Key Factors for Modeling Jet Fuel-Contaminated Site to Assess NSZD in Subtropical/Tropical Climates

Abstract #: 249
GROUP 3

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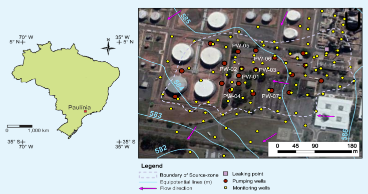
SITE CONTEXTULIZATION

A large jet fuel-impacted site is located in the municipality of Paulínia, São Paulo, Brazil. The estimated volume of LNAPL is nearly 520 m3.

The Cenozoic shallow aquifer is composed of coarse to fine sand lenses interfingered with clayey sandy lithologies deposited in a meandering river depositional environment dominated by floodplain facies. The hydraulic conductivity ranged from 1.2 x 10-7 to 2.4 x 10-4 m/s.

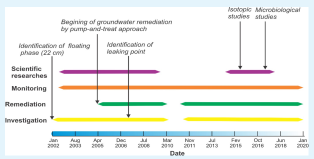
The contextualization of contamination has been described in several works, notably by Teramoto and Chang (2017), Isler et al. (2018), Teramoto and Chang (2019), Hidalgo et al. (2020), and Teramoto et al. (2020).



In February 2002, a 22-cm floating phase was recorded in a monitoring well during a site characterization survey. The study site underwent a detailed investigation because of the potential risk of LNAPL. A total of 104 monitoring wells were installed between 2002 and 2015 to assess LNAPL spread.

The exact spill location was identified only in July 2007 after a series of hydraulic (leakage) tests. A small diameter jet fuel pipe was identified as the leakage.

Activities regarding investigation, monitoring, groudwater remediation, and scientific researches were conducted between 2002 and 2017 proveding relevants insights with respect to NSZD in tropical/subtropical climates.



OBJECTIVES

Current understanding and research findings regarding LNAPL fate in the subsurface has been mainly conducted in the Northern Hemisphere, particularly in the United States and Canada, which are characterized by temperate and cold climates. Some key assumptions and conceptual models formulated in temperate climates could potentially guide to inaccurate diagnose of field data in tropical and subtropical climates. To describe the main findings obtained in 15 years of studies in a jet-fuel contaminated site, we present the main features controlling specificities of NSZD in tropical and subtropical climates.

NUMERICAL APPROACH

To predict the temporal change in the BTEX concentration in both the aqueous and non-aqueous phases within the LNAPL source zone, in which the LNAPL is mostly entrapped, we developed a numerical model within the representative elementary volume (REV) that represents a discrete portion of the LNAPL source zone. The temporal change in the BTEX concentration is driven by interphase mass transfer from the LNAPL to groundwater and biodegradation in the aqueous phase.The non-linear system of equations is solved numerically using the Gauss-Seide l iterative method, with central weighting of time until convergence is reached. Additional procedures were added to reproduce the effect of water table fluctuations in the REV-scale model.

$$C_{i,eq,t} = \gamma_i \left(M_{i,t} / \sum_{j=1}^{m} M_{j,t} \right) \cdot S_{i,sub}$$

$$E_{i,t} = A \cdot k_i \cdot (C_{i,eq,t} - C_{i,t})$$

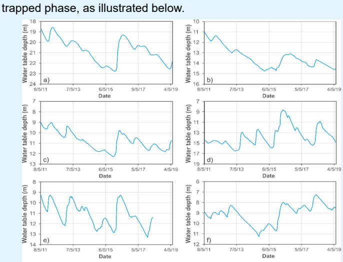
$$M_{i,t} = M_{i,t-1} - \frac{\Delta t}{2} \cdot (E_{i,t} + E_{i,t-1})$$

$$C_{i,t} = \frac{\left(C_{i,t-1} e^{-\lambda \frac{\Delta t}{2}}\right) + \frac{\Delta t}{2V_w} \cdot \left(A \cdot k_i \cdot C_{i,eq,t-1} + E_{i,t-1} - Q \cdot C_{i,t-1} e^{-\lambda \frac{\Delta t}{2}}\right)}{1 + \frac{\Delta t}{2V_w} \cdot (Q + A \cdot k_i)}$$

Where $C_{i,t}$ = aqueous concentration of compound i, $C_{i,eq,t}$ = equilibrium aqueous concentration of compound i, $M_{i,t}$ = mass in moles of the compound i (M), γ_i = activity coefficient of compound i, V_w = volume of water in the porous medium, k_i = coefficient of mass transfer ($L T^{-1}$), Q = flow ($L^3 T^{-1}$), A = interface area (L^2), $S_{i,sub}$ = solubility of compound i (M/L^3), and $E_{i,t}$ = exchange term of compound i (M/T). λ = first-order decay coefficient. The values of C_i, $C_{i,eq}$, M_i, and E_i, are marked by subscript t and t-1 to account for current time step and previous time step, respectively.

RESULTS

High amplitude of water table fluctuation is a common hydrologic phenomenon observed in tropical and sub-tropical climates. Differences between minimum and maximum recorded water table level easily exceeds 3 meters in a decadal cycle. As result of the high amplitude of water table fluctuation, the majority of LNAPL is distributed as entrapped phase, as illustrated below.



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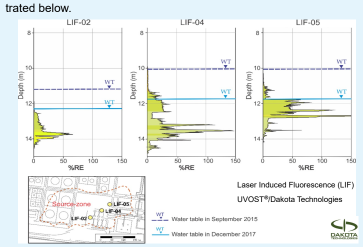
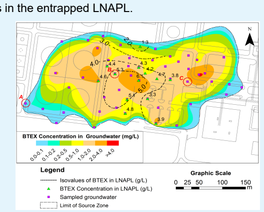
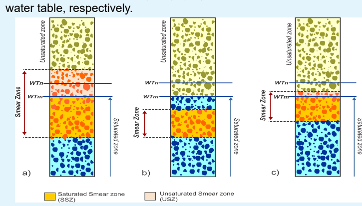


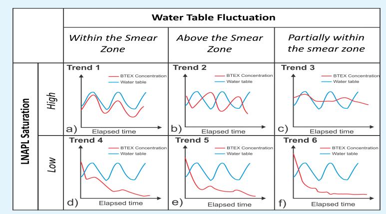
Because of the entrapment condition, partitioning to groundwater comprises themain process governing the LNAPL depletion. The concentration in the aqueous phase reflects the molar fraction of these compounds in the entrapped LNAPL.



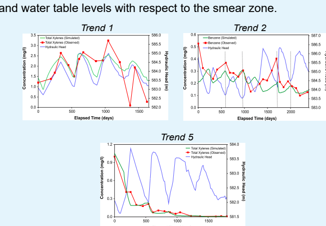
The water table can fluctuate partially within, completely within or above the smear zone. The smear zone is subdivided into two portions denominated the unsaturated smear zone (USZ) and saturated smear zone (SSZ), lying above and below the water table, respectively.



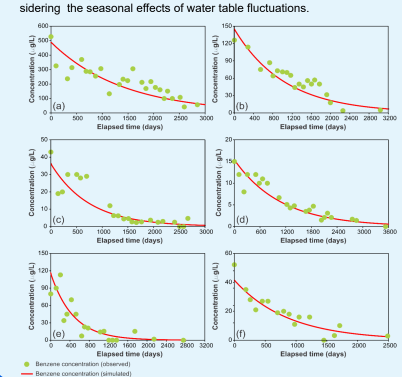
In the case of high LNAPL saturation, the mass of releasable BTEX in pores is large and the depletion trend is subtle. When LNAPL saturation in pores is low (<20%), the BTEX mass is also low, resulting in relatively faster depletion of BTEX, following a fickian first-order decreasing trend. Theoretically, the dissolved BTEX concentration based on combinations of the LNAPL saturation and water table fluctuations with respect to the smear zone follow 6 distinct trends.



The modeled concentration trend is capable of reproducing the field observations, confirming that the variation in concentration over time is a result of fluctuations in LNAPL saturation and water table levels with respect to the smear zone.



Phenomenologically, the changes in the evolution of BTEX concentration within the LNAPL source zone may be attributed to LNAPL saturation and water table fluctuations within, above, or below the smear zone. However, for NSZD purposes, long-term modeling of BTEX decline may be conducted without considering the seasonal effects of water table fluctuations.

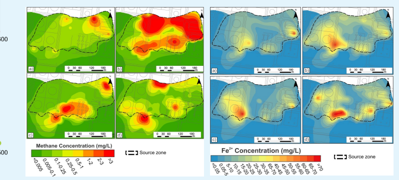


Owing to the abundance of iron in the aquifer, which is typical of lateritic aquifers in tropical environments, biodegradation via dissimilatory iron reduction is an important mechanism for BTEX mineralization. The overall reaction of hydrocarbon mineralization under iron reduction in a system buffered by the high partial pressure of CO_2 is described below:

$$C_7H_8 + 36FeOOH + 14H_2O + 65CO_2 \rightarrow 72HCO_3^- + 36Fe^{2+}$$

Direct interspecies electron transfer (DIET) between putative iron reducers and methanogens is an important metabolic pathway of hydrocarbon degradation in ecosystems with depleted electron acceptors, and this may play a role in hydrocarbon oxidation at the study site. Equation below describes the biodegradation of toluene through methanogenesis:

$$C_7H_8 + 5H_2O \rightarrow 4.5CH_4 + 2.5CO_2$$



CONCLUSIONS

- The findings on the Brazilian jet fuel-contaminated site serve as a reference guide for evaluating and understanding hydrocarbon contaminated sites in tropical and subtropical regions;
- Key factors controlling NSZD in subtropical/ tropical climates are large groundwaterr table fluctuation, which favors LNAPL entrapment, and high groundwater temperature (> 20 °C);
- Due to the entrapment condition, Natural Source Zone Depletion (NSZD) is primarily governed by the removal of soluble compounds from LNAPL to groundwater through interphase mass transfer;
- The modeling of LNAPL depletion by dissolution is the most appropriate approach for describing NSZD in tropical/subtropical climates;
- Rapid biodegradation is facilitated by high groundwater temperature, with dissimilatory iron reduction and methanogenesis being the main processes involved in hydrocarbon mineralization.

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