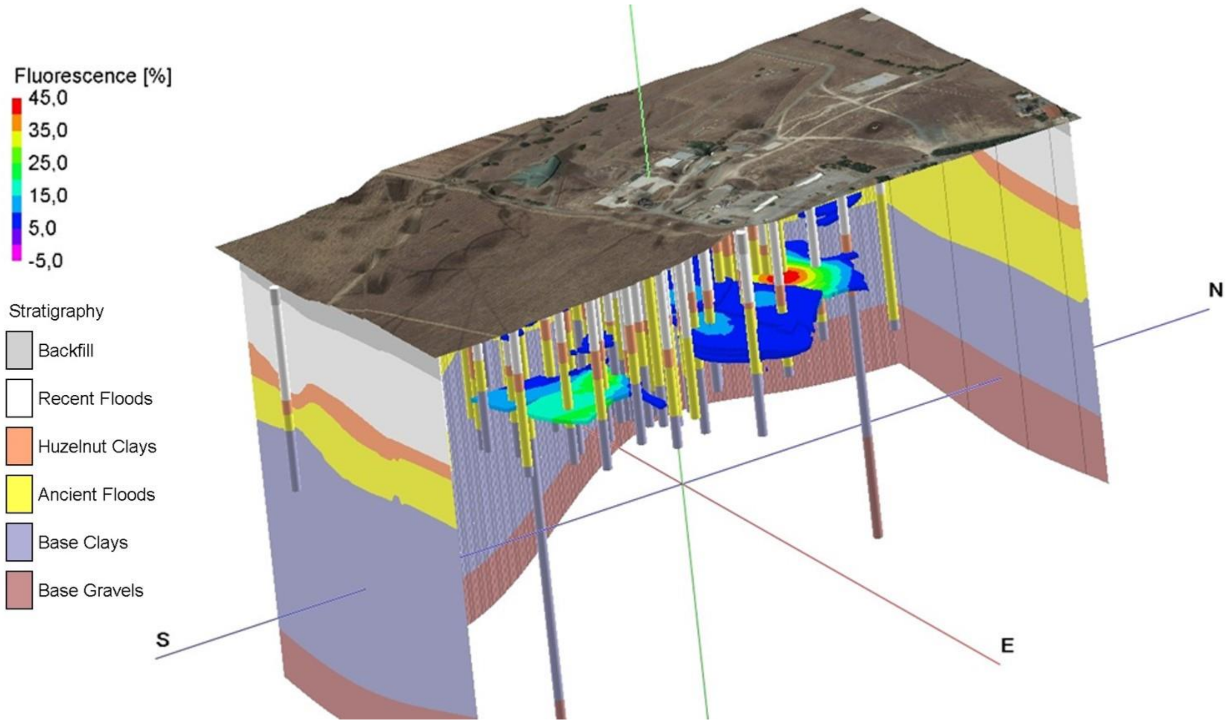


Figure 63. Multi-source model of Decimomannu military base.

Three-dimensional visualization, geospatial analysis, and integration of geo-referenced data contribute to the continuous convergence of different types of geomodelling. The hydrogeophysical model acts as the interface through which the user can access, analyze, and process geospatial data. This gives the user a rapid and intuitive way to access vast amounts of data in large and complex models (Jones et al., 2009; Harvey et al., 2017). The construction of a multidisciplinary geodatabase and the realization an integrated model face the simultaneous integration of the information relating to the hydrogeochemical sphere in all its dimensions (Ciampi et al., 2019$_a$). This ensures the interchangeability of information in the multidisciplinary nature of the elements involved. Their interaction and the high-resolution characterization of environmental variability capture the hydrogeological uniqueness, the geophysical peculiarity, and the contamination dynamics (Harris et al., 2004; Suthersan et al., 2016). The fusion of multi-modality data and the combination of different survey technique is relatively straightforward. ''Stitching'' data sets can form composite models (Chiabrando et al., 2019). In many cases we may be armed with data from multiple modalities, measuring different properties, in different configurations, with different depths of investigation. Rather than treating each data set independently, we should endeavor to formulate a single coherent image (model) of the subsurface (Pollard et al, 2004). Coupled hydrogeophysical approaches go some way toward achieving this goal, but no generalized method currently exists, and more work is needed to provide practical solutions that do not depend on substantial a priori knowledge of the superface (Binley et al., 2015). This research proposes a refinement method for 3D modeling with multi-source data integration. By stepwise refinement on multiple data, the approach increases the accuracy of 3D models gradually and effectively. The applied method clearly displays the effectiveness of the adopted procedure for the harmonization and the restitution of the different elements. Visualizing volume data is very important to enable intuitive understanding of 3D structures, making them easier to analyze and share (Jones et al., 2009). The hydrogeophysical model shows data-driven elements and multi-layer objects (Binley et al., 2015). The multitemporal and multidisciplinary geodatabase enabled integrated management, representation and analysis of different data types (geological, hydrological, chemical, and physical) to reach a high-resolution characterization of underground geological heterogeneities, aquifers, preferential flow paths, and contaminated areas (Ciampi et al., 2019$_a$). The 3D stratigraphic model depicts the hydrogeological setting (Abbaspour et al., 2000; Jones et al., 2009; Hunkeler, 2016). The geophysical model, obtained from the ERT profiles, strengthens the geological model (Crook et al., 2008). The contamination status evolution shows a decreasing trend of hydrocarbons concentrations in groundwater. Monitoring data and GC-MS analysis reveal the presence of contaminants in the residual phase, highlighting the aging of the product which constituted the primary fuel spills (Lekmine et al., 2017; Fedotov et al., 2019; Teramoto et al., 2019). The progressive aging of the contamination sources corresponds to an impoverishment of the more mobile and degradable fractions (Totsche et al., 2003) with the accumulation of fractions characterized by higher molecular weight (Lekmine et al., 2017). The mass of residual fraction absorbed on solid matrix is not capable of releasing water-soluble components. Residual fractions are characterized by limited mobility and are therefore difficult to remove by using pumping wells. The interpretation of contaminant behavior and dynamic has strong implications for the reliability of the CSM. The accurate characterization of the residual phase's real characteristics affect the selection and adoption of an effective remediation strategy. The low hydrocarbon concentrations measured in groundwater in the last year demonstrate the inefficiency of the hydraulic barrier installed in the site for the removal of this kind of contaminants. Integrative investigations, which were realized through LIF surveys, track the secondary sources of pollution with high spatial resolution and reveal that contamination distribution is heavily affected by subsurface heterogeneity and hydraulic processes. The multi-source model reveals the sequestration of contaminants and the entrapment of residual phase along the smear zone due to the water table fluctuations. The rich data set, and the data-driven models comprise, collect, and establish a connection between the environmental variables. They optimize the contribution of each aspect and support unequivocally the design of an effective and sustainable intervention. The realization of the pilot test showed a remarkable reduction of contaminat mass, which is hardly removable with traditional extraction techniques. The applied method clearly displays the effectiveness of the adopted technology for the removal of this contaminant class. The multi-source model represents the tool supporting the decision-making process and enables the design of the remediation strategy in full-scale.

The results of full-scale intervention provide information on the long-term trend of the groundwater treatment on the site of the Bologna railway station. The post-application image clearly indicates an improvement in the qualitative state of groundwater, which led to achieve the site-specific remediation targets. Previous studies underline that suspended questions remain to be answered regarding the effectiveness of activated carbon-based amendments, given the lack of both field data and evidence of biodegradation process (Fan et al., 2017). The results obtained in the last intervention area (Figure 52) clearly highlight the occurrence and the persistence of biodegradation. Plumestop™ and HRC™ combined injection into groundwater representss an innovative remediation operation, being the first of its kind, realized on a large scale, in the European territory. Intervention monitoring played a fundamental role, to validate the performance of the implemented remediation strategy. The reduction of CAH concentrations below the CSC testifies the effectiveness of the adopted remediation technology for the abatement of chlorinated solvents, through a combined action of contaminant absorption and biodegradation processes (Ciampi et al., 2019$_b$). Based on literature, additional uncertainties reside in how subsurface heterogeneity may affect the design, implementation, and monitoring of this technology (Fan et al., 2017). The remedial investigation phase primarily focuses on the characterization of subsurface geology and contaminant distribution (Kueper et al., 2014). The remediation of polluted sites cannot prescind from the integration of the geological-hydrogeological and chemical data, considering the geological-technical characteristics of the subsoil, the hydraulic properties of the aquifers, which are possible pathways of the contamination and the potential pollution of the environmental matrices (Suthersan et al., 2016). These peculiar aspects are unique site-specific elements, according to which it is possible to select a targeted intervention for remediation (Samouelian et al., 2005). Multitemporal and multidisciplinary geodatabase enabled integrated management, representation, and analysis of different data (geological, hydrogeological, hydrogeochemical, and geophysical) to reach a high-resolution characterization of underground geological heterogeneities, aquifers and preferential flow paths (Harris et al., 2004). The geological and chemical peculiarities addressed the design, the sizing, and the configuration of intervention strategy from the engeenering point of view. The multidisciplinary geodatabase and the integrated data modeling supported the planning of the interventions, playing an essential role for the design of a targeted, efficient, and economically sustainable remediation strategy. The hydrogeological uniqueness and chemical peculiarities supported the selection of a remediation technology and the identification of the application points. From the implementation perspective, field applications should continuously stress on adequate site characterizations for remedial design. The verification of the amendment distribution should be part of the performance monitoring. The distribution of activated carbon-based amendments is one of the key factors that determine the success of the remedy (Fan et al., 2017). The multidisciplinary geodatabase and the integrated data modeling supported the design, the sizing, and the configuration of the intervention strategy. In fact, the injection mode strongly depends on geological, hydrogeological, and operational characteristics, and particularly critical is the possible presence of preferential flow pathways. The geophysical model, obtained from the three ERT profiles, strengthened the geological model and provided the necessary high-resolution details. Electrical resistivity tomography measurements indicated that the geological site structure, the hydrogeology and the injected product may be discriminated based on altered electrical properties (Crook et al., 2008; Atekwana and Atekwana, 2010; Binley et al., 2015). The realization of the injection stations and the injection of the PlumeStop™ were made on the base of the most suitable configuration. The pilot test, appropriately coordinated through the multidisciplinary and multitemporal data management model, was checked in the implementation phase in terms of yield, through ERT, soil and groundwater sampling. Geophysical surveys and monitoring activities were realized in near real time to control the effectiveness of the intervention, in terms of capacity of product diffusion. The field test provided an impressive picture, illustrating how in situ remediation actions affected different portion of the subsurface, as an effect of subsoil hydraulic heterogeneity (Ciampi et al., 2019$_b$). The study of the pilot test provided the elements for the verification of the efficiency, for the optimization of the intervention layout, and for the design of an optimized full-scale intervention. The operating project provided an innovative remediation strategy for sites contaminated by chlorinated DNAPLs. The remediation strategy implied the creation of "reactive" zones capable of reducing significantly and permanently the concentration of chlorinated solvents in groundwater through the combined action of adsorption and biodegradation. The results of full-scale intervention furnished evidences about an intense biological dechlorizing activity. At present, concentrations of chlorinated solvents higher than those established by the legislation are not recorded in groundwater. This clearly demonstrates the effectiveness of the technology implemented for the reduction of chlorinated solvents. The data-driven model comprises, collects, and establishes a connection between the environmental variables, to optimize the contribution of each aspect supporting the design, implementation, and validation of the remediation techniques. The hydrogeophysical model and the thematic database act as integrated and continuously updated tools, able to manage and calibrate in progress the intervention modalities according to innovative approaches during the remediation phases, from the pilot site to the full-scale intervention. The multi-source model, the data fusion, and the integrated approach furnish a demonstration of the biodegradation processes in conjunction with contaminant adsorption for in situ subsurface remediation of chlorinated solvents with activated carbons and illustrate how geological heterogeneity affects reagent distribution.

Based on the geological and hydrogeological characteristics of the healily contaminated industrial site, a 26 m deep GCW (Johnson and Simon, 2007) was designed to obtain in situ vertical groundwater circulation cells, by drawing groundwater from two lower screened sections (PNS1 and PNS2) of a multiscreened well separated by packers, and discharging it through an upper screened section (PNS9). The pressure gradient between two hydraulically separated screen sections in the well induced a circulation flow in the aquifer (Xiang and Kabala, 1998; EPA, 1998). The groundwater moves through the treatment zone both horizontally and vertically, and consequently the low-permeable layer is constantly penetrated by the vertical flow of the GCW (Petrangeli et al., 2016). The results of the characterization identified a large source of contamination below an operative industrial warehouse. A significant mass of residual DNAPLs (Leharne, 2019) was contained in an area with complex hydrogeological settings. Residual CAHs resulted and were associated with the low permeability layers (Christ et al., 2010; Luciano et al., 2010). Clayey silts act as a persistent slow-releasing secondary contamination source kinetically controlled by slow back-diffusion mechanisms (Lapworth et al., 2018). The analysis of the data related to the pilot test emphasized how the concentration of chlorinated solvents in the water pumped from the low permeability layer was notably greater than that measured at the point corresponding to the high permeability horizon (Petrangeli et al., 2016). Although the volumetric flow rates were remarkably lower, the masses mobilized by the less permeable zone appeared almost two orders of magnitude higher than those corresponding to the most transmissive zone of the aquifer (Pierro et al., 2017). The flow dynamics induced by the GCW (Johnson and Simon, 2007), for a physical/mechanical effect, clearly favored the mobilization of the adsorbed/trapped contaminants (Harris et al., 2004; Abdel-Moghny et al., 2012) in the solid matrix. This potentially decreases the exhaustion (remediation) time of the trapped fractions in the areas with a lower permeability, i.e., the slow-release persistent secondary sources that are not influenced by the traditional pumping action (Petrangeli et al., 2016). The site-specific hydrogeological setting shows a multilayered heterogeneous aquifer, which consists of materials that vary in their water-transmitting properties laterally and vertically (from fine-to-medium sands with an intercalation of less permeable sandy silt to clayey silt layers with a permeability in the range of 10−8–10−5 m/s). In this situation, trapped DNAPL in low permeability zones acts as a continuous, persistent source for releasing contaminants into the more permeable layers by slow back-diffusion (Lapworth et al., 2018). The contamination present at the site consists of quantities of pooled or trapped DNAPL (hotspots), and various dissolved plumes are generated from the residual phase (Christ et al., 2010; Luciano et al., 2010). Site characterization surveys have also indicated that natural attenuation is already ongoing in the investigated site—the presence of 1,2-DCE and VC indicates an intense but incomplete microbial dechlorination activity, which has led to the formation of toxic compounds, such as VC (Aulenta et al., 2005). Due to the decreasing reductive dechlorination rate, under anaerobic conditions, an accumulation of cis-DCE or VC is often observed at CAH contaminated sites (Aulenta et al., 2002). The hydrogen atoms replace the chlorine atoms one after the other, resulting in the typical dichlorination sequence from PCE, via TCE, cis-DCE and VC down to ethane. The rate of reductive dichlorination decreases with the decreasing number of chloroatoms, causing an accumulation of cis-DCE or VC (Tiehm and Schmidt, 2011). Compounds with a higher degree of chlorination, like TCE, were certainly used in the past as industrial solvents, and therefore constitute the primary contaminants. They have been detected at lower concentrations, presenting an intense biological dechlorizing activity. It is a well-known fact that one of the requirements for a successful in situ bioremediation implementation for chlorinated DNAPLs is homogenous electron donor distribution (Aulenta et al., 2007). In this case, the conventional addition methods were not suitable because of the geochemistry and the hydrogeology of the site. Traditional injection approaches are often limited by the preferential migration of injected fluids through the more permeable zones (Harris et al., 2004), while distribution through less permeable and contaminated layers is usually limited. Conventional injection approaches (either continuous or pulsed) were not applicable at the investigated site, owing to complex aquifer geological characteristics. Injected fluids would preferentially migrate through easily permeable zones, and thereby prevent fluids from reaching less permeable layers where significant masses of contaminants were accumulated (Pierro et al., 2017). The use of groundwater circulation well (GCW) technology could advantageously improve the distribution of soluble electron donors by creating an effective three-dimensional circulation cell in the aquifer (Tatti et al., 2019). This three-dimensional water flow is established by installing a multiple screened well, where a packer is inserted to isolate the screen intervals hydraulically. Groundwater is extracted from one screen, and after a generic treatment, is circulated back into the aquifer through another screen, thereby creating the circulation cell (Petrangeli et al., 2016). The pressure gradient between the hydraulically separated screen sections induces a circulation flow in the aquifer, forcing water through less permeable layers that are not usually affected by conventional pumping and injection systems (Hunkeler, 2016). In fact, even though an intensive pumping is active for twelve years to avoid any contaminant spreading outside the site, dissolved CAH concentrations remain significantly high. On the other hand, the remediation technology of a groundwater circulation well (Hunkeler, 2016) allows the creation of in situ vertical groundwater circulation cells. This technology enhances the mobilization of pollutants from a less accessible, low-permeable zone, where a significant mass of contaminants is strongly retained (Pierro et al., 2017). In this regard, the traditional pump and treat approach could mostly remove contaminants from the more transmissive zones of an aquifer, but it has a negligible effect on the contaminant mass stored in low permeability media which is slowly released by back-diffusion (Lapworth et al., 2018). Moreover, coupling GCW with the continuous production of electron donors should allow the improvement of the biological reductive dechlorination inside the less permeable layer, thus, potentially reducing the remediation time (Petrangeli et al., 2016).

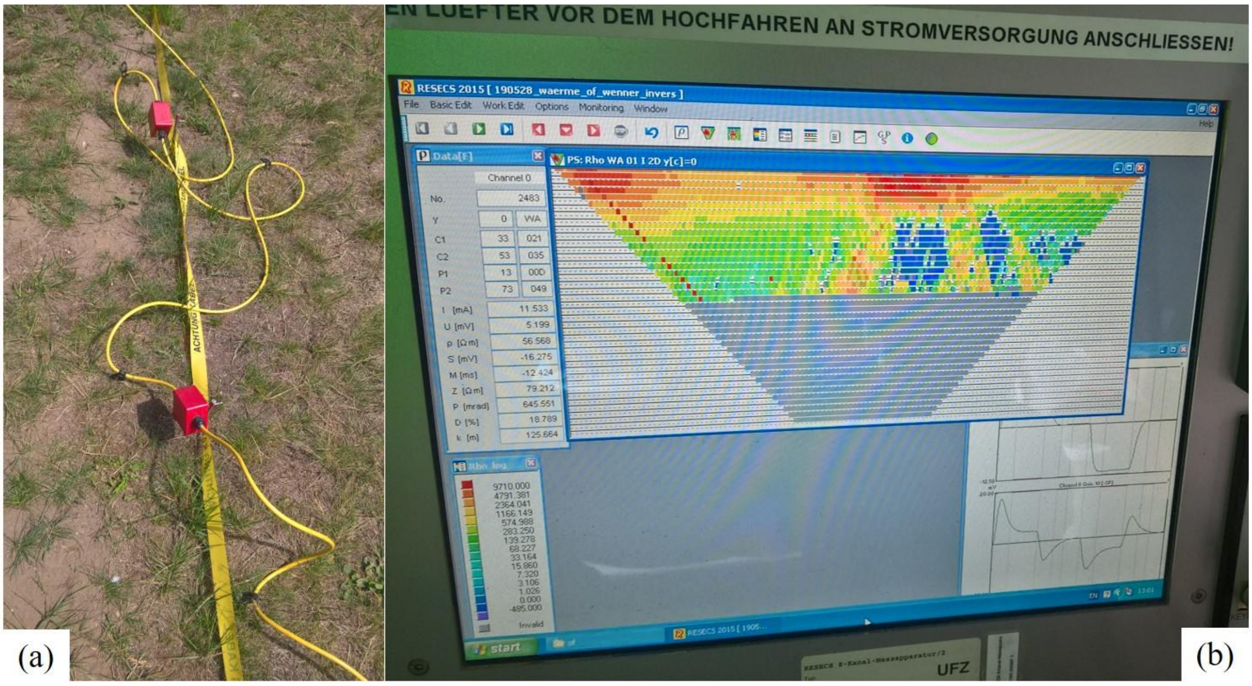
The three real cases are an exemplification of the management, processing and integrated interpretation of data. Multi-source conceptual model, high resolution characterization, monitoring, and optimization in pilot testing lead to the selection of an effective remediation strategy, based on the geological uniqueness and chemical-physical peculiarities. Original remediation projects were profoundly modified in the three sites following the implementation of the developed management platform. The integrated modeling and joint analysis of data related to different disciplines revealed the limitations of traditional remediation technologies. The thesis highlights the need for a large amount of multi-source data to build a reliable and high-resolution conceptual model, and to design effective remediation strategies with innovative technologies. The design of innovative characterization techniques and remediation strategies was made possible through the implementation of the integrated multidisciplinary dashboard. The thematic cockpit is able to manage heterogeneus data during the different phases (from the characterization to the technique inmplementation) and to bring together multidisciplinary information in an unique interface supporting unequivocally the decision-making process. Different information related to the hydrogeophysical sphere must be integrated and taken into consideration when developing a reliable remediation strategy for contaminated sites. The construction of a multidisciplinary geodatabase and the realization an integrated model face the simultaneous integration of the information relating to the hydrogeochemical sphere in all its dimensions.

4.1 The Research Period Abroad

During the last year of PhD course, I had the opportunity to work for the Department Monitoring and Exploration Technologies (MET) at the Helmholtz Centre for Environmental

Research – UFZ in the period from May 2nd, 2019 until July 5th, 2019 as part of an internship. In this framework, my activities at the UFZ were completely inserted in the contest of my PhD research. The activities carried out in the UFZ Research Center and in three experimental sites aimed to reach a high-resolution characterization of the underground geological heterogeneity, aquifer, preferential flow pathways, and transport routes. Field surveys focused on the use of direct sensing investigation and electrical resistivity tomography investigations (ERT). A detailed list of the activities carried out follows:

- Realization of two electrical resistivity tomography (ERT) prospecting lines, at the Wittstock site. The ERT investigations aimed at discriminate the geological site structure, the hydrogeology and the injection of hot water into the subsoil, based on the electrical properties of the subsoil (Figure 64);



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C2	53	035
P1	13	000
P2	73	049
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U [mV]	5.199	
ρ [Ωm]	56.568	
S [mV]	-16.275	
M [ms]	-12.424	
Z [Ωm]	79.212	
P [mrad]	645.551	
D [%]	18.789	
k [m]	125.664	

Figure 64. Geophysical prospection line realized at the Wittstock site (a) and ERT data collected in real time (b).

- Implementation of 82 vertical surveys with soil optical color screening tool (SCOST) technology at the UNESCO Pestenacker archaeological site. Direct push methods provide many alternative sampling and sensing tools for site investigation. Direct push-driven spectral colorimeter allows for direct in situ sensing of color, the reflectance response of an induced optical signal to any material. During this experience, the potential of in situ colorimetric proxy sensing for (geo) archaeological applications was investigated;

- Test and calibration of optical image profiler (OIP) in the “pilot test”, inside the UFZ. The OIP system detect fluorescent and NAPL substances and provides a vertical profile of electrical conductivity of the subsoil;
- Realization of a tracer test coupled with optical image profiler (OIP) surveys at the site of Selbitz. The field test aimed at discriminate the diffusion of a tracer (uranin-injected into a piezometer) inside the shallow aquifer of the site. The high resolution characterization provided by fluorescence vertical profiles highlighted the presence of the tracer at particular depths, with great detail. The second configuration of the tracer test has also foreseen the use of SCOST technology (with the aim of identifying the chromatic variations due to the injection of fluorescein) and the implementation of slug test (for the parameterization of the aquifer horizon).

The experimental work deepened the knowledge about direct push surveys, geophysical exploration and management of multidisciplinary data to obtain an in-depth knowledge of underground heterogeneity and subsurface processes. The research accomplished at the UFZ underlined the importance of coupling more investigation technologies to capture the geological uniqueness and hydrogeochemical peculiarities of the subsoil at site-specific scale. All laboratory, field and modeling activities validated the methodological approach used for the remediation of contaminated sites also in other fields of application. The integration of heterogeneous data within a single information dashboard unequivocally supported all the study phases. The geodatabase oriented the location of the surveys, optimizing the decision-making process and the exchange of information between professionals belonging to the different scientific spheres. The application of this methodology on other sites and contexts tested its reliability and accuracy.

5. CONCLUSIONS

The research significantly contributed to the optimization, management, and monitoring of polluted site remediation interventions with innovative techniques. The acquisition and construction of multidisciplinary data storage models was able to harmonize the different elements and to return in "near real time" pre-processed information, useful for the analysis, management, and optimization in pilot test and / or full site of innovative solutions for the remediation. The research project developed a methodology for the integrated management of the various data sources, with particular reference not only to the characterization phase, but also to experimentation and monitoring at a site-specific scale. The joint management of different origin data and the contributions of the different skills lead to integrated data management processes, also in order to design, in a targeted and ergonomic way, any integrative investigations and / or (re) calibrate the modalities of intervention during the test phase. The optimization of databases reduced processing times and encouraged and coordinated the exchange of information between the various disciplines for the purpose of identifying gaps to be filled or to confirm what emerged during the characterization phase, laboratory and / or field experimentation, and adoption of innovative remediation technologies. The faced challange by the PhD project filled the knowledge gaps and lead to the advancement of new knowledge on sustainable remediation technologies, by analyzing the different aspects involved in the environmental arena. In the context of remediation of contaminated sites, simultaneous management of multi-source data is a gap which, although of a predominantly methodological nature, has important implications on the efficiency of the selection, planning and control of remediation operations. The integration and combined analysis of geognostic, hydrogeological, geophysical, and chemical data within the geodatabase facilitates the development of conceptual models that consider extension and degree of contamination, geological, hydrogeological, and chemical-physical parameters that condition the mobility and distribution between the phases of pollutants. The geological model acsts as an integrated and continuously updated tool, able to optimize the investigations during the characterization phase, support the choice of the strategies in planning phase, managing and calibrating in progress the intervention modalities according to innovative approaches during the remediation phase. Depending on geological contexts and contaminant characteristics it is possible to evaluate the applicability of the intervention options in an efficient way from the economic point of view, the timing and the invasiveness of the survey, to achieve the design of targeted, effective, efficient, and economically sustainable remediation interventions. The spatial data storage model used for processing and editing dynamically integrates different data sources from the characterization phases to the intervention implementation. The multi-source model manages the operativity and optimizes the layout in the phase of passage from pilot test to full scale experiment of remediation interventions with innovative technologies. The three-dimensional geodatabase acts as an integrated and continuously updated tool, effectively supporting, managing, and calibrating the implementation of an effective remediation strategy according to innovative approaches. The 3D pseudo-real visualization captures the high resolution characterization of geological eterogeneity and contaminated bodies at the scale of pollution mechanisms and decontamination processes. The physicochemical and data-driven model, which links geophysical signals to contaminant characteristics within contaminated porous media, explains the observed contaminant-geophysical behaviour. The interpretation of contaminant dynamic has strong implications for the reliability of the CSM, affecting the selection and the performance of remediation strategies. The display of integrated data allows a real-time interaction with the multi-source model (and the 3D geodatabase), to extract useful information for the decision-making processes during the different stages of remediation. The rich data set, and the data-driven models comprise, collect, and establish a connection between the environmental variables. They optimize the contribution of each aspect and support unequivocally the design and the adoption of an effective and sustainable clean-up intervention.

The proposed research activity was applied to real cases such as the Decimomannu military airport, the Bologna high speed railway station and an industrial site operating in northern Italy.

At the Decimomannu NATO base, the multitemporal and multidisciplinary geodatabase enabled the integrated use of geological, hydro-chemical and geophysical data and highlighted the need for a large amount of multi-source pictures to build a reliable and high-resolution conceptual model. The simultaneous integration of the information relating to the hydrogeophysical sphere in all its dimensions, the overlapping of knowledge, and the high-resolution characterization of environmental variability capture the hydrogeological uniqueness, the geophysical peculiarity, and the contamination dynamics. The hydrogeophysical model and the thematic database act as integrated and continuously updated tools, able to harmonize and valorize different information. The research emphasizes the contributions of multiple lines of evidence and innovative approach to leading to refinement of conceptual site models. The application of data fusion to the characterization of contaminated sites, incorporating geologic knowledge, geophysical data, geochemical analysis, direct sensing investigations, hydraulic test data, and observation of head reduces uncertainly associated with subsurface interpretation and provides precious insights. The high-resolution hydrostratigraphic reconstruction captures the variability of the geological heterogeneities. The electrical resistivity model refines the geological model. The geophysical result is consistent with the hydrogeological conceptualization. The reconstruction of the evolution of groundwater quality coupled with comparative analyzes conducted both on the fresh product and on the supernatant reveal the presence of an old and aged product. The incorporation of LIF investigations provided not only confirmation that residual phase is present, but also evidences not previously available about the distribution and behavior of LNAPLs in the soil matrix. The pumping action carried out by the hydraulic barrier wells and the seasonal oscillation of the water table favored the redistribution of the product in the residual phase along the smear zone. The multi-source model reveal that contamination distribution is heavily affected by subsurface heterogeneity and hydraulic processes. The gradual refinement of the conceptual model, which combines hydrogeophysical methods, innovative investigations and laboratory analysis, accentuates the limitations of traditional sampling techniques in the identification of secondary sources and in the interpretation of the actual state of contamination of a polluted site. The combination and the integration of the data-driven models effectively support the decision-making process and the definition of the possible remediation strategies to proceed then with the implementation of the one considered most suitable. On the basis of the results obtained and after integration into the reference geological model, it was possible to define the remediation strategy and the location of the interventions to be implemented on the pilot scale. An in situ enhanced chemical desorption strategy increased the desorption of hydrocarbons adsorbed to saturated soils or at the capillary fringe and raised the product recoverability in a separate phase. The hydrocarbons were rendered available in the dissolved phase or in a separate phase with lower viscosity, allowing a subsequent rapid and effective physical recovery. The pilot test, appropriately coordinated through the multidisciplinary and multitemporal data management model, was checked in the implementation phase in terms of yield, through ERT and groundwater sampling. ERT measurements represented a tool for intervention optimizing and performance monitoring. Geophysical surveys and groundwater sampling were realized to control the effectiveness of the intervention, both in terms of product diffusion capacity and in terms of effective reduction of pollutant concentrations. The study of the pilot test provided the elements for the verification of the efficiency, for the optimization of the intervention layout, and for the design of an optimized full scale intervention. The treatment carried out with the pilot test clearly reveals the mobilization of the petroleum product which constitutes the secondary contamination source. The case study is considered of interest as it illustrates an example of how it is possible to optimize the removal of LNAPL contaminants when they are substantially no longer recoverable by conventional technologies. Analysis of all data clearly shows that traditional extraction techniques are ineffective in removing secondary sources of fuel contamination. The integrated approach evidently shows that traditional characterization techniques are not able to consider the natural "aging" of potential secondary sources of contamination. The resulting data from characterizations carried out many years prior is used as an informational basis for the design of the interventions and is often insufficient to identify the best remediation strategy, affecting the effectiveness of interventions.

The Bologna railway station represents a case of integrated use of geological, hydro-chemical and geophysical data to support the high-resolution characterization, the design of remediation intervention, the monitoring and the validation of a pilot test, and the implementation of an effective remediation strategy in full-scale. The hydrogeophysical model and the thematic database act as integrated and continuously updated tools, able to optimize the investigations during the characterization phase, support the choice of the strategies in planning phase, managing and calibrating in progress the intervention modalities according to innovative approaches during the remediation phase. The high-resolution lithostratigraphic reconstruction caught the variability of the geological heterogeneities, that exert a decisive action on the contamination dynamics and decontamination mechanisms. The integration of geophysical evidence strengthened and refined the 3D geological/hydrogeological model. The hydrogeological uniqueness and chemical peculiarities supported the selection of a remediation technology and the identification of the application points. The indications obtained by the conduction of the pilot test optimized the full-scale operations. The operating project provided an innovative remediation strategy for sites contaminated by chlorinated DNAPLs. The remediation strategy implied the creation of "reactive" zones capable of reducing significantly and permanently the concentration of chlorinated solvents in groundwater through the combined action of adsorption on micrometric activated carbon, which is injectable directly into the groundwater, degradation of organic contaminants, stimulation of the dechlorinating biological activity by addition of an electron donor. The results that led to the achievement of the objectives and to the project closure derive from the integration of multidisciplinary data, using a multiscale approach. The multidisciplinary geodatabase, the integrated hydrogeophysical model, and the field test are an expression of the holistic approach followed from the characterization phases up to the adoption of remediation strategy. Supporting a holistic, multidisciplinary and integrated approach means working in the direction of a renewed and necessary "contamination of knowledge". “Contamination” is realized by promoting an interdisciplinary action that involves the dynamic interchangeability of the different scientific spheres to evaluate and design targeted, effective, and economically sustainable remediation interventions. This research represents the first completed example in European territory for the remediation of an aquifer contaminated with chlorinated solvents by a combination of adsorption and biodegradation.

The results obtained at the heavily contaminated industrial site provides some evidence about the effectiveness of a composite hydrogeochemical database for the integrated management, representation and analysis of heterogeneous data, enabling the appropriate selection, design and optimization of an effective remediation strategy. The integrated geodatabase represents an effective “near real time” decision support system (DSS) able to manage and release data during the different remediation phases—from the characterization to the implementation of technique. The research highlights the need for a large amount of multi-source data to build a reliable and high-resolution conceptual model, and to design effective remediation strategies with innovative technologies. The 3D geological/hydrogeological model was refined and strengthened by integrating the hydrochemical evidence. The high-resolution hydrogeochemical characterization highlights the association of a significant mass of contaminants with lenses of fine materials with very low permeability, in the saturated zone, which act as slow-release sources of contaminants. 1,2-DCE and VC were identified as the main pollutants of the groundwater and were detected in concentrations of up to 100 mg L−1, indicating the presence of residual areas of DNAPL acting as persistent secondary sources. The complete multidisciplinary and multitemporal characterization has recognized the areas affected by residual contamination, and has supported the choice, the sizing and the configuration of the remediation technology to be deployed. The realization of a pilot test is functional for the evaluation of the effective contaminant mobilization. Results from the field test demonstrate the important mobilization of contaminants from the low permeability zone, and the possibility of distributing electron donors to enhance in situ the natural attenuation mechanisms based on biological reductive dichlorination. The GCW allowed the extraction of water from the very low permeability layers by mobilizing the contaminants (residual DNAPL) trapped/adsorbed in these areas. The GCW can also be operated in the "reverse flow" configuration (groundwater is recirculated from the bottom to the top). Changing the recirculation configuration could prove beneficial, by enhancing the mobilization of pollutants from less accessible zones. The results obtained during the experimentation will support a definitive design choice for the full-scale intervention, determining the remediation of the entire identified contamination source. The implementation of the strategy in full scale will verify the effectiveness of the adopted technology for the persistent, low permeability contaminant source zones. Pilot testing was properly coordinated through the multidisciplinary and multitemporal data management model, and controlled in the execution phase in terms of yield. The integrated data cockpit reflects the interdisciplinary action that involves the contribution and collaboration of the different scientific spheres to guarantee valid results in qualitative terms. The geodatabase represents the link that favors the dynamic interchangeability of information in the multidisciplinary nature of the elements involved in the hydrogeochemical arena. The central system to organize/return even heterogeneous data is a support tool for the evaluation and design of targeted, effective and economically sustainable remediation interventions.

The results suggest that in order to enhance sustainable and effective remediation adoption, it is imperative to employ continued effort to develop the mixed understanding of all the aspects involved in the environmental arena in all its dimensions. In this sense and in the context of a digital world, one of the future developments of the doctoral project is the production of models in virtual reality (VR). I'm exploring the virtual reality for the representation of conceptual models, in collaboration with Arcadis (Figure 65).

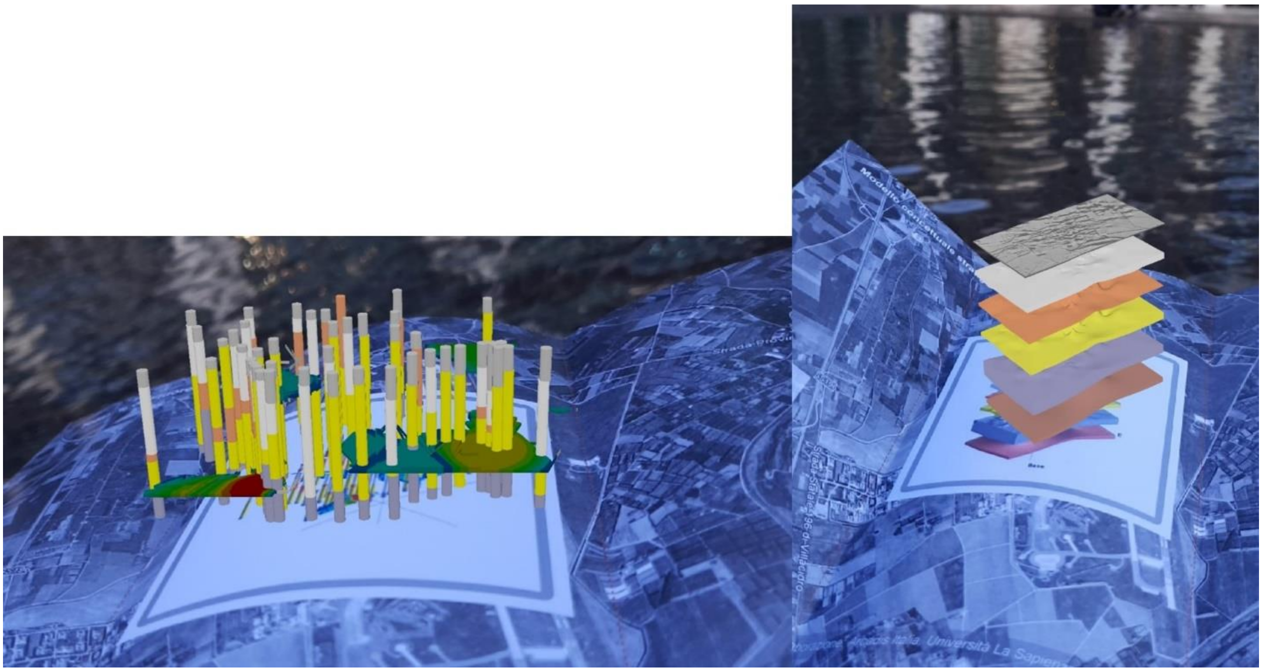

Figure 65. Representation of Decimomannu multi-source model through the VR.

Smartphones and tablets with are equipped with applications for augmented virtual reality (Figure 66).

Figure 66. Use of smartphones and tablets with Augmented VR App.

I'm moving in the direction of holograms, to obtain a three-dimensional representation of the solid models realized through the geodatabase (Figure 67).

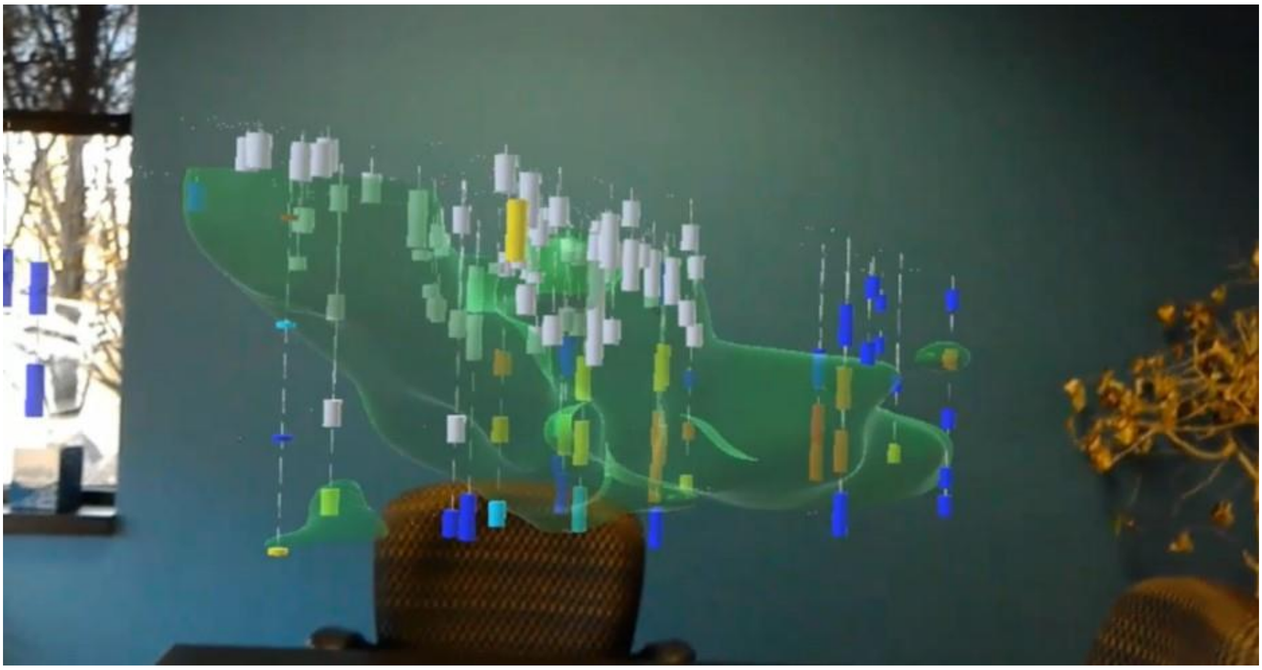

Figure 67. 3D Augmented Virtual Reality (hologram)

Visualizing volume data is very important to enable intuitive understanding of 3D structures, making them easier to analyze and share. The holographic display method shows transparent and multi-layer objects. The hologram illustrating the multi-source model will represent the tool supporting the decision making process. The next frontier is harnessing artificial intelligence and can revolutionize the remediation of contaminated sites. The integrated model works by combining disparate sources of knowledge typically found at most contaminated sites: geological and drilling data, drilling reports, geophysical surveys, historical information, hydrological measurements, chemical analysis, and the reams of internal data contained in process logs, reports, and studies. The digital model synthesizes those massive amounts of data with the knowledge older geologists and engineers have accumulated from years of field experience. The rich data set and the data-driven models comprise, collect, and establish a connection between the environmental variables, optimizing the contribution of each aspect to support unequivocally the the design of an effective and sustainable remediation strategy.

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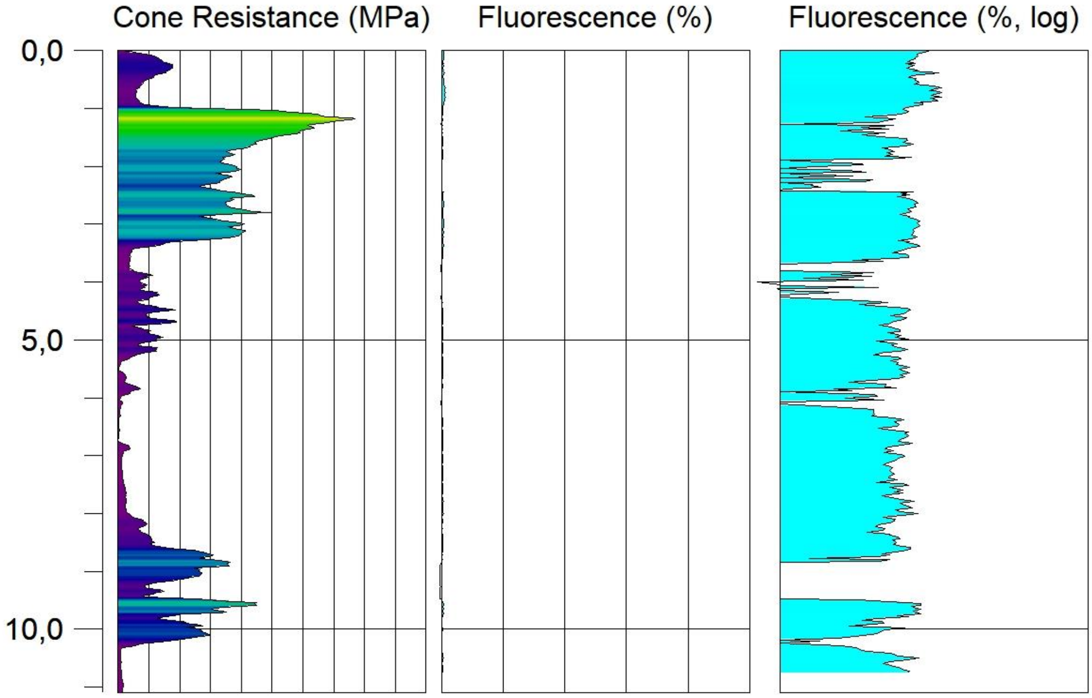
7. ANNEX 1

VERTICAL PROFILES RELATED TO CONE RESISTANCE AND FLUORESCENCE, OBTAINED AT THE LIF-CPT SURVEY POINTS

LIF-CPT00



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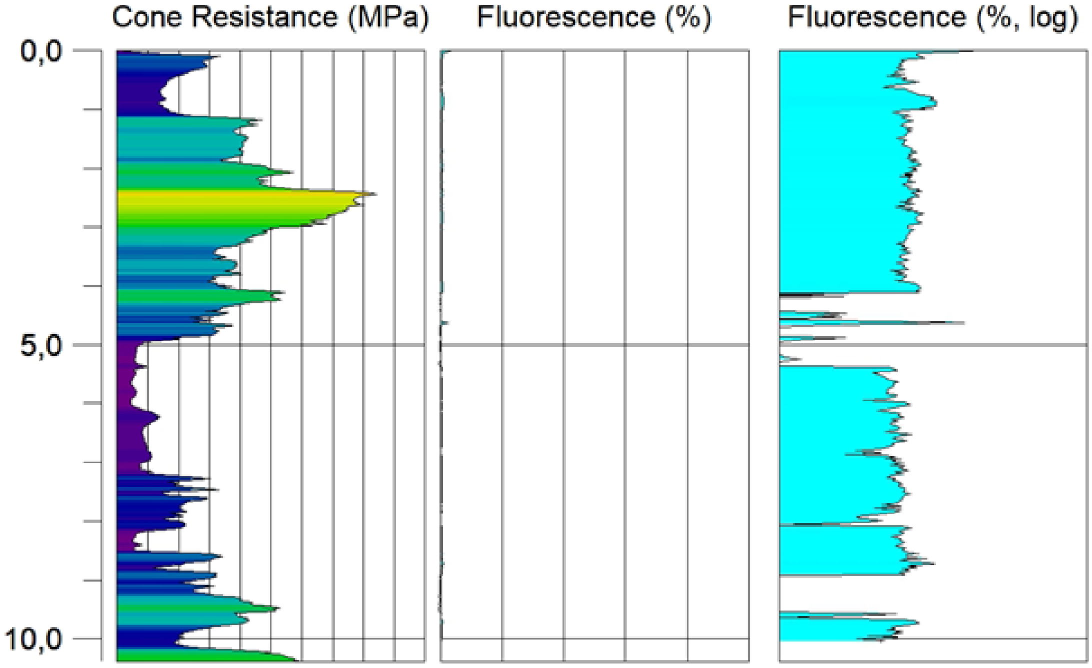

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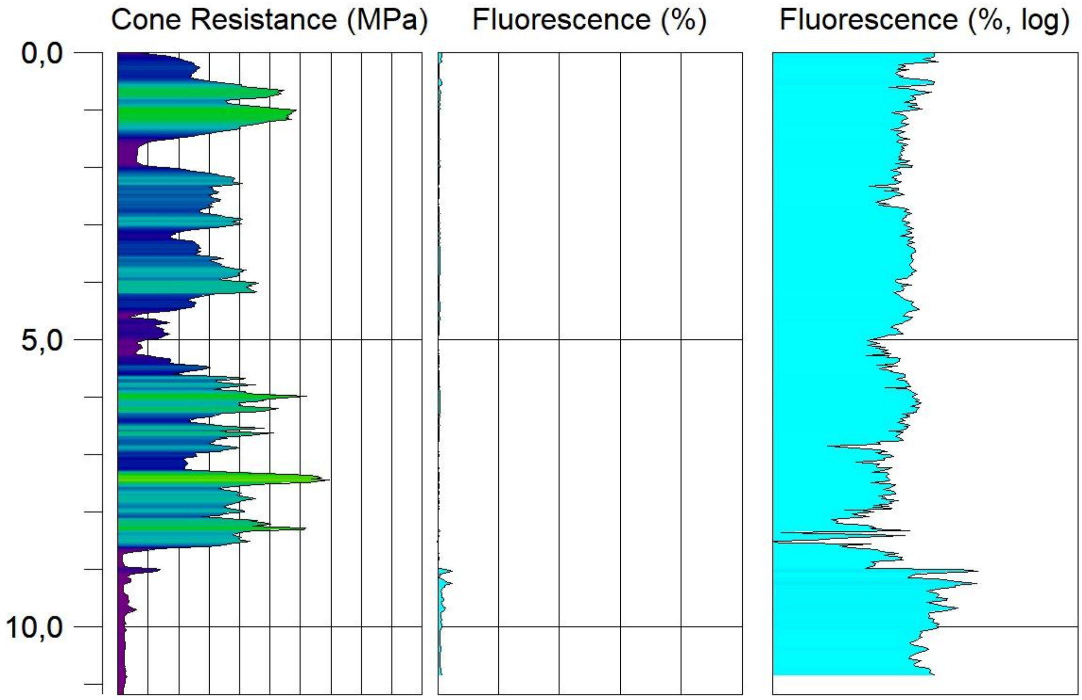

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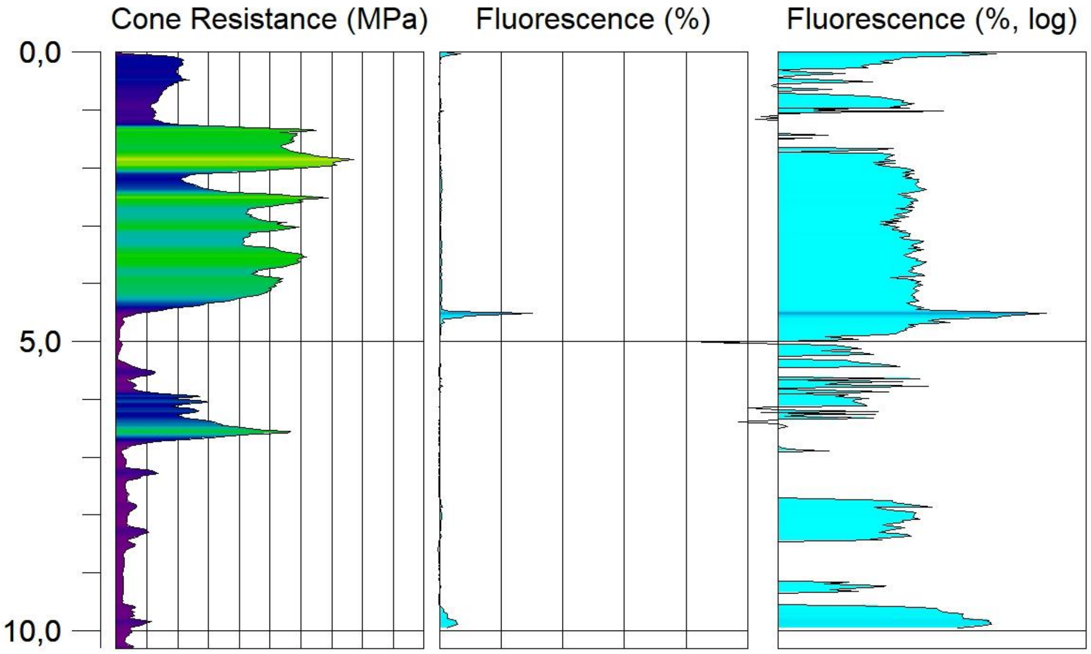

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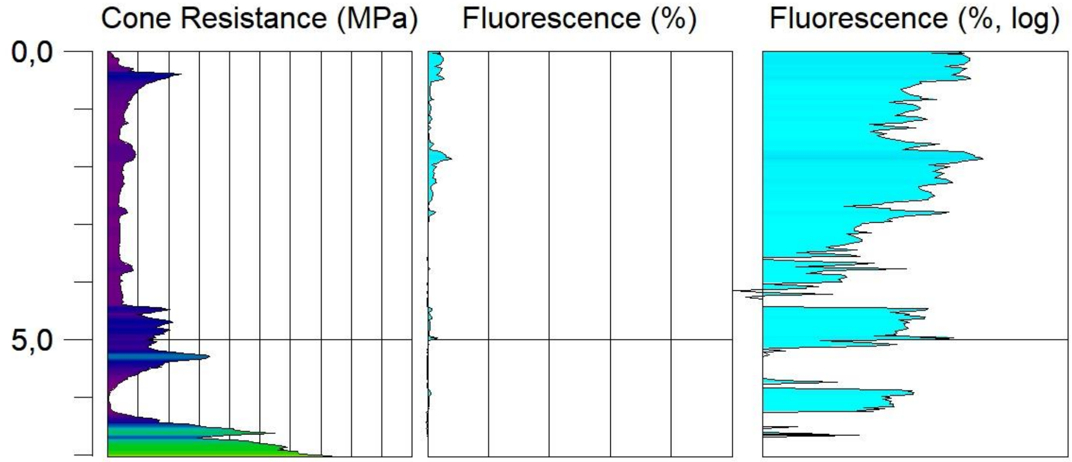

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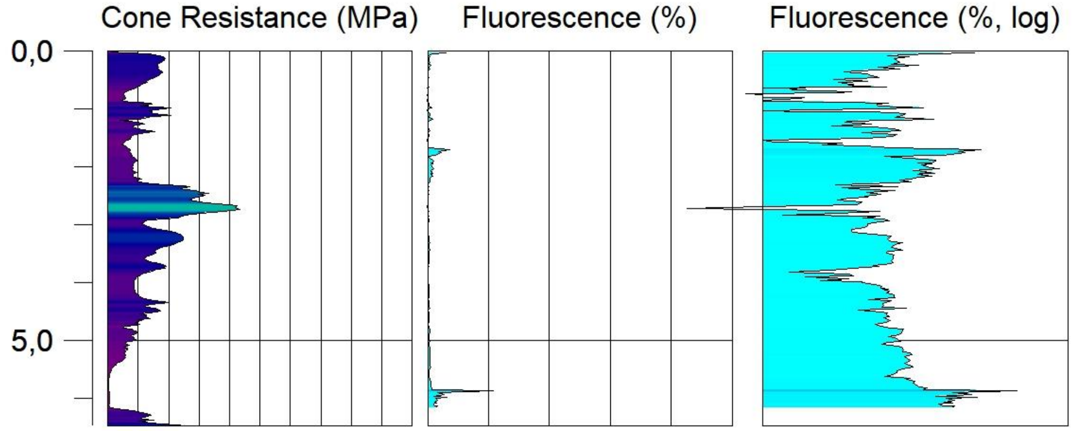

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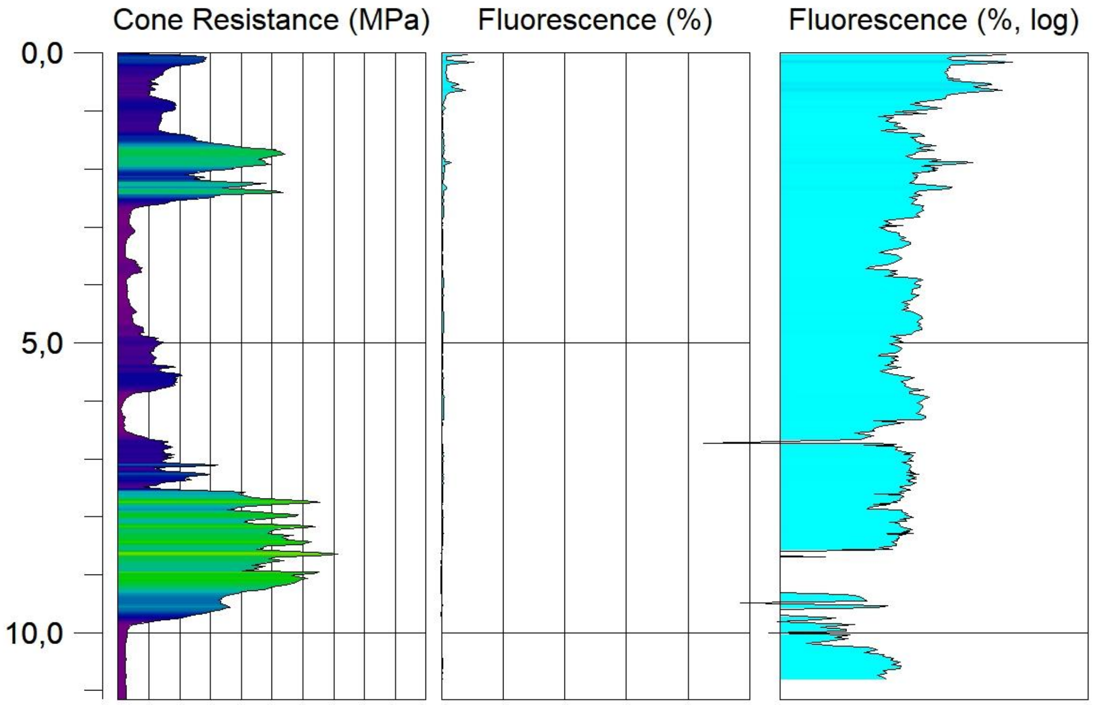

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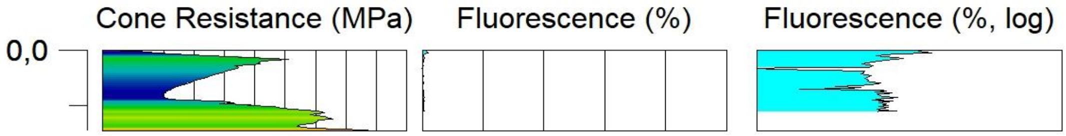

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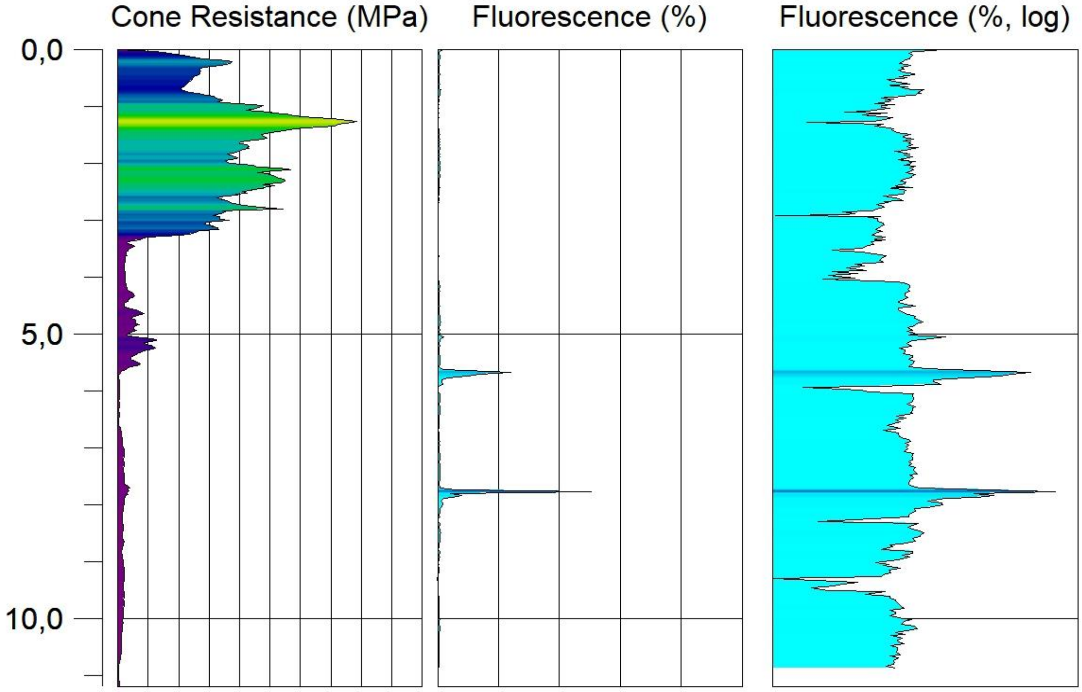

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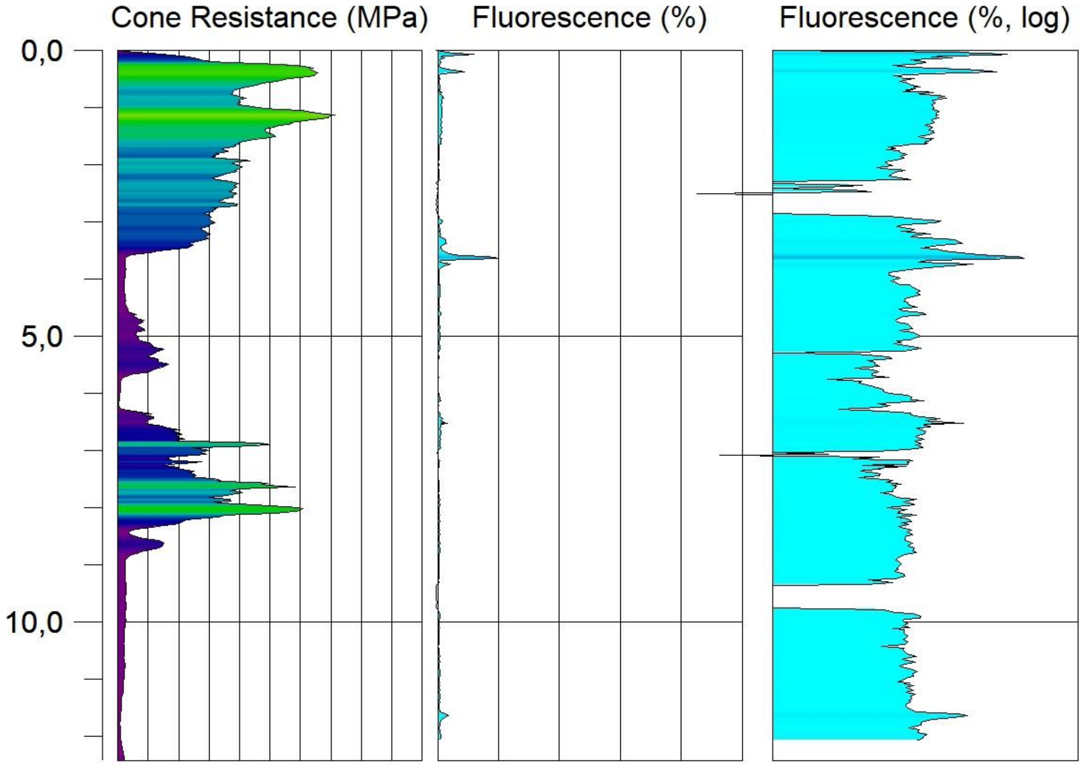

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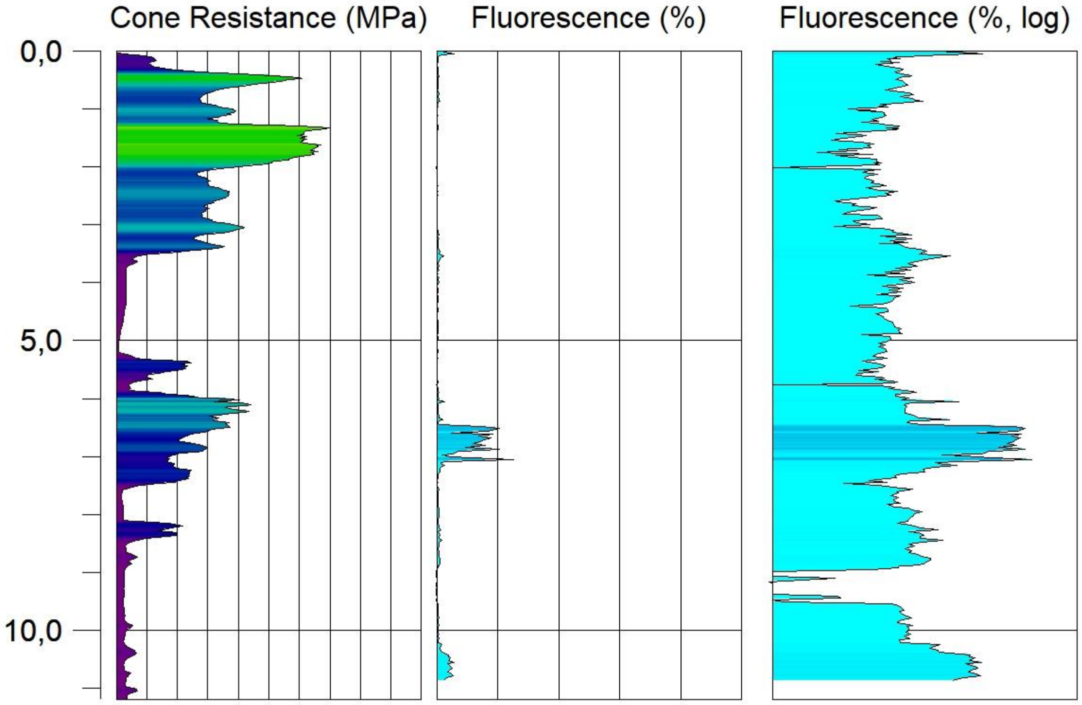

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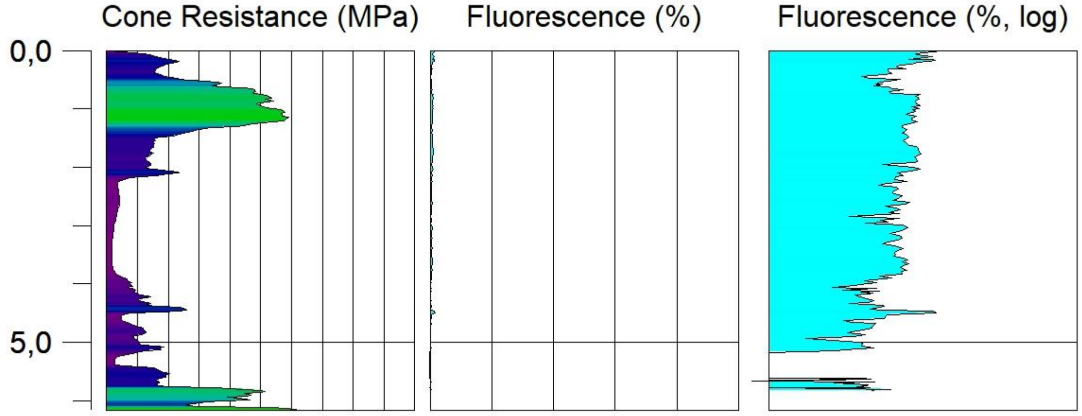

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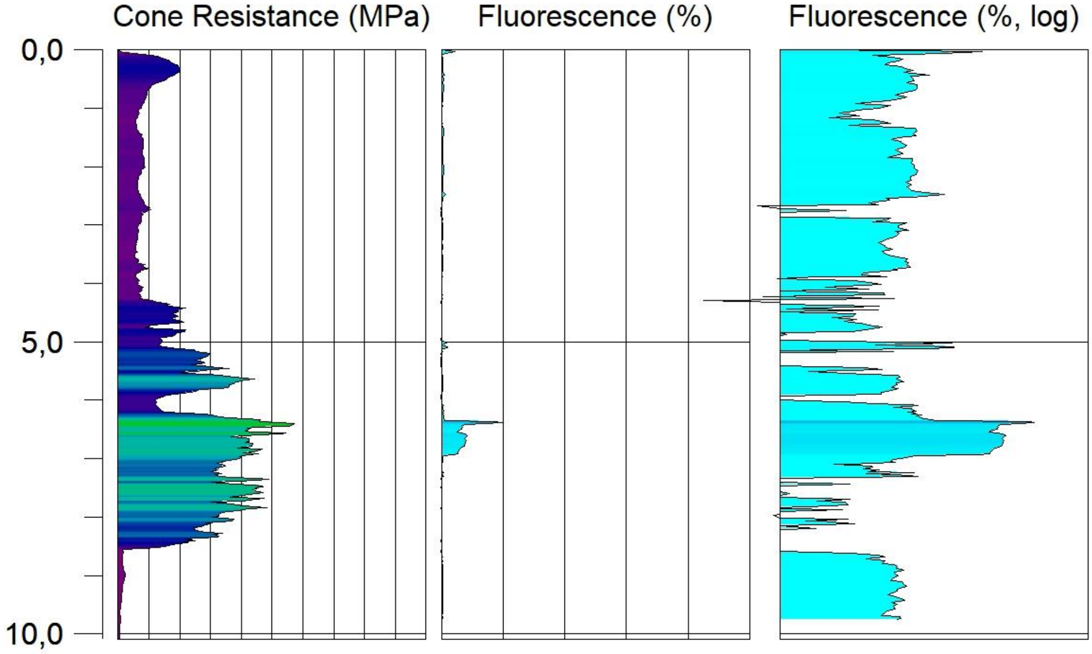

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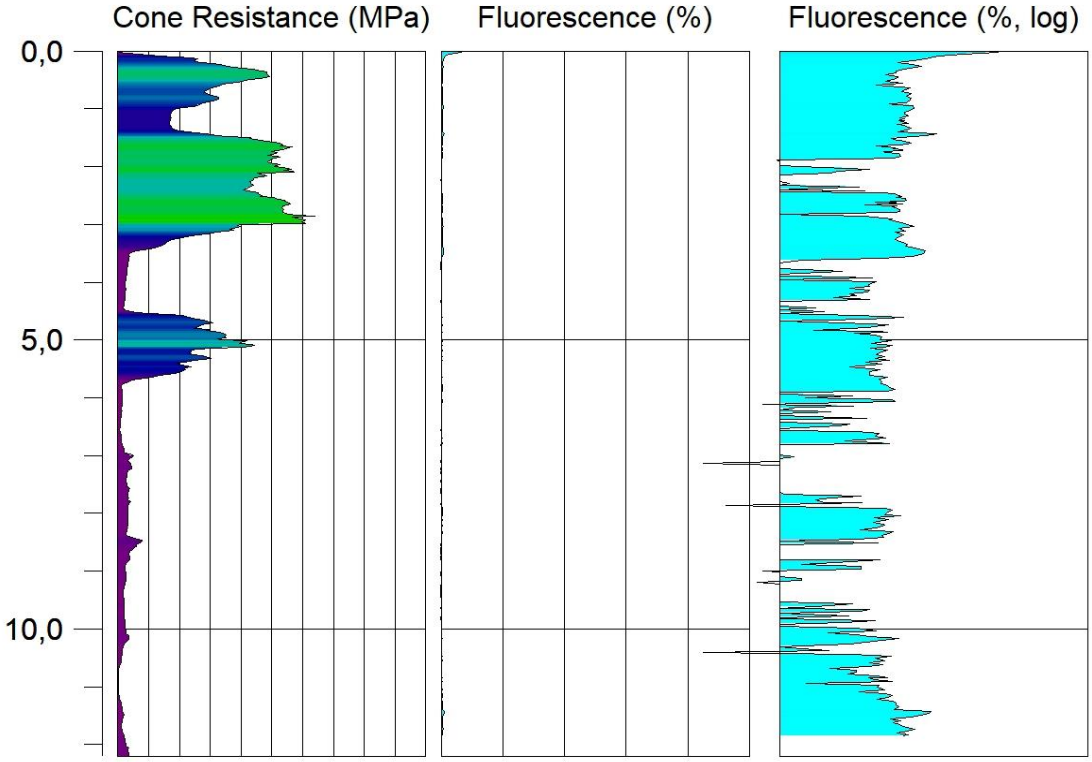

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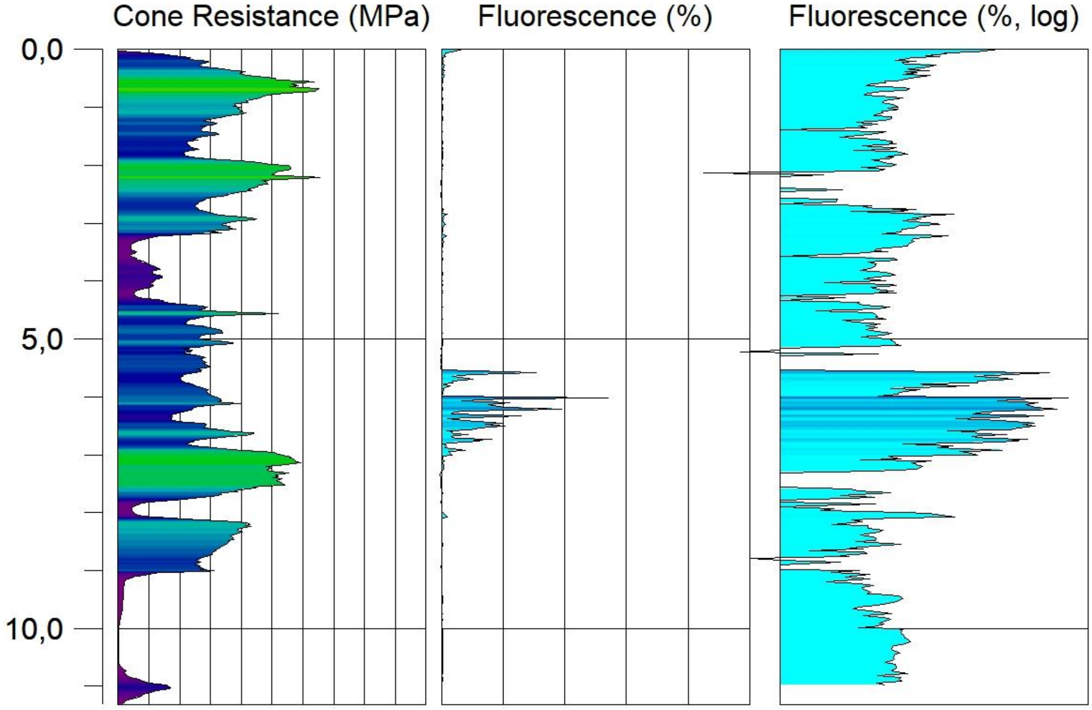

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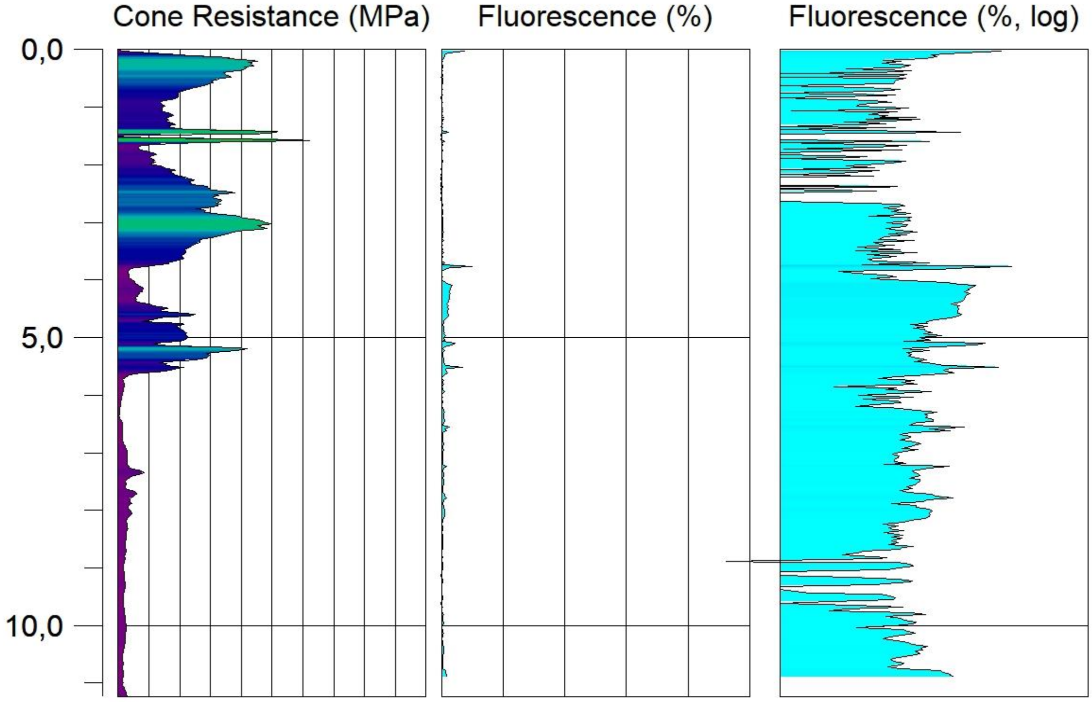

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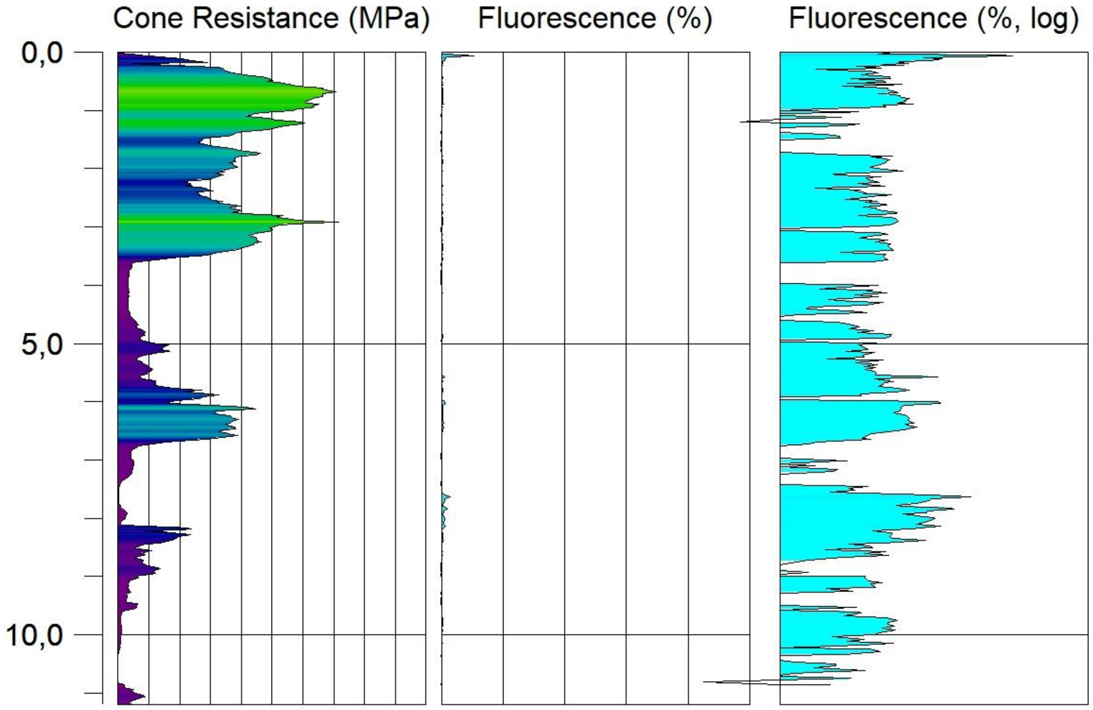

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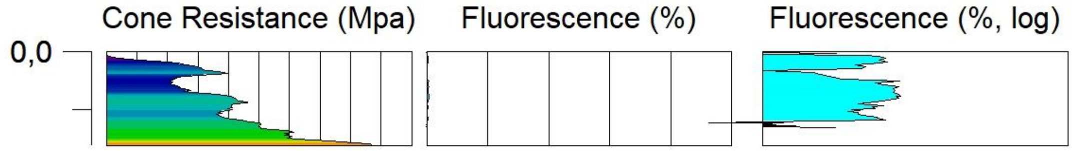

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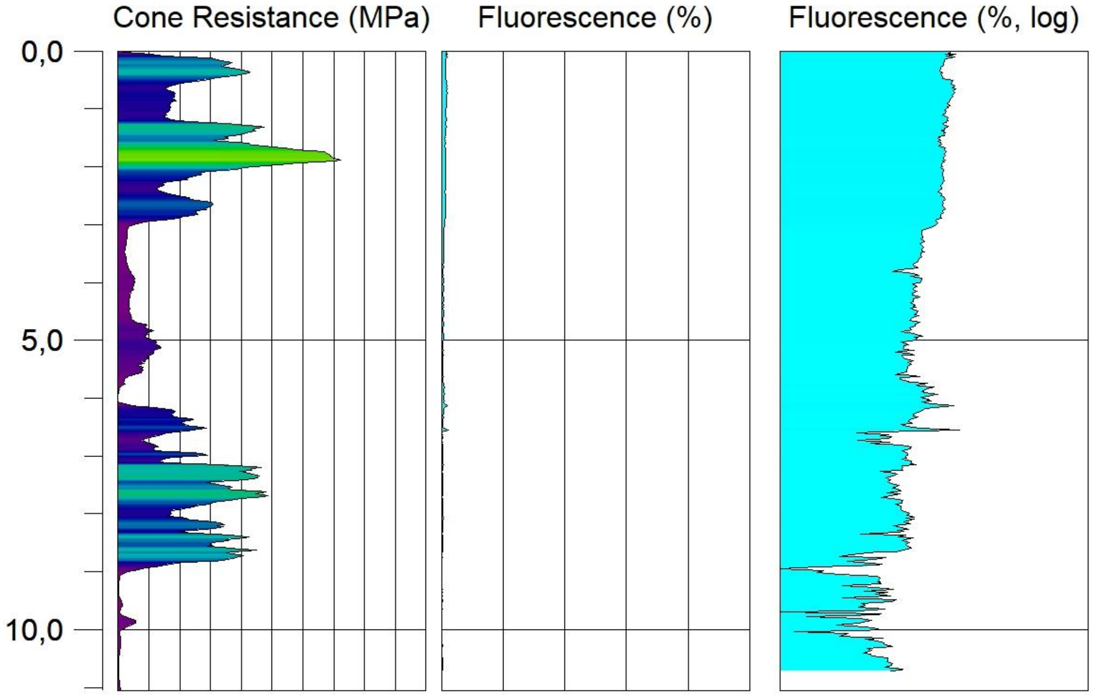

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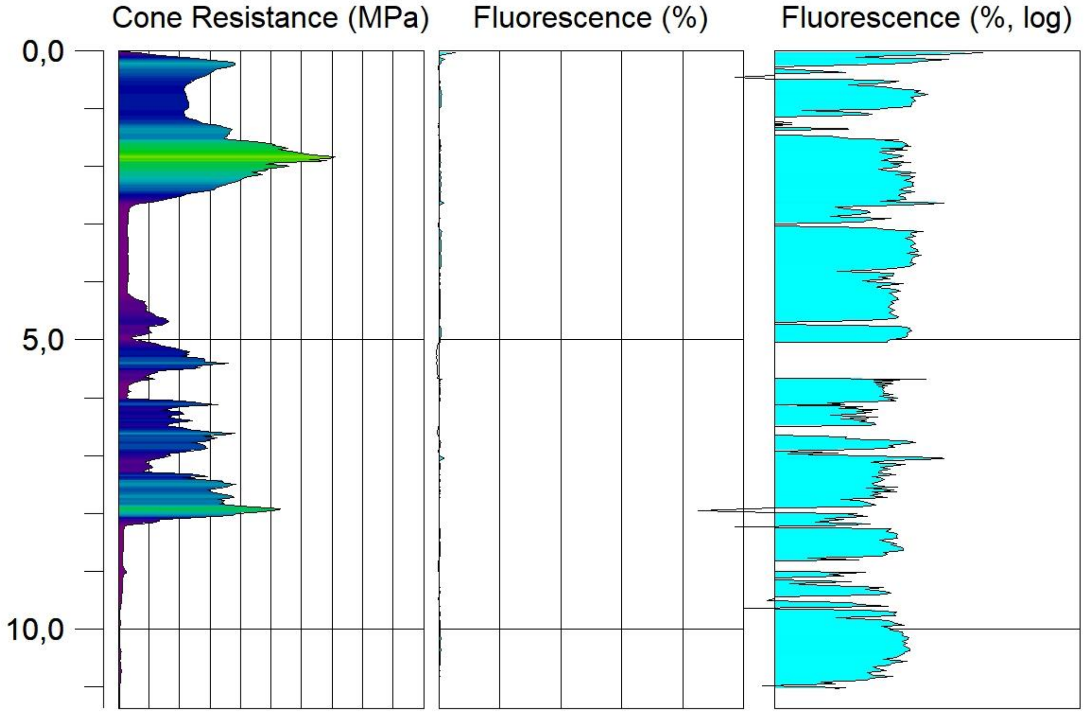

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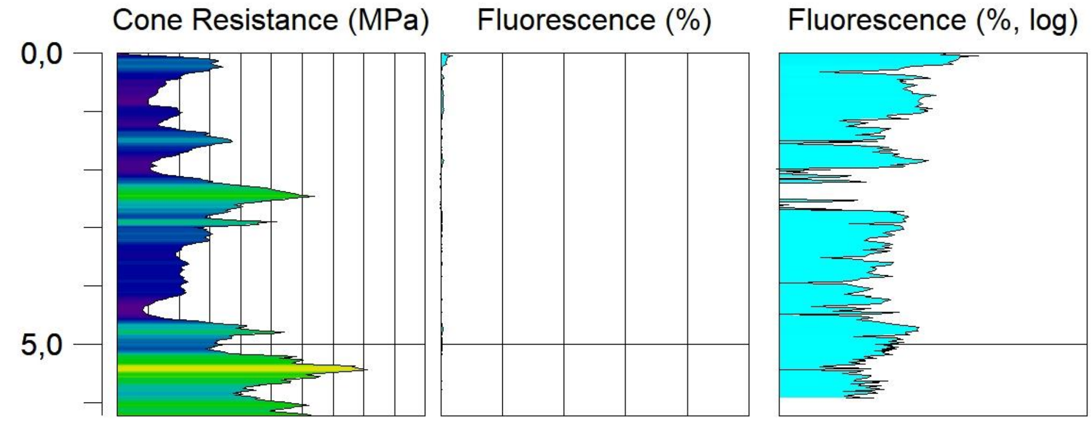

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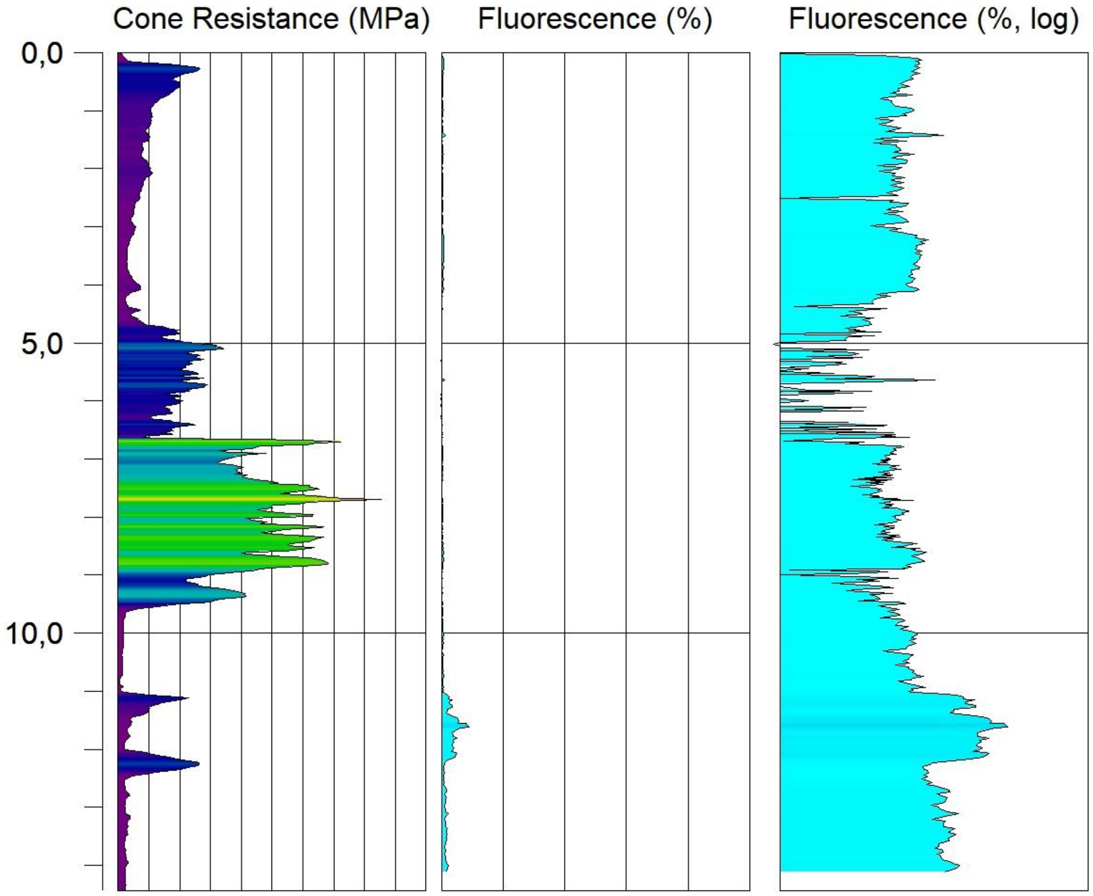

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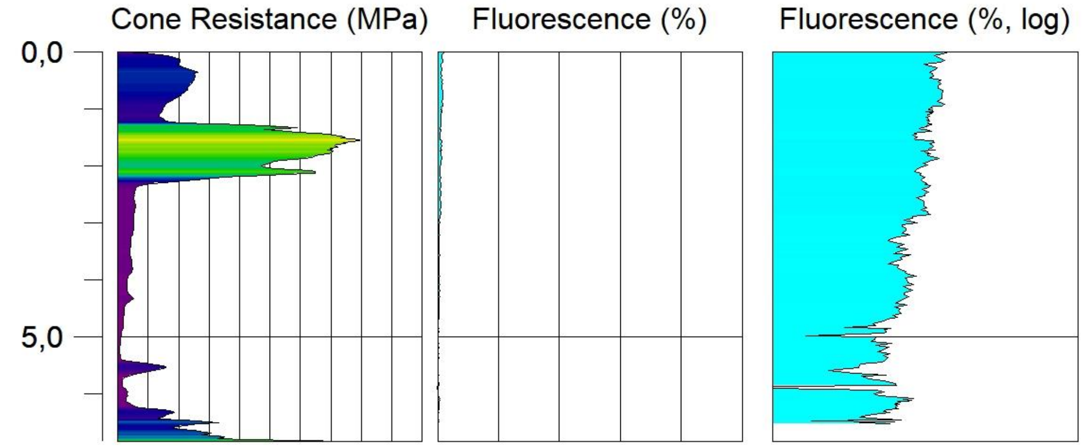

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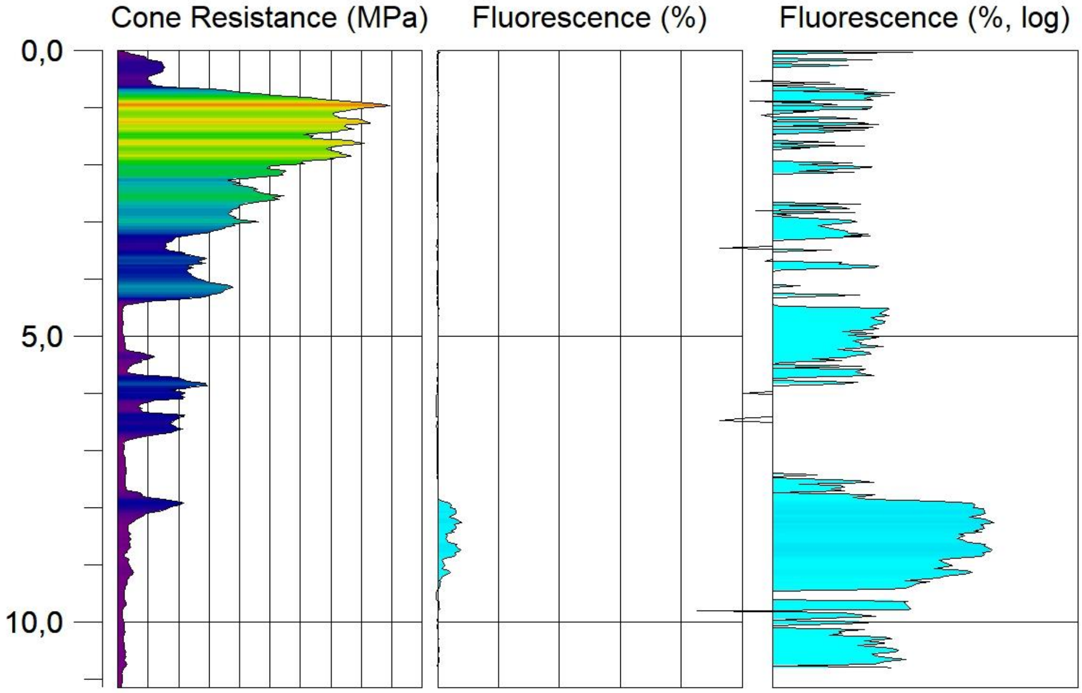

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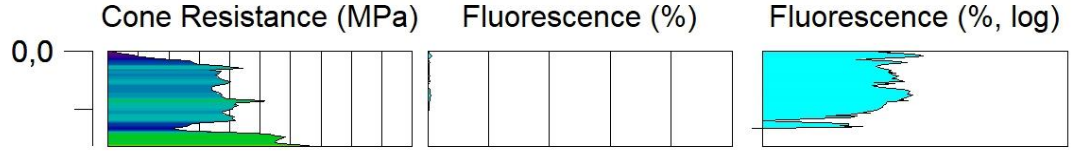

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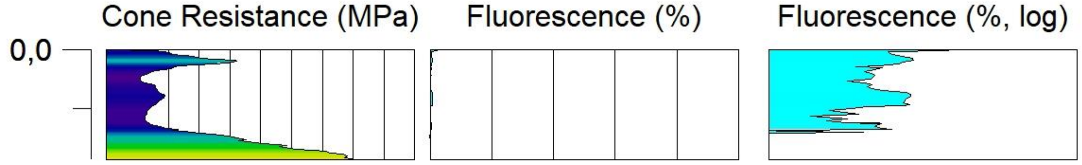

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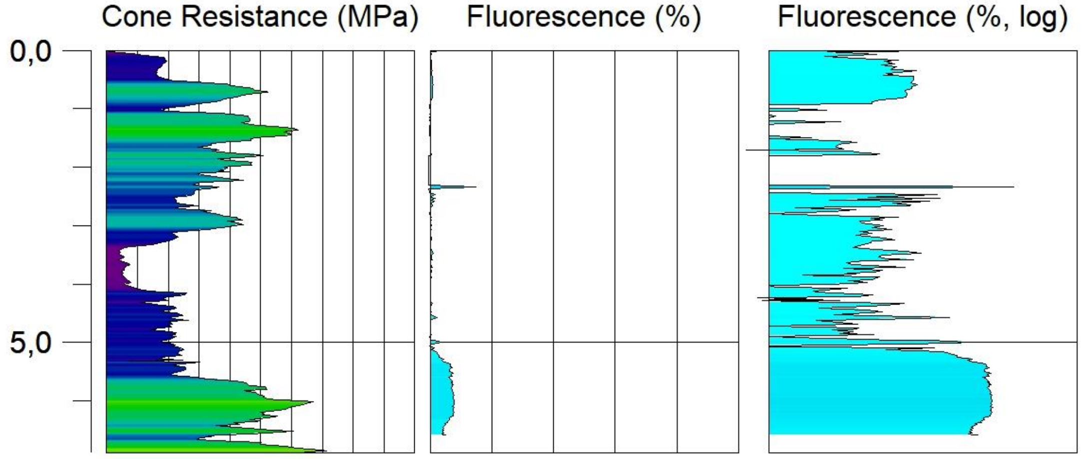

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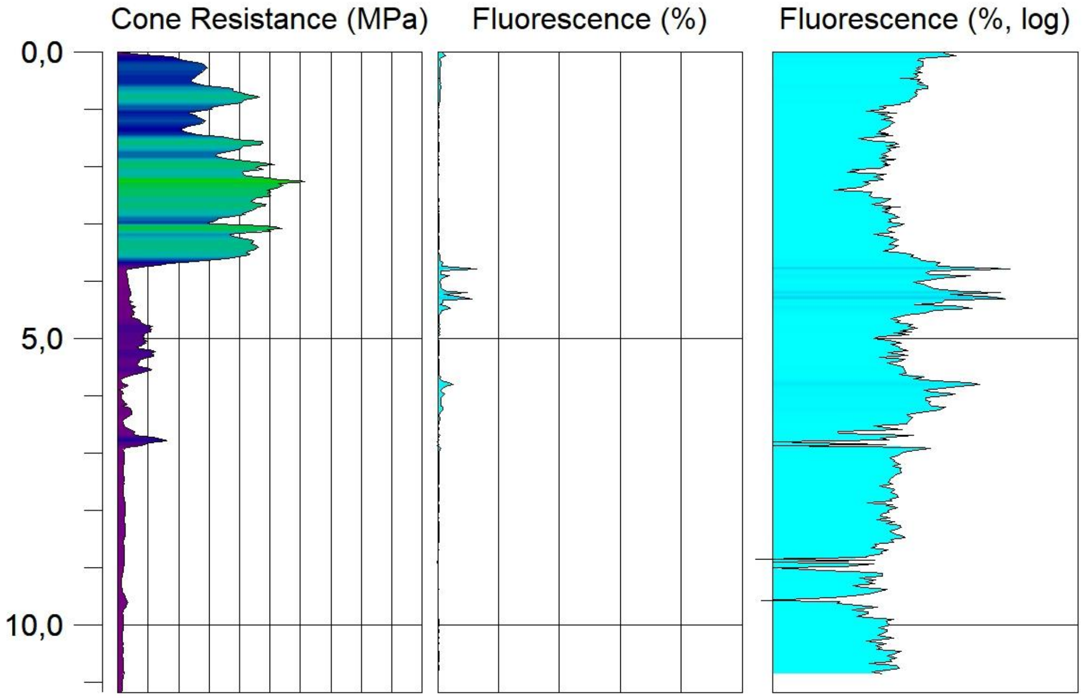

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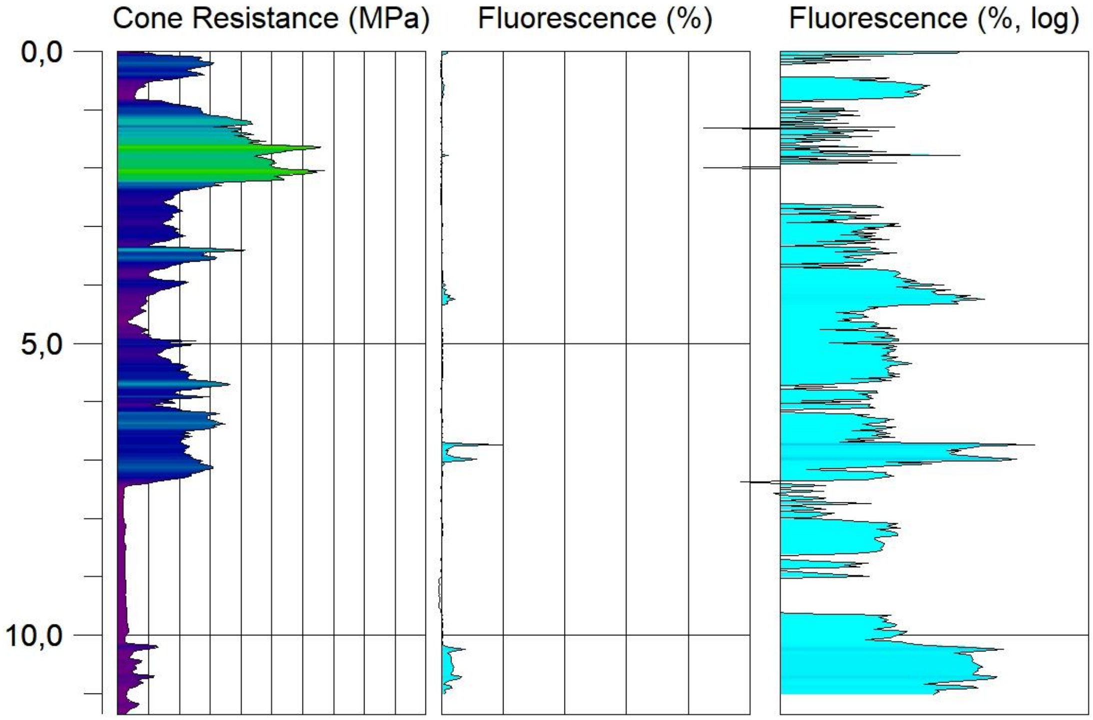

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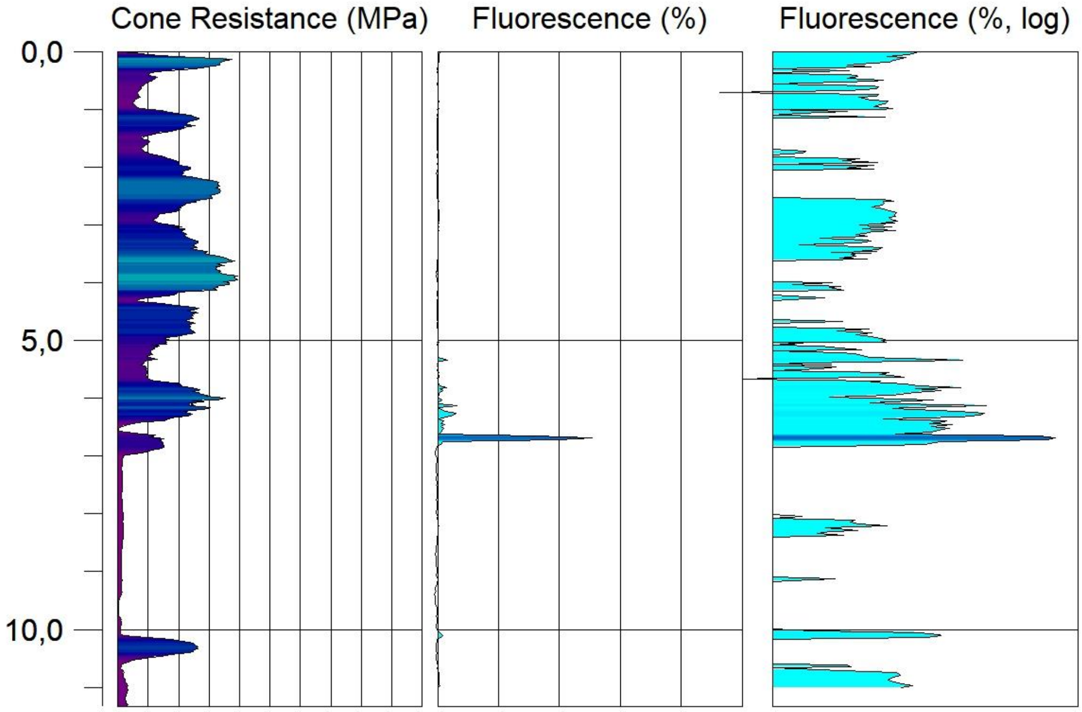

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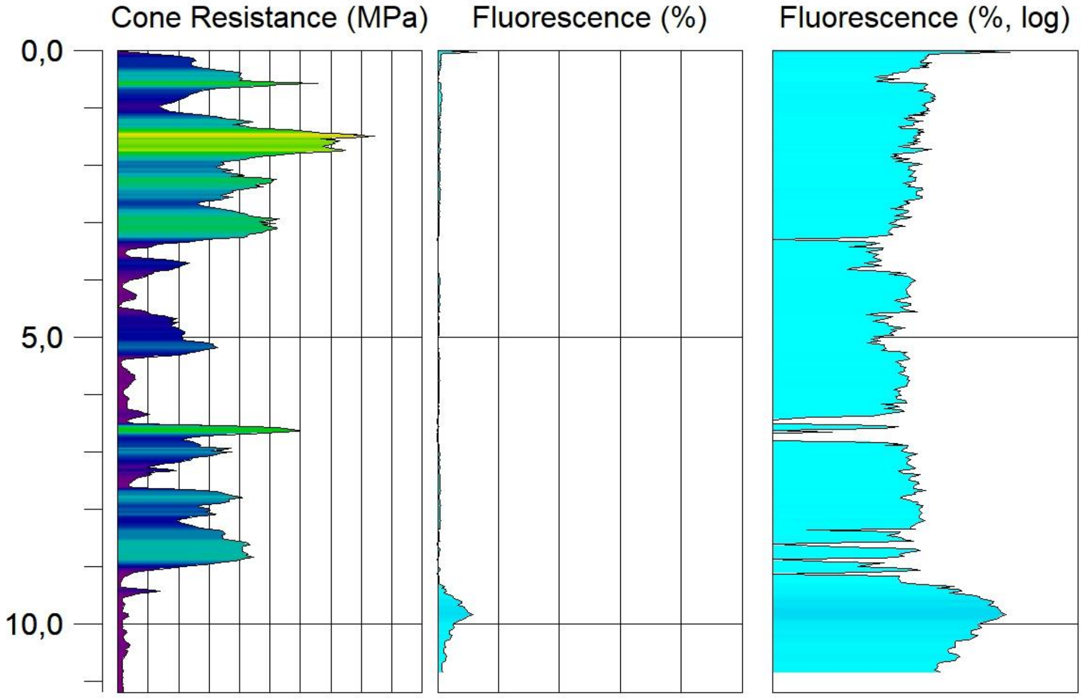
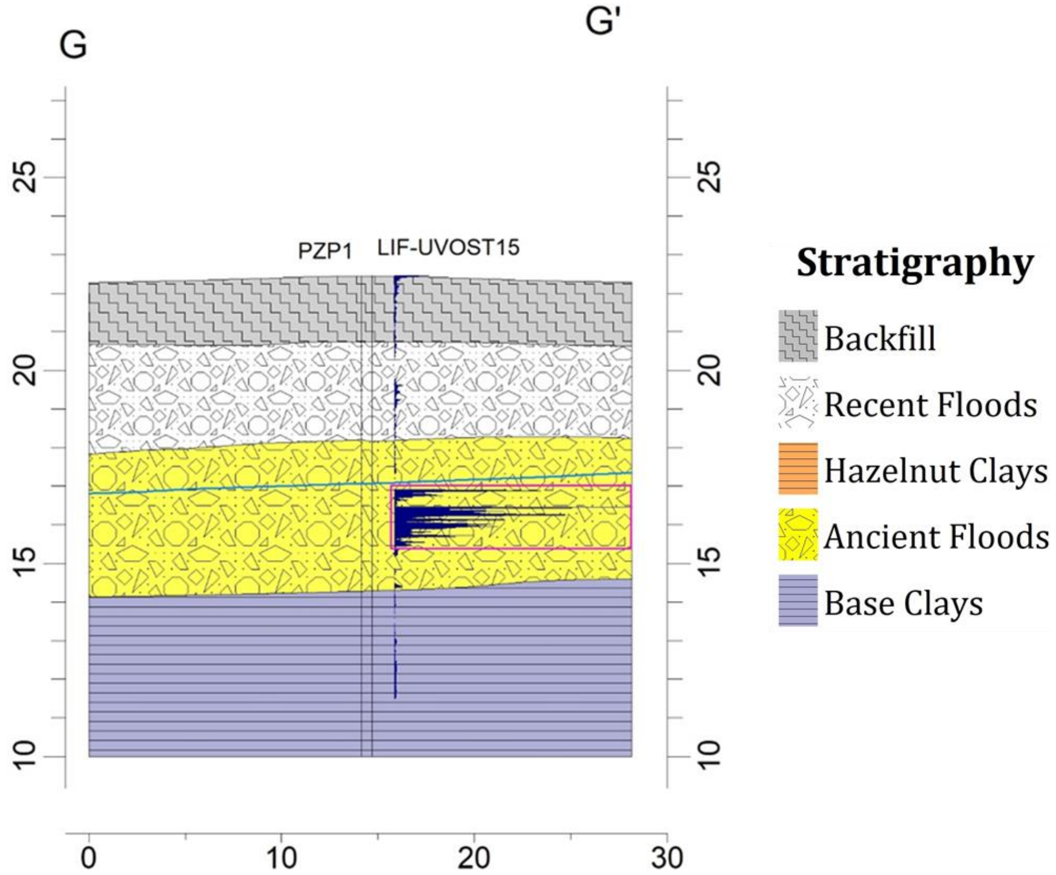


8. ANNEX 2

GEOLOGICAL SECTIONS REALIZED IN CORRESPONDENCE OF THE POINTS IDENTIFIED FOR THE IMPLEMENTATION OF THE REMEDIATION INTERVENTION IN FULL SCALE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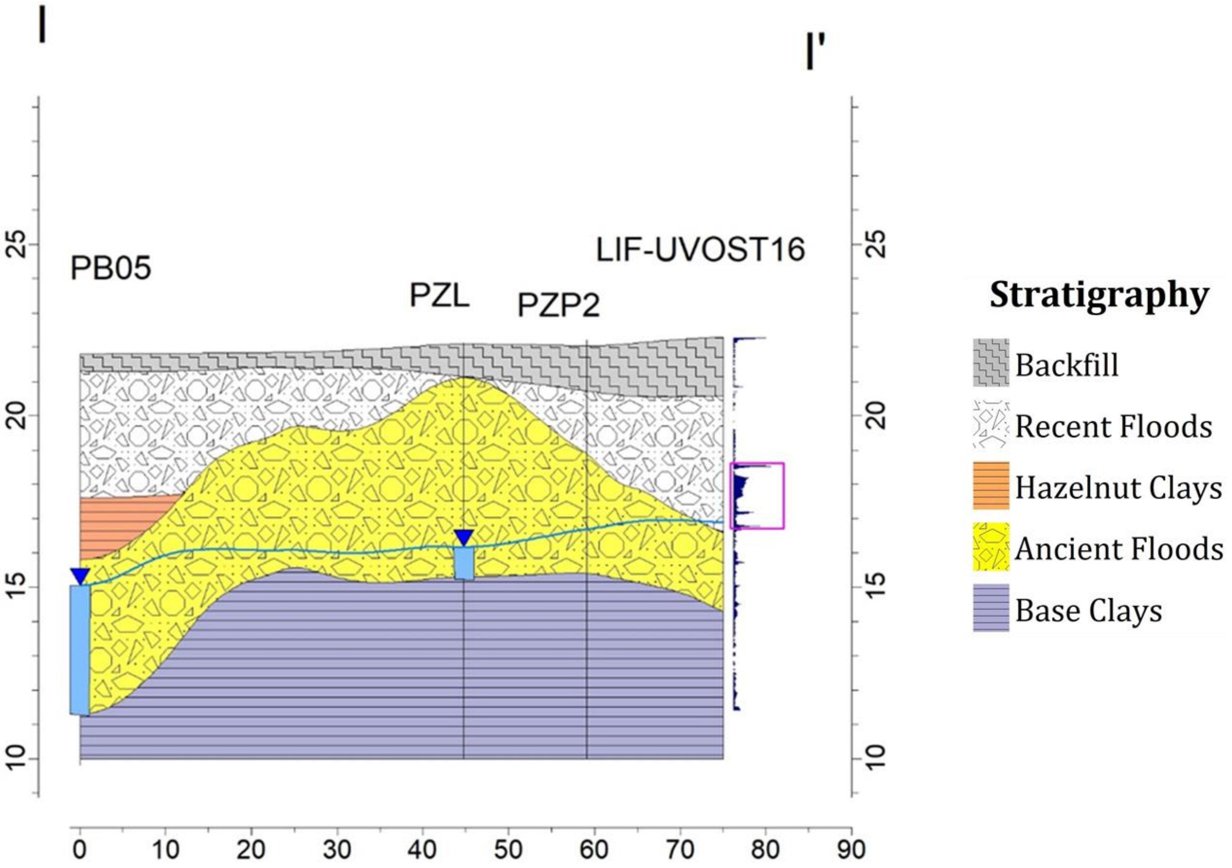
Stratigraphy
Backfill
Recent Floods
Hazelnut Clays
Ancient Floods
Base Clays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80
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Stratigraphy
Backfill
Recent Floods
Hazelnut Clays
Ancient Floods
Base Clays