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Superfund Ground Water Issue

Facilitated Transport

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The Regional Superfund Ground Water Forum is a group of ground-water scientists representing EPA's Regional Superfund Offices, organized to exchange up to date information related to ground-water remediation at Superfund sites. Facilitated transport is an issue identified by the forum as a concern of Superfund decision-makers.

Any process that has the potential to speed the transport of a pollutant beyond what is expected based solely on considerations of idealized Darcian flow and equilibrium sorptive interactions with an immobile solid phase has been broadly termed, "facilitated transport". Hydrodynamic dispersion, a transport mechanism which fits this description of facilitated transport, is not discussed herein.

Research and literature indicates that hydrophobic organic contaminants (HOC's)(i.e., PCB's, DDT, dioxins, polynuclear aromatic hydrocarbons (PAH's)) and heavy metals have a high affinity for mobile subsurface particles and that such an attraction may alter the mobility of the contaminant. Facilitated transport is a relatively new area of study in the field of contaminant transport. Considerable research and interest is currently focused in this area. Although incompletely understood at this point, the effects of facilitated transport at Superfund sites may range from paramount to negligible. There may be an abundance of field data currently available that identifies both the occurrence and the importance of these transport mechanisms. However, relatively little information is available in the scientific literature which attempts to correlate the occurrence of these transport mechanisms with field data.

Most Superfund Sites are characterized as having the following conditions: a complex mixture of organic and inorganic wastes; highly variable chemical and physical characteristics; a broad range of chemical concentrations; and a broad spectrum

of soil and hydrogeological characteristics. Therefore, several facilitated transport mechanisms may be occurring simultaneously at any site.

Idealized laboratory experiments reported in the literature have been designed to simulate specific physical and chemical conditions. These laboratory conditions have allowed researchers to control the variables which affect the behavior of contaminants in the subsurface and to identify the mechanisms which are likely to occur in the field. An understanding of the various mechanisms of facilitated transport will provide a more thorough understanding of the fate and transport of contaminants in the ground water and ultimately will provide the framework for further development of ground-water remediation technology. The following is a brief technical overview of facilitated transport prepared in support of the Regional Superfund Ground Water Forum.

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Cosolvent Effects

Many releases from land disposal or waste storage systems consist of a mixture of water and organic compounds. High concentrations of organic compounds or solvents in water have significant potential for facilitated transport of usually immobile HOC's. An HOC which partitions into a solvent may exhibit increased mobility, above which is typically predicted from idealized Darcian flow and adsorption/desorption kinetics, due to its intimate association with the mobile solvent. In a mixed solvent (cosolvent) system, organic solutes are subjected



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to a wide range of chemical and physical processes which ultimately determine how a particular solute will be distributed and transported in the subsurface.

In a mixed solvent system consisting of water and one or more water miscible organic compounds (i.e., methanol, acetone, methyl ethyl ketone, etc...), sorption of HOC's onto the solid phase does not follow the same sorption behavior as seen for water without the solvent mixture. Instead, as the fraction of cosolvent in the mixture increases, the solubility of the HOC increases exponentially (6). Correspondingly, the sorption coefficient decreases logarithmically and the retardation factor decreases drastically (6,7,15,16,18,22). As the sorption coefficient decreases, less HOC will be sorbed onto the solid phase and subsequently becomes more mobile. The decrease in the sorption coefficient has been shown to be a function of the increased solubility of the hydrophobic compound in the cosolvent (18). In one set of laboratory column studies, the breakthrough curves for some pesticides in a cosolvent system were equal to that of a conservative tracer, suggesting no measurable retardation of the pesticide had occurred (16). This mechanism of facilitated transport is significant at cosolvent concentrations above a few percent. Therefore, the effects of this transport mechanism are expected to be greater near the source, prior to dilution. A model has been developed to quantitatively describe the sorption and transport of hydrophobic organic chemicals in an aqueous and mixed solvent system (18).

Research has shown that an organic cosolvent can also accelerate the movement of metals through a soil matrix. Based on the results of laboratory soil column experiments, ethylene glycol was shown to increase the rate of cadmium migration through three soils compared to water, while 2-propanol increased the rate of cadmium migration through two of the three soils (19). This research indicates that metal contaminants may be found deeper in soils than originally expected because of cosolvent effects.

Immiscible flow of solvents and petroleum fluids in the subsurface has been observed at numerous waste disposal sites. The presence of a mobile immiscible phase can facilitate the transport of HOC's in both the saturated and unsaturated zones. The impact of this facilitated transport mechanism has been described utilizing an analytical chemical transport model (5). Using this method of analysis, it was observed that ignoring the presence of organic compounds moving either with the ground water or as a separate phase could greatly underestimate the mobility of chemicals.

Colloidal Processes

The transport of contaminants in ground water has typically been characterized as a mass balance of the contaminant governed by the partitioning of the contaminant between the mobile aqueous phase and the immobile solid phase. However, under certain conditions, small solid phase particles and macromolecules, which exist in some subsurface environments, are transported in the aqueous phase and have been characterized as mobile sorbent.

Colloids, defined as particles with diameters less than 10 micrometers (20), are widely recognized as mobile particles in both the unsaturated and saturated zones of the subsurface.

Many hydrophobic organic contaminants, generally considered to be highly retarded due to strong interactions with immobile aquifer material, have a high affinity for the mobile colloidal material. Consequently, the association between the contaminant and colloid ultimately affects the transport of the contaminant (12). Research has found that batch adsorption experiments which are often relied upon to predict the adsorption potential of a compound may give misleading results if consideration is not given to the presence of the nonsettleable particulate phase or macromolecular phase (9). Furthermore, current solute transport models that assume partitioning between a mobile aqueous phase and a stationary organic carbon or mineral phase may significantly underestimate contaminant mobility (2).

The significance of dissolved colloidal material to the fate of contaminants depends on the following factors: (a) the identity and concentration of dissolved colloidal matter; (b) the nature of the interaction between the contaminants and the dissolved colloidal matter; and (c) the mobility of the colloidal matter in an aquifer (11).

Ground water typically contains a few mg/l dissolved organic matter, but the dissolved organic matter may reach a few hundred mg/l in surface water and ground water near a dump site (11). Consequently, the potential effects of facilitated transport is likely to be greater in waste disposal areas. The nature of the interactions between contaminants and colloidal material are diverse. Colloids typically are divided into two groups: organic and inorganic and the contaminants which colloids interact with are typically divided into three groups: organic compounds, metals, and radionuclides. Therefore, it is apparent that there are many interactions which may occur in a complex mixture of colloids and contaminants. The various interactions between colloidal material and contaminants are further discussed below. The mobility of a diverse range of colloidal matter has been reported by one reviewer to occur in the ground water under a variety of conditions (13). However, the ability to accurately assess the mobility of colloidal material in the subsurface is difficult and at present, is incompletely understood.

Organic Colloids

Natural and anthropogenic organic colloids occurring in the subsurface can assume the role of either the sorbent in the adsorption-desorption and cation exchange mechanisms or the solvent in a solvent-cosolvent scenario. Organic colloids range in size over several orders of magnitude. There are at least three general classes of organic colloids: (a) biocolloids, such as bacteria, spores, and viruses, (b) macromolecules, such as high molecular weight polymers, humic substances, pulp fibers, proteins, and (c) nonaqueous-phase liquids, such as oil droplets or detergent micelles (12,21).

Organic Colloids: Interactions with Metal Contaminants

The association of metals with organic matter is a relationship that has been documented repeatedly both in the field and the laboratory. Due to the large surface area per unit mass and anionic surface functional groups associated with some organic colloidal material, metals have a significant potential to be adsorbed. Due to the association with mobile colloidal matter, the metal may become more mobile.

The complexation of metal ions with organic colloids is reported in the literature to vary considerably with a number of experimental variables. Complexation increases at higher pH's and higher humic substance concentrations and decreases at higher ionic strengths. Generally, complexation also varies with the nature of metal ion (12).

The chemical and/or physical reaction which influences the metal complexation with organic colloids is a reversible process. Parameters which influence reversibility include: pH, ionic strength, and metal and organic compound concentrations. Complexation reversibility may have important repercussions when ground water from various flow regimes mix together in common hydrogeological units. When complexation reactions are reversed, the fate and transport mechanisms associated with the complexation may change accordingly.

Although the association between organic matter and metals has been investigated intensively, little information is available on this association with respect to transport in a porous media system. This is an area of considerable research effort at the present time.

Organic Colloids: Interactions with Organic Contaminants

Organic colloids are reported to associate with HOC's by: (a) sorbing organic contaminants; (b) behaving as a solvent to the organic contaminant; and (c) participating in ionic exchange reactions with cationic organic compounds. The association of the mobile organic colloidal matter results in the increased mobility of the contaminant through the porous media. A summary report on the role of colloids in contaminant transport processes indicates that the sorption of organic contaminants onto colloids appears to be a simple partitioning process between the water and the organic colloidal phase. This sorption process is also found to be mathematically predictable (12).

Hydrophobic organic contaminants have a high affinity for association with organic macromolecules, i.e., humic substances. Enhancement of the solubility of HOC's by the organic macromolecules can be accounted for by a partition-like interaction of the HOC's with the macromolecule (3,11). Enhanced solubility, also referred to as apparent solubility, as used in reference to colloids describes the increased contaminant concentration in an aqueous sample due to the presence of colloids. These two terms do not describe a condition where the water solubility, i.e., the physical constant, of a contaminant increases. Instead, the suspended colloids provide a mechanism whereby the chemical stays associated with the solid phase while suspended in the liquid phase.

The apparent solubility of the HOC's increases with an increase in the colloid concentration (12) and with a decrease in HOC solubility. Therefore, the greater the concentration of organic colloids, and the more hydrophobic the compound, the greater the potential mobility of the contaminant by this facilitated transport mechanism. Additional organic colloid features which have been reported to affect the apparent solubility of the HOC's include: molecular size, polarity, and molecular configuration (3). In a laboratory column experiment where an aqueous mixture of organic macromolecules and hexachlorobenzene were introduced together, the transport of the hexachlorobenzene occurred more rapidly than in a mixture without macromolecules (1). The presence of hydrophilic

macromolecules may change the relative mobility of HOC's by an order of magnitude in low organic carbon soils (2).

Several polar organic contaminants are characterized as cationic (positively charged). The sorption of these contaminants onto the solid phase is governed by both electrostatic and hydrophobic forces. Therefore, the retention of these contaminants not only depends on its physical and chemical characteristics and the colloid organic carbon content, but also on the cation exchange capacity of the colloid.

Surfactants

Aggregates of surfactant molecules or micelles may be classified as organic colloids or organic microdroplets that may interact with both metal and organic contaminants and increase the mobility of these contaminants. At critical concentration levels, surfactants form discrete structures called micelles. Micelles are distinctly different from the bulk aqueous phase, and in most instances, serve as efficient media for the partitioning of hydrophobic pollutants (17). The micelle then can strongly influence the transportation of the contaminants (14). The existence of such micelles in leachates has yet to be demonstrated (17).

Presently, there is little information in the literature which correlates the facilitated transport of organic contaminants by organic colloids with field data. However, the literature does contain several publications of laboratory studies which demonstrate facilitated transport processes involving colloids (1,3,11,23).

In conjunction with the numerous interactions which may occur between colloids and contaminants is the high degree of variability and uncertainty of the chemical, physical, and biological subsurface environment. Consequently, estimating the effects of facilitated transport in the field is often difficult. However, the concept of facilitated transport of trace organic compounds helps rationalize the occurrence of hydrophobic contaminants 30 meters below waste disposal sites in Ohio (1), a distance much greater than predicted by conventional sorption theory.

Inorganic Colloids

Inorganic colloids include clay, metal oxides, and inorganic precipitates in the sub-micrometer size range (12). These colloids occur both naturally and from anthropogenic sources. Anthropogenic formation of ferrous phosphate colloids was reported to occur when sewage-derived phosphate combined with the ferrous iron that was released from aquifer solids (8). These colloids were detected in the ground water downgradient from the disposal site indicating that the colloids were mobile in the aquifer system.

Although most Superfund sites do not contain radioactive wastes, radionuclide research of inorganic colloids is useful to identify facilitated transport mechanisms. The transport of clay particles has been reported to vary with the ionic strength of the aqueous environment. Laboratory column experiments indicate that clay particles passing through porous media are increasingly retained as the salinity of the solution is increased. Additionally, saline aqueous solutions are less likely to adsorb cesium from solution and, once adsorbed, are less likely to desorb into saline water (4). These studies show that kaolinite colloids pass readily

through various soil media and readily adsorb cationic radionuclides, indicating that facilitated transport may potentially occur at high level radioactive waste repositories.

Little information is currently available concerning the association between inorganic colloids and organic contaminants. Due to both the existing data base concerning organic contaminant sorption to typical subsurface mineral surfaces (12) and to inorganic colloidal transport, the scientific framework suggests facilitated transport is a viable transport mechanism. Further research is necessary to elucidate specific mechanisms and the importance of this particular colloid-contaminant association.

Practical Considerations

The potential role of facilitated transport should be considered while assessing the areal and vertical extent of contaminants in the ground water, particularly if the following pertain: the contaminant is known to associate strongly with organic or inorganic surfaces (e.g., hydrophobic organic compounds, metals); the ground water contains a relatively high concentration of dissolved organic carbon, total dissolved solids, or total suspended solids; the aquifer is relatively porous or fractured, and flow rates are relatively high; or aqueous chemistry undergoes natural or contaminant associated alterations that could mobilize colloidal particles (12). Facilitated transport has the potential to disperse contaminants which are usually relatively immobile thereby increasing problems associated with contaminant migration control. On the other hand, low sorption of contaminants in the saturated zone material is desirable from the standpoint of ground-water remediation in that solute removal by pumping to the surface is facilitated (2).

There are several areas related to field work which must be given special consideration to determine whether facilitated transport may be playing an important role in contaminant transport. These areas are as follows (12):

Drilling Methods

Drilling operations, by nature, disrupt the subsurface environment. Drilling may redistribute material and create fine particles as a result of the associated abrasive activities. In addition, many drilling techniques involve the injection of foreign materials into the borehole such as drilling muds, water, and compressed air. The particles introduced into the system may become associated with the contaminants entering the well screen area. Depending on numerous factors surrounding the particle-contaminant association and sampling technique, the contaminant may be undetected in the ground water. Augering is the least disruptive technique available for shallow holes in unconsolidated material. In deeper holes or harder materials, casing drive techniques may be required. However, there will be occasions when the more traditional drilling methods are necessary. Careful evaluation of the impacts of the drilling technique and materials is essential to evaluate contaminant transport in the well area.

Well Construction

Materials used in the construction of recovery or monitoring wells may have an impact on the subsurface chemical environment. Sampling artifacts may arise through contact of various well

materials with the water that is drawn into the well and sampled. In particular, the sand pack may act as a source of fine particles. As previously discussed, these particles may result in the contaminant being undetected. If the sand (filter) pack is constructed with very fine material, it may function as a filter medium effectively removing larger colloids that may have contaminants adsorbed to their surface.

Well Development

One purpose of well development is to remove drilling muds and fine particles introduced or created during the course of well construction. This process involves dislodging and transporting the particles from the system. Although the objective is to remove the artificially placed particles, this activity may introduce naturally occurring particulate material into the well area. However, every type of drilling operation alters the characteristics of formation materials in the vicinity of the borehole. Therefore, well development is generally recommended to eliminate the particulate matter potentially available to interfere with contaminant transport to the well.

Well Purging

The well is a conduit for the surface atmosphere to artificially contact the ground water. Ground water in the area of the well is in contact not only with the atmosphere, but with the construction material of the well. Additionally, the ground water in the well becomes stagnant and unrepresentative of actual ground-water quality. For these reasons, it is standard practice in ground-water sampling to purge a predetermined volume of water from the well before taking the sample. The purpose is to draw in fresh and presumably representative formation water to be sampled. Excessive rapid pumping, however, may create a dramatically different ground-water gradient and flow pattern from the natural state and affect the distribution of suspended particles in the sampled water. Recently, field methods were implemented during a ground-water investigation to distinguish whether colloidal particles were introduced during sampling operations or if the colloids were truly suspended and moving with the ground water in-situ (10). This was performed by using very low pumping rates to purge the well in conjunction with a dissolved oxygen sample handling technique to prevent the atmospheric exposure of ground-water samples. These steps yielded ground-water colloid suspensions which the researchers believed were representative of ground-water quality.

Sample Handling

Perhaps the single most important aspect of ground-water sampling that has paramount effects on the detection of contaminants resulting from facilitated transport is filtering the ground-water sample. Essentially, filtering the sample (usually with a 0.45 micron filter) removes some of the colloid and macromolecule material which may be responsible for contaminant transport. Therefore, when the filtered sample is analyzed, there is reduced probability that the contaminant will be detected in the ground water. Further discussion on the repercussion of filtering ground-water samples can be found in Superfund Issue Paper No. 1, entitled, "Ground Water Sampling for Metal Analyses."

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