

Methodological approach for the estimation of recoverable LNAPL volumes in aquifer and for the analysis of residual phase behaviour in laboratory

Approccio metodologico per la stima dei volumi di LNAPL recuperabili in falda e per l'analisi del comportamento della fase residuale in laboratorio

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Riassunto: Le fasi libera e residuale sono le più abbondanti fasi di LNAPL (fase liquida leggera non acquosa) nel sottosuolo; perciò la stima del volume della fase libera e la comprensione del comportamento della fase residuale sono fondamentali al fine di un'efficace bonifica.

La stima del volume della fase libera presente in un sito contaminato è stata effettuata attraverso l'applicazione del Modello del Pancake e del Modello dell'Equilibrio Verticale. Tale stima mostra una notevole differenza tra i due modelli e tra i diversi metodi usati per la delimitazione dell'area. In particolare, i volumi stimati sono più bassi per il Modello dell'Equilibrio Verticale e la maggior differenza si osserva per maglie 200x200. I risultati evidenziano anche alcuni punti critici come il valore della porosità efficace; infatti l'analisi di sensitività mostra che una riduzione di questo parametro produce una variazione del volume stimato fino al 20%.

Il comportamento della fase residuale è stato analizzato attraverso test in colonna a scala di laboratorio realizzati usando tre differenti materiali porosi e il toluene come contaminante. La maggior saturazione residua e la minor dissoluzione nei materiali più fini dimostrano l'influenza del mezzo poroso sul comportamento del toluene. La minor dissoluzione è confermata anche dalla modellazione realizzata usando sia l'approccio tradizionale che quello basato sui dati sperimentali. L'analisi di rischio, condotta usando l'approccio tradizionale e un nuovo approccio sperimentale, mostra che quest'ultimo permette di ottenere un indice di pericolo più affidabile che tiene conto delle condizioni sito-specifiche.

Keywords: LNAPL, free phase volume, dissolution column test, risk assessment.

Parole chiave: LNAPL, volume della fase libera, prove in colonna di dissoluzione, valutazione del rischio.

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Abstract: Free and residual phases are the most abundant phases of LNAPL (light non aqueous phase liquid) in the subsoil; therefore the free phase volume estimation and the understanding of residual phase behaviour are fundamental for an effective remediation.

The volume estimation of free phase present in a contaminated site was carried out through the application of the Pancake Model and the Vertical Equilibrium Model. This estimation shows a remarkable difference between the two models and between the different delimitation area methods employed. In particular, the estimated volumes are lower for the Vertical Equilibrium Model and the higher difference is observed for a 200x200 mesh. The results underline also some critical points as the amount of the effective porosity; indeed the sensitivity analysis shows that a reduction of this parameter produce a variation of the estimated volume until to 20%.

The behaviour of residual phase was analysed through lab-scale column tests carried out using three different porous media and toluene as contaminant. The higher residual saturation and lower dissolution in finer materials reveal the influence of porous media on toluene behaviour. The lower dissolution is confirmed also by the modelling realized using a traditional approach and an approach based on experimental results. The risk analysis, carried out applying a traditional approach and a new experimental approach, shows that the last one allow to have a more reliable hazard index which contemplates the site specific conditions.

Introduction

LNAPLs (light non aqueous phase liquids) are the most common and harmful contaminants in groundwater being potential long-term sources of contamination and carcinogenic or toxic for human health (Bacocchi et al. 2010).

In the vadose zone, immediately following the release, LNAPLs typically migrate downwards under the gravity influence. This vertical migration up to the water table continues only if the capillary forces exceed the residual soil retention capacity. Once the LNAPL reaches the capillary fringe, the contaminant starts spreading laterally unless sufficient LNAPL potential energy exists for it to displace water and penetrate the water table (Brost and DeVaul 2000; CL:AIRE 2014). This condition happens when LNAPL reaches and exceeds the entry pressure, which is inversely proportional to the pore throat radius. The entry pressure, capillary, viscous and gravity forces are some of the key factors that control the behaviour of LNAPL and its partitioning in the free phase (liquid separated phase immiscible in water) and in the residual phase (adsorbed to solids particles). The residual phase is immobile (Feenstra 2005) and its saturation is lower than residual saturation, which is the fraction of available soil pore volume occupied by the immobile LNAPL (ASTM 2000). Contrarily, if the LNAPL saturation exceeds the residual saturation, the LNAPL becomes mobile (free phase) and can be transported in the subsoil.

Since free and residual phases represent the 99% of LNAPL in the subsoil, the first action to be conducted in a contaminated site is the recovery of the free product. Nevertheless, the complete recovery of all the LNAPL is difficult and usually causes the further development of the residual phase that can serve as long-term source of dissolved hydrocarbon plumes. Based on the above, it is necessary to quantify the free LNAPL volume present in the site and to understand the behaviour of residual phase, in order to have an effective remediation of the site.

To reach this goal, a contaminated site was used to estimate the volume of the free phase through the application of two different conceptual models: Pancake Model and Vertical Equilibrium Model. Although the Pancake Model has been overcome by more reliable methods, such as Vertical Equilibrium Model, in this paper it is adopted because of its easy application when site-specific data are not available. At the same time, the behaviour of residual phase was evaluated flanking the case study by column tests, carried out using different porous media and toluene.

The case study

The case study is a site of about 3.3 km², characterized by a diffused contamination by LNAPLs in free and dissolved phases and undergoing remediation through a horizontal barrier and a hydraulic barrier (consisting of 85 pumping wells and 20 Hot Spot pumping monitoring wells). In addition to wells of hydraulic barrier, in the site there are also 321 monitoring wells (95 m average spaced) used for groundwater level monitoring, for the evaluation of free LNAPL thickness

and for LNAPL and groundwater sampling. Stratigraphic logs allow identifying four different geological units (Pleistocene - Holocene): sands unit; clay-silty unit; sands and gravel unit; grey clay unit. The geological units correspond with four major hydrostratigraphic units: shallow aquifer; aquitard; deep aquifer and aquiclude (Mastrocicco et al. 2012). Only the unconfined shallow aquifer, characterized by sands and silty sands, is contaminated and subject to remediation.

In the contaminated monitoring wells, three different free LNAPL types have been detected: 1) gasoline (more of 70% of C₆-C₉); 2) diesel (more of 70% of C₁₀-C₃₀); 3) mixture of gasoline and diesel. In particular, in 54% of contaminated monitoring wells has been detected diesel, in 26% gasoline and in 20% mixtures of them.

In June 2013, the supernatant was unconfined (there is not a confining layer in the formation that prevents LNAPL movement upward) and its thickness measured in some of the monitoring wells ranged from few centimetres to 1.15 m without a homogeneous distribution (Fig. 1).

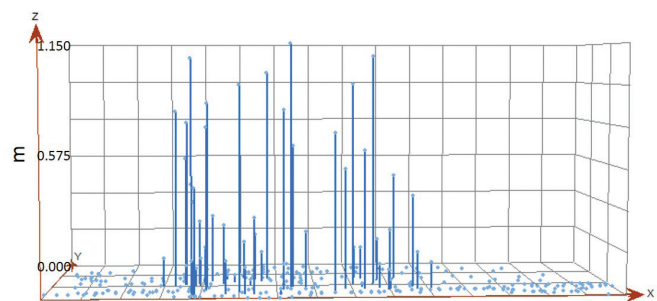


Fig. 1 - 3D representation of free LNAPL thicknesses (m) measured in the monitoring wells at June 2013.

Fig. 1 - Rappresentazione 3D degli spessori (m) di LNAPL libero misurati nei piezometri a Giugno 2013.

Materials and Methods

Two different conceptual models have been developed for the free phase volume estimation: Pancake Model and Vertical Equilibrium Model.

According to the Pancake Model, the migration of LNAPL to the water table and its lateral spreading through the capillary fringe creates a buoyant pool above the water table, with uniform and constant saturation, and consequently in the monitoring wells, an apparent thickness is observed (CL:AIRE 2014; Dippenaar et al. 2005; Gruszczenski 1987; Testa and Paczkowski 1989). This apparent thickness is higher than real thickness in the aquifer, due to the absence of the capillary fringe in the well that conducts to a lower level of water table in the well and hence to a more easily flow of free product in it (Hughes et al. 1988). This difference is related also to other factors, such as LNAPL density, volume of LNAPL release and grain size distribution of the aquifer that influences the capillary fringe (Testa and Paczkowski 1989). Owing to the difference between apparent and real thickness, it is necessary to correct the thickness measured in the well applying correction factors. In the case study, baildown tests

have been used to calculate the exaggeration factor (EF), in order to estimate the real thickness of free phase in the aquifer. This EF is calculated as the ratio between measured thickness and real thickness which is obtained by the baildown test chart applying the Gruszczenski or Hughes methods if, during the baildown test, respectively both supernatant and water or only supernatant are pumped (Gruszczenski 1987; Hughes et al. 1988).

Applying the Pancake Model, the procedure to obtain the free LNAPL volume consists of:

- 1) identification of monitoring wells with supernatant and its measured thickness;
- 2) identification of LNAPL and soil types present in the monitoring well;
- 3) identification of EF through baildown test;
- 4) application of an average EF and determination of real thickness in the monitoring wells where baildown tests have not been carried out, considering the LNAPL type present in the well;
- 5) determination of the specific thickness as the product of real thickness and effective porosity in function of soil type present in the well;
- 6) determination of the area of interest of monitoring wells;
- 7) estimation of free LNAPL volume as the product of specific thickness for area and sum of all volume obtained for every area.

The average EF is obtained considering the type of supernatant present in the monitoring wells; namely, the EF applied to monitoring wells not investigated and characterized by gasoline, has been obtained by the average of exaggeration factors derived by baildown tests realized in the monitoring wells with gasoline. The same procedure has been performed for the other LNAPL types. The average EF, obtained following this procedure, are 5.40 for mixtures of gasoline and diesel, 5.59 for gasoline and 7.9 for diesel.

The area for the volume estimation is calculated using two different methods: Thiessen polygons and grid at regular square mesh (100 m x 100 m and 200 m x 200 m). The mesh size is due to the available data; specifically the size has been chosen to have at least one or more points in the same cell. Thiessen polygons have been built by ArcGIS (ESRI Inc.) considering all the monitoring wells located in the site, therefore every monitoring point is associated to a polygon. In addition, in order to understand the influence of Thiessen polygons construction, new polygons have been reconstructed using both monitoring and pumping wells located in the site. However, the use of pumping wells can be considered less reliable for a correct volume estimation, since the pumping influences the measured product thickness and the LNAPL characteristics because of different LNAPL types mixing in the well.

For each Thiessen polygon a free LNAPL volume has been calculated, instead of the grid with regular mesh method, an average specific thickness has been associated to every mesh considering all the monitoring points present in the mesh.

The Vertical Equilibrium Model can be used only when

there is not persistence of release of contaminant (Lundegard and Mudford 1998), i.e. like the scenario considered in the study site. This model assumes that there is not a discrete layer of LNAPL floating on the water table, but that LNAPL can penetrate below the water table. In addition, the LNAPL saturation varies with the depth because the pore fraction occupied by product is less than 100% due to the presence of air and water (ITRC 2009; Lundegard and Mudford 1998). The saturation profile, whose shape depends on the capillary properties of the soil and the LNAPL characteristics, influences the LNAPL thickness in the monitoring well and its specific volume in the aquifer. Therefore, the Vertical Equilibrium Model requires the knowledge of the saturation profiles to calculate the specific volume. These profiles can be obtained using LDRM program (LNAPL Distribution and Recovery Model, distributed by American Petroleum Institute), a software which requires information about characteristics of LNAPL and affected aquifer (API 2007).

In the Vertical Equilibrium Model, the first two steps of the procedure followed for the free LNAPL volume estimation coincide with the first two steps used in the Pancake Model. Successively, it has been necessary collect data related to the parameters required by LDRM. These parameters, as product thickness, ground surface elevation, water table elevation, LNAPL density (average value) and LNAL viscosity (average value) have been derived from laboratory and field data. Instead, because of lack of site-specific data, surface interfacial tensions, N and α Van Genuchten parameters result from API (2006), effective porosity from Fetter (2001) and Kresic (2006), hydraulic conductivity and irreducible water saturation from the software HYDRUS (Šimůnek et al. 2013). Once all needed parameters are entered in LDRM, this provides the saturation profile, the specific volume (D_n) and the recoverable specific volume (R_n). Right now, as in the Pancake Model, the areas of interest of monitoring wells are defined using Thiessen polygons and grids at regular square mesh (100x100, 200x200). In this case, the Thiessen polygons reconstructed using both monitoring and pumping wells have not been considered. The reason is that the Vertical Equilibrium Model requires equilibrium conditions that can not be respected in the pumping wells due to possible presence of vertical gradient. Even the last procedure step coincides with the Pancake Model procedure and the free LNAPL volume is given by D_n for area. In this case, due the possibility to have the R_n , also the total free recoverable LNAPL volume has been calculated.

Since some parameters are derived from literature and they are not site-specific data, a sensitivity analysis has been carried out for one of this: effective porosity. This analysis has been performed, using both the conceptual models, applying a value of 0.20 instead of 0.25 for sands and a value of 0.15 instead of 0.20 for sands and silty sands.

Results and Discussion

The specific product thickness, obtained applying the Pancake Model, vary from 0.05 cm to 5.5 cm; instead, the

specific volume (D_n) and the recoverable specific volume (R_n), provided by LDRM based on Vertical Equilibrium Model, vary respectively from 0 cm to 8.58 cm and from 0 cm to 6.01 cm.

Based on these results, applying the procedure described above, the total volume of free product (Table 1) has been calculated using Thiessen polygons and grids at 200x200 m and 100x100 m mesh.

The application of the Vertical Equilibrium Model shows that about 70% of the product present in the site can be removed by pumping.

The comparison of results, derived applying the two conceptual models and the different methods to calculate areas, shows a difference of thousands of cubic meters.

The Vertical Equilibrium Model obtained values are lower than the Pancake Model results, probably due to the different LNAPL saturations considered in the two models (100% in the first one, lower and variable with depth in the last one).

In addition, the use of the different delimitation area methods leads to a significant difference of the estimated volumes. In particular, in both models, the higher volumes were estimated applying the Thiessen polygons, whereas the lower volumes were obtained using the 100x100 m regular mesh. Moreover, the difference between volumes estimated with the Pancake Model and the Vertical Equilibrium Model varies from 37% (100x100 m mesh and Thiessen polygons) to 51% (200x200 m mesh). These results allow supposing that the application of smaller cells can lead to a reduction of the differences, but at this stage, the average distance of 95 m between the available monitoring wells do not permit to use smaller cells and confirm this theory.

The Thiessen polygons method reveals another discrepancy, related to the construction method of these polygons; in fact, since they are created as a function of the distance and spatial distribution of the monitoring wells, they have different shape and dimension and this fact influences the volume calculation. The demonstration of the influence of Thiessen polygons construction method to the volume estimation is given also by the comparison of volumes obtained considering only the piezometers and those obtained considering both piezometers and wells; indeed this comparison shows a difference of about 2200 m³ between the two volume estimations. For this reason, the area delimitation represents a critical point in the free LNAPL volume estimation.

Another critical point, in this estimation, is the lack of some site-specific data as e.g. the effective porosity. Indeed, the effective porosity sensitivity analysis results show that the reduction of this parameter provides a reduction of about 20-22% of specific volume for sands and of about 25% for sands and silty sands leading to a reduction of total free LNAPL volume (m³) of about 20%. These results show as an unsuitable value of a parameter, e.g. effective porosity, can significantly influence the volume estimation leading to an inaccurate quantification of free LNAPL present in a site and this can compromise the success of a remediation.

Column test

As said above, the residual phase can serve as long-term source of dissolved hydrocarbon plumes and so, it is fundamental understand its behaviour and impact on the water quality, in order to accurately plan and realize an effective remediation coupled with a good cost/benefits ratio. At this aim, lab-scale column tests were performed.

Materials and Methods

The lab-scale column tests were carried out using different porous media (glass spheres, sandy soil A with 9% of silt and 1% of clay, sandy soil B with 14% of silt and 2% of clay) and toluene as contaminant.

The sandy soils, reconstructed in laboratory mixing different fluvial deposits and rock avalanche deposits, consist mainly of quartz, calcite, feldspars, muscovite and augite, and had a low total organic carbon (TOC), namely $0.192 \pm 0.01\%$ in soil A and $0.189 \pm 0.01\%$ in soil B.

The hydraulic conductivity, estimated by HydrogeoSieveXL (Devlin 2015) was approximately $6 \cdot 10^{-5}$ m/s in soil A and $3 \cdot 10^{-5}$ m/s in soil B.

Toluene (C₆H₅CH₃) (99.8% Sigma-Aldrich), characterized by a density, lower than that of water (856 g/L), and a solubility in water of 526 mg/L at 20°C (EPA 2015), was chosen due to its widespread presence in hydrocarbon-contaminated sites.

Fluorobenzene (C₆H₅F) (99% Sigma-Aldrich) was used as internal standard in static headspace gas chromatography-mass spectrometry (HSS-GC-MS) analysis. For analysis procedure, see Frollini et al 2016.

The experimental procedure consists of packing the cylindrical column (12.7 cm x 2.9 cm), with 6.7 cm of dried

Tab. 1 - Free LNAPL volume (m³) estimated applying the Pancake Model and the Vertical Equilibrium Model.

Tab. 1 - Volume di LNAPL libero (m³) stimato applicando il Modello del Pancake e il Modello dell'Equilibrio Verticale.

Delimitation area method	Free LNAPL Volume (m ³) Pancake Model	Free LNAPL Volume (m ³) Vertical Equilibrium Model
Thiessen Polygons (monitoring wells)	9002	5679
Thiessen Polygons (monitoring wells + pumping wells)	6856	-
Regular square mesh 200x200 m	8744	4288
Regular square mesh 100x100 m	4831	3024

soil (glass spheres in the control test) inserted between glass-microfibre filters and glass spheres of different dimensions (see Frollini et al. 2016 for details).

Once the column was packed, it was saturated, using a peristaltic pump, with deionized water (produced by reverse osmosis) from the bottom. This procedure allows removing gas bubbles trapped in the porous media and estimating (based on the water trapped in the column) the pore volume (PV) of the column that ranged from 20 ml to 30 ml. The second step considered the toluene introduction from top into the column to simulate the movement of contaminant into the saturated zone, until the water present in the column was completely displaced by toluene, indicating complete saturation with the organic liquid (Powers et al.1992; US EPA 1990). Once column was saturated with toluene, it was flushed from the bottom with deionized water at relatively flow rates (from 0.5 to 1 ml/min) for approximately 25 PV to displace the free toluene phase. Completed this step, the residual saturation was calculated as the ratio between volume of toluene remained in the soil and volume of toluene injected in the soil. The column test continued with the flush of deionized water into the column and with the analysis of effluent water, in order to assess the dissolution kinetics of toluene.

Analytical modelling of the experimental results flanked column tests. The results were modelled using a first order kinetic model and a traditional approach (Frollini et al. 2016). In the first case, the cumulative mass released by the soil is function of toluene concentration measured at the column outlet and of the water volume fed into the column; in the second one, it is function of solubility of the contaminant in water and of the water volume fed into the column.

The ratio between theoretical cumulative mass assuming saturation condition and the experimental cumulative mass, both calculated for a specific number of pore volumes delivered (n_{pv}^*), provides the correction factor (CF). The higher is the CF values obtained, the greater will be the overestimation of the mass release calculated assuming equilibrium conditions between the eluate and the LNAPL.

Finally, the experimental results were used also to perform a risk analysis. In particular, an effective hazard index (HI_{eff}) was calculated; it is directly proportional to hazard index (HI) estimated with traditional approach (ASTM-Risk-Based Corrective Action) and inversely proportional to the correction factor (CF) which is function of the pore volumes delivered (n_{pv}^*) (Frollini et al. 2016). The expected pore volumes delivered in field (n_{pv}^*) are directly correlated with groundwater velocity and exposure duration, and inversely correlated with the length of the source along groundwater direction and the effective porosity in the saturated zone.

Results and Discussion

The results of lab-scale column tests show that the residual saturation is function of the grain size distribution; indeed, residual saturations for glass spheres, soil A and soil B were respectively 36%, 70% and 77%, indicating an

inversely proportion between residual saturation and grain size dimension. The influence of soil properties on residual saturation is more remarkable if control test and soil tests are compared, rather than soil A test with soil B test. This difference is because the grain size distribution of soil A and soil B are similar (small difference of clay and silt percentages), whereas the glass spheres used in the control test are very different with respect to the two soils. The higher saturation in soils than in the control test can be due to the higher capillary forces that act in the soils to hold toluene rather than to the organic carbon, because, as shown above, the percentage of TOC present in soils were very low. Dissolution profiles (Fig. 2) show that the solubility of toluene in water was never reached during the test, except in some cases in the first samples collected by control test and soil A test. Conversely, in the soil B test, the solubility was never reached. In addition, it was observed that the concentration of toluene decreases more quickly with the increase of particle size. In the control test after approximately 50 PV the toluene concentration quickly dropped to less than 100 mg/L, instead in the soil tests this concentration is reached after 225-250 PV (Frollini et al. 2016). In addition, the reduction of toluene concentration is more gradual in the soil B (finer soil) due to capillary forces that in the finer soil are higher, holding more toluene leading to higher residual saturation and lower dissolution of residual phase.

First-order modelling results show a good correlation (ranging from 0.9680 to 0.9977) between the measured and simulated data (Fig. 2). Conversely, the traditional approach, which assumes that the eluate from the residual LNAPL is saturated with toluene, may lead to an overestimation of the true dissolved toluene concentration in water.

Risk analysis results (Fig. 3) highlight that the traditional ASTM-RBCA approach provides a unique value for both soil A and soil B. In addition, this HI value (180) does not change with the variation of source-zone length and groundwater velocity. This fact is due to the absence, in the ASTM-RBCA, of CF that is function of the mentioned parameters and can reach values of 200 (soil A) and 400 (soil B) at 10000 pore volumes delivered (n_{pv}^*). Hence, the traditional approach can lead to an overestimation of the HI for human health, especially in scenarios characterized by higher groundwater velocity and for sources characterized by lower lengths along the groundwater direction. Indeed, in these circumstances, the HI_{eff} is very lower than the HI estimated with the traditional approach (Fig. 3) and varies from soil A to soil B. As shown in figure 3, the HI_{eff} ranges from 0.2 to 148.9 in soil A and from 0.1 to 122.1 in soil B.

Based on these findings, it was also found that the approach proposed in some countries (Carlon 2007) to estimate the risk to groundwater resources based on conservative concentration thresholds may provide an inaccurate perception of the effective impact on groundwater quality. Indeed, the use of steady-state transport models combined with linear equilibrium partitioning model can be considered representative only of the very early stages after the contamination event.

Conversely, a risk assessment procedure, especially if coupled with the approach proposed in this work, that evaluates the risk based on the effective cumulative dose over the entire exposure duration, can account the observed rapid decrease, after a relatively short time, of contaminant concentrations in groundwater.

Conclusion

LNAPLs are a key environmental issue in contaminated sites due to their chemical-physical characteristics and their

possible negative effect on human health and ecosystems. In the subsoil, these contaminants are present for 99% as free phase (a mobile phase removable from subsoil by pumping) and residual phase (an immobile phase that cannot be pumped). The abundance of these phases in the subsoil and the difficulties encountered in their removal, lead to the necessity to quantify free LNAPL volume present in a site and to the need to understand the behaviour of residual phase. These will allow optimizing the planning and management of remediation and hence to achieve the goal, namely an

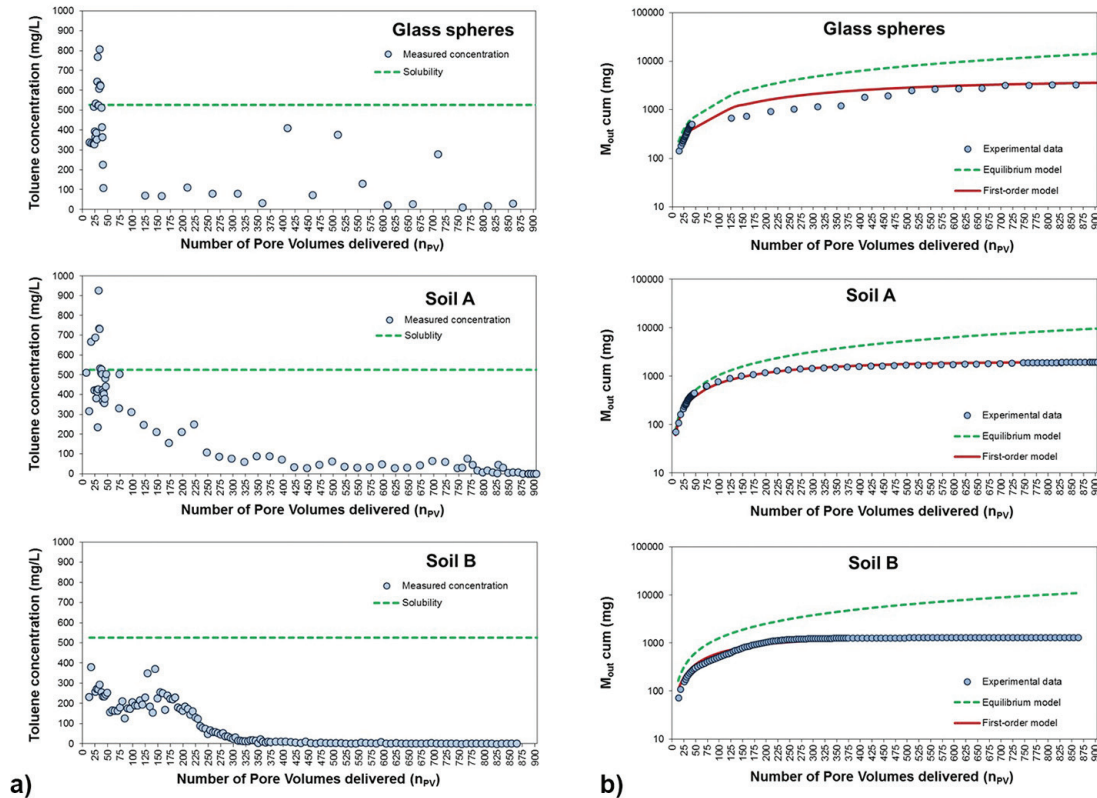


Fig. 2 - a) Dissolution profiles: Toluene concentration vs n_{pv} ; b) M_{out} (cum) vs PV. Experimental data, first-order model and expected release assuming equilibrium conditions (modified from Frollini et al. 2016).

Fig. 2 - a) Profili di dissoluzione: concentrazione del toluene vs n_{pv} ; b) M_{out} (cum) vs PV. Dati sperimentali, modello del primo ordine e rilascio atteso assumendo condizioni di equilibrio (modificata da Frollini et al. 2016).

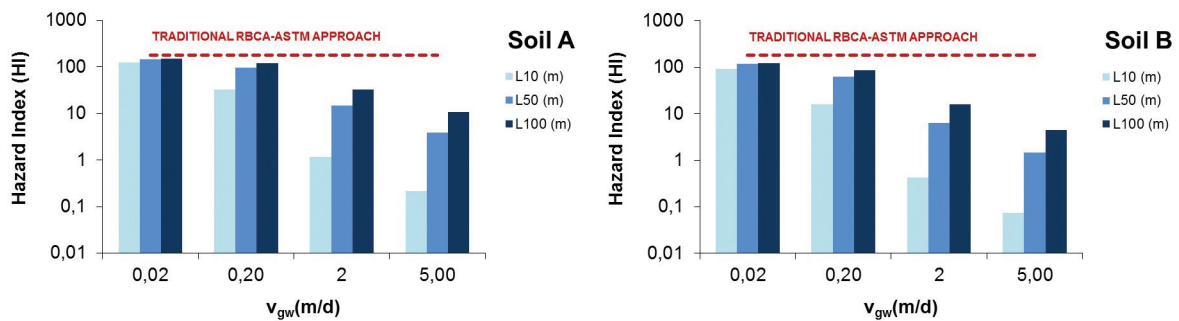


Fig. 3 - Risk analysis. Hazard Index of the soil A and soil B considering different groundwater velocity (v_{gw}) and different source-zone lengths (L10=10 m; L50=50 m; L100=100 m) (modified from Frollini et al. 2016).

Fig. 3 - Analisi di rischio. Indice di pericolo del suolo A e del suolo B ottenuto considerando differenti velocità dell'acqua (v_{gw}) e diverse lunghezze della zona sorgente (L10=10 m; L50=50 m; L100=100 m) (modificato da Frollini et al. 2016).

effective remediation considering also the cost/benefits ratio.

In this paper, methods and results for the free phase volume estimation and for the understanding of toluene residual phase behaviour have been shown.

The results of free phase volume estimation, obtained applying the Pancake Model and the Vertical Equilibrium Model, show some possible critical points, such as the area delimitation method, the presence of different types of LNAPL and the lack of some site-specific data as effective porosity. Indeed, the sensitivity analysis carried out for effective porosity shows that a variation of this parameter can produce a reduction until to 20% of the estimated volume. At the same time, the choice of a method, rather than another for the area delimitation, can provide a difference in the estimation up to almost 50%.

The experimental results obtained by lab-scale column tests show that the actual concentration released by residual phase of toluene is clearly below the solubility. In addition, the employment of different porous media, allows observing that the residual saturation and the release kinetics of the contaminant are affected by the soil properties. In particular, the finer materials host the majority of the toluene mass, leading to higher residual saturation and lower dissolution. This condition reflects in a remarkable reduction of HI_{eff} for the finer soil. Therefore, the proposed approach for the HI_{eff} evaluation can provide a more reliable hazard index considering the site-specific conditions.

It is hopeful that this integrated approach can be used in forthcoming studies, using different contaminants and porous media, in order to achieve more detail and clear knowledges on the dynamics that occur in a contaminated site, as to realize more efficient and effective remediation also more economically viable.

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REFERENCES

- API (2006) API Interactive LNAPL guide version 2.0.4. <http://www.api.org/oil-and-natural-gas/environment/clean-water/ground-water/lnapl/interactive-guide>.
- API (2007) LNAPL Distribution and Recovery Model. Volume 1. Distribution and recovery of petroleum hydrocarbon liquids in porous media. API Publication Number 4760, January 2007, American Petroleum Institute, Washington D.C.
- ASTM (2000) Standard Guide for Risk-based Corrective Action, ASTM, West Conshohocken, PA, 2000, E2081-00.
- Baciocchi R., Berardi S., Verginelli I. (2010) Human health risk assessment: Models for predicting the effective exposure duration of on-site receptors exposed to contaminated groundwater. *Journal of Hazardous Materials* 181:226-233.
- Brost E.J., DeVaul G.E. (2000) Non-aqueous phase liquid (NAPL) mobility in soil. *Soil & Groundwater Research Bulletin*, June 2000, n. 9, American Petroleum Institute.
- Carlson C. (2007) Derivation methods of soil screening values in Europe. A review and evaluation of national procedures towards harmonization. European Commission, Joint Research Centre, Ispra, EUR 22805-EN, 306 pp.
- CL:AIRE (2014) An illustrated handbook of LNAPL transport and fate in the subsurface. CL:AIRE, London. ISBN 978-1-905046-24-9 <http://www.claire.co.uk/LNAPL>
- Devlin J.F. (2015) HydrogeoSieveXL: an Excel-based tool to estimate hydraulic conductivity from grain-size analysis. *Hydrogeology Journal* 23: 837-844.
- Dippenaar M.A., Sole M.D., Van Rooy J.L., Du Troit G.J., Reynecke J.L. (2005) Determining actual LNAPL plume thickness: review and case study in fractured aquifer. *Bulletin of Engineering Geology and the Environment* 64: 347-360.
- EPA (2015) US Environmental Protection Agency, Toxicity and chemical/physical properties for Regional Screening Level (RSL) of Chemical Contaminants at Superfund Sites. <https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-may-2016>
- Feenstra S. (2005) Soil sampling in NAPL source zones: challenges to representativeness. *Environmental Forensics* 6 (1): 57-63.
- Fetter C.W. (2001) Applied Hydrogeology. Fourth edition. Prentice Hall, Inc.
- Frollini E., Piscitelli D., Verginelli I., Baciocchi R., Petitta M. (2016) A methodological approach to assess the dissolution of residual LNAPL in saturated porous media and its effect on groundwater quality: preliminary experimental results. *Water Air Soil Pollution*: 227-379. doi:10.1007/s11270-016-3077-7
- Gruszczenski T. S. (1987) Determination of a realistic estimate of the actual formation product thickness using monitor wells: A field bailout test. In Proc. Conf. on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration, Natl. Ground Water Assoc., Dublin, OH, 235-253
- Hughes J. P., Sullivan C.R., Zinner R. E. (1988) Two techniques for determining the true hydrocarbon thickness in an unconfined sandy aquifer. In Proceedings of the National Water Well Association of Ground Water Scientists and Engineers and the American Petroleum Institute Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration, vol. 1, 291-314
- ITRC (2009) Evaluating LNAPL remedial technologies for achieving project goals. Interstate Technology and Regulatory Council, LNAPLs Team. <http://www.itrcweb.org/guidance/getdocument?documentid=48>
- Kresic N. (2006) Hydrogeology and Groundwater Modeling. Second Edition. CRC Press, ISBN 0849333482, 9780849333484, 828 pp.

- Lundegard P. D., Mudford B. S. (1998) LNAPL volume calculation: parameter estimation by nonlinear regression of saturation profiles. *Groundwater Monitoring & Remediation*, 18: 88-93.
- Mastrocicco M., Colombani N., Sbarbati C., Petitta M. (2012) Assessing the effect of saltwater intrusion on petroleum hydrocarbons plumes via numerical modelling. *Water, Air and Soil Pollution* 223 (7): 4417-4427.
- Powers S.E., Abriola L.M., Weber W.J. (1992) An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: steady state mass transfer rates. *Water Resources Research* 28 (10): 2691-2705.
- Šimůnek J., Šejna M., Saito H., Sakai M., Van Genuchten M.Th. (2013) The HYDRUS-1D Software Package simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. http://www.pc-progress.com/Downloads/Pgm_hydrus1D/HYDRUS1D-4.08.pdf
- Testa S.M. and Paczkowski M. T. (1989) Volume determination and recoverability of free hydrocarbon. *Groundwater Monitoring & Remediation* 9: 120-128.
- U.S. EPA (1990) Laboratory investigation of residual liquid organics from spills, leaks, and the disposal of hazardous wastes in groundwater. EPA/600/6-90/004