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A Review on Transport Modeling Of VOCs In Subsoil

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ABSTRACT: Volatile Organic Compounds (VOCs) are the most common subsurface environment contaminants usually in the form of Non-Aqueous Phase Liquids (NAPL) through Leaking Underground Storage Tanks (LUSTs) and pipelines, accidental spills, land disposal sites, and industrial waste impoundments. VOCs are toxic, mutagenic and carcinogenic. Hence, VOCs in subsoil pose a serious threat of groundwater contamination. Organic compounds, owing to their persistence and volatility, present unique environmental problems in the vadose zone of soils. The uncertainty in transport mechanisms and subsoil environment pose a serious challenge in developing transport model for VOC compounds. Apart from advection and dispersion, VOC also undergo several complex chemical reactions such as adsorption, degradation, volatilization and ionic exchange. The transport mechanisms and transport modeling studies for VOCs are largely based on extensive field studies and relevant laboratory experiments. The focus here is to review the role of transport mechanisms and modeling aspects of organic compounds in petroleum fuels and other such liquids and liquid wastes that have the potential to migrate through subsoil to groundwater and also to atmosphere by vapor diffusion.

KEYWORDS: VOCs, NAPL, Subsurface environment, Vadose zone, Transport mechanisms.

I. INTRODUCTION

Over the past centuries, organic compounds have been used widely in industries, and large amounts of organic wastes are expelled carelessly into the subsurface from leaking storage tank, accidental spill of petroleum hydrocarbons, agricultural pesticides usage, etc. Most of these volatile organic compounds (VOCs) are toxic even when the concentrations are in several part-per-billion (ppb)[1]. Sources of liquid disposal or discharge include liquid chemical waste and, or wastewater disposal lagoons/pits, effluent soakaways, infiltration/injection facilities and leaking sewers. Liquid wastes may contain water-miscible or immiscible NAPL VOCs with perhaps high solid/sediment contents better described as semi-liquids, liquid slurries or sludges [2]. Non-biodegradable VOCs can reach the water table through rapid vapor phase diffusion or transport in the aqueous phase [3]. Contaminants present in a waste matrix from a shallow matrix in the unsaturated zone above the water table can migrate to the ground surface and the water table. On an annual basis, the net movement of water in the unsaturated zone is downward into the water table [4].

In recent years a number of numerical models have been developed for predicting the movement of organic vapors in soils. These models have ranged from single-phase single component models that include dispersion and advection to three-phase (water–organic–gas) multicomponent compositional models that include advection, dispersion, capillary forces, and interphase partitioning of organic species between any of the phases present. All of these models are based on the assumption that Fick’s law is an adequate representation of gas-phase diffusion [5]. The transport of VOC through subsoil is accompanied by bio-geo chemical reactions due to the fact that the soil minerals are made up of chemically active and inert compounds. And also it comprises of microbial and organic matter upto certain depth in vadose zone. This leads to complex reactions when VOC is introduced into subsoil environment. But it may prove challenging to differentiate abiotic and biotic reaction contributions, particularly where products are similar, or several abiotic and biotic pathways exist [6].

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Scope of Review: Subsoil is a complex and uncertain environment. The transport mechanisms that govern the fate and transport of any contaminant released depends on a wide range of variable factors which are complex in nature. The transport mechanisms vary from place to place and time to time. Hence, prediction of VOC transport in subsoil need extensive and detailed field and lab studies with precise knowledge on basics of subsoil modeling concepts. The available literature and number of studies in this respect are very limited. Hence it is intended to shed light on the basic mechanisms of VOC transport modeling in subsoil environment.

II. LITERATURE SURVEY

Transport modeling of VOCs in subsoil environment

Fate and transport of fuel components in the subsurface at leaking underground storage tank (LUST) sites are determined by their physical and chemical characteristics and by the hydrogeological and geochemical conditions at the site [7]. Soil VOCs are difficult to describe because they occur in several phases such as gaseous, aqueous, sorbed and NAPL. The key controlling processes that influence the fate of contaminants at spill sites are the dissolution of the residual multi-component source; mass transfer of the dissolved organics from the residual zone to the flowing groundwater; transport in the groundwater by advection, dispersion and diffusion; sorption; and chemical and biological transformations [8]. During the migration of NAPL VOCs through the unsaturated zone, a certain amount of the liquid is retained in the soil by capillary forces. This trapped fraction is known as residual saturation, and may occupy 2-20% of the available pore space [9],[10]. Volatilization of this trapped liquid may result in significant vapor transport away from the NAPL source and contamination of clean soil or groundwater [9], [10], [11], even if the water table is very deep. Vapor transport occurs by both advection and diffusion and is influenced by partitioning between liquid and vapor phases and by sorption onto soil particles [10].

NAPL migration in the unsaturated zone is a complex multi-phase flow problem with various factors promoting the formation of shallow NAPL source zones. NAPL may partially penetrate the unsaturated zone and be restricted to shallower horizons due to layering or dissipation of heads driving NAPL movement [2].

Mass Transfer mechanisms: Spills of liquid hydrocarbons, referred to as NAPL, are known to contaminate the subsurface environment. During a spill event, bulk NAPL infiltrates horizontally and vertically until it becomes trapped in pores as isolated blobs, droplets, or ganglia. If bulk NAPL becomes entrapped below the water table, flowing ground water will dissolve soluble NAPL components and transport them away from the spill zone. Transport of these dissolved NAPL components is controlled by several processes including advection, dispersion, sorption onto aquifer materials, and liquid-liquid partitioning [12]. The lack of affinity for water causes fuel to attach, or sorb, readily to almost any type of soil [13]. The time required to remove a volatile liquid from a bed of sand by evaporation is directly proportional to the square of its depth. It takes four times as long to remove a volatile liquid by evaporation from a 200mm depth of sand as from a depth of l00mm. Also, the time for evaporative removal is inversely proportional to the partial pressure of the volatile liquid [14]. Depending on their water solubility and the composition of the entire NAPL phase, individual compounds slowly dissolve out of the NAPL phase into the flowing groundwater. This phenomenon can in many cases be described by Raoult's law, which states that the saturation concentration of a substance in groundwater at equilibrium depends on the molar fraction of that substance in the mixture. Components of higher solubility are removed from the source zone preferentially, thus their mole fraction decreases over time and subsequently the concentrations of these compounds emanating from the source zone decreases. Whereas, less soluble compounds within the contaminant mixture increase in their mole fraction over time, and their concentrations in the flowing groundwater also increase. In general, higher groundwater flow rates result in larger amounts of NAPL being removed from the source zone [8].

Basics of VOC transport modeling: Transport modeling of VOC in any environment is a set of natural processes or mechanisms which may be the combination of biotic and abiotic and that are occurring either simultaneously or in a sequence. In the case of VOCs, volatilization is a governing factor in vertical transport in subsoil environment. Temperature

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and density of VOC are the key factor that governs the rate of volatilization. The process occurs through vapor diffusion and advection. The vapor transport either retards or enhances the downward movement VOCs into groundwater.

VOC diffusion coefficients in the gas phase are up to 4 orders of magnitude greater than those in the aqueous phase. Hence the presence of air causes diffusive fluxes in the unsaturated zone to be significantly greater than those in the saturated zone [15]. Vapor advection is driven by pressure or vapour–density gradients and may be responsible for more rapid and extensive gas and VOC transport at sites than can be accounted for by diffusion alone [16],[17],[18].

Sorption is also one of the mechanisms which is a reversible phase-partitioning process that may lead to retardation of VOC migrating in mobile gas and aqueous phases [2].

Biodegradation of VOCs occurs when suitable bacteria, carbon sources, terminal electron acceptors and nutrients are present and factors such as moisture, pH and temperature are conducive. The vast majority of VOC biodegradation research has been undertaken in the saturated zone and has been driven by monitored natural attenuation interests, both for petroleum Aromatic Hydrocarbons and Chlorinated Aliphatic Hydrocarbons at contaminated sites generally [19].
The basic processes that are included in VOC transport model formulation are:

1. Advective-dispersive transport in the mobile water.
2. Diffusional mass transfer within the gaseous phase.
3. Instantaneous mass transfer between water and gaseous phases residing in mobile region and similarly between water and gaseous phases residing in immobile region.
4. Instantaneous mass transfer between water and solid phases in mobile region and in immobile region.
5. Diffusional mass transfer between mobile water and immobile water.
6. First order degradation in water and solid phases present in mobile as well as immobile region.

Mass transfer between gas and liquid phase will be assumed to be instantaneous and governed by Henry's Law [20].

III. MODELLING CASE STUDIES

The fate and transport of petroleum-hydrocarbon contaminants in subsurface environments can be characterized by multiphase multicomponent simulation models. A number of modeling works have been undertaken over the past decades, aiming to characterize Petroleum contaminants fate and transport processes in subsurface environments [21]. Vertical migration through the unsaturated zone is represented by a one-dimensional solution to the advection–dispersion equation, which is used to calculate the solute flux at the water table. This is coupled to a solution to the three dimensional advection–dispersion equation in Laplace space to represent the subsequent lateral groundwater transport [22].

Extensive field, laboratory and modeling studies have contributed the whole scenario or significant part of the problem in understanding the transport of VOCs are discussed in this section. Case studies that have comprehensively addressed the problem of leached VOC plume generation, transport and attenuation in the unsaturated zone are rare. This lack of comprehensive transport modeling studies represents a key research need.

Transport mechanism studies for describing natural attenuation and remediation potential at a crude oil spill site, Bemidji, Minnesota, US located on a glacial outwash. The study included multicomponent gas transport, solute transport, and the most relevant biogeochemical reactions [23]. Similar studies were conducted at Hanford site, Washington State to determine the role of complex mechanisms such as geochemical, biological and hydrological factors involved in transport of NAPL and carbon tetrachloride compounds into deep groundwater reserves at 100m below the surface [24].
A thorough study of immobile flow in unsaturated porous media was performed and a theory was proposed stating that the immobile zone is not fully immobile and it in fact carries a minor flow. Such minor flows are critical in practical conditions as it can transport the contaminant through vadose zone to the ground water below. A numerical model was developed to represent this phenomenon [25].

[26] Illustrated the application of a 1-D finite difference model VLEACH that assesses the effect of leached, volatile and sorbed contaminants through vadose zone into groundwater. It primarily describes the vertical transport rates of VOC tri-chloro ethylene in vadose zone. The study concluded that a high source concentration of VOC will lead to significant downward advective gas phase transport in a soil with high air permeability. 1-D and 3-D analytical models were developed to simulate steady state and transient leaching from shallow VOC sources and apply their models to site investigation data. The models included the essential processes inherent to the VOC leaching scenario: advection (water phase vertical flow), dispersion, sorption, water/air phase partitioning (volatilization), first-order degradation in the water phase [27].

Majority of the models in the literature neglect the effect of air flow on contaminant transport in unsaturated soil or assume a constant pore air pressure equivalent to the atmospheric pressure. A finite transport model was developed to address factors such as; Water flow, Air flow, Contaminant transport due to the transient flow of water and Contaminant transport due to the combined effect of transient flow of water and air are considered. It was applied to assess the potential transport of petroleum based contaminant site at Southwest of England. A thorough study of immobile flow in unsaturated porous media was performed and a theory was proposed stating that the immobile zone is not fully immobile and it in fact carries a minor flow. Such minor flows are critical in practical conditions as it can transport the contaminant through vadose zone to the ground water below. A numerical model was developed to represent this phenomenon [25].

IV. CONCLUSIONS

Unlike other liquid contaminants, VOCs in subsurface environment undergo a complex multiphase transport which is brought about by advection, diffusion, volatilization, adsorption, absorption and dissolution. Volatilization is the major transport factor which governs the depth of penetration of such contaminants due to ambient air temperature and relative variations in soil temperature. The effect of VOC volatilization reduces exponentially with increase in subsoil depth, hence increases transport of such contaminants into groundwater in case of deeper contaminant source. And also the downward transport of VOCs in unsaturated soil is affected by presence of air in unsaturated zone of subsoil. The case studies with detailed modeling of VOC transport in subsoil environment are not conducted extensively. Hence, the need for extensive lab and field studies are required to establish a benchmark in transport of such complex contaminants in subsoil and groundwater.

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