A Review on Bio Degradation of VOC's in Subsoil

Sadashiva Murthy B. M[*], Udayashankara T. H[*]
* Professor - Department of Environmental Engineering,
SJ College of Engineering,
Mysore-570006.

Adarsh S. V[**]
** Research Fellow - Department of Environmental Engineering,
SJ College of Engineering,
Mysore-570006.

***Abstract* :- Bioremediation can remove petroleum products from soil that has been contaminated by leaking underground storage tanks, abiotic processes such as evaporation can contribute significantly to the overall removal process. Biodegradation is an important natural attenuation mechanism since it is the only process whereby there is a reduction in total hydrocarbon mass is achieved. It is learnt that more than 200 species of bacteria, yeast and fungi are capable of degrading petroleum hydrocarbons. The inclusion of biodegradation in vadose zone transport of BTEX (benzene, toluene, ethyl-benzene and xylene), and fuel hydrocarbons has been studied. Based on the observed soil vapor profile, first-order biodegradation rates were observed for diffusion and bio decay. Degradation rates were found to compare well to other reported laboratory and field data, however, there is still significant uncertainty regarding biodegradation rates. The main intention of this review was to evaluate biodegradation as significant process in vadose zone to degrade VOC's naturally over a relatively small depth interval.**

Keywords: VOCs, Biodegradation, BTEX, Vadose Zone, Degradation Rate.

1. INTRODUCTION

The need to provide treatment for soils contaminated with hazardous materials from accidental spills and land based handling operations has become increasingly apparent. Many of these hazardous materials contain VOCs that volatilize and pass through the soil as a vapor. To develop adequate treatment and control for volatile air emissions and to predict the fate of chemical constituents in soil, it is necessary to understand the fundamental processes and interactive mechanisms that occur in soil. Such knowledge can be utilized both to provide criteria for designing soil decontamination processes and to evaluate the feasibility of soil biofilters as an alternative bioremediation technology at hazardous waste sites and for industrial vapors and exhaust gases (English C.W. et al., 1991). A major concern with the presence of hazardous compounds in soils is the movement of contaminants into groundwater. Evidence for vadose zone biodegradation of BTX or fuel hydrocarbons has been seen at a limited number of field sites, several analytical models for hydrocarbon vapor transport that include biodegradation have been proposed which include a model incorporating vapor-phase and aqueous-phase diffusion and aqueous-phase advection, subject to sorption and first-order decay, (Jury et al., 1990), and a model for steady-state vapor-phase diffusion, subject to first-order decay, (Johnson et al., 1998). Incorporating biodecay in models simulating soil vapor transport to indoor air, in some instances, reduces predicted exposure concentrations by several orders-of-magnitude. Therefore, sound evaluation of biodegradation potential is essential. Multiple lines of evidence should be considered while evaluating vadose zone intrinsic biodegradation, as typically conducted for dissolved hydrocarbon fate in groundwater. Lines of evidence include: field measurements indicating that hydrocarbon vapor concentrations are being attenuated beyond levels that would be expected for other non-destructive mechanisms, ii. Geochemical data showing the depletion of electron acceptors and generation of metabolic by-products, and iii. Laboratory studies. BTEX (Benzene, Toluene, Ethyl-Benzene and Xylene), generally including benzene, toluene, ethyl benzene and o, m, p-xylene, is a class of toxic organic pollutants in lakes and rivers. In addition, BTEX in water environment makes different migration and transformation process with its physical and chemical properties and environmental conditions, such as volatilization, microbial degradation, photolysis, hydrolysis, and sorption. In recent years, the pollution of BTEX has been getting worse along with industrial development (Lizhi-ping et al., 2010). oil contamination such as BTEX in soil and groundwater may be generated by accidental spills from deliberate dumping, leaching of older landfills, leaking of underground storage tanks, trucks and pipelines or residue of oily wastewater irrigation, When gasoline comes into contact with water, BTEX will rapidly partition out of the fuel and enter into water because of their high aqueous solubility. Once in the water, they are rapidly transported and do not adsorb to sediment or other organic material because of their low octanol - water partition coefficient. BTEX, which are considered to be priority pollutants, are volatile organic compounds (VOCs), most of them can volatilize from water into air. The residue in water or soil can be biodegraded, and the half time of benzene was about a few days or several months. In the vadose zone, the ground consists of soil particles (solids), voids (pores), air, and water. The soil properties such as porosity, moisture content, pore geometry, horizontal and vertical soil layering and other

features may influence diffusion or volatilization. The diffusion rate of volatile compounds is expected to decrease with increasing moisture content in soil. The presence of a thin soil layer of high moisture content reduces the gaseous concentrations of benzene and toluene and stopped the migration of ethylbenzene and m-xylene vapors. Additionally, biodegradation is other important effectors that cannot be overlooked (Chen Wei-sheng et al., 2010). The prevalence of hydrocarbon-contaminated sites and the high degree of toxicity and aqueous mobility of hydrocarbons has resulted in numerous investigations into the fate of hydrocarbons in the subsurface. A number of electron acceptors in subsurface environments can be utilized by bacteria to mediate the oxidation of hydrocarbons; however, the rates of degradation can vary significantly under different electron-accepting conditions (Krumholz et al., 1996). In the absence of oxygen, the oxidized forms of inorganic species are used by microorganisms as electron acceptors. In most sand and gravel aquifers, Fe (III) oxides are abundant, yet the spatial distribution of sedimentary iron may be heterogeneous at scales ranging from the entire formation, which may be tens of meters thick, to individual depositional layers that may be only a few centimeters thick. As degradation reactions progress in a contaminated aquifer, the distribution of solid-iron phases can change over time and space, altering the biogeochemical processes that affect the fate and transport of hydrocarbons, Characterization of the small-scale spatial variability of biogeochemical processes provides insight into how naturally occurring microbes degrade hydrocarbons in contaminated aquifers and may improve estimates of hydrocarbon degradation rates. It has been demonstrated that closely spaced sampling is required to identify microbiological processes in contaminated aquifers (Isabelle M. Cozzarelli et al., 1996). Microbiological degradation of the vapors can naturally attenuate the pollutants and prevent or reduce the groundwater contamination at spill sites where the residual fuel is retained above the groundwater. Knowledge of the biodegradation rates and kinetics of volatile organic compounds (VOCs) in the unsaturated zone is thus a prerequisite for groundwater risk assessment. For biodegradable compounds, natural attenuation in the vadose zone is difficult to assess. Aerobic biodegradation can lead to vertical gradients of oxygen in vadose zones of a few meters thickness. The correct prediction of natural attenuation thus depends very much on the proper design of experimental approaches that take into account the possible reductions in oxygen concentrations. (Patrick Hohener et al., 2006).

2. INTRINSIC BIODEGRADATION

Diffusion, sorption, and biodegradation, for non-recalcitrant VOCs, are generally thought to have the most significant effect on VOC fate and transport within the zone. Biodegradation is an important natural attenuation mechanism since it is the only process whereby there is a reduction in total hydrocarbon mass. More than 200 species of bacteria, yeast, and fungi capable of degrading

petroleum hydrocarbons have been identified, with *Pseudomonas* spp. and *Corynebacterium* spp. thought to be the two major bacterial agents. Aerobic biodegradation of petroleum hydrocarbons will occur in the vadose zone providing there is sufficient oxygen indigenous microbes that produce enzymes capable of degrading the compound of interest, soil moisture, nutrients and appropriate pH, temperature and salinity conditions, and no inhibiting materials. (Ian Hers et al., 2000)

Conceptually, there are several ways in which a building or other similar surface barrier, Could affect intrinsic biodegradation. For aerobic degradation of VOCs, the ability of oxygen to diffuse, or be transported through advection to below the building is of 2 critical importances. Oxygen replenishment will be a function of the diffusivity and Permeability of near surface soils and the subsurface building structure, and gradients driving these processes. Advective transport of soil gas through shallow soil can occur as a result of changes in atmospheric pressure and temperature gradients (Massman and Farrier, 1992.)

A building or other low permeability structure will also eliminate surface water infiltration below the structure footprint and potentially promote long-term drying of the soil. While there is little, direct study of the effect of soil moisture on intrinsic biodegradation, bioventing studies suggest that biodegradation rates are significantly reduced for low moisture contents (Zwick et al., 1995.)

3. ESTIMATION OF FIELD BIODEGRADATION RATES

Although there is evidence for VOC biodegradation at the site, no simple method is available to extract directly biodegradation rate coefficients from the measured concentration profiles in the field. At the Vaerlose field site, the geometry of the experimental setup (depth of source center, depth of water table) and the relatively isotropic porous medium led to vapor contour shapes in the approximated form of (hemi) spheres. Data was selected the for m-xylene on day 30, which show almost hemispherical contours, to test whether the point by point interpretation of plume data with the steady-state solution of the radial-symmetric analytical reactive-diffusive transport model gave useful estimates of the apparent first-order biodegradation rate coefficients. This evaluation of degradation rates for m-xylene on day 30 yielded degradation coefficients which varied extremely. The variability probably reflected only partially the true spatial variability of the degradation rate, and more likely also the local analytical errors and local variability in soil parameters. Furthermore, it was recognized that the land surface boundary condition affected the profiles in the vertical direction, giving high rates near the surface erroneously affected by mass loss to the atmosphere. In order to obtain rate data without bias in shallow depths and near the source where concentration gradients are small, the rate analysis was performed at the source depth (1.05 m) and with a method integrating over larger lateral distances. Since the absolute lateral attenuation distances varied from less than 2 m to over 18 m between

compounds, the concept of the compound-specific relative distance for attenuation by a factor of 1000 (0.001) was used. The attenuation factor 0.001 was chosen because it ensured to investigate a large integrating volume around the source and kept at the same time a safe margin with respect to the analytical detection limit of the data. Data analyzed from day 30, 70 and day 87 in analysis to cover the period in which plumes were stable and biodegradation activity was highest. Due to the discrete lateral spacing of soil gas probes, an uncertainty of the lateral attenuation distance r0.001 is imposed, together with the uncertainty of the tortuosity-corrected diffusion coefficient. The other compounds, which had larger lateral migration distances, yielded rates which compare fairly well, but are subjected to higher uncertainty. The deviation of the fast-degrading compounds may originate from the fact that the plume shapes were not always (hemi) spheres as assumed by the model, but rather laterally elongated spheres, which indicates that diffusion was not isotropic. It should be noted, furthermore, that the spacing of soil gas probes near the source was denser than at larger distances, and the r0.001 was thus measured with a better accuracy for these fast degrading compounds. (Patrick Höhener et al., 2006).

Given the current rudimentary understanding of biodegradation kinetics of chemicals in soils, especially with respect to combination with fate and transport, the system was modeled simply, by assuming a first order biodegradation rate constant. First-order biodegradation rate needs consistent definition in many cases, it was assigned based on total soil concentration .The rate constant was based on soil moisture concentration. If the zone of oxygen and VOC consumption is restricted to the top shallow depth of the vadose zone, and diffusion is the only transport mechanism for oxygen through the vadose zone, then the governing equation is:

$C(z) = c0 - (c0 + A\hat{U}) z / L + Az2$ (1)

where $c(z)$ is the oxygen concentration (%) at depth z (m), D is the effective diffusion coefficient for oxygen through the pore space of the vadose zone (m2 s"1), y is the zero-order oxygen consumption rate (% s"1), and $A = y/(2D)$). It was noted that C0 is the oxygen concentration at the ground surface, i.e. $c(z) = C0$ at $z = 0$, and L is the depth at which the oxygen concentration is zero, i.e. $c(z) = 0$ at $z = L$. Soil gas profiles measured at approximately steady state indicated that oxygen consumption, carbon dioxide production and biodegradation of hydrocarbon vapors occurred in a shallow and thin depth-interval of the vadose zone. Zero-order oxygen consumption rate coefficients and apparent hydrocarbon biodegradation rates calculated from the steady state profiles were high. Several issues remain including: the characteristic times to achieve steady state, diurnal and other oxygen concentration fluctuations at shallow depths, and the role of other oxidisable organic matter, (Davis .G.B et al., 1998).

Monitoring at the site, that processes affecting fate and transport below the building can be divided in three zones based on depth below ground surface consisting of primarily diffusion in the deep zone, biodegradation and diffusion in the mid-depth zone, and advection, biodegradation and diffusion in the shallow zone. First-

order degradation coefficients were estimated for the mid-depth zone by fitting model-predicted BTX concentrations, based on an analytical solution for one-dimensional (1-D).Steady-state diffusion and reaction, to measured BTX concentrations. The vapor profile between about 0.5 and 0.8 m depth was used since BTX attenuation was significant and approximately log-linear over this interval. The BTX vapor profiles below and adjacent to the building were also consistent over time suggesting approximate steady-state conditions, A first-order model was considered appropriate based on the log-linear BTX vapor profile and presence of sufficient O for biodegradation based on the BC. Steady-state vapor-phase diffusion and reaction for a homogeneous soil can be represented by the following equation

$D_g^{eff} \partial^2 C_g / \partial Z^2 = G = (k_w^1 \theta_w / H^1) C_g$

Where D_g^{eff} is the effective vapor-phase diffusion coefficient ($L^2 T^{-1}$), C_g is the vapor concentration (mol L^3) and G is the first-order rate of mass consumption (mol $L^{-3} T^{-1}$), k_w^1 is the first-order degradation rate based on the pore-water concentration (T^{-1}), θ_w is the water-filled porosity(L^3), and H is Henry's Law Constant (dimensionless).(Ian Hers et al., 2000).

A reactive transport model, incorporating a multispecies bio chemical model was developed for modeling the natural attenuation of a fuel hydrocarbon plume present. The model describes sequential degradation pathways for BTEX using multiple terminal electron accepting processes including aerobic respiration denitrification. Model calibration consisted of fitting the flow model to the observed hydraulic head distribution and simulating the distribution of various chemical species. The hydraulic conductivity distribution and reaction rate constants were estimated based on this calibration process. The calibration results suggest that the location of LNAPL (light non-aqueous phase liquids) distribution coincide with the low hydraulic conductivity zone. The calibrated first order decay rate constants for BTEX biodegradation using different electron acceptor processes as calculated from model are 0.051,0.031,0.005,0.004,and 0.002 day^{-1} for aerobic respiration,denitrification,fe(III) reduction are most important contributors for BTEX degradation, with methanogenesis the least significant process, aerobic respiration results in the remaining 30% of BTEX degradation. (Guoping lu et al., 1999)

4. BTEX ATTENUATION

Importance of long-term monitoring and examination of processes at a small spatial scale when assessing the natural attenuation of hydrocarbons, Concentrations of ethylbenzene and ortho-xylene in ground water, examination of the patterns in the hydrocarbon well data for the crude-oil contaminated aquifer shows that there were periods of several years, during which hydrocarbon concentrations in the heart of the contaminant plume showed decreases for many compounds. If these were the only data available, one might have concluded that hydrocarbons near the source were being depleted and the long-term potential for hydrocarbon transport would have

been underestimated. Temporal data collected at closely spaced vertical intervals, however, indicate that hydrocarbon concentrations (e.g. ethylbenzene) have spread out, consistent with a vertical thickening of the plume. Previously undetected hydrocarbons, such as ortho-xylene, are migrating in narrow zones in the aquifer, as the microbial degradation reactions shift from iron reduction to methanogenesis. It is apparent that the availability of an electron acceptor, such as Fe (III) oxides in this system, has a significant impact on the transport of hydrocarbons down gradient and away from the crude-oil source. Examination of changes in the distribution of this electron acceptor at the plume scale and at the core scale provides insight into the progression of biogeochemical zones. This type of information is needed in order to predict the long-term impact of hydrocarbon spills on aquifer chemistry and to assess the potential for hydrocarbon transport through the aquifer. (Isabelle M. Cozzarelli et al., 2001)

A reactive transport model, incorporating a multispecies biochemical model describes sequential degradation pathways for BTEX using multiple terminal electron accepting processes including aerobic respiration, and methanogenesis. Model calibration consisted of fitting the flow model to the observed hydraulic head distribution and simulating the distribution of various chemicals species as observed in data set as the initial condition. The hydraulic conductivity distribution and reaction rate constants were estimated based on this calibration process. The calibration results suggest that the location of LNAPL distribution coincide with the low hydraulic conductivity zone. (Guoping lu et al., 1999).

5.   CONCLUSIONS

This review shows the importance of long-term monitoring and examination of processes at a small spatial scale when assessing the natural attenuation of hydrocarbons in a contaminated site. Multiple lines of evidence should be considered while evaluating vadose zone intrinsic biodegradation, as typically conducted for dissolved hydrocarbon fate in groundwater. The correct interpretation of kinetic biodegradation parameters in unsaturated batch experiments remains a difficult task, This type of information is needed in order to predict the long-term impact of hydrocarbon spills on aquifer chemistry and to assess the potential for hydrocarbon transport through the aquifer. Abiotic losses pose problems when working in short incubations with large soil/headspace ratios and changes in microbial communities pose problems when working in long-term incubations with low soil/headspace ratios. In situ field methods such as tracer injections or isotope methods for rate determination should be further developed.

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