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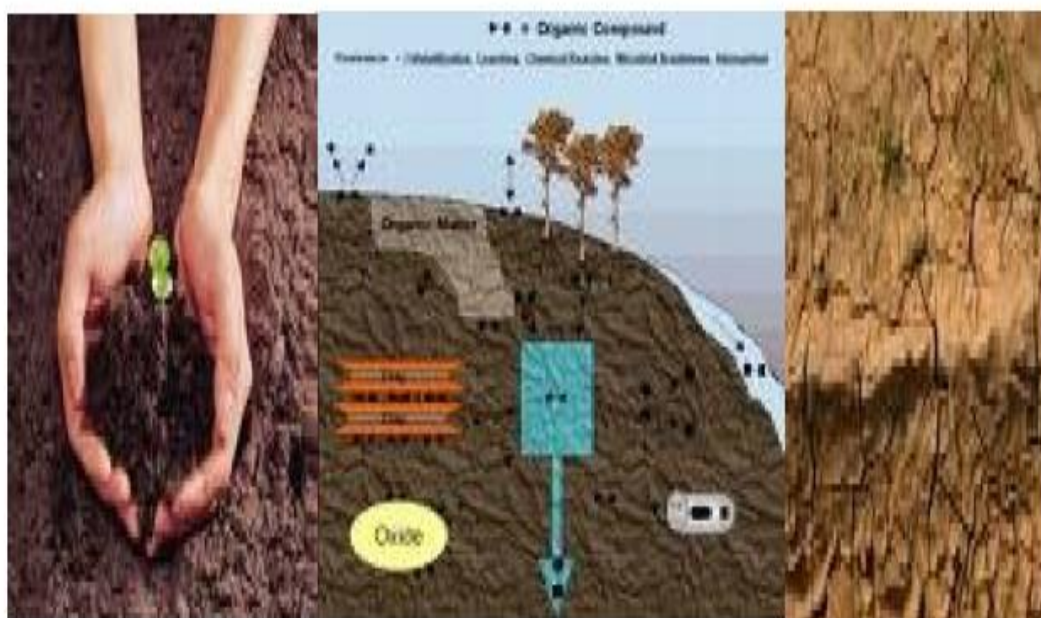**Water Resources Engineering Department**

SOIL POLLUTION

POLLUTION MECHANISMS AND SOIL-POLLUTANTS INTERACTION

For Post graduate Students 2020\2021

Faculty of Engineering

Mustansiriyah University

Environmental Engineering Department

1. Introduction

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

.**Retention on and within the soil body**

.**Infiltration, diffusion and transport by soil solutions**

.**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 of only chemical and biological processes, by which pollutants are transformed or stored as residues in the interstitial space. Figure 8.1 shows a schematic overview of the three groups of processes. A summary of the processes involved in soil pollution may be given in Fig. 8.2.
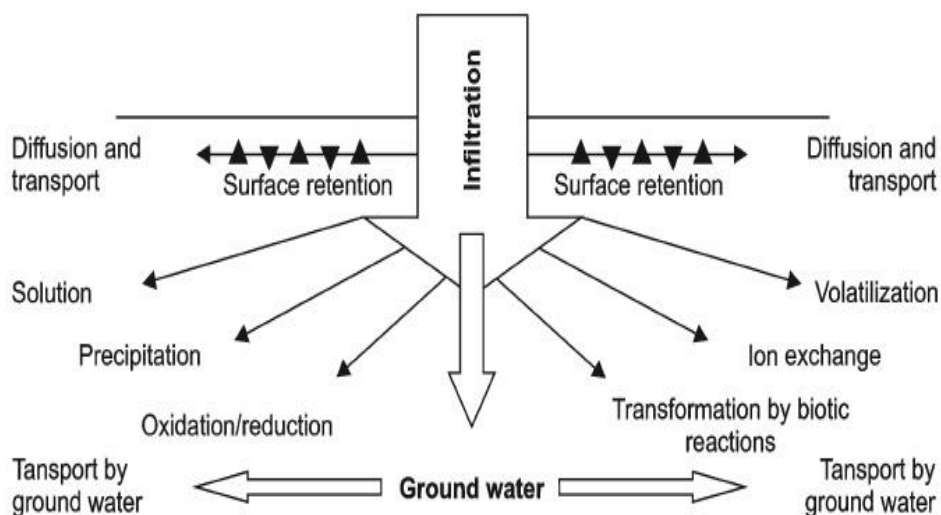

Fig. 8.1 A schematic overview of the processes representing soil-pollutant interactions
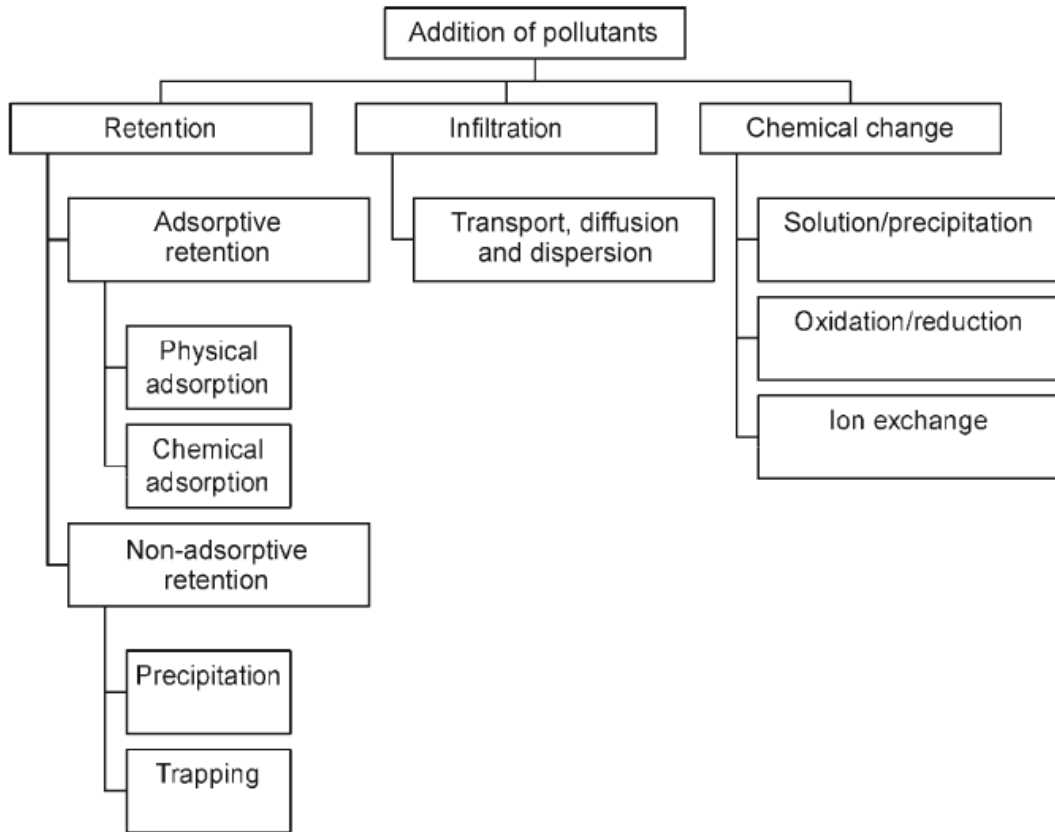
Fig. 8.2 A summary of the mechanisms involved in soil pollution

2. Physical Processes and Mechanisms of Pollution

Upon encountering soil grains, pollutants 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 physical chemical mechanisms of pollutant retention on the surface of soil grains. In the following, these phenomena will be treated in some detail.

2.1. Adsorptive Retention

Molecules of pollutants can be retained on the surfaces of soil grains in two ways. In physiosorption, or physical adsorption, molecules of pollutants will be attached to the surfaces of soil grains by Van der Waal forces, which are known to be weak long range forces. The amounts of energies involved in such attachments 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.

Normally various adsorbents exist in the 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.

2.1.1. 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 (Fig. 8.3a). Guoy and Chapman, 1910 cited in Atkins (1978)) and further workers, in the following years, modified this theory to a form that culminated into the diffuse double layer model. According to this 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. 8.3b. One part of the double layer (A in Fig. 8.3b) is firmly attached to the

surface of the colloid substance and thus becomes an integrated part of it. The second part

Fig. 8.3 a Helmholtz double layer; b Gouy-Chapman diffuse double layer
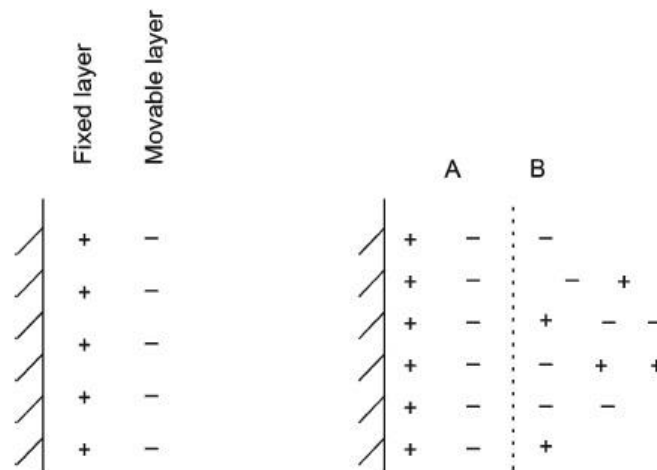
(B in Fig. 8.3b) lies in the surrounding phase. Thus the potential drop between the solid surface and the surrounding phase is formed of two parts: (i) a part between the solid surface and the firmly attached layer A; (ii) and another part between layer A and the bulk of the surrounding phase. This second potential drop is called the electro kinetic or zeta potential (represented by the Greek letter).

2.2. Chemical Adsorption or Chemisorption

As it was stated before, the 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.

2.3. 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 later shown, 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, then the 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, Kd (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:

$$S = KdC$$

where S = amount adsorbed (μg/g solid),

C = concentration of substance to be adsorbed in the ambient solution (μg/ml), and

Kd= distribution coefficient.

Another coefficient, also widely used in problems of soil pollution, is the organic carbon partition coefficient (Koc). It is derived by dividing the distribution coefficient (Kd) by the percentage of the organic carbon present in the system (Hamaker and Thompson 1972).

Accordingly

$$Koc= Kd / (\% \text{ organic carbon})$$

where Kd is the distribution coefficient.

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

2.4. 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 cations, the phenomenon will be described as cation exchange, otherwise we speak of anion exchange. Cation exchange plays a dominant role in the soil environment, while anion exchange processes are very rare. This is because anions, as acid radicals, may in the 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:

$$Ca^{2+}A + 2Na^+ \rightleftharpoons 2Na^+A + Ca^{2+}$$
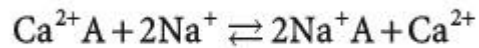
Classic examples of soil components showing marked cation-exchange behavior are the clay minerals; especially the montmorillonites and illites. They possess a negatively charged repetitive structural framework, having well defined, negatively charged sites, occupied by singly or doubly charged cations. A great variety of materials, other than the clay minerals, exhibit the same behaviour. Among these, include most silicate minerals, silicate glasses, arsenates, vanadates, molybdates and related species.

The CEC of an ion-exchanger is normally defined as the equivalent mass (in milliequivalents) of exchangeable cation per 100 g of exchanger at pH = 7.

In Table 8.1, the CECs 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 CECs, and normally cause the enrichment of soil water in NaHCO3، due to their tendency for sodium replacement with other cations. Montmorillonite، which occurs in various soils, is normally considered as the most important cation exchanger in the weathering zone.

2.5. Ion Selectivity

Natural cation exchangers do not attract all ions with the same intensity. This preference، or selectivity, depends principally on the cationic concentration in the solution، 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 valence (II or III). The general series of ion-preference may be represented as follows:

H+>Rb+> Ba2+> Sr2+>Ca2+>Mg2+>K+>Na+> Li+
←—— stronger ATTACHMENT weaker ——→
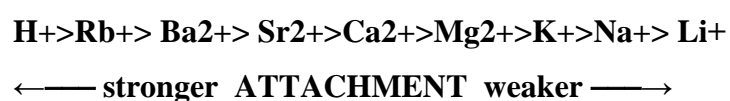
2.1.1. Factors Affecting Adsorption

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 summarize all these factors as follows:

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 proportion of other silicates in the mineralogical composition.

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 mm delivered only 10% of the whole content.

3. Humic Substances and Their Distribution in the Soil

Humic substances containing carboxyl and phenolic hydroxyl functional groups increase the 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 a positive influence on the CEC 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 the 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 with an acidic character which may increase the exchange capacity of the soil.

2.1.2. Nonadsorptive Retention

1. Trapping

The entrapment of solid particles and large dissolved molecules in the pore space of the soil forms one of the major mechanisms in the retention of pollutants in the soil. This type of retention occurs following the three mechanisms shown in Fig. 8.6, drawn after J.

R. Boulding (1995). The figure illustrates the three mechanisms, which may be concisely described as follows:

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, clogging the soil pores.

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 to pass through.

Physical-chemical trapping. The limitation of the flow, through the clogging of the 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.
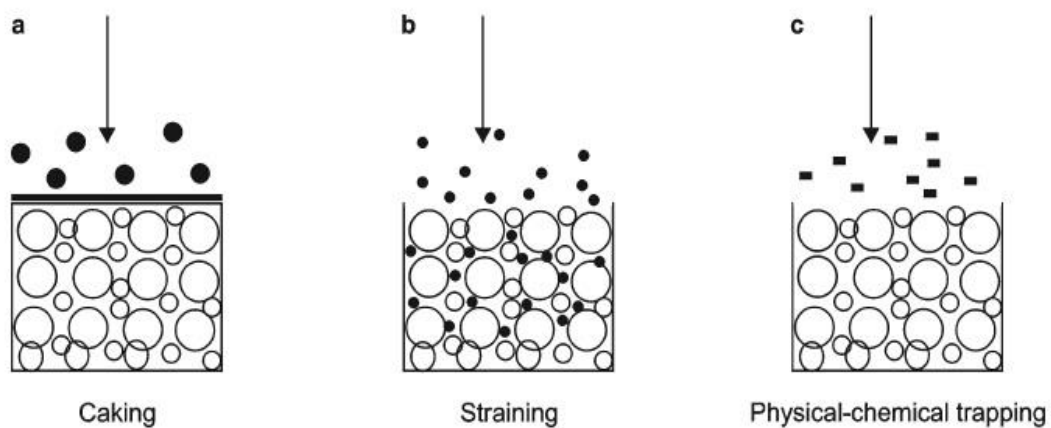

Fig. 8.6 Trapping mechanisms in porous media (based on Boulding 1995, after Palmer and Johnson 1989)

3. Precipitation

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

4. 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 the groundwater. 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 the groundwater, the contaminants spread horizontally and vertically by joining the main cycles of the geochemical flows. Fortescue (1980), following the pioneering work of Kozlovskiy (1972), classified the patterns of material flow in landscapes into three main categories which may be described as follows (see also Fig. 8.7):

Main migrational cycle (MMC). This type of flow resembles the one familiar in geochemical cycles, i.e. the chemical substances are predominantly transported in a vertical direction upward from the soil to plants and animals, and then downward from plants and animals to the soil, approaching a steady state (Fig. 8.7a).

Landscape geochemical flow (LGF). This involves a progressive transport of material parallel to the soil surface (see Fig. 8.7b). It takes place within a prism (Landscape prism: Fortescue 1980), including portions of the atmosphere, the pedosphere، and the lithosphere, as shown in Fig. 8.7. An example of chemically active air migrants in the LGF is carbon dioxide and other gases that would dissolve in soil water، causing a shift in its chemical constitution.

Extra landscape flow (ELF). A third type of material flow in landscapes is 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 Fig. 8.7c.
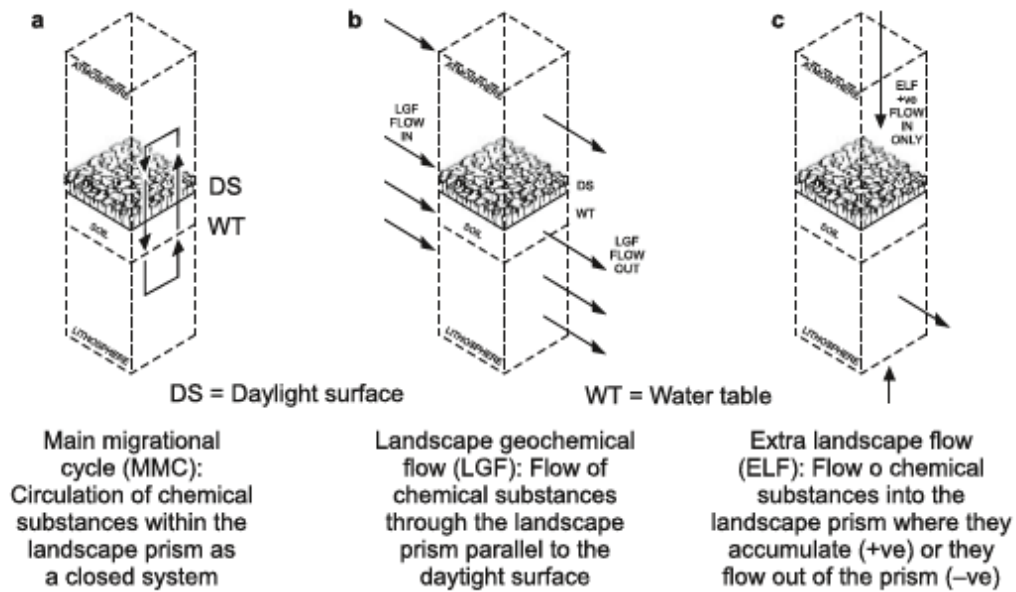
Fig. 8.7 Illustration of the three flow patterns according to Fortescue (1980)

2.2. Contaminants Transport

The 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 groundwater; (2) dispersion, movement caused by the irregular mixing of fluids during advection.

Advection

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

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

where Q is the total discharge of fluid per unit time (cm3 s^{-1}), A is the cross-sectional area of flow path (cm2), l is the length of the flow path, ρ is the density of fluid (g cm–3, η is the dynamic fluid viscosity (mPa s), h2–h1 is the hydraulic head or pressure drop across the flow path (g cm–2), K is the permeability constant in Darcies.

<u>Dispersion</u>

Besides advection, contaminants may be transported in the 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 aquifer2. Figure 8.8 shows in a schematic way the different mechanisms involved in spread processes of contaminants through dispersion.
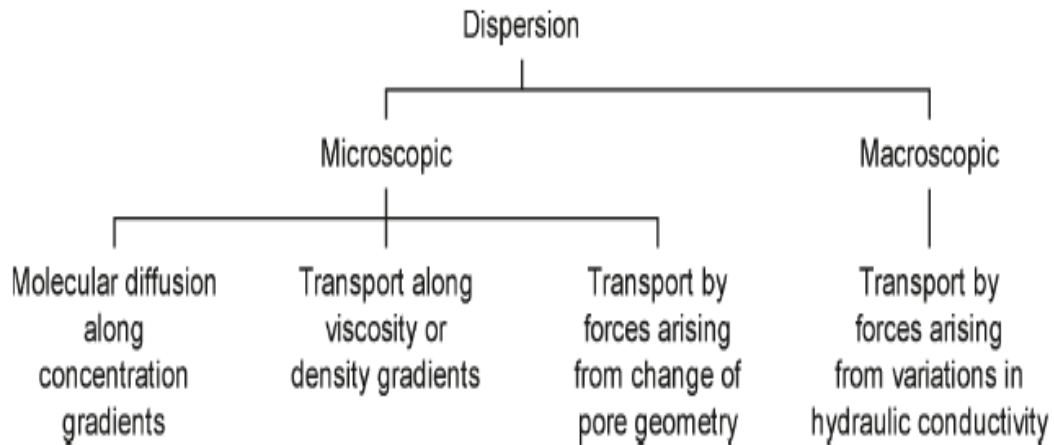

Fig. 8.8 Dispersion processes in soil