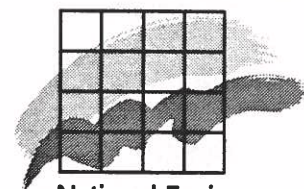


Ministry of
the Environment



National Environmental
Research Institute

Migration Chemistry

Chemical and Physico-chemical
Processes Influencing the Migration
Behaviour of Pollutant

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RESUMÉ

Transport kemi, dvs betydningen af kemiske -, biokemiske - og fysisk-kemiske reaktioner på transporten af forurenende stoffer i miljøet, er et samspil mellem den konkrete forurenende forbindelse og egenskaberne af det omgivende miljø, som f.eks. pH, redoxforhold, og indholdet af organisk materiale. Det store antal mulige forurenende stoffer i sammenhæng med forskellige geologiske medier og de forskellige kemiske -, biokemiske - og fysisk-kemiske reaktioner gør en forudsigelse af disse processers betydning for mobiliteten af de forurenende stoffer til et særdeles komplekst emne.

Rapporten summerer en lang række af potentielle forurenende stoffer samt forskellige kemiske -, biokemiske - og fysisk-kemiske reaktioner, der a priori kan forventes at have indflydelse på transportfænomener, såsom diffusion/dispersion/konvektion, sorption/desorption, udfældning/opløsning, omdannelse/nedbrydning, biokemiske reaktioner og kompleksdannelse. Denne sidste reaktion omfatter både kompleksdannelse mellem metalioner og non-polære organiske forbindelser med naturligt forekommende organiske makromolekyler.

De enkelte reaktionstypers indflydelse på transportprocessen er belyst baseret på teoretiske studier ved anvendelse af computerprogrammet COLUMN2. Betydningen af kemiske -, biokemiske - og fysisk-kemiske reaktioner på migrationen af forurenende stoffer er entydig, idet disse reaktioner tilsyneladende kontrollerer transporten i det terrestriske miljø. Idet det simple K_D koncept bryder sammen, foreslås at migrationsprocessen beskrive ved alternative koncepter som kemisk dispersion, gennemsnitlig udvaskningstid og effektiv retention.

SUMMARY

Migration chemistry, i.e. the influence of chemical -, biochemical - and physico-chemical reactions on the migration behaviour of pollutants in the environment, is an interplay between the actual nature of the pollutant and the characteristics of the environment, such as pH, redox conditions and organic matter content. Thus, the wide selection of possible pollutants in combination with varying geological media, as well as the operation of different chemical -, biochemical - and physico-chemical reactions makes the prediction of the influence of these processes on the mobility of pollutants a rather complex subject.

The report summarizes a wide range of potential pollutants in the terrestrial environment as well as a variety of chemical -, biochemical - and physico-chemical reactions, which a priori can be expected to influence the migration behaviour, comprising, diffusion/dispersion/convection, sorption/desorption, precipitation/dissolution, transformations/degradations, biochemical reactions and complex formation. The latter comprises the complexation of metal ions as well as non-polar organics to naturally occurring organic macromolecules.

The influence of the single types of processes on the migration process is elucidated based on theoretical studies by application of the computer code COLUMN2. The influence of chemical -, biochemical - and physico-chemical reactions on the migration behaviour is unambiguous, as these processes apparently control the transport of pollutants in the terrestrial environment. Thus, as the simple, conventional K_D concept breaks down, it is suggested that the migration process should be described in terms of the alternative concepts chemical dispersion, average-elution-time and effective retention, respectively.

1. INTRODUCTION

A wide variety of chemical and physico-chemical reactions can be expected to occur in the terrestrial environment. The processes comprise e.g. radioactive decay, precipitation/dissolution, redox equilibria, degradation, hydrolysis, complex formation, colloid formation and sorption/desorption. Sorption is a common denotation for a number of chemical mechanisms, e.g. ion exchange, causing the movement of pollutants to be delayed, however, not eliminated.

For convenience all these mechanisms are often characterized by a single coefficient quantifying the equilibrium between liquid and solid phase. However, other processes may influence the transport, e.g. redox reactions, complex and colloid formation.

The wide selection of pollutants, in combination with varying geological media, as well as different combinations of chemical and physico-chemical processes makes the prediction of the influence of chemical reactions on the mobility of pollutants a very complex subject. It is, however, possible theoretically to predict the migration of pollutants taking the operation of chemical and physico-chemical processes into account (Nielsen et. al., 1985). In order to evaluate the possible importance of the single processes a detailed knowledge of the characteristics of a given pollutant, i.e. the reactivity related to these processes is crucial.

From a theoretical point of view all processes can in principle be regarded as more or less sophisticated combinations of first- and second-order reactions. In practice, on the other hand, the majority of second-order reactions will involve the macro-components in the ground water, the concentrations of these being up to several orders of magnitude higher than those of the micro-components under investigation. Hence, these reactions can be treated as pseudo first-order reactions with respect to micro-components. In Table I the different types of reactions that should be taken into account are summarized.

TABLE 1.

Characterization of elementary reactions which may influence the migration. (FO: first-order, PFO: pseudo first-order, SO: second-order)

Reaction	Type	Forward	Backward
Radioactive Decay chains	$A \rightarrow B \rightarrow \dots \rightarrow C$	FO	
Sorption/Desorption	$A \rightleftharpoons B$	FO	FO
Precipitation/Dissolution	$A \rightleftharpoons B$	FO	FO
Redox Reaction ^a	$A \rightleftharpoons B$	PFO	PFO
Degradations	$A \rightarrow B_i$	FO	-
	$A + X \rightarrow B_i$	SO/PFO	-
Substitutions ^b	$A + B \rightarrow B$	SO/PFO	-
Hydrolysis	$A + OH \rightarrow B$	PFO	-
Complex Formation ^c	$A + L \rightleftharpoons AL$	SO/PFO	FO
Colloid Formation ^d	$nA \rightarrow A_n$	SO	-

- a) The redox potential will generally be controlled by the macro composition of the ground water (e.g. by the Fe(II)/Fe(III) couple).
- b) the substitution reaction may be of importance in cases of organic pollutants.
- c) In the case of complex formation, which can be expected to influence the migration behaviour of metal cations significantly, it is to be expected that in most cases it can be treated as a PFO reaction, owing to a large excess of the ligand, and/or a constant concentration of the latter (e.g. naturally occurring ligands in ground water).
- d) Colloid formation can in principle be regarded as a consecutive series of SO reactions

In the following the single chemical and physico-chemical processes will be discussed, followed by a theoretical evaluation of the influence of these processes on the migration behaviour of pollutants in the environment, i.e. "chemical dispersion".

The theoretical investigations have been carried out by application of the COLUMN2 computer code (Nielsen et al., 1985). COLUMN2 solves in one dimension the migration equation [1]

$$\partial c_i / \partial t = (D_i / R_f(i)) \partial^2 c_i / \partial x^2 - (V / R_f(i)) \partial c_i / \partial x + F(c_i, t) \quad [1]$$

taking into account possible chemical and physico-chemical reactions ($F(c, t)$). The program has been verified in the INTRACOIN study (Intracoin, 1984).

In risk assessments one is generally concerned with total quantities, however, COMUMN2 calculations are based on concentrations. Introducing the flow velocity, V , in COLUMN2 (interstitial velocity through the pores of the porous media), total quantities eluted from the columns can be derived (Nielsen et al.,1985).

In all the investigated systems identical 2 m long square input pulses of 1 mol m^{-3} have been started at the first points just outside the column, total column length applied was 100 m and the flow velocity was 1 m/y (Fig.1).

Two different types of plot are used to visualize the migration behaviour of the species, i.e. profiles of liquid phase concentrations in the column as the migration process progresses (typically with 20 years intervals) and concentration in the fluid eluted from the column as a function of time.

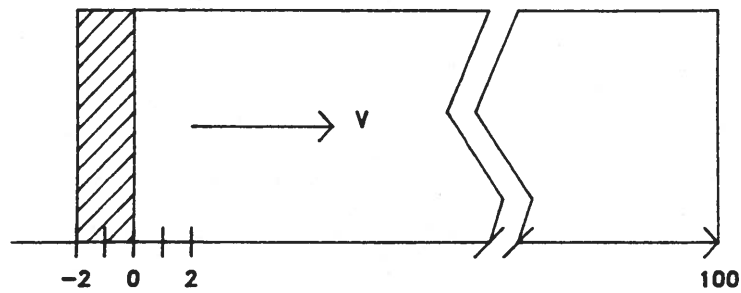


Fig.1: Schematic diagram of the column and input pulse.

2. POTENTIAL POLLUTANTS

The potential pollutants can roughly be divided into two main classes, as is inorganic pollutant, i.e. primarily metals, and organics. However, the eventual migration behaviour will be controlled by the same type of processes, cf. Table 1, although distinct species-specific differences obviously prevail. For laboratory as well as for controlled in-situ studies the application of radioactively labelled species is advantageous.

2.1 Metallic Pollutants

In relation to nuclear waste a distinction has to be made between high level waste, which typically will be deposited in deep geological formations, and medium and low level waste, which will be found in more shallowly located repositories. In the case of HLW the long-lived transuranium elements as americium, plutonium and neptunium are of major concern in addition to long-lived fission product as iodine and technetium.

In the case of MLW and LLW these waste forms will mainly consist of reactor waste, i.e. compacted solid waste, solidified ion exchange resins, filter materials and/or evaporates from water purifications systems in LWR's, etc. In general it is not foreseen that any α -contaminated waste will be present; however, minor accidents may result in α -contaminated LLW and MLW. If LLW from reprocessing or fuel fabrication operations is included α -emitting nuclides will be present. Decommissioning waste may contain special nuclides.

Only limited knowledge of typical concentrations of long-lived radionuclides in reactor waste is available, although some reports on estimates and investigations have appeared (NAEP, 1981, Roukola, 1981, SKBF/KBS, 1982, USEPA, 1977).

Based on values obtained from these reports the potential hazard has been estimated for a burial facility used at a steady rate for disposal of waste from six 1-GW LW-reactors in 30 years. (Ca. 54.000 m³) (Brodersen, pers. comm.) The potential hazard associated with the waste is calculated by dividing accumulative activity in the repository with the ALI values (ALI, 1980-82).

In figure 2 the potential hazard, given as ALI's, is depicted as function of time assuming linear input to the burial facility for 30 years, whereafter no further use takes place. The fresh reactor waste will contain considerable amounts of short-lived isotopes, which, however, have been neglected here.

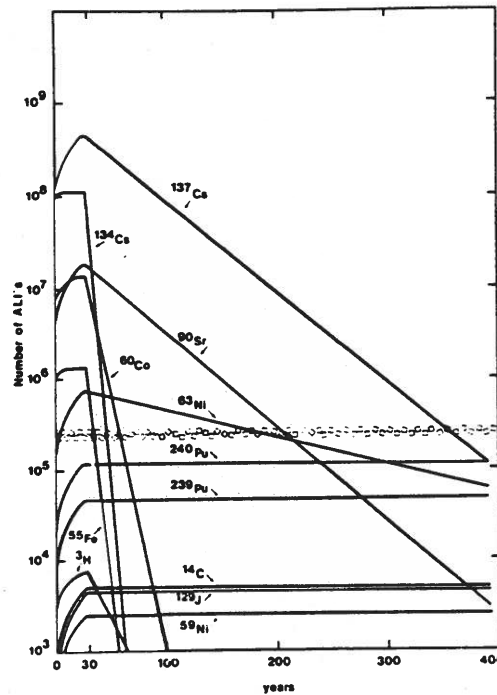


Fig.2: Potential hazard as function of time for 54.000 m³ conditioned reactor waste from ca. 120 GW-y produced on LWR's (---) visualizes the potential hazard due to natural activity (i.e. U+Th daughters) in 54.000 m³ ordinary concrete).

It is seen (Fig.2) that cesium, strontium, nickel, and to a minor extent cobalt apparently are the radionuclides of concern. After ca. 200 years only cesium plays any significant role. However, it must be remembered that the curves in figure 2 are partly guesswork and even minor changes may result in for example larger contributions from α -activity. It should also be remembered that use of other types of reactors may change the isotope content. Thus, in the case of breeder reactors substantial increase in α -activity could a priori be expected, whereas the use of HWR will result in an increase in tritium of several orders of magnitude. In addition, a recent study (Pinner et al., 1984) suggest ¹⁴C to be of major concern.

In addition to metals originating from nuclear activities, a series of heavy metals has to receive attention (Coughtrey et al 1983a, 1983b, 1983c, 1984a, 1984b, 1985, Ure and Berrow, 1982). Of major concern in this respect are cadmium (NAEP, 1980), mercury (NAEP, 1987a), lead (Nielsen and Christiansen, 1987, NAEP, 1987b), nickel (NAEP, 1985, Adriano, 1986), zinc (Hansen and Tjell, 1981), cobber (Hansen and Tjell, 1981), chromium (NAEP, 1985, Adriano, 1986) and arsenium (NAEP, 1985, Adriano 1986).

One of the main sources for heavy metal pollution of the terrestrial environment, apart from leachates from wastes dumps, is atmospheric deposition, e.g. as a result of the use of leaded fuels. In relation to agricultural areas fertilizer, feeding stuff and mineral blends as well as the possible application of sewage sludge may lead to metallic pollution.

2.2 Organic Pollutants

It has in recent years been realized that the constantly increasing production and consumption of organic chemicals constitute a potential hazard for polluting the ground waters, which eventually may lead to contamination of water courses and drinking water supplies. The nature of organic contaminants in the terrestrial environment is manifold, comprising pesticides, herbicides, insecticides, detergents, a variety of oil products, residues from chemical production plants etc.etc.

The increasing agricultural use of organics most probably constitute a major source of potential ground water pollution. Annually large amounts of different pesticides are spread, however, larger amounts accidentally slopped locally, ploughing (to avoid evaporation), as well as increasing precipitation, increases the possibility of contamination of lower lying layers and, hence, the ground water.

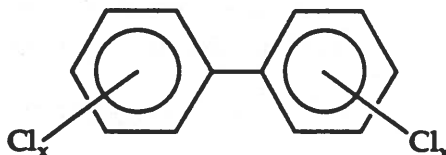
Other important sources for ground water contamination are different types of waste disposal sites, as dumping-grounds, and sub-surface waste repositories. The typicality is well illustrated by the current discussion in this field, including the attempts to map disposal sites throughout the country.

2.2.1 Aliphatic- and aromatic hydrocarbons

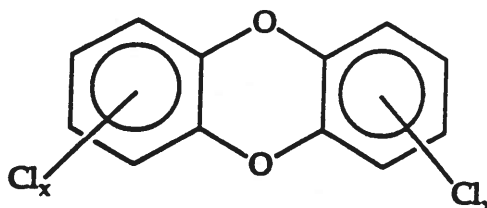
These compounds are the main components in oil products. Aromatic hydrocarbons are furthermore widely used as solvents. A special type, to which special concern should be payed, is the polycyclic aromatic hydrocarbons (PAH), typically found in stack and exhaust gasses. Contamination of ground waters with hydrocarbons may result in unpleasant tasting and smelling drinking water. Several of the members of this class of compounds are recognized, or strongly suspected as carcinogens.

2.2.2. Halogenated hydrocarbons

Halogenated hydrocarbons are to some extent used as pesticides, and several members of this class of compounds are widely used as solvents. Additionally, halogenated hydrocarbons are found as components in e.g. gasoline. Due to their stability and insulation properties polychlorinated biphenyles (PCB) have been extensively used in e.g. transformers.

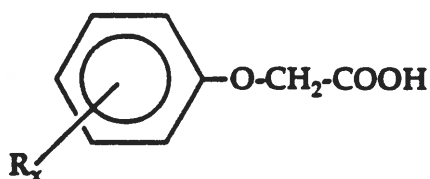
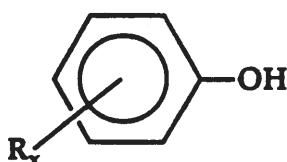


Dioxins, e.g. 2,3,7,8-tetrachloro dibenzo-p-dioxin (TCDD) are formed by various combustion processes, e.g. of municipal wastes and as unwanted by-products in the syntheses of certain chloride containing chemicals.



2.2.3 Phenolic compounds

Compounds belonging to the phenolic class are used as herbicides. In addition they are found as decomposition products from pesticides and oil products. The compounds are, as toxins and/or carcinogens injurious to health.



2.2.4 Carboxylic acid derivatives

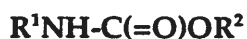
Compounds belonging to this class of compounds are to a certain extent used as herbicides, and are in general toxic.



Both simple aliphatic carboxylic acids, e.g. trichloroacetic acid ($R^1 = CCl_3$), and aromatic derivatives, as 2,5-dichloro-6-methoxybenzoic acid (Dicamba) as well as carboxylic acid esters are used.

2.2.5 Carbamic acid derivatives

Carbamic acid derivatives, as e.g. carbamates, are to a certain extent used as herbicides and insecticides

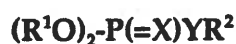


2.2.6 Anilin derivatives

Anilin derivatives are used as herbicides. However, they may also appear as decomposition products. They are generally injurious to health.

2.2.7. Phosphoric acid derivatives

Members of this class of compounds are used as insecticides.



Both the simple phosphoric acid esters ($X=Y=O$) as well as the thiono ester ($X=S, Y=O$) and the dithio esters ($X=Y=S$) are used.

2.2.8. Heteroaromatic compounds

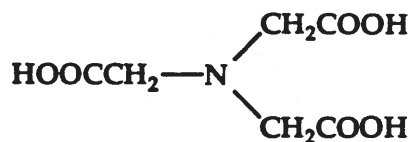
In addition to the above mentioned classes of compounds it can be mentioned that a variety of heteroaromatic compounds, as e.g. triazines, are used e.g. as herbicides. They are all toxic.

2.2.9 Multidentate chelating agents

A special type of organic compounds of great interest in connection with environmental pollution appears to be multidentate chelating agents as NTA (nitrilotriacetic acid), EDTA (ethylenediaminetetraacetic acid), and DTPA (diethylenetriamine pentaacetic acid) as well as some of their degradation products. (Means and Alexander, 1981, Toste and Myers, 1986, Means et al. 1980).

These compounds, which are not toxic as such, are receiving widespread use in a variety of industrial applications, because of their ability selectively to form very strong complexes with numerous metal ions. The industrial use of these compounds causes their entrance into natural water systems, where they will solubilize and, hence, act as a vehicle for e.g. heavy metals.

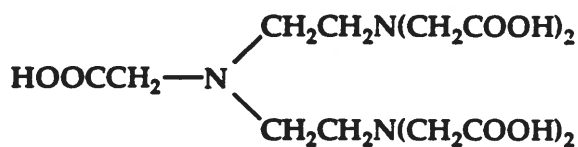
A major problem concerning chelating agents as EDTA etc. are their apparent persistence in the environment due to rather slow degradation rates. Hence, considerable concern about the possible release of these species to the environment is strongly emphasized.



NTA



EDTA



DTPA

Of major concern in connection with nuclear energy is, in this context the extensive use of chelating agents. The list of chelating commonly used in nuclear operations, i.e. which compounds can be expected to be found in nuclear wastes in rather comprehensive (Toste, personal comm.):

CIT:	citric acid
CDTA:	trans-1,2-cyclohexanediamine-tetraacetic acid
DCTA:	1,2-diamino cyclohexane-N,N-tetraacetic acid
DTPA:	diethylene-triamine-pentaacetic acid
EDTA:	ethylenediamine-tetraacetic acid
GLUC:	Gluconic acid (pentahydroxycaproic acid)
HEDTA:	N-hydroxyethylenediamine-triacetic acid
HEIDA:	hydroxyethylimino-diacetic acid
NTA:	nitrilotriacetic acid
TEA:	triethanol amine
TTHA:	tetraethylenetriamine-hexaacetic acid

A broad selection of these species as well as a range of their degradation products, many of which also exhibit pronounced complexing abilities towards metal ions, has been identified in nuclear waste forms and leachates (Toste, personal comm.)

3. RETENTION MECHANISMS

3.1 Diffusion, Dispersion, Convection

In cases where a waste repository is in contact with stagnant water, the only possibility for transport of contaminants will be diffusion through the aqueous phase, the mean pathway being given by

$$x = \sqrt{2Dt} \quad \text{m}$$

where D is the diffusion coefficient (m^2/years) and t the time (years) in which the process has proceeded.

Typically the diffusion coefficient, D , in pure water is found to be in the order of $0.03\text{-}0.06 \text{ m}^2/\text{y}$. However, in porous media effects as constrictivity and tortuosity may significantly decrease the D value (cf. Carlsen et al.1981).

However, in near surface layers, where contamination often can be monitored, ground water movement will in general not be neglectible. Hence, dissolved species will be subjected to the transport of dissolved species in flowing ground water systems, the so-called convection. In addition a series of mixing and dilution processes, one of which is diffusion, takes place. The effect of these processes is summarized as dispersion. The result of dispersion is, as is of diffusion that concentration differences decrease and the dissolved material is diluted. It has been shown (Marsily et al. 1982) that the dispersion is varying as a function of time as well as on average travelled distance.

Introducing chemical and physico-chemical processes, e.g. interactions between the pollutants and the geological material, may significantly change the migration behaviour of the latter. The effects of the chemical and physico-chemical processes, which give important contributions to the dispersion, are summarized in the so-called chemical dispersion, (Carlsen et al. 1987)

Diffusion of a radionuclide in a groundwater flow in a porous media is normally slower than in the unconfined fluid; however, the dispersion coefficient, D_i , increases with increasing ground water velocity, V . A typical value of dispersion coefficients of radionuclides (metal ions) in water at ambient temperature is around $10^{-9} \text{ m}^2/\text{s} \sim 0.03 \text{ m}^2/\text{y}$.

Retention may be due to several physico-chemical processes already mentioned: sorption/desorption, precipitation/-dissolution, and ion exchange. The effects of these processes are in general combined in a single retention factor, R_f assuming equilibrium between the radionuclide on the solid phase and in

solution, respectively, the corresponding distribution coefficient, $K_D(i)$ (M^3/kg) being related to $R_f(i)$ by:

$$R_f(i) = 1 + K_D(i) (1 - \epsilon) \rho / \epsilon \quad [2]$$

where ϵ is the porosity and ρ the bulk density of the solid phase (cf. e.g. Carlsen et al., 1981; Jensen, 1982; Neretnicks, 1980; Anderson et al., 1984; or Eriksen and Jacobsen, 1984).

In Figure 3 the effect of increased retention, i.e. $R_f > 1$ is visualized. It is seen that increasing the R_f values decrease the mobility of the migrating species proportionally to the R_f value and the peaks become broader, as a result of the increased residence time in the column.

The effect of a decrease in D which is a narrowing of the concentration profile as expected, is elucidated in Figure 4.

Finally, it should be remembered that a decrease in groundwater velocity (for constant D) causes pronounced increased dispersion, due to the time effect, i.e.. increased residence time in the column (Fig.5).

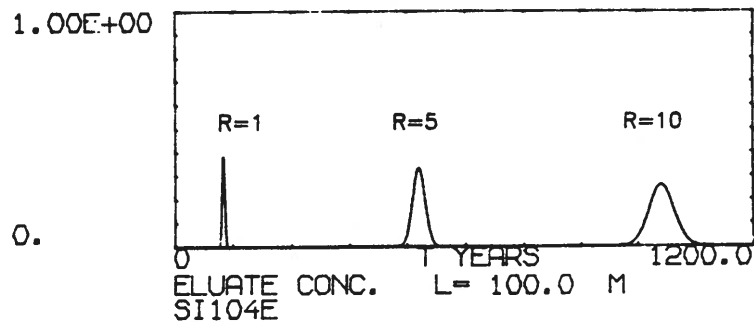


Fig.3: Elution curves of compound A. Initial concentrations: $[A]_0 = 1$. Retention factors: $R_f(A) = 1, 5, 10$, respectively. $V = 1m/y$, $D = 0.03m^2/y$.

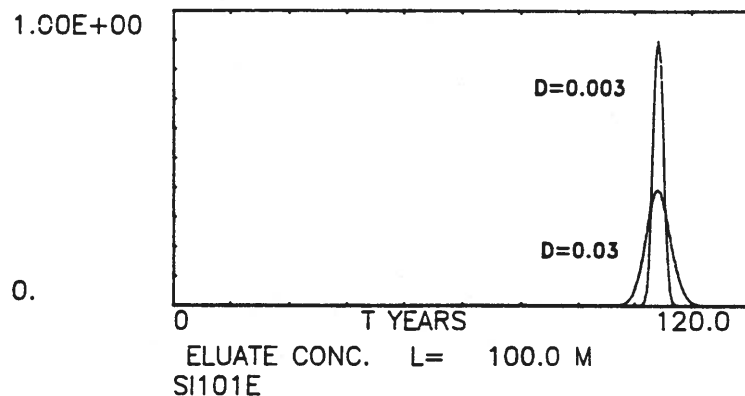


Fig.4: Elution curves of compound A. Initial concentrations: $[A]_0 = 1$. Retention factor: $R_f(A) = 1$. $V = 1m/y$, $D = 0.03$ and $0.003 m^2/y$ respectively.

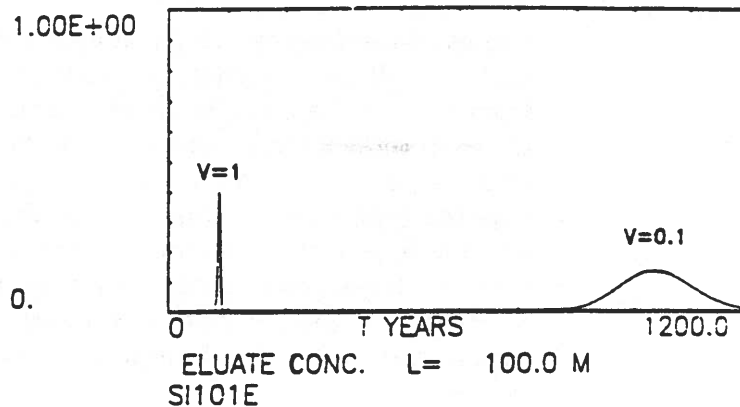


Fig.5: Elution curves of compound A. Initial concentrations: $[A]_0=1$. Retention factor: $V = 1$ and 0.1 m/y, respectively, $D= 0.03$ m^2/y .

3.2 SORPTION/DESORPTION

Both inorganic as well as organic species are sorbed onto solid surfaces. Thus, the sorption/desorption process constitute as a major retardation mechanism influencing the migration behaviour of pollutants with groundwater.

Several factors influence the sorption of pollutants to geological material, such as pH and ionic strength and the composition of the solid phase, e.g. clay content and the fraction of organic carbon in the soil.

In the case of metallic pollutants ion exchange is one of the more important mechanisms by which positively charged ions are retained in soil. The exchange process is relatively rapid and reversible. Thus, ion exchange with soil fines is a process of major importance for the retention of metallic pollutants, e.g. radionuclides, in geologic formations. For a given clay material, with a given particle size distribution, the physico-chemical variables of primary importance for the sorption of trace amounts of a given metal ion are: 1° The selectivity of the ion exchanger towards the metal ion defined as the standard Gibbs free energy of exchange between the metal ion and a reference ion (e.g. a calcium ion), 2° The concentration level and chemical composition of the aqueous phase from which the radionuclide is sorbed, 3° The ionic composition of the exchangeable ions present in the clay particles and 4° The acidity of the ground water (e.g. hydrogen ions may compete with other ions for the exchange sites on the clay material).

The clay minerals of interest in connection with geologic disposal of radioactive waste covers a wide spectrum of mineral structures and ion exchange properties. Some minerals of the smectite type have rather high ion exchange capacities (50-150 meg/100 g) resulting mainly from isomorph substitutions in the structural units of the mineral and exchangeable ions located at the internal

planes of the mineral. Other minerals, of the kaolinite type, have rather small ion capacities (3-15 meg/100 g) probably originating from broken chemical bonds on the surface of the particles, i.e. the total capacity apparently should be proportional to the surface area rather than to volume, as is the case for minerals of the smectite type. Clay minerals of the illite type are believed to be intermediate in ion exchange properties (10-40 meg/100 g), however, the three types of clays are expected to have a profound influence on both selectivity, concentration -, and composition dependence of the distribution coefficients.

In general metal ions are strongly sorbed to clay minerals by ion exchange giving rise to a rather effective retardation.

Other types of sorption occur, however, the bonding being significantly less strong. Consequently the retardation efficiency is decreased accordingly.

A special type of sorption, which may influence the migration of metallic pollutants significantly, is the association with colloidal material. The possible engagement of colloidal clay material, diminishing the sorption of radionuclides by ion exchange to soil fines was discussed by Bo and Carlsen (1981). In recent years a European research program within the MIRAGE project has concentrated on the role of colloids in the transport of radionuclides in geological formations (cf. Billon et al. 1991 and references therein).

In the case of organic pollutants the sorption to geological material is significantly less dominating than in the case of metal ions, however, still of major importance.

In the case of ionizable species as e.g. carboxylic acids and amines especially ionic strength and pH are dominant factors. Typically the sorption process in case of these types of compounds involves elimination and addition of a proton, respectively (Leonard et al., 1976). The sorption of a wide variety of energy-related organic pollutants, including several carboxylic acids, has been reported by Reinbold et al. (1979).

In the case of ionizable organic pollutants sorption to the clay minerals constitutes the more important reaction, due to their omnipresence and their surface characteristics, the latter, however, being strongly dependent of the clay type (Calvet, 1980). The sorption efficiency of clay minerals is closely connected to the clay structure, where the crystal lattice is negatively charged. Owing to this feature the clay minerals are neutralized by sorbed positively charged ions, which may be exchanged by other cations. It has been emphasized (Calvet, 1980) that the ion composition at the clay surface significantly influences the sorption characteristics.

The importance of the water content in the soil has been reported (Hance, 1979, Calvet 1980). Surfaces which bind water as ligand preferentially to organics, will consequently exhibit an increase ability towards sorption of organic compounds in zones with relatively low water contents than in those with high water contents.

In cases where the geologic media, e.g. soil, exhibit a significant fraction of organic carbon (f_{oc}), the latter plays a major role in determining the sorption of organic pollutant, especially those of non-polar, hydrophobic character (Schwarzenbach, 1982, Schwarzenbach and Westall, 1981, 1984, Frost 1969, McCall et al. 1981, Means et al., 1980, 1982).

The sorption has been expressed in terms of partition coefficients K_p , derived as the ratio between the concentration of the pollutant sorbed on the solid phase (C_s) and in solution (C_{sol})

$$K_p = C_s / C_{sol}$$

The partition coefficients are often normalized to the fraction of organic carbon, f_{oc} , of the solid phase, i.e.

$$K_{oc} = C_s / f_{oc} \cdot C_{sol}$$

Thus K_{oc} is the organic carbon normalized partition coefficient, corresponding to the partition of the pollutant between a liquid phase and a theoretical solid phase of 100% organic carbon ($f_{oc}=1$)

In order to evaluate the ability of organic pollutants to be sorbed on the organic fraction in soil and sediment the liquid - liquid partition between water and octanol (K_{ow}) is generally used as reference case. A series of relations, in general strongly substance dependent, has been developed to obtain K_{oc} partition coefficient from the corresponding K_{ow} 's (Schwarzenbach 1982, Schwarzenbach and Westfall, 1981, 1984, Karickhoff et al., 1979). Some authors have introduced a relation, possibly linear, between K_{ow} and the solubility X_{sol} (McCall et al. 1981, Rao et al., 1983, Karickhoff, 1981, Means et al., 1980)

$$K_{oc} = f(K_{ow}) = g(X_{sol})$$

K_{ow} and, thus, K_{oc} has been related to normalized retention times obtained by liquid chromatography, using acetone as a reference (Rao et al., 1983).

Attempts have been made to relate K_{ow} values to structural characteristics of the pollutants (e.g. Schwarzenbach, 1982), which, however, shall not be discussed further in the present context.

It should be noted that in cases of very low, or even zero content of organic carbon, the dominant factors for sorption of organic

compounds are the specific surface area and the actual nature of the mineral surface (Schwarzenbach 1982)

It is strongly emphasized that not only the fraction of organic carbon of the solid phase plays an important role in determining the partition between the liquid and solid phases, but also the dissolved organic matter (DOM) and particulate organic matter (POM) have to be taken into account. Thus, a pronounced binding of non-polar, hydrophobic organic pollutants to dissolved and particulate organic matter has been reported (Carter and Suffet, 1982, 1983, Caron et al., 1985, Caron and Suffet, 1989, Henry et al., 1989, Hassett and Anderson, 1982, Brownawell and Farrington, 1985, Hunchak-Kariouk and Suffet, 1991) hereby decreasing the sorption of these compounds to soils and sediments.

Consequently the migration potential will increase. The concentration of the pollutants in solution can accordingly be regarded as the sum of the concentrations of the free pollutants, C_{aq} and that of the pollutant "complexed" to the DOM, C_{doc} . Consequently K_{oc} can be expressed as

$$K_{oc} = C_s / (C_{aq} + C_{doc}) \cdot f_{oc}$$

Introducing a DOM/water partition coefficient, K_{doc} , normalized to the DOM concentration in the bulk aqueous phase, $[DOC]_w$, i.e.

$$K_{doc} = C_{doc} / C_{aq} [DOC]_w$$

gives the following expression for K_{oc} , thus, taking into account the "complexation" between the pollutant and the DOM.

$$K_{oc} = C_s / C_{aq} (1 + K_{doc} [DOC]_w) \cdot f_{oc}$$

The "complexation" reaction will be discussed in more detail later

The interaction between low molecular organics and POM can be treated analogously (Hunchak-Kariouk and Suffet, 1991).

In Table 2 logarithmic K_{oc} values for selected potential organic pollutants are given.

TABLE 2.

Logarithmic partition coefficients for selected organic pollutants.

Aromatic hydrocarbons:

Benzene	1,98 ^d
Pyrene	4,80 ^d
	4,92 ^c
Tetracene	5,81 ^c

Halogenated hydrocarbons:

1,3-Dichloropropene	1,41 ^a
Ethylene dibromide	1,51 ^a
Tetrachloroethylene	2,32 ^{c,d}
Chlorobenzene	2,59 ^{c,d}
Lindane	3,11 ^a
DDT	5,14 ^{c,d}
	5,38 ^a
2,4,5,2',4',5'-PCB	5,34 ^{c,d}

Carboxylic acid derivatives:

Dicamba	no sorption
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Anilin derivatives:

Trifluralin	3,59 ^a
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Carbamic acid derivatives:

Urea:

Fenuron	1,59 ^b
Monuron	1,92 ^a
	2,13 ^b

Fluometuron	2,24 ^b
Monolinuron	2,37 ^b
Diuron	2,59 ^b
Linuron	2,92 ^b

Carbamates:

Carbofuran	1,46 ^b
Chlorpropham	2,77 ^b
Carbaryl	2,36 ^b

Phosphoric acid derivatives:

Malathion	3,25 ^b
Parathion	3,06 ^{c,d}
	3,85 ^b
	4,00 ^a
Methyl parathion	3,85 ^b
Chlorpyrifos	4,13 ^b
	4,15 ^a

Heteroaromatic compounds:

Uraciler:

Terbacil	1,66 ^b
Bromacil	1,86 ^b

Triaziner:

Simazine	2,20 ^b
Atrazine	2,23 ^a
	2,24 ^b
Cyanazine	2,28 ^b
Propazine	2,32 ^b
Trietazine	2,74 ^b
Ipazine	3,06 ^b

a: McCall et al. 1981

b: Rao et al. 1983

c: Schwarzenbach and Westall 1981

d: Schwarzenbach 1982

In sum it can be concluded that sorption constitute as a retention mechanism of major importance controlling the migration behaviour of both inorganic and organic pollutants.

Finally, it should be mentioned that in connection to the possible role of organics in the migration of metallic pollutants, it is noteworthy that complexes of metal ions with rather large organic ligands may act as "organics" in the ground water system, as the species "looked upon from without" may appear as organic rather than metallic. Thus, the sorption, and hence, the migration behaviour of these complexes possibly follows the laws for sorption of organic compounds to geological material.

3.3 Precipitation/Dissolution

The actual solubility of potential pollutants in groundwater is obviously a limiting factor with regard to the possible concentration levels to be discussed. From a theoretical point of view the precipitation/dissolution type of reaction can be considered identical to the above discussed sorption/desorption process (cf. Table1).

The solubility of pollutants in groundwater systems depends strongly on groundwater composition, i.e. both the bulk concentrations of the macro elements as well as the physical characteristics such as pH and redox conditions.

The solubilities as well as solubility products are listed in standard reference books on physical constants for inorganic and organic compounds as e.g. Handbook of Chemistry and Physics (Chemical Rubber Company).

To evaluate the solubility as function of pH and it is valuable to construct so-called concentration-limit diagrams (Jensen, 1982).

In figure 6 the concentration-limit diagram for technetium is depicted

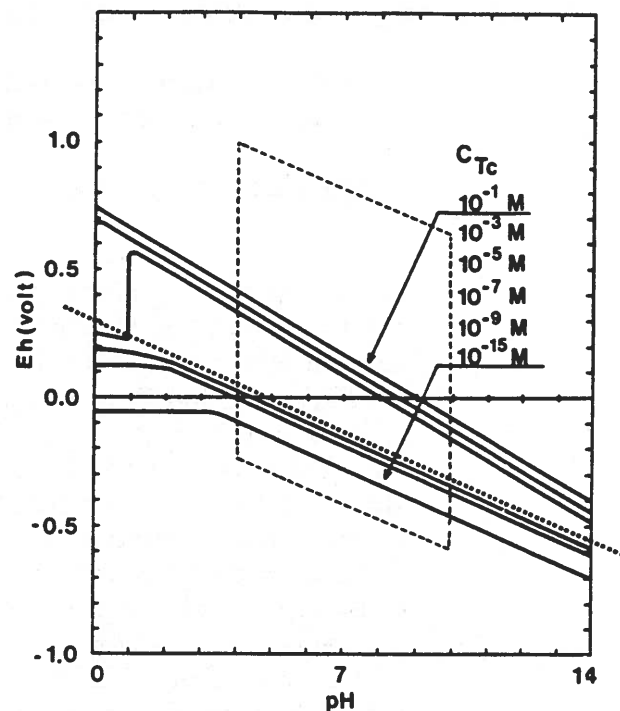


Fig.6: Concentration-limit diagram for Technetium as function of pH and EH. The dotted line denotes the border-line between TcO_2 (above) and elemental Tc (below) as solid phase. The area defined by the broken line corresponds to pH/EH conditions normally to be expected in the environment.

It is noteworthy in this context to realize that the ongoing change in acidity of groundwater, due to the global acidification may have a severe impact on the level of environmentally potential hazardous species. Thus, it can be expected that acidification of groundwater will result in dissolution of e.g. alumina possibly leading to undesired human health effects.

3.3.1 Migration behaviour

Both the sorption/desorption and precipitation/dissolution processes are simple first order equilibria reactions of the type $A \rightleftharpoons B$ (cf. Table 1). Also redox equilibria (vide infra) like $TcO_4^- + 4H^+ + 3e^- \rightleftharpoons TcO_2 + 2H_2O$ or $Pu^{III} \rightleftharpoons Pu^{IV}$ are recognized as important examples of an $A \rightleftharpoons B$ system. If one of the two rate constants in the $A \rightleftharpoons B$ system, k_1 or k_{-1} , is very slow this system will turn into a simple $A \rightarrow B$ system or even the reference case depending on the starting concentrations of A and/or B, respectively.

If both components have the same retention factors the system will approach equilibrium with contributions of A and B as determined by the equilibrium constant $K = k_1/k_{-1}$, the two species migrating with the same speed.

If there is a difference in retention factors, i.e. $R_f(A) \neq R_f(B)$, it appears necessary to distinguish between two cases:

- 1° The equilibrium is reached rapidly compared to residence time in the porous medium, and
- 2° The equilibrium is reached only slowly, it reached at all.

In the first case significantly chemical dispersion for both species can be observed as visualized in Figure 7, depicting the eluate concentration profiles for the A=B system exhibiting $k_1=k_{-1}=0.1 \text{ y}^{-1}$, $R_f(A) = 1$, and $R_f(B) = 2$. It should here be strongly emphasized that from a simple K_D approach component A would be expected to be eluated after 100 years whereas component B should appear in the eluate after 200 years. In Figure 7 it is unambiguously demonstrated that A and B appear in the eluate simultaneously after 150 years. Hence, the chemistry apparently causes a break down of the K_D -concept. It is emphasized that this "average-elution-time law" is not associated with the equality of k_1 and k_{-1} , but observed as long as both reactions are rapid compared to the residence time in the porous medium, i.e. $k_{\pm j} \gg V/LR_f \equiv V_{\text{eff}}/L$. In general the migration of species obeying the "average-elution-time law" can be ascribed to a common retention factor, the "effective retention factor, R_f^{eff} ", applying to all components in the equilibrium system. R_f^{eff} can easily be obtained from the single R_f values.

$$R_f^{\text{eff}} = \left(\sum_i^n R_f(i) \right) / n \quad [3]$$

In the second case pronounced tailings are observed (Fig.8). Simultaneously it is noted that under these conditions the equilibrium system no longer obey the "average-elution-time-law". However, in both cases of equilibrium it is emphasized that the chemical dispersion affects both components.

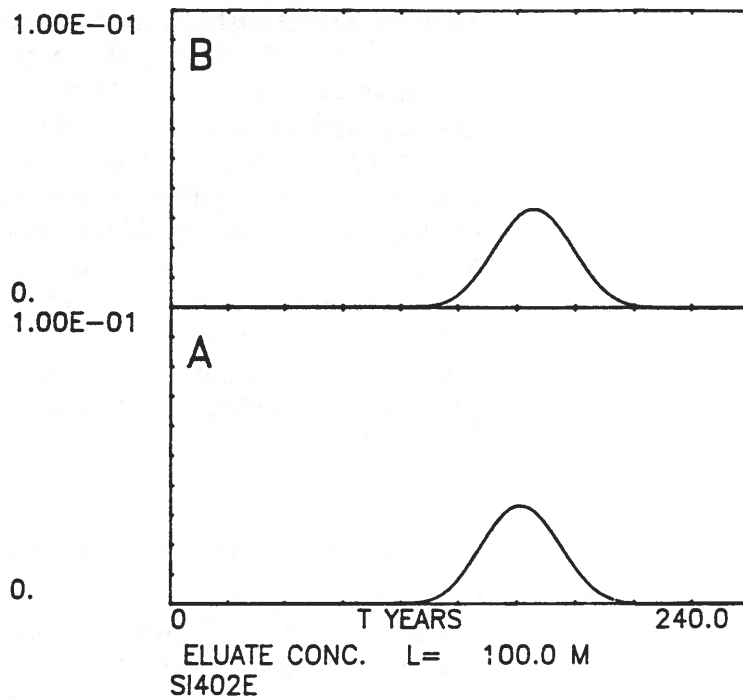


Fig.7: Elution curves of compounds A and B. Initial concentrations: $[A]_0=1$, $[B]_0=0$. Retention factors: $R_f(A) = 1$, $R_f(B) = 2$. Rate constants: $k_1=k_{-1}=0.1 \text{ y}^{-1}$. $V= 1 \text{ m/y}$, $D= 0.03 \text{ m}^2/\text{y}$.

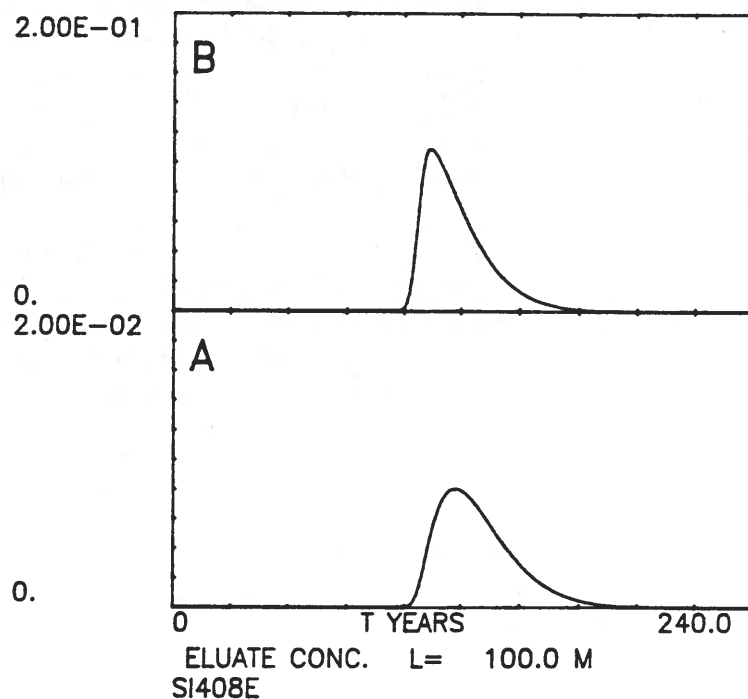


Fig.8: Elution curves of compounds A and B. Initial concentrations: $[A]_0=1$, $[B]_0=0$. Retention factors: $R_f(A) = 2$, $R_f(B) = 1$. Rate constants: $k_1=0,1$ and $k_{-1}=0.01 \text{ y}^{-1}$. $V= 1 \text{ m/y}$, $D= 0.03 \text{ m}^2/\text{y}$.

More extended systems as the double equilibrium system $A \rightleftharpoons B \rightleftharpoons C$ could represent redox equilibria involving three separate oxidation states, or a redox equilibrium combined with complex formation equilibrium, e.g. $TcO_4^- + 4H^+ + 3e^- \rightleftharpoons TcO(OH)_2 \rightleftharpoons \frac{1}{2}Tc_2O_2(OH)_4$ can be studied analogously (Carlsen et al., 1987). Since this system consists of two superposed equilibria, it is obvious that certain combinations of values of the respective k_1 , k_{-1} , k_2 and k_{-2} will cause the system to appear as a single equilibrium system (i.e. $A \rightleftharpoons B$). This will be the case for low values of k_{-1} or k_2 . On the other hand if k_2 is low this system degenerates into the $A \rightleftharpoons B \rightarrow C$ system. In all investigated examples nearly identical pictures are developed independently of the initial concentrations of A and/or B.

3.4 Transformations/Degradations

Transformations and degradations are important reactions in relation to migration of pollutants, since these reactions with time will reduce the actual concentration of the pollutants eventually eliminating the latter as potential hazards. However, it has to be considered that the transformation/degradation products may well be hazardous as well. Thus, transformations/degradations of primary pollutants have a priori to be regarded as a production with time of secondary pollutants.

In the case of metallic pollutants radioactive decay chains and redox systems are important processes, which affect the migration behaviour. These reactions, however, are almost exclusively related to radionuclides, as e.g. plutonium, neptunium and technetium exhibit quite different characteristics (solubility, sorptivity, complexity) dependent of the actual oxidation state.

To elucidate the pH-Eh dependence, so-called predominance diagrams advantageously can be constructed (Jensen, 1982). In Figure 9 and 10 the neptunium speciation as function of Eh and pH are visualized in carbonate free and carbonate containing aqueous solutions, respectively (Nilsson and Carlsen, 1989.)

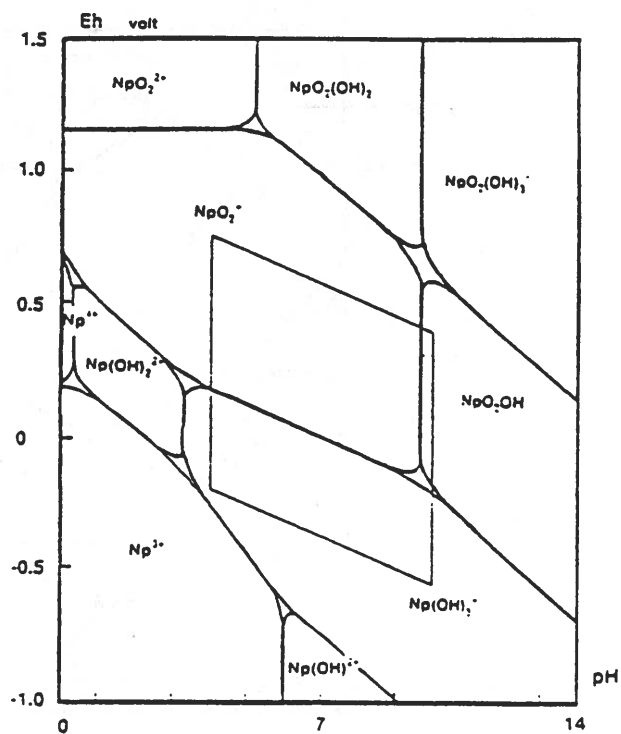


Fig.9: Neptunium speciation as a function of pH and Eh in a carbonate-free aqueous solution. The border lines denote areas within which the indicated Np-species constitutes >50% of the total amount of neptunium present. The area defined by the parrallelogram corresponds to pH/Eh conditions normally to be expected in the environment.

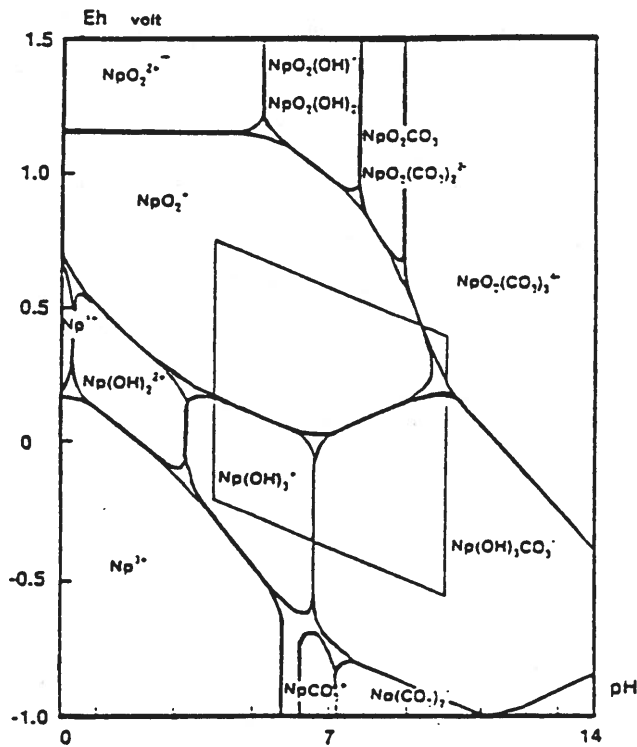


Fig.10: Neptunium speciation as a function of pH and Eh in an aqueous solution saturated with carbon dioxide at a partial pressure of $10^{-3.5}$ atm corresponding to atmospheric conditions. The border lines denotes areas within which the indicated Np-species constitutes >50% of the total amount of neptunium present. The area defined by the parallelogram corresponds to pH/Eh conditions normally to be expected in the environment.

Turning to organic pollutants the stability, and, hence, the persistence of artificially introduced organic species in the terrestrial environment is of crucial interest in connection with the evaluation of the potential hazard of these species. Not only an ultimate degradation of the organic species into water and carbon dioxide has to be considered. Important is the possible formation of complexing agents through chemical or microbial transformations, as well as the eventual fate of these compounds. The importance of this discussion has continuously increased simultaneous with the increased use of e.g. pesticides.

The decomposition of organic compounds in the terrestrial environment can take place either chemically, microbiologically or photochemically induced. However, the latter type of reaction probably should receive only minor attention (Leonard et al., 1976. Rao et al., 1983). Only in the very top layers of the soil, light can play a dominant role in the transformation of adsorbed organic compounds (Gäb et al., 1983). Chemical degradation will lead to smaller molecules, whereas the ultimate transformation into water and carbon dioxide probably takes place only as a result of microbiological decomposition (Rao et al., 1983).

Often the degraded products exhibit characteristics that make them potential hazards, i.e. a short half life does not necessarily exclude a compounds as important. Furthermore, an enhanced mobility of the degradation products is often observed, which should be taken into account as well. Typically the half life of organic compounds introduced into the environment as a result of agricultural use ranges from a few days to a year, except in the case of chlorinated hydrocarbons, as e.g. DDT, where half lifes of more than 10 years can be observed (Laskowski et al., 1983). In Table 3 half-lives for selected organic pollutants are given.

TABLE 3. Half-lives of selected organic pollutants^a

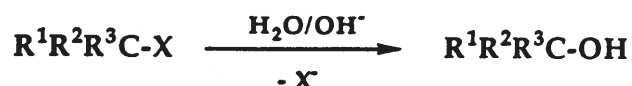
	$t_{1/2}$ (days)
<u>Halogenated hydrocarbons:</u>	
Endrin	4300
DDT	3800
Heptachlor	2000
Dieldrin	1000
Lindane	6000
<u>Phenol derivatives:</u>	
2,4D	4
<u>Carboxylic acid derivatives:</u>	
Dicamba	20
<u>Anilin derivatives:</u>	
Alachlor	7
<u>Carbamic acid derivatives:</u>	
Monuron	170
Diuron	200
<u>Phosphoric acid derivatives:</u>	
Chlorpyrifos	60
Parathion	15
Malathion	1
<u>Heteroaromatic compounds:</u>	
Atrazine	130
Diazinon	30

a: Laskowski et al., 1983

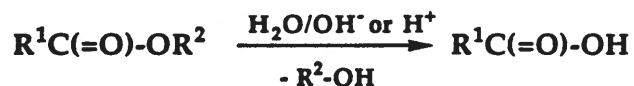
3.4.1 Chemical degradation

The more important chemical reactions involved in the degradation and/or transformation of organic compounds in the terrestrial environment appear to be hydrolysis, oxidation and reduction (Leonard et al., 1976, Terce, 1981). Typical examples of hydrolytical transformations are (Schwarzenbach, 1982).

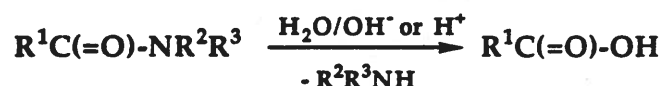
Halocarbones:



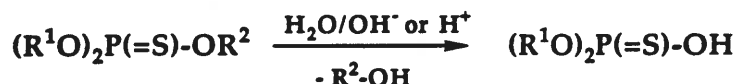
Carboxylic acid esters:



Amides:



Thiophosphoric acid esters:



It appears evident that hydrolysis reactions as illustrated above certainly do not produced "harmless" species.

The reaction rates are, not surprisingly, dependent of temperature, pH, redox potential, soil humidity as well as the possible sorption onto organic or mineral matter, especially clay material, which may catalyze the degradation or, in other cases stabilize the adsorbed organic compounds (Leonard et al., 1976, Laskowski et al., 1983, Terce, 1981).

Of special interest are the stability of the stronger complexing species, which may cause significant enhanced mobility of metallic pollutants.

The multidentate ligands as NTA, EDTA, DTPA and HEDTA has been found to be rather stable species at temperatures up to 220-260°C, whereas their hydrous sodium salts decompose at significant lower temperatures (Wendtland, 1960). In aqueous solution the species appear to be thermally labile at temperatures above 200°C (Venezky and Moniz, 1969, Martell et al., 1975). Toste (personal comm.) studied the possible transformation routes of a series of the multidentate ligands. Apparently a wide variety of products can be expected. However, many of the thermally produced breakdown products appear to be quite good chelating agents. Hence, thermal degradation do not necessarily decrease the overall concentration of strongly chelating agents significantly.

3.4.2 Microbiological degradation

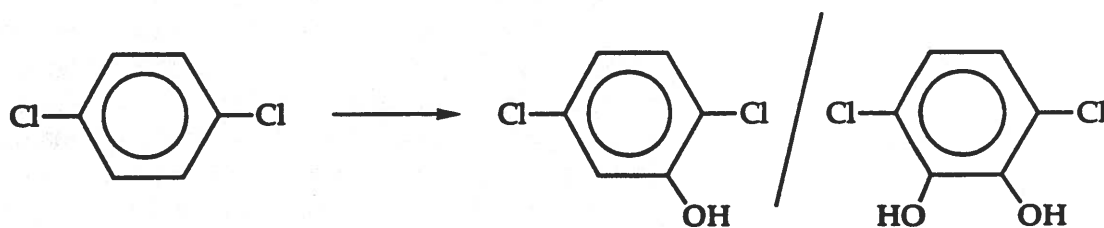
Primarily organic compounds in the terrestrial environment are degraded as a result of microbiological activity. Alexander (1973) defined biodegradation as "the conversion by biological agencies of a complex organic material into one or more simpler substances". Thus, the microbiological degradation may be subdivided into three categories according to the degree of degradation:

- Ultimate biodegradation, where the original organic compounds are converted into inorganic material, i.e. carbon dioxide, water, ammonia and salts.
- Primary degradation, where the degradation products still exhibit organic character, but the characteristics of the original species, e.g. the chelating ability, are no longer evident.
- Secondary degradation, where the degradation products exhibit similar characteristics as the original compounds, i.e. chelating agents are degraded into species still exhibiting chelating ability.

Obviously the importance of the secondary degradation must be emphasized, since such reactions will increase the persistence of organic pollutants in the environment, as well as e.g. complexing ability.

The microbial activity may involve a wide variety of reactions as oxidation, reduction, cleavage of ether bonds, hydrolysis reactions, ring cleavage reactions, dehalogenations and N-dealkylations.

Oxidation:



Reduction:



Dehalogenation:



The rates of microbiological degradations appear as an interplay between the ecology of the microbial population and the structure of the organic compounds, which may be affected by soil composition, pH, temperature, soil humidity, the concentration of organic carbon and other nutrients, the adsorption of the organic compounds, redox potential and dissolved oxygen (Leonard, 1976, Haider, 1983, Kobayashi and Rittmann, 1982).

Generally speaking, it can be concluded that increasing temperatures result in increased degradation rates. Similarly increased contents of organic carbon and nutrients in the soil afford increase in adsorption of most organic compounds, which will limit or even prevent degradation (Hance, 1979, Fournier and Catroux, 1981)

With regard to microbiological degradation the geosphere can be subdivided in three sections: 1° the aerobic, and hence, biologically active zone, 2° the underlying oxygen deficient zone, and 3° the anaerobic zone, with only minor biological activity. It is, however, emphasized that even in deep geological formations, microorganisms have been found (West and McKinley, 1984)

Obviously, compounds administered to the surface of the soil must pass through the biologically active zone, and, hence, be subjected to aerobic degradation, in order to reach the ground water. However, in cases where aerobic degradations do not operate, i.e. chemical disposal sites, an increased risk of ground water contamination develops, since the anaerobic degradations in most cases appear to be significantly slower than the aerobic. Hence, leachates from conventional dumping sites for chemical wastes constitute a potential source for introducing pollutants to the ground water system.

As mentioned previously carboxylic acids and phenols should, in addition to the multidentate complexing agents, receive attention. These compounds can be expected to be introduced to the ground water through an aerobic decomposition of aliphatic and aromatic hydrocarbons. If carboxylic acids or phenols (as well as alcohols and glycols) reach the anaerobic zone, which appears conceivable due to their relatively high mobility, which is a result of the pronounced polar nature of these species, they appear to be quite persistent, and will undergo only slow anaerobic degradation (Hoeks et al., 1984)

The biodegradability of NTA, EDTA and DTPA has been comprehensively reviewed by Means, Kucak and Crerar (1980). They concluded that degradation rates of all three chelates were not rapid enough, even under ideal laboratory conditions, to preclude concern about their release to the environment, and that biodegradation, if slow or incomplete, may be an inadequate barrier to their various undesirable environmental consequences. Hence, Means et al. (1980) as well as Toste (personal comm.) advocate for a destruction of chelates by thermal or chemical means prior to discharge to the environment as highly desirable.

3.4.3 Migration behaviour

The transformation/degradation reactions can from a theoretical point of view be regarded as simple $A \rightarrow_x B / (\Sigma B_i)$ reactions.

The $A \rightarrow B$ system represents an irreversible conversion of A to B. A simple radioactive decay like $^{226}\text{Ra} \rightarrow ^{222}\text{Rn}$ is an example of a simple $A \rightarrow B$ system. Also thermally or catalytically induced degradations of e.g. organically complexed radionuclides as well as microbial transformations may be represented by this system. The case where the two retention factors are equal, $R_f(A) = R_f(B)$, appears trivial since variation in the rate constant, K_1 , will determine the rate by which A is converted to B, the two compounds migrating with the same speed. In cases where $R_f(A) < R_f(B)$, i.e. compound A migrates faster than compound B, some B will be produced at positions where previously produced B has not yet reached. Thus, part of the species B will apparently move faster than anticipated based on the value of $R_f(B)$ alone (Fig.11).

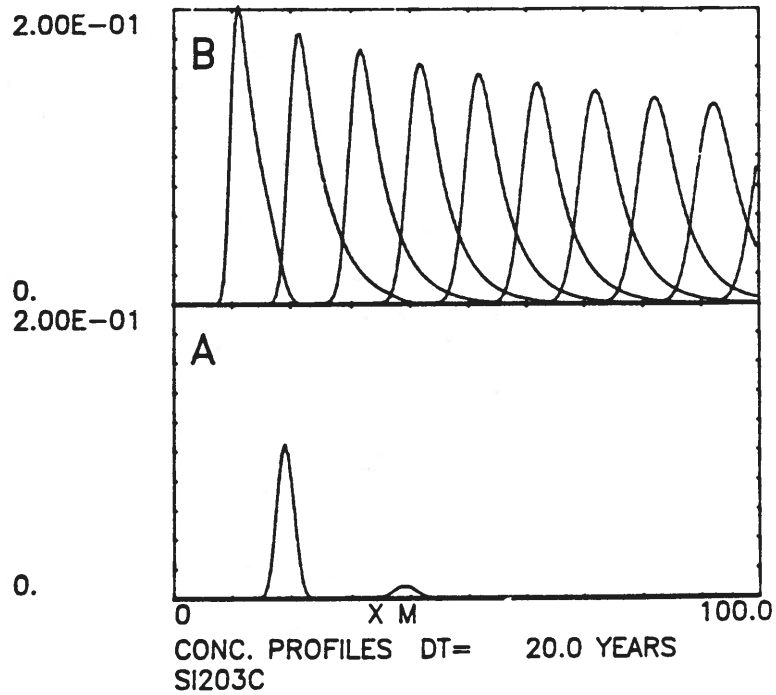


Fig.11: Concentration profiles of compound A and B initial concentrations: $[A]_0 = 1$ and $[B]_0 = 0$. retention factors: $R_f(A) = 1$, $R_f(B) = 2$. Rate constant: $k_1 = 0.1 \text{ y}^{-1}$. $V = 1 \text{ m/y}$, $D = 0.03 \text{ m}^2/\text{y}$.

On the other hand, if $R_f(A) > R_f(B)$ i.e. B migrates faster than A some B will be produced at positions that B has already passed. hence, part of the compound B will apparently move slower than expected from the $R_f(B)$ value (Fig. 12.)

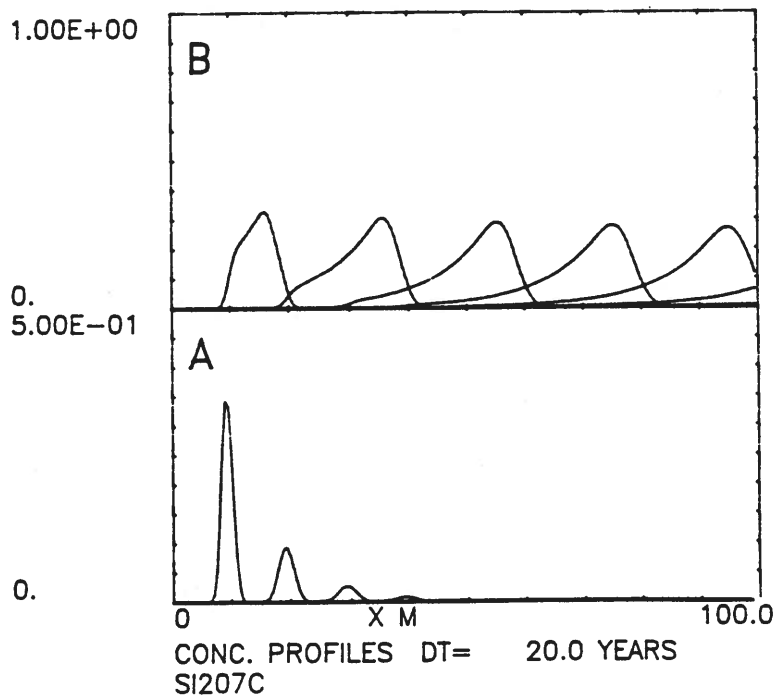


Fig.12: Concentration profiles of compounds A and B. Initial concentrations: $[A]_0 = 1$ and $[B]_0 = 0$. Retention factors: $R_f(A) = 2$, $R_f(B) = 1$. Rate constant: $k_1 = 0.1 \text{ y}^{-1}$. $V = 1 \text{ m/y}$, $D = 0.03 \text{ m}^2/\text{y}$.

In cases where the $A \rightarrow B$ conversion rate decreases to a value where the half life of A ($\tau = \ln 2 / k_1$) becomes comparable to the residence time of the porous media, the tailing effect becomes highly significant as demonstrated by Figures 13 and 14. The term "chemical dispersion" is suggested for this effect since it effects the migration behaviour of B as would a strong increase in the dispersion coefficient.

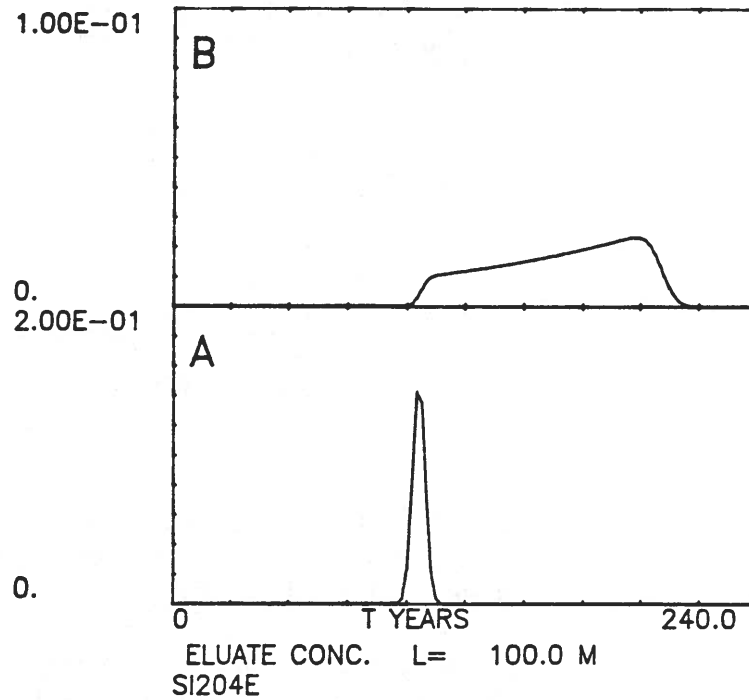


Fig.13: Elution curves of compounds A and B. Initial concentrations: $[A]_0 = 1$, $[B]_0 = 0$. Retention factors: $R_f(A) = 1$, $R_f(B) = 2$. Rate constant: $k_1 = 0.01 \text{ y}^{-1}$. $V = 1 \text{ m/y}$, $D = 0.03 \text{ m}^2/\text{y}$.

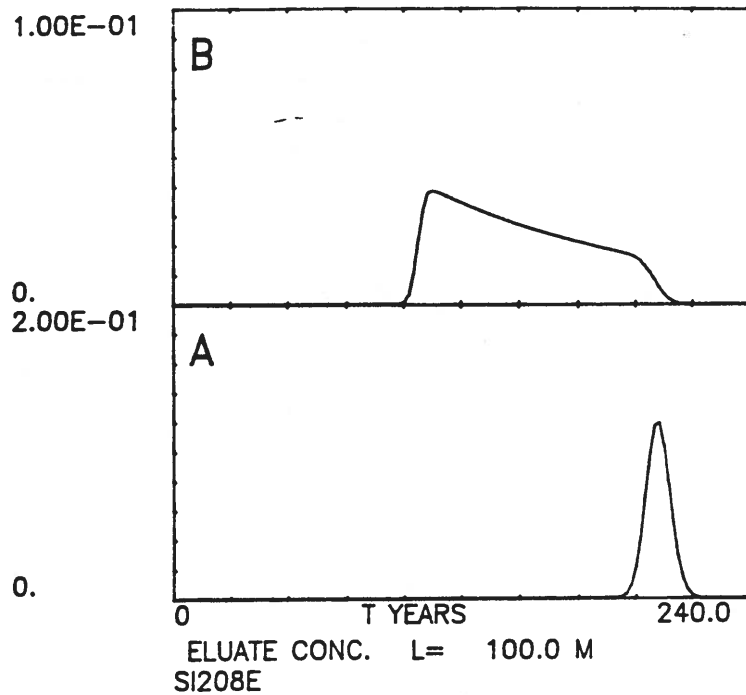


Fig.14: Elution curves of compounds A and B. Initial concentrations: $[A]_0 = 1$, $[B]_0 = 0$. Retention factors: $R_f(A) = 2$, $R_f(B) = 1$. Rate constants: $k_1 = 0.01 \text{ y}^{-1}$. $V = 1 \text{ m/y}$, $D = 0.03 \text{ m}^2/\text{y}$.

Turning to a two step reaction sequence $A \rightarrow B \rightarrow C$, this system appears as two consecutive $A \rightarrow B$ systems corresponding to an irreversible reaction sequence, e.g. a radioactive decay chain as $^{239}\text{U} \rightarrow ^{239}\text{Np} \rightarrow ^{239}\text{Pu}$ or consecutive chemical/microbial transformations. Hence, the trends observed for the $A \rightarrow B$ system are, not unexpected refound here, Increased relative retention of one of the species results in chemical dispersion of the eventual product C, the effect being significantly more pronounced in cases where one of the two processes $A \rightarrow B$ or $B \rightarrow C$ is slow. Figures 15 and 16 are shown as examples. Thus, C is retarded relative to A and B and the rate constants k_1 ($A \rightarrow B$) and k_2 ($B \rightarrow C$) being 0.1 y^{-1} and 0.01 y^{-1} (Fig.15) and 0.01 y^{-1} and 0.1 y^{-1} (Fig.16), respectively. The resulting eluate profile of C appears identical in the two cases.

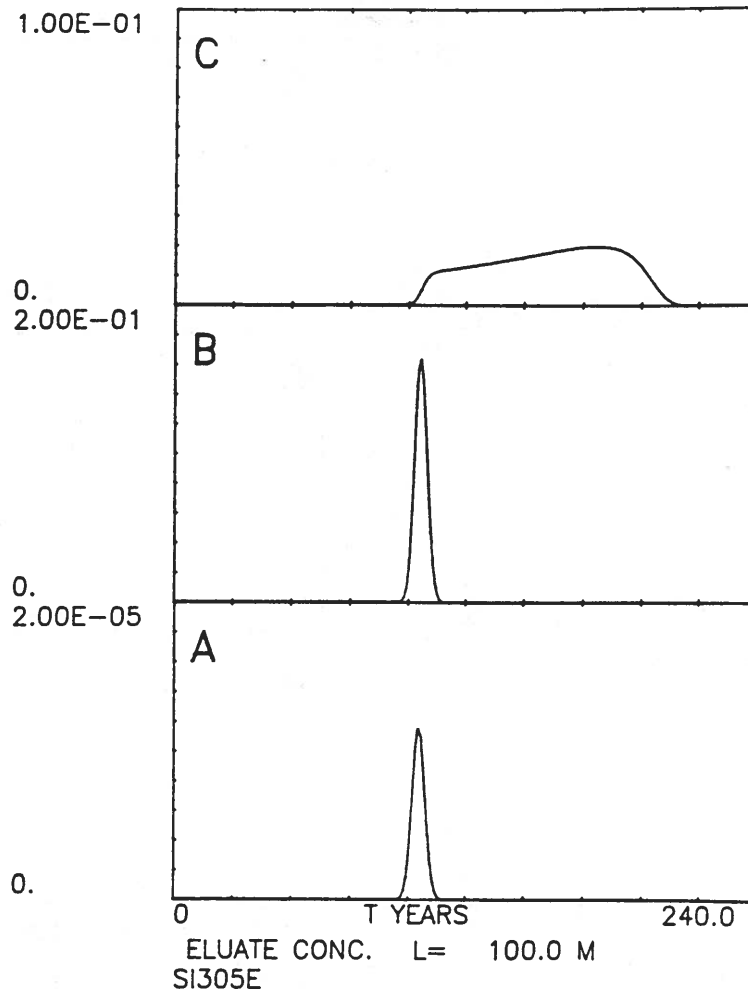


Fig.15: Elution curves of compounds A and B. Initial concentrations: $[A]_0 = 1, [B]_0 = 0, [C]_0 = 0$. Retention factors: $R_f(A) = R_f(B) = 1, R_f(C) = 2$. Rate constants: $k_1 = 0.1$ and $k_2 = 0.01 \text{ y}^{-1}$. $V = 1 \text{ m/y}$, $D = 0.03 \text{ m}^2/\text{y}^{-1}$.

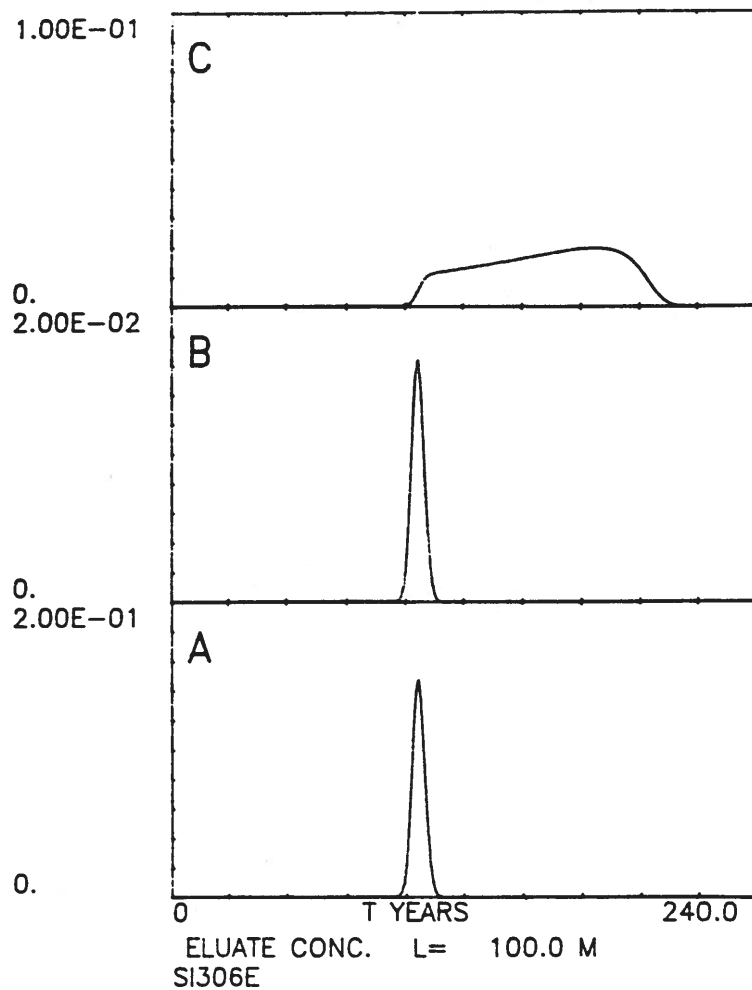


Fig.16: Elution curves of compounds A and B, and C. Initial concentrations: $[A]_0 = 1, [B]_0 = 0, [C]_0 = 0$. Retention factors: $R_f(A) = R_f(B) = 1, R_f(C) = 2$. Rate constants: $k_1 = 0.01$ and $k_2 = 0.1 \text{ y}^{-1}$. $V = 1 \text{ m/y}$, $D = 0.03 \text{ m}^2/\text{y}$.

The mixed $A \rightleftharpoons B \rightarrow C$ reaction system describes a system where the equilibrium between A and B is accompanied by an irreversible transformation of B to C. An example could be $\text{Pu}^{\text{III}} \rightleftharpoons \text{Pu}^{\text{IV}} \rightarrow \text{colloidal-Pu}$, where the irreversible transformation is inclusion of Pu^{IV} in colloidal-Pu.

This system is apparently a superposition of the systems $A \rightleftharpoons B$ exhibiting rate constants k_1 and k_{-1} , and $B \rightarrow C$ with rate constant k_2 . Depending on the relative values of k_1 , k_{-1} and k_2 this system always degenerates into one of simple systems according to the following scheme: (Carlsen et al., 1987)

k_1	k_{-1}	k_2	degenerates to:
fast	ur	fast	$A \rightarrow B \rightarrow C$
ur	ur	slow	$A \rightleftharpoons B$
slow	ur	ur	non-reacting system

ur (unrestricted): means that the actual value of this rate constant only to a very minor extent influences the overall picture.

3.5 Biochemical Reactions

Apart from the above discussed microbial transformation/degradations, reactions involving extra cellular enzymes may contribute significantly to the environmental fate of pollutants, or even take part in the natural production of potential hazardous chemicals.

Rook (1974) reported that chlorination of natural water lead to the formation of chloroform and other potentially hazardous chlorinated hydrocarbons. In nature enzymatically mediated chlorination reaction reactions are conceivable.

A series of investigations (Asplund et al., 1989, 1991, in press., Christiansen, 1990, Christiansen and Carlsen, 1991a, 1991b., Carlsen and Lassen, 1992, Hodin et al 1991., Asplund and Gimvall, 1991.) have indicated that naturally occurring extracellular peroxidases may be responsible for the formation, and thereby the occurrence, of organohalogenes of non-anthropogenic origin in soil. Both low and high molecular weight compounds are apparently formed.

In connection with iodine an increasing concern about the possible transport of long-lived radionuclides with groundwater has drawn attention to the presence of organoiodine compounds in the terrestrial environment (Christiansen and Carlsen, 1989). Strong evidence of microbial formation of organic iodine compounds has been presented (Behrens, 1982, 1985, 1986), whereas direct reactions between inorganic iodide and soil organic matter have been considered less plausible.

In laboratory studies it has been demonstrated (Christiansen and Carlsen, 1991a, 1991b) that humic acids can be iodinated either by elemental iodine or iodide by action of peroxidases in the presence of hydrogen peroxide. The iodinated humic acids exhibit a uniform distribution of the iodine independent of molecular size fractions. It appeared that the iodination reaction can be rationalized as an equilibrium reaction applying to a rather simple model, although it seems to involve different types of reactions as well as different types of sites in the humic acids.

It has not been possible unequivocally to rationalize the enzymatically controlled reactions, i.e. to elucidate to what extent the reactions are to be formulated as a direct interaction between the humic acids and enzyme-iodine complexes or as primary enzymatically controlled formation of elemental iodine, which subsequently reacts with the humic acids leading to the iodinated species.

In attempts to evaluate soil organic matter as a potential sink for radioiodine in the terrestrial environment, it seems appropriate to distinguish between soluble and solid organic matter. It appears the iodinated humic acids can be precipitated as such, however, when dissolved at least part of the iodine will be released to the liquid phase as a result of the equilibrium reaction. Hence, it was concluded that if conditions where dissolved soil organic matter is precipitated and subsequently dissolved prevail retention of iodide may be observed, the migration behaviour being controlled by an effective retention factor as recently discussed by Carlsen et al. (1989).

It has in analogous studies (Carlsen and Lassen, 1992) unambiguously been demonstrated that humic acids can be chlorinated by chloride by action of chloroperoxidase and hydrogen peroxide, the reaction probably proceeding with hypochlorous acid as the actual chlorinating species.

The possible role of halogenated humic material in the formation of low molecular weight organo halogen containing compounds has been elucidated by Lassen et al (1991a).

It was demonstrated that organic as well as inorganic chlorine and iodine are released when precipitated chlorinated and iodinated humic acids are dissolved at different pH. For both chlorine and iodine the release increases with increasing pH. However, the release is significantly higher for chlorinated than for iodinated humic acid. The amount of AOX in soil decreases during storage at pH values above 8.5; suggesting the release of inorganic chlorine, in agreement with the estimated halogenability as function of pH.

In the case of organic pollutants, the possibility of incorporation in humic acids by covalent bonding has to be taken into account, concurrent to sorption of the organic species onto solid humic acids.

It has been argued (Stevenson 1972, 1982, Schnitzer, 1981, Varadachari and Ghosk, 1984) that humic substances are formed by polymerization of simple monomeric species, such as hydroxy phenols, originating from the decomposition of plant components. Thus, it appears reasonable to assume that other compounds of phenolic nature can be incorporated into an existing humic acid structure. Recently Sakar et al., (1988) reported on the enzymatic coupling of 2,4-dichlorophenol to fulvic acids.

The incorporation of phenol units into the humic acid skeleton has been investigated by studying the interaction between phenol (spiked with ^{14}C -phenol) and humic acids in solution in the presence of enzymes of the peroxidase group and hydrogen peroxide (Lassen et al., 1991b, Carlsen et al., 1992) The reaction apparently gives rise to incorporation of phenol moieties in the humic acid structure. In fig.17 the chromatographic trace (UV-detection) of the humic acid solution before addition of the other reactants (i.e. phenol, horseradish peroxidase and hydrogen peroxide) and that of the resulting reaction mixture are depicted together with the radioactivity trace corresponding to the latter. Unambiguously, the latter trace demonstrates the incorporation of ^{14}C -phenol in the humic acids

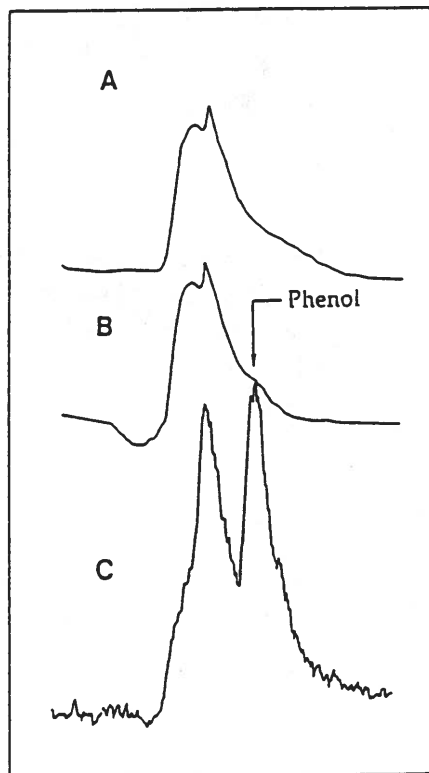


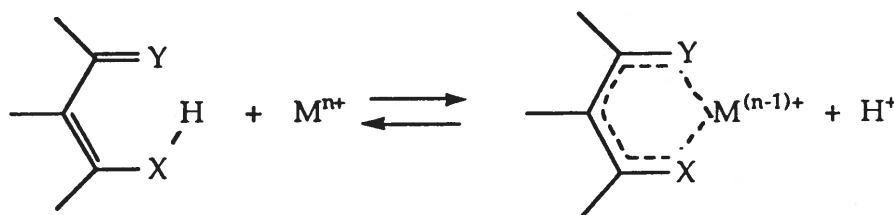
Fig.17: Chromatographic traces of A (UV-detection): humic acid solution before reaction, B (UV-detection) and C (radioactivity-detection): the resulting reaction mixture.

In sum it must be concluded that the possibility of biochemical reactions involving enzymatic catalysis should be taken into account in order comprehensively to evaluate the migration behaviour of pollutants in the environment.

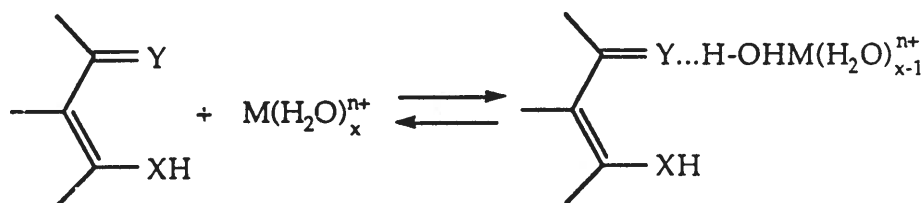
3.6 Complex formation

In recent years an increasing awareness of the possible importance of complexation of metal ions with organic ligands present in groundwater has developed, due to the possible mobilization effect (Carlsen, 1989).

In cases of the naturally occurring organic acids as humic- and fulvic acids, as well as in the cases of the artificially introduced organics of the multi-dentate type as NTA, EDTA etc., chelation unambiguously is the predominant reaction leading to complex formation, as illustrated by:



The reaction between hydrated metal ions and hetero atoms in the organic ligand may take place, however leading to relatively weak interactions by hydrogen bonding. Most probably this type of metal ion - ligand interaction will be limited to the case of $Y=O$:



Complexes formed as a consequence of this type of interactions are, similar to the formation of π -type complexes, most probably so weak that they can be left out of consideration in discussing the influence of organics in the migration of metal ions within the ground water system.

Finally the "salt formation" type of complexation, as result of a possible reaction between a metal ion and e.g. an isolated carboxylic group, shall be illustrated. This type of complexation is potentially of interest, due to the fact that several low-molecular weight organic acids, e.g. simple carboxylic acids, may be present in terrestrial ground waters.



Obviously, a detailed knowledge of the thermochemistry involved in these complex formation reactions is crucial in order to evaluate the eventual importance of the presence of certain organics in the ground water system.

The general reaction between a metal ion, M , and an organic ligand, L , is given by the following equation, i being the average number of ligands per metal ion.



Applying the mass action law gives:

$$\frac{[\text{ML}_i]}{[\text{M}][\text{L}]^i} = \beta$$

where β is the stability constant of the complex. In the cases of e.g. humic acid complexes, where most probably a variety of different types of complexing sites at the same ligands molecule will be involved in binding the metal ions, the term **Interaction Constant**, is suggested as appropriate for β (Carlsen, 1985).

It is important to note that in cases where the ligand appears as an anion of a weak acid, as typically for organic ligands, β will be observed to be pH dependent, the ligand concentration being given by:

$$\frac{[\text{HL}]}{[\text{L}]} = \frac{[\text{H}^+]}{K_a} = \frac{10^{-\text{pH}}}{K_a}$$

where K_a is the dissociation constant for the protonated ligand.

Typically the ligand concentration will be significant greater than the radionuclide concentration. Hence, the ligand concentration $[\text{L}]$ can be approximated by the total ligand concentration $[\text{L}^{\text{tot}}]$, which means that

$$\beta[\text{L}^{\text{tot}}]^i = \frac{[\text{ML}_i]}{[\text{M}]}$$

In other words, if the interaction constant, β , and the number of ligands per metal atom in the complex, i , are known, the molar ratio of complexed metal to uncomplexed metal can be approximated as the product of the interaction constant and the total ligand concentration raised to the i 'th power. Obviously, low concentrations can be compensated by high interaction constants, and vice versa.

Knowing the composition of a given ground water, and, hence, the concentrations of the single potential ligands, organic as well as inorganic, we have, by applying the above equation an excellent tool for comparing the complexing capacities of the different involved ligands. By this method, we can get a fair estimate of the type, or types of complexes, which will dominate the collective amount of radionuclide complexation.

As an example americium complexation in a ground water containing equal concentrations of natural occurring acetate and humic acid, both 10^{-3} molar, and minor amounts, e.g. 10^{-6} molar of EDTA. The $\log\beta$ values for the Am-acetate, Am-humate - and Am-EDTA complexes have been determined to be 2.0 (Martell and Smith, 1977), 7.3 (Bertha and Choppin, 1978), and 17.8 (Martell and Smith, 1974), respectively. These figures give rise to the following calculations:

Acetate:

$$\frac{[\text{Am-acetate}]}{[\text{Am}]} = \beta[\text{acetate}] = 10^{2.0} \times 10^{-3} = 0.1$$

Humate:

$$\frac{[\text{Am-humate}]}{[\text{Am}]} = \beta[\text{humate}] = 10^{7.3} \times 10^{-3} = 2 \times 10^4$$

EDTA:

$$\frac{[\text{Am-EDTA}]}{[\text{Am}]} = \beta[\text{EDTA}] = 10^{17.8} \times 10^{-6} = 6.3 \times 10^{11}$$

Hence, it is unambiguous that even very small amount of EDTA will dominate the collective amount of americium complexation, whereas the rather weak acetate complex will play a very minor role in the present context.

In the course of time a wide variety of techniques have been introduced for studying soluble metal complexes. However, due to the complicated nature of humic and fulvic acid, special requirements are often necessary in order to obtain the desired data. It is outside the scope of this report to discuss, and still less to evaluate these techniques. However, it seems reasonable to list the

more applied methods, which comprise ion-exchange equilibria (Schubert, 1948, Ardakani and Stevenson, 1972, Maes et al., 1988) potentiometric titration (Stevenson, 1977, Takamutsu and Yoshida, 1978), application of ion-selective electrodes (Bresnahan et al., 1978, Takamutsu and Yoshida 1978), spectroscopic measurements (Schnitzer and Hansen, 1970), liquid-liquid partition (Geering and Hodgson, 1969), gel filtration (Hirata, 1981), and dialysis (Carlsen, 1985, Truitt and Weber, 1981, Rainville and Weber, 1982, Carlsen et al., 1984)

One of the major problem in connection with the determination of interaction constants for metal ion - humic/fulvic acids interactions is the estimation of the ligand concentration [L]. In the course of time [L] has been expressed in terms of molar units (Schnitzer and Hansen, 1970, Schnitzer and Skinner, 1967), amount of ligand material (Tan et al., 1971), and concentration of complexing sites (Bertha and Choppin, 1978, Chielewska, 1969). The latter seems to be the more appropriate, as it unambiguously characterizes the humic/fulvic acid sample more satisfactorily than an average molecular weight. However, application of the amount of ligand material, given as g/L, as a measure of the ligand concentration, certainly do exhibit some advantages, since this figure typically will be the more easily achievable, e.g. from ground water samples. Thus, no extensive characterization of the ligand material will be necessary. In addition, knowing the complexing capacity W, in eq/g, the corresponding interaction constant can easily be derived from the equations

$$\beta = \beta' \times W^{-i}$$

or

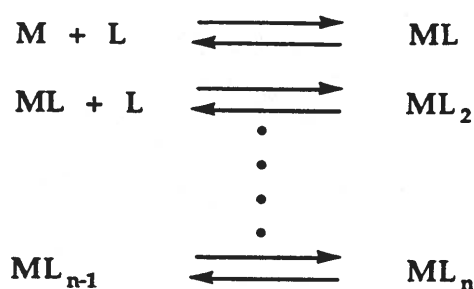
$$\log\beta = \log\beta' - i\log W$$

where β and β' denoted the interaction constants corresponding to ligand concentrations based on complexing capacity and weight per litre, respectively, and i being the average number of ligands per metal atom.

The complexing capacity of the ligands is defined as the maximum number of metal ion equivalents that can be bound per weight unit of the ligand.

Obviously the complexing capacity will be dependent of the nature of the metal ion, e.g. the coordination number of the ion, as well as of the stability of the complex.

The above described complexation reaction, giving rise to a complex of the general type ML_i , i not necessarily being an integer, reflects a stepwise complexation, whereby complexes of the types ML , ML_1 , ML_2 , ..., and ML_n are formed.



The corresponding stepwise interaction constants are given by

$$\beta_1 = \frac{[M]}{[M][L]}$$

$$\beta_2 = \frac{[ML_2]}{[ML][L]}$$

$$\beta_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

which gives the overall interaction constant

$$\beta = \prod_{i=1}^{i=n} \beta_i$$

It should be noted that the above equations for nearly all practical uses in the present context appear quite sufficient. However, the more accurate treatment requires the use of ion activities of the involved species rather than concentrations, e.g. $(M) = \gamma_M[M]$ where γ_M is the activity coefficient. Thus, the above derived interaction constants are the so-called concentration- or conditional interaction constants. The values of these interaction constants will vary with the ionic strength of the solution. Upon dilution, i.e. decreasing the ionic strength μ , the true thermodynamical interaction constant β^t will approach the conditional interaction constant β , as the activity coefficient $\gamma_{ML}/\gamma_M\gamma_L^i$ will approach unity.

$$\beta^t = \beta(\gamma_{ML}/\gamma_M\gamma_L^i)$$

Finally it can be mentioned that the true thermodynamical interaction constant β^t is related to the standard Gibbs free energy change of the reaction according to

$$\Delta G^\circ = -RT \cdot \ln \beta^t = \Delta H - T^\circ \Delta S^\circ$$

where R is the gas-constant (8.31 J/mol.K), T the absolute temperature. ΔH° and ΔS° denote the reaction enthalpy and the reaction entropy, respectively.

In contrast to the conditional interaction constants, which appear to be fairly easily obtained, by a variety of possible techniques as mentioned above, the true thermodynamic interaction constants are often extremely difficult to determine, due to the lack of activity-coefficient data. However, methods to derive stability constants at zero ionic strength have been developed, based on the application of a Debye-Hückel equation and the Davies equation as reported by Phillips (1982). We shall, however, not discuss this further in the present context, but only refer to the relevant literature on the subject.

Very recently a highly interesting approach towards an estimation of stability constants has been reported by Brown and co-workers (Brown and Sylva, 1987, Brown and Wanner, 1987). The approach is based on estimation of metal ion complex formation constants from properties of the reacting metal ion, such as ionic charge, radius and electronic structure, and ionic charge and pK_a of the acid of the ligand.

The theory, which shall not in detail be described here, introduces the electronicity concept, reflecting the "freeness" of the valence electrons and describes quantitatively, the ability of a ligand to complex a metal ion (Brown and Sylva, 1987). The theory has successfully been applied to a series of metal-ion-complexes with inorganic ligands as hydroxide, halogenide, sulphate, carbonate and hydrogen carbonate, as well as to organic ligands as oxalate, formate, acetate, benzoate catecholate, ethylenediamine, glycinate, glycolate and phenolate (Brown and Wanner, 1987). Unfortunately, no attempt to apply this potentially rather effective method to humic- and fulvic acid complexes, an area of obvious interest, has been done.

Several factors will influence the stability of organic metal complexes as derived by e.g. metal ion - humic acid interactions. Apart from the obvious influence due to differences in the nature of the metal ions, e.g. charge and complexation mode and ligands involved, two factors are of major significance. These are ionic strength and pH.

The influence of ionic strength on metal ion - humic- and fulvic acid complexes has been investigated by Schnitzer and Hansen (1970) and Stevenson (1976). In both cases a pronounced decrease in stability of the complexes with increasing ionic strength of the solution could be observed. A similar trend can generally be noted (Phillips, 1982)

The influence of pH on the complexation of metal ions with organic acids, e.g. humic and fulvic, acids has been studied by a manifold of groups (see e.g. Takamutsu and Yoshida, 1978, Bresnahan et al., 1978, Truitt and Weber, 1981, Rainville and Weber, 1982, Kerndorff and Schnitzer, 1980, Ong et al., 1970, Saar and Weber, 1979). With very minor exceptions it is generally found that complex stability increases with increasing pH, in agreement

with the enhanced availability of the actual ligand, i.e. the anion of the organic acid.

It can be mentioned that some reports on complex stability as a function of the metal ion/ligand concentration ratio have appeared for humic and fulvic acids (Truitt and Weber, 1981, Kerndorff and Schnitzer, 1980, Saar and Weber, 1979) only minor effects could be observed. However, Saar and Weber (1979) noted a trend towards an increase in stability with decreasing metal to ligand ratio.

Finally, a special feature associated with metal ion complexes with ligands of humic origin shall be mentioned, as is the effect of molecular weight. Thus, it appears that an increase in the capacity of metal ion fixation by decreasing molecular weight operates (Banerje, 1979, Toledo et al., 1981). It is suggested that this variation is due to the presence of a greater number of functional sites on the exposed surface area per unit mass of the low molecular weight compounds as compared to the high molecular weight species (Banerje, 1979, Toledo et al. 1981). Moreover, configurational aspects may play an important role (Banerje, 1979).

In the course of time a wide variety of stability constants for metal ion complexes with low-molecular-weight ligands has been reported. A major comprehensive source in this context is the work by Martell and Smith: "Critical Stability Constants" (Martell and Smith, 1974, 1975, 1977). Also comprehensive publications devoted to more specific topics have appeared e.g. dealing with acetylacetone, (Stary and Liljenzin, 1982), acidic organophosphorous extractants (Kolarik, 1982), NTA (Andereg, 1982), aminoacids (Petitet, 1984) and ethylenediamine (Paoletti, 1984). In a recent paper (Jensen and Jensen, 1985) the complex formation of metal ions with low-molecular acidic ligands, e.g. citric acid, commonly found in ground waters was studied. Metal ion - humic/fulvic acid interaction constants have been compiled by Carlsen (1989).

During the last years it has been elucidated that a strong "complexation" between non-polar, hydrophobic organic pollutants as PCB, DDT, dioxins and PAH and humic material takes place (Carter and Suffet, 1982, 1983, Caron et al, 1985, Caron and Suffet, 1989, Henry et al, 1989, Hassett and Anderson, 1982, Brownawell and Farrington, 1988, Hunchak-Kariouk and Suffet, 1991). Also slightly polar substances, as 1-naphthol has been reported to be complexed by humic-and fulvic acids (Chem. et al., 1992). The association of organic pollutants to humic substances may lead to a masking of these species by the organic matter possible resulting in a decrease in toxicity of the pollutants to certain, however, not necessarily all organisms in the environment. It is important to note that this association may result in an enhanced persistence of the pollutant, however, with a decreased toxicity. From an analytical point of view, it should be mentioned

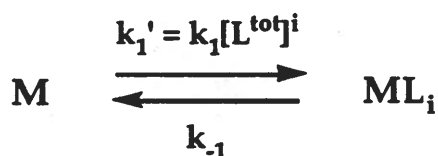
that the "complexed" organic pollutants may escape detection if the "complexation" has not been taken into account. The influence of this association/"complexation" on the migration behaviour of organic pollutants in the environment can be expected to mimic that for metal ion-humic acid complexation. Thus, the "complexation" may well explain why surface-administrated organic chemicals, e.g. pesticides in some cases have been found at significant depths.

The general reaction between a pollutant, M, and an organic ligand, L, has been discussed (vide supra). Typically under environmental conditions the ligand concentration will be significant greater than the pollutant concentration. Hence, the ligand concentration, [L] can be approximated by the total ligand concentration [L^{tot}], which means that

$$\frac{[ML_i]}{[M]} = \beta [L^{tot}]^i = \frac{k_1 [L^{tot}]^i}{k_{-1}} = \frac{k_1' [L^{tot}]^i}{k_{-1}} = \frac{k_1'}{k_{-1}} = \beta$$

β' is the apparent interaction constant of the complex expressed as the ratio between the pseudo-first order rate constant for the formation of the complex and the first order rate constant for the dissociation of the complex, respectively.

Thus, the complexation reaction can be described as an A \rightleftharpoons B pseudo-first order equilibrium system, i.e.



3.6.1 Migration behaviour

Migration of pollutants were calculated through a column of 100 m length, the ground water velocity is assumed to be 1 m/y and the dispersion coefficient is fixed to 0.03 m²/y. The initial concentrations at the entrance of the column of the uncomplexed, [M]₀, and the complexed, [ML_i]₀, pollutant molecules were assumed to be 1 mol/m³ and 0 mol/m³, respectively. The pollutant, M, was introduced to the column as a single pulse.

Equilibrium systems exhibiting apparent equilibrium constants ranging from 0, i.e. no complexation, to 1000 have been reported (Carlsen et al., 1989). In all cases, taking a study of Pagenkopf (1978) into account, both reactions involved are fast compared to the residence time of the equilibrium system in the column under investigation.

In agreement with the general assumption (*vide supra*) it is assumed that the complexed pollutant migrate through the column without retention, i.e. $R_f(ML_i) = 1$, whereas the retention factor of the uncomplexed pollutant was varied in the range from 1 to 100. However, one set of calculations, assuming a certain retention of the complex, applying $R_f(ML_i) = 5$, has been carried out.

First of all it can be stated that independently of the ratio between the rate constants, i.e. the apparent stability constant, well as of the applied retention factors for the free pollutant and the complex, respectively, both parties of the equilibrium system migrate through the column with the same speed, controlled by an *effective retention factor*. Hence, the two species of the system will accordingly be eluted from the exit of the column simultaneously. This fact is demonstrated by the representative set of elution curves depicted in Figure 18. The curves in Fig.18 visualize the elution of an equilibrium system exhibiting an apparent stability constant equal to 100, the retention factors of the free metal ion being 2 and 10, respectively. In both cases the retention factor of the complex was fixed equal to 1. It is noted that the M/ML_i equilibrium system of course is subject to the increase in dispersion by increased retention, i.e. increased residence time in the column.

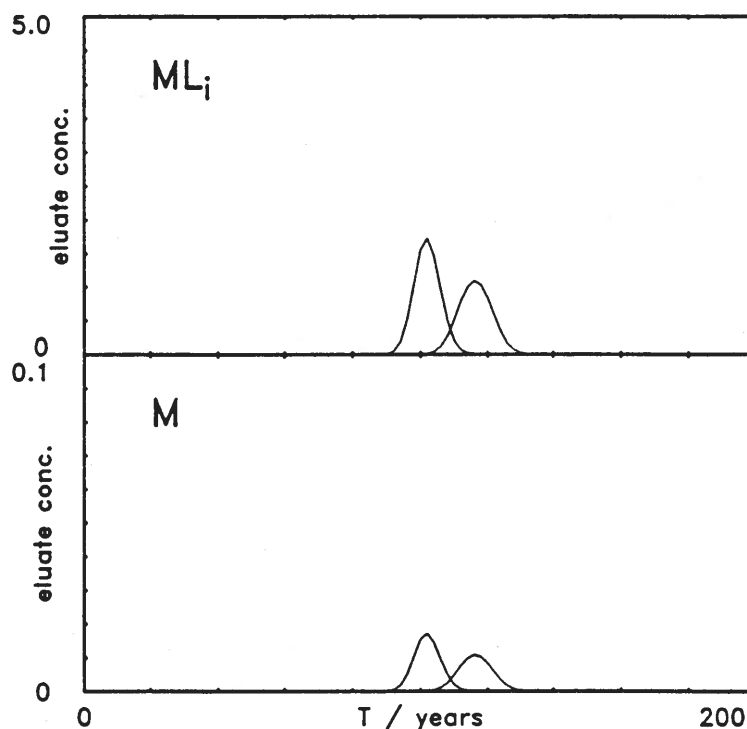


Fig.18: Elution curves for the components of a M/ML_i equilibrium system (apparent stability constant equal to 100) exhibiting $R_f(M)$ equal to 2 and 10, respectively, $R_f(ML_i)$ in both cases being 1.

Unambiguously it can be noted that the elution time increases for an increased pollutant retention. The calculated values, referring to the retention factors mentioned in Table 4 are 102, 110, 115, 150, and 200 years, respectively. It can additionally be noted that the actual value of the apparent stability constant is nicely reflected by the ratio between the eluate concentrations of the complexed and non-complexed metal ions. This feature appears as a common trend for fixed stability constants as summarized in Table 4.

TABLE 4.
Average Elution Times as a Function of Apparent Stability Constant and Retention Factors

k_1'	k_1	β'	$R_f(M)$	$R_f(ML_i)$	$T_{elution}$
1	1	1	2	1	151
			5	1	300
			10	1	561
			50	1	2657
			100	1	5171
5	1	5	2	1	117
			5	1	168
			10	1	257
			50	1	959
			100	1	1780
10	1	10	2	1	110
			5	1	143
			10	1	185
			50	1	500
			100	1	959
50	1	50	2	1	104
			5	1	115
			10	1	125
			50	1	200
			100	1	294
100	1	100	2	1	102
			5	1	110
			10	1	115
			50	1	150
			100	1	200
500	1	500	5	1	103
			10	1	103
			100	1	121
			1000	1	112
1000	1	1000	5	1	102
			10	1	102
			50	1	107
			100	1	112

Table 5 gives the calculated average elution times for a series of equilibrium systems, the apparent interaction constant varying from 1 to 10000. In all cases the retention factors for the free pollutant and the complex were fixed equal to 100 and 5, respectively.

TABLE 5. Average elution times as a function of apparent constant.

k_1'	k_1	β'	$R_f(M)$	$R_f(ML_i)$	$T_{elution}$
1	1	1	100	5	5308
5	1	5	100	5	2175
10	1	10	100	5	1507
50	1	50	100	5	685
100	1	100	100	5	592
10000	1	10000	100	5	500

Apart from the above mentioned effect of increased metal ion retention, the figures in the above two Tables unambiguously demonstrate, for fixed retention factors for the species involved, a significant decrease in elution time as function of increased apparent stability of the complex. The calculated average elution times given in the above two Tables should be compared to the theoretically obtained values for the two species, assuming no interaction. These values are given by $L R_f(i)/V$, L and V being the column length and ground water velocity, respectively. For the system studied the values are given by $100 R_f(M)$ and $100 R_f(ML_i)$, respectively. The two mentioned effects are visualized in Figure 19 and 20, showing the calculated average elution time as function of the retention factor (fixed complex stability) for the free pollutant and the apparent interaction constant (fixed pollutant retention), respectively.

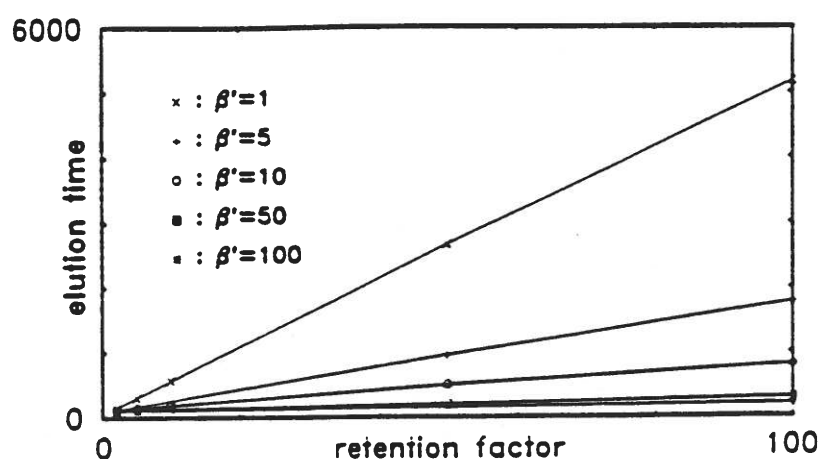


Fig.19: Average elution time for the M/ML_i equilibrium system as function of the retention factor for the free metal ion (fixed complex stability).

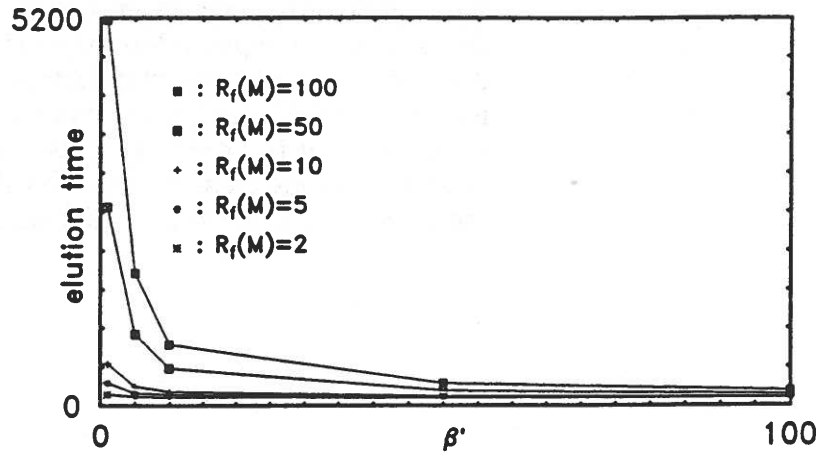


Fig.20: Average elution time for the M/ML_i equilibrium system as function of the apparent stability constant of the system (fixed metal ion retention).

Based on the data summarized in Figure 20, it is concluded that the following limiting values for the effective retention factors apparently apply to the migration of an equilibrium system through a column:

$$R_f^{\text{eff}} \rightarrow R_f(M) \text{ for } \beta' \rightarrow 0$$

$$R_f^{\text{eff}} \rightarrow R_f(\text{ML}_i) \text{ for } \beta' \rightarrow \infty$$

It is suggested that the following formula applies to the effective retention factors as function of the individual retention factors for the free pollutant and the complex and the apparent interaction constant, respectively. It should be noted that apart from obeying the above mentioned limiting conditions, the formula also agree with that proposed earlier (Carlsen et al., 1987) for the more simple systems, exhibiting only minor differences in retention factors.

$$R_f^{\text{eff}} = (R_f(M) + \beta' R_f(\text{ML}_i)) / (1 + \beta')$$

Application of this formula gives the following effective retention factors for the equilibrium system summarized in Table 5, the values given in parentheses are those obtained by the COLUMN2 calculation: 5250 (5308), 2083 (2175), 1364 (1507), 686 (685), 594 (592), 501 (500). Similar comparisons can be made using the systems summarized in Table 4.

In the introductory remarks it was stated that a wide variety of experimental data strongly suggest that organically complexed pollutant are subjects to very limited sorption only, if any at all. The above described calculations unambiguously demonstrate the influence of complexation on the migration of pollutant in the terrestrial environment. Increasing the apparent interaction con-

stant of the complex, either as a results of high true stability of the complex or by increased ligand concentrations, significantly decrease the effective retention of the equilibrium system. Hence, it is concluded that the naturally occurring organic ligands, i.e. humic- and fulvic acids, which form strong to very complexes with pollutant (vide supra), apparently must be expected to exhibit a pronounced influence on the migration behaviour of radionuclides, leading to an increased migration speed.

4 CONCLUSION

A wide range of possible chemical and physico-chemical processes, which a priori can be expected to influence the migration behaviour of pollutants in the environment has been discussed both from an experimental and theoretical point of view.

The study unambiguously discloses the importance of "chemistry" in predicting the migration behaviour of pollutants in the terrestrial environment.

The investigation of these reaction systems that in principle cover all possible processes, demonstrates that the interplay between retention characteristics and interconversion rate constants controls the migration behaviour. It has been shown that the K_D -concept breaks down and new concepts have been introduced: chemical dispersion, tailing, the average-elution-time law, and, hence, the effective retention.

This study suggests that besides estimation of retention characteristics for pollutants, kinetic information on processes like complex formation, and redox equilibria is of great importance, in order properly to predict migration behaviour.

Finally, the study reveals that prediction of pollutant migration in cases where chemical and/or physico-chemical reactions appear can be achieved based on the knowledge of reaction type, retention and kinetics.

The study has demonstrated rather drastic effect as results of minor changes only in retention factors. Hence, applying K_D -values, and hereby R_f -values as found in nature most probably will result in rather extreme effect of e.g. chemical dispersion, which eventually may diminish the potential hazard of leached of leached pollutants.

In sum it can be concluded that significant amount of data are needed for the eventual evaluation of the migration behaviour of pollutants in the environment. The major part of these data, can advantageously be obtained applying various nuclear techniques, e.g. radiochromatography.

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Publications:

NERI publishes professional reports, technical instructions, reprints of scientific and professional articles, a magazine of game biology and the Annual Report.

Included in the annual report is a review of the publications from the year in question. The annual reports and an up-to-date review of the year's publications are available on application to NERI