Journal of Advances in Science and Technology

Vol. V, Issue No. IX, May-2013, ISSN 2230-9659

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AN INTERNATIONALLY INDEXED PEER REVIEWED & REFEREED JOURNAL

Journal of Advances in Science and Technology
Vol. V, Issue No. IX, May-2013, ISSN 2230-9659

A Comparative Analysis on Transport of Pollutants through Soils to Ground Water

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Abstract – Three simplistic models are developed for evaluating the transport of organic pollutants through soil to ground water. The models consider mobility and first-order degradation. The first calculates linear sorption/desorption of the pollutant and first-order degradation without considering dispersion. The second is similar to the first but also considers dispersion.

A quantitative understanding of the transport of pollutants in groundwater is of great importance from the environmental perspective. Some environmental pollution scenarios involving groundwater contamination are very real. For example, one may encounter a situation where an underground storage tank is leaking hydrocarbons into an aquifer at a constant rate. Similarly, an overturned oil tanker spilling fuel that might flow through the sandy soil and find its way to the groundwater aquifer leading to its contamination.

The main focus of the present experimental study was to investigate the effect of the molecular diffusivity of the tracer on the dispersive transport or the spread of the pollutant. This was achieved using two different salt tracers of significantly different diffusivities. Pulse injections of tracers were made and their concentrations were monitored in situ downstream with the help of specially designed conductivity probes.

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INTRODUCTION

Large-scale problems of soil and groundwater contamination are the direct result of the development of the modern industrial society. The production of organic chemicals has increased immensely. More important are the changes in the types of compounds produced and the uses of these chemicals. In the past, chemicals used in agriculture were derived principally from animal wastes, plant residues, and minerals.

Today a wide assortment of petroleum-derived compounds is used as pesticides and herbicides. Many compounds, in some cases after extensive worldwide use, have been found to be toxic to wildlife and fish (e.g., DDT), highly toxic to mammals (e.g., phosphate-based pesticides such as Parathion), or carcinogenic (e.g., halogenated compounds such as polychlorinated biphenyls and dibromochloro-propane).

The most common sources of groundwater pollution are perhaps leaking under-ground storage tanks, landfills, and waste-disposal ponds. Serious soil and groundwater contamination problems also result from spills and improper disposal of toxic materials. For example, accidents during transport of chemicals may result in spillage of large quantities of pure products on small areas of ground. Left untreated, the chemicals can percolate into the soil and eventually may contaminate the local groundwater. Many sites throughout the industrial world exist where chemicals accidentally or intentionally leaked, deposited, or were disposed of in soils have contaminated groundwater aquifers or rendered large tracts of land unusable and dangerous to humans and other forms of life. In order to gauge the magnitude of environmental damage caused by even small amounts of pollutant finding its way to groundwater.

Contaminants or pollutants released into the environment rarely remain at the point of discharge. Transport through mechanisms of advection, dispersion, and interphase transfer normally takes place. In most cases, contaminant mixtures are involved and individual species may be transported at significantly different rates. Successful hazardous-waste management and site remediation therefore requires an understanding of contaminant fate and transport. Different aspects of contaminant transport have been an active area of research . A good deal of literature is also available suggesting effective remediation strategies for different types of contaminations. For example, factors affecting the chemical remediation of oil contaminated water-wetted solid has been recently reported. However, the present work is mainly concerned with the transport of contaminant in a saturated porous medium with a superimposed groundwater flow. In particular, the issue of the molecular diffusivity on the dispersive transport of the contaminant is examined.

After reaching the soil-solid surfaces, before, while, or after being subjected to biologically or chemically induced transformation, or retained by the soil constituents as absorbed or bound residues, the pollutants are redistributed in the soil profile as solutes and or water-liquids immiscible, in gaseous form or adsorbed on colliods and other fine particles. The extent of this redistribution and the kinetics of redistribution are controlled by both soil and pollutant properties, by the environmental conditions, and by the management of the polluted lands. During the transport of the pollutants through the unsaturated media, the pollutants undergo dispersion, diffusion, adsorption and transformation.

A tremendous amount of research has been devoted to the modeling of transport processes. The validation of the proposed models was done mainly by using parameters obtained in laboratory experiment. The present research work along with soil column laboratory experiments has been further extended to develop the model and test it to the field condition using laboratory experiments for certain parameters required to run the model under field conditions

TRANSPORT OF CHEMICALS IN GROUNDWATER

Volatilization - Volatilization occurs in whether the vadose zone or saturated zone when the dissolved contaminants and non-aqueous phase contaminants exposed to gas. The factors affecting volatilization include solubility of the compound, molecular weight and water-saturated state of the geological media. The evaporation rate must be measured fundamentally in order to determine pollutions transporting into the atmosphere, changes of the pollution load in the vadose zone and groundwater. The process that the contaminants of deep soil volatilize to the atmosphere can be assumed as one-dimensional diffusion, which can be described with Fick's second law. Volatilization of the water-soluble organic matter, such as benzene dissolved in water is generally described by Henry's Law.

Adsorption - Adsorption in Soil and sediment makes an important influence on the behavior of organic pollutants. The mobility and biological toxicity reduced as organics are detained in the soil and sediment. Generally, adsorption is affected by sediments and soil properties, such as organic percentage, the type and quantity of clay minerals, cation exchange, pH and the physical and chemical properties of the contaminants.

Biochemical processes - Microorganisms may play an important role in contamination transformations within groundwater and on the soil. They can act as catalysts for many types of reactions. When modeling biochemical reactions in groundwater, additional processes must be considered.

These include the changes in the availability of substrate for the microorganisms to utilize and reactions on the particles that the microorganisms are attached to. When microbial reactions are significant, there is a possibility of clogging of pores due to precipitation reactions or to biomass accumulation.

Microorganisms not only influence chemical reactions, but may be contaminants themselves. There is much current uncertainty about the fate and survival time of viruses, bacteria, and larger enteric organisms in groundwater. Distribution of microorganisms will vary greatly with depth. Potential outbreaks of waterborne diseases due to biologic pollutants are of particular concern where there is land disposal of human waste (often via septic tanks) and animal waste. The potential for transmittal of waterborne diseases in groundwater is particularly high in areas of rapid velocities such as karst regions.

POLLUTANT TRANSPORT

Solutes are transported by molecular diffusion and mass low, whatever their properties are. For pollutants with low solubility and for soil with high adsorption capacity, the rate-limiting parameters are dissolution and/or release and/or diffusion. Hydrodynamic dispersion - including both diffusion and mass low - determines solute spreading in soil and other porous media in accordance with water velocity variations. At low average water luxes in uniform soil, this process is relatively unimportant; it becomes dominant over diffusion at high water fluxes or in structured soils where there are substantial variations in water velocities. Pollutants being adsorbed on the soil solid phase do not move freely with water through the soil. For example, Jury(1983) showed that the travel time for an adsorbed chemical, tA, is related to the travel time for a non-adsorbed or mobile chemical, tM, by

$$t_\lambda = \left\{ \frac{1+pKd}{\theta} \right\} tm = Rt_m$$

where p is the soil dry bulk density, K is the solid/ liquid partition or distribution coefficient of the interacting chemical, A is the volumetric water content, and R is a generalized sink term modified for specific reactions.

Under field conditions, the movement of pollutants often does not follow the anticipated general pattern. Soils with a high content of clay may shrink and crack when subjected to wetting and drying cycles. Then, when a pollutant is applied, followed by rainfall or irrigation, the pollutant will partially leach into the soil through cracks and large pores. During transport through these large pores or cracks, only a portion of the solid phase - the external surface - comes in contact with the solute and the amount retained on the soil is relatively small (Yaron et al., 2012).

SATURATED AND UNSATURATED RANSPORT

Once a chemical has been released into the ground and has either moved through the unsaturated zone or directly entered the saturated zone, saturated transport processes will deter-mine if, how fast, and at what concentration a chemical reaches a supply well. A great deal of research has been carried out on understanding and modeling these processes. There is increasing recognition that chemical transport must be viewed as a stochastic process.

The same elements of uncertainty are present for saturated transport as for unsaturated transport. The important differences are that in saturated transport, water content equals porosity, hydraulic conductivity is no longer a function of water content or head, gravity rather than suction head is the driving force, and the scale of concern may be much larger.

In many cases, the receptor medium for release of a contaminant will be the unsaturated zone. In contrast to the saturated zone, pores in the unsaturated zone are not completely saturated with liquid. This fundamentally affects the processes governing flow and chemical transport. A number of processes will affect the contaminant within the unsaturated zone before it enters the saturated groundwater system and potentially is tapped by supply wells.

The uncertainties in characterizing releases just described lead to uncertainties in defining the source terms and initial and boundary conditions for modeling unsaturated transport. Analogously, uncertainties in characterizing unsaturated transport processes lead to uncertainties in defining the source terms and initial and boundary conditions for modeling saturated transport.

TRANSPORT PHENOMENA

At the soil-pore scale, there are two transport mechanisms that can move solutes through the medium: diffusion and convection. The molecular diffusion process whereby material move from a higher to lower concentration region as a result of random molecular motion. The rate of transfer of material is proportional to the concentration gradient normal to the direction of movement. Since solutes are not distributed uniformly through the soil, solution concentration gradients will exist and solutes will tend to diffuse from where the concentration is higher to where it is lower. Conditions in the soil system that may affect solute diffusion in soil are follows:

(i) The diffusion coefficient cannot be assumed to be independent of concentration;

(ii) Diffusion is confined to certain segments of the system (a molecule will not diffuse through a solid soil particle);

(iii) Sorption of the diffusing substance by soil particles often occurs; and

(iv) The diffusion coefficient is dependent upon temperature and a number of soil properties such as mineral composition, bulk density, and water content.

The mobile fraction of the adsorbed phase of an organic molecule may also contribute to diffusion. The adsorbed molecules may be divided into an immobile fraction and a mobile fraction, which contribute to diffusion and has the same apart mobility as molecules in solution. Since diffusion coefficient of organic molecules in soil remains low even over a large range of moisture content, biological degradation may occur during the diffusion process. The rate of decomposition at any distance as a function of time (t) to be dependent on the local concentration of the chemical and on microbial activity. The variation in the soil water content can influence the effective molecular diffusion of organic pollutants in two ways:

(a) By determining the air-filled porosity, thus controlling the gas diffusion-liquid diffusion ratio for a given organ pollutant (for given solubility and vapour tension values),

(b) By modifying pollutant adsorption. The general trend is for adsorption to decrease as water content increases, and this effect is probably greater at low water contents, because of the more pronounced competition between pollutant and water molecules. Convection refers to the transport of a dissolved chemical by virtue of a bulk movement of the host water phase. In general, the convective transport of solute is described by considering the two components of convective low: mean pore water velocity and deviations from the mean, induced by variations in the low regime within the soil. Hydrodynamic dispersion refers to the motion of solute due to small-scale convective fluctuations about the mean motion (Bear 2003). The hydrodynamic dispersion process results from the microscopic nonuniformity of low velocity in the soil conductive phase and includes both diffusive and convective transport.

CONCLUSION

Groundwater is a geological agent and a renewable natural resource vitally important for man and nature. Travel (or transport) of pollutants in the environment involves airborne transport through the atmosphere and waterborne transport through the hydrosphere. The hydrosphere includes surface water components of the hydrologic cycle (streams, lakes and reservoirs) and subsurface water components (vadose zone and groundwater zone). Subsurface transport will be addressed both from the point of view of the potential contamination of potable groundwater resources, and in terms of its role as a migration path from the land surface tosurface-water bodies. The water - bearing rocks themselves have their own protective properties. Different natural attributes that affect the vulnerability of groundwater include recharge, soil, unsaturated zone and saturated aquifer.

The transport of pollutant model is developed keeping in view the pollution potential of the study area for prediction. The travel of pollutant from the surface of the soil passes through the soil media i.e., unsaturated zone, then enters the aquifer media i.e., saturated zone after covering the capillary zone between these two zones. The transport of pollutant through the unsaturated zone is studied theoretically and the computer model is developed as explained. One-dimensional low model is selected considering the movement of pollutant which is dominant as vertical flux.

From results presented in the foregoing, one might be tempted to conclude that individual species in a mixture of contaminant would still transport at the same rate even if their molecular diffusivities are significantly different. It should however be kept in mind that using a non-porous packing material for the construction of the porous media in the present experimental study is gross approximation of the actual

field situation. Its clear consequence is the elimination of both internal and external mass transport resistances. Both these mechanisms are clearly sensitive to the molecular diffusivity of the ant species present in the system.

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