

**Category B:** Sites, which according to their previous use (depots, target shooting areas, fuel stations, Ware houses, car depots, Parking areas, Workshops, Barracks) are considered as potential sites for high contamination. Further investigations are required.

**Category C:** low risk sites, which are not initially considered as contaminated. These include: administrative buildings, transit areas, housing areas, cultural centres, and guest houses. According to the same study (SCHÄFER et. al., 1996) following qualitative assessment, for soil pollutants, ( Table 23 ) has been determined for representative sites:

Class	Number of samples and detected pollutants					
	>= 300	100-299	30-99	10-29	5-9	<5
Soil	Petro-leum Products	Xylene, Pb, Zn, Ni BTEX	Cr, Fe, Cu, Mn, Cd, K, Mg, Na, Hg, Ca, Al, Ethylbenzene, Toluene, Benzene, Ammonium comp. Nitrates, Chlorides	Nitrites, PAH	Chrysene, Fluoranthene, Pyrene, Anthracene, Benzo[a]pyrene, perylene	Chlorinated hydrocarbons, Indeno [1,2,3cd]pyrene, Tetra-chloroethane, Naphthalene Phenols, Phosphates, F <sub>2</sub> , Acenaphthalene.
Soil air		BTEX	Toluene, Benzene, Ethylbenzene	Chlorinated hydrocarbons, Trichloroethane		Tetrachloroethane, AOX
Ground water		BTEX, Ethylbenzene, Pet. Products, Chlorinated hydrocarbons, Dichloroethane, Tetrachloroethane	AOX	Al, Pb, Ca, Cr, K; Cu, Mg, Mn, Na, Zn, Sulphate s, Nitrites, PAH, Tetrachloromethane	Trichloroethane, Trichloroethane, Methane, Nitrates, Phosphates, Hg, Cl <sub>2</sub> , Ni,	

BTEX = Benzene, Toluene, Ethylbenzene, Xylene, AOX= Absorbed Organic Halogens

**Table 24.** Pollutants at abandoned military sites in Berlin. (After SCHÄFER et. al., 1996)

## Chapter 8

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### Pollution Mechanisms and Soil – Pollutants interaction

Pollutants behaviour and interaction with soil comprise various physical, chemical, and biological processes that take place in all three (solid, gas and liquid) components of the soil medium. They generally include three main groups of processes:

1. Retention on, and within the soil body
2. Infiltration, diffusion and transport by soil solutions
3. Alteration, transformation, and initiation of chemical changes within the soil.

While the first two groups include mainly physical processes, by which pollutants are transported and distributed in the soil, the third group comprise only chemical and biological processes by which pollutants are transformed or stored as residues in the interstitial space. Figure 56 shows a schematic overview of the three groups of processes.

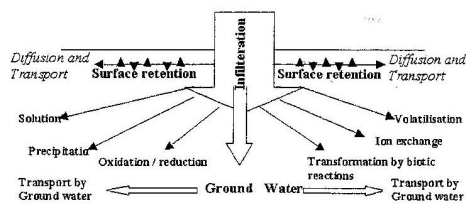


Fig. 56 A schematic overview of the processes representing soil-pollutant interactions

Physical processes of soil /pollutant interactions are those processes including transport and retention. They depend mainly on the physical parameters of the medium (temperature, grain size, electric charges etc.), while chemical processes depend largely on the type of pollutants and their chemical nature. Both groups of processes are further classified according to the mechanisms involved.

As for biological or biologically controlled soil pollution processes, we may include all processes of biotransformation, and biodegradation, each depending on the microbial ecology, the depth, and the oxygen availability at the site of pollution. A summary of the processes involved in soil pollution may be given as in Figure 57.

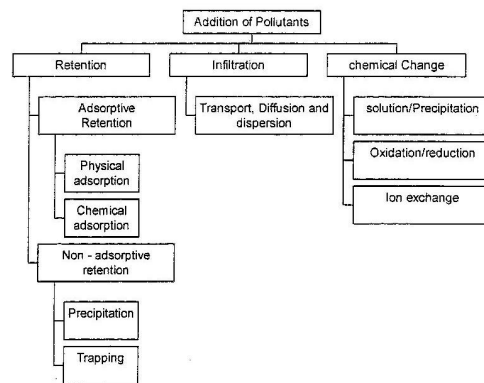


Figure 57 A summary of the mechanisms involved in Soil Pollution

### 8.1 Physical processes and mechanisms of pollution

Pollutants on encountering soil grains will either be retained by adsorption on the surface of these grains, or be accumulated in their intergranular space, where they may form concentrations retaining their original chemical composition or substances that have been altered by various chemical reactions. Pollutants retained thus on the soil surface or in its interstitial space may be organic, inorganic, or a mixture or complexes of both. They reach the soil in various physical conditions as solutes, water-immiscible liquids or suspended particles. The mechanisms of their interaction with the soil will thus depend upon physical parameters prevailing in the soil medium such as temperature, moisture content or salinity of the soil water, as well as upon their own physical and chemical properties.

Adsorption and its accompanying phenomena are considered as the most important physico-chemical mechanisms of pollutants retention on the surface of soil grains. In the following, these phenomena will be treated in some details.

### 8.1.1 Adsorptive retention

Molecules of pollutants can be retained on the surfaces of soil grains in two ways. In physical adsorption, which is also known as physisorption, molecules of pollutants will be attached to the surfaces of soil grains by Van der Waal forces, which are known to stand for a long range, yet weak interaction. The amounts of energies involved in such attachment are normally of low magnitudes and are not sufficient for bond breaking. Thus, pollutant molecules sticking to the soil surface will retain their chemical identities, although they might be stretched or bent on account of their proximity to the surface.

In chemisorption or chemical adsorption, the pollutants attach themselves to the grain surfaces as a result of the formation of a chemical (usually covalent) bond. In this case, the energy of attachment is very much greater than in physical adsorption. Thus, a molecule undergoing chemisorption can be torn to satisfy valency considerations arising from bond formation with the surface atoms. Although it is very difficult to differentiate between physical and chemical adsorption, one can generally say that the amount of physically adsorbed material decreases with increasing temperature, while this relation for chemically adsorbed material is reversed.

Normally various adsorbents exist in soil medium. Some examples of these are given by clay minerals, zeolites, iron and manganese hydrated oxides, aluminium hydroxide, humic substances, bacterial mucous substances, and plant debris. Many rock forming minerals such as micas, feldspars, some pyroxenes, and some amphiboles are also considered as good adsorbents of pollutant molecules.

The capability of clay minerals and colloids in general to adsorb foreign molecules on their surfaces is attributed partially to their high surface energy, and partially to the existence of a net surface charge ( $\sigma_s$ ), which may be caused by some functional groups (e.g.,  $M-OH$ ). These normally possess charges that are dependant in sign and magnitude on the composition of the ambient liquid phase, as well as on the nature of the surface they are bound to. Such net charges attract ionic pollutants to the surfaces of the adsorbent material. However, non-ionic pollutants

can also be adsorbed by soil grains. This occurs principally through electrostatic forces.

### *The theory of diffuse double layer (DDL)*

To explain the adsorption of charged particles on the surfaces of solids, HELMHOLTZ (1879) assumed an electrical double layer of positive and negative charges at the surface of separation between the colloidal particle and the dispersion medium. The double layer according to Helmholtz consists of one layer firmly attached to the surface of the particle and a second oppositely charged layer at a monomolecular distance from the particle in the surrounding medium (Figure 58a). Guoy and Chapman (1910) and further workers in the following modified this theory to culminate in the diffuse double layer theory. According to the Gouy-Chapman model, the charges on the surface of the solid are not balanced by a single movable layer in the surrounding phase, but by a layer more diffuse in character, that extends into the ambient phase as shown in Fig. 58b. One part of the double layer (A in Figure 58b) is firmly attached to the surface of the colloid substance and thus becomes an integrated part of it. The second part (B in Figure 58b) lies in the surrounding phase. Thus the potential drop between the solid surface and the surrounding phase is formed of two parts (i) between the solid surface and the firmly attached layer A (ii) between layer A and the bulk of the surrounding phase. This second potential drop is called the electro kinetic or zeta potential (represented by the Greek letter  $\xi$ ).

The theory explains the formation of the double layer through the argument that the surfaces of colloids are considered as planar surfaces upon which electrical charges are uniformly distributed. The colloid surface with its layer of net charge, on encountering the front of approaching liquid or gaseous phase, will be faced by a layer of equal but opposite charges made by the ions to be absorbed on the surface of the colloid. This will cause that the approaching ions (if possessing an opposite charge) will be attached on the colloid surface. Following the electrostatic attachment of the oppositely charged ions on the colloidal surface another process

will take place viz.; the repulsion of the similarly charged ions, which in this case will be drifted by diffusion to form a layer further from the surface of the colloid. Thus, two layers will surround the colloid surface; one of them is the layer of attracted opposite charges (called the layer of counter ions) and a diffusive layer of repelled ions migrating towards the ambient liquid or gaseous phase. The double layer theory is suitable to explain adsorption of ionic pollutants on the surface of soil particles; especially in connection with ion exchange mechanisms. This will be explained below in some details.

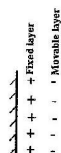


Fig. 58a Helmholtz double layer

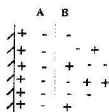


Fig. 58b . Gouy-Chapman diffuse double layer

#### Chemical Adsorption or Chemisorption

As it was stated before, formation of covalent bonds during chemical adsorption makes the energy of attachment very much greater than in the case of physical adsorption. A molecule undergoing chemisorption can be torn to satisfy valency considerations arising from bond formation with the surface atoms.

Generally the amount of adsorbed material in physical adsorption is inversely proportional to temperature. This relation is reversed in chemical adsorption

In Chemisorption, molecules undergoing this process normally lose their identities as the atoms are rearranged (Hassett and Banwart, 1989).

#### The extent of adsorption (Adsorption isotherms)

The extent of adsorption depends upon the exposed surface area of the adsorbent as well as upon the concentration of the sorbate in the soil solution (partial pressure in case of gases) and the temperature of the medium. As it will be shown later the adsorption process arrives at equilibrium, when the number of molecules adsorbed will be equal to the free ones in the surrounding medium. If measured adsorption data are plotted against the concentration values of the adsorbate in the surrounding medium a graph known, as the *adsorption isotherm* can be obtained.

The simplest isotherm is the *linear distribution coefficient*,  $K_d$  (also called linear partition coefficient), which is widely used to describe adsorption in soil and near surface aquatic environments. According to this equation, the amount of contaminant adsorbed is directly proportional to the concentration of the adsorbate in the ambient solution. It has the form.

$$S = K_d C$$

Where:  $S$  = amount adsorbed ( $\mu\text{g/g}$  solid)

$C$  = concentration of substance to be adsorbed in the ambient solution ( $\mu\text{g/mL}$ )

$K_d$  = distribution coefficient.

Another coefficient, also widely used in problems of soil pollution, is the *organic carbon partition coefficient* ( $K_{oc}$ ). It is derived by dividing the distribution coefficient ( $K_d$ ) by the percentage of organic carbon present in the system (HAMAKER & THOMPSON, 1972).

Accordingly:

$$K_{oc} = K_d / \% \text{ organic carbon,}$$

where  $K_d$  is the distribution coefficient.

Readers, interested in the application of  $K_d$  to explain adsorption processes of organic pollutants in soil environment, are referred to Karickhoff (1984).

### The Langmuir Isotherm

This isotherm was originally developed to describe adsorption of gases on homogeneous surface and can be derived as follows:

For an adsorbent surrounded by a gaseous phase, gas molecules crashing on the exposed surface will be trapped only if they quickly dissipate their energy into the vibrations of the underlying lattice. Otherwise, they will be bounced back to the surrounding phase. The rate of collisions with the surface, that will successfully lead to adsorption is called the *sticking probability* and is given by the relation.

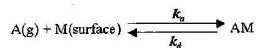
$$s = \frac{\text{rate of adsorption of molecules by the surface}}{\text{rate of collision of molecules with the surface}}$$

The sticking probability depends upon the exposed surface area, it drops to smaller values as the surface sites get filled. The extent of surface coverage is given by the relation:

$$\theta = \frac{\text{number of adsorption sites filled}}{\text{number of adsorption sites available}}$$

At the time when equilibrium is attained between molecules sticking on the surface and molecules free in the gas phase,  $\theta$  will depend on the pressure of the gas. This relation between  $\theta$  and the pressure at a given temperature delivers what we called above the *adsorption isotherm*.

Assuming that every adsorption site is equivalent and that the ability of a molecule to attach itself to the surface is independent of whether the neighbouring sites are occupied or not, we may represent the dynamic equilibrium between the adsorbed molecules and the free ones by the equation:



where  $k_a$  and  $k_d$  are the rate coefficients for adsorption and desorption respectively.

If the fractional coverage is denoted by  $(1 - \theta)$ , then the number of vacant sites will be given by  $N(1 - \theta)$ , where  $N$  is the total number of sites.

Since the rate of adsorption is proportional to the pressure of A ( $P_A$ ) as well as to the number of vacant sites, we may represent it by the equation:

$$\text{Rate of adsorption} = k_a P_A N (1 - \theta)$$

The rate of desorption, however, is proportional to the number of adsorbed species  $N\theta$  so that it can be represented by the equation:

$$\text{Rate of desorption} = k_d N \theta$$

At equilibrium:

Rate of adsorption = Rate of desorption, i.e.

$$k_a P_A N (1 - \theta) = k_d N \theta$$

solving for  $\theta$ , we get:

$$\text{Langmuir isotherm: } \theta = K P_A / (1 + K P_A)$$

The Langmuir isotherm was originally developed to describe the adsorption of gases on solids. However in dealing with solutes in soil water  $P_A$  is replaced by  $C_A$ , so that we get:

$$\text{Langmuir isotherm: } \theta = K C_A / (1 + K C_A)$$

$\theta$  stands for the amount adsorbed per unit mass of adsorbent and  $C_A$  for the concentration of adsorbate in solution.

At low degrees of surface coverage the graphical relation between  $\theta$  and the concentration of adsorbate is given by a straight line. However, this was found to deviate gradually as the adsorption sites are increasingly occupied by the molecules of adsorbate (Figure 59). Such deviation hints to the fact that following assumptions underlying the derivation of the Langmuir isotherm are quite unrealistic.

- The energy of adsorption is equal for all sites and is independent of the degree of surface coverage.
- The adsorbed entities are attached to the surface at definite homogeneous localised sites  
Forming a monolayer with no interaction between adjoining adsorbed molecules.
- The energy of adsorption is independent of temperature.

These consideration and the observation that the energy of adsorption logarithmically decreases with increasing coverage of the adsorbent surface led to the empirical derivation of the *freundlich equation*, that modifies Langmuir isotherm to fit more realistic conditions.

This is given by  $\theta = K C^{1/n}$  where  $K$  and  $n$  are empirical constants

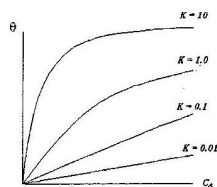


Fig. 59 . The Langmuir isotherm for several values of  $K$

### The Brunauer, Emmet and Teller (BET) isotherm

This equation was developed to allow for multilayer adsorption, which is characteristic for phenomena of physisorption. It has the form:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C_h} + \frac{(C_h - 1)P}{V_m C_h P_0}$$

$P$  stands for the equilibrium pressure at which a volume  $V$  of a gas is adsorbed.

$P_0$  is the saturation pressure of the gas.

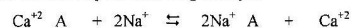
$V_m$  the volume of gas corresponding to a mono-molecular layer.

$C_h$  is a constant related to the heat of adsorption of the gas on the adsorbent.

### 1. Adsorption of ionic pollutants.

According to the diffuse double layer model (ddl), soil grains surrounded by a gaseous or liquid environment will be faced by a front of one or more layers of counter ions (ions of opposite charge) or co-ions (ions of similar charge). Many soil components (e.g. clay minerals) have a marked tendency of replacing some of their ions with similar species from the ambient medium (solution or gaseous phase). When the species lost or gained are cations, the phenomenon will be described as cation exchange, otherwise we speak of anion exchange. Cation exchange plays a dominant role in soil environment, while anion exchange processes are very rare. This is because anions as acid radicals may, in presence of hydrogen, lead to dissociation of adsorbent materials such as the clay minerals.

A cation exchange process between an adsorbent and the surrounding soil solution is a reversible process. It can be represented, for an adsorbent (A), by a simple reversible equation as shown by the following example:



Classic examples of soil components showing marked cation-exchange behaviour are the clay minerals; especially the montmorillonites and illites. They possess a negatively charged repetitive structural framework; having a well defined negatively charged sites occupied by singly or doubly charged cations. A great variety

of materials other than the clay minerals exhibit the same behaviour. Among these are included most silicate minerals, silicate glasses, arsenates, vanadates, molybdates and related species.

Cation exchange capacity of an ion-exchanger is normally defined as the equivalent mass (*in milliequivalents*) of exchangeable cation per 100 gm of exchanger at pH = 7.

In table 25 cation exchange capacities (CEC) of some soil components are given. These are clay minerals and zeolites in the first place. Zeolites may occur in soils formed on volcanic substrates. They exhibit high cation exchange capacities and normally cause enrichment of soil water in  $\text{NaHCO}_3$  due to their tendency for sodium replacement with other cations. Montmorillonite that occurs in various soils is normally considered as the most important cation exchanger in the weathering zone.

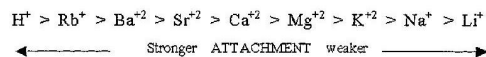
Rock forming mineral or sediment	Cation exchange capacity (meq /100 gm at pH 7)
Kaolinite	3-15
Halloysite ( $2\text{H}_2\text{O}$ )	5-10
Halloysite ( $4\text{H}_2\text{O}$ )	40-50
Illite (Hydrous mica)	10-40
Chlorite	10-40
Glauconite	11-20
Palygorskite	20-30
Allophane	25-50
Montmorillonite	80-150
Silicagel	80-150
Vermiculite	100-150
Zeolite	100-130
Organic substance in soil and recent sediments.	150-500

Table 25 .Cation exchange capacities of some soil components After Carroll, D. (1959) and Grim (1968)

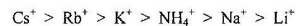
#### Ion selectivity:

Natural cation exchangers do not attract all ions with the same intensity. This preference or selectivity depends principally on cationic concentration in the solu-

tion, the cationic dimensions, as well as on the structural properties of the exchange surface. It has been generally postulated that cations of higher valency and those held tightly in their crystal lattice are preferred by soil components. Hydrogen, however, forms an exception to this rule. It behaves in the course of ion exchange as if it were of higher valency (II or III). The general series of ion-preference may be represented as follows:



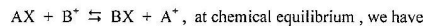
Among monovalent cations, the preference takes place according to the following series:



On soil organic compounds multivalent cations are generally preferred to monovalent cations and transitional group metals to the strongly basic metals.

A quantitative measure for the selectivity of an exchanger towards a pair of monovalent cations (or its tendency to bond one of them more strongly than the other) can be derived using the Law of Mass Action as follows:

assuming the exchange reaction to be:



$$\frac{[\text{A}^+][\text{BX}]}{[\text{B}^+][\text{AX}]} = K_{AB}$$

Rearranging we get:

$$\frac{[\text{A}^+]}{[\text{B}^+]} = K_{AB} \frac{[\text{AX}]}{[\text{BX}]}$$

Where,  $\text{A}^+/\text{B}^+$  is the ratio of ion activities in the solution, (AX) and (BX) refer to the concentration of  $\text{A}^+$  and  $\text{B}^+$  in the exchanger in moles per unit weight of ex-

changer (they may also be expressed in mole fraction) and  $K_{AB}$  is the selectivity constant, which expresses the inequality of the activity ratios of the cationic pair. Following example illustrates the use of the relation:

*Example:* (i) The ratio of ionic activities of  $A^+$  and  $B^+$  in a solution was found to be 1. The mole fraction of both species in the exchanger is also equal to unity. What is the selectivity of the exchanger?

In this case according to equation (12)  $K_{AB} = 1$ , therefore the exchanger has no selectivity and both  $A^+$  and  $B^+$  are bonded to it with equal strength.

(ii) If in the same example  $K_{AB} = 10$  and the ratio of ion activities in solution  $A^+/B^+ = 1$

which ion will be represented by higher occupation on the exchanger?

In this case  $(AX)/(BX) = 0.1$  i.e. the exchanger is by far largely occupied by  $B^+$ .

(iii) under what condition can equal occupation occur in case (ii)?

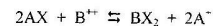
This can only happen if  $A^+/B^+ = 10$ , while  $(AX)/(BX)$  will be equal to unity.

J.F. Walton, after studying the results of various experimental works, replaced equation 12 with the following empirical relation which is basically the same; except for the empirical exponent  $n$ .

$$\frac{[A^+]}{[B^+]} = K'_{AB} \left( \frac{(AX)}{(BX)} \right)^n,$$

$[A^+]$  and  $[B^+]$  are the activities of cations in solution;  $(AX)$  and  $(BX)$  are the concentrations of ions in the exchanger,  $n$  is an empirical exponent and  $K'_{AB}$  is the exchange constant.

For a monovalent-divalent ion exchange, the reaction can be written:



Accordingly, the empirical equation takes the form:

$$\frac{[A^+]^2}{[B^{++}]} = K'_{AB} \left( \frac{(AX_2)}{(BX_2)} \right)^n$$

For exchange involving more than two cations, following relation holds:

$$\frac{[A^+]}{[B^+][C^+]} = K'_{AB} K'_{AC} \left( \frac{(AX)}{(BX)(CX)} \right)^{n+m}$$

#### Factors affecting adsorption:

The intensity of adsorption depends upon several factors including physical and chemical properties of the pollutants themselves as well as the soil matrix, composition, and surface properties. It is generally possible to summarise all these factors as follows

- Mineralogical composition of the soil
- Grain size distribution in the soil
- The content and distribution of humic substances in soil
- Chemical and physical properties of the soil solution
- Cation exchange capacity of organic and mineral components
- The pollutants, their nature and chemical constitution
- To the above we may add external conditions such as climatic conditions and agricultural practices.

In the following each of these groups and collective factors will be shortly discussed



### 1. Mineralogical composition of the soil

As mentioned before, clay minerals are the most important adsorbents in the soil environment followed by some silicates and organic components. Accordingly, the intensity of adsorbance in soils will largely depend on the clay content of the soil as well as on the share of other silicates in the mineralogical composition. The negative framework of the clays consists essentially of sheet structures of aluminium silicates in which the exchangeable cations occupy interlayer positions or are located adjacent to the particle surfaces (section 2.1.3). Structural properties of individual clay minerals play normally the principal role in determining selectivity, intensity, and mechanism of adsorption on these substances. In this respect we identify following types of adsorption on clay minerals

a) Adsorption on planar external surfaces as in kaolinite: Here the tetrahedral layers are strongly held by hydrogen bonds, leaving only the external surfaces as available sites for ion exchange

b) Exchange in the interlayer space: Here the ability of the layers to swell on hydration will contribute to the feasibility of ion exchange in the interlayer space as in montmorillonite. In addition, the bonding of adjacent layers by cations such as in vermiculite will lead to cation exchange if size conditions are fulfilled.

Cation exchange capacities of clays, however, can considerably increase in presence of other mineral matter such as Al and Fe hydroxides. TERCE and CALVET (1977) found that the two hydroxides increase the adsorptive capacity of montmorillonite.

### 2. Soil matrix (grain size distribution)

It has generally been observed that the rate of adsorption is higher on finer sediments than on coarser ones. Kennedy and Brown (1965) found that the content of total calcium and sodium in a sandy sediment was represented by about 90% in the grain size fraction of 0.12 - 0.20 mm, while the coarser fraction of 0.2 - 0.50 delivered only 10% of the whole content. Malcolm and Kennedy (1970) interpreted this behaviour by the slow diffusion rates in coarse fractions compared to

the fine ones. Despite the fact that concentration of certain cations in finer sediment fractions is also known from other sediments (e.g. carbonates), following possibilities should be taken in consideration when interpreting this phenomenon for silicates. In case of sandy sediments, when Ca and Na are concerned, relative hardness of certain silicate minerals (e.g. feldspars) and their lower resistance to abrasion, relative to harder silica compounds with low Na and Ca content (e.g. Quartz), may control the distribution of such cations between the different grain size fractions in the same sandy layer. To attain better bases for interpretation, mineralogical composition of the different grain size fractions, must be determined using X-ray diffraction methods. However, one should also bear in mind that the high surface area, and hence high surface energy, of fine sediments supplies an excellent interpretation for the higher rates of ion adsorption on them.

### 3. Humic substances and their distribution in the soil.

Humic substances containing carboxyl and phenolic hydroxyl functional groups increase the cation exchange capacity (CEC) of the soil. In general, the presence of active functional groups (e.g. carboxyl, hydroxyl, carbonyl, methoxy and amino groups) is thought to be of positive influence on the cation exchange capacity of a soil.

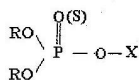
### 4. Chemical and physical properties of the soil solution

A major part of pollutants, however, passes in solution or in particulate form to the vadose or even saturated groundwater zone. In presence of clays, water molecules are adsorbed on their surfaces to form hydration shells; these provide adsorption sites for pollutant molecules. Water adsorbed on clay molecules generally has higher rates of dissociation providing surfaces of acidic character (Yaron, Calvet and Prost, 1996) that may increase the exchange capacity of the soil. Mechanisms by which pollutants are transported to deeper horizons of the soil are collectively called *infiltration*. They form the major mode of pollutants spreading as reported by Calvet, 1984, who found out that pesticides are transported to the adsorbing

surfaces by water. Descending contaminated fluids that might end in joining the vadose or saturated zones of ground water are generally known as *leachates*. In the vadose zone leachates spread horizontally in the direction of ground water flow. Such movements are controlled by the laws governing transport phenomena in ground water and will be discussed later.

#### 5. The pollutants, their nature, and chemical constitution.

The composition and nature of contaminants control to a considerable extent not only solution and diffusion processes, but also adsorption on the soil grains. Such control may be explained by the fact that ion exchange and hydrolysis reactions are particularly sensitive to the parameters (pH, Eh) of the chemical environment created by the contaminants in their direct vicinity. An example of this may be provided by the adsorption of organophosphorus pesticides on clay surfaces. As mentioned before (p. 74), organophosphorus pesticides are members of the phosphoric acid ester group, having the following general formula:



General formula of organophosphorus compounds

where the two alkyl groups (R) may be methyl or ethyl but they are the same in any given molecule. X (the leaving group) is generally a complex aliphatic cyclic group. It was found that adsorption of organophosphorus compounds on clay surfaces is influenced by the nature of the constituent group X (Yaron, 1978). This is due to the fact that such esters are stable at pH- values  $\leq 7$  i.e. at neutral or acidic media, but they are susceptible to hydrolysis under alkaline conditions, where the P-O-X ester bond breaks down. The rate of this process is related to the nature of the group X.

#### 8.1. 2 Nonadsorptive retention

1. **Trapping:** Entrapment of solid particles and large dissolved molecules in the pore space of the soil forms one of the major mechanisms of retention of pollutants in the soil. This type of retention occurs following three mechanisms as shown in figure 60, drawn after J. R. BOULDING (1995). The figure illustrates the three mechanisms, which may be shortly described as follows:

##### a) Caking

This may occur physically when the pollutant particles are larger than the soil pores. In this case, the entrapped particles form a layer (cake) on the surface where the pore sizes become too small. Caking may also result from biological activities through which particles cluster in bigger lumps that clog the soil pores.

##### b) Straining

Straining occurs, when pollutant particles are about the size of the soil pores. They move down the pores until they are entrapped at the entrance to a pore, which is too small

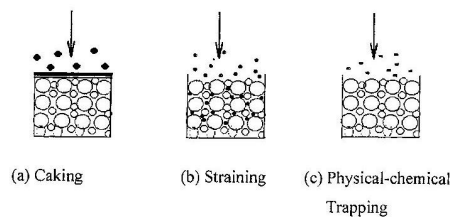


Fig. 60 . Trapping mechanisms in porous media (based on J. Russel Boulding, 1995 after Palmer and Johnson, 1989)

### c) Physical – chemical trapping

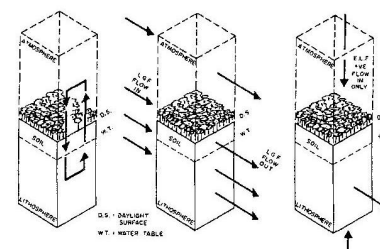
Limitation of flow through clogging of pore space may occur because of physical or chemical transformation, such as the production -by chemical reactions- of new products having molecular sizes that exceed that of the soil pores. An example is the flocculation of colloidal material resulting from the precipitation of iron and manganese oxides.

### Precipitation

Retention of contaminants in soil may often occur through passing of contaminants from a dissolved form to an insoluble form in the course of geochemical reactions taking place within the soil pores. Precipitation reactions are controlled by acid-base equilibria and redox conditions. They are reversible and may lead to dissolution of formerly precipitated compounds if conditions are changed. A further discussion of these types of reactions will be given later at the section dealing with transformations.

### Infiltration:

This is perhaps the most common mechanism of contamination of soil solutions in the vadose zone as well as deeper regions of the saturated zones of ground water. As fluids move downward under the influence of gravity, they dissolve materials to form leachates that contain inorganic and organic constituents. As they reach the saturated zone of ground water, the contaminants spread horizontally and vertically by joining the main cycles of geochemical flows. FORTESCUE (1979), following the pioneer work of KOSLOVSKIY (1972), classified patterns of material flow in landscapes into three main categories which may be described as follows (see also Figure 61)



a) Main migrational cycle (MMC): Circulation of chemical substances within the landscape prism as a closed system. b) Landscape geochemical flow (LGF): Flow of chemical substances through the landscape prism parallel to the daylight surface. c) Extra landscape flow (ELF): Flow of chemical substances into the landscape prism where they accumulate (+ve) or out from the prism (-ve).

Fig. 61 Illustration of the three flow patterns according to FORTESCUE (1980)

### a) Main migrational cycle MMC:

This type of flow resembles the one familiar in geochemical cycles i.e. chemical substances are predominantly transported in a vertical direction upward from soil to plants and animals and then downward from plant and animals to soil approaching a steady state (figure 61a)

### b) Landscape Geochemical Flow (LGF)

This involves a progressive transport of material parallel to soil surface (see figure 61 b). It takes place within a prism (Landscape prism: Fortescue, 1980), including portions of the atmosphere, the pedosphere, and the lithosphere as shown in Figure. An example of chemically active air migrant in the LGF is carbon dioxide and other gases that would dissolve in soil water, causing a shift in its chemical constitution.

### c) Extra Landscape Flow (ELF)

A third type of material flow in landscapes is the Extra landscape flow (ELF). Applying this to soils as a portion of the landscape prism, we may define it as the flow of chemical substances into the soil where they would be accumulated (+ ve flow) or out of it (-ve flow). See figure 61 c.

## 8.2 Contaminants transport

Spreading and transport of contaminants during any of these cycles of geochemical flows occurs according to two principle transport mechanisms: (1) advection, movement caused by the flow of ground water; (2) dispersion, movement caused by the irregular mixing of fluids during advection.

### 1. Advection:

This is the mechanism controlling fluid flows in soil and underlying earth layers. It is quantified by Darcy's law:

$$Q = \frac{-K\rho}{\eta} \frac{A(h_2 - h_1)}{l}$$

Where  $Q$  is the total discharge of fluid per unit time ( $\text{cm}^3 \text{s}^{-1}$ );  $A$  is the cross sectional area of flow path ( $\text{cm}^2$ );  $l$  is the length of the flow path;  $\rho$  is the density of fluid ( $\text{g cm}^{-3}$ );  $\eta$  is the dynamic fluid viscosity ( $\text{mPa s}$ );  $h_2 - h_1$  is the hydraulic head, or pressure drop across the flow path ( $\text{g cm}^{-3}$ );  $K$  is the permeability constant in darcies.

### 2. Dispersion

Besides advection, contaminants may be transported in soil by hydrodynamic dispersion, which is defined as the net effect of a variety of microscopic, macroscopic, and regional conditions that influence the spread of a solute concentration front through an aquifer<sup>3</sup>.

<sup>3</sup> Op. cit.

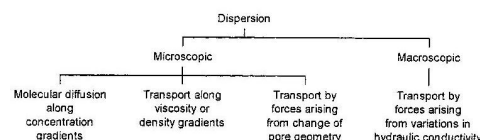


Fig.62 Dispersion processes in soil

Figure 62 shows in a schematic way the different mechanisms involved in spread processes of contaminants through dispersion.

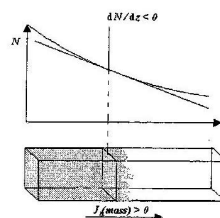


Fig. 63. Flux of particles down a concentration gradient (Atkins, 1978)

### 8.2.1 Microscopic Dispersion: Molecular Diffusion

On microscopic scale, dispersion may occur due to: a) molecular diffusion along concentration gradients, b) Transport along viscosity or density gradients or c) transport by forces arising from change of pore geometry. Transport process by diffusion occurs in gases liquids and solids. A contaminant dissolved in soil water may diffuse along concentration gradients in the fluid to attain uniform concentration in a given portion of the pore space, which will again contribute to the geochemical gradient in neighbouring regions. Gases in the soil air resulting from volatile components of contaminants such as fuel spills will diffuse as well throughout the pore system. The rate of diffusion (matter transport) was found to

be proportional to the concentration gradient. This relation finds its mathematical expression in **Fick's First Law of Diffusion**:

$$J_z(\text{matter}) = -D (dN / dz)$$

It states that the flow of matter along an axis ( $z$ ) is proportional to the concentration gradient along the axis (see Fig. 63)

Density and viscosity changes in soil fluids control transport of contaminants in the pore space. This follows from the fact that mobility in pore space is related to other physical parameters such as temperature, density, and viscosity. Diffusion constant is related to viscosity via **Stokes-Einstein relation**:

$$D = kT / 6 \pi \eta a;$$

Where  $D$  = diffusion coefficient,  $T$  = absolute temperature,  $\eta$  is the viscosity and  $a$  is the radius of flow cylinder.

KAUFMAN & MCKENZIE (1975) reported that the apparent hydraulic conductivity of an injection zone in the Floridan aquifer receiving hot organic wastes increased about 2.5 times due to temperature differences. OBERLANDER (1989) also reported that density variations might cause errors in estimations of flow directions.

#### Transport by forces arising from change of pore geometry

In Darcie's law (see above),  $K$  the permeability constant describes permeability – the property by which fluids are allowed to pass through a medium without change in the structure of the medium or displacement of its parts. Permeability depends largely on soil texture and the geometry of its pores. Generally, it is related to porosity by the following theoretical relation:

$$\phi = a + b \log k$$

Where  $\phi$  is the porosity and  $k$  is permeability. However, permeability may change without change of porosity due to properties inherent in the geometrical organisation of the pores, such as the small-scale roughness of the pore walls or the path length the fluid must follow during transport. The latter is commonly known as the **tortuosity factor**. In calculating the mass flux of vapour in soils,

JURY & FLUHLER, 1992 make allowance for reduced cross sectional area and increased path length of gas molecules in soil by introducing a tortuosity factor in Fick's first law, so that it takes the following form:

$$J_g = \xi_g(a) D_g^a \partial C_g / \partial z$$

Where  $J_g$  is the gas flux,  $D_g^a$  the binary diffusion coefficient of the vapour in air, and  $\xi_g(a)$  is the tortuosity factor.

Porosity, however, may change in a way that enhances transport or triggers off higher transport rates. Such cases occur when the soil in some of its parts is fractured or has dissolution cavities. In such cases, forces arising from change of pore geometry may lead to an enhancement of transport processes.

#### 8.2.2 Macroscopic Dispersion

The classical advection/ dispersion model for contaminant transport in soil is only valid for dispersion on a micro scale i.e. so long the pore system of the soil is considered. A different physical situation is encountered in soils where due to particle aggregation or development of cracks, the hydraulic conductivity is considerably changed. An example of this is the situation in clay rich soils when consecutive cycles of wetting and drying, produce shrinkage cracks, in the soil body, that eventually serve as preferential routs for fluid transport. During Transport through cracks and large pores, retention on soil surfaces is reduced to a minimum; because in this case only a small portion of the soil surface encounters the fluid.

#### 8.3 Behaviour of Non-aqueous Phase Liquids (NAPL's) in soils

Synthetic organic solvents, which are insoluble or slightly soluble in water, are grouped in one category of contaminants known collectively as Non-aqueous Phase Liquids – shortly NAPL's. In fact, one uses the term NAPL for all immiscible pure chemicals that may contaminate the soil. The behaviour of this category in soils depends on various factors, such as the degree of saturation of the soil, the density and viscosity of the NAPL relative to water and the volume or

dimension of spill introduced into the landscape. As in case of aqueous phase liquids, contaminants of this category may be retained on the soil surface, spread in the vadose zone or if added in great volumes, may infiltrate the soil to reach the ground water table at the saturated zone. Transport of NAPL's follows principally the same hydrologic principles controlling permeability in porous media. Absolute permeability is independent of the nature of the fluid; it depends only on the medium which is described through its coefficient of permeability  $k$ , given by the equation:

$$k = N l^2,$$

where  $N$  is a dimensionless number depending on pore space characteristics such as grain shape and packing (it may be constant for a given soil) and  $l$  is the length of the pore structure of the soil (a factor related to grain size).

If different phase fluids such as gas, an organic solvent, and water are present, the fluids create complex mutual interferences; a so-called effective permeability for each phase ( $k_g$ ,  $k_o$ ,  $k_w$ ) would control material transport. Absolute permeability of the medium, as given by the above-mentioned equation, ceases to be the only control factor for transport in the medium.

It would also be found that  $k_g + k_o + k_w < k_{abs}$ , because the mutual interferences are retardative and not enhancing. This clearly shows that the validity of Darcy's law is restricted to single phase homogeneous or laminar fluid flow.

In cases of NAPL spills on water-saturated soils, water and NAPL would be competing for flow within the pore system as mentioned before. In such cases, the NAPL drives the pore-water into finer and finer spaces where capillary forces would hold it. Soil air and any existing gaseous phases are also driven out of the pore-space in the course of this process, so that at the end the central portion of the pore would be filled with non-aqueous phase liquids, while irreducible pore-water, held by capillary forces, forms a thin layer lining the pore (see Figure 64). At this point, the fluid saturation with respect to water decreases to almost zero while the fluid saturation with respect to NAPL would reach to maximum. The fluid saturation is defined as the fluid volume expressed as a fraction of the total pore space.

The velocity of transport of a given fluid is directly proportional to its fluid saturation in the medium. In cases of small spills on a soil not fully saturated with water, the volume of NAPL would not be enough to expel all the water out of the pores. This leads to a distribution of the fluid saturation of the soil between the NAPL and the pore water followed by a depression of the transport velocities of both to a level lower than the expected one in case any of them was holding sway in the pore space. A certain fraction of the NAPL adheres to soil particles in the vadose zone forming the so-called residual saturation. This may be later transported by dissolution or be volatilised in the pore space.

The Behaviour and transport patterns of NAPL's depend on two important factors. These are the relative density of the NAPL with respect to water (lighter or denser than water) and the size of spill. In the following, both classes will be discussed separately.

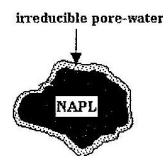


Fig. 64. Non-aqueous phase liquid (NAPL) displacing water in pore space

#### NAPL's, lighter than water (LNAPL's)

**a) Small spills:** LNAPL's may, in case of small spills, be retained on grain surfaces within the vadose (unsaturated) zone. Further penetration can only follow, if the LNAPL, retained as residual saturation, is dissolved by penetrating waters and carried in solution to deeper parts of the site contaminated. This is often the case with contaminants such as benzene, toluene, or xylene.

A further path of LNAPL's residual saturations to deeper horizons of a soil may be provided by evaporation and diffusion within the soil pore space.

**b) Large spills:** Larger spills of LNAPL's will normally be followed by dispersion both in vertical and horizontal directions. At the beginning, contaminants reaching the water table may change the wetting properties of water (i.e. changing capillary pressure and/or viscosity at the interfaces in the system mineral-water-NAPL) leading to a collapse of the capillary fringe (see fig 91, p. 187). Such a dramatic change will normally be followed by a depression of the water table. However, when the discharge of NAPL stops, the contaminant flows preferentially in a horizontal direction in the vadose zone until residual saturation is reached. This leads to a relief in the upper horizons, making it possible for the water table to rebound to its original level (PALMER & JOHNSON, 1989).

#### **NAPL's, denser than water (DNAPL's)**

**a) Small spills:** Denser Non-aqueous Phase Liquids would, due to their denser nature, displace water on their way to deeper parts of the vadose zone, yet the confrontation between the NAPL with water which is more viscous than the contaminant, results in an unstable liquid – water boundary, forming viscous fingers penetrating the vadose zone until residual saturation is reached. Penetrating waters and dense vapours affecting the capillary fringe, may help forming a contaminant plume. At places, where the chemicals are held in place between the soil grains, aggregates of NAPL may persist forming local concentrations, known as ganglia.

**b) Large spills:** Depending on the dimensions of the spill, the contaminant may either be dispersed around or near the water table until residual saturation is reached or penetrate deeper into the saturated zone, forming pools at the surface of impermeable layers.

Surface tension between NAPL's and the water wetting the surfaces of soil grains makes it difficult for both phases to mix and reduces largely their miscibility. This, together with the low solubility of NAPL's, makes these pollutants to dissolve very slowly in ground water. A variety of processes, including the following, have been proposed to increase their dissolution rates.

#### **a. Flushing with hot water:**

The reasoning behind this process is the possibility of increasing chemical solubility of the NAPL's through decreasing water viscosity. However, IMHOFF *et al* (1995a) found that this process has a very little effect on the dissolution rate of NAPL's at contaminated sites.

#### **b. Steam injection:**

HUNT *et al* (1988) demonstrated through experimental work that steam injection in porous media (sand) was very effective in removing immiscible pure phase liquids such as trichloroethylene, toluene, and gasoline. This method is very effective, yet it is connected to high energy-costs. According to LOGAN B.E (1999), the energy from 6.8 L of fuel oil would be necessary to clean one cubic meter of contaminated aquifer.

#### **c. Flushing with solvents:**

Some solvents e.g. methanol are capable of decreasing the interfacial tension between NAPL's and water, leading to mixing of the two phases and hence increasing the chemical solubility of the pure phase. IMHOFF *et al* (1995b) used different concentrations of methanol – water solution and found out that using a 60% methanol solution decreased the surface tension to 25% of its original value, thus largely increasing the chemical solubility of the pure phase contaminant in water.

#### **d) Flushing with surfactants**

Like in the above mentioned methods, the reasoning here depends upon changing the wetting properties of water especially decreasing the interfacial tension between water and the pure contaminant phase. Surfactants can largely decrease the interfacial pressure, through partitioning of the pure phase into surfactants micelles. This may be followed by an increase of the chemical solubility of the NAPL.