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INTEGRITY OF FINE-GRAINED LAYERS TO DNAPL MIGRATION IN MULTILAYERED AQUIFERS: ASSESSMENT IN A PCE-CONTAMINATED ALLUVIAL SYSTEM, USING HIGH-PRECISION SIMULATIONS

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EXTENDED ABSTRACT

I composti organici clorurati contaminano ampiamente le falde acquifere in tutto il mondo. Appartengono ai cosiddetti DNAPL, sono più densi dell'acqua, con una bassissima solubilità, e possono migrare per effetto della pressione e della forza di gravità attraverso i mezzi insaturi e saturi, fino a raggiungere il substrato impermeabile.

Il presente studio riguarda lo sviluppo di un modello numerico tridimensionale finalizzato a studiare ed analizzare l'impatto atteso in conseguenza del rilascio di percloroetilene (PCE) in sistemi acquiferi multistrato caratterizzati dalla giustapposizione di strati più permeabili (ghiaia e sabbia) e strati a bassa permeabilità (limo e argilla).

In dettaglio, sulla base di un modello geologico tridimensionale di sottosuolo ed idrogeologico concettuale, viene sviluppato un modello numerico 3D utilizzando il codice numerico CactusHydro, introdotto in (Feo & Celico, 2021; Feo & Celico, 2022). Si basa su un metodo conservativo ad alta risoluzione che cattura le discontinuità (*High-Resolution Shock-Capturing* HRSC) e che permette di seguire la dinamica temporale di un fluido immiscibile multifase in un mezzo poroso preservando, in modo accurato, le discontinuità di concentrazione. In particolare, CactusHydro risolve le equazioni che descrivono la dinamica della migrazione di un fluido multifase in un mezzo poroso composto da una fase non acquosa (n), acqua (w) ed aria (a) in una zona variabilmente satura. Durante la migrazione, la fase DNAPL è considerata immiscibile e gli effetti della volatilizzazione, biodegradazione o dissoluzione non vengono considerati. CactusHydro tratta il movimento verticale ed orizzontale del contaminante nella zona variabilmente satura come accoppiati ed è numericamente definito come una zona unica (non separando il movimento verticale da quello orizzontale poiché l'equazione del flusso include entrambe le zone).

Il modello qui presentato simula la migrazione di DNAPL con l'obiettivo di prevedere (*i*) la distribuzione dei prodotti liberi in acquiferi multistrato (fino a diverse centinaia di metri di spessore), e quindi (*ii*) la distribuzione di possibili fonti di inquinamento a lungo termine per acque sotterranee più o meno profonde. Nel dettaglio, in questo primo lavoro è stato simulato un primo scenario, con lo scopo di prevedere quale effetto abbia un primo orizzonte semipermeabile sul processo di migrazione verso il basso di PCE in fase pura. Il sito del test è l'acquifero alluvionale della pianura parmense (Nord Italia), dove il percloroetilene (PCE) è stato recentemente rilevato nelle acque sotterranee (Zanini *et alii*, 2019; Zanini *et alii*, 2021), suggerendo quindi l'esistenza di sorgenti di DNAPL. La simulazione ha consentito di accertare che il sistema multifalda oggetto di simulazione è vulnerabile rispetto ad un approfondimento dei percorsi di migrazione di PCE in fase pura, benché siano necessari tempi molto lunghi (circa un anno) perché il DNAPL riesca ad oltrepassare gli orizzonti semipermeabili.

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ABSTRACT

Chlorinated organic compounds widely contaminate aquifer systems worldwide (Doherty, 2000). They belong to the so-called DNAPLs (dense non-aqueous phase liquids), are denser than water, and have very low water solubility. Thus, they can migrate under pressure and gravity forces through the unsaturated and saturated porous medium until they reach a bottom aquiclude (Mercer & Cohen, 1990). They are usually detected in industrial and urban areas, persist in the environment, and are linked to toxic effects.

The behavior of chlorinated organic compounds in the subsurface has been studied since the early 1980s, *e.g.*, (Parker *et alii*, 1987; Kueper *et alii*, 1989). Some numerical models, including migration and remediation of alluvial aquifers (Guadano *et alii*, 2022), using the MT3DMS numerical code (Zhou *et alii*, 2023; Zheng & Wang, 1999), have been written to simulate their migration in aquifer systems.

The dynamics of a spilled DNAPL migration in a variably saturated zone can be described using numerical simulations for the governing equations of immiscible phase fluid flow in a porous medium. These are coupled with conserved partial differential equations for each fluid flow, based on the Darcy equation, together with the conservation of mass and an equation of state. They are written as a function of each fluid flow's saturation, capillary pressure, density, viscosity, permeability, and porosity.

Since each phase's capillary pressure and permeability are a function of the saturation, these equations are non-linear, with a dominant hyperbolic advection term proportional to gravity and the pressure gradient. It is responsible for forming sharp (shocks) front and rarefaction, which can create significant errors in the output results if not treated with conservative numerical solutions methods.

The present study deals with the three-dimensional (3D) numerical model implemented to analyze the expected impact of perchloroethylene (PCE) releases in multilayered aquifer systems characterized by the juxtaposition of more permeable layers (gravel and sand) with low-permeability layers (silt and clay).

A 3D numerical model is developed using the numerical code CactusHydro, introduced in (Feo & Celico, 2021; Feo & Celico, 2022). It is based on the high-resolution shock-capturing flux (HRSC) conservative method to follow sharp discontinuities accurately and temporal dynamics of a three-phase immiscible fluid flow in a porous medium. CactusHydro resolves the governing equations that describe the migration of an immiscible phase fluid flow in a porous medium composed of non-aqueous (*n*), water (*w*), and air (*a*), and a variably saturated zone. The migration of the spilled DNAPL is considered immiscible, and the effects of the volatilization, biodegradation, or dissolution are not considered. CactusHydro treats the vertical and horizontal movement of the contaminant in the variably saturated zone as a whole and is numerically resolved as a unique zone (not separating the vertical movement from the horizontal one since the flow equation includes both zones).

The model presented here simulates the DNAPL migration with the aim of predicting (*i*) the free-product distribution in multilayered aquifers (up to several hundred meters thick) and then (*ii*) the distribution of possible long-term pollution sources for shallow and deep groundwaters. A first scenario was simulated in detail, with the scope of understanding whether the interposition of a low-permeability layer between two higher permeability horizons can influence the vertical migration of DNAPLs. The test site is the alluvial aquifer of Parma Plain (Northern Italy), where perchloroethylene (PCE) was recently detected in groundwater (Zanini *et alii*, 2019; Zanini *et alii*, 2021), therefore suggesting the existence of DNAPLs sources. The results demonstrated that the PCE can migrate downward through low-permeability layers, even though a very low velocity was estimated.

Keywords: *DNAPL migration, high precision numerical simulations, groundwater contamination.*

INTRODUCTION

Chlorinated organic compounds widely contaminate aquifer systems worldwide. They belong to the so-called DNAPLs (dense non-aqueous phase liquids), are denser than water, with very low water solubility, and can migrate under pressure and gravity forces through both the unsaturated and the saturated medium until reaching a bottom aquiclude (*e.g.*, Mercer & Cohen, 1990). They are usually detected in anthropized areas due to their application in dry cleaning, metal degreasing, and chemical production. They persist in the environment and negatively impact on human health (*e.g.*, Henschler, 1994; Volpe *et alii*, 2007).

The present study deals with the three-dimensional (3D) numerical model implemented to analyze the expected impact of perchloroethylene (PCE) releases in multilayered aquifer systems characterized by the juxtaposition of more permeable layers (gravel and sand) with low-permeability layers (silt and clay). The method was introduced by (Feo & Celico, 2021; Feo & Celico 2022) and validated through a laboratory experiment (Feo *et alii*, 2023) and several applications (Feo *et alii*, 2023a; Feo *et alii*, 2023b; Feo *et alii*, 2023c; FEO *et alii*, 2023d). It is based on the high-resolution shock-capturing flux (HRSC) conservative method (Kurganov & Tadmor, 2000; Lax & Wendroff, 1960; Hou & Lefloch, 1994) to follow sharp discontinuities accurately and temporal dynamics of three-phase immiscible fluid flow in a porous medium. CactusHydro is based on the Cactus computational toolkit (Allen *et alii*, 2011; Goodale *et alii*, 2002), an open-source software framework for developing high-performance computing (HPC) simulation codes, and the data are evolved on a cartesian mesh using Carpet (Schnetter *et alii*, 2004; Schnetter *et alii*, 2006).

HYDROGEOLOGICAL FEATURES AND PCE CONTAMINATION AT THE STUDY AREA

Parma Plain has been recognized as an ideal test site for the simulation purposes of this work. The area is characterized by a continuous multilayer aquifer system composed of alternating fine-grained materials (clays and silts) and coarse-grained bodies (gravels and sands). These geological strata are part of the alluvial units that filled the basin between the Alps and Apennines (Po Plain) during the Pleistocene till the present (see Fig. 1). Sedimentation processes of the Parma sector of this sedimentary context is primarily a consequence of the depositional dynamics originating from the Apennine watercourse (*e.g.*, Taro River, Baganza Stream, and Parma Stream). The alternance of sediment grain size is linked, among other things, to climatic cycles and shifting riverbeds (Regione Emilia-Romagna & Eni-Agip, 1998; Pinardi *et alii*, 2023). In this multilayer aquifer groundwater, flowing almost entirely in the gravel and sand strata, exhibits a predominant southwest-to-northeast verse from the Apennine to the central Po Plain and consequently toward the Adriatic Sea (Zanini *et alii*, 2019; Feo *et alii*, 2023c; Pinardi *et alii*, 2023) (see Fig. 2). Concerning groundwater contamination, PCE was detected from 2002 to 2019 with concentrations up to 23 $\mu g/L$ (Zanini *et alii*, 2019; Zanini *et alii*, 2021) using institutional monitoring wells (Parma Municipality) and

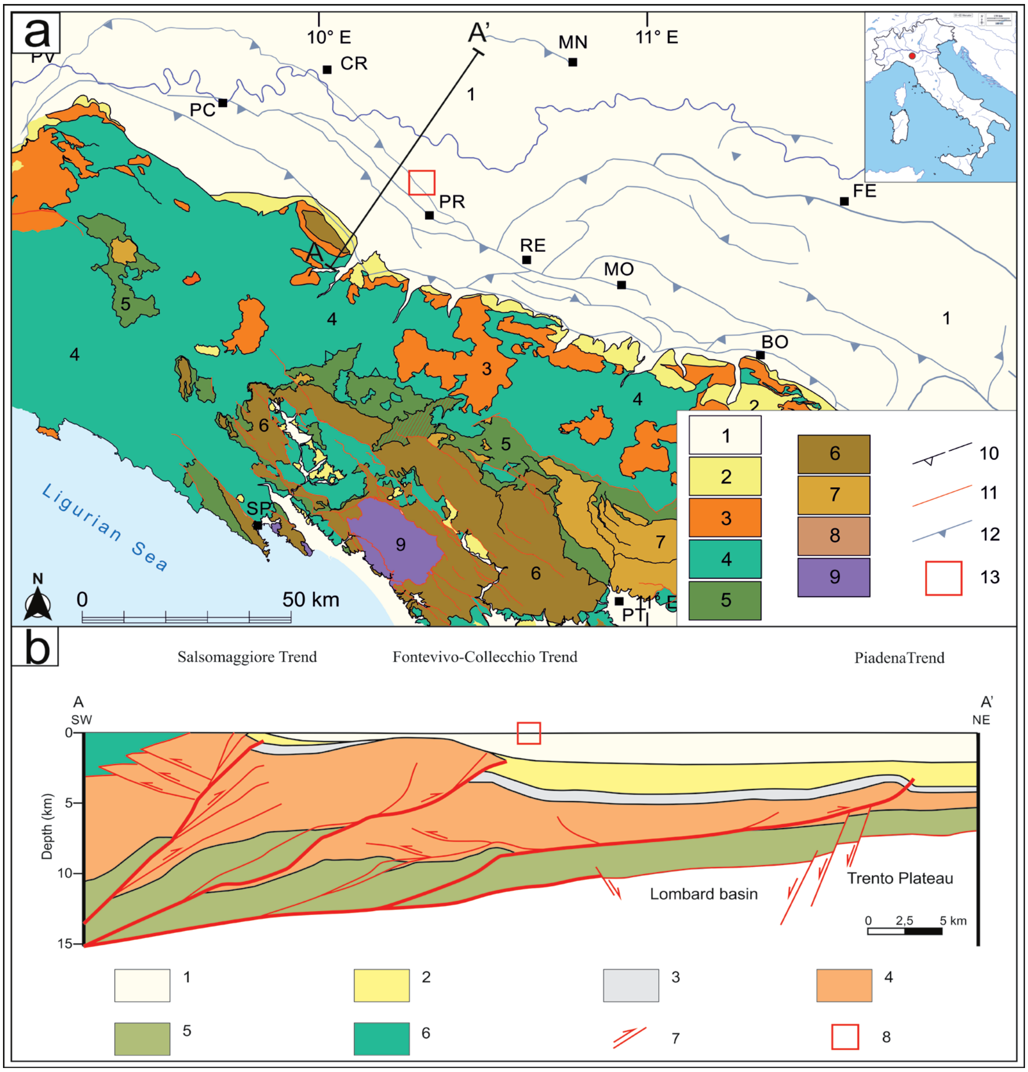

Fig. 1 - *Geological setting at basin scale, (1a) geological map modified from (Conti et alii, 2020) and (1b) geological cross section modified from (Livani et alii, 2018).1.a. Legend: [1] Quaternary Deposits; [2] Miocene-Pleistocene succession; [3] Epiligurian succession; [4] Ligurian Units; [5] Subligurian Units; [6] Tuscan Nappe; [7] Cervarola/Falterona Unit; [8] Rentella Unit; [9] Tuscan Metamorphic Units; [10] Thrusts; [11] Faults; [12] Subsurface thrust fronts below the Po Plain; [13] Study area geological context.1.b. Legend: [1] Pleistocene foredeep units; [2] Middle-Upper Pliocene foredeep units; [3] Lower Pliocene foredeep units; [4] Upper Eocene-Miocene foredeep units; [5] Norian-Middle Eocene passive margin units; [6] Allochtonous Allochthonous units; [7] Faults/Thrusts; [8] Study area geological context*

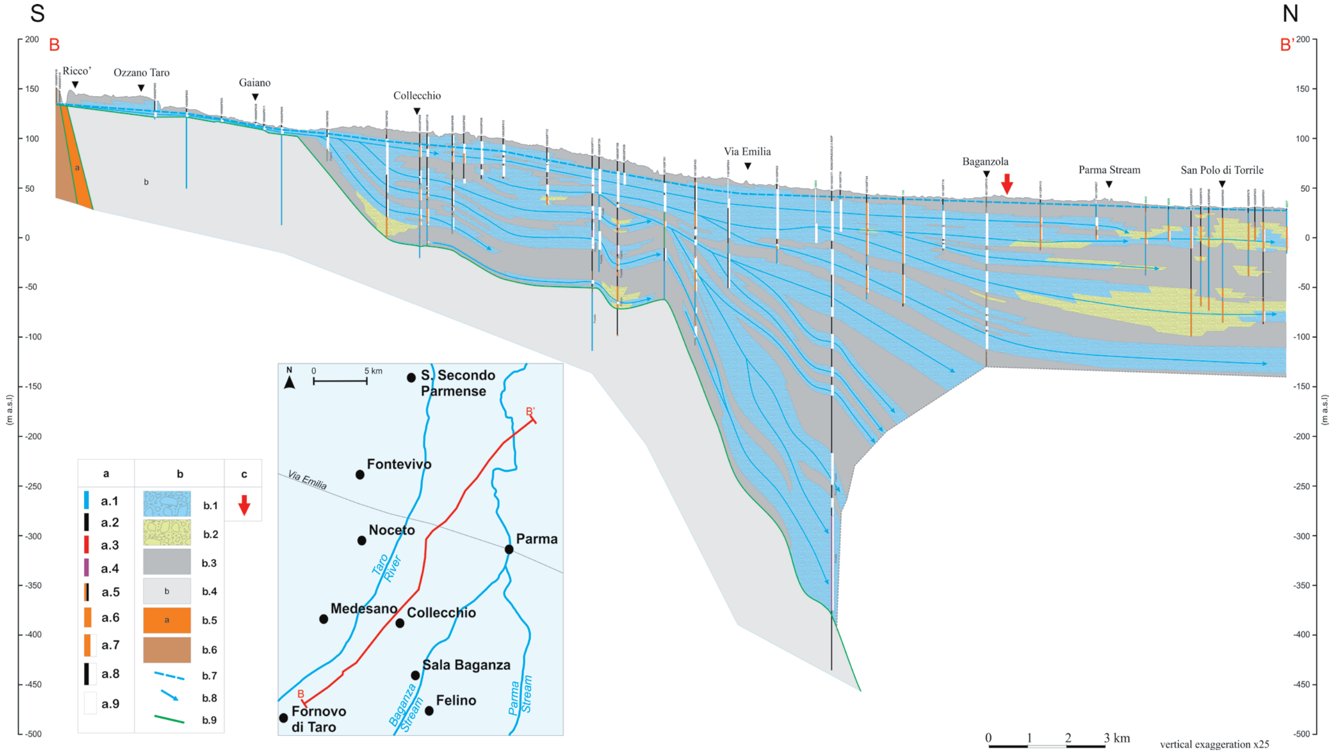

Fig. 2 - *The hydrogeological section at basin scale modified from (Pinardi et alii, 2023). Legend: [a] Borehole's simplified stratigraphic column symbols (a.1. Grey or light blue clay or silt; a.2. Yellow or brown blue clay-silt; a.3. Red or orange clay-silt; a.4. Peat; a.5. Silt; a.6. Sand; a.7. Gravel and sand; a.8. Gravel and clay-silt; a.9. Gravel); [b] Hydrogeological complexes and symbols (b.1. Gravel prevalence - Pleistocene/Holocene; b.2. Sand prevalence - Pleistocene/Holocene; b.3. Silt and clay prevalence - Pleistocene/Holocene; b.4. Clay – Pliocene; b.5. Clay – Messinian; b.6. Turbidite – Oligocene/Miocene; b.7. Hydraulic Head; b.8. Groundwater flow line; b.9. Stratigraphic contact); [c] Study area geological context*

piezometers drilled within the AMIIGA CE32 research project (UE INTERREG program). The PCE concentrations cyclically varied over time, with the highest detected in early recharge and the lowest concentrations in late recession (see Fig. 2; Feo *et alii*, 2023c).

The detection of PCE for over two decades, the cyclic variation of its concentrations over time, and the nearly constant peak concentration observed in different hydrologic years suggest one or more free-product DNAPL pools' upgradient regarding the observation wells used in (Zanini *et alii*, 2001). Therefore, taking into consideration (*i*) the layered hydrogeological setting of the whole system, as well as (*ii*) the existence of low-permeability layers interbedded within the coarse-grained ones (Ducci *et alii*, 2023), a 3D high-precision numerical model has been implemented to simulate the DNAPL migration and forecast its possible propagation towards the deep aquifer.

Concerning the hydraulic properties of the system, (Zanini *et alii*, 2019; Zanini *et alii*, 2021) determined a hydraulic conductivity varying from 1.2×10^{-5} to 4.9×10^{-5} m/s (mean 2.3×10^{-5} m/s; median 1.7×10^{-5} m/s) in coarse-grained horizons, and from 9.3×10^{-9} to 1.3×10^{-7} m/s (mean 1.6×10^{-7} m/s; median 9.7×10^{-8} m/s) in fine-grained layers.

HYDROGEOLOGICAL PARAMETERS OF THE NUMERICAL MODEL USING CACTUSHYDRO

The geological setting adopted for the simulation has been reconstructed by interpolating subsurface stratigraphic data using Leapfrog Geo software. This first passage allowed us to obtain three-dimensional top and bottom surfaces of aquifers and aquitards object of modeling. Consequent to the results obtained, a 3D numerical model has been developed using the numerical code CactusHydro, introduced in (Feo & Celico, 2021; Feo & Celico, 2022). CactusHydro resolves the governing equations that describe the migration of an immiscible phase fluid flow in a porous medium composed of non-aqueous (*n*), water (*w*), and air (*a*), and a variably saturated zone. The migration of the spilled DNAPL is considered immiscible, and the effects of the volatilization, biodegradation, or dissolution are not considered. CactusHydro treats the vertical and horizontal movement of the contaminant in the variably saturated zone as a whole and is numerically resolved as a unique variably saturated zone (not separating the vertical movement from the horizontal one since the flow equation includes both zones).

Table 1 shows the DNAPL (PCE) phase properties such as density, viscosity, and the hydrogeological parameter details

Parameter	Symbol	Value
Absolute permeability	k_1	5.102×10^{-12} m^2
Absolute permeability	k_2	5.102×10^{-14} m^2
Rock compressibility	c_R	4.35×10^{-7} Pa^{-1}
Porosity	ϕ_0	0.37
Water viscosity	μ_w	10^{-3} kg/(ms)
Water density	ρ_w	10^3 kg/m^3
DNAPL viscosity	μ_n	0.844×10^{-3} kg /(ms)
DNAPL density	ρ_n	1643 kg/m^3
Air viscosity	μ_a	1.8×10^{-5} kg /(ms)
Air density	ρ_a	1.225 kg/m^3
Van Genuchten parameters of SWRC	(n, m)	$\left(2.68, 1 - \frac{1}{2.68}\right)$
Irreducible wetting phase saturation	S_{wir}	0.045
Surface tension air–water	σ_{aw}	7.199×10^{-2} N /m
Interfacial tension non-aqueous–water	σ_{nw}	4.44×10^{-2} N/m
Capillary pressure air–water at zero saturation	p_{caw0}	676.55 Pa
Capillary pressure air–non-aqueous at zero saturation	p_{can0}	259.83 Pa

Tab. 1 - *Definitions of the parameters used in the numerical simulations of a DNAPL (PCE) migration in a variably saturated zone*

used in the numerical simulations. In particular, the density of the PCE contaminant is ρ_n = 1643 kg/m^3, and therefore denser than water. We also considered two different values of absolute permeability based on the values of the hydraulic conductivity previously mentioned. They are k_1 for a hydraulic conductivity of 5.0×10^{-5} m/s in a coarse-grained horizon and k_2 for a hydraulic conductivity of 5.0×10^{-7} m/s in fine-grained layers.

The van Genuchten parameter (Van Genuchten, 1980; Parker *et alii*, 1987) is $\alpha = p_c / \rho_w g^{-1}$, where p_c is the capillary pressure head. For "sand", the value is α = 0.145 cm^{-1} = 14.5 m^{-1}, and the capillary pressure between air and water, at zero saturation, gives:

$$p_{caw} = \rho_w g / \alpha = (10^3 \text{ kg / m}^3 \; 9.81 \text{ m / s}^2) / (14.5 \text{ m}^{-1}) = 676.55 \text{ Pa}.$$

Using the value of the interfacial tension $\sigma_{nw} = 4.44 \times 10^{-2}$ N/m and $\sigma_{aw} = 7.199 \times 10^{-2}$ N/m we have that $\beta_{nw} = \sigma_{aw} / \sigma_{nw} = 1.62$, and $p_{cnw} S_w = p_{caw} / \beta_{nw} = 417.62$ Pa. Then, the capillary pressure at zero saturation is $p_{can} = p_{caw} - p_{cnw} = 259.83$ Pa.

3D NUMERICAL SIMULATIONS RESULTS USING CACTUSHYDRO

The 3D numerical model developed in this study describes the scenario of a free-product PCE released into the environment that migrates downward in the variable saturated zone and forecasts its possible propagation towards the deep aquifer.

It is based on the reconstruction through interpolating the points of several surfaces that represent the existence of low permeability layers interbedded within the coarse-grained ones. See Fig. 3 for details. Between the red surface A_1 with georeferenced coordinates and the brown surface G_1, A_2 (cyan) and G_2 (purple), and A_3 (yellow) and G_3 (gray), the absolute permeability is k_1, while the rest has an absolute permeability k_2 (See Table 1 for details). The base aquiclude is impermeable with a permeability value of 5.102×10^{-19} m^2. The groundwater table surface is colored in blue.

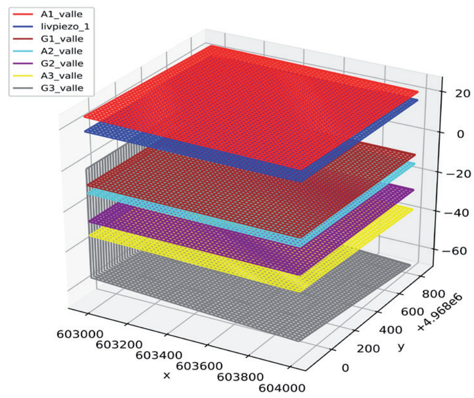

Fig. 3 - *The seven surfaces with georeferenced coordinates. Between the red surface A_1 and the brown surface G_1, A_2 (cyan) and G_2 (purple), and A_3 (yellow) and G_3 (gray), the absolute permeability is k_1, while the rest has an absolute permeability k_2 (See Table 1 for details)*

Initially, we consider a fixed volume of PCE (of density ρ_n = 1643 kg/m^3) released in the subsurface that migrates downward in the variably saturated zone. Figure 4 shows the interpolating cubic grid geometry used in this paper. We assume a variably saturated zone to be a parallelepiped of 80.0 m long, from x = [-40.0,40.0] m (left-hand side), 40.0 m wide from y = [-40.0,40.0] m (right-hand side), and 66.0 m depth from z = [32.0,-66.0] m. We then consider a spatial resolution of $dx = dy = dz = 2.0$ m and a time step resolution of $dt = 0.2$ s. The PCE is positioned at (x, y, z) = (0,0,20.0) m. The porous medium is composed of an unsaturated dry zone (air-DNAPL), the one depicted in white in Fig. 2, and a saturated one, the one depicted in blue, separated by a groundwater table surface (as shown in Fig. 3). The green color in the bottom represents the base aquiclude of the aquifer (Pliocene clay). The green color on the upper side represents the atmosphere.

After being released into the environment at atmospheric pressure, the DNAPL migrates downward into the unsaturated zone under the influence of gravity. Figure 5 shows the three-dimensional numerical simulation results of the saturation contours, $\sigma_n = S_n \phi$, at different times for the three-phase immiscible fluid flow (water + DNAPL + air) in a dry unsaturated zone. The saturation contours are viewed in the z - x plane on the left-hand side and the z - y plane on the right-hand side.

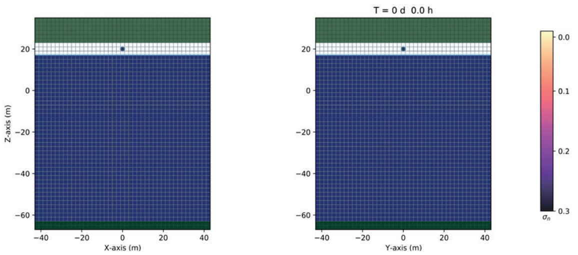

Fig. 4 - Example of the 3D interpolated grid geometry used in the numerical simulations of a three-phase immiscible fluid flow (water + DNAPL + air) and a spatial resolution of 2.0 m at different times. The grid dimension is 80 m ×80 ×98 m, at the initial time t = 0 s. The immiscible contaminant is situated on top of the interpolating cubic grid in the z-x plane view (left-hand side) and the z-y plane view (right-hand side), respectively. The green color in the bottom represents the conceptual base aquiclude of the aquifer. The green color on the upper side represents the atmosphere. The white color is the unsaturated aquifer. The blue color is the saturated one

The first panel represents the time $t = 1$ day and 21.5 hours (the initial time $t = 0$ s is depicted in Fig. 4) in which the PCE has already reached the groundwater table and entered in the saturated zone. Being denser than the water, it continues its migration downward. Due to an irreducible water saturation (see Table 1), part of the DNAPL remains trapped in the porous medium and does not move downward.

The groundwater flows from southwest to northeast at a basin scale (Pinardi *et alii*, 2023) with a hydraulic gradient equal to 0.00072, causing the contaminant to move slightly to the right. See the second panel of Fig. 5 (the left-hand side) at the time $t = 15$ days and 4.1 hours, while it remains symmetric in the z - x plane for all times (the right-hand side).

After 151 days and 16.9 hours (the third panel), the contaminant has reached the G_1 surface (see Fig. 3), where there is a low permeability (k_2). That is why the contaminant creates a sort of pool at around $z = -10$ m on top of the layer formed by the surfaces G_1 and A_2. Eventually, it continues to move downward in depth. In the fourth panel (after 310 days and 16.1 hours), the contaminant has reached the top of the G_2 surface, where the permeability is again k_2 between G_2 and A_3. That is why it creates a second pool at around $z = -27$ m.

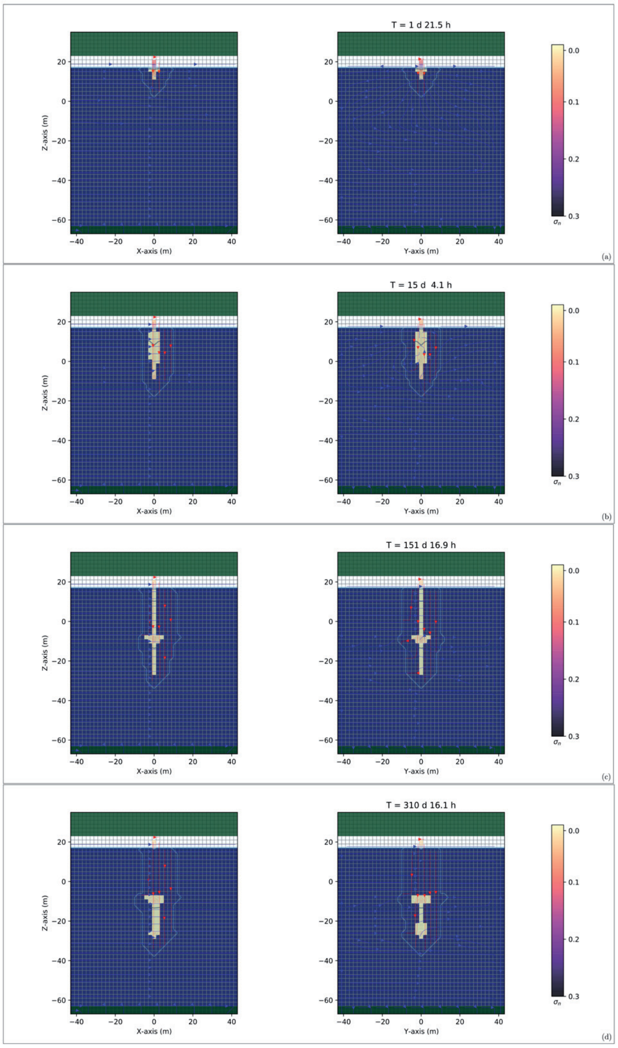

Fig. 4 - 3D numerical results on the saturation contours ($\sigma_n = S_n \ \phi$) of the three-phase immiscible fluid flow (water + DNAPL + air) in a variably saturated zone and a spatial resolution of 2.0 m at different times. The DNAPL migrates in depth through the low permeability layers interbedded within the coarse-grained one. The green color in the bottom represents the base aquiclude of the aquifer. The green color on the upper side represents the atmosphere. The white color is the unsaturated aquifer. The blue color corresponds to the saturated one.

CONCLUSIONS

In this work, we presented the first results of a 3D numerical modeling investigation on the migration of a free-product DNAPL (PCE) released in a multilayered aquifer system characterized by the juxtaposition of more permeable layers (gravel and sand) with low-permeability layers (silt and clay). The 3D numerical model is developed using the numerical code CactusHydro, introduced in (Feo & Celico, 2021; Feo & Celico, 2022). It is based on the high-resolution shock-capturing flux (HRSC) conservative method to follow sharp discontinuities accurately and temporal dynamics of a three-phase immiscible fluid flow in a variably saturated porous medium. The test site is the alluvial aquifer of Parma Plain (northern Italy), where PCE was recently detected in groundwater (Zanini *et alii*, 2019; Zanini *et alii*, 2021), therefore suggesting the existence of DNAPL sources.

The numerical results indicate that this numerical approach can simulate the PCE contamination migration and predict, among others, the free-product distribution in multilayered aquifers (up to several hundred meters thick) and the distribution of possible long-term pollution sources for shallow and deep groundwaters. The case study demonstrated that the PCE can migrate downward through low-permeability layers, even though a very low velocity was estimated. The following steps of this research will examine (i) the possible migration of PCE through deeper horizons within the multilayered aquifer system and (ii) the role of the slope of low permeability horizons in the contamination migration using the CactusHydro numerical code.

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