

APPENDIX E

CONTAMINANT PERSISTENCE AND MOBILITY FACTORS

1. INTRODUCTION

When assessing the potential for a particular Class V well to adversely affect a USDW it is important to consider the mobility and persistence of the contaminants (biological and chemical) found in the injectate. Understanding the mobility and persistence characteristics of particular contaminants helps in determining the likelihood that a contaminant of concern will reach a point where people might be exposed (e.g., a private drinking water well).

This appendix is a compilation of information taken from the literature regarding the mobility and persistence of biological and chemical contaminants likely to be encountered in fluids released into Class V wells. It was prepared to assist readers in understanding scientific principles behind the factors that affect the mobility and persistence of specific chemicals observed in injectate of the different types of Class V wells covered in Volumes 1 through 23 of this report. The reader, however, is advised to use caution when interpreting the information presented below for particular biological and chemical contaminants. Specifically, numerous site-specific factors (including waste stream characteristics, hydrogeologic parameters, and injection well operations) can have a significant impact on the actual mobility and persistence of these chemicals in the “real world.” The reader, therefore, should not use the information presented in this appendix for the purpose of analyzing the behavior or possible impacts of these chemicals at an actual site. Depending on site-specific conditions, the actual mobility and persistence of a given chemical at a given site may be higher or lower than discussed below.

1.1 Mobility

Mobility refers to a biological or chemical contaminant’s ability to move within soil or ground water over time. A contaminant may move under the influence of gravity as with light or dense non-aqueous phase liquids, or under the influence of ground water flow as with dissolved constituents. As the contaminant moves through a porous medium, conditions within the medium tend to resist the mobility of the contaminant. For example, molecules (e.g., cations and pesticides) tend to adsorb onto particles of the porous medium in proportion to their concentration in ground water. Adsorption also depends on the physical and chemical characteristics of the medium such as carbon content and pH. Dissolved contaminants also exhibit the tendency to diffuse within the solute, although diffusivity is a minor mechanism of mobility in the case of rapid ground water flow such as with injection wells.

Ground Water Transport of Contaminants

The movement of most toxic contaminants in the ground water is affected by chemical reactions that cause transfer of contaminant mass between the liquid and solid phases or conversion of dissolved species from one form to another. The chemical attenuation of inorganic contaminants occurs mainly by adsorption, precipitation, oxidation, or reduction. Organic contaminants can be adsorbed or degraded by microbiological processes. Biological contaminants can be attenuated by both chemical and microbiological

In addition to chemical factors affecting adsorption, physical factors such as ground water hydraulic gradient, hydraulic conductivity, porosity, and bulk density also affect mobility. Because the point of injection for many Class V wells is within a permeable, coarse-grained unit, or karst or a fractured unit in some areas, conditions are likely to be present that would allow constituents in injectate to be highly mobile. Constituents may travel significant distances when there are extensive formation voids and/or fractures.

In other settings where the receiving formation contains substantial clay or silt content, and does not include solution cavities or fractures, the mobility of some constituents may be “retarded.” This is especially true for many metals, which, depending on pH and other site-specific factors, can undergo fixation and adsorption processes that decrease mobility within the soil-ground water system.

1.2 Persistence

Persistence is the ability of a biological or chemical contaminant to remain unchanged in composition, chemical state, and physical state over time. Persistence depends on chemical structure, conditions in the aquifer conducive to degradation such as microbial population, nutrients available to support microbial growth, and the type and quantity of ions in the background ground water. In some cases, the degradation of one constituent occurs along with a chemical change in another as when electrons are accepted by manganese ions in the breakdown of petroleum hydrocarbon. In this case, the relatively immobile manganese³⁺ becomes mobile manganese²⁺.

Persistence can be expressed in terms of half-lives, or the time it takes for a chemical to change one-half of its mass to a different form or compound. The half-life is an empirical, global measurement that encompasses all of the operable degradation mechanisms. Accordingly, the half-life of a chemical is expressed as a range of values for a particular medium.

2. BIOLOGICAL CONTAMINANTS

The mobility and persistence of biological contaminants including, protozoa and parasites, bacteria, and viruses from septic tank effluent, sewage treatment effluent, storm water effluent, wastewaters from food processing facilities, and other wastewaters are affected by the operation of treatment units (e.g., septic tanks and settling basins) preceding the injection well (or drainfield), the injection rate (or loading pattern), and characteristics of the subsurface environment.

2.1 Bacteria and Parasites

Many soils are capable of physically filtering (or straining) parasites (cysts and eggs) and bacteria as the effluent moves through soil pores because of their relatively large size. One of the most important factors in removal of bacteria is the pore size of the soil matrix, with smaller pores being better able to remove bacteria. Bacteria, which have many nutritional requirements, usually die off once filtered from the effluent because of a lack of nutrients. Cases have been reported of active bacteria (from septic tank effluent) traveling distances of up to 300 feet in sandy aquifers, 2,800 feet in gravelly

aquifers, and 3,300 feet in limestone bedrock (Kaplan, 1991). Note that this movement is believed atypical for properly sited, designed, operated, and maintained septic systems. In addition to movement, bacteria may simply persist. For example, enteric bacteria have been observed to survive from 10 to 100 days in soil depending on the moisture content, temperature, organic matter, pH, sunlight, and antagonism from native soil microflora present in the soil (Canter and Knox, 1985). Generally, bacteria removal is enhanced by low effluent loading and frequent drying periods between doses.

2.2 Viruses

Viruses are less easily filtered. The major means of virus removal is through adsorption onto soil particles. Virus adsorption is greatly affected by the pH of the soil-water system. This effect is due primarily to the amphoteric nature of the protein shell of the virus particles. At low pH values, below 7.4 units, virus adsorption by soils is rapid and effective. In addition, coarser soils with higher pH values were less effective in adsorbing viruses. Higher pH values considerably decrease the effectiveness of virus adsorption by soils because of increased ionization of the carboxyl groups of the virus protein and the increasing negative charge on the soil particles. Virus adsorption also is influenced by other soil characteristics such as clay content, silt content, ion exchange capacity, and particle size. Adsorption also can differ as a function of virus type and strain due to the variability in the configuration of proteins in the outer capsid of the virus since this will influence the net charge on the virus (which affects the electrostatic potential between virus and soil) (USEPA, 1984).

Dry soils may also inactivate viruses (Kaplan, 1991). One study found virus removal in soils to be three times greater in unsaturated conditions than in saturated conditions (Powelson and Gerba, 1994). The implication of this finding for Class V injection systems (e.g., large-capacity septic systems) is that if ground water mounding beneath these systems were to reach the infiltrative surface, it could result in saturated flow conditions, possibly allowing greater concentrations of viruses to travel to ground water. Ground water mounding reduces the distance from the bottom of the system to the water table (MN Pollution Control Agency, 1984). This distance is a critical factor in the treatment of sanitary wastes and effluents because the unsaturated soil above the water table filters and absorbs contaminants, including parasites, bacteria, and viruses (Price, 1988).

The ambient environment is an important factor for effective virus removal. Research by Scandura and Sobsey (1997) determined that the risk of viral contamination is greatest in the most coarse (sand) soils, when water tables are most shallow (smallest vadose zones or unsaturated soils) and in winter when temperatures are at the lowest. However, extensive reductions of enteric viruses, bacteria, and nutrients are possible if the site has soils with clay content at or exceeding 15 percent, if the vadose zone is at or exceeds 3.28 feet, and if the injection well does not inject directly into a saturated zone (or in the case of large-capacity septic systems, the drainfield distribution lines do not become submerged).

Initial virus removal or inactivation can be reversed by changing environmental conditions. Heavy rainfall can induce saturated soil conditions or significant temperature changes (Yates, 1987).

Viral organisms may persist in temperatures as cold as -20 °C, but can be inactivated by high temperatures (exceeding 31°C) (Harris, 1995; Yates, 1987). Viruses have been observed to travel more than 600 feet and survive as long as 170 days (Canter and Knox, 1985). Like bacteria removal, virus removal is enhanced by low pH and ionic strength (Canter and Knox, 1985). Virus adsorption also depends on the strain of the virus. A different strain of the same virus may adsorb to a different extent and/or at a different rate. According to Yates, (1987), infectious viruses are not normally present in effluent, and are only shed in the feces of infected individuals. However, this would make larger systems more likely than smaller ones to contain such viruses. At the 1998 Ground Water Protection Council annual forum, Mr. Michael Rapacz (MA Department of Environmental Protection) presented evidence that viruses can remain active for up to two-years of ground water transport. His findings are supported by other research, including an article in Ground Water which found that: (1) viruses could travel as fast, or faster than inorganic contaminants; and (2) the combination of the virus sorption processes and long survival times resulted in the presence of viable seed virus for more than nine months (DeBorde, et al., 1998).

Finally, with regard to possible human immunodeficiency virus (HIV) transmission, recent studies concerning the survivability of HIV in wastewater suggest that HIV can survive in wastewater. For example, researchers recently found that HIV remained stable through 48 hours and remained infectious for 96 hours in water and wastewater, and concluded that the presence of HIV in wastewater cannot be dismissed without further investigation through field studies (Casson, et al., 1997).

3. CHEMICAL CONTAMINANTS

The mobility and persistence of chemical contaminants, like biological contaminants, are dependent on many factors. Some of the most important factors are chemical-specific parameters.

3.1 Inorganic Contaminants

The mobility of inorganic compounds, especially metals, is difficult to determine due to the many reactions inorganic compounds can have with the various soil components. The mobility of metal compounds is strongly influenced by soil type (e.g., texture) and the corresponding pH and cation exchange capacity (CEC) of the soil. Soil type or composition is a very important factor in heavy metal fixation reactions. Clays are extremely important in adsorption reactions because of their high CEC. In addition, soils high in humus or other organic matter also exhibit good exchange capacity. The type of clay mineral present also is an important factor. Many sorption reactions take place at the surface of iron and aluminum hydroxides and hydroxy oxides, and therefore, the iron and aluminum content of soils becomes an essential factor governing the ability of a soil for heavy metal immobilization (USEPA, 1984).

Soil texture or soil particle size is another factor that can influence the fixation of metals by soils. In general, finely textured soils immobilize trace and heavy metals to a greater extent than coarse textured soils. Also, finely textured soils usually have a greater CEC, which is an important factor in

heavy metal fixation. Soil texture has been found to influence the transport of mercury, lead, nickel, and zinc (USEPA, 1984).

Soil pH plays a very important role in the retention and mobility of metals in soil columns. The pH is a controlling factor in sorption-desorption reactions and precipitation-solubilization reactions. In addition, the CEC of soils generally increases with an increase in pH. Even with a soil that has a high affinity for a specific metal, the degree to which the metal is fixed is a function of pH. Soil pH has been determined to be a major factor along with CEC for the fixation of lead by soils. Soil pH also influences the retention of zinc, molybdenum, mercury, and copper (USEPA, 1984).

The oxidation-reduction or redox potential of a soil is very important in determining which species of an element is available for sorption, precipitation, or complexation. In general, the reduced forms of a metal are more soluble than the oxidized form. The redox potential of a soil system is usually altered through biological activity and a change in redox potential is many times correlated with changes in pH. Reducing conditions may be associated with a low pH resulting in the formation of CO₂ and organic acids from the microbial degradation of organic matter. A reducing environment typically exists in saturated soils underneath septic tank systems or injection zones. The anaerobic conditions would enhance the mobility of metals in system effluents. Iron is a good example of a metal which readily undergoes redox reactions. In the oxidized or ferric state, iron is reduced under anoxic conditions, the ferrous form, which is more soluble, predominates (USEPA, 1984).

Metals added to a soil/ground water system will undergo fixation and adsorption processes, which directly effect the mobility of the metal. Fixation reactions include chemisorption (where the metal forms a covalent bond with a mineral surface), solid state diffusion (irreversible penetration into mineral pore spaces), and precipitation (insoluble solid formation). Of the three, precipitation is the fixation reaction that has the most significant impact on a metal's fate and mobility and therefore a brief discussion is provided below in Section 3.1.1. Adsorption processes also play a significant role in mobility and some basic information is provided below in Section 3.1.2. While fixation and adsorption reactions can be discussed separately in theory, in practice they can be very difficult to measure independently. Solid state diffusion plays a relatively minor role and therefore is not discussed further. Changes in soil environmental conditions over time, such as degradation of the organic waste matrix, changes in pH, redox potential, or soil solution composition, due to various remediation schemes or to natural weathering processes, also may enhance metal mobility (McLean and Bledsoe, 1992).

3.1.1 Precipitation

Precipitation of a given metal species depends on the Eh (reduction-oxidation potential) and pH of the soil/ground water system, as well as the presence of anions and competing cations that exceed the solubility product constant. pH is a measure of the hydrogen ion concentration in the soil/ground water system, expressed as the negative log of the hydrogen ion concentration. When used together, an Eh/pH diagram can be developed for a given metal, which indicates the species that a given metal will exist as under various Eh and pH conditions.

Metal precipitation is also dependent on the presence of anions that cause the metal to form insoluble inorganic compounds. For example, based on the Eh/pH diagram for barium, one could assume that barium is soluble at all pHs and all Ehs. However, the presence of sulfate or phosphate ions will cause the barium to form insoluble barium sulfate or barium phosphate, and therefore be removed from solution and become immobile. Solubility product constants are indicators of the tendency of a given compound to form in solution on the basis of the concentrations of the individual cation and anion of a product. Other cations may also be present in the system which compete for the anions by precipitating at lower concentrations.

3.1.2 Adsorption

Adsorption is defined as the accumulation of a metal at the surface of soil particles. Adsorption reactions include cation attraction, complex formation, and anion adsorption/ exclusion. Often metal adsorption occurs in the presence of clays. Clay surfaces possess negative charges, while most dissolved metals possess positive charges. Thus, clay will tend to remove metals from solution by a process called cation exchange. Cation exchange is a surface-charge driven phenomenon. Metal ions can also form complexes with molecules or ions containing free pairs of electrons. The molecule or anions with which a metal forms the complex with is called the ligand. Two important organic ligands in nature are humic and fulvic acids. The general affinity of cations for humic acids as a whole decreases in the following order: trivalent cations > divalent cations > monovalent cations. Fulvic acids are water soluble, but cations such as Fe^{+3} , Al^{+3} , Cr^{+3} , Pb^{+3} , Cu^{+2} , Hg^{+2} , Zn^{+2} , Ni^{+2} , Co^{+2} , Cd^{+2} , and Mn^{+2} can form water-insoluble complexes with fulvic acid.

Soil particles can also possess positive surface charges. The edges of alumino-silicate clay minerals, or oxide surfaces, and organic matter can all possess positive charges, depending on the pH of the surrounding water. Positive surface charges will tend to accumulate anionic species such as phosphate, arsenate, molybdate, selenite, sulfate, borate, silicic acid, fluoride, halides, and nitrate.

Most soil surfaces, however, are predominately negatively charged. Typically, negatively charged constituent anions in solution are repulsed by the negatively charged surfaces. This repulsion leads to a process called anion exclusion which increases mobility for some compounds. Anionic species such as phosphate, arsenate, molybdate, selenite, sulfate, borate, silicic acid, fluoride, halides, and nitrate will therefore migrate faster through the soil because of the repulsion forces present.

3.1.3 Behavior of Specific Inorganics

The behavior of some of the more common inorganic constituents found in Class V injectate is discussed below.

Arsenic (in the soil environment) exists as either arsenate or arsenite. Arsenite is the more toxic form of arsenic. The behavior of arsenate in soil is analogous to that of phosphate, because of their chemical similarity. Like phosphate, arsenate forms insoluble precipitates with iron, aluminum, and calcium. Iron in soils is most effective in controlling arsenate's mobility. Arsenite compounds are

reported to be 4-10 times more soluble than arsenate compounds. Arsenate adsorption by kaolinite and montmorillonite approaches maximum at pH 3-4 units, followed by a gradual decrease in adsorption with increasing pH. The adsorption of arsenite is also strongly pH-dependent, with an increase in sorption of arsenite by kaolinite and montmorillonite over a pH range of 3-9 units and a maximum adsorption by iron oxide at pH 7. The adsorption of arsenite has been found to be rapid and irreversible and iron oxide, redox, and pH were the most important properties in controlling arsenite adsorption by soils (McLean and Bledsoe, 1992).

Both pH and the redox are important in assessing the fate of arsenic in soil. At high redox levels, arsenate predominates and arsenic mobility is low. As the pH increases or the redox decreases, arsenite predominates. The reduced form of arsenic is more subject to leaching because of its high solubility. The reduction kinetics are, however, slow. Formation of arsenite also may lead to the volatilization of arsine and methyl-arsines from soils. Under soil conditions of high organic matter, warm temperatures, adequate moisture, and other conditions conducive to microbial activity, the reaction sequence is driven towards methylation and volatilization. Arsenite can be oxidized to arsenate and manganese oxides are the primary electron acceptor in this oxidation reaction (McLean and Bledsoe, 1992).

Cadmium may be adsorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide, and phosphate. Evidence suggests that adsorption mechanisms may be the primary source of cadmium removal from soils. In soils and sediments polluted with metal wastes, the greatest percentage of the total cadmium was associated with the exchangeable fraction. Cadmium concentrations have been shown to be limited by cadmium carbonate in neutral and alkaline soils. As with all cationic metals, the chemistry of cadmium in the soil environment is to a great extent controlled by pH. Under acidic conditions cadmium solubility increases and very little adsorption of cadmium by soil colloids, hydrous oxides, and organic matter takes place. At pH values greater than 6 units, cadmium is adsorbed by the soil solid phase or is precipitated, and the solution concentrations of cadmium are greatly reduced. Cadmium forms soluble complexes with inorganic and organic ligands, in particular with chloride ions. The formation of these complexes will increase cadmium mobility in soils (McLean and Bledsoe, 1992).

Chlorides are extremely mobile due to their anionic form (Cl) and solubility (USEPA, 1984).

Chromium exists in two possible oxidation states in soils: the trivalent chromium and the hexavalent chromium. Forms of hexavalent chromium in soils are as chromate ion, predominant at pH less than 6.5 units, or CrO_4^{2-} , predominant at higher concentrations (>10mM) and at pH 2-6 units. The dichromate ions pose a greater health hazard than chromate ions. Both hexavalent chromium ions are more toxic than trivalent chromium ions. Because of the anionic nature of hexavalent chromium, its association with soil surfaces is limited to positively charged exchange sites, the number of which decreases with increasing soil pH. Iron and aluminum oxide surfaces will adsorb CrO_4^{2-} at acidic and neutral pH values. The adsorption of hexavalent chromium by ground water alluvium is due to the iron oxides and hydroxides coating the alluvial particles. The adsorbed hexavalent chromium is, however, easily desorbed with the input of uncontaminated ground water, which indicates nonspecific adsorption

of hexavalent chromium. The presence of chloride and nitrate has little effect on hexavalent chromium adsorption, whereas sulfate and phosphate inhibit adsorption. The presence of sulfate enhances hexavalent chromium adsorption to kaolinite and BaCrO_4 may form in soils at chromium contaminated waste sites. No other precipitates of hexavalent chromium compounds of chromium have been observed in a pH range of 1.0 to 9.0 units. Hexavalent chromium is highly mobile in soils and is one of the only metals to be highly mobile in alkaline soils. However, clay soil, containing free iron and manganese oxides, significantly retards hexavalent chromium migration. The parameters that correlated with hexavalent chromium immobilization in soils are free iron oxides, total manganese, and soil pH, whereas the soil properties, cation exchange capacity, surface area, and percent clay have no significant influence on hexavalent chromium mobility (McLean and Bledsoe, 1992).

Trivalent chromium forms hydroxy complexes in natural water, including Cr(OH)_2^+ , Cr(OH)_3^0 , and Cr(OH)_4^- . Trivalent chromium is readily adsorbed by soils and is least mobile in soils at a pH of 5 units. Hydroxy species of trivalent chromium precipitate at pH 4.5 units and complete precipitation of the hydroxy species occurs at pH 5.5 units. Hexavalent chromium can be reduced to trivalent chromium under normal soil pH and redox conditions. Soil organic matter has been identified as the electron donor in this reaction. The reduction reaction in the presence of organic matter proceeds at a slow rate at environmental pH and temperatures, and may require years in natural soils. The rate of reduction increases with decreasing soil pH. Soil organic matter is probably the principal reducing agent in surface soils. In subsurface soils, where organic matter occurs in low concentration, Fe(II) containing minerals reduce hexavalent chromium; however, this reaction only occurs in the subsurface soil with a pH less than 5 units, decreasing to a pH of 2.5 units (McLean and Bledsoe, 1992).

Trivalent chromium can be oxidized under certain conditions prevalent in some soils. The presence of oxidized manganese which serves as an electron acceptor is an important factor in this reaction. Industrial use of chromium also includes organic complexed trivalent chromium, which when complexed with soluble organic ligands, will remain in the soil solution. In addition to decreased trivalent chromium adsorption, added organic matter also may facilitate oxidation of trivalent chromium to hexavalent chromium (McLean and Bledsoe, 1992).

Copper is retained in soils through exchange and specific adsorption mechanisms. At concentrations typically found in native soils, copper precipitates are unstable. This may not be the case in waste-soil systems and precipitation may be an important mechanism of retention. Copper is adsorbed to a greater extent by soils and soil constituents than most other metals, with the exception of lead. Copper, however, has a high affinity for soluble organic ligands and the formation of these complexes may greatly increase copper mobility in soils (McLean and Bledsoe, 1992).

Lead (in the soluble form) when added to the soil reacts with clays, phosphates, sulfates, carbonates, hydroxides, and organic matter such that lead solubility is greatly reduced. At pH values above 6 units, lead is either adsorbed on clay surfaces or forms lead carbonate. Of all the trace metals commonly found in Class V injectate, lead is retained by the soils and soil constituents to the greatest extent under well defined, simple matrices. A decreased sorption of lead has been demonstrated when

lead is in the presence of complexing ligands and competing cations. Lead has a strong affinity for organic ligands and the formation of such complexes may greatly increase the mobility of lead in soil (McLean and Bledsoe, 1992).

Mercury distribution (including elemental mercury, mercurous ions, and mercuric ions) in the soil is dependent on soil pH and redox potential. Both the mercurous and mercuric mercury cations are adsorbed by clay minerals, oxides, and organic matter. Adsorption is pH dependent, increasing with increasing pH. Mercurous and mercuric mercury are also immobilized by forming various precipitates. Mercurous mercury precipitates with chloride, phosphate, carbonate, and hydroxide. At concentrations of mercury commonly found in soils, only the phosphate precipitate is stable. In alkaline soils, mercuric mercury will precipitate with carbonate and hydroxide to form a stable solid phase. At lower pH values and high chloride concentration, HgCl_2 is formed. Divalent mercury also will form complexes with soluble organic matter, chlorides, and hydroxides that may contribute to its mobility (McLean and Bledsoe, 1992).

Under mildly reducing conditions, both organically bound mercury and inorganic mercury compounds may be degraded to the elemental form of mercury. Elemental mercury can readily be converted to methyl or ethyl mercury by biotic and abiotic processes. These are the most toxic forms of mercury. Removal of mercury from a leachate is generally resultant through volatilization and/or precipitation rather than adsorption by clays; removal increases with increased pH. The amount of mercury removed by volatilization appears to be affected by the solubility of the mercury compounds added to the soil. Volatilization is also found to be inversely related to soil adsorption capacity (McLean and Bledsoe, 1992).

Nickel does not form insoluble precipitates in unpolluted soils and retention of nickel, is therefore, exclusively through adsorption mechanisms. Nickel will adsorb to clays, iron oxides, manganese oxides, and organic matter and is thus removed from the soil solution. The formation of complexes of nickel with both inorganic and organic ligands will increase nickel mobility in soils (McLean and Bledsoe, 1992).

Nitrogen compounds will usually oxidize to nitrate in the soil through the process of biological nitrification. This process often takes place in the aerobic environment just below the clogging mat of the soil absorption system. After organic nitrogen or ammonium has been oxidized to nitrate, denitrification, the process by which nitrate is converted to nitrogen gas or nitrous oxide, may also occur. This process requires an anaerobic environment, which may be found deeper in the soil, along with a supply of labile (constantly undergoing or likely to undergo chemical change; unstable) organic carbon to act as an electron donor (Robertson and Cherry, 1995). Soil characteristics, such as texture and structure, will primarily influence the availability of oxygen in the subsurface, and therefore, the amount of denitrification that is likely to occur (Wall, 1991). Some studies have found that ground water in areas where properly operating septic systems were underlain by poorly drained soils had much lower nitrate concentrations than in comparable areas with well drained soils (Ritter and Churnside, 1984; Miller, 1972). Permeable soils immediately below a soil absorption system with poorly drained soils in the lower soil horizons would optimize conditions for reducing nitrate

concentrations. With sufficient soil organic matter and available carbon, the denitrification process in the soil beneath septic systems can remove up to 90 percent of the nitrate from the wastewater (Eastburn and Ritter, 1984).

Denitrification is the process of removing combined nitrogen from soil and water by reducing nitrate to release nitrogen gas to the atmosphere. The removal of nitrate from an effluent stream by denitrification requires an anaerobic environment, the presence of facultative, heterotrophic microorganisms, and a source of organic carbon. During the decomposition of organic matter, after the supply of oxygen is exhausted from aerobic microbial respiration, microorganisms continue to respire organic matter as long as nitrate is present. The nitrate is reduced to the level of nitrite by bacteria (e.g., pseudomonas, achromobacter, bacillus, micrococcus). These nitrites may then be further reduced to nitrogen gas (Eckenfelder, 1980).

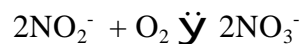


This can be expressed as:



The rate of denitrification relative to the presence of dissolved oxygen is significantly influenced by the pH of the mixture. Under alkaline conditions, denitrification is promoted by strict anaerobic conditions. However, under acidic conditions active denitrification occurs in the presence of dissolved oxygen (Eckenfelder, 1980). A carbon supply (e.g., methanol) that is supplied by untreated sewage, or an industrial wastewater can increase the rate of denitrification, but is not normally used for those systems.

Nitrification, which requires the input of oxygen, consists of two oxidizing steps that are performed by two types of chemoautotrophic bacteria collectively called nitrifiers, (e.g., nitrosomonas for the first step; nitrobacter for the second) (Benefield, 1982). Ammonia is oxidized to produce nitrites, hydrogen ions, and water. In the second step, nitrites can be oxidized further to nitrates.



This can be expressed as:



The nitrifiers are extremely sensitive to changes in pH and will require additional alkalinity (via an external source) when insufficient natural alkalinity is present. Compared to an effluent with a large ammonia concentration, a nitrified effluent is more preferable for surface discharge to reduce the oxygen demand on receiving waters.

Phosphorus is easily retained in soils due to chemical changes and adsorption. Phosphate ions become chemisorbed on the surfaces of iron and aluminum minerals in strongly acid to neutral systems, and on calcium minerals in neutral to alkaline systems. As the concentration in the soil solution is raised, there comes a point above which one or more phosphate precipitates may form. In the pH range encountered in septic tank leach fields, for example, hydroxyapatite is the stable calcium phosphate precipitate. However, at relatively high phosphorous concentrations similar to those found in septic tank effluents, dicalcium phosphate or octacalcium phosphate are formed initially, followed by a slow conversion to hydroxyapatite. Therefore, both chemical precipitation as well as chemisorption is involved in phosphorus retention in soils. Phosphates can be removed at practically all pH ranges and the removal mechanism is primarily related to the formation of relatively insoluble phosphate compounds of aluminum, iron, and calcium. The rate at which phosphorous is sorbed from solution onto the surfaces of soil constituents has been shown to consist of a rapid initial reaction followed by an important, much slower, reaction which appears to follow first order kinetics. Since the removal involves chemisorption, it is possible to exceed the sorptive capacity of the soil based on either long term use of an injection system or the application of high hydraulic loading rates. Movement of phosphorous through soils columns is minimal until all sorption sites are occupied. Thereafter, movement through the soil continues to increase, depending upon the injection rate and the pH of the soil (USEPA, 1984).

Selenium behavior in soils has received much attention in recent years. Studies were stimulated by the high incidence of deformity and mortality of waterfowl at the Kesterson Natural Wildlife Refuge in California that resulted from the input of agricultural drainage water from the western San Joaquin Valley that was high in selenium. Such studies have led to a better understanding of the distribution and movement of selenium in soils and ground water (McLean and Bledsoe, 1992).

Selenium exists in the soil environment in four oxidation states: selenide, elemental selenium, selenite, and selenate. The concentration and form of selenium in soils is governed by pH, redox, and soil composition. Selenate is the predominant form of selenium in calcareous soils and selenite is the predominant form in acidic soil. Selenite binds to sesquioxides, especially to iron oxides and its removal increases with decreasing pH. Selenite adsorption decreases dramatically in the presence of phosphate and organic acids, but appears to be unaffected by the presence of sulfate or chloride. Precipitation is not a major mechanism of retention of selenite in soils. Manganese selenite may form, however, in strongly acidic environments (McLean and Bledsoe, 1992).

Selenate dominates under alkaline conditions. In contrast to selenite, selenate is highly mobile in soils. Selenate is adsorbed by amorphous iron oxide with the maximum removal at pH of 4.5 units; adsorption decreases with increasing pH. Selenate seems to be adsorbed by weak exchange mechanisms similar to sulfate, in contrast to selenite that is specifically adsorbed by soils and soil

constituents. No stable precipitates of selenate are expected to form under the pH and redox conditions of most soils (McLean and Bledsoe, 1992).

Similar to other anionic species, selenium is converted to the elemental form. This conversion can provide an effective mechanism for attenuation since mobile selenate occurs only under well aerated, alkaline conditions. Organic forms of selenium are analogous to those sulfur, including seleno amino acids and their derivatives. Like sulfur, selenium undergoes biomethylation forming volatile methyl selenides (McLean and Bledsoe, 1992).

Silver as a cation will participate in adsorption and precipitation reactions. Silver is very strongly adsorbed by clay and organic matter and precipitates of silver, AgCl, Ag₂SO₄, and AgCO₃, are highly insoluble. Silver is highly immobile in the soil environment (McLean and Bledsoe, 1992).

Zinc is readily adsorbed by clay minerals, carbonates, or hydrous oxides, with the largest percent of total zinc being associated with iron and manganese oxides. Precipitation is not a major mechanism of retention of zinc in soils because of the relatively high solubility of zinc compounds. Precipitation may become a more important mechanism of zinc retention in soil-waste systems. As with all cationic metals, zinc adsorption increases with pH. Zinc hydrolyzes at pH greater than 7.7 units, and these hydrolyzed species are strongly adsorbed to soils surfaces. Zinc forms complexes with inorganic and organic ligands that will affect its adsorption reactions with the soil surface (McLean and Bledsoe, 1992).

It is important to remember that in addition to the chemical factors affecting adsorption, physical factors such as ground water hydraulic gradient, hydraulic conductivity, porosity, and bulk density also affect the mobility of compound. To estimate mobility of a given inorganic compound a geochemical speciation analysis, which incorporates many of the processes discussed previously, can be performed. A well-known model developed by the U.S. Geological Survey, called PHREEQ, can be used to perform a speciation analysis. An on-line interactive version of PHREEQ called Web-PHREEQ is available at the following website:

<http://www.ndsu.nodak.edu/instruct/sainieid/geochem/webphreeq/web-phreeq.shtml>.

3.2 Organic Contaminants

In addition to the general processes described above for inorganic contaminants, the mobility and persistence of organic contaminants is also affected by decomposition resulting from biological degradation by soil microorganisms. Two chemical reactions which may occur in soil are hydrolysis and neutralization of organic compounds. Microbial processes are usually the dominant decomposition pathway for organic contaminants. Thus, most of the factors which affect the degradation of organic contaminants in soil, exert their influence by affecting the microbial metabolism or soil microflora in the soil (ERT, 1984).

3.2.1 Half-lives

The term half-life is used to indicate the persistence of a chemical in the soil. The half-life of the compound is the time required for the concentration of the compound to decrease to one half of its initial value. Half-lives can be estimated from first-order kinetics if first-order rate constants are known for the contaminants of interest. Similarly, the time required for the compound to decrease to 1% of its initial level can also be estimated.

The degradation of most chemicals in the soil will follow a first-order reaction ($d_c/d_t = -KC$). The reaction indicates that at any one time, the rate of degradation is proportional to the concentration of the chemical in the soil. First-order kinetics generally apply where the concentration of the chemical being degraded is low relative to the biological activity in the soil. At very high chemical concentrations, Michaelis-Menten Kinetics seem to apply and the rate of decomposition changes from being proportional to the concentration to being independent of concentration. If the degradation rate is known at a specific temperature, rates for other temperatures can be estimated from the following relationship (ERT, 1984):

$$K_{T_2} = K_{T_1} 2^{(T_2-T_1)}$$

where 2 = temperature correction factor (1.08)

T_1, T_2 = temperatures in °C

K_{T_2}, K_{T_1} = specific decomposition rate at corresponding temperatures.

This equation is only an approximation, however, over the limited range of temperatures found in the soil, the above relationship can be utilized for practical purposes (ERT, 1984).

3.2.2 Sorption and Desorption of Organics

The sorption of organic constituents in soil may be the most important factor affecting the fate of these compounds in soil systems. Adsorption to soil constituents will affect the rate of volatilization, diffusion, and leaching, as well as the availability of these compounds to microbial or chemical degradation, or uptake by plants and other organisms. Adsorption is a process in which a solution component is concentrated at the solid-solution interface (ERT, 1984). The properties of a contaminant (or sorbate) has a profound impact on its sorption behavior; these properties include (Piwoni and Keeley, 1990):

- C water solubility
 - C polar/ionic character
 - C octanol/water partition coefficient
 - C acid/base chemistry
 - C oxidation/reduction chemistry
- Contaminant Characteristics*

In discussing sorption it is useful to divide chemicals into three groups. Although there are many ways to divide chemicals into subgroups, for this purpose three categories are presented which transcend normal boundaries between inorganic and organic species. These are: (1) ionic or charged species, (2) uncharged species, and (3) uncharged nonpolar species. Organic contaminants have representatives in all three sorption categories. Many of the more common organic ground water contaminants are the nonpolar species, including trichloroethylene, tetrachloroethylene, the chlorinated benzenes, and the more soluble components of hydrocarbon fuels such as benzene, toluene, and xylene. Other important organic contaminants including many of the pesticides, phenols, and dyes exist in solution as either charged or polar molecules. Still other, larger organics, such as surfactants, can have both polar and nonpolar ends within the same molecule. The environmental mobility of contaminants with these distinctive properties has been less thoroughly studied than nonpolar organics; therefore, site specific investigations may provide the most reliable information for their transport characteristics (Piwoni and Keeley, 1990).

Soil Characteristics

If one avoids the difference between positive and negative charges, a simple rule of sorption might be: for charged species, “opposites attract” and for uncharged species, “likes interact with likes.” Likes refers to the three categories of contaminants and to the properties of the soil matrix. Some of the most important characteristics of soil affecting the sorptive behavior of subsurface materials include:

- C mineralogy
- C permeability/porosity
- C texture
- C homogeneity
- C organic carbon content
- C surface charge
- C surface area

Soil, in its natural state, is primarily composed of sand, silt, clay, water, and a highly variable amount of natural organic carbon. The latter profoundly complicates a soil’s sorptive properties. The combination of these characteristics describes the surfaces offered as sorptive sites to contaminants in water passing through the subsurface matrix. For example, silts and clays have much higher surface areas than sand, usually carry a negative charge, and almost invariably associate with natural organic matter (Piwoni and Keeley, 1990).

It can be deduced that sandy materials offer little in the way of sorptive surfaces to passing contaminants while silts and clays, particularly those having substantial amounts of organic matter, provide a rich sorptive environment for all three categories of contaminants. Even the most porous and highly productive aquifers, composed of sands and gravels, usually have some fine grained material, and a few percent of silts and clays can result in a substantial increase in the sorptive behavior of the aquifer material (Piwoni and Keeley, 1990).

Fluid Media Characteristics

Under most contamination situations, the primary transporting fluid is water. One of the most important properties of this solvent phase is pH for it dictates the chemical form and, therefore, the mobility, of all contaminants susceptible to the gain or loss of a proton. As an example, pentachlorophenol will primarily be an uncharged polar molecule in an aqueous solution whose pH is below about 4.7 units and an anion when the pH is above that value, increasing its solubility from 14 to 90 mg/l. Other characteristics of water that can influence the behavior of contaminants include the salt content and the dissolved organic carbon content. Chlorides, for example, which are not usually of much concern when dealing with organic contaminants, can have an important effect on the mobility of various metals. Dissolved organic matter, at relatively high concentrations found in many leachates, has a significant effect on the mobility of most nonpolar organics (Piwoni and Keeley, 1990).

Implications of These Characteristics

Although somewhat simplified, it can be assumed for the purposes of this discussion, that charged and polar species tend to interact with charged and polar surfaces, and nonpolar compounds interact with nonpolar components of soil, usually the natural organic carbon. In order to make a first estimate of the significance of sorption at a site, it is necessary to determine the polar and nonpolar nature of the material which the contaminant will come into contact. This is usually done by measuring CEC and the natural organic carbon content, respectively (Piwoni and Keeley, 1990).

The CEC provides an estimate of the total negatively-charged sites on the surface of the soil. It is determined by measuring the mass of a standard cation, usually ammonia, that displaces another cation held by the soil. Under normal field conditions these sites will be occupied by cations common to the flowing or percolating water, such as Na^+ , K^+ , Ca^{2+} , and Mg^{2+} . Larger organic cations and highly-charged metal ions like Hg^{2+} or Cr^{3+} will be preferentially retained at these sites by “exchanging” with their normal occupants. Thus, large organic cations and heavy metals would not normally be expected to move far through soils with a measurable CEC. At contaminated sites, however, conditions may not be “normal” and Hg^{2+} (for example) may be codisposed of with high levels of chloride salts. The Hg^{2+} may be replaced through a complexation reaction by the neutral complex HgCl_2 or the negative ion HgCl_3^- , both of which move through the soils more quickly than the cationic form (Piwoni and Keeley, 1990).

For organic compounds there are two general cases where the affinity of the sorbate for the sorbent is greater than the affinity of the solute for the solvent and significant adsorption results. In the first case, there is a strong positive attraction between the sorbate (i.e., the contaminant that adheres to the sorbent, or sorbing material) and the sorbent (i.e., the soil), and these forces of attraction overcome even a fairly strong solute-solvent interaction. The sorption of organic cations or polar organic molecules by swelling clay minerals is an example of this type of adsorption. In the second case, adsorption results not because of strong adsorbate-adsorbent interaction, but rather because of a weak solute-solvent interaction which results in adsorption (ERT, 1984).

The adsorption of nonpolar aromatic hydrocarbons of low water solubility by soil organic matter is an example of the second type of adsorption. This type of adsorption has been called “hydrophobic adsorption” because of the emphasis on the weak solute-solvent interaction in determining the degree of adsorption in aqueous systems. Hydrophobic adsorption increases as compounds become less and less polar (i.e., as chain length, molecular volume, molecular weight, and carbon number increases). The effect of all these properties on the solute-solvent interaction is integrated into the water solubility of the compound (ERT, 1984).

Adsorption equilibria are frequently described by the empirical Freundlich equation:

$$X/M = KC_e^{1/n}$$

where X/M = amount (X) of adsorbed chemical per unit amount of adsorbent (M)

C_e = equilibrium solution concentration of the chemical

K = Freundlich adsorption coefficient, and

n = constant related to adsorption intensity.

Hydrophobic sorption has been shown to be highly correlated with the organic carbon content of the soil. When the sorption of hydrophobic compounds is expressed as a function of the organic carbon content of the soil, a constant K_{OC} , is generated which is a unique property of the compound being sorbed (ERT, 1984):

$$K_{OC} = (K_p)/(f_{OC})$$

where K_{OC} is equal to the partition coefficient (K_p) divided by f_{OC} , the fractional mass of organic carbon in the soil. This constant is independent of other soil properties and is only dependent on the nature of the adsorbing species. Thus, if the K_{OC} has been determined for a hydrophobic compound, the sediment/water partition coefficient (K_p) can be estimated for a variety of soils if the organic carbon content of each soil is known (ERT, 1984).

Many studies have investigated the relationship between the organic matter and the organic carbon content of the soil. Recent studies indicate that organic matter in subsurface soils is approximately 2.5 times greater than organic carbon. The influence of the water solubility of a chemical has been examined by numerous investigators and they found that the adsorption of hydrophobic compounds increases with decreasing water solubility. The adsorption of more polar compounds also increases with decreasing water solubility, but only within an individual class of chemicals (ERT, 1984).

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