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A REVIEW OF PROCESSES AFFECTING THE FATE OF
CONTAMINANTS IN GROUNDWATER

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RÉSUMÉ

Ce document examine les processus hydrologiques et hydrochimiques qui
influent sur l'évolution des matières contaminantes dans les eaux
souterraines. Le transport de ces substances est régi par des phénomènes
hydrogéologiques, tandis que les réactions chimiques, comme la sorption,
l'hydrolyse et la biodégradation, inhibent ou atténuent ces matières. Un
résume les résultats des recherches menées en Europe et en Amérique du Nord
au cours des dernières années pour que les non initiés puissent se
familiariser avec le domaine de la pollution des eaux souterraines.

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ABSTRACT

The hydrological and hydrochemical processes controlling the fate of contaminants in groundwater flow systems are reviewed. The transport of these contaminants is controlled by hydrogeological phenomena, while chemical reactions, such as sorption, hydrolysis and biodegradation, act to retard and/or attenuate these substances. The results of recent research by European and North American workers are summarized for the benefit of readers unfamiliar with groundwater pollution.

INTRODUCTION

Twelve years ago Cherry et al. (1975) introduced the term "contaminant hydrogeology" to describe the study of the hydrologic and chemical processes controlling the migration and attenuation of contaminants in groundwater flow systems. Since that time the field of contaminant hydrogeology has grown rapidly. The purpose of this review is to familiarize the nonspecialist reader with the literature of contaminant hydrogeology, in particular the current theories concerning the transport, retardation and transformation of contaminants in groundwater flow systems.

The contaminants of greatest concern to hydrogeologists and public health officials are those which are simultaneously toxic, mobile and persistent in the subsurface. Few toxic inorganic contaminants are particularly mobile in the subsurface; the principal exceptions being inorganic oxyanions such as those of arsenic, hexavalent chromium, etc. Despite this, the hydrogeology of inorganic contaminants has received most attention over the past 25 years due to concerns about the extreme toxicity of the radionuclides involved with radioactive waste disposal. However, the present decade has seen the rapid development of interest in the fate of toxic organic chemicals in the subsurface due to their discovery in many hazardous waste sites and their persistence and mobility in the subsurface.

This paper begins with a review of the transport processes affecting the mobility of contaminants in aquifers, i.e. those bodies of granular or fractured materials which can transmit groundwater and contaminants. The second section describes the contaminant retardation processes controlling solute mobility and concentration, i.e. solubility, sorption and desorption. Finally, the various abiotic and biotic transformation reactions which affect the persistence of both inorganic and organic contaminants are described.

CONTAMINANT TRANSPORT PROCESSES

Solute Transport by Groundwater

The average velocity of a nonreactive or conservative contaminant (i.e. one which does not undergo retardation or attenuation) is identical to that of the groundwater transporting it (Bear, 1972, p. 23):

$$V_{GW} = q/n \tag{1}$$

where V_{GW} is the average linear groundwater velocity (L/T), q is the specific discharge of groundwater through a unit area of granular medium (L³/L²T) and n is the porosity (dimensionless).

Reactive contaminants are those whose average velocity is less than that of groundwater because of their reaction (i.e. sorption) with aquifer materials. This reaction results in their distribution or partitioning between the aquifer matrix and the groundwater. Their average velocity (V_c) is given by (Freeze and Cherry, 1979, p. 404):

$$V_c = \frac{V_{GW}}{R_f} = \frac{V_{GW}}{1 + (\rho_b K_p/n)} \tag{2}$$

where R_f is the dimensionless retardation factor, ρ_b is the bulk density of the granular medium (M/L³) and K_p is the partition or distribution coefficient (K_D) of the contaminant (L³/M) as described by the slope of an equilibrium linear adsorption isotherm (see Tinsley, 1979, p. 18, or Freeze and Cherry, 1979, p. 403).

The generalized equation which describes the mass balance of a contaminant with concentration C (M/L³) in uniform, steady flow in the x direction in a saturated granular medium is given by the transport equation (e.g. Bear, 1972):

$$R_f \frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} - V_{GW} \frac{\partial C}{\partial x} - \lambda R_f C \tag{3}$$

where t is time, D is the coefficient of hydrodynamic dispersion (L²/T) and λ is a first-order rate constant (T^{-1}). As written above the dispersion coefficient is a tensorial measure of the distribution of velocities about the mean value (i.e. V_{GW}) due to heterogeneities in the granular or fractured medium, drag forces exerted by the grains on the groundwater, molecular diffusion, etc. The term containing V_{GW} is known as the advective flux and results from solute transport governed by groundwater advection. The first-order rate constant may symbolize either a biotic or an abiotic (e.g. hydrolysis or radioactive decay) transformation process.

Transport in Granular Media

The structure of most granular aquifer formations, e.g. of glaciofluvial or alluvial origin, is three-dimensionally heterogeneous and anisotropic, and may be characterized by its grain-size and hydraulic-conductivity distributions. The hydraulic conductivity, K, forms a second rank symmetrical tensor which may be approximated by its statistical description of the spatial variability (Dagan, 1982; Gelhar and Axness, 1983).

In horizontally stratified aquifers the principal directions of anisotropy coincide with the horizontal and the vertical coordinate axes. If the groundwater flow is predominantly parallel to the bedding, the distribution of K governs the residence-time and the transport-velocity distributions of nonreactive contaminants between two points of interest in a groundwater flow system (Mercado, 1967; Pickens and Grisak, 1981). The residence time of the groundwater corresponds to that of a conservative contaminant because the latter does not, in theory, undergo chemical retardation or biological attenuation. Figure 1 shows schematically the effect of the grain size and the hydraulic conductivity in different aquifer layers on the average linear groundwater flow velocity. Parts b, c and d of Figure 1 are cumulative distribution functions which give the probability of obtaining a value smaller than or equal to some value of the discrete random variables d, K, V and C.
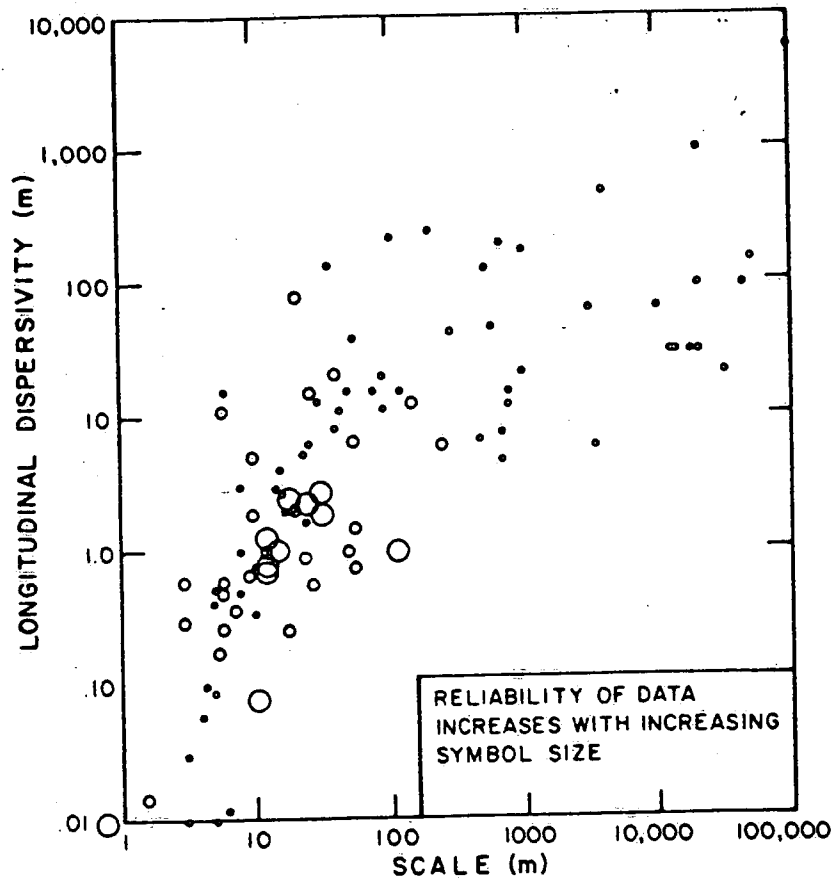
Figure 2   The scale of observation versus longitudinal dispersivity for the saturated zone: reliability classification (from Gelhar et al., 1985).

Our understanding of fluid flow and contaminant transport in such media is based on the conceptual model of laminar flow between planar parallel plates which together form a fracture, the so-called parallel plate model (see Snow, 1968; Gale, 1977 and Witherspoon et al., 1980). Starting with the Navier-Stokes equation for the one-dimensional flow in the x-direction of a viscous, incompressible fluid (i.e. groundwater), one may derive the following expression relating the velocity (V_{GW} in L/T) through the parallel plate fracture to the fracture width, which is usually identified as 2b (Eagleson, 1970; Gale, 1977):

$$V = (w/12\mu) \ (2b)^2 \ dh/dx \qquad\qquad (4)$$

where w is the specific weight of water, μ is the dynamic viscosity and dh/dx is the hydraulic gradient.   By integrating over the width of the fracture, one obtains the cubic law describing the dependence of the flow rate in such fractures to the aperture width:

$$Q = (w/12\mu) \ (2b)^3 \ dh/dx \qquad\qquad (5)$$

Because flow and transport properties of fractured media are dominated by this fracture or aperture width, two different approaches have developed to study the hydrogeology of fractured media.   One direction of research aims at laboratory and field tracer experiments with single fractures in those situations in which such fractures appear to dominate the hydraulic properties of the rock, e.g. Neretnieks et al., 1982; Novakowski et al., 1985.   The second approach treats the fractured rock mass as being equivalent to a porous medium with flow of groundwater and contaminants through a network of interconnecting fractures, e.g. Endo et al., 1984; Smith and Schwartz, 1984.

The first substantial advance in recent understanding of solute transport in fractured media came from the work of Grisak and Pickens (1980) and Neretnieks (1980) who simultaneously extended the concept of dual--porosity media introduced by Barenblatt et al. (1960). They showed that solute transport through fractured geological materials, e.g. tills, clays, shales, and granites, may be described by advective-dispersive transport in the fractures with accompanying diffusive transport into and out of the adjacent geological matrix (see Figure 3A). This "matrix diffusion" results in substantial retardation of the solute front as shown in Figure 3B; the effect being dependent upon the aperture width of the fracture, the porosity of the matrix and both the molecular diffusion coefficient and the sorption of the contaminant within the matrix. The principal application of matrix diffusion theory has been in the assessment of radionuclide transport through fractured rocks which comprise the intended repository for radioactive wastes, for example, the granitic rocks of the Canadian and the Scandinavian Shields.
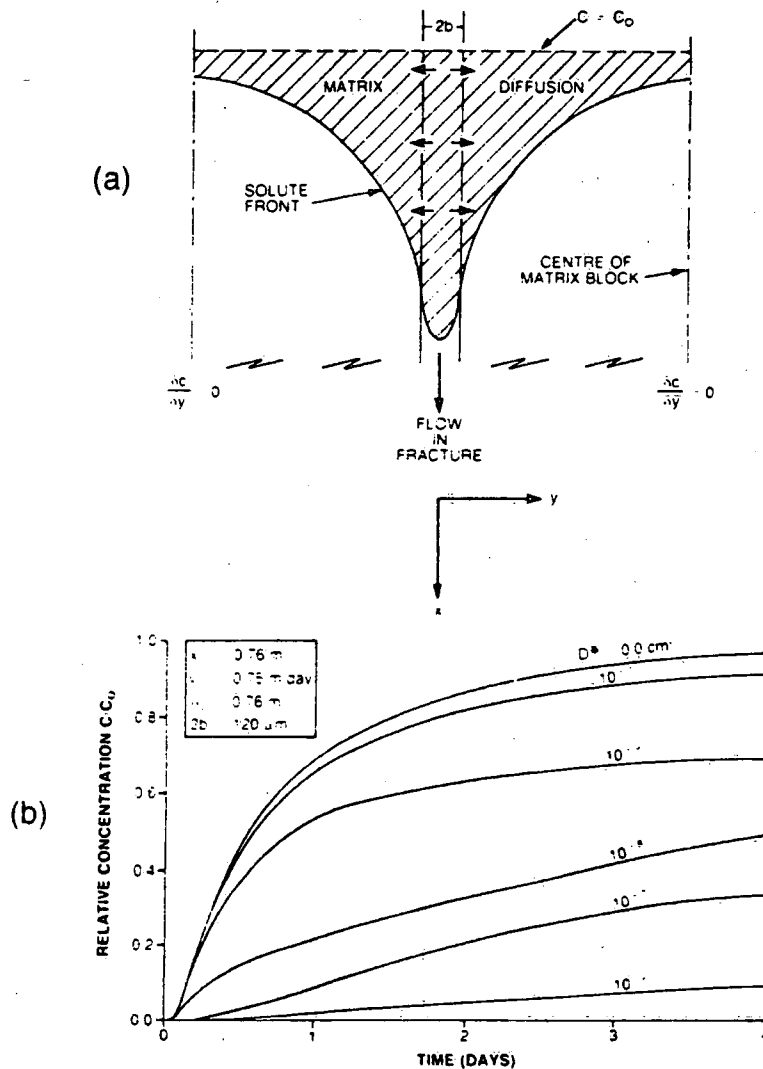

Figure 3   (a) Schematic of solute transport in a fracture of aperture 2b, with a constant source input, C_0, and periodic boundary condition of zero concentration gradient (C/y = 0) at centre of matrix blocks.

(b) Effect of matrix diffusion on solute breakthrough curves obtained at distance 0.76 m from source with a range of matrix diffusion coefficients representative of most geologic media (from Grisak and Pickens, 1980).

The majority of the efforts made to understand the phenomena of groundwater contamination has involved dissolved contaminants. However, many problems relate to the transport of non-aqueous phase liquids (NAPL). While the study of the migration of NAPL through aquitards and aquifers has been of concern in Europe for many years (e.g. Schwille, 1975), most recently interest has developed in North America (e.g. Faust, 1985). Toxic components dissolved from NAPL are probably transported from dumpsites bordering the Niagara River into Lake Ontario. The flow of NAPL in aquifers is dependent upon the viscosity and density of the NAPL, the relative permeability of the medium to the various states of saturation of the NAPL (see Figure 4a) and the related capillary pressures.

In experimental studies, Schwille (1984) has shown the effects of positive and negative density differences between NAPL and the groundwater. The experiments included gasolines ($\rho < 1000$ kg/m^3) and chlorohydrocarbons (CHC; $\rho > 1000$ kg/m^3). Faust (1985) has presented a model for such systems and applied it to the leakage of such non-aqueous phases, which could represent the migration from leaking storage tanks or from dumpsites. Both authors point out that the greater danger arises from dense, low-viscosity immiscible contaminants (DNAPLs) which tend to travel fast and deep as is
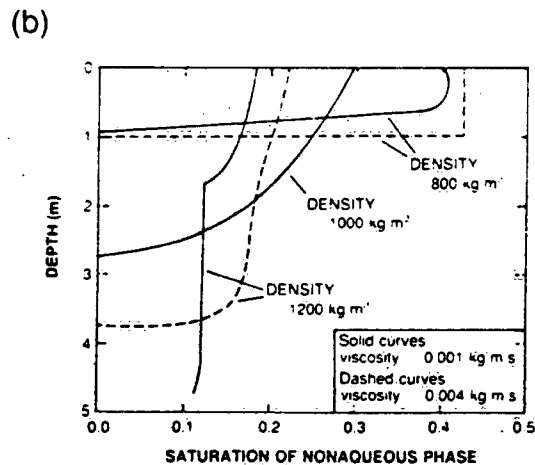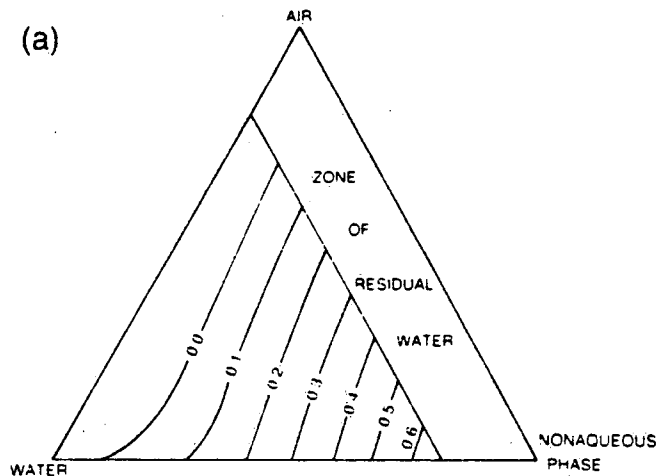
(a)

(b)

Figure 4   (a) Ternary diagram showing the relative permeability of the nonaqueous phase as a function of phase saturations.

(b) Saturation profile of nonaqueous phase below a hypothetical source (located at the upper left-hand corner of figure) 0.317 years after leakage began for specified homogeneous phase densities and dynamic viscosities (from Faust, 1985).

shown in Figure 4b, to eventually reach the bottom of aquifers. "An estimate of the form and extent of CHC 'lenses' is practically impossible" (Schwille, 1981). Low-density, viscous liquids (LNAPLs), however, "tend to remain at shallow depths and are more amenable to corrective measures such as excavation or pumping-recirculation strategies" (Faust, 1985).

CONTAMINANT RETARDATION PROCESSES

Inorganic and organic solutes are usually retarded during their transport through groundwater flow systems by chemical reactions at the surfaces of the aquifer materials. This has been observed for such diverse contaminants as cations like strontium-90 (Pickens et al., 1981) and calcium and magnesium (Valocchi et al., 1981) and hydrophobic neutral organics such as trichloroethylene and tetrachloroethylene (Schwarzenbach et al., 1983). This phenomenon is usually expressed by the retardation factor shown in equation 2. The chemical reaction causing retardation may be (1) an adsorption reaction like ion exchange or specific adsorption, or (2) a solubility-controlled reaction such as precipitation or coprecipitation or (3) a hydrophobic reaction which results in the uptake of sparingly soluble organic molecules by aquifer materials.

Adsorption

The effects of adsorption processes on groundwaters have long been observed at waste disposal sites and quantified in terms of the retardation factor and the distribution coefficient (see eq. 2). For example, Patterson and Spoel (1981) and Reynolds et al. (1982) evaluated the retardation of radiostrontium (i.e. Sr-90) at the Chalk River Nuclear Laboratories in Ontario by laboratory batch and/or column experiments to measure R_f and K_D. Such lab measurements and the associated predictions are based upon two principal assumptions:

1. that local chemical equilibrium is attained between dissolved and sorbed Sr-90 both in the lab experiment and in situ, and
2. that the lab and in-situ adsorption isotherms are linear.

Considering the first assumption, the adsorption of Sr-90 at Chalk River is demonstrably partially irreversible and consequently process is a nonequilibrium one (Jackson and Inch, 1983). Furthermore, the same kind of specific adsorption reactions that contributed to the nonequilibrium adsorption of Sr-90 at Chalk River have been observed in the adsorption of Cr(VI) in alluvial aquifer materials in Colorado (Stollenwerk and Grove, 1985) and in glaciofluvial aquifer materials on Long Island (Ku et al., 1978). In addition, the experimental results of James and Rubin (1979) indicate that, should the coefficient of hydrodynamic dispersion be significantly larger than the molecular diffusion coefficient for the ion of interest, then local chemical equilibrium will not be attained. This would seem to be the general case.

Considering the second assumption, Reynolds et al. (1982) indeed showed evidence of a linear adsorption isotherm for radiostrontium with K_D = 15 mL/g, similar to the in-situ value of 10 mL/g measured by Jackson and Inch (1983). Manipulation of the latter's in-situ Sr-90 data yield adsorption isotherms that are essentially linear; departures from linearity appear to be due more to variations in the adsorption capacity of the aquifer materials than to variations in ionic competition.

Consequently, the R_f approach will continue to be used to obtain first approximations of contaminant transport (e.g. Johnston et al., 1985), i.e. ones in which dispersion may be neglected (Valocchi, 1984). More complex solutions will require consideration of adsorption/desorption kinetics and of the reversibility of the reactions (Rubin, 1983).

While adsorption reactions such as those described above will significantly retard inorganic contaminants, other reactions, such as the complexation of transition metals in groundwaters by organic ligands can result in the migration of toxic contaminants in quantities much larger than

anticipated. Killey et al. (1984) have described a situation at Chalk River in which sorbed Co-60 was desorbed and transported through a sand aquifer to a nearby stream following the disposal of complexing agents into the disposal site into which the radiocobalt was disposed. While much of the Co-60 is irreversibly adsorbed, most of the dissolved radiocobalt is in solution as a hydrophilic, anionic organic complex.

Solubility Controls

It was not until the mid-1960s that geochemists began to study the solubility of metals in groundwaters. They began with an assessment of the solubility controls on iron, which causes numerous quality problems in potable groundwater supplies. Because iron has two oxidation states in natural waters, this assessment went hand-in-hand with the development of hydrogeological interest in oxidation-reduction (i.e. redox) processes in groundwater flow systems.

The electrochemical evolution of groundwater was first studied in detail in the West by Back and Barnes (1965) of the U.S.G.S., who showed that the measured platinum electrode potential, E_H, decreased down the hydraulic gradient in groundwater samples taken from a confined aquifer system. As the E_H value decreased in such systems, oxide minerals such as $Fe(OH)_3$ and MnO_2 become thermodynamically unstable, dissolve and release any sorbed or coprecipitated metal ions associated with them. Further decreases lead to sulfate reduction and the precipitation or coprecipitation of metals as metal sulfides (e.g. Jackson and Patterson, 1982). Conversely in a shallow, unconfined aquifer, it is possible that the infiltration of dissolved oxygen in groundwater recharge will cause the oxidation of sulfide minerals and/or the oxidation of reduced groundwaters leading to the precipitation of metal ions as oxide coatings on the aquifer matrix (Champ et al., 1979).

Recent field studies by the University of Waterloo at the Borden landfill and the Elliot Lake uranium mine-tailings disposal area, both in Ontario, have considerably added to our knowledge of the role of solubility processes in controlling metal-ion contamination. Nicholson et al. (1983) pointed out that carbonate minerals, such as siderite ($FeCO_3$), could also control the solubility of metal ions in leachate at Borden. Dubrovsky et al. (1985) identified solubility controls on iron by siderite and jarosite ($KFe_3(SO_4)_2(OH)_6$) and on aluminum by allophane, $Al(OH)_3$, and basaluminite in pyritic tailings at Elliot Lake.

Consequently, studies on the solubility of transition metals in contaminated groundwaters require a complete understanding of the redox state of groundwater and the redox chemistry of the metal ion in question, as well as its propensity to form complex ions. For example, Theis and Richter (1979) undertook a comparison of solubility and adsorptive controls on heavy metals in fly-ash leachate contaminating shallow groundwater. They concluded that sorption by Fe(III) and Mn(IV) oxides controlled the mobility of Cd, Ni and Zn, while precipitation accounted for the observed concentrations of Cr(III), Cu and Pb.

It should be noted that the chemical forces responsible for solute precipitation and coprecipitation are the same forces that control adsorption; "there are no others available" (Parks, 1975). The equality of solubility controls, such as coprecipitation, and adsorptive processes can be demonstrated by the following example of James and Parks (1975). Assume that, somewhere in a contaminated aquifer, Zn^{++} is adsorbed to the surface of HgS, mercuric sulfide, a trace mineral in the aquifer. The adsorption reaction may be written as follows:

$$Zn^{++} + HgS = ZnS + Hg^{++}; \quad K_{ex} \qquad (6)$$

where K_{ex} is the ion exchange constant. If elsewhere in the same aquifer, Zn^{++} is coprecipitated with the HgS in a solid solution rather than "adsorbed" from groundwater, then the coprecipitation reaction is defined by D, the distribution ratio (Stumm and Morgan, 1981, pp. 288-9):

$$D = \frac{K_{SO} \text{ (for HgS)}}{K_{SO} \text{ (for ZnS)}} \tag{7}$$

where K_{SO} is the solubility product for the particular compound. However, the two reactions are equivalent in terms of their mass action expressions:

$$D = K_{ex} = \frac{(ZnS)(Hg^{++})}{(Zn^{++})(HgS)} \tag{8}$$

and therefore the processes are equivalent, or as Parks (1975) writes "the same forces responsible for ... compound formation are responsible for adsorption". Just as the mass action expressions show no difference between the processes, neither would a retardation factor for Zn^{++} show any difference, precisely because the chemical bonds that retard the zinc ion do not differ between "adsorption" and "coprecipitation".

In the example above it is assumed that the solubility product is well defined, however, this is often not the case. Consider the actinide metals produced during nuclear fission, which are substances of extreme toxicity. The fate of such metals in radioactive wastes, which may in future be stored in mined rock repositories and from which the radionuclides may be potentially leached, can only be assessed if the relevant thermodynamic constants for each radionuclide are known. In the case of thorium, i.e. Th-232, the reported solubility product of ThO_2 (as $Th(OH)_4$) varies from 10^{-23} to 10^{-54}. We consider the value of 10^{-49} of Wagman et al. (1977) to be the most reliable because the solid phase was identified as crystalline ThO_2 by electron diffraction analysis and the value is probably consistent with reliable hydrolysis constants at low pH. This variability is further complicated by the absence of reliable stability constants for the soluble thorium species at typical groundwater pH's, i.e. the anionic thorium hydrolysis products. Given such uncertainties, the role of the hydrogeologist in predicting solute transport is doubly difficult.

Hydrophobic Bonding

Most of the toxic organic chemicals identified in groundwaters beneath hazardous waste sites are hydrophobic, i.e. they are sparingly soluble in water, and neutrally charged. If neutral, organic molecules (M) are to dissolve in groundwater, they must distort or disrupt the structure of the water molecule created by the strong hydrogen bonds between water molecules (Tanford, 1980):

$$2(H_2O - H_2O) + (M - M) = 2(H_2O-M-H_2O) \tag{9}$$
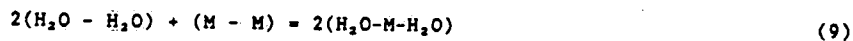
which reaction is biased to the left because of the hydrogen bonding. If nonpolar aquifer materials are added to the above system, sorption occurs due to this same hydrophobic effect, a process called hydrophobic bonding:

$$H_2O + M + OS = H_2O + M-OS \tag{10}$$

where OS refers to organic sorbents, i.e. the nonpolar aquifer materials of greatest importance (Karickhoff, 1984). Such sorption may be considered as like dissolving in like.

Karickhoff (1984) has pointed out that this sorption reaction is thermodynamically controlled by the activity coefficient of the molecule in groundwater, which is a measure of the molecule's affinity for water. Because it is not feasible to measure this activity coefficient, numerous expressions have been developed which correlate readily measurable or available parameters, such as the octanol-water partition coefficient - K_{OW}, with observed levels of sorption.

The most useful of these expressions for hydrogeological purposes is that of Schwarzenbach and Westall (1981), who used a linear free energy relationship to relate the partition coefficients of a nonpolar solute z in different aqueous/nonaqueous solvent systems:

$$\log K_{SW}^z = a \log K_{RW}^z + b \qquad\qquad (11)$$

where K_{SW}^z is the partition coefficient of z between the solvent S and water (W) and K_{RW}^z is that for a reference solvent R, usually octanol, hence K_{ow}, the octanol-water partition coefficient. The slope constant a is a measure of the lipophilicity of solvent S relative to R, and hence, when the solvent is sedimentary organic matter, it is a measure of its capacity for sorption. For compounds $2.6 < \log K_{ow} < 4.75$ in contact with alluvial aquifer materials, Schwarzenbach and Westall found that the value of a varied from 0.50 to 0.71. The intercept constant is a function of the units in which K is measured.

Schwarzenbach and Westall went on to describe the sorption of chlorinated benzenes by sediments with $f_{oc} > 0.001$ by the following relationship:

$$\log K_p^z = 0.72 \log K_{ow}^z + \log f_{oc} + 0.49 \qquad (r^2 = 0.95) \qquad (12)$$

where f_{oc} is the weight fraction of organic carbon and K_p^z is the partition (or distribution) coefficient of z in units of ML/g. This value of the partition coefficient may be used in the retardation equation (eq. 2) to estimate the retardation factor of an organic contaminant in a porous medium of known porosity and bulk density; the relationships between K_{ow} and R_f and between K_{ow} and the relative ionic velocity (V_c/V_{GW}) are shown in Figure 5.
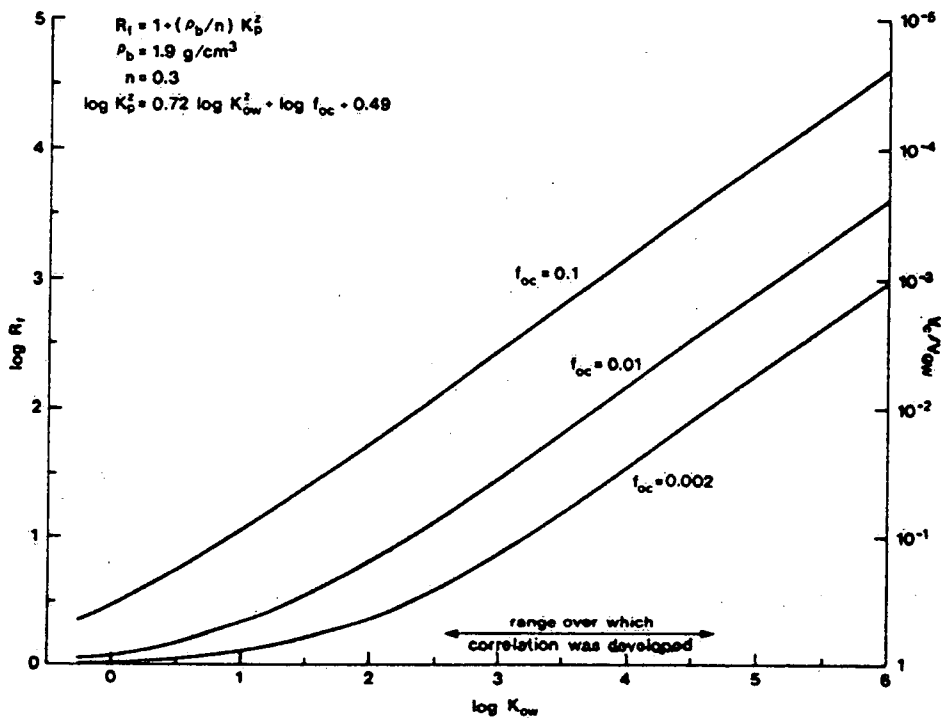

Figure 5   Variation of the retardation factor with the octanol-water partition coefficient for various concentrations of sedimentary organic carbon using equation 12.

A recent field experiment (Mackay et al., 1986) conducted by Stanford University and the University of Waterloo at Canadian Forces Base Borden, Ontario has provided a test of the Schwarzenbach/Westall predictive equation (eq. 12). In this natural gradient tracer test, 12,000 L of tracer solution was injected into a shallow sand aquifer and monitored for a three-year period. The solution contained two nonreactive tracers, chloride and bromide, and five halogenated organic chemicals, bromoform (BROM), carbon tetrachloride (CTET), tetrachloroethylene (PCE), 1,2-dichlorobenzene (DCB) and hexachloroethane (HCE). Some 5,000 monitoring points were employed to monitor the path of tracers and nearly 20,000 samples were collected and analysed. All organic tracers were retarded during the tracer relative to the inorganic tracers. Retardation factors from the field data of this test, from equation 12 and from laboratory batch sorption experiments are presented in Table 1.

TABLE 1   Comparison of retardation factors for the Borden tracer test (Curtis et al., 1986). Predicted values are from equation 12 with $f_{oc}=0.0002$. The field values are from the analysis of breakthrough curves (temporal) and from spatial mapping of the plume (Roberts et al., 1986).

Compound	log K_{ow}	Predicted	Batch	Field Data	
				Temporal	Spatial
CTET	2.7	1.3	1.9±0.1	1.6-1.8	1.8-2.5
BROM	2.3	1.2	2.0±0.2	1.5-1.8	1.9-2.8
PCE	2.6	1.3	3.6±0.3	2.7-3.9	2.7-5.9
DCB	3.4	2.3	6.9±0.7	1.8-3.7	3.9-9.0
HCE	3.6	2.3	5.4±0.5	4.0	5.1-7.9

The retardation factors from Equation 12 are significantly smaller than the field values. A similar phenomenon is apparent in the data of Jackson et al. (1985, their table 5) from the Gloucester, Ontario landfill in which the mobility of six organic compounds with log K_{ow} values from -0.27 to 2.7 (CTET) were analyzed. Curtiss et al. (1986) ascribe this to the neglected sorption of the organic tracers onto the mineral fraction of the aquifer materials, which may be significant at low f_{oc} concentrations such as at Borden. The batch results are relatively good vis-a-vis the field values; the laboratory experiments produced essentially linear and, for HCE, reversible isotherms.

The above methods allow approximate estimates of contaminant mobility under conditions of low-level contamination, such as at the front of an advancing plume. However, in the immediate vicinity of a landfill or other location with high levels of organic contamination, contaminant concentrations will likely be substantially higher and estimates of contaminant retardation significantly more uncertain. In heavily contaminated porous media sorption isotherms may be strongly nonlinear and microbial activity much reduced resulting in greater mobility of the contaminant (Rao and Davidson, 1979). Furthermore, as the fraction of organic solvent to groundwater increases in the contaminated pores, the retardation factor exponentially approaches unity (Rao et al., 1985).

CONTAMINANT TRANSFORMATION PROCESSES

Despite the seemingly adverse conditions for degradation of toxic contaminants in the subsurface, degradation does occur over time by physical, chemical and microbiological processes. Because of the present concern about the persistence of halogenated organic chemicals in groundwater, we shall concentrate this discussion on that particular class of contaminant. The principal reaction types are shown in Figure 6.

It should be noted that some transformation reactions depend only upon the atomic instability of the contaminant, i.e. radionuclides. Others depend only upon certain physical and chemical properties of the groundwater (e.g. pH, E_H and T); these relatively slow processes include hydrolysis reactions which involve a component ion of the water molecule. A third type occur more

rapidly due to the catalytic effects of microbially-produced enzymes; such reactions are commonly biological transformations. In this latter case it is probable that the principle constraints on microbial proliferation and enzymatic function are groundwater temperature, redox conditions and nutrient availability (Champ et al., 1979).

Abiotic Transformation

There are several abiotic transformation processes of interest to the hydrogeologist. The first is that of radioactive decay, with which hydrogeologists are perhaps the most familiar on account of their work on the migration and attenuation of radionuclides in the subsurface (e.g. Pickens et al., 1981; Reynolds et al., 1982; Killey and Munch, this issue). The second is that of oxidation, an example of which, the thio-oxidation of aldicarb in a sandstone aquifer is described by Priddle et al. in this issue. A third type of abiotic reaction is the substitution of the halogen atom of a contaminant by an HS group; Schwarzenbach et al. (1985) have described the occurrence of such reactions in groundwaters containing H_2S beneath a chemical plant in Switzerland. The fourth is the hydrolysis of halogenated hydrocarbons, which is summarized below.

We assume that all transformations occurring in groundwater without microbial catalysis may be described by a general rate law such as (Tinsley, 1979):

$$\text{rate of degradation} = \frac{(-dC)}{(dt)} = k[A]^n[B]^m \qquad (13)$$

where C and t are as defined, k is a rate constant associated with the concentrations of components A and B and the order of the reaction is equal to the sum of the exponents (n+m). Should only component A be involved in the transformation and n=1, as is the case with radioactive decay, equation 13 becomes the simple first order reaction which yields, by integration, the half life of the reaction, $t_{1/2} = 0.693/k$.

Several hydrolysis reactions relevant to groundwater pollution have been documented. Mabey et al. (1983) have pointed out that some polyhalogenated alkanes of environmental interest undergo OH^--induced hydrolysis to yield an alkene and HHal by a dehydrohalogenation reaction of the kind shown in Fig. 6. These include the pesticides 1,2-dibromo-3-chloropropane or DBCP (Burlinson et al., 1982) and 1,2,-dibromoethane (Vogel and Reinhard, 1986) and several chlorinated ethanes (Walraevens et al., 1974). However, the rates of these reactions at pH 7 may be slow. At 25°C, 1,1,1-trichloroethane hydrolyses with a half life of less than 1 year (Mabey et al., 1983), while DBCP has a half life of 141 years at 15°C (Burlinson et al.) and chloroform has a value of 3500 years at 25°C (Mabey and Mill, 1978).
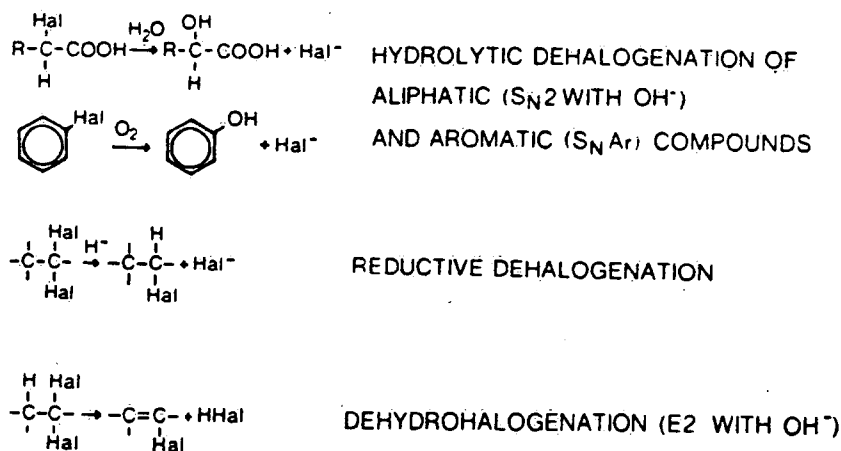

HYDROLYTIC DEHALOGENATION OF ALIPHATIC (S_N2 WITH OH^-) AND AROMATIC (S_NAr) COMPOUNDS

REDUCTIVE DEHALOGENATION

DEHYDROHALOGENATION (E2 WITH OH^-)

Figure 6   Reactions important in the transformation of organic pollutants (after Hill, 1978).

Recent studies of the microbial transformation of the common organic pollutants of groundwater clearly indicate that the redox (oxidation-reduction) environment is the controlling variable. Assuming that groundwater temperature and dissolved nutrient concentrations are capable of supporting microbial growth and enzymatic function, it is likely that chlorinated aromatic compounds will be biodegraded under aerobic conditions while halogenated aliphatic compounds will be biotransformed only in anoxic environments (McCarty et al. 1984), which commonly result from groundwater contamination.

Oxygenated groundwaters are likely to be found in the recharge areas of granular aquifers (Champ et al., 1979; Freeze and Cherry, 1979) but, on occasion, may be observed at depth within groundwater flow systems (Winograd and Robertson, 1982). In such oxic environments aromatic hydrocarbons, such as benzene, toluene, phenols, chlorobenzenes and chlorophenols, are likely to undergo biotransformation (Wood, 1982; Wilson and McNabb, 1983; Bouwer, 1983). In anoxic conditions, if oxygen is not present on the aromatic ring or in a substituent of the ring (e.g. OH$^-$, COOH), then the cleavage of the ring (i.e. biodegradation) appears unlikely (Bouwer and McCarty, 1983b). However, there is evidence that nitrate can substitute for oxygen as an electron acceptor (Zeyer et al., 1986) in the biodegradation of toluene and m-xylene.

Field studies of aromatic hydrocarbons are consistent with the above hypothesis. Ehrlich et al. (1982) have shown that phenolic compounds undergo anaerobic biodegradation in groundwaters containing 2-20 mg CH_4/L; because phenols contain -OH groups this observation appears to confirm Bouwer and McCarty's (1983b) conclusion concerning the importance of oxygen-containing functional groups in the anoxic biotransformation of aromatic compounds. Schwarzenbach et al. (1983) observed the biotransformtion of alkylated and halogenated aromatic compounds under oxic conditions but, significantly, noted that 1,4-dichlorobenzene appeared not to be biotransformed during periods of denitrification within the aquifer.

Once the available molecular oxygen in groundwater has been reduced, redox reactions result in the sequential reduction of nitrate, manganese and iron oxides, sulfate and dissolved carbon dioxide (Champ et al., 1979; Jackson and Patterson, 1982). Therefore denitrification conditions are mildly reducing compared with environments within which sulfate reduction and methane fermentation occur. In reducing environments reductive dehalogenation and dehydrohalogenation reactions are known to biodegrade halogenated aliphatic compounds. The best documented occurrence of these reactions is the biotransformation of DDT to TDE by reductive dechlorination and of DDT to DDE by dehydrochlorination (Hill, 1978).

From laboratory studies it appears that halogenated aliphatics undergo anaerobic dehalogenation by processes similar to DDT degradation. Bouwer and McCarty (1983a, b) showed that with an acclimation period, carbon tetrachloride and three brominated trihalomethanes were degraded in the presence of denitrifying bacteria; furthermore chloroform, carbon tetrachloride and 1,2-dichloroethane were almost completely transformed to CO_2 by biological oxidation under methanogenic conditions. Vogel and McCarty (1986) presented evidence for the reductive dechlorination of tetrachloroethylene to trichloroethylene under methanogenic conditions and proposed a sequence of dehalogenation reactions leading to CO_2.

The results of field studies in Europe and California are consistent with the foregoing conclusions. Biotransformation of trihalomethanes ($t_{1/2}$: 3-6 weeks) and chlorinated ethanes and ethenes ($t_{1/2}$: 5-9 months) was observed in an anoxic aquifer receiving reclaimed municipal wastewater (Bouwer, 1983). Piet and Zoeteman (1980) also reported that trihalomethanes (20-100 ppb) are "eliminated" under anoxic conditions during passage through sand dunes. Schwarzenbach et al. (1983) concluded that chloroform, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene were persistent under oxic and seasonally anoxic conditions during infiltration of river water to an alluvial aquifer.

Recently, Klecka and Gonsior (1984) reported the reductive dehalogenation of carbon tetrachloride, chloroform and 1,1,1-trichloroethane (i.e. all having three or more chlorine atoms attached to the same carbon) by

by reaction with a naturally-occuring pigment, Fe(II)-porphyrin, dissolved in an anoxic redox buffer. Since such porphyrins are a component of proteins in most living organisms and are likely present in the decay products of organic matter, reduced iron porphyrin systems may play an essential role in the degradation of halogenated organic compounds in groundwater. For example, Criddle et al. (1986) speculated that the aerobic biotransformation of hexachloroethane to tetrachloroethylene during the Borden tracer test (Mackay et al., 1986) was mediated by such an iron porphyrin system.

In summary, therefore, some rules of thumb concerning the likelihood of contaminant transformation may be put forward. In oxidizing environments (i.e. ones containing oxygen and/or nitrate) aromatic compounds will be biotransformed; in such conditions aliphatic halides are not degraded, however exceptions may occur should iron-porphyrin systems mediate the reactions. In anoxic conditions halogenated aliphatics and aromatics with oxygen-containing functional groups will undergo degradation.

CONCLUSIONS

World-wide interest in groundwater pollution has emerged in the 1980's with the discover of halogenated solvents migrating from hazardous waste sites and of pesticides contaminating drinking water wells and with the difficult international task of finding safe subsurface repositories for hazardous chemical and radioactive wastes. These problems have focussed the attention of hydrogeologists, engineers, chemists and microbiologists on the processes controlling the transport, retardation and transformation of contaminants in groundwater flow systems. If these groups are to integrate successfully their knowledge into the idealized schema presented in Figure 7, then much additional research is required. In particular, conceptual advances are needed to allow the development of physically-based models of transport in large-scale, heterogeneous aquifer systems, to incorporate both kinetic and equilibrium sorption reactions for such aquifers, particularly when they are composed of mixed sorbents and, finally, to determine rate constants for the transformation of the priority pollutants.
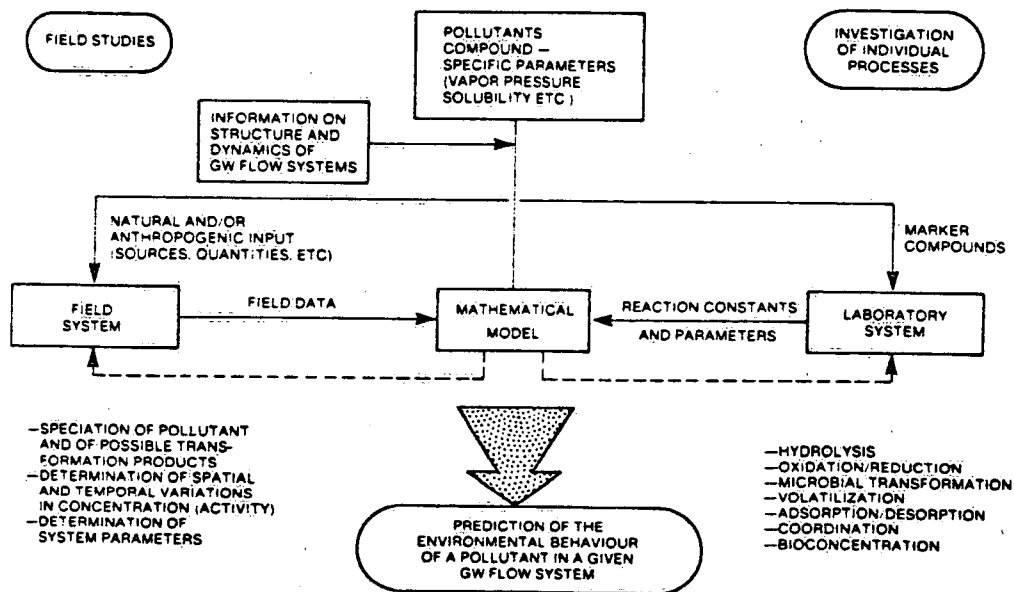

Figure 7   Idealized schema for predicting the environmental behaviour of pollutants in groundwater flow systems (after Stumm et al., 1983).

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