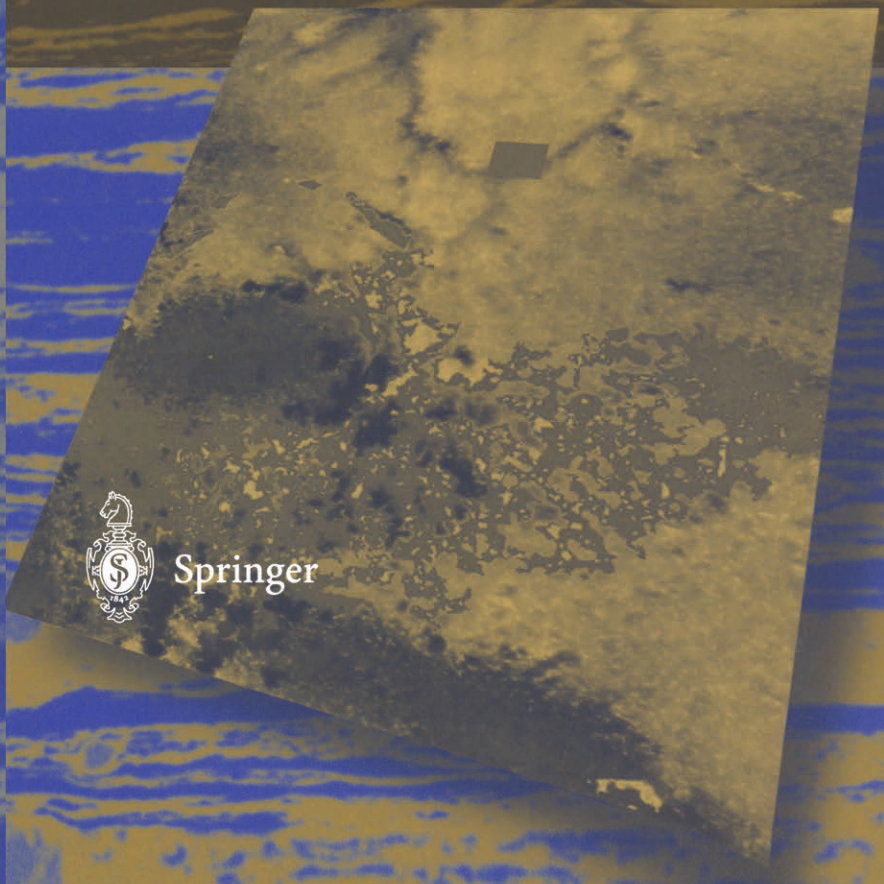
Ibrahim A. Mirsal

Soil Pollution

ORIGIN, MONITORING & REMEDIATION



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With 112 Figures

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To Gabi, Miriam and Jasmin

Preface

Who ever has enjoyed following the legendary duel between the Egyptian Pharaoh and his magicians (Alchemists) on one side, and Moses and his brother Aaron on the other, as it is vividly narrated by the Bible, must have realised, that people (at least those living at, or near the eternal battle fields of the middle East) have always had knowledge about the terrible consequences of soil pollution by chemicals. This knowledge must have existed long before Moses and his Pharaoh. Nobody knows when did it start, yet it must have been born at very early times, reaching back to the dawn of human conscious.

As history teaches, human knowledge explodes in logarithmic dimensions, and times have come when pollution attained alarming levels, with pollutants from industrial and military sources becoming a threat to life wherever it exists on this Earth. At the end of the 20^{th} century, states started projects for pollution control and remediation, major Universities changed their programs to accommodate environmental studies at central positions in their curricula and nations forgot their differences and came together to sign the Chemical Weapons Convention (CWC) and other treaties allowing pollution control on world wide scale.

The present book is designed as a contribution to understanding the origins, mechanisms and consequences of the environmental setbacks brought about by soil pollution. It is based on university lectures, that the author has held in the last twenty years at the University of Marburg, Germany, the University of the Philippines, Manila, Philippines and Bogaziçi University in Istanbul, Turkey.

This book is useful for students of Earth Sciences, Environmental Sciences and Agriculture, as well as for professionals of all these fields, who are seeking an integration of all the isolated parts they have learnt about soil pollution. It may also be of help for members of environmental NGO's and environment community officers.

I wish to acknowledge with gratitude my indebtedness to the members of my family for their support and patience during the preparation of this book My thanks are also due to many of my colleagues and students in Manila and Istanbul. I am particularly indebted to the library staff of Bogaziçi University, Istanbul, who always offered me their assistance and support in searching for the required literature.

Finally, I wish to thank all individuals and departments, who helped to produce this work.

Ibrahim A. Mirsal

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Part 1

Soil – Its Nature and Origin

Soil is essentially a natural body of mineral and organic constituents produced by solid material recycling during a myriad of complex processes of solid crust modifications, which are closely related to the hydrologic cycle. It is the interface at which all forces, acting on the Earth's crust meet to produce a medium of unconsolidated material that acts as an environment for further changes and developments keeping pace with the evolution of the global Earth system as a whole. It offers shelter and habitat for countless number of organisms and provides incubation and living medium for plants, while perfectly playing its role in the universal cycle of material flow between the four main geospheres (atmosphere, lithosphere, hydrosphere and biosphere). For this reason, some authors consider soil as a separate geosphere and give it the name pedosphere. The pedosphere, is formed by, and is eternally changing by weathering forces, which despite their complicated nature and intricately structured processes are found to belong to few basic types, the Nature of which and importance for the evolution of our Earth environments will be the subject of close inspection in the first few chapters of the present work.

Chapter 1

The Origin of Soil

1.1 Physical or mechanical weathering

Physical and biological agents, such as wind, running water, temperature changes, and living organisms, perpetually modify the Earth's crust, changing its upper surface into products that are more nearly in equilibrium with the atmosphere, the hydrosphere, and the biosphere. Earth scientists sum up all processes through which these alterations take place under the collective term ***weathering.*** One speaks of mechanical weathering in case the dominant forces are mainly mechanical such as the eroding action of running water, the abrading action of stream load or the physical action of wind and severe temperature fluctuations. Similarly, one speaks of biological weathering when the forces producing changes are directly or indirectly related to living organisms. Of these, we can mention several examples such as the action of burrowing animals, penetration forces of plant roots, and the destructive action of algae, bacteria, and their acid-producing symbiotic community of the lichens or simply the destructive action of man, who continuously disturbs the Earth's crust through various activities.

Processes of disintegration, during which mantle rocks are broken down to form particles of smaller size, without considerable change in chemical or mineralogical composition are known as physical weathering processes. Changes of this

type prevail under extreme climatic conditions as in deserts or arctic regions. They are also prevailing in areas of mountainous relief. The most prominent agents of physical weathering are:

a) Differential stress caused by unloading of deep-seated rocks on emerging to the surface.
b) Differential thermal expansion under extreme climatic conditions.
c) Expansion of interstitial water volume by freezing, that leads to rupture along crystal boundaries.

Other mechanical agents enhance the effect of mechanical weathering. These may include processes such as gravity, abrasion by glacial ice or wind blown particles.

1.2 Chemical weathering

Chemical weathering depends principally on the presence of water. It is initiated largely by the preceding physical weathering; since disintegration of the solid material leads to activation of the solid phase and eventually to more favourable energetic conditions for subsequent chemical alterations. The effect of chemical weathering is by far more decisive in the geologic cycle, whereby dramatic changes may completely obliterate the parent rock and vast geomorphologic changes may occur. Chemical weathering is normally performed through one of the following chemical reactions:

a) Oxidation: In the vadose (aerated) zone (fig.91, p. 187) where most processes leading to soil formation take place, availability of oxygen, water, and dissolved gases leads to a dominance of oxidation reactions leaving their finger prints on the formed soil horizons represented by the characteristic colours of the resulting products. The typical yellow, brown, or red colour of soil in some warm areas (e.g. Mediterranean terra rossa) is due largely to the oxidation of ferrous iron in the minerals pyroxene, amphibole, and olivine into ferric iron. Beside Fe^{+2}, Mn^{+2}

and S^{+2} are the most commonly affected elements by oxidation. They are normally oxidised to Mn^{+4} and S^{+6}. Other examples are V, Cr, Cu, As, Se, Mo, Pd, Sn, Sb, W, Pt, Hg, and U.

A good example of oxidation reactions during weathering is the oxidation of pyrite to form sulphuric acid, which attacks the rocks (see equation 1.1), developing solution pits and stains.

$$2\ Fe\ S_2 + 2\ H_2O + 7\ O_2 \leftrightarrows 2\ Fe\ S\ O_4 + 2\ H_2\ S\ O_4 \qquad (1.1)$$

Oxidation functions most effectively in the vadose zone, yet in some places oxidation fluids can descend to depths far below the water table before their oxidising power is consumed (Rose et. al., 1979).

b. Hydration and hydrolysis: Hydration and hydrolysis are the most important processes encountered during soil formation by weathering. While in hydrolysis a proper chemical reaction between water and the mineral substance takes place to produce or consume a proton (H^+) or an electron $(OH)^-$, water in hydration forms an envelope around the cations to form a hydrate – a compound in which it is integrated within the crystalline structure of the substance. A typical example of hydration is the conversion of anhydrite ($CaSO_4$) into gypsum ($CaSO_4 .2H_2O$).

Clays that, together with organic substance and other colloidal matter, give soil its characteristic nature are typical products of hydrolysis processes steering the change of aluminium or iron silicates into clay minerals and / or iron oxides. An example of this is the reaction of the mineral albite in the course of weathering with weak acids to yield kaolinite (clay), silica and Sodium ions (Na^+).

$$2NaAlSi_3O_8 + 2H^+ + H_2O \leftrightarrows Al_2Si_2O_5\ (OH)_4 + 4\ SiO_2 + 2\ Na^+ \qquad (1.2)$$

Albite Kaolinite

The protons involved in this reaction are generally provided by naturally occurring acids, such as carbonic acid or by the rather abundant humic acids. The released

Na-cations will be sorbed on the surface of colloidal particles or released to the solution. SiO_2 precipitates as colloidal silica or quartz.

1.3 Weathering by biological agents

Biological effect is a factor, which has never been absent in any soil forming process during weathering. It is always there, whether the dominant processes were mechanical or chemical; it always accompany emergence and evolution of soil. One needs only to consider the mechanical forces exerted by intruding roots, or the enormous work of worms and rodents in mixing and disintegrating rock bodies in the upper surface environment to realise how important this factor is for soil formation and its later evolution. The chemical dimension of biological weathering vary from simple dissolution reactions occurring at the extensive acidic environment at root tips, to complex biochemical processes by which certain elements are extracted, concentrated or bound into complex by plants or by bacterial action. As an example, we may take the oxidation of iron and sulphur or the fixation of nitrogen by bacteria.

1.4 Factors controlling soil formation

Climate: Weathering in general and soil formation processes in particular are dependent largely on climatic factors. These, not only control the main processes and directions in the main cycles of material flow, but also affect organic addition, and the rate of mineral transformation via crystal lattice break down. S. ROSS, (1989) found that in such transformations the rates of chemical reaction double for every 10°C rise in temperature and that the maximum rate of organic matter decay takes place in the temperature range from 25- 35°C. This may also follow from the observation that, on a global level, the rate of mineral transformation and organic matter decay increase from high to low latitudes.

Biota: Actually, the role of organisms cannot be discussed apart from the climatic control effect, since these are generally related to bio geographical conditions. Aside from the mechanical work done by rodents and burrowing animals, the chemical reactions triggered off by bacteria and plant roots play, as mentioned before, a crucial role in the process of soil formation

Parent material: Since the principal source of soil is the pre-existing rock or parent material, the main control on soil formation will be directly related to the susceptibility of this material to weathering processes and the chemical and physical changes accompanying them. Physical properties such as hardness, cleavage, porosity and grain size form primary factors determining whether water can percolate into a rock layer to initiate its disintegration into an unconsolidated material or its decomposition into a different mineralogical constitution, properties and characteristics of the resulting soil will also be directly related to parent material. Soils formed on parent material highly resistant to weathering will normally have relatively less thickness than those formed on easily weathered landscapes. They also contain more regolith or stony material than the latter.

1.5 Morphology of soil

One of the characteristic properties of soil is the organisation of its constituents into layers related to present day surface. Each of these layers, which may easily be identified in the field through colour or texture, reflects subtle differences in chemical properties and composition, of which the most significant are pH, organic matter content, mineral assemblages, and metal concentrations, especially Fe and Mn.

Soil layers, normally referred to as horizons, may range from few centimetres to a meter or more in thickness. They are classified according to their position in profile, which is also closely related to their mineralogical constitution and grain size into few basic types as shown in figure 1.

At the top of the profile, a layer of partially decomposed organic debris is referred to as the O-horizon (also A_0). It contains about 20-30 % organic matter, derived from plant and animal litter. In this region, the principle process of soil formation, known as humification i.e. complete change of organic debris into soil organic matter, takes place. The resulting material (humus) made of a mixture of organic substances, which is characterised by its dark colour and rather acidic nature, is mainly produced by the work of consumers and decomposers among the micro- organisms, living in the site of soil formation.

In best-developed soils, rendering ideal profiles, three main horizons follow. They form a transition between the O-horizon and the base of the profile, made of the parent material, which is given the name R-horizon. This may be rock *in situ*, transported alluvial, glacial or wind blown overburden or even soil of a past pedological cycle.

The three middle horizons, identified by the letters A, B, and C, are composed of sand, silt clay and other weathered by-products (table 1 presents a description of grain size). They represent two main subsequent stages of soil formation, whereby the lowest one (C-horizon) represents the stage nearest to the parent material. It is made up of partially or poorly weathered bedrock having minimum content of organic matter and clay. The A and B- horizons are viewed together as representing the real soil emerging from the complete weathering of the C-horizon. They are summed together under the name solum.

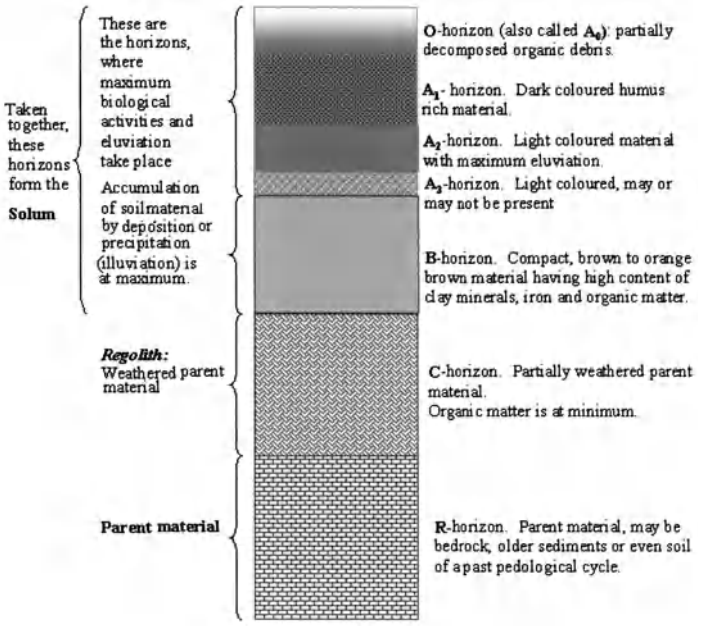


Fig. 1. Diagrammatic representation of a hypothetical soil profile

Grain Size	Unconsolidated sediment	Lithified rock
> 80 mm	Boulders, cobbles	Congolomerate (Breccia if angular)
> 2 mm	Pebbles, gravel	
0.5 - 2.0 mm	Coarse sand	Sandstone
0.02 t0 0.05 mm	Medium to fine sand	Sandstone
0.002 to 0.02 mm	Silt	Siltstone (mudstone)
< 0.002 mm	Clay	Shale

Table 1. Grain sizes of clastic sediments and related rock types

The A-horizon, which is generally a dark coloured horizon, rich in organic matter, may in some cases have a structure made up of three identifiable subdivisions known as A_1, A_2, and A_3. Marked colour differences resulting from leaching processes make it possible to identify these subdivisions in the field. In fact, the resolution of the A-horizon into a dark upper layer containing humus with mineral grains (A_1) and an underlying light coloured horizon with little organic matter is due to leaching processes initiated by water percolating downward through the rich organic material on the top of the A-horizon. On its course downwards, water carrying in solution organic acids and complexing agents generated in the humus by bacterial action performs a process of leaching known as eluviation – a word from Latin meaning "to wash out". Eluviation, enhanced by carbonic acid resulting from the decay of humus, displaces bases (Ca, Na, Mg, K) from the exchange sites of clay minerals. These bases move down the soil profile as colloidal particles, dissolved ions or as free ions complexed with hydroxyl. Silica is also leached in the course of eluviation. It is largely dissolved as silicic acid or colloidal silica. Resistant primary mineral matter, however, remains behind in the upper soil (ROSE et al. 1979)

Material dissolved in the A-horizon finds in some cases its way to the saturated zone of ground water, yet the greatest part of it is normally redeposited in the underlying layers forming the B-horizon. In this process, known as illuviation (from the Latin to wash in), colloidal material and metal oxides are deposited or precipitated in the B-horizon, resulting in an enrichment of its layers in clay and aluminium oxide. Fe oxides, if present, give the horizon its red or yellow brown colour.

Chapter 2

Soil Constituents

Generally speaking Soil is a three dimensional system, made of a solid, a liquid and a gaseous phase, each in an amount depending on the abundance of its constituents and their kinetic roles in the complex series of reactions, leading to soil formation. Figure 2 illustrates the composition by volume of an average soil.

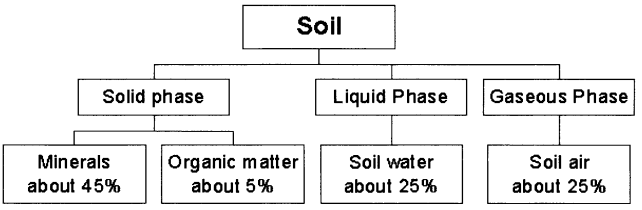


Fig. 2. Composition by volume of an average soil

2.1 The mineral solid phase

Mineral matter in soil depends largely on the nature and composition of the parent rock. However, since about three fourths of the earth's crust is made up of silicon and oxygen, we find that silicate minerals occupy a central position in any description of the mineral constituents of a given soil. All silicates are formed of a fundamental structural unit, comprising one silicon ion (Si^{+4}) and four oxygen ions O^{-2}, closely surrounding the silico in a tetrahedral lattice, as shown by figure 3.

The tetrahedra may, based on their net and residual charges, combine in a multi-form of combinatorial structures and three-dimensional arrangements to form various kinds and varieties of silicates, which can be categorised into the following fundamental groups:

1.Orthosilicates: These are discrete units of individual or grouped tetrahedra, made of one, two, three or six tetrahedra per unit – a property, which, as we can see later, is used for further classification of the group

2.Chain silicates: In this group individual tetrahedra catinate together, by sharing the four tetrahedrally co-ordinated oxygen atoms with the neighbouring silicon atoms, to form infinite chains of formula $(SiO_3)^{-2}{}_n$,

3.Sheet silicates: In this group three co-ordinated oxygen atoms at the corners of a tetrahedron are shared with adjacent silicon atoms, resulting in the formation of a sheet or a layer of tetrahedra connected together at the three basal corners.

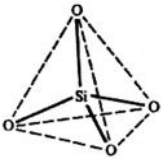


Fig. 3. A Silicate Tetrahedron

4.Frame work silicates: These are formed, if all four oxygen atoms per SiO^4 tetrahedron are shared with adjacent tetrahedra in a framework structure. In the following, each of these four silicate groups or classes will be discussed in some detail.

2.1.1 The orthosilicates

The orthosilicates comprise two subcategories — nesosilicates and sorosilicates. In the first category, the SiO_4 - tetrahedra occur as separate units, without shared oxygen atoms, and are linked by metallic cations. This structure (Figure 4a) is not

very common in minerals. However, some minerals like olivine, $(Mg, Fe, Mn)_2 Si O_4$, which is an important constituent of basalt, adopt it. Other minerals, made of single silicon tetrahedra are zircon $ZrSiO_4$, topaz $Al_2 (FOH)_2 SiO_4$, and the garnets, with the general formula:

$M^{II}_3 M^{III}_2 (SiO_4)_3$, where M^{II} can be Ca^{2+}, Mg^{2+} or Fe^{2+}, and M^{III} is Al^{3+}, Cr^{3+}, or Fe^{+3}. This group of minerals occurs in soils formed on igneous rocks due to their higher resistance to weathering. The sorosilicates, themselves, may further be classified into two groups — the pyrosilicates and the cyclosilicates . In the pyrosilicates, (also called disilicates) discrete groups of two tetrahedra share one of the co-ordinated oxygen atoms to form the disilicate anion Si_2O_7 (see fig 4b). An example is the mineral hemimorphite that has the general formula $Zn_4 (OH)_2 Si_2 O_7$. It sometimes occurs in soils formed on limestones. However, generally minerals having this structure are quite rare. In the cyclosilicates (the second category of the sorosilicates), three or six tetrahedra may share one or more of their co-ordinated oxygen atoms to form a trigonal ring, $Si_3 O_9$, (Figure 4c) or a hexagonal ring Si_6O_{18} (Figure 4d). Sorosilicates forming trigonal rings are represented by minerals like wollastonite, $Ca_3Si_3O_9$, or rhodonite, $Mn_3Si_3O_9$. Cyclosilicates having hexagonal ring structures are represented by minerals like beryl, $Be_3Al_2Si_6O_{18}$, or dioptase $Cu_6Si_6O_{18}. 6H_2O$.

Figure 5 summarises the classification of the orthosilicates.

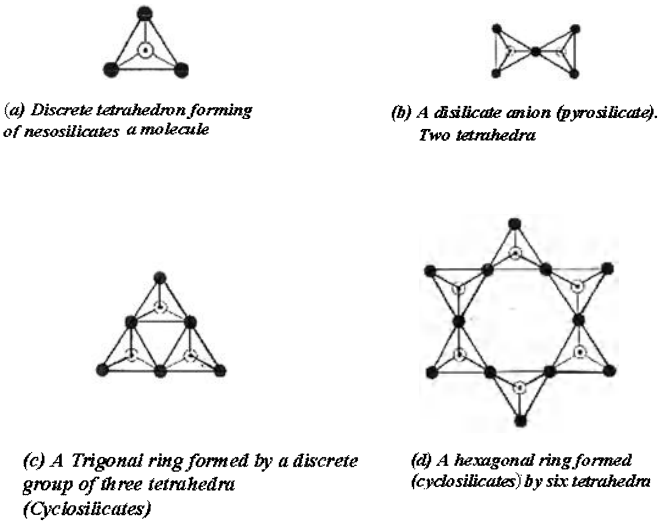


Fig. 4. Structure of the orthosilicates

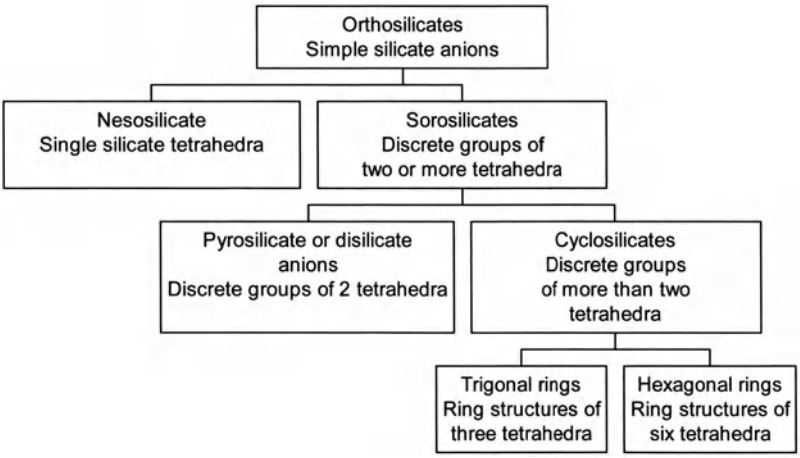


Fig. 5. Classification of the orthosilicates

2.1.2. Chain silicates or inosilicates:

This group derives its structure from the self-association of metasilicate anions $(Si\ O_3)^{2-}$ into infinite chains of formula $(SiO_3)_n^{2n}$. The simplest of these is the string-like chain characteristic of the pyroxenes. In this arrangement, the silicon atoms share two of the four tetrahedrally co-ordinated oxygen atoms with adjacent silicon atoms (Figure 6). Examples of the pyroxenes include enstatite, $Mg\ Si\ O_3$ and diopside, $Ca\ Mg\ (Si\ O_3)_2$. If further sharing of oxygen atoms occurs by half of the silicon atoms, a double chain or band structure is formed. This is the structure of the amphiboles. Amphiboles are more complicated, containing the basic $(Si_4O_{11})^{6-}$ repeating unit as well as metal and hydroxide ions. Examples of the amphiboles are tremolite, $Ca_2\ Mg_5\ (OH)_2\ Si_8\ O_{22}$ and actinolite, $Ca_2\ (Mg, Fe)_5\ (OH)_2\ Si_8\ O_{22}$.

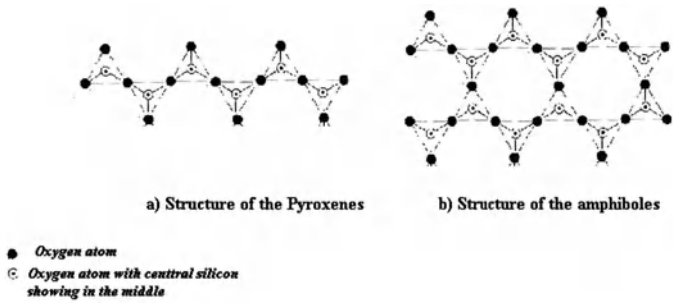


Fig. 6. Structure of the Chain silicates

2.1.3. Sheet silicates or Phyllosilicates:

If a complete sharing of the three basal oxygen atoms in a silicon tetrahedron is established, a layer or a sheet structure, made of various associated tetrahedra, and

having an empirical formula $(Si_2O_5)_n$, would result, creating a completely new type of silicates, known as the phyllosilicates or the sheet silicates. Connections between the central silicon atoms in the individual tetrahedra lead to the appearance of a network of hexagonal holes on the sheets, lending them a pronounced pseudo hexagonal symmetry (Figure 7).

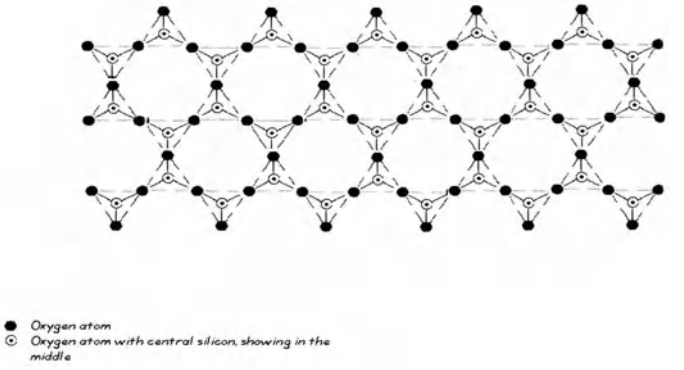


Fig. 7. Structure of the Phyllosilicates. Observe the hexagonal network of holes

The apical atoms of the tetrahedra contemplating neutrality, form ionic-covalent bonds with other metal cations. They commonly associate themselves into octahedral sheets of Gibbsite $(Al_2 OH_6)_n$, or *Brucite* $[Mg_3 (OH)_6]_n$. Gibbsite sheets are formed by edge-to-edge linking of two octahedra of Al equidistantly surrounded by six OH groups (see Figure 8). Edge-to-edge association of three octahedra of $[Mg (OH)_6]$, results in the formation of *Brucite sheets*, which are also of octahedral structure, having an empirical formula: $[Mg_3 (OH)_6]_n$.

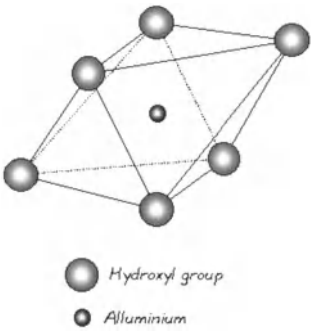


Fig. 8. Diagrammatic representation of an Allumina octahedron

The bonding of silica tetrahedral sheets (also known as siloxane sheets) with gibbsite or brucite octahedral sheets makes the basic structural units for the clay minerals, which are considered the most important group of mineral constituents of soils. These fundamental units (known as layers) are of two types; the first one (Figure 9a), called here (for the sake of convenience) doublet structure while the other (also for convenience, called triplet structure) is made of a 2:1 lattice, comprising an octahedral brucite sheet sandwiched between two siloxane sheets (Figure 9b)

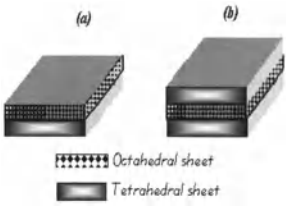


Fig. 9. A doublet layer (1:1), an octahedral sheet linked to a tetrahedral (siloxane) sheet. (b) a triplet layer (2:1) an octahedral sheet sandwiched between two tetrahedral sheets

Classification of the clay minerals

Before explaining the fundamentals of clay mineral's classification in detail, the terms used henceforth will be shortly recapitulated. There are three fundamental elements delineating the structure of clay minerals — sheets, layers and stacks. The ***sheets*** are structurally of two types (tetrahedral silica and octahedral Al-OH or Mg-OH sheets). Combinations of sheets make the ***layers***, of these there are also two types — "doublets", made of a tetrahedral sheet linked to an octahedral one and "triplets" made of an octahedral sheet sandwiched between two tetrahedral ones. A ***stack*** is a combination of layers alternating in a vertical direction. Layers in a stack may all be of the same type or they may be different, in which case the clay mineral is called a mixed layer-clay. The alternation of layers in a stack may follow a regular Rhythm or may be random. Figure 11 summarises these relations:

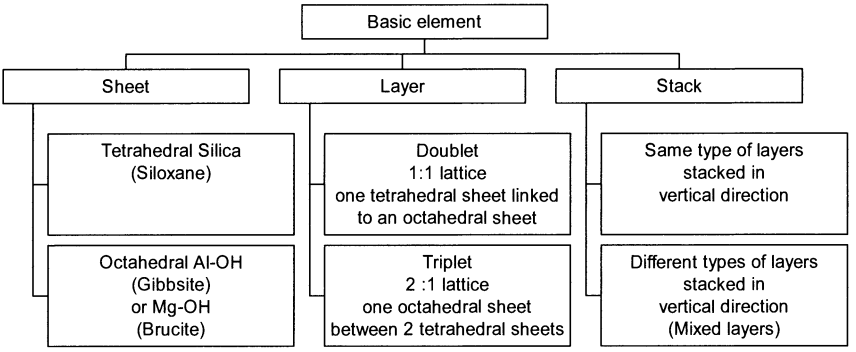
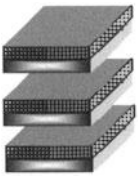


Fig. 10. Chart summarising the main basic structural elements of the clay minerals

Clay minerals are classified according to the type of layer structure (doublets or triplets), the interlayer or basal spacing between the unit layers, and the inter layer components or species. Accordingly, following groups are identified:

A. The Kaolinite group: This group is made of stacks of doublets (see above). The main member of the group is the mineral kaolinite, which has the composition $(OH)_8Al_4Si_4O_{10}$. Another member of this group is halloysite, having almost the same composition except for having two layers of water molecules within the stack. Figure 10 represents the structure of the group.



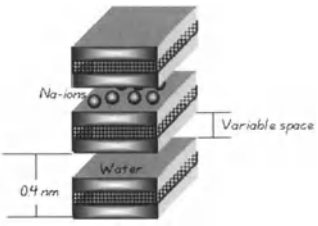


Fig. 11. Structure of the kaolinite group

Fig. 12. Structure of the montmorillonite group

B. The Montmorillonite group

This group is made of triplets stacked in vertical direction (Figure 12). It has the empirical formula $(OH)_4\ AL_4\ Si_8\ O_{10}$. n H_2O. Mg^{+2}, Fe^{+2}, or any other divalent cations substitute generally for Al^{+3} in the octahedral sheet, producing a rest charge, which is normally balanced by accommodating Ca^{+2}, or Na^{+}, between the layers. The interlayer space in this group provides a shelter not only for neutralising ions, but also for organic material as well as for varying amounts of water, making the lattice expandable to accommodate variable numbers of water molecules. The interlayer ions may be displaced by other dissolved ions when their solutions enter the interlayer space. This property makes members of the montmorillonite group include smectite, in which Fe^{+2} and Mg^{+2} substitute for Al^{+3} and nontronite with Fe^{+3} replacing Al^{+3}

C. The Illite (Hydromica) group

The illite or hydromica group (also known as muscovite group) is represented by its main member illite. It has the general formula: $OH_4\ K_y\ (Al_4.\ Fe_4.\ Mg_4.\ Mg_6)\ (Si_{8-y}\ Al_y)\ O_{20,}$ and has a structure made of stacked triplets (Figure 13). However, about three quarters of the tetrahedral positions in the siloxane sheets are occupied by Al^{+3} rather than Si^{+4}, leaving a net layer charge of about –2 on

each layer. This rest charge is balanced by accommodating K-ions in the interlayer space, making the interlayer bonding much stronger than the weaker ionic bonding in montmorillonite and rendering the illite lattice, unlike that of montmorillonite, non expandable.

D. The chlorite group:

The chlorite group can be structurally viewed as being derived from montmorillonite by inserting a sheet of Mg $(OH)_6$ (brucite) between each two adjacent montmorillonite layers (Figure 14). This case in which a single sheet functions by itself as a layer is substantiated by the observation that montmorillonite is altered to chlorite in Mg-rich seawater, that can provide the Mg- ions required to produce brucite sheets.

Fig. 13. Structure of the illite group

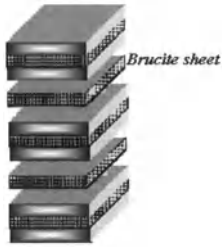


Fig. 14. Structure of the chlorite group

E. Mixed layer clays:

This group has a structure resulting from ordered or random stacking of the basic clay mineral groups in a vertical direction. It might be alternation between stacks of doublets with stacks of triplets (e.g. Kaolinite-Illite) or as it is the case in chlorite, just a regular alternation of triplets with a single brucite or gibbsite sheets or even an alternation between stacks of chlorite and illite. The alternations may

be regular following a fixed Rhythm like in chlorite or irregular like in some minor soil constituents

Factors controlling the formation and alteration of clay minerals

The principal factors, controlling formation and alteration of clay minerals are the chemical composition of the parent material and the physicochemical environment in which the process takes place. Kaolinite for instance, having only Al and Si as cations will be formed in an environment, where bases are continuously removed from the solution, giving rise to a residue with high Al/Si-ratios (Kaolinite has the highest Al/Si-ratio among the clay minerals). Such an environment as here described, should be acidic and having a very active percolation of fluids to provide the effective removal of the bases. Kaolinite develops, therefore, much readily in relatively humid climates with free drainage and enhanced percolation of ground water.

Contrary to Kaolinite, formation of members of the montmorillonite group (of low Al/Si-ratio: about 0.5:1 and high content of Fe, Mn, Na, Ca, Mg, and K), warrants a retainment of the bases. This can readily occur in a neutral or a slightly alkaline environment of impeded drainage or high evaporation rates. Accordingly, montmorillonite is considered as a typical product of weathering in water logged terrain or semi-arid climates. The mere occurrence of montmorillonite in a landscape retains the poor drainage character of the soil due to its expandable lattice and its capacity to accommodate and retain water molecules.

2.1.4. Framework silicates or tectosilicates:

In this category, complete sharing of all four oxygen atoms per Si O_4 tetrahedron is attained, giving rise to a framework structure. Minerals like quartz and the feldspars, which are very common in most soils, adopt this structure. Quartz is made up of Si-O tetrahedra linked through the O^{2-} ions. It has the general formula $(SiO_2)_n$ or silicon dioxide. The name quartz stands actually for a mineral species under which about 300 varieties are included. The feldspars are far more important, as rock constituents are, than any other group of minerals; in fact, they may

be compared in igneous rocks to all other groups combined, since they constitute nearly 60% of such rocks and serve as the basis for their classification. They undergo ***isomorphic substitution***, which is one of the fundamental properties of silicate minerals. In this process, an ion may be replaced by another ion, in the silicate lattice, causing an imbalance in the electric charge of the crystal. To re-establish electric neutrality, extra ions or ionic species are incorporated or expelled from the crystal lattice. In feldspars a considerable part of the Si^{4+} ions are replaced by Al^{3+} ions with extra base cations like Ca^{2+}, Na^{+} or K^{+} to re-establish neutrality. The chief chemical types of feldspars are: K Al Si_3O_8 (orthoclase and microcline), Na Al Si_3O_8, (albite), and Ca Al_2 Si_2O_8 (anorthite). Natural crystals of microcline and of orthoclase contain 10 to 25% Na Al Si_3O_8. Albite and anorthite are completely miscible with each other and form mix-crystals (in all proportions), known as plagioclase feldspars, which are stable at any temperature. They normally contain 5 to l5 % K Al Si_3O_8.

Accessory soil minerals Apart from silicate minerals, non-silicate minerals of minor occurrence may play an important role in the development of soil properties. Among those most widely distributed in soils are the oxides of iron and aluminium, which are often lumped under the collective term "sesquioxides". Limonite, $Fe_2O_3.nH_2O$; hematite, Fe_2O_3; goethite, $Fe_2O_3.H_2O$; diaspore, $Al_2O_3.H_2O$ and gibbsite, Al_2O_3, best exemplify the sesquioxides.

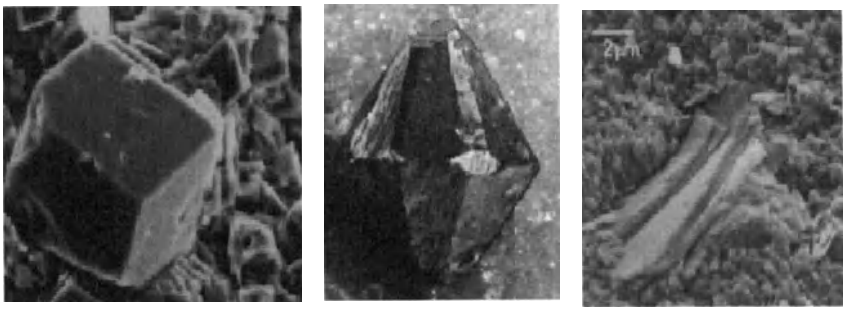


Fig. 15. SEM –photographs of some detrital accessory crystals in soil :(a) calcium carbonates (b) anatase (titanium oxide) and (c) detrital mica

Hydrous Fe and Al oxides attain their highest concentrations in soils under humid tropical conditions. However, Fe-concentrations will principally depend on the *Eh* of the environment, such that under oxidising conditions iron not required for clay formation be precipitated as hydrated ferric oxide, while under reducing conditions ferrous iron is removed in solution. Other accessory minerals occurring in soils developed on recent volcanic deposits are anatase, TiO_2 and amorphous silica.

2.2 Organic matter and soil organisms:

A major agent determining the character of the entire soil profile is humus, which is generally concentrated in the upper horizons. Brady (1974) has defined Humus as:

"A complex and rather resistant mixture of brown or dark brown amorphous and colloidal substances modified from the original plant tissues or synthesised by various soil organisms."

It is principally the product of decay of surfacial organic debris (litter), together with the decomposition products of roots within the uppermost soil horizons. In average soils, humus contains 4- 6% organic substances, which, in turn, are made of 85% dead matter, 8.5% living roots and rootlets and about 6.5% soil organisms.

2.2.1.Soil organisms: These are generally classified according to their biological activities in soils into producers, consumers, and decomposers. Decomposers form the basis of the nutritive chain among the three groups. They produce, by degradation of organic litter, the primary resources (CO_2, N_2, O_2 ...etc.) used by the producers to synthesise complex nutritive material, which in turn will be consumed by the group of consumers. All three groups work hand in hand to change and continuously develop the soil profile. Soil organisms may also be classified according to their size into microfauna (< 200 μm), mesofauna (200- 1,000 μm), and macrofauna (> 1,000 μm). Table 2 illustrates the approximate distribution in volume % of soil organisms in the organic fraction of an average European soil.

Class of organisms	Vol. % in humus of an average European soil
Bacteria and actinomycetes	50
Fungi	25
Lumbrscid worms	14
Macrofauna	5
Mesofauna	2.5
Microfauna	3.5

Table 2. . Distribution of soil organisms in average European soils

I Macrofauna living on and in the soil includes large molluscs, beetles, large insect larvae, as well as vertebrates like moles, rabbits, foxes, and badgers. These normally bury deep in the soil and feed on other smaller organisms. Moles in particular consume a great deal of smaller soil dwellers.

II. Mesofauna: Soil dwellers of this category belong to four main groups — nematodes, arthropods, annelids and molluscs (see Figure 16). ***Nematodes***, the unsegmented roundworms (also called eelworms) are about 0.5 to 1 mm in length. They are considered as the smallest soil fauna next to protozoa. In a soil block of 1 m^2 surface area and 30-cm depth, $10^6 - 2 .10^7$ individuals of these worms, with a total weight between 1 and 20 g may be present. They feed on plant debris, bacteria and in some cases on protozoans.

a) Arthropods, as shown by Table 3, comprise various categories. To these, we count acari (mites), colembola (springtails), myriapods (centipedes and millipedes), isopods (wood lice), beetles, insect larvae, and termites. Among these categories, the mites and springtails are the most abundant; especially in acidic litter, where they may form 80% of the soil organisms. Both mites and springtails feed on plant debris, bacteria and fungi. Table 3 summarises some information on selected soil arthropods. The numbers are based on a soil block of 1 m^2 surface area and 30 cm depth. Ants and termites are most abundant in tropical soils. They are very active soil mixers. Earth pillars heaped by termites (termintaria) may reach several meters in height.

Group	Number of indiv.	Total weight in gm.	Characteristics
Mites	10^5 – 4.10^5	1 – 10	Common in acidic litter
Spring tails	5.10^4 – 4.10^5	0.6 – 10	Abundant with mites
Centipedes (chilopods)	50 – 300	0.4 – 2	Carnivorous
Millipedes (diplopods)	100 – 2000	0.05 – 1	Herbivorous
Isopods (wood lice)	50 – 200	0.5 – 1.5	Typical decomposers

Table 3. Some data on small arthropods in soils

b) Annelida (ringed worms) is the name of the phylum to which the segmented earthworm, the leech, and the nereis belong. The Lumbrscid worms (the earthworms) represent the first class of soil annelids. These occur in countless numbers in moist soils all over the world, emerging only at night and retreating under ground in the morning. Darwin made their activities the object of a careful study and concluded that: "*it may be doubted if there are any other animals which have played such an important part in the history of the world as these lowly organised creatures*." Indeed, the quantity of earth burrowed, mixed and brought up from below and deposited on the surface by these worms has been estimated to be as high as 18 tons per acre per year or if spread out uniformly about 3 cm in 10 years. The effects of worms on the soil include beside bringing out deeper parts of the soil to the surface and exposing them to the air, improving the drainage through the intricate net of burrows and adding (in the form of excretory waste) a great deal of organic material to the soil. Their numbers in European soils are estimated to be between 80 and 800 with a total weight of 40 to 400 grams per square meter. Some giant earthworms are found in tropical regions, especially in Australia. ***Megascolecides australis*** may be 3 m long. It lives in burrows with volcano-shaped openings. The ***enchytraeid*** or potworms are the second class of soil annelids. They are smaller than the earthworms (0.1 - 5.0 cm) and have a thread like

appearance. Potworms feed on algae, fungi, bacteria, and other soil organic materials. They may attain numbers as high as 200,000 individuals per square meter. ***Mesofaunal molluscs*** (2 - 20 mm) found in soils include slugs and snails. Their numbers per square meter may range between 50 and 1000. They feed on plants, fungi, and faecal remains.

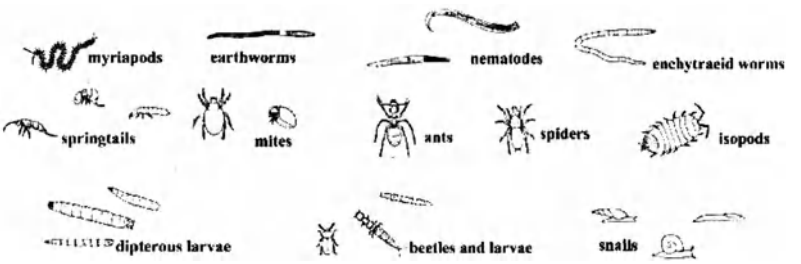


Fig. 16. some of the common mesofauna in European soils

III. Micro-organisms (Micro fauna and micro flora): These are mainly represented by four groups — bacteria, fungi, algae and protozoa. All four groups occur in great numbers in soils (see Table 4).

Group	Number of individuals / m^{-2}	Total weight in gm.
Bacteria	10^{12} - 10^{15}	50 - 500
Fungi	10^{10} - 10^{12}	100 - 1000
Algae	10^{6} - 10^{10}	1 - 15

Table 4. Number of individuals and total weight of microorganisms in a soil block of 1 m^2 surface area and 30 cm depth (after Klötzli, 1993)

A. Bacteria: These are normally unicellular organisms with cellular sizes between 0.0001 and 0.02 mm. Accordingly, they are the smallest organisms visible under the light microscope. They occur, due to their tremendous reproduction rates, in very high numbers (about 10^{12} - 10^{15}. m^{-2}) mostly in water films surrounding the soil particles. According to their morphology, Bacteria are classified into three main classes– Eubacteria, Chlamydobacteria and Actinomycetes.

a. Eubacteria This is the most representative class of bacteria and can be further subdivided into spherical bacteria (cocci) and rod-shaped (bacilli) bacteria. Prominent examples of this group are the bacteria responsible for nitrogen fixation in the soil - ***nitrobacter.***

b. Chlamydobacteria (thread- shaped bacteri) In this class the bacterial cells are attached together by a filament (filamenatum) into a linear chain similar to bead strings. Iron-bacteria, playing a very important role in weathering and diagenesis of sediments belong to this class.

c. Actinomycetes In this class, rod like cells are united to form stellar forms of bacteria, which in their vegetative stage of reproduction resemble fungi, consisting of fine branching filaments (about 1 μm in diameter). These morphological peculiarities make it difficult to determine the real systematic position of these organisms, yet Actinomycetes are considered as an independent class of the bacteriophyta.

Another method of classification of bacteria is their susceptibility to staining by the so-called Gram solution (after the Danish bacteriologist H. C. J. GRAM, 1853-1938). Bacterial cells, stained by this solution are called gram-positive; others are collectively termed gram-negative.

The effects of bacteria on the soil are many. They decompose a wide range of materials under various conditions. Examples of these range from oxidation of Fe^{+2} and reduced sulphur compounds under catalytic action of ***Thiobacillus ferrooxidans*** to the formation of nitrogen-fixing nodules on the roots of leguminous plants by ***Rhizobium sp.*** Some bacteria are also capable of metabolising a wide range of chemicals. Example here is given by ***Pseudomonas***, a species capable of metabolising pesticides.

B. Fungi: Mycophyta or Fungi are, like the bacteriophyta, in their overwhelming majority parasitic, depending for their carbon needs on nutritive material synthesised by other organisms. They are characterised by filamentous structures (hyphae), which are about 0.5 - 10 μm in diameter and which grow into a dense network called mycelium. Fungi live mostly in the surface layers of the soil,

preferring acidic conditions yet some of them live symbiotically in plant tissues. They may, under favourable (acidic) conditions, be responsible for the decomposition of up to 80% of the soil organic matter.

C. Algae: These are photosynthetic organisms confined largely to the upper surface of the soil. They include Cyanophaceae (blue green algae) and Chlorophaceae (green algae). Blue green algae regulate the nitrogen cycle in the soil.

D. Protozoa A variety of protozoa, like rhizopoda, ciliates, and flagellates live in water films surrounding the soil particles. They control the numbers of bacteria and fungi on which they live. Table 5 shows the numbers and total weights of some protozoa in a soil block of 1 m^2 surface area and 30 cm depth.

Group	Number of indiv. / m^2	Total weight in gm.
Flagellates	$5.\ 10^{11}$ — 10^{12}	10 — 100
Rhizopoda	10^{11} — 5.10^{11}	10 — 100
Ciliates	10^{6} — 10^{8}	10 — 100

Table 5. Some data on soil protozoa

2.2.2. Dead organic matter: Soil organic matter formed by metabolic action of the soil organisms as well as by the break down of pre- existing organic material can be classified into four main classes:

A) Organic compounds free from nitrogen (other than lipids)

B) Nitrogen compounds

C) Lipids

D) Complex substances including humic acids

A. Organic compounds free from nitrogen:
a) Nitrogen free aliphatic compounds

Carbohydrates are the most important representatives of this class of soil organic substance. Plants and soil organisms depend upon them for their structural material, which eventually ends up as important soil constituents. It is estimated that about 5 - 30% of the soil carbon exist as Carbohydrates. These have a fundamen-

tal general empirical formula $C_x (H_2O)_y$, where x and y can be equal or different numbers.

i. Monosaccharides (simple sugars): The simplest structure demonstrating the property of optical activity, which is one of the fundamental properties of carbohydrates, is ***glycolic aldehyde*** $C_3 (H_2O)_3$ or $CH_2OH - CHOH - CHO$; and it is by repeating the central group (CHOH) that further simple carbohydrates can be deduced. The most important of these are the ***pentoses*** [$CH_2OH (CHOH)_3 CHO$] and the ***hexoses*** [$CH_2OH (CHOH)_4 CHO$]. However, because the (CHOH) can be arranged in a multitude of spatial constellations, we may have a variety of compounds with the same composition but having different structural formulae. ***Arabinose*** (from ***gum arabic***); xylose, wood sugar, and ***ribose*** (component of nucleic acid) are all pentoses, while ***glucose***, ***mannose*** and ***galactose*** all have the hexose composition and still differ in their structural formulae. Monosaccharides are usually decomposed in soils by the catalytic action of bacteria. They break up into organic acids; the number and nature of which depend on the microflora present.

ii. Oligosaccharides: These are produced by condensation of molecules of one or more kinds of monosaccharides. Accordingly, we may have ***disaccharides*** (cane sugar, maltose, and lactose), ***trisaccharides*** (raffinose) or the more complicated ***tetra-***, ***penta-*** and ***hexasaccharides.***

iii. Polysaccharides: These are formed by condensation of an infinite number of lower carbohydrates. Examples are starch, glycogen, and cellulose.

b) Nitrogen free aromatic compounds:

It is known that numerous low molecular weight ***phenols*** and ***quinones*** are liberated from dead vegetable matter. These may be utilised by fungi in building molecules with greater number of aromatic rings. It is also known that fungi (during the decomposition of lignin) produce extracellular phenol oxidases (enzymes, section 9.4)), which catalyse the introduction of hydroxyl groups into the phenol rings, giving rise to some aromatic soil constituents.

B. Nitrogenous organic compounds

a) Proteins and amino acids

The most important nitrogenous organic compounds, found in soils are proteins and amino acids. It is estimated that about 20 - 50% of organic nitrogen in soils exists as amino acids. These are compounds that contain carboxyl, –COOH and amino group, $–NH_2$. Thus many of them are neutral, but can react as acids or bases according to the conditions prevailing. Polymerisation of amino acids produce chain polymers known as polypeptides; very long chains of polypeptides are known as proteins. Both proteins and amino acids persist in the soil by being absorbed on the surfaces of clay minerals or being incorporated in other organic material. Proteins in soils ultimately break down, through bacterial or fungal action, into Methane, CH_4; amines (compounds similar to ammonia, NH_3 in which a part or all the hydrogen has been replaced by organic groups); urea, $NH_2 – CO – NH_2$; Carbon dioxide or water. Figure 17 summarises the breakdown series of the proteins.

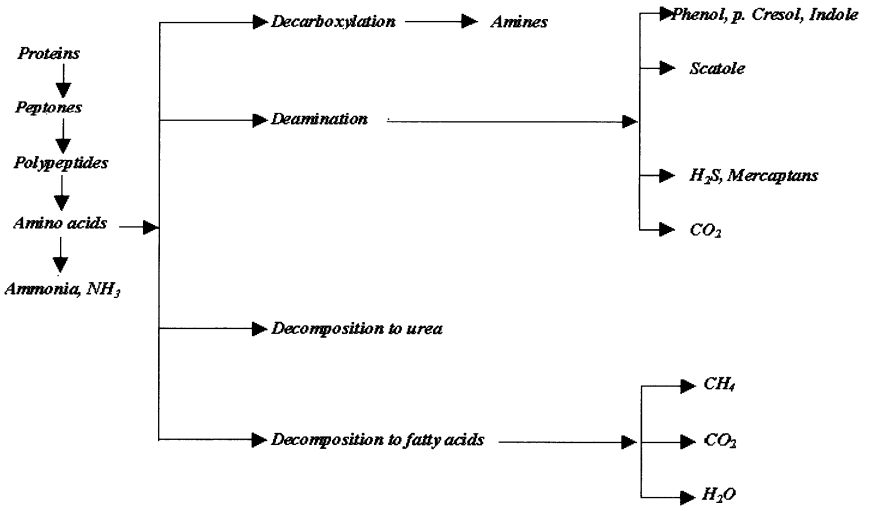


Fig. 17. Breakdown series of the proteins

We should, however bare in mind that not only decomposition takes place. In some cases, bacteria may resynthesize the simple molecules generated by protein decomposition

b) Skeletal nitrogen substances

These include cartilage of vertebrates and chitin of invertebrates. They are unlikely to decompose and persist in an almost unchanged state in the soil. Cartilage is a mucoprotein, conjugated with chondrotin sulphuric acid. Chitin is a polymer made of a chain of an indefinite number of N-acetyl glucosamine groups.

C) Lipids: Lipids are esters of fatty acids, yet many of them contain combined phosphoric acid. On hydrolysis, they yield the parent acids with glycerol, aliphatic alcohols, carbohydrates, nitrogenous bases, or sterols. Lipids are resistant to decomposition.

D) Complex substances including humic acids:

The bulk of organic material in most soils and natural water systems is probably composed of humic substances. These substances are not chemically fully understood due to their molecular complexity. They are defined as dark - coloured, acidic, complex organic material of high molecular weight, lacking the specific physical and chemical characteristics of simple organic compounds (SCHNITZER, 1976). · They consist essentially of insoluble, heterogeneous polymers and have an approximate composition, (on an ash free basis) of 44-53% carbon, 40-47% oxygen, 3.5-5.5% hydrogen, and 1.5-3.5% nitrogen, with molecular weights ranging from several hundred to perhaps several thousand. Humic substances in general, account for around 60- 80% of the organic substances in the soil. They occur, due to their high surface area, in enormous distribution as colloidal material or as coatings on clay and other sediments. Processes through which humic materials form include degradation of plant material as well as synthetic activities of

microorganisms. Humic acids, according to their solubility under different pH-conditions, are classified into three groups. These are humic ***acids***, which are soluble in dilute alkali (NaOH), but are precipitated on acidification of the extract; ***fulvic acids***, which remain in solution on acidification of the alkaline extract; and ***humin***, which is insoluble in both dilute base and acid. The three groups differ in molecular weight, with fulvic acid having the lowest molecular weight and the highest content of–COOH, –OH, and –C = O groups. Humic acids are all in a position to bind metals both by chelation as well as by complexing to a single site on the molecules. However, the strength of polymer bonding among the individual units of a group is directly proportional to the molecular weight.

2.3 The liquid phase – soil water

Principally, soil water is derived from two sources: precipitation and groundwater; each contributing to the amount of moisture in the soil within the regime of a sensitive dynamic equilibrium depending mainly on the climate and the water balance between the atmosphere and the plant-soil system. The amount of water lost to the atmosphere comprises the sum of water transferred by evaporation and that transferred by plant transpiration, both forming together the ***evapotranspiration***. This depends directly on the climatic conditions as well as the properties of the plant-soil system. Evapotranspiration that would take place under optimum conditions of precipitation and soil moisture capacity is known as the potential evapotranspiration, shortly Potet; it can be determined by empirical methods. Under ideal conditions Potet will be equal to the actual amount of water transferred to the atmosphere by evapotranspiration in the region under consideration, which is known as ***ACTET***; in other cases when ***POTET*** is not met by ***ACTET***, the considered area will suffer a moisture shortage. The difference between ***POTET*** and ***ACTET*** in this case is known as the deficit or simply ***DEFIC***. Still in other cases when ***POTET*** is fully satisfied, yet the soil still receives water input, a situation will arise where water oversupply will lead to the formation of surface puddles and/or a recharge of the ground water reservoir. This water surplus is shortly known as ***SURPL***. To

establish an account or water budget for a given region all the foregoing quantitative factors are united in the following simple equation, known as Thorntwait's water-balance equation (after C.W. THORNTHWAITE, 1899 - 1963):

$$PRECIP = (POTET - DEFIC) \quad + SURPL \pm \Delta STRG \qquad (2.1)$$
$$ACTET$$

Where ***PRECIP*** stands for precipitation and Δ***STRG*** for the soil moisture storage or the amount of water, that is stored in the soil and is accessible to plant roots. Indeed, not all water stored by the soil can be classified in this category; for soil moisture comprises two main types: the type available to plant roots, which is held in the soil by surface tension and cohesive forces and is known as ***capillary water***; and the type inaccessible to plant roots, which is known as ***hygroscopic water***. This is made up of thin films of water molecules held tightly to the surfaces of soil grains by hydrogen bonds. Soils containing predominantly hygroscopic water and none or very little amounts of capillary water are not in a position to support plant growth. They are said to be at ***wilting point***. Whereas, soils having pores full of capillary water are generally said to be at ***field capacity.*** In case of water oversupply to the soil, the amount of water percolating downward to join the ground water reservoir will be termed ***gravitational water.*** A soil, in which all gravitational water is drained out, contains the maximum level of capillary water and is consequently at field capacity. Based on the principles of water balance, the U.S. Soil Conservation Service recognises the following five soil moisture regimes

i) Aquic this is the case, when the soil is constantly wet like in bogs marshes and swamps. An aquic environment is a reducing one, virtually without dissolved oxygen. It is characterised by perennial stagnant water.

ii) Aridic (Torric) This regime occurs mainly in arid or semiarid climates, where soils are dry more than half of the time. Soil temperatures at a depth of 50 cm lie above 5°C. This regime is characterised by thin soils allowing high rates of

evaporation and/or surfaces sealed by dryness, so that infiltration and recharge are inhibited.

iii) Udic The water balance in this regime is characterised by a moisture surplus at least during one season of the year. If the surplus exists throughout the year, the regime is called ***perudic***. The soil is always in a position to support plants due to its rich reservoir of capillary water.

iv) Ustic, this regime occurs in semiarid and tropical wet climates. It is intermediate between aridic and udic regimes. The water balance reveals a prolonged deficit period following the growing season.

v) Xeric, this is the regime characterising the Mediterranean climate: dry and warm summer, rainy, and cool winter. In every six of ten years, there are (under this regime) at least 45 consecutive dry days during the four months following the summer solstice.

Composition of Soil waters:

Soil solutions contain a wide range of dissolved and /or suspended organic and mineral solid and gaseous substances. Organic substances include all minor amounts of soluble and suspended organic compounds. These, together with minor amounts of dissolved silica and some pollutants such as heavy metals (Pb, Zn, Cd....etc.), belong to the minor constituents of the soil water. The major constituents of soil water include dissolved salts in mobile ionic form and gaseous compounds such as CO_2. This may be derived from the atmosphere by being dissolved in precipitation, or from the soil air, as a product of respiration of soil organisms. It also may be the product of internal chemical reactions (e.g. as a product in the protein decomposition series). Mobile ions resulting from the dissolution of mineral substance include basic cations such as Ca^{2+}, Na^{+}, K^{+}, $NH4^{+}$, and Anions such as NO^{3-}, PO_4^{3-}, Cl^{-}. These are provided by external sources as well as by internal chemical processes taking place within the soil (weathering, diagenesis, decomposition and synthesis of organic matter). Chloride ions and to a lesser extent, sulphate ions (SO_4^{2-}) may be provided by atmospheric sources in-

cluding air borne marine salts and acid deposition. Under acidic conditions, cations of Fe and Al may also constitute a considerable part of the active cations in soil water. The concentrations of ions in the soil solution, however, depend mainly on the soil-pH, its oxidation status and the affinity to processes such as adsorption, precipitation and desorption. Lower pH values result in diminished metal adsorption capacities, which will in turn lead to higher metal concentrations in the solution. An important factor in determining the soil pH is the concentration of CO_2 in the soil solution. It provides the solution with H^+ through the reaction:

$$H_2O + CO_2 \leftrightarrows H_2CO_3 \leftrightarrows H^+ + HCO_3 \qquad (2.)$$

Soil water in equilibrium with CO_2 in soil air has pH values often below five. This acidity arises mainly from the following main sources:

a) Organic acids produced during degradation of organic matter.
b) Natrification processes, where NH_4^+ is converted into NO_3^-.
c) Release of H^+ by plants in exchange for nutritive base cations.
d) Sulphide oxidation.
e) Pollution through industrial and urban emissions.

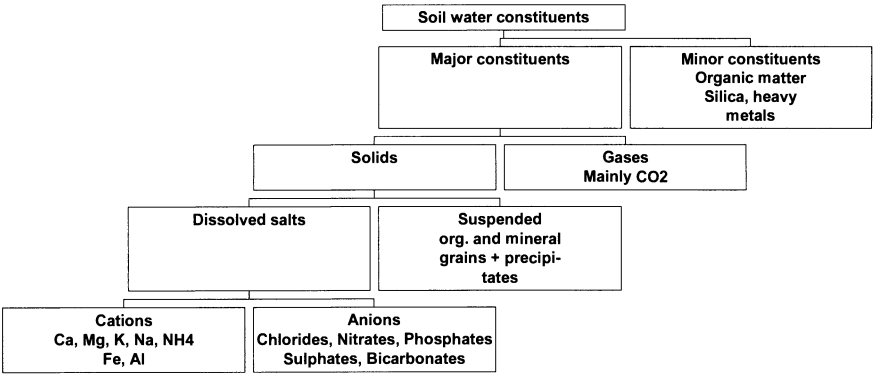


Fig. 18. Schematic diagram, showing the principal constituents of soil water.

2.4 The gaseous Phase — Soil air, origin, composition and properties:

Soil air or soil atmosphere is the characteristic name given to the mixtures of gases moving in the aerated zone above the water table (fig. 91, p. 187) and filling the soil pores, where these are not already occupied by interstitial water. Mass flow of these gases in the aerated zone will be wholly controlled by atmospheric factors such as temperature, pressure, and moisture conditions. As far as major constituents are concerned, soil air has a composition slightly different from that of atmospheric air (see table 6). While soil air contains 1 - 6% less oxygen by volume than atmospheric air, we find that it contains about 10 to 150 times more CO_2 .

SYSTEM	C OMPOSITION		
	Nitrogen	Oxygen	Carbon dioxide
Atmospheric air	78%	21%	0.03%
Soil air	78%	15 – 20%	0.25 – 5.0%

Table 6. Major constituents of soil air and atmospheric air in volume *%*

These differences in the concentration of CO_2 and O_2 between soil air and the atmosphere result in partial pressure gradients between the two systems along which CO_2 moves from the soil to the atmosphere while oxygen flow takes place in the opposite direction. Gas exchange between soil air and the atmosphere occurs also along temperature gradients and in sites where rainwater introduces atmospheric gases into the soil. Beside the major constituents, minor or trace amounts of other gases may occur in the soil air, originating from deep-seated sources or as products of organic or mineral reactions in the soil environment. Examples of these are trace amounts of CO (Carbon monoxide) and CS_2 (Carbon disulphide) occurring in soils overlying geothermal sites in Utah (HINKEL *et al.*, 1978). By contrast, light Hydrocarbons such as methane, CH_4, H_2, H_2S, CO, and water vapour are mainly produced within the soil body as products of degradation of organic material (SCHLEGEL, 1974). Traces of the extremely toxic gas ***Dimethyl mercury,*** generated by bacterial activities may under extremely reducing conditions occur in the soil.

Chapter 3

Soil properties

3.1 Physical properties

Colour: Colour is the most obvious trait in a soil profile. It may in many cases be indicative of soil composition. Red and yellow colour hues are generally indicative of enrichment in ferric iron, while grey hues may result of higher concentrations of Aluminium oxides and silicates. Black currents are generally caused by abundant organic material. Under warm temperate conditions, however, soils containing less than 3 % of humus may have deep black colours. Soil colours are generally described according to a standard colour chart (Munsel colour chart), having 175 colour hues.

Texture: Texture is the term referring to the size and organisation of the soil particles. Individual particles known as soil separates, may be described, according to their grain size, as soil components (less than 2 mm in diameter) or simply as cobbles, pebbles or gravel if they are larger than this. Soils may be classified according to their textures in different classes depending on the ratio of sand: clay: silt (Figure 19). A hypothetical soil made of equal parts of these 3 components is termed loam. A loam can be further described as sandy, clay, or silty loam according to the dominant component.

Structure: Soil structure refers to the aggregation or arrangement of primary soil particles. Structure is important because it can partially modify or overcome aspects of soil texture. The term ***ped*** (as it was mentioned before) describes an indi-

vidual unit of soil aggregates; it is a natural lump or cluster, with clay and humus holding the particles together. Peds separate from each other along zones of weakness, creating voids that are important for moisture storage and drainage. Spherical peds have more pore space and greater permeability.

They are therefore more productive for plant growth than are coarse, blocky, prismatic, or platy peds, despite comparable fertility (see Figure 20).

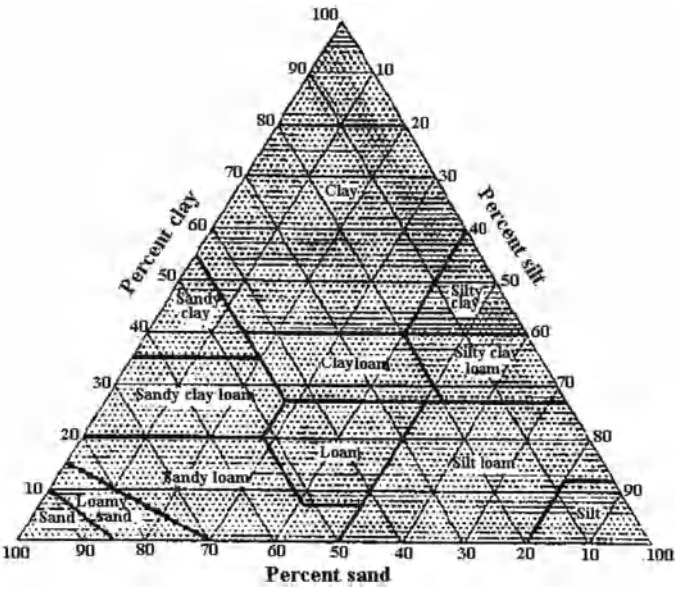


Fig. 19. Textural classification of soils (United States Dep. Of Agriculture)

Terms used to describe soil structure include fine, medium, or coarse, with structural grades of adhesion within aggregates ranging from weak, to moderate, to strong.

Consistence: Cohesive properties of a soil such as resistance to mechanical stress and manipulation under varying moisture conditions are grouped under the heading consistence.

Wet soils are variably sticky. Plasticity is roughly measured by rolling a piece of soil between the fingers and thumb to see whether it rolls into a thin strand.

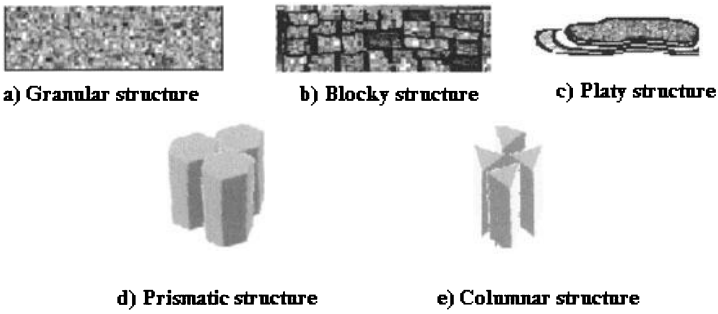


Fig. 20. Essential types of soil structure

Moist soil implies that it is filled to about half of field capacity, and its consistence grades from loose (noncoherent), to friable (easily pulverised), to firm (not crushable between thumb and forefinger). Finally, a dry soil is typically brittle and rigid, with consistence ranging from loose, to soft, to hard, to extremely hard. The segmentation that occurs in various soil horizons is a function of consistence and usually is described as continuous or discontinuous. Soils are variously noted as weakly or strongly cemented or indurate (hardened). Calcium carbonate, silica, and oxides or salts of iron and aluminium can all serve as cementing agents.

Porosity: Grain size and pore volume are the most important factors controlling the percolation of water and ventilation within the soil. Porosity, as a measure of the percentage of volume of pore space with respect to the total volume, can be indirectly calculated using the following equation:

$$\text{Porosity} = 1 - \frac{\text{(Bulk) density}}{\text{(Particle) density}} \times 100 \qquad (3.1)$$

Porosity can also be directly determined from the volume of water contained in a saturated undisturbed soil core of a given volume. The weight of the saturation water is determined through the difference between the wet and dry volume of the core. Porosity in this case will be calculated as follows:

$$\text{Porosity (\%)} = \frac{Ws - Wd}{V} \times 100 \qquad (3.2)$$

Where (Ws) stands for the weight of the water-saturated core, (Wd) for the weight of the dry core and (V) represents the volume of the same.

Related to porosity is the pore size distribution. It is a very important physical parameter, that stands in direct relation to water retention and related properties such as drainage and aeration of a given soil and hence to its agricultural productivity. Pore size distribution can be determined from the so-called moisture retention curves (s. Figure 21).

Moisture retention curves are established by determining the volumetric water content at various points over a range of tensions or suctions applied to an undisturbed soil core (HALL *et al.* 1977). This depends on the fact that the volume of water removed from an undisturbed soil core at a given tension is directly proportional to the pore size.

According to Figure 20, the total porosity of the core under investigation is 50 % and of this, 27 % of pores are > 20 µm in diameter, 15% are 2.0 — 20 µm and 10% are < 0.2 µm.

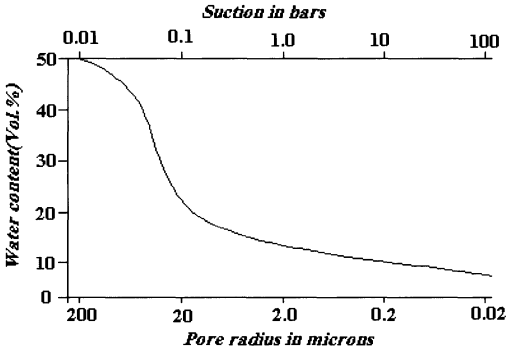


Fig. 21.A characteristic moisture retention curve (Drawn after Ellis and Mellor, 1995)

3.2 Chemical properties:

Based on their chemical composition and the degree of Agricultural exploitation, soils may display certain chemical properties, which are not only diagnostic for their origin and environmental parameters but also very sensitive indicators of

there land use value. The most prominent of these are the degree of soil acidity (pH) together with ion exchange and cation adsorption capacities, which are very important factors for plant nutrition potentials of the soil. In fact, these properties are closely related to one another as we may see by looking at them.

Soil acidity [pH]

Soil-pH is usually measured in a standard suspension of 1: 2.5 (weight to volume) of soil in distilled water or in dilute solution of calcium chloride (0.01 M). Besides being closely related to the ion exchange properties of soil (see below), soil acidity is related to other properties such as organic content and clay mineralogy of the soil. It also has a direct relationship to the availability of metals as it affects their solubility and their capacity to form chelates in the soil. In this sense, Al^{+3} ions play an important role in controlling the concentration of hydrogen ions in soil waters and hence the level of soil acidity (pH). This effect is brought about by hydrolysis when H^+ ions would be generated through following reaction:

$$Al^{+3} + H_2 \leftrightarrows Al(OH)_2^+ + H+ \qquad (3.3)$$

Hydroxy-aluminium

Positively charged hydroxy-aluminium species may undergo further hydrolysis to produce additional H^+ ions, leading to higher acidity of the soil.

$$Al(OH)_2^+ + 2H_2O \leftrightarrows Al(OH)_3 + 2H^+ \qquad (3.4)$$

Gibbsite

Thus, aluminium hydrolysis in readily acidic soils will promote further acidity. Such a phenomenon is characteristic for humid, clay rich soils.

Soils of acidic character are generally rich in calcium and/or magnesium, because calcium and magnesium may precipitate as carbonate increasing the buffering capacity of the solution, according to the following reaction:

$$Ca^{+2} + CO_2(g) + H_2O \leftrightarrows Ca\,CO_3 + 2\,H^+ \qquad (3.5)$$

Sodium does not have the same property as calcium and magnesium and that is why alkaline soils will be rich in sodium rather than calcium and magnesium. This dependence of soil pH-value on the availability and nature of the base cations makes it transient i.e. changing in short term as well as in long spans of time, according to the availability and saturation of the base cations $Ca^{2+,}$ Mg^{2+}, Na^{+}, and K^{+}. The input of these bases by atmospheric agents (precipitation), geochemical conditions (weathering), or agronomic activities (fertilisers) would eventually lead to fluctuations of the pH-value.

A general pattern, however is that ***water dominated soils*** (soils of humid regions) have low values of pH, because their content of organic and carbonic acids is often subject to replenishing and recharge by rain fall. Under these conditions, the acids, in the way mentioned above for alumino-silicates, attack minerals, producing more acidity.

Under arid conditions, however, minerals which are salts of weak acids and strong bases would domain the system, producing higher levels of alkalinity and causing the soil pH to raise to values between 9 and 10 or even more. Desert soils, having such elevated values of pH are referred to as ***rock dominated soils***. One should however be careful in dealing with soil pH-values above 10, since these may indicate contamination with strong bases such as Na OH or Ca $(OH)_2$, though in some cases like in some regions in Northwestern Egypt this extreme elevation might be due to dissolution of such minerals as nahcolite ($Na\ HCO_3$) or natron : (Na_2CO_3. 10 H_2 O).

Ion exchange

Exchangeable cations are those held between the layers of clay minerals (see figures 12 and 13) as well as those held on the surfaces of clays and organic particles (clay-humus complex or exchangeable complex), by virtue of the high surface energy resulting from the immense surface area of these finely divided substances. In case of clay minerals cations occupying interlayer positions, possess permanent positive charges that satisfy structural conditions of the crystal lattice.

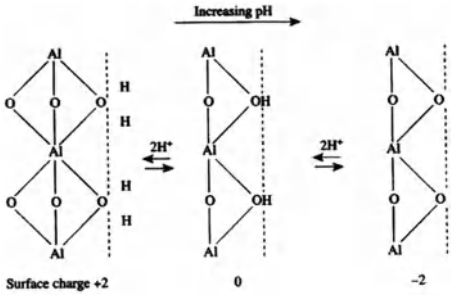


Fig. 22. Influence of pH on surface charge in aluminium oxide (White, 1997)

They may be replaced by other cations of similar size but of lower valency giving rise to isomorphous substitution, which is not directly dependent of soil pH. In case of the clay humus complex in general, surface charges are not governed solely by structural considerations. They result largely from surface reactions such as reversible dissociation of surface groups or functional groups of organic compounds and since these reactions are pH dependent, the charges would vary according to the prevailing pH. This can be illustrated by the reaction of Aluminium " oxyacids " under different conditions of Acidity. Two of these compounds are known to occur in soils — Al $(OH)_3$ [Gibbsite - some times called simply Aluminium hydroxide] and its anhydride H Al O_2.

As illustrated by Figure 22, the anhydride, which is amphoeteric would produce different species according to whether it reacts under acidic or alkaline conditions. Under acidic conditions the edge Hydroxyl groups may take up H^+ ions to produce the positively charged hydroxy aluminium with a charge of +2 while removal of H^+ from these groups under alkaline conditions produces a negatively charged species with a charge of -2. Such negatively charged colloidal particles are known as ***micelles***. They act like giant anions that attract cations to their surfaces resulting in the formation of an ***electrical double layer*** (made of the negatively charged layer on the micelle and the positively charged layer of adsorbed cations) around each of them. Cations closer to the negatively charged layer will be attracted

stronger than those at a greater distance and that is why cations with a smaller radius of hydration will be preferentially adsorbed and less readily replaced.

Another factor controlling adsorption and replacement is the valency — cations with a high valency have a high energy of adsorption and are therefore adsorbed in preference to lower valency cations. The following sequence is generally accepted for preferential adsorption of base cations: $Ca^{+2} > Mg^{+2} > K^{+} > Na+$. These cations will be less readily replaced and that is why they are represented in soil composition by a similar sequence of concentration

$$Ca^{+2} > Mg^{+2} > K^{+} > Na+$$
$$80\ \% \quad 15\ \% \quad 1\%\ .\ \ 1.8\%$$

Beside this, anion adsorption and replacement may occur. It is even more common under certain conditions.

Cation exchange capacity (CEC):

Cation exchange capacity of soils (CEC) is generally measured by the cation yield of the soil through extraction with an ammonium acetate solution. It is also a measure of the surface negative charge as well as the potential for cation adsorption. CEC is generally expressed in

Meq. per 100 g of soil. Its value depends largely on organic and clay content of the soil as well as acidity and clay mineralogy of the same.

Anther quantitative attribute of cation exchange in soils is the property known as the ***percentage base saturation***, which is simply a measure of the proportion of exchangeable bases on the soil exchange complex. It can be calculated from the following equation:

$$\text{Base saturation (\%)} = \frac{(Ca^{+2} + Mg^{+2} + K^{+} + Na^{+})}{CEC} \times 100 \qquad (3.6)$$

The difference between CEC and total exchangeable base content provides a measure of exchangeable hydrogen content. For more information on this, the student should consult Rowell, 1994

$$\text{Exchangeable } H^{+} = \text{CEC} - (Ca^{+2} + Mg^{+2} + K^{+} + Na^{+}) \quad (3.7)$$

Metal binding by small organic molecules, which are largely composed of polymeric weak acids of the type of humic and fulvic acids takes place through the formation of outer sphere complexes by binding the metal to the carboxylic or phenolic groups (see Figure 23).

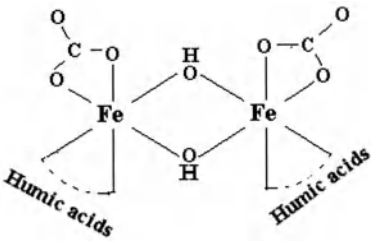


Fig. 23,Bonding of metals on humic substances by chelation (From Mirsal, 1995)

The cation exchange capacity of organic soil is largely due to organic matter and its contribution to the CEC of mineral soil may be > 200 meq / 100 gm of organic matter (BLOOM, 1981).

Oxidation-Reduction status:

The redox potential (Eh) or oxidation-reduction status is an indicator of the degree of soil aeration or the amount of oxygen present in the soil atmosphere. It can be directly measured by inserting an appropriate electrode in the soil. In aerobic soils, electrons produced during respiration combine with oxygen. Under anaerobic conditions however, oxygen is unavailable and other chemical compounds must act as electron receptors. Ferric iron compounds often take on this role, undergoing reduction to ferrous iron compounds.

Chapter 4

Soil Classification and Soil Types

4.1 Soil Classification

There are various soil classification systems in use worldwide. The most recognised among these are the system of Soil Taxonomy developed by the US Soil Conservation Service and that of the United Nations Food and Agricultural Organisation (FAO). Both may be approximately brought into proper relations despite the different approaches adopted by their authors.

Most authors adopt the system of Taxonomy, developed by the US Soil Conservation Service. It depends on the systematic description of a ***unit soil series (polypedon),*** made of an indefinite number of pedons and representing a certain locality / area, with a distinctive characteristic soil that differentiates it from its surroundings. A profile of such a series, that may or may not be a combination of both A & B- horizons ***(solum),*** comprises normally two diagnostic horizons — ***the Epipedon*** and the ***subsurface diagnostic horizon***.

The epipedon is the portion of the soil formed at the surface and may extend through the A-horizon or even include parts of B-horizon. It is normally dark in colour and contains high amounts of organic matter. Morphological as well as chemical characteristics of epipedons allow their classification in different types that can be used for soil classification. Table 7 shows the most important of these.

Epipedon	Characteristics
Mollic (A) – from mollis: soft.	Humus rich, dark coloured, base cation rich
Anthropic (A) – from anthropos: related to humans.	Similar to mollic but modified by continuous land use.
Umbric (A) – from umbra: shadow or dark coloured	Dark coloured mollic epipedon, having low base cation content
Histic (O) – from histos: tissue.	Thin layers of peat or muck, water saturated at least 30 consecutive days a year
Plaggen (A) – from plaggen: Sod.	Human made, produced by long continued manuring; less than 50 cm thick
Ochric (A) – from ochros: pale	Light coloured, hard and massive when dry, characterised by low humus content

Table 7. Major types of epipedon -- based on Christopherson (1992) after Soil Taxonomy, Agricultural Hand Book No. 436, U.S. Dept. of Agriculture, 1975

The subsurface diagnostic horizon (2nd type) is that portion of the solum formed below the surface at varying depths. It may include parts of the A- and / or B-horizons. As in the case of the epipedon the subsurface diagnostic horizons can be classified into various types (see Table 9), which may be further used in classifying soils according to the presence or absence of the diagnostic horizons, characterising the soil of the area or locality under consideration. Soils are classified according to the soil taxonomy system into eleven major groupings called ***orders*** (Table 8). Orders are devised into ***sub-orders*** (47) and these are further subdevided into great groups, bringing the whole taxonomy to about 225categories.

Name	Characteristics
Argillic– from Argilla: white clay	Illuviated clay accumulation.
Agric – from ager: field	Illuvial layer formed below cultivation.
Natric – from natrium: sodium	Argillic having high sodium content.
Spodic – from spodos: wood ashes	Accumulation of organic matter, high in Fe and Al.
Placic – from plax: flatstone	Thin, dark-reddish, iron-cemented pan.
Cambic – from cambiare: to exchange	Altered or changed through physical or chemical conditions.
Oxic– from oxide	Weathered material made of Fe and Al oxides, less than 30 cm in thickness.
Duripan – from durus: hard	Silica cemented hard pan, cannot be softened by water.
Fragipan – from fragilis: brittle	Weakly cemented brittle pan; loam texture.
Albic – from Albus: white	Light coloured pale layer deficient in clay, Fe and Al.
Calcic – from calcium	Accumulation of $CaCO_3$ or Ca Mg $(CO_3)_2$.
gypsic – from gypsum	Accumulation of hydrous calcium sulphate (Gypsum).
Salic – from salt	Accumulation of soluble salts (more than 2%)
Plinthite – from plinthos: brick	Iron pan, hardened by wet dry cycles; deficient in humus

Table 8. Major types of subsurface units-- based on Christopherson (1992) after Soil Taxonomy, Agricultural Hand Book No. 436, U.S. Dept. of Agriculture, 1975

Major soil grouping	Formative element	Connotation
Acrisols	L. acer, acetum: acid	Low base saturation
Alisols	L alumen	High aluminium content
Andosols	Jap. An(dark), do (soil)	Dark (rich in volcanic glass)
Anthrosols	Gr. Anthropos (man)	Related to human activities
Arenosols	Gr. Arena (sand)	Coarse textured
Calcisols	L. calx (lime)	Calcium carbonate rich
Cambisols	L.Cambiare (to change)	Changes in colour, structure and consistence
Chernozems	Rus.Chern: black, zemlia: (Earth or land)	Black, rich in organic matter
Ferralsols	L. ferum, alumen	High sesquioxide content
Fluvisols	L.fluvius: river	Alluvial deposits
Gleysols	Rus.Gley (mucky soil mass)	Excess water
Greyzems	AS. Grey, Rus: zemlia	Uncoated silt and quartz with organic rich layers
Gypsisols	L. Gypsum	Calcium sulphate rich
Histosols	Gr. Histus: tissue	Fresh or partly decomposed organic matter
Kastanozems	L.castana (chestnut), Rus. Zemlia	Organic rich, brown coloured
Leptosols	Gr. Leptos(thin)	Weakly developed , shallow soils
Lixisols	L.lixivia (washing)	Clay rich, weathered
Luvisols	L. lueve (to wash)	Clay accumulation
Nitisols	L. Nitidus (shiny)	Shiny ped faces
Phaeozems	Gr. Phaeos (dusky) Rus. Zemlia	Organic rich, dark coloured
Planosols	L.Panus (flat, level)	Seasonal surface water logging on levels
Plinthosols	Gr. Plinthos (brick)	Mottled clayey material, hardenon exposure
Podzols	Rus. Pod: (under), Zola: (ash)	Strongly bleached horizons
Podzoluvisols	Podsols and luvisols	
Regosols	Gr. Rhegos (blanket)	Loose mantle of material
Solonchaks	Rus. Sol (salt)	Salty area
Solonetz	Rus. Sol(salt), etz (strong)	
Vertisols	L.vertere (to run)	Turnover of surface soil

L = Latin, Jap = Japanese, Gr. = Greek, Rus. = Russian, AS = Anglo Saxon

Table 9 . The major soil groupings in the FAO-UNESCO- System

From S .Ellis and A. Mellor, (1995)

Soil survey staff soil orders	FAO-Unesco main soil groupings
Alfisols	Luvisols
Andisols	Andosls
Aridisols	Glacisols, Gypsisols, Solonchaks, Solonetz
Entisols	Arenosols, Fluvisols, Leptosols, Regosols
Histosols	Histosols
Inceptisols	Cambisols
Mollisols	Chernozems, Greyzems, Katstanozems, Phaeozems
Oxisols	Alisols, Ferralsols, Nitosols, Plinthosols
Spodosols	Podzols
Ultisols	Acrisols, Lixisols
Vertisols	Vertisols

Table 10. Approximate relationship between the Soil Survey Staff soil orders and the FAO-UNESCO major soil groupings

4.2 Description of the soil orders of soil Taxonomy

1.Alfisols: Wide spread soils in Western Europe, often highly fertile and rich in humus. In low-lying areas, water logging may present problems leading to compaction by heavy trafficking.

2.Andisols: Fine textured soils developed from parent material of volcanic origin. Andisols have a high ion exchange capacity and often contain considerable amounts of organic matter. Fresh, weatherable minerals from the parent material are in most cases abundant. They occur on steep slopes in mountainous regions in east Africa, New Zealand, Southeast Asia, and Central America. If poorly managed, they show a high susceptibility to erosion.

3.Aridisols: Soils developed in arid and semi arid regions. Soil water is restricted and cultivation is impossible without irrigation. Aridisols mostly possess a high content of sodium, leading to toxicity for plants and / or aggregate dispersion and consequent breakdown of soil structure.

4.Entisols: Shallow, poor soils occurring under restricted conditions of soil formation, such as in cold and exposed environments. They mostly have a low water holding capacity and poor content of organic matter.

5.Histosols: Mostly waterlogged soils, developed on wetlands. They are of different varieties. Some of them are acidic and nutrient poor, while others are very rich in nutrient organic matter. Draining of histosols for cultivation poses great environmental problems due to oxidation of organic matter after exposure to the atmospheric air and the consequent danger for wetland habitats.

6.Inceptisols: These are rather poor soils, wide spread in many regions of south Asia, Amazonian region in South America, some parts of the USA as well as in the Sahel zone in Africa. If carefully managed, Inceptisols can be successfully used to produce high agricultural yield, as it is the case in south Asia, where they are used for high yield rice production. In the Sahel zone in Africa, however, overgrazing of these soils lead to immense drought problems and erosion.

7.Mollisols: These soils are often developed on loess parent material. They are quite common in grassland – environments, such as in central North America Eurasia and Argentina. They are fertile, yet their often-lengthy exposure to drought makes them susceptible to wind erosion.

8.Oxisols: These are developed in equatorial regions. They often lack distinct horizons — a property which reflect an advanced stage of development and an intensive change due to large amounts of vegetation. They generally contain large amounts of organic matter and exhibit a clear lack of mineral substances. Oxisols are common in equatorial regions of South America, Asia, and Africa. Typical oxisols are reddish and yellowish in colour due to the iron and aluminium oxides left behind after the leaching of soluble soil constituents. Base cations are also removed by illuviation resulting in very low CEC - values.

9.Spodosols: These are coarse textured; highly leached acidic soils having a surface of poorly decomposed plant remains. They are wide spread in cool temperate regions and are rarely used for productive agricultural purposes.

10.Ultisols: Soils dominated by kaolinitic clays and containing few weatherable minerals are said to be at the ultimate or end stage of weathering or simply ultisols. These are acidic and of low nutrient status. They are common in humid warm temperate to tropical environments

11.Vertisols: These are soils containing swelling clays — a property that makes them brittle on drying, and extensively swelling when wet. These physical properties may pose management problems, when the soil is used for agricultural production. They are mostly rich in nutrients and are highly fertile. Vertisols are particularly common in Australia, India, Sudan, as well as in the southern coastal regions of the USA.

Chapter 5

Soil Degradation

5.1 Physical Degradation

5.1.1 Erosion

Soil erosion occurs when the rate of removal of soil by water and / or wind exceeds the rate of soil formation. Soil formation is generally a very slow process with rates ranging around 1 cm/ 100 - 400 years. This makes about 0.1 - 1.3 t / ha .In areas with intensive land use or deforestation, erosion may be enhanced by human activities, yet we should bear in mind that erosion in general is a natural process, that has always been taking place on earth's surface. To differentiate between natural erosion and erosion induced by human activities, we call the former background erosion. It is almost in equilibrium with soil formation (< 1.0 t / h / a) in plain areas and a little bit higher in mountain regions. The harm caused by human induced erosion is that it seriously disturbs this balance.

Many models have been proposed to quantify the extent of soil erosion. However, we should always be aware of the fact that models may differ according to geographical, climatic, and geologic conditions. The soil loss equation used by many authors provides a general tool for modelling and predicting of erosion phenomena. In this equation, soil-erosion rate is considered a function of five factors:

$$E = R.K.L.S.C.P \qquad (5.1)$$

Where E *stands for mean annual soil loss*

R stands for rainfall erosivity index

K stands for soil erodiblity index

L stands for slope length

S stands for slope steepness

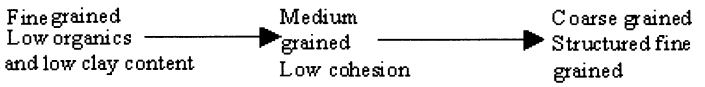
C stands for cropping factor (The ratio of soil loss under a given crop to that from bare soil)

P stands for Conservation practice factor

(Loss where contouring and strip are used to that They are not used)

Besides ignoring the human factors and socio - economic conditions, this equation as we said before cannot be used without adaptation to special hydrologic and morphological conditions. MORGAN, 1968, discusses other models.

Soil erodiblity is a measure of the soil resistance to detachment and transport. It depends particularly on soil texture, organic content, structure, and permeability. Generally, soils with low contents of clay and organic matter are more readily eroded than soils with a higher content of the same. The following rule holds for most soil types:



Higher erodibility Lower erodibility

Erosivity is a measure of the potential of the eroding agent to erode and is commonly expressed in kinetic energy. In case of rainfall, this will be related to the intensity of rainfall as well as to the size of raindrops. The most widely used in-

dex is the one known as EI_{30}. This is a compound index of kinetic energy and the maximum 30 minutes rainfall intensity. Wind erosivity indices are based largely on the velocity and duration of the wind. Erosion induced by human activities depends upon various factors such as land use, overgrazing in pasturelands and deforestation. In the developing world, however socio-economic factors add to the reasons of enhanced erosion.

Management and remediation of soil erosion can be achieved according to one of the following soil conservation strategies

:**a) Agronomic practices:** These aim to minimise the period of exposure to erosion when the soil is left bare, by encouraging the cultivation of dense vegetation cover and plant root network.

b) Soil management techniques: These aim to increase the resistance of the soil to erosion by following techniques that improve and maintain the soil structure. Such methods apply mainly processes such as mulching, reduced or zero tillage and addition of synthetic soil conditioners e.g. PVA (polyvinyl alcohol), PAM (polyacryl amide) and PEG (polyethylene glycol).

c)Mechanical techniques: The main strategy here is to reduce the energy of the eroding agent through modifying the surface topography. This is attained by geotechnical methods such as ***bunding***, terracing or constructing diversionary spillways to direct water away from areas that are highly susceptible to erosion.

Table 11 **shows** an overview of effectiveness of various soil conservation strategies mentioned above (Ellis and Mellor, 1995)

Practice	Control over					
	Rain splash		Runoff		Wind	
	D	T	D	T	D	T
Agronomic measures:						
Improving vegetation cover	#	#	#	#	#	#
Increasing surface rough ness	–	–	#	#	#	#
Increasing surface depression storage	+	+	#	#	–	–
Increasing infiltration	–	–	+	#	–	–
Soil Management:						
Fertilisers, manures, soil conditioners,						
Bio-engineering techniques	+	+	+	#	+	#
Sub soiling, drainage	–	–	+	#	–	–
Mechanical measures:						
Contouring, ridging	–	+	+	#	+	#
Terraces	–	+	+	#	–	–
Shelterbelts	–	–	–	–	#	#
Waterways	–	–	–	#	–	–

– = no control; + = moderate control; # strong control; D = detachment phase; T = transport phase .

Table11. Effectiveness of some soil conservation strategies

After Morgan, 1980

5.1.2 Compaction

Compaction is the mass reduction of soil and is generally expressed in dry bulk density, porosity, and resistance to penetration. Compacted soils are normally of a higher bulk density than comparable uncompacted ones (>1.5 g/ cm^3 compared to 1 to 1.5 g/cm^3 in uncompacted soils).

Compaction, which occurs under high vertical pressures, is related to many factors pertaining to soil properties such as texture clay content and clay mineralogy. Clays due to their sheet structures are highly susceptible to volume reduction. This leads in clay rich soils (on application of vertical high pressures) to the formation of highly compacted horizons at shallow depths (20 - 30 cm). These hori-

zons, known as cultivation pan, empede drainage and hamper the formation of plant root networks. They also delay and may completely stop germination.

5.1.3 Soil crusting

In silty soils, the impact of soil drops may lead to the formation of thin crusts on the soil surface. These lead, like in compaction, to delayed germination, increased run-off and reduced infiltration.

5.2 Chemical degradation

5.2.1 Acidification

Like all other problems of soil, acidification has an anthropogenic dimension as well as a natural one, arising from back ground factors. Natural processes that lead to acidification range from long-term base leaching and microbial respiration to nitrification and plant growth.

Base leaching attains a maximum in regions, where precipitation exceeds evapotranspiration. It is also enhanced by higher concentrations of CO_2 in rain-water and by decomposing materials such as humic and fulvic acids in the soil.

Plant growth contributes to soil acidity because plant-nutrition depends upon the exchange of nutrient base-cations for H^+ and thus increases the soil acidity. Nitri-fying bacteria also help in lowering the pH of the soil by oxidation of ammonium according to the equation:

$$NH^{+4} + 1.5\,O2 \leftrightarrows NO^{-}_{3} + 4H2\,O \qquad (5.2)$$

Anthropogenic processes leading to acidification are principally related to land use practices such as needle leaf afforstation and excessive use of inorganic Nitrogen fertilisers.

5.2.2 Salinisation and sodification

In regions, where evapotranspiration is higher than precipitation, soil water flow will be driven by capillary action in an upward direction and eventually, due to evaporation, saline precipitates will be formed in the interstitial pores of the soil, leading to salt accumulation between the soil grains. This phenomenon is known collectively as salinisation. In cases, where the parent material of the soil is rich in sodium, salinisation will also lead to the increase of sodium in the soil water leading to ***sodification*** as this is termed by soil scientists.

Saline soils are generally formed in low lying flood plains, where the water table is high, sodic soils, in contrast, occur commonly on slopes immediately above valley floors and flood plains. Both types, however, are widely observed in semiarid regions.

Classification of soils as saline, sodic or both mainly depends on physical properties such as Ec_e - the electrical conductivity of a saturated extract of the soil and ESP-- the exchangeable sodium percentage, which is related to soil acidity. Table 12 shows an outline of the soil type in relation to these two properties.

PH	Ece	ESP	Soil type
8.5 or less	4 or more	Less than 15%	Saline
8.5 or less	4 or more	15 % or above	Sodic-saline
8.5 – 10	Less than 4	15 % or above	Sodic

Table 12.Relation of soil type to salinity and sodicity

As the table shows, sodic soils are alkaline and have generally a lower electrical conductivity relative to saline ones. In contrast, saline soils have a wide range of pH- values ranging from acidic to slightly alkaline, yet they are characterised by higher electrical conductivity.

Part 2

Soil Pollution – an overview

Pollution is defined ***as the introduction by man into the environment of substances or energy forms liable to cause hazards to human health, harm to living resources and Ecological systems, damage to structures or amenity or interference with legitimate uses of the environment*** (HOLDGATE, 1979).

The major source of pollution is human activities releasing pollutants to the soil (see Figure 24) this may include point sources and /or area loadings. Pollution processes may be intentional such as landfills and spray irrigation of sewage or unintentional such as spills and leaks.

Soil pollutants are generally classified into two main types. These are ***Macropollutants,*** which normally occur or are introduced into the soil in great amounts and ***Micropollutants,*** usually occurring or introduced in small or trace quantities, yet they are in a position to modify the nature of some key biochemical reactions of the soil biota. Micropollutants can be

Toxic at very low concentrations and often involve chronic effects (TARRADELLAS & BITTON, 1997). Fig 24 summarises the main types of chemical pollutants in soils.

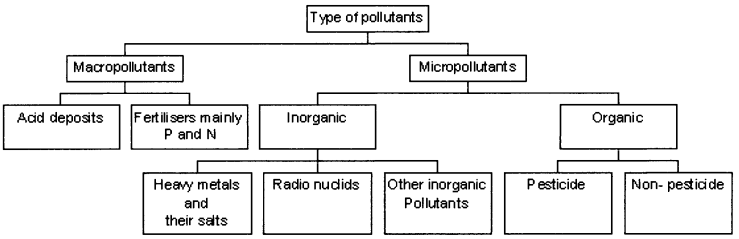


Fig. 24 . Main types of chemical pollutants in Soil

1. Macropollutants

These are largely introduced by acid rain as well as by fertilising salts and ions. They are generally defined as naturally occurring or introduced molecules of local and / or temporal distribution that cause the soil composition to deviate from the normal background values. As mentioned before, fertilisers based on compounds of plant macronutrients (e.g. N, P, and K) belong to this group. The fate of fertilisers in soils depends upon several factors, yet generally the following five possibilities represent almost all-alternative pathways of fertilisers in a given soil:

1) Plant and animal uptake
2) Adsorption and exchange in the soil
3) Leaching and loss in soluble form through drainage.
4) Volatilisation and loss to the atmosphere
5) Surface loss in solid form by erosion and runoff.

Plants generally do not recover all-nutritive compounds. The degree of recovery depends mainly on the type of fertiliser as well as on soil and plant characteristics. We should however mention, that nitrogen fertilisers are considered one of the most serious environmental problems; due to their intensive use in almost all parts of the world, leading to growing contamination of the ground water which in turn, enhance eutrophication of continental and coastal

turn, enhance eutrophication of continental and coastal waters. Phosphate fertilisers can also create serious environmental problems; since phosphates normally contain considerable amounts of cadmium and these may be concentrated in soils through intensive use of phosphate fertilisers.

According to STIGLIANI AND ANDERBERG, 1993, the concentration of cadmium has doubled in the soils of the Rhine basin between 1970 (350 g/ha) and 1990 (700 g/ha), probably due to phosphate fertilisation. Beside this, a great deal of phosphate is introduced into the soil by sodium polyphosphate-based complexing agents in detergents and by other sources such as animal excreta.

When sewage sludge is used as a fertiliser, Pollution problems would be intensified, due to presence of persistent chemicals such as residues of chlorinated pesticides and PCB's. Such chemicals can be concentrated in sludge because they (as olephilic substances) are apt to be absorbed by the hydrophobic groups of lignin and humic substances in the digested sludge. Groups thus attached to lignin or humic substances are stable to processes of chemical and biochemical degradation (LIU & CHAWLA, 1976).

2. Micropollutants

Heavy metals in soils are collectively known, if their amounts are higher than the normal background values, as micropollutants. The term "heavy metals" is generally applied for the group of metals and metalloids with an atomic density greater than $6g/cm^3$. Most of these elements are essential for plant and / or animal nutrition. Examples here are given by Boron, copper, iron, manganese, molybdenum, silicon, vanadium and zinc which are essential for plant metabolism and by copper, cobalt, iodine, iron, manganese, molybdenum, selenium and

Zinc, which are required by animals. This shows actually, that not only excesses of heavy metals in soils will cause environmental problems but also deficiencies of these may lead to serious imbalance of the soil-plant-animal system. However, excess concentrations of heavy metals in soils may be toxic.

Chapter 6

Major types of soil pollutants

6.1 Heavy metals and their salts:

Natural concentrations of heavy metals in soils depend primarily on the type and chemistry of the parent materials from which the soils are derived. However, anthropogenic inputs may lead to concentrations highly exceeding those from natural sources. Average concentrations of some heavy metals in the Earth's crust, in some sediments and generally in soils are shown in Table 13.

Element	Mean crust	Mean sediment	Average shale	Deep-sea clay	shallow water sediments	River suspended sediments	Sand stone	Lime-stone	Soil
Iron	4.1%	4.1%	4.7%	6.5%	6.5%	4.8%	2.9%	1.7%	3.2%
Titanium	0.6 %	0.4%	0.5%	0.5%	0.5%	0.6%	0.4%	0.03%	0.5%
Vanadium	160	105	130	120	145	170	20	45	108
Chromium	100(?)	72	90	90	60	100	35	11	84
Nickel	80(?)	52	68	250	35	90	9	7	34
Zinc	75	95	95	165	92	350	30	20	60
Copper	50	33	45	250	56	100	30	5.1	26
Cobalt	20	14	19	74	13	20	0.3	0.1	12
Lead	14	19	20	80	22	150	10	5.7	29
Tin	2.2	4.6	6.0	1.5	2	---	0.5	0.5	5.8
Cadmium	0.11	0.17	0.22	0.42	--	1	0.05	0.03	0.6
Mercury	0.05	0.19	0.18	0.08	--	--	0.29	16	0.1

Table 13. Elemental composition of the Earth's crust and sediments — *only Iron and manganese are in percent all other elements are in µg/g.* (Modified after SALOMONS and FÖRSTNER, 1984)

From the table, we can conclude that lead; cadmium, tin, and mercury are the most abundant metallic pollutants introduced into soil by anthropogenic activities. The mean concentration of cadmium in soils is six times its mean concentration in the crust. Concentrations of lead, mercury, and tin in soils attain double their mean values in the Earth's crust.

Relations between metal concentration in soils and their parent material were investigated by BOWEN (1979) and later discussed by MARTIN and COUGHTREY (1982).

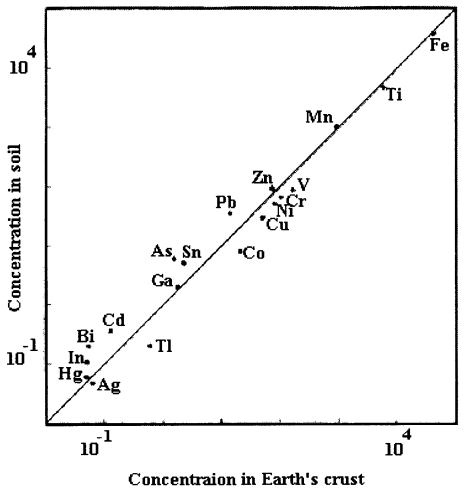


Fig. 25 . Relationship of recorded concentrations of various metals in soils with average concentrations in the Earth's crust. (Martin and Coughtrey, 1982)

Figure 25 taken from MARTIN and COUGHTREY (1982), p. 155 shows that iron, titanium, manganese, zinc, gallium, silver, and mercury show a close relationship between parent material and soil concentrations while thallium, cobalt, copper, nickel, chromium and vanadium are somewhat depleted in soils relative to parent rock. In the mean time indium, bismuth, cadmium, tin, and arsenic seem to be enriched in soil relative to the original material. Most studies dealing with vertical distribution in soil profiles report a tendency of several metals to be concentrated in the upper layers or horizons of many soils of open and woodland. This was reported by BURTON & JOHN (1927), who studied the vertical distribution of lead,

cadmium, copper, and Nickel in some soils in Wales, as well as by WILKINS (1978), who reported higher concentrations of lead in surface soil layers of 500 sites in the U.K.

The surface enrichment of metals in soils may be the result of fallout of wind-transported pollutants, concentration of metals by plants from lower horizons or chemical complexing of metals by organic compounds.

6.2. Other inorganic pollutants

Elements like Aluminium, Beryllium, and Fluorine are considered as environmental pollutants if they occur in excessive quantities in soils. Attention was drawn to aluminium, when in July 1988; 20 tons of aluminium sulphate was accidentally introduced into the water supply of the Camelford District of Cornwall. This led to serious toxic effects on fish and other aquatic biota. Excessive concentrations of aluminium as well as fluorine in soils lead to abnormal concentrations of these two elements in some plants. The tea plant is an example of natural accumulators of aluminium as well as fluorine. Aluminium is brought in connection with some diseases such as Alzheimer (**senile dementia**) or kidney dysfunction. Since hydrous aluminium oxide is used for water treatment, the World Health Organisation (WHO) set a tolerance level of 200 µg /l for the concentration of Al in drinking water[1]. Fluorine, also, despite of being added to many public water supplies to improve dental health, can at concentrations higher than 3 - 6 mg/l in drinking water, cause a toxic condition called **skeletal fluorosis**, which deforms the limbs. Crippling occurs at concentrations higher than 10 mg /l.

6.3 Radionuclides

Since 1954, there has been an increasing pollution of soils with radioactive nuclides. These are natural or technically produced elements with unstable nuclei

[1] WHO, (1993): Guidelines for drinking water quality, Vol.1, Recommendations, WHO, Geneva.

that spontaneously alter their compositions through radioactive decay in a series of successive nuclear reactions, ultimately leading to a stable configuration. Decay of unstable nuclei takes place according to one of the following mechanisms:

a. Gamma decay: Emission of gamma ray
b. Alpha decay: Emission of alpha particle
c. Beta decay: Emission of electron by nuclear neutron
d. Electron capture: Capture of electron by nuclear proton
e. Positron emission: Emission of positron by nuclear proton

The rate at which the nuclei of a sample decay is known as the ***activity*** of the considered radioactive nuclide. If (N) is the number of nuclei present in the sample at a given time, its activity R would be given by : $R = - dN / dt$

The SI unit of activity is named after Henri Becquerel, who discovered radioactivity in 1896.

1Becquerel = 1 Bq = 1 event / s. In practice, however the activities encountered are so high that it is more appropriate to use MBq (10^6 Bq) and GBq (10^9 Bq).

The ***Curie*** is the traditional unit of activity. It is arbitrarily defined as:

$$1 \text{ curie} = 1 \text{ Ci} = 3.70 \times 10^{10} \text{ events /s} = 37 \text{ GBq}$$

1 Ci is nearly the activity of 1 g of radium $_{88}R$ (few % less).

The majority of radioactive nuclides occurring in nature are members of exactly four radioactive series, with each series consisting of a succession of daughter products all ultimately derived from a single parent nuclide. The reason for this is that α decay reduces the mass number of a nucleus by 4. Accordingly, nuclides, the mass numbers of which, are all given by: A *(Mass number)* = 4n where n is an integer, will be in a position to decay into one another in descending order of mass number. The same holds for nuclides with mass numbers

$$A = 4n + 1 \text{ , } A = 4n+2 \text{ and } A = 4n+3$$

This allows them to have exactly four series named after their parent nuclides. Table 14 summarises the data of the four series.

Mass numbers	Series	Parent	Half-life. yr.	Stable end product
4n	Thorium	$^{232}_{90}Th$	1.39×10^{10}	$^{208}_{82}Pb$
4n + 1	Neptunium	$^{237}_{93}Np$	2.25×10^{4}	$^{209}_{83}Bi$
4n + 2	Uranium	$^{238}_{92}U$	4.51×10^{9}	$^{206}_{82}Pb$
4n + 3	Actinium	$^{235}_{92}U$	7.07×10^{8}	$^{207}_{82}Pb$

Table 14 . The four radioactive series

Apart from artificial sources of radioactivity in soils, natural sources of radionuclides such as cosmic radiation or terrestrial radiation derived from radioactive decay of some elements in the earth's crust contribute to the radiation emission from landscapes. It is estimated that natural radioactive emissions from soils have intensively increased during the last 200 years since the beginnings of the industrial revolution. This increase is mainly due to displacement of sediments in the upper crust by mining activities, road building, and other construction activities. Also industrial activities such as cement production, and metal treatment industries intensify the release of radionuclides into the atmosphere and the upper soil. The more or less even distribution of background values of radioactivity observed in certain regions is due to the absorption of naturally occurring radioactive particles by humans and living organisms through water air and nutritive substances. Figure 26 shows these relations in a schematic way. The intensity of background radiation (radiation from natural sources) in a given region depends generally on the geological conditions as well as on the topographic relations prevailing in a given region. However, soil pollution by artificially produced radioactivity occurs through handling, transporting, testing, and using of nuclear materials in warfare and industry. The main sources are nuclear power stations, atomic tests, belligerent activities, and major nuclear accidents.

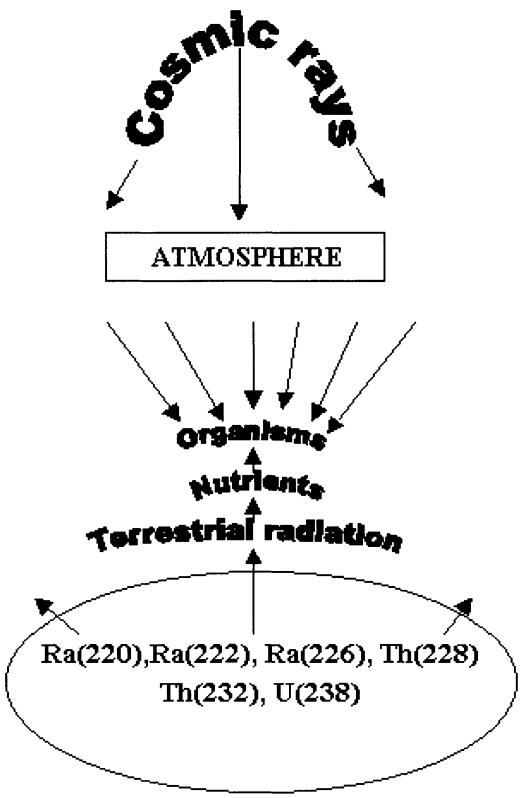


Fig. 26 . Natural sources of radioactivity

6.4 Weapon tests and belligerent activities

The distribution of nuclear debris has increased on a worldwide scale since thermonuclear devices first contaminated the Earth's atmosphere after the nuclear bombardment of Hiroshima and Nagasaki by the American air force at the end of Second World War.

PIERSON (1975) studied the abundance of ^{90}Sr in fallout from the atmosphere from 1955 to 1970. The study revealed (Figure 27) that the distribution curve represents three phases: a phase up to 1959, another from 1961 to 1962 and the third one from 1966 – 1970. Peaks of deposition rate are observed immediately after the first and second phases and a levelling during the third phase when the rate of injection into the stratosphere has been in fortuitous balance with the rate of depletion of the reservoir.

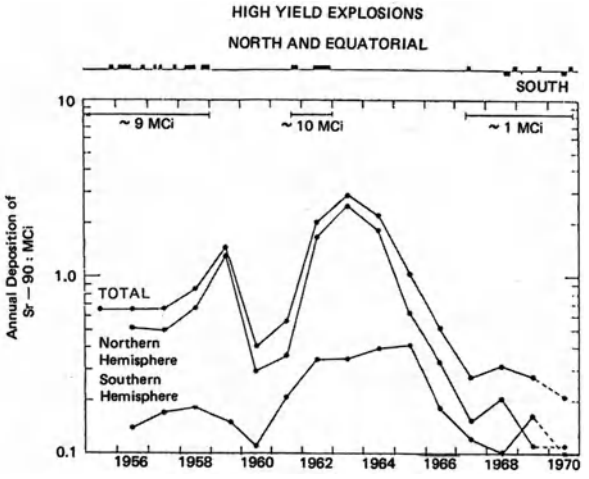


Fig. 27 . Annual deposition of ^{90}Sr in the period 1955- 1970 (PIERSON, 1975)
After FORTESCUE, (1980)

A more detailed study was the one carried out by the Federal Agency of Environment in Berlin- Germany *" Umweltbundesamt – Berlin."* The study representing a series of measurements of atmospheric radioactivity between the years 1958 and 1992 (Figure 27) shows clearly a relation between the average daily radioactivity in the atmosphere and surface nuclear tests. The year 1963 for example was a

year of exceptionally high radioactivity in the atmosphere. This is interpreted to be a result of the nuclear tests of the years 1961/ 1962 in which highly explosive Hydrogen Bombs were tested on surface. The retardation of one year between the increase of radioactivity in Berlin and the tests can be understood if we consider the residence time of the debris in the upper atmosphere. In the 1970's, the higher values of radioactivity can be attributed to the Chinese and French nuclear tests. In the 1980's, first came a period of decreasing atmospheric radioactivity, where we observe for example that the radioactivity in 1963 was thousand times as high as that of the years 1982-1985. Later in the year 1986 an increase of radioactivity up to the level of the nuclear tests years (1961/1962) was caused by one single incident - namely the major accident of Chernobyl.

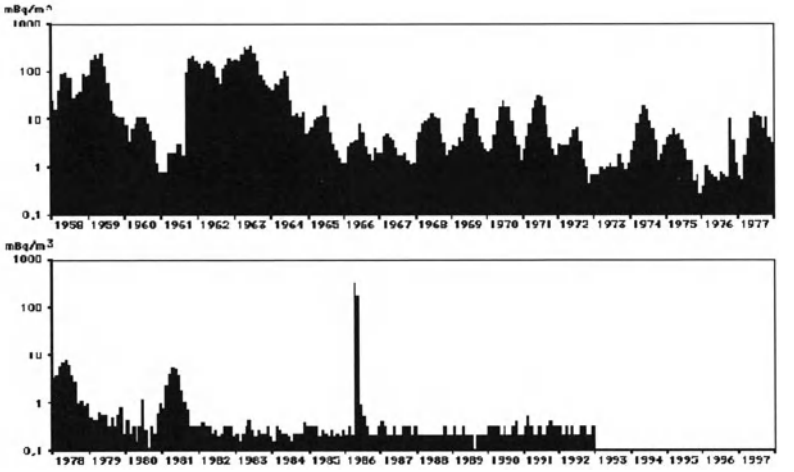


Fig. 28 . Radioactivity in soils between the years 1958 and 1992 (Umweltbundesamt Belin)

6.5 Major nuclear accidents

Between the years, 1957 and 1993, major nuclear accidents have occurred and contributed to the pollution of soil and atmosphere with nuclear debris. Some of these accidents are listed in table 15 (ALWAYS & AYRES, 1997) together with their level of risk as given by the scale of the International Atomic Energy Agency. The scale is from 1 to 7 in increasing order of risk.

Level	Nuclear accident
7	Chernobyl, 1986
6	Ural mountains, waste explosion, 1958
5	Fire at Windscale (Sellafield), 1957 and Three mile island, USA, 1979
4	Fatal accidents at Los Alamos, Wood River, and Idaho Falls (1945-64)
3	Unauthorised release at Vandellos, Spain, 1989,Tomsk-7, Russia, 1993
2	Incidents at UK Magnox stations, 1968,1983,1989
1	Management deficiencies in waste reprocessing, Windscale, 1986

Table 15 .some nuclear accidents as placed on the LAEA scale of risk

(After ALWAY & AYRES, 1997)

Inspection of table 15 shows that the accident in Chernobyl was the most serious and perhaps the most investigated, due to its proximity to many European centres with highly sophisticated research facilities. Accordingly, the Chernobyl disaster will be discussed here in some detail.

On The 26th of April 1986, the core of one of the reactor-blocks in Chernobyl caught fire causing a great increase in temperature and emission of radioactive nuclides reaching an altitude of up to 1500 m in the atmosphere. As a result and together with high wind speed, radioactive debris was dispersed over an immense area in central and south Europe thousands of kilometres away from Chernobyl. Table 16 shows the distribution of ^{137}Cs and ^{131}I in some of these countries together with their distance from the region of the catastrophe.

Countryaffected	Distance from Chernobyl (Median km)	Activity in Soil (kBq/m^2)	
		$^{137}Cs^a$	^{131}I
Austria	1250	23	120
Norway	2000	11	77
UK	2250	1.4	5.0
France	2000	1.9	7.0
Ireland	2750	5.0	7.0

[a] With ^{134}Cs

Table 16 . Spread of ^{137}Cs and ^{131}I from Chernobyl

(Umweltbundesamt, Berlin)

During the first two days, prevailing easterly winds carried the nuclear debris mainly to Hungary and Austria and on the 2nd of May, as wind changed its direction to the south also parts of Germany were affected (Figure 28). Measurements of atmospheric radioactivity in Berlin between the 27th of April and the 12th of May 1986 showed that the accident had brought the burden of radioactive nuclides in the atmosphere to maximum values, comparable to those measured in the years 1962/1963 (Figure 29).

Washout by rainfall brought additional load of radionuclides to the soil. Measurements after the first rainfall following the accident in some stations in Berlin showed that additional burdens of ^{137}Cs, depending on precipitation intensity, varied between 860 and 5600 Bq / m^2. Additional burdens of radioactivity were between 430 and 2600 Bq / m^2.

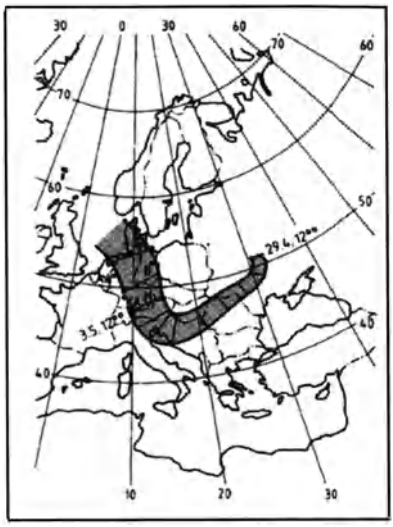


Fig. 29 . Diffusion of Emissions on 29 April 1986 at an Altitude of 1,500 m. Lines Marked in the Shaded Area Indicate Intervals of 12 Hours. NEIDER, R. (1986)

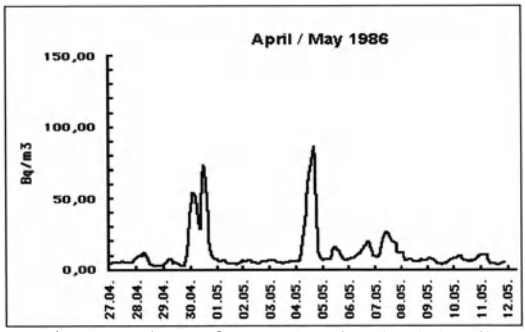


Fig. 30 . Daily maximum values of natural and artificial radioactivity in the air from 27 April to 12 May 1986 (Umweltbundesamt, Berlin)

Chapter 7

Sources of Soil Pollution

Pollution of soil may arise from a wide range spectrum of sources. These might be discrete point sources or diffuse sources and the pollution process itself may be deliberate as in fertilisation processes or following an accident as in the case of radio nuclear accidents or oil spills. Figure 31 summarises the main sources of soil pollution.

7.1 Pollutants of agrochemical sources

Pollutants from agrochemical sources include fertilisers, manure, and pesticides. To these, we may add the accidental spills of hydrocarbons used as fuels for agricultural machines. As it was mentioned before, the main pollution effect caused by fertilisers and manure is the introduction of heavy metals and their compounds into the soil. Examples of these are the introduction of As, Cd, Mn, U, V and Zn by some phosphate fertilisers or the soil contamination with Zn, As and Cu when poultry or pig manure materials are used. Organic compounds used as pesticides, however, are of more far reaching effects for the whole community depending on soil ecology. The use of pesticides in Agriculture has been steadily increasing in the last 40 years. Figure 32 shows that except for a short decrease in worldwide sales at the beginning of the 1990's, the market is growing since 1992 (TARADELLAS et.al.1977). According to the British Food and Environmental Act, 1985, a pesticide is defined as " any substance or preparation prepared or used for any of the following purposes:

a) Destroying organisms harmful to plants or to wood or other plant products
b) Destroying undesired plants
c) Destroying harmful creatures

Pesticides applied to plants or harmful organisms living on soil may (by successive adsorption and elution) move down the soil column, where they would be bound within the latticework of clay minerals or adsorbed on to soil organics. They may also join the soil water or the gas phase in the interstitial space, if the active ingredients are of suitable volatility.

The degree of penetration or sorption of pesticides into the tissues of their living targets whether animals or plants, provides one of the basis for their classification. According to this, pesticides that remain as superficial deposits exerting only a local contact action are known as ***contact pesticides***, while those with a local internal movement within the cuticles of leaves or the epidermis of animals are known as ***quasi-systemic***. Pesticides that directly penetrate through the outer layers and are transported around the organisms of their targets are classified as ***systemic*** pesticides.

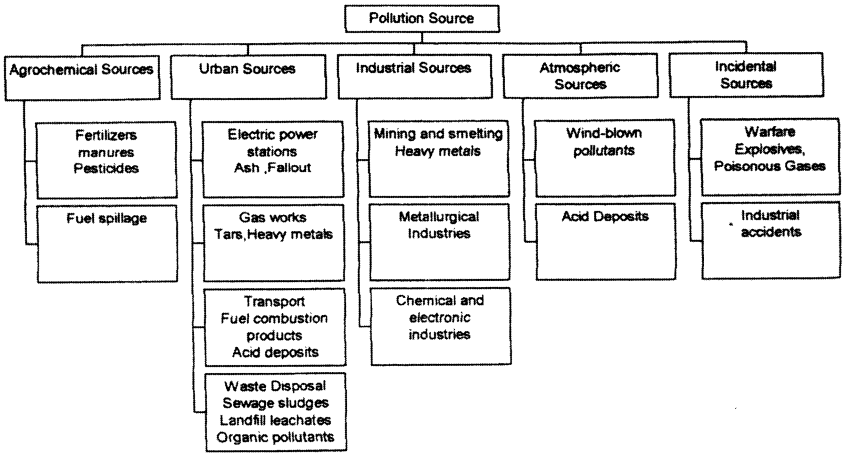


Fig. 31 . Sources of soil pollution

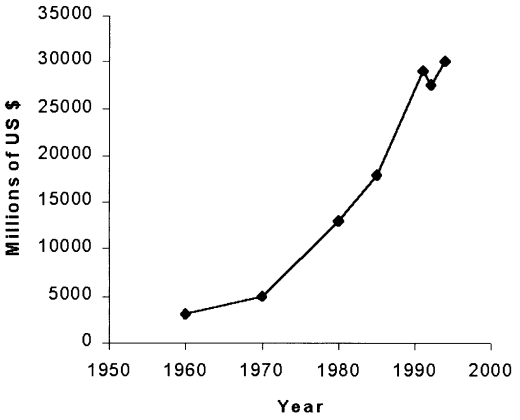


Fig. 32 . Evolution of pesticide market in millions of U.S $ between 1960 and 1994

However, pesticides are generally classified into the following groups according to their mode of action and the specific organisms they are used to combat:

1) Insecticides: These are chemical compounds used to kill insects, whether specifically for a given type or generally for a variety of insects

2) Herbicides are chemicals used to combat or suppress the growth of all or certain types of plants

3) Fungicides are chemicals used to kill or suppress the growth of all kinds or of a certain type of fungus.

7.1.1 Insecticides

The worldwide use of insecticides has been greatly increasing in Agriculture and other fields since the end of Second World War. Nowadays, there is a great number of commercial formulations for these products, yet they belong principally to four groups of organic compounds, providing a fundamental scheme for their classification. These are the organophosphorus compounds, the organochlorines, the carbamates, and the pyrethroids.

A) Organophosphorus compounds are technically nerve poisons, the basic technology of which was developed during Second World War in Germany and Brit-

ain. They are used in many different ways in Agriculture and animal hygiene. Some of them are used as fumigants; others are contact poisons, while still others are used as systemic pesticides.

Two prominent examples of this group are tetraethyl pyrophosphate –TEPP (Figure 32 a) and the warfare agent sarin (Figure 33 b) both of which are highly toxic for mammals.

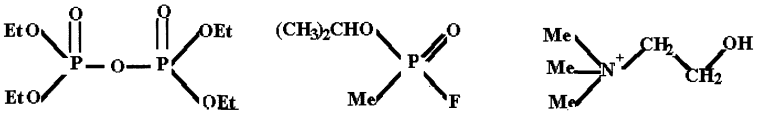


Fig. 33 . Organophosphorusn pesticides

The toxic action of organophosphates arises from their disruption of the nervous system by inhibiting the enzyme cholinestrase, responsible for the establishment of nervous transmission. To this category, we may add a group of organophosphates with an ester function (Phosphorothionates) known as proinsecticides. These are only toxic to animals producing high levels of special enzymes, known as mixed function oxidases (MFO).

Most organophosphorus pesticides have the general structural formula shown in figure 33 a, 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. Table 17 taken from HASSAL, 1982 shows 6 possible variations of the general formula with examples of the commercial products related to each of them.

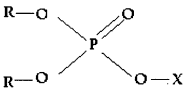
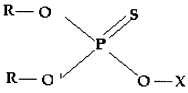
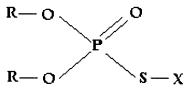
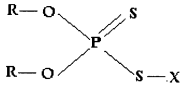
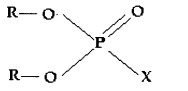
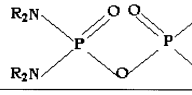
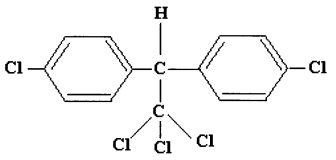
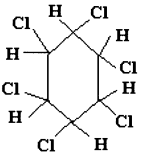
Compound	Structural formula	Example (commercial product)
1. Organophosphates		Chlorfenvinphos, Dichlorvos, Mevinphos Phosphamidon
2. Thionphosphates (Phosphothionates)		Bromophos, Diazinon, Fenitrothion Parathion, Primiphos (methyl and ethyl)
3. Thiophosphates (Phosphothiolates)		Demiton- S-methyl, Oxydemeton-methyl, Vamidothion
4. Dithiophosphates (phosphorothiolothionates)		Azinophos-methyl, Dimethoate, Disulfoton, Malathion, Menazon, Phorate.
5. Phosphonates		Trichlorphon, Butonate.
6. Pyrophosphoramides		Schradan

Table 17 . Chemical groups of organophosphorus insecticides after Hassal (1982)

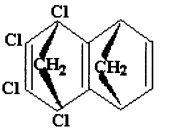
B) Organochlorines: During World War II, a group of organochlorine compounds were found to be very effective in controlling pests responsible for diseases such as malaria and yellow fever. These compounds being cheap, easy to produce and (at that time thought to be) safe to man and other warm-blooded animals, were hailed as the best pesticides ever found by man. They belong to three chemical families: the DDT family (Figure 34a), the BHC- family (Figure 34b) and the cyclodiene family (Figure 34 c).



a) DDT-Family (e.g) DDT)



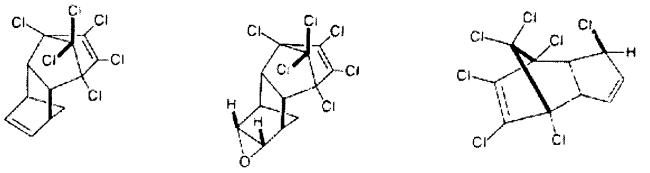
(b) BHC-Family Only γ-BHC



(c) Chlorinated cyclodiene family e.g. Aldrin

Fig. 34 . The three families of organochlorine pesticides

DDT (Dichlorodiphenyl trichloroethane) was first described by OTHMAR ZEIDLER in 1874, yet its use as insecticide was established 60 years later by the Geigy chemical industries. The principal representative of the BHC family is often called Lindane (after van der Linden, who discovered some of the BHC isomers). It is prepared by adding three molecules of chlorine to benzene activated by UV irradiation and is superior to DDT in controlling soil pests. Aldrin (Figure 35 a), Dieldrin (Figure 35 b) and heptachlor (Figure 35 c) are stereochemically related compounds belonging to the cyclodiene family, which were effectively used for controlling locusts.



(a) Aldrin **(b) Dieldrin** **(c) Heptachlor**

Fig. 35 . Members of the cyclodiene family

Despite the fact that organochlorine compounds have been effectively used in the past in agriculture and hygiene, the later discovery (in the late fifties) of their persistence in the environment and their indiscriminate killing of beneficial as well as harmful insects, has led to an emotional discussion about their use. This ended with a ban on their application in many developed countries. The ban decision is justified by the fact, that the stability resulting from the inactive nature of the C–C, the C–H and the C–Cl bonds forming these compounds make them very persistent and hence dangerous for humans and animals. To this, we should also add the observation that due to their partition coefficients that favour the accumulation in biolipids, they tend to accumulate in body lipids of organisms exposed to their action. At present, organophosphorus and carbamate insecticides are largely replacing organochlorines.

C. Carbamates: These are derivatives of carbamic acid NH2 – COOH, of which about 40 commercial compounds, used as insecticides, molluscicides, or nemato-

cides, are on sale. Their toxic effect, like that of the organophosphates, arises from their disruption of the nervous system by inhibiting cholinesterase. Carbamates used as insecticides possess the general structure shown in figure 36 However, they may be classified according to their mode of action and chemical structure into three sub-groups as shown in figure 37.

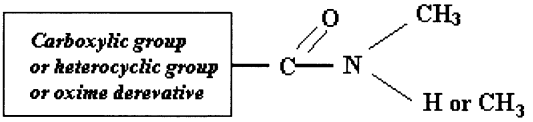
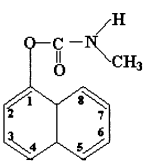


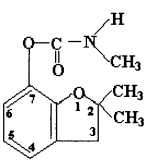
Fig. 36 . General structure of the carbamate insecticides

Carbamates are directly applied to the soil to control nematodes and snails or in order to be absorbed by root systems of weeds, where they operate as systemic pesticides after being translocated within the plant. Toxic and health damaging effects of carbamates insecticides have been reported by many authors e.g. ANGER & SETZER (1979).



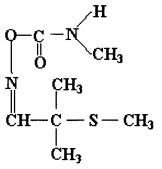
Carbaryl

Subgroup1:
Aryl N-methyl carbamates
example: 1-naphthyl N-methyl carbamate



Carbofuran

Subgroup2:
Heterocyclic mono or dimethyl carbamates.
example:
2,3-dihydro-2,2 dimethyl benzofuran-7-yl N-methyl carbamate



Aldicarb

Subgroup3:
Oxymes, the OH-group of which has been carbamylated.
example:
2-methyl-2(methylthio) propionaldehyde O-(methyl carbamoyl) oxime

Fig. 37. Subgroups of carbamate insecticides

According to HASSAL (1982), mild carbamate poisoning can affect behavioural patterns, reducing mental concentration and slowing the ability to learn. Protein deficiency accentuates these symptoms. This renders their effect highly precarious; especially for poor farm workers and children in countries of the third world, where food shortage and protein lack is always a result of the bad economic conditions.

Beside the above-mentioned synthetic carbamates, some naturally occurring carbamate e.g. ***Physotigmine*** were used in studying the toxic effect of carbamate compounds on insects and other organisms. Physotigmine is extracted from the Calabar bean

D. Natural and synthetic pyrethroids:

Pyrethroids are originally quite effective natural pesticides, which were extracted from ***Chrysanthemum cineraria folium*** – a plant that was for centuries grown in Persia specially to obtain these substances. Nowadays the main producers of natural pyrethrum are Kenya and Tanzania. This is simply because Pyrethrum plants give larger yields of pyrethrin, when grown on volcanic ash at high altitudes (1500 – 3500 m) in tropical zones. Natural pyrethroids extracted from the dried pyrethrum flowers comprise four active ingredients known as pyrethrins I and II and cinerins I and II. The elucidation of the structure of natural pyrethroids made it possible to produce synthetic substances related to the pyrethroids and possessing similar or even higher insecticidal characters than the natural compounds. Some of these are preferred due to their lower toxicity, less persistence and higher stability to light. Synthetic pyrethroids belong to four groups known as: the alethrin, bioresmethrin, permethrin, and the fenvalerate groups.

E. Some other natural insecticides:

Beside natural pyrethroids, some other plant-derived compounds were used as insecticides in the Far East and South America. Of these, we may mention nicotine, [1-methyl-2 (3′-pyridyl) pyarrolidine] (Figure 38) and rotenone.

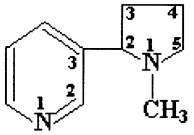
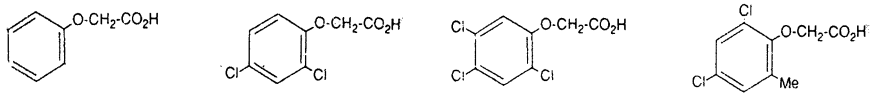


Fig. 38 . Nicotine structure

7.1.2 Herbicides

The use of chemical weed control agents is a disputable problem among environmentalists since selectivity of these agents has never been completely achieved. After 1945, however, a considerable number of commercial organic compounds with some degrees of selectivity have replaced the older traditional herbicides such as copper sulphate solutions; dilute sulphuric acid and petroleum oil. Main herbicides belong to one of the following groups:

1.Organochlorine compounds In this group, one encounters principally, derivatives of phenoxyacetic acid (Figure 39 a); such as 2,4 – dichlorophenoxyacetic acid, known as 2,4-D (Figure 39 b); 2,4,5 trichlorophenoxyacetic acid, known as 2,4,5 T (Figure 39c) or 2-methyl-4, 6-dichlorophenoxyacetic acid, known as MCPA (Figure 39 d).

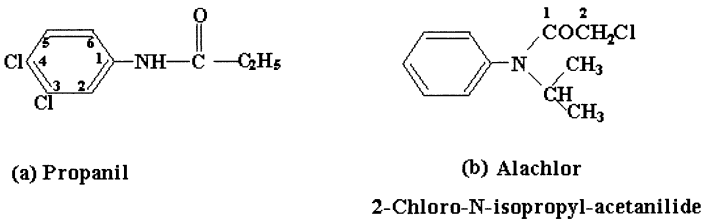


(a) Phenoxy-acetic acid **(b) 2,4-dichlorophenoxy-aceticacid** **(c) 2,4,5- Trichlorophenoxy-acetic acid** **2-methyl-4,6 dichloro phenoxyacetic acid**

Fig. 39 . Organochlorine compounds

Organochlorine derivatives of phenoxyacetic acid mimic natural growth hormones in weeds, leading to over-production of RNA and death of the plants because their roots will not be able to deliver sufficient nutrition to support their abnormally induced growth. The US army sprayed during the war against Vietnam millions of acres of woodlands with an equal mixture of 2,4-D and 2,4,5- T code-named Agent Orange, causing persistent environmental damage.

Beside derivatives of phenoxyacetic acids, derivatives of aniline major high among organochlorine herbicides. Examples of these are Propanil (Figure 40a) and alachlor (Figure 40 b).



(a) Propanil

(b) Alachlor

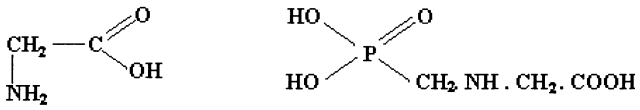
2-Chloro-N-isopropyl-acetanilide

Fig. 40 . Aniline derivatives used as organochlorine herbicides

Both propanil and alachlor are organochlorine derivatives of acetanilide (Figure 39a). The US EPA prohibited use of alachlor in 1987 due to its carcinogenic character.

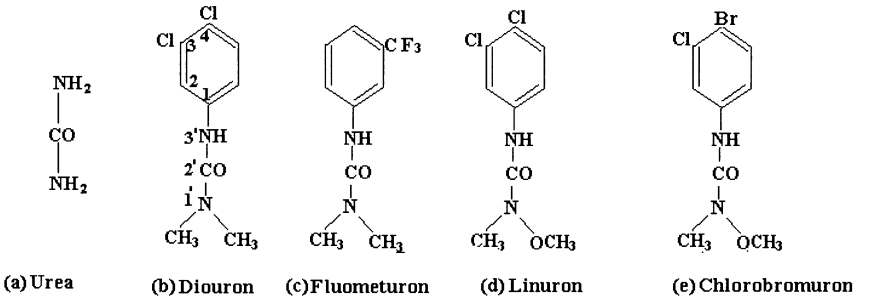
2. Organophosphorus Herbicides:

Organophosphorus herbicides, known as glyphosates, due to their effectiveness against weeds and their non-carcinogenic character, are widely used in agriculture. A glyphosate (Figure 41 b) is a modified glycine (Figure 41a). It mimics glycine and hence can be accepted by peptides, where it works as a synthesis inhibitor. It has a half-life in soil of about 60 days and is excreted by mammals unchanged.



a) Glycine *b) Glyphosate*

Fig. 41. Glycine and its glyphosate derivative



(a) Urea
(b) 3'- (3,4-dichlorophenyl)- 1,1' -dimethyl urea
(c) 3'- (3- trifluoromethylphenyl) - 1',1' dimethyl urea
(d) 3'-(3,4- dichlorophenyl)- 1'-methoxy-1'-methyl urea
(e) 3'-(4-bromo-3chlorophenyl)-1'-methoxy-1'-methyl urea

Fig. 42 . Urea herbicides (Ureides)

Derivatives of carbamic acid

Examples are several derivatives of urea (Figure 42 a) such as Diuron (42b), Fluometuron (42c) Linuron (42d), and Chlorobromuron (42e)

4. Triazine derivatives:

Triazines are compounds in which 3 nitrogen atoms are incorporated into the benzene ring (Figure 43 a). Derivatives of these, like atrazine (Fig 43 b) and simazine (Figure 43 c) are used as systematic weed control agents of relatively low toxicity for mammals.

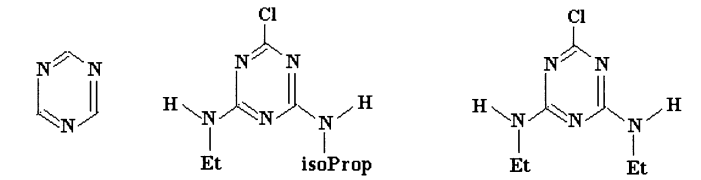


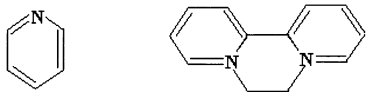
Fig. 43 . Triazine derivatives

Water solubility of both atrazine and simazine is enhanced by enzymatic action of soil organisms leading to replacement of the chloro-substituent by a hydroxyl

group. The same was also found to occur through dealkylation of these compounds by UV radiation. Accordingly, and after discovering that the use of triazine base herbicides polluted water supplies in the Thames Valley, the UK- government has banned use of both compounds. Some EU countries have also done the same.

5. Pyridine derivatives:

In pyridine, one nitrogen atom is incorporated into a benzene ring (Figure 44a). Bipyridyl (Figure 44b) known under the name Diquat is used as systemic herbcide.



(a) Pyridine (b) Diquat

Fig. 44 . Pyridine derivatives

6. Aliphatic compounds:

There are few aliphatic compounds, used as herbicides. Of these, the product known under the commercial name ***dalapon*** (Figure 45) was found useful in controlling the couch grass. It is not persistent; because of being readily hydrolysed to pyruvic acid (figure 166)

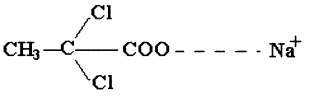


Fig. 45 Dalapon

7.1.3 Fungicides

Fungicides comprise a group of chemicals ranging from inorganic to organic compounds of comparable structures as the foregoing pesticides. Of these, the followings are examples:

1. Inorganic and organic compounds of heavy metals

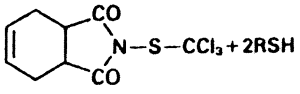
Examples are mixtures of copper bearing inorganic compounds (e.g. Bordeaux mixture) or organometallic compounds such as organotins, which may be represented by Tributyltinacetate (Figure 46a) or triphenyltinacetate (Figure46b)

(a) Tributyltinacetate (b) Triphenyltinacetate

Fig. 46 . Structure of some organotins

2.Derivatives of phthalic acid

Example here is given by phthalimide (figure 47), which is a compound produced by the reaction of phthalic acid with ammonia. This is marketed under several commercial names (e.g. Captan, Captafol).



Captan

Fig. 47 . Phthalimide

3. Benzimidazoles:

Benzimidazole (Figure 48), a compound related to histamine, which is known for its blood pressure reducing character, is used as a systemic fungicide. The pen-

tagonal ring in histamine is known as imidazole ring. Its fusion with a benzene nucleus gives the benzimidazole.

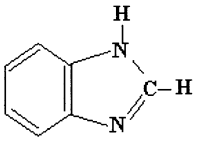


Fig. 48 . Structure of Benzimidazole

4. Derivatives of barbituric acid

Barbituric acid (Figure 49) gives on treatment with phosphorus oxychloride followed by reduction with hydroiodic acid a group of compounds known as the pyrimidines. These are used as fungicides.

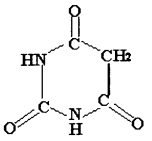


Fig. 49 . Structure of Barbituric acid

7.1.4 Fuel spills in farms:

Fuels through accidents or careless handling in farms may pollute soils. Fuels used in Agriculture machines are mostly petroleum products that may contain organic contaminants like benzene; heptane, hexane; isobutane, toluene, phenol, tetraethyl, and tetramethyl lead *and* zinc (anti knocking compounds). Soil pollution by petroleum hydrocarbons will be discussed later under a separate heading.

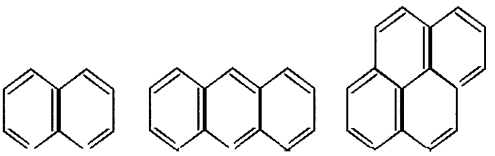
7.2 Soil pollutants of urban sources:

Soil pollution by materials of urban sources is a problem as old as urbanisation itself. Archaeological studies show that, through construction and demolition of

domestic concentrations and public centres of human activities (temples, sport arenas. etc.), a great deal of polluting substances were always dumped or disposed of on soils, resulting in their physical or chemical degradation. The damage of soil in those ancient days was of limited scale, yet since the beginnings of the industrial revolution it has taken dimensions that are hardly controllable in modern times. According to BRIDGES (1991), considerable quantity of construction materials (concrete, gypsum, asbestos...etc.) may come into contact with the water table and ultimately lead to changes in the chemistry of soil waters. The main sources of urban soil pollution, however, are power generation emissions, releases from transport means and waste disposal.

7.2.1 Power generation emissions:

Emissions from power generation plants include Co_x, NO_x, SO_x, UO_x and polycyclic aromatic hydrocarbons (PAHs, see figure 50) from coal-fired power stations and radionuclides from nuclear power plants. These may be introduced into the soil either directly as fall-out (dry deposition) or in a wet form after being dissolved in precipitation.



Naphthalene *Anthracene* *Pyrene*

Fig.50. Some polycyclic aromatic hydrocarbons (PAH's)

A number of organic and inorganic soil pollutants including tars, CN, spent iron oxides Cd, As, Pb, Cu, sulphates and sulphides may be released in sites of abandoned gas stations. The most abundant radionuclides found in soils, originating from nuclear power generation are ^{137}Cs and ^{134}Cs.

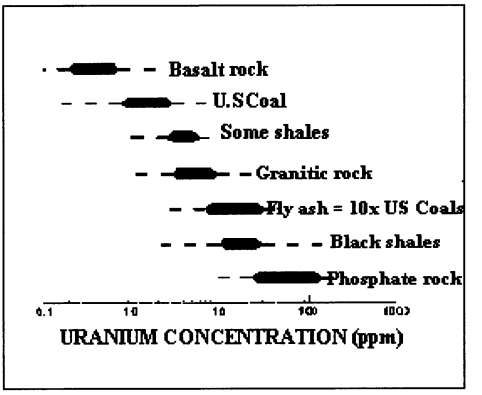


Fig. 51. Uranium in fly ash as compared to other Earth materials

In soils with a high CEC (Cation exchange capacity) and pH-values near 7.0, these radionuclides are normally absorbed onto clays and humic materials.

Electric power generation in coal-fired power plants contribute not only to addition of inorganic and organic pollutants to the soil through air born fly ash, but it also adds to the radioactive nuclides content of the soil. In the USA, many studies have been done on the concentration of uranium in fly ash, showing that uranium in fly ash may reach concentration of between 1-10 ppm (see figure 51)[2]. Despite the fact that, these concentration may not represent severe danger to individuals and life in general, chemical conditions under which uranium may be leached from fly ash and be concentrated in soil are still not completely understood.

Studies done in Germany show a high potential of pollution by heavy metals through deposition of flay ash on soils. Table 18 shows the contribution of heavy metals in emissions from coal-fired power stations to the content of the same in all emissions in the western part of the country

[2] Central Region Energy Team- Fact Sheet FS-163-97, October 1997

Pollutant	Contribution in (Wt. %)	
	1982	1990
As	38	27
Cd	7	7
Cr	12	4
Cu	22	8
Hg	11	14
Ni	5	4
Pb	8	1
Se	1	1
Zn	7	6

Table 18. Contribution of heavy metal emissions from coal-fired public power plants to total emissions in the western part of Germany

7.2.2 Soil pollution through transport activities:

Transport activities in and near urban centres constitute one of the main sources of soil pollution, not only because of the emissions from internal combustion engines and petrol spills, but rather from these activities and their accompanying changes as a whole. To explain this, we should consider the breath taking increase in high way construction projects all over the world. One also should not ignore the secondary or satellite land use activities attracted to the sites of newly constructed highways such as gas stations, moles, shopping centres and all other services offered to car owners and commuters.

In fact, the impact of high ways on the hydrogeologic environment may cause considerable transformations on the terrain leading to physical and/or chemical degradation of soil. According to RICHARD R. PARIZEK, 1973, these may be summarised in the following:

a) Water quality changes due to sediment damage to surface and ground water supplies.

b) Pollution due to high way activities such as accumulations of oils, chemicals, and hazardous substances through accidental spills.

c) Pollution resulting from maintenance activities requiring the use of chemicals such as weed and insect control compounds as well as salts used to control the formation of ice in winter.

d) During highway construction road, cuts may expose pyrite-bearing strata that in turn would produce acid and other chemically polluted waters.

e) Enhanced new economic activities attracted to the highway site may result in producing huge amounts of roadside litter and debris.

The principle contribution of transport activities to soil pollution is caused by emissions from vehicles and aeroplanes; especially supersonic ones. Emissions from transportation means driven by internal combustion engines, include oxides of carbon, nitrogen and sulphur as well as some heavy metals. These pollutants may be transported to the soil by deposition of particulate matter or by being washed from the atmosphere. Table 19 shows, as an example, the yearly amount of pollutants emitted by vehicles in the region of Berlin- Germany (reference year 1993).

Emission	Total weight in tons
Hydrocarbons	25,461.7
Benzene	1,279.5
Carbon dioxide	3,424,519.4
Carbon monoxide	144,196.5
Nitrogen oxide	19,024.8
Exhaust particles	1,135.5
Abrasion dust (tyres)	1,290.9
Elemental Carbon (exhaust + tyre abrasion dust)	873.5
Sulphur dioxide	1,398.2

Table 19 Yearly total emissions by vehicles (motorcycles are not included) in the region of Berlin: Total transportation capacity 12,151.8 million vehicle-km /year and total fuel consumption of 1,138,046.1 tons (reference year 1993)*

* Source : Umweltbundesamt ,Berlin

Sulphur and Nitrogen oxides on oxidation by photochemical reactions in the atmosphere react with water droplets in the air to produce strong acids such as HNO_3 and H_2SO_4. These acids produce by reaction with bases (existing in the atmosphere mainly as particulate matter) a mixture of basic and acid radicals that dissolve in the rain, forming what has been known as the phenomenon of acid rain, causing great devastation in soils and plants.

As the concentration of these radicals together with carbon dioxide in surface and pore water approaches equilibrium a great deal of change in the chemical environment of soil takes place, leading to drop of pH and to increasing acidity of the soil. As a result increasing intensity of weathering combined with the release of toxic, Al-ions from clay minerals as well as leaching of nutrients from the upper soil take place. Figure 52 shows a summary of the process involved.

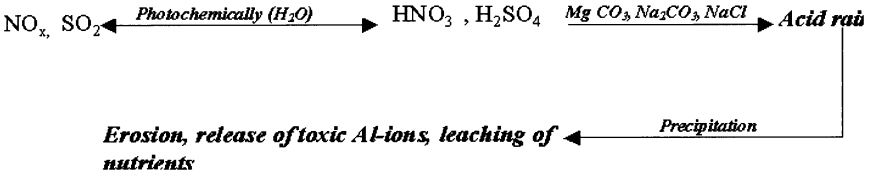


Fig. 52 . Formation of acid rain

7.2.3 Soil Pollution by Waste and sewage sludge

Of all urban sources contributing to soil pollution, waste and sewage sludge disposal occupies a central role in this environmental problem. In highly developed OECD countries despite of retreating rates of population growth, the production of waste is still increasing; especially in the industrial sector. In developing and under-developed countries, high rates of population growth and increasing waste and sludge production, combined with lack of municipal services, create a dangerous situation. Even in some of the OECD countries like Poland and Hungary, this is still posing a problem. The percentage of population served by municipal waste services, in these two countries, during the early nineties was between 55 % for Poland and 36 % for Hungary compared to 100 % in most of the EU countries and

the United States. Waste produced by households is known collectively as municipal waste to differentiate it from waste originating from industrial processes. It includes various types of materials that may contribute to changing the environment of soil. Table 20 shows the composition (%)of Municipal waste in both France and Turkey in the year 1993 as published by the EOCD.

Country	Paper and paper board	Food and garden waste	Plastics	Glass	Metals	Textile and others
France	30	25	10	12	6	17
Turkey	6	64	3	2	1	24

Table 20 Municipal waste in both France and Turkey in the year 1993 as published by the EOCD.

Municipal waste disposal by landfills and incineration may in both cases lead to concentration of heavy metals such as Cd, Cu, Pb, Sn and Zn either directly from landfill leachates that may be polluting soil and under ground waters or by ash fallout from incinerating plants. To this we may add the effect of landfill gases that may pass to neighbouring soils, causing a change of their soil air environment.

The disposal of sludge produced by sewage treatment poses a great problem as well; since in almost all developed countries the disposal of this sludge by dumping at sea is being phased out and the principal method of disposal is now shifting to land use. In fact, the mere use of sludge to amend soils is an advantageous process in itself. It adds essential organic matter as well as useful nutritive elements like phosphorus and nitrogen to the soil. Yet, pollutants such as heavy metals, which are normally concentrated in the sludge may accumulate within the soil and eventually would be taken up by food crops as leafy vegetables, which are known to preferentially take up cadmium – one of the heavy metals that are normally abundant in sewage sludge.

To reduce the hazard of soil pollution through sewage sludge the EC-Directive 86/278/EEC has sets the maximum permissible concentrations of heavy metals and other elements in sewage sludge amended soils. Table 21 shows some of these figures.

Element	Maximum concentration (mg/kg dry solids)	Maximum rate of addition over 10 year period (kg / ha)
Cd	3	0.15
Cr	400 (provisional)	15 (provisional)
Hg	50	3
Pb	300	15
Zn	300	15
Ni	50	3

Table 21 The EC maximum permissible concentrations of heavy metals in sewage sludge amended soil (taken from Alloway B.J and Ayres D.C, 1994)

Beside heavy metals, sewage sludge may include various organic micro-pollutants such as PAHs (polycyclic aromatic hydrocarbons), PCDDs (polychlorodibenzo-p-dioxin- Figure 53), and PCDFs (polychlorodibenzofuran- figure 54).

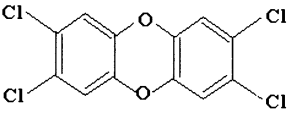


Fig. 53 .2,3,7,8 TCDD (Polychlorodibenzo-p-dioxin)

PCDDs or simply the ***dioxins*** are represented by over twenty isomers of a basic chlorodioxin structure and can be differentiated from each other through the number and positions of the chlorine atoms in a molecule. The most common form of dioxins is the 2,3,7,8- tetrachlorodibenzo-p-dioxin (Fig 53). Dioxins are considered the most toxic manmade chemicals.

PCDFs such as 2,3,7,8-tetrachlorodibenzofuran (Figure 54) compare in toxicity to 2,3,7,8- tetrachlorodibenzodioxin and are considered as examples of the most lethal synthetic chemicals.

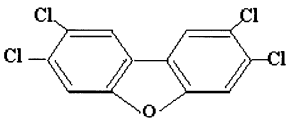


Fig. 54 . 2,3,7,8- Tetrachlorodibenzofuran

The above-mentioned substances are synthetic chemicals and none of them has been found to form as a result of any natural process. Their main sources are the following activities:

a) Municipal waste incineration
b) Chemical industry
c) Coal combusting power plants
d) Iron and steel industry
e) Car traffic
f) Hospital ovens
g) Forest industry.

7.3 Soil pollution through chemical warfare

Use of poisonous chemicals or irritating smokes against rival troops is as old as war itself. Reports about poisoning water resources or burning sulphur to irritate the enemy are known from battles dating back to the ancient Greeks. Indeed, like a modern biological and chemical attack, the curse of Moses on the Egyptians appeared, when he inflicted them with the plague of red tide (probably producing neurotoxins) that poisoned their waters and killed their fish. The Bible, vividly, reports on this, using the following words: "*...and the waters that were in the*

river were turned to blood. And the fish that were in the river died; and the river stank and the Egyptians could not drink of the water of the river."
Exodus 7: 20-21.

Yet, the systematic use of lethal chemical weapons as they are known today is relatively a recent matter. It started and was developed by European chemists during the early stages of First World War (1914 - 1918). At the beginning, the French used shells filled with ethyl bromoacetate in August 1914, and the Germans followed on 27th October 1914 at Neuve-Chappelle by using the "Ni-Schrapnell" 105 mm shell, which consisted of lead balls embedded in powdered o-dianisidine chlorosulfonate.

However, the turning point, which most historians consider as the starting event of modern systematic chemical warfare, came when the Germans discharged on the 22nd of April 1915 at 5 PM, 180,000 kg of chlorine gas at Ypres from 5,730 cylinders on the line between Steenstraat on the Yser Canal through Bixschoote and Langemark, to Polecappelle. The gas cloud carried by wind forced the French and Algerian troops in the opposing trenches to flee, after suffering heavy casualties. Prof. Fritz Haber, chief of the German chemical warfare service during World War I, directed this attack, which was the first of its kind. Haber, a chemistry Professor, Nobel laureate and famous for his discovery of ammonia synthesis by the combination of nitrogen and hydrogen, is often referred to as the father of modern chemical warfare.

After a second attack on 24th April 1915 against Canadian troops at Ypres, the Germans employed for the first time on 31st May 1915, chlorine on the eastern front at Bolimow, near Skierniewice, 50 km south east of Warsaw. For this attack, they employed 12,000 cylinders, releasing 264 tons of chlorine along a 12 km line. It is assumed that nearly 200 chemical attacks during World War I using gas released from cylinders were carried out; the largest of these occurred in October 1915 when the Germans released 550 tons of chlorine from 25,000 cylinders at Rhiems.

It is estimated that, beside the grievous environmental pollution caused by chemical weapons during World War I, employing 125,000 tons of chemical warfare agents caused about 1,296,853 casualties. A great number of people in battle regions developed serious symptoms that lasted for lengthy times after the war. The use and advancement of chemical weapons in World War I, was only a gambit for the horrific developments in this field during World War II and the subsequent years, known as the years of the cold war. During those years, chemists armed with the experience and knowledge, they collected during World War I, discovered lethal agents that are more effective in mass killing and destroying of natural resources. The development and use of herbicides and nerve agents culminated and showed its horrible face in the use of defoliation agents in Vietnam by the Americans, causing pollution of immense forest regions and genetic damage of people for many generations to come.

The history of nerve agents goes back to the few years preceding World War II at the end of 1936 when Dr. Gerhard Schrader of the *I. G. Farbenindustrie* laboratory in Leverkusen first prepared Tabun (ethyl dimethylphosphoramidocyanidate, (see page 99). Tabun, a nerve poison was very fast identified by the Nazis as a potent Warfare agent and they started in 1942 producing it on wide scale. By the end of 1944, the Nazis had produced 12,000 tons of Tabun: 2,000 tons loaded into projectiles and 10,000 tons loaded into aircraft bombs. They stockpiled this arsenal mainly in Upper Silesia and in abandoned mineshafts in Lausitz and Saxony. The Red Army approaching Silesia in august 1944 forced the Germans to flee abandoning the production sites and tons of liquid nerve agents were simply poured into the River Oder. It is believed that the Soviets captured both the full-scale Tabun plant and the pilot plant of another nerve poison – sarin, which is like Tabun an organophosphorus compound (O-Isopropylmethylphosphonofluridate – fig. 33b). According to some reports, the Soviets resumed production at both captured plants in 1946.

The Americans have also been active during the fifties and early sixties of the last century developing new nerve agents. The main compound of these was used

(under the code name *Agent Orange* as defoliating agent in Vietnam (YOUNG & REGGIANI,1988). Agent Orange is a mixture of herbicides, containing equal amounts of **2,4-dichlorophenoxy acetic acid (2,4-D)** and **2,4,5-trichlorophenoxy acetic acid (2,4,5-T)**, see figure 55. Operations of the American Air Force against Vietnam involving the use of Agent Orange were stopped in May 1970, after opposition grew inside the USA.

Realising the potential catastrophic consequences of chemical warfare for humanity, world powers started negotiating a Convention on the Prohibition of the Development, Production, Stockpiling, and Use of Chemical Weapons and on Their Destruction. After twenty years of negotiations, the convention known as the CWC (Chemical Weapons Convention) was opened for signature in Paris, France on 13 January 1993 and entered into force on 29 April 1997.

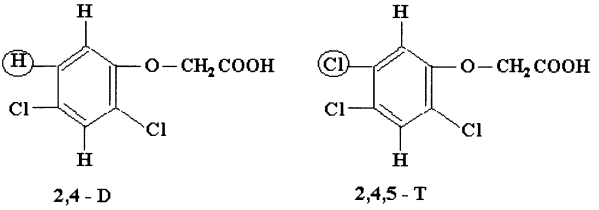


Fig. 55 . The two main ingredients of agent orange

7.3.1 Pollutants, toxic chemicals, and chemical weapons:

According to the CWC: ***a toxic chemical*** is defined as "Any chemical, which through its chemical action on life processes can cause death, temporary incapacitation or permanent harm to humans or animals. This includes all such chemicals, regardless of their origin or of their method of production, and regardless of whether they are produced in facilities, in munitions or elsewhere." ***Precursor materials*** used to produce toxic chemicals were also precisely defined in the chemical weapons convention (CWC) as: " Any chemical reactant which takes part at any stage in the production, by whatever method, of a toxic chemical. This includes any key component of a binary or multi-component chemical system."

In a classification of three categories (schedules), toxic or potentially toxic substances were classified according to their potentiality of being used as chemical weapons, or precursors of these. The Schedules do not define the chemicals in terms of specific properties, but classify them according to general accepted usage. Where a chemical is placed in the schedules, depends upon whether or not it's use as a chemical weapon is legal or illegal according to the Ratified CW Convention (DAVID R. HUFF, 1997)

Schedule 1; Chemicals can be listed here, if few or no peaceful uses have yet been identified for any members of them.

Schedule 2; Chemicals listed here are dual-Use Chemicals of Limited Use.

Schedule 3; Chemicals listed here are Dual-Use Chemicals of Extensive Use.

The Convention allows for future change of listing, if technical or legal developments require this.

Schedule1: Chemical Warfare Agents and Their Precursors.

In this schedule, all substances that have been produced stockpiled or used as chemical weapons as defined in article II of the convention are classified. Furthermore, substances of similar chemical structure that may be potentially of use as chemical weapons or can be precursors of them are included. Principally, following toxic chemicals and their precursors were listed on schedule 1:

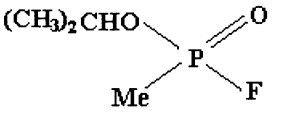
I. Organophosphorus compounds:

All nerve agents belong chemically to this group. They have rapid effects both when absorbed through the skin and via respiration. For a short description of these compounds, see page 74. Following organophosphorus compounds are on schedule 1:

a) Fluorinated organophosphorus compounds

O-Alkyl ($\leq C_{10}$, incl. Cycloalkyl) alkyl (Me, Et, n-Pr, i-Pr)- phosphonofluoridats

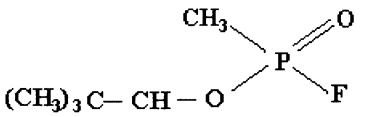
Example 1: ***Sarin*** also written ***Zarin***: This is a colourless liquid, odourless in pure form and readily soluble in water and all organic solvents. It is a powerful cholinesterase inhibitor having the chemical formula: $C_4 H_{10} F O_2 P$ with the following structure:



Structural formula of Sarin

Example 2: ***Soman***

Soman - also having the code name GD, has the chemical name methylphosphonofluoridic acid 1,2,2-trimethylpropyl ester and the molecular formula $C_7H_{16}FO_2P$. It has the following structural formula:



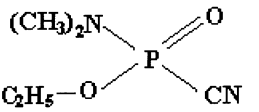
Structural formula of Soman

Soman was discovered in Germany in 1944, its laboratory testing was in progress in Germany at the end of World War II. Thus, it has never been used in combat, but was produced and stockpiled by the Soviet Union after the war. Soman – a colourless liquid when pure, has a yellow-brown colour as an industrial product.(Franke,1967) The pure compound has a fruity odour, but as an industrial product, it may have a camphor-like odour, resulting from impurities.

b. Esters of dimethylphosphoramidocyanidic acid

O-Alkyl (<C_{10}, incl. Cycloalkyl) N, N-dialkyl (Me, Et, n-Pr or I-Pr) phosphoramidocyanidates.

Example: ***Tabun.*** A colourless to brown liquid, which was discovered by Schrader in 1936, Tabun is slightly soluble in water but soluble in all organic solvents. It is an O-Ethyl N,N-dimethylphosphoramidocyanidate having the chemical formula $C_5H_{11}N_2O_2P$ with the following structure:

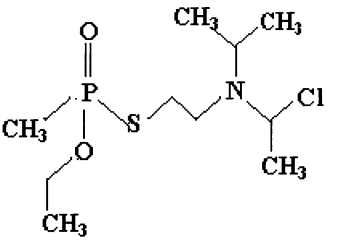


Structural formula of Tabun

c. Sulphonated organophosphorus compounds

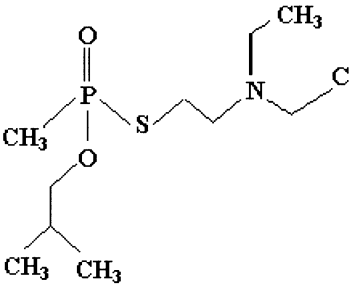
O-Alkyl (incl. Cycloalkyl) S-2-dialkyl (Me, Et, n-Pr or i-pr) aminoethyl alkyl (Me, Et, n-Pr or i-pr) phosphonothiolates and corresponding alkylated or protonated salts

Example: VX .The lethal nerve agent codenamed VX, has the chemical name methylphosphonothioic acid, *S*-[2-[bis (1-methylethyl)amino]ethyl]- *O*-ethyl ester, with the molecular formula $C_{11}H_{26}NO_2PS$, having the following structure.



Structural formula of VX

VX belongs to phosphorylthiocholine class of compounds, which was discovered independently by Ranaji Ghosh of ICI, by Gerhard Schrader of Bayer, and by Lars-Erik Tammelin of the Swedish Institute of Defence Research in 1952-1953. As a result of intensive research, by the U.S. at Edgewood Arsenal, VX was developed and stockpiled by the United States. A closely related compound referred to as V-gas was also manufactured and stockpiled by the Soviet Union. V- gas has the following structural formula.



Structural formula of V-gas

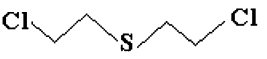
II-Mustards

Mustards are chemicals that contain a 2-chloroethylgroup attached to a **sulphur atom** (reactive alkyl chlorides.) or to a nitrogen atom. One can, accordingly, speak of sulphur mustards and nitrogen mustards:

Sulphur Mustards:

Sulphur mustards belong to the group of chlorinated thioethers. They may be regarded as derivatives of hydrogen sulphide in which chlorinated alkyl groups replaced the two hydrogen atoms.

Example 1: ***Mustard gas*** — Bis (2-chloroethyl) sulphide, has the chemical formula $C_4H_8Cl_2S$, with the structure:



Structural formula of Mustard gas

Mustard gas ***(also known as H, yperite, sulphur mustard, Kampfstoff Lost)*** was the most important vesicant poison gas used during the First World War.

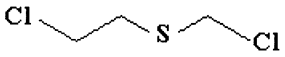
The Germans first used it on the night of 12-13 July 1917 near Ypres in Flanders (PAXMAN AND HARRIS, 1982). The French followed in June 1918, while the British extended their arsenal to include it in September 1918. Documented uses of mustard in later times, according to (COMPTON 1988), include Morocco 1925(by the French), Ethiopia, 1935 (by the Italians), China between 1934 and 1944 (by the Japanese) and during the Iran-Iraq war (by both sides). Although no chemical warfare agents were used during World War II in Europe or in the Pacific(FRANKE,1967), there was a release of mustard into Bari harbour in Italy in 1943 (COMPTON, 1988). During the years of the cold war, the Soviet Union and the United States stockpiled considerable arsenals of this lethal weapon.

Mustard or *Kampfstoff Lost*, as the Germans used to call it, is a heavy liquid (b.p. 217°C). Its vapour attacks skin and lung tissues producing blisters and burns. It can be rendered innocuous by Bleaching powder. As a soil pollutant, however, Mustard has a precarious effect; since it can persist in polluted lands (even if it is covered by water) for decades.

Following compounds belong to the sulphur mustards and are all listed on schedule 1 of the CWC as chemical weapons:

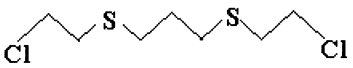
- Bis (2chloroethylthio) methane

- 2-Chloroethylchloromethylsulfide

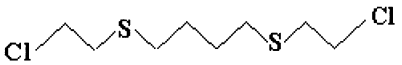


- Sesquimustard: 1,2-Bis (2-chloroethylthio) ethane

- 1,3-Bis(2-chloroethylthio)-n-propane

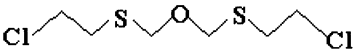


- 1,4-Bis(2-chloroethylthio)-n-butane

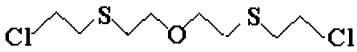


- 1,5-Bis(2-chloroethylthio)-n-pentane

- Bis(2-chloroethylthiomethyl)ether

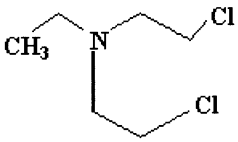


- O-Mustard: Bis (2-chloroethylthioethyl) ether

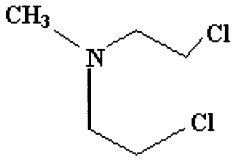


b. Nitrogen mustards:

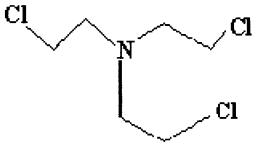
- HN1: Bis(2-chloroethyl)ethylamine



- HN2: Bis(2-chloroethyl)methylamine



- HN3: Tris (2-chloroethyl) amine



All the nitrogen mustards are liquids with fish odour and either practically insoluble in water e.g. NH1, sparingly soluble (NH2: 0.16 g /l) or slightly soluble (NH3, 16 g/l). The accident in Bari harbour (Italy) during WWII that killed 85

American soldiers seems to had been due to release of nitrogen mustards formerly stored by the American Navy on one of its warships.

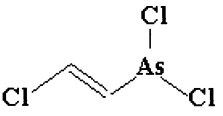
III- Lewisites

Lewisite (L, 2,chlorovinyldichloroarsine, 2-chlorovinylarsonous dichloride) has the chemical name (2,chloroethenyl) arsonous dichloride with the molecular formula $C_2H_2AsCl_3$.

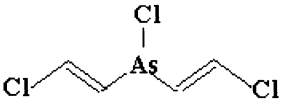
Lewisite was discovered near the end of World War I by a team of Americans headed by Capt. W. Lee Lewis working at Catholic University in Washington DC. (Paxman and Harris,1982). It was never used in the operations of World War II. However, after the War, Lewisite was considered obsolete by the major powers because of the discovery that 2,3-dimercaptopropanol ("British anti-Lewisite") was an inexpensive and effective antidote to lewisite exposure. Crude Lewisite has a strong penetrating geranium odour; the pure compound is odourless.

Lewisite is a complex mixture of several compounds, all of which occur as *cis*- and *trans*-isomers. These are classified in three main isomers L1, L2, and L3. In chemical agent grade Lewisite, the L-1 isomer generally predominates. The three isomers have following structures:

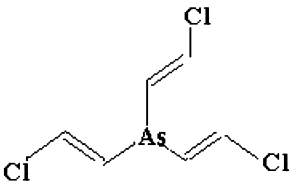
L1: 2-Chlorovinyldichloroarsine



L2: Bis (2-chlorovinyl) chloroarsine

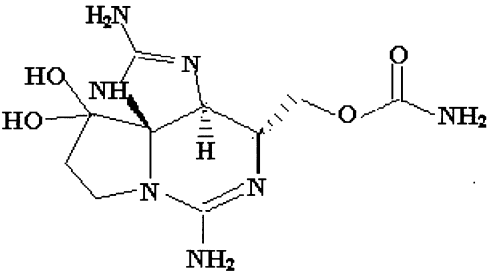


L3: Tris (2-chlorovinyl) arsine



IV- Saxitoxin and Ricin

These are the only two naturally occurring neurotoxins listed as Schedule 1 Chemical Warfare Agents. Saxitoxin is related to the deadly PSP (paralytic shell-fish poison), which is a potent neurotoxin, produced by various algae (*Gonyaulax species*). Saxitoxin, the major component of PSP, is responsible for respiratory paralysis, which in 8 % of cases results in death. It blocks the sodium ion channels in nervous and muscle membranes. The lethal dose in humans lies between 1 to 3 mg. Numbness and respiratory arrest can occur after oral ingestion of as little as 0.5-1.0 μg of saxitoxin.

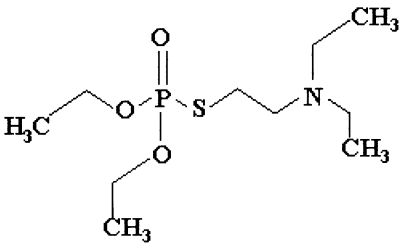


Structural formula of Saxitoxin

Schedule 2: Dual-Use Chemicals of Limited Use.

The following 3 toxic chemicals, are the leading members of schedule 2 for chemical weapons use.

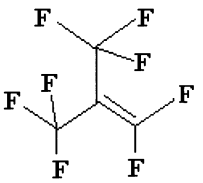
1. Amiton: O, O-Diethyl S- [2-(diethylamino) ethyl] phosphorothiolate and corresponding alkylated or protonated salts



Structural formula of Amiton

Amiton is an organophosphorus insecticide that was first synthesized in the 1950's. The EPA due to its high toxicity banned its use in agriculture.

2. PFIB (Perfluoroisobutylene) 1,1,3,3,3-Pentafluoro-2- (trifluoromethyl)-1-propene



Structural formula of PFIB

PFIB is a gas of no commercial use. It is formed as a by-product during the production of some perfluorinated polymers (e.g. Teflon), and is as toxic as phosgene ($COCl_3$).

3. BZ: 3-Quinuclidinyl benzilate :

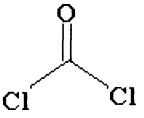
Structural formula classified

Besides toxic chemicals, known as previously used weapons or those, which are considered as potential CW agents, schedule 2 includes various precursors that may be used for the production of chemicals listed in schedule 1 or schedule 2.

Schedul 3: Dual-Use Chemicals of Extensive Use.

The four toxic chemicals ***Phosgene, Cyanogen chloride, Hydrogen cyanide***, and ***Chloropicrin*** are the most notable among members of schedule 3. They may be shortly described as follows:

1.Phosgene: Carbonyl dichloride



Structural formula of Phosgene

Phosgene owes its name to the first method of its preparation by the action of sunlight on carbon monoxide and chlorine. The word phosgene means formed by light. It is used as a starting material for the preparation of some agrochemicals and in the dye chemistry. Physiologically, it is a powerful respiratory poison. Due to this property, it was used as a chemical weapon during First World War.

2.Cyanogen chloride

$$Cl—C\equiv N$$

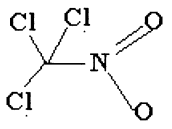
Cyanogen chloride is a poisonous, lacrymatory gas, which can be condensed at 13°C and readily trimerises to cyanuryl chloride. Cyanogen Chloride acts by blocking cell respiration, and causes death within a short time if high concentrations are inhaled. In the chemical industry, however, it is considered an important synthetic intermediate for the production of many organic compounds.

3.Hydrogen cyanide

$$HC\equiv N$$

Like Cyanogen Chloride, hydrogen cyanide causes death by blocking cell respiration. It is an important synthetic intermediate and was sometimes used as a pesticide.

4.Chloropicrin: Trichloronitromethane (nitrochloroform: CCl_3—NO_2)



Structural formula of Chloropicrin

Chloropicrin, which can be prepared by the action of concentrated nitric acid on chloroform, is a heavy liquid, boiling at 112°C. It is a severely irritating lacrymatory agent, which is also used as a soil sterilizer, a grain disinfectant, and an intermediate in organic syntheses. Schedule 3 has also seven nerve agent precursors listed, which have extensive applications in the chemical industry, mostly in the production of insecticides and as chlorinating agents.

Soil pollution by military activities during the cold war:

It is perhaps not completely true or even false when we classify pollution by military and belligerent activities as incidental sources of pollution as we did in the foregoing section. This is because of one undeniable fact, that the First and Second World Wars were, at least in Europe, only a prologue for an extended period of pollution through troop concentrations, training and stockpiling of armaments on both sides of the confrontation line between East and West. The need for armaments and munitions by less developed countries involved in regional and civil conflicts in Africa, Asia and Latin America boosted the arms industry and increased the areas planted by land mines to horrible dimensions (e.g. Afghanistan). While the extensive use and handling of modern warfare agents by badly or insufficiently trained personnel, in the third World, rendered many regions in these countries uninhabitable due to pollution by heavy metals, fuels, oil products, explosives and various dangerous organic pollutants.

After the Second World War Germany became the main confrontation field between the Eastern block on one side and the Nato nations on the other. The coun-

try with a total area of 35 million ha was divided into two States — The Federal Republic of Germany (25,000,000 ha) and the German Democratic Republic with an area of 15,000,000 ha. Until the end of the cold war (1990), 960,000 ha (about 2.8% of the total area of the country) were used for military training by both eastern and western forces. Table 22 shows the contingents in ha, which were assigned to each:

Area	Stationed troops
253,000	Federal Defence Force „Bundeswehr" W. Germany
200,000	Armies of the West Alliance: USA, Britain, France, Canada, Belgium, and Holland
240,000	National People's Army (NVA), E. Germany
250,000	West Group of the Soviet Armed Forces (WGT)

Table22. Contingents assigned to eastern and western forces in Germany during the cold war

According to a study made on behalf of the German Federal Agency for the Environment in Berlin *(Umweltbundesamt, Berlin)*, The following pollution risk assessment (Table 23) was proposed for the whole region of Berlin East and West. The Assessment was also done for military sites formerly used by the Soviets and their allies as well as for sites, which were used by the forces of the West Alliance.

Category	West Berlin		East Berlin		All Berlin	
	No. of sites	Area (ha)	No. of sites	Area (ha)	No. of sites	Area (ha)
A	17	300	16	300	33	1 070
B	15	280	35	220	50	500
C	21	280	57	130	78	400
Total	53	1 330	108	650	161	1 970

Table 23. Pollution risk assessment for abandoned military sites in Berlin (Schäfer et al 1996)

Category A: Sites of proven high contamination or sites of highly probable contamination

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	Petroleum Products	Xylene, Pb, Zn, Ni BTEX:	Cr, Fe, Cu, Mn, Cd, K, Mg, Na, Hg, Ca, Al, Ethylbenzene, Toluene, BenzeneAmmonium comp. Nitrates, Chlorides	Nitrites, PAH	Chrysene, Fluoranthene, Pyrene, Anthracene, Benzo[a]-Pyrene, perylene	Chlorinated hydrocabons, Indeno [1,2,3cd]-pyrene Tetrachloroethane, Naphthalene Phenols, Phosphates, F_2, 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,MnNa, Zn,Sulphates, Nitrites, PAH, Tetrachloromethane	Trichloroethane,Trichloro- Methane, Nitrates, Phosphates, Hg,Cl_2,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

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.

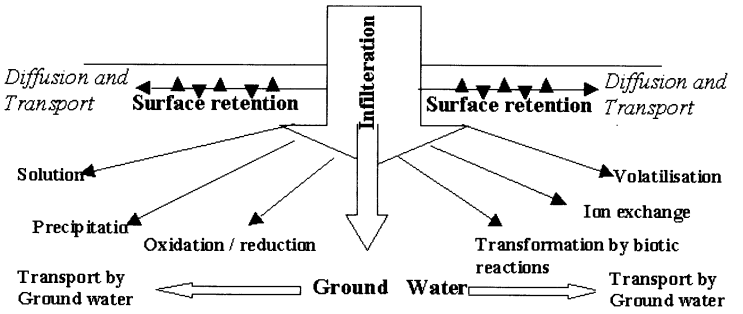


Fig. 56 A schematic overview of the processes representing soil-pollutant interactions

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.

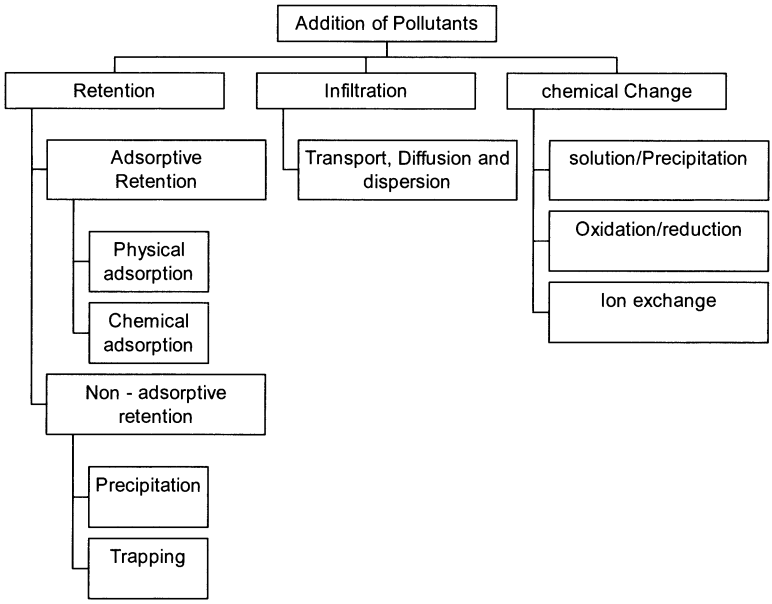


Figure57 A summary of the mechanisms involved in Soil Pollution

8.1 Physical processes and mechanisms of pollution

Pollutants on encountering soil grains will either be retained by adsorption on the surface of theses 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 physiosorption, 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 week 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 them selves 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 (σ_s), which may be caused by some functional groups (e.g., M–OH). These normally posses 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

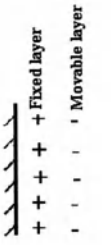
can also be adsorbed by soil grains. This occurs principally through electrostatic forces.

The theory of diffuse double layer (DDL)

To explain the adsorption of charged particles on the surfaces of solids, HELMHOLZ (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 Helmholz 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 58 a). 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 ξ).

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.



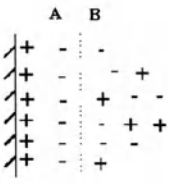


Fig. 58a Helmholz double layer **Fig. 58b** . Gouy-Chapman diffuse double layer

Chemical Adsorption or Chemisorption

As it was stated before, formation of covalent bonds during chemical adsorption mqkes the energy of attachement 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 (µg/g solid)

C = concentration of substance to be adsorbed in the ambient solution (µg/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.

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

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:

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

At the time when equilibrium is attained between molecules sticking on the surface and molecules free in the gas phase, θ will depend on the pressure of the gas. This relation between θ 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:

$$A(g) + M(\text{surface}) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} AM$$

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:

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:

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 θ, we get:

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

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 :

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

θ, 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 θ 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*

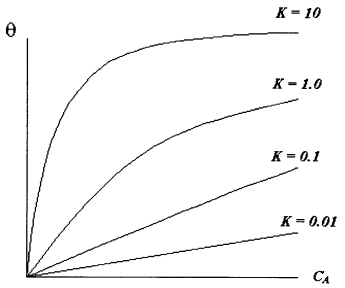


Fig. 59 . The Langmuir isotherm for several values of K

The Brunauer, Emmet and Teller (BET) isotherm

This equation was developed to allow for multilayer adsorption, which is charateristic for phenomena of physiosorption .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:

$$Ca^{+2}\ A \quad + \quad 2Na^{+} \quad \leftrightarrows \quad 2Na^{+}\ A \quad + \quad Ca^{+2}$$

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 $NaHCO_3$ 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 ($2H_2O$)	5-10
Halloysite ($4H_2O$)	40-50
Illite (Hydrous mica)	10-40
Chlorite	10-40
Glaukonite	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 valence (II or III). The general series of ion-preference may be represented as follows:

$$H^+ > Rb^+ > Ba^{+2} > Sr^{+2} > Ca^{+2} > Mg^{+2} > K^{+2} > Na^+ > Li^+$$

$$\longleftarrow \quad \text{Stronger ATTACHMENT weaker} \quad \longrightarrow$$

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

$$Cs^+ > Rb^+ > K^+ > NH_4^+ > Na^+ > Li^+$$

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:

$AX + B^+ \leftrightarrows BX + A^+$, at chemical equilibrium , we have

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

Rearranging we get:

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

Where, A^+/B^+ is the ratio of ion activities in the solution, *(AX)* and *(BX)* refer to the concentration of A^+ and 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^+ an 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:

$$2AX + B^{++} \leftrightarrows BX_2 + 2A^{+}$$

Accordingly, the empirical equation takes the form:

$$\frac{[A^+]^2}{[B^{++}]} = K'_{AB}\left(\frac{(A_2X_2)}{(BX_2)}\right)^n$$

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

$$\frac{[A^+]^2}{[B^+][C^+]} = K'_{AB}\,K'_{AC}\left(\frac{(AX)}{(BX)\,(CX)}\right)^{n+m}$$

Factors affecting adsorption:

The intensity of adsorption depends upon several factors including physical and chemical properties of the pollutants them selves 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.

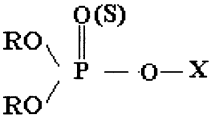
4.Chemical and physical properties of the soil solution

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 sits 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 lows 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 ≤ 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

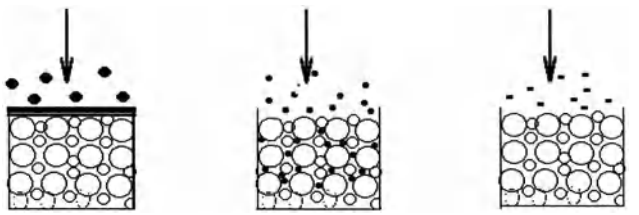
1. Trapping: Entrapment of solid particles and large dissolved molecules in the pore space of the soil forms one of the major mechanisms of retention of pollutants in the soil. This type of retention occurs following three mechanisms as shown in figure 60, drawn after J. R. BOULDING (1995). The figure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

a)Caking

This may occur physically when the pollutants 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



(a) Caking (b) Straining (c) Physical-chemical Trapping

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

c) Physical – chemical trapping

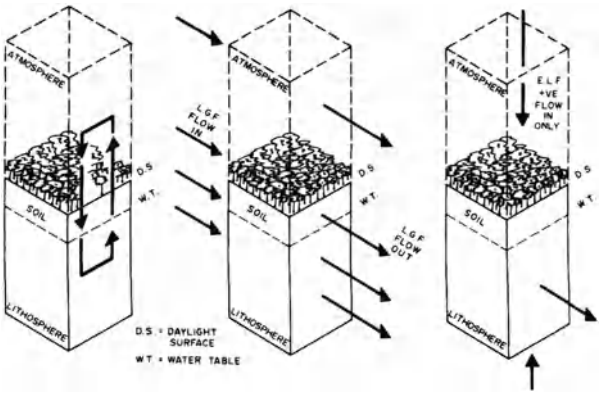
Limitation of flow through clogging of pore space may occur because of physical or chemical transformation, such as the production -by chemical reactions- of new products having molecular sizes that exceed that of the soil pores.
An example is the flocculation of colloidal material resulting from the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

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

Where Q is the total discharge of fluid per unit time ($cm^3\ s^{-1}$); A is the cross sectional area of flow path (cm^2); 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 – h_1 is the hydraulic head, or pressure drop across the flow path (g cm^{-2}); 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[3].

[3] Op. cit.

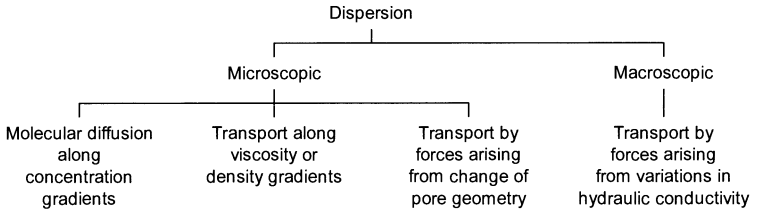


Fig.62 Dispersion processes in soil

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

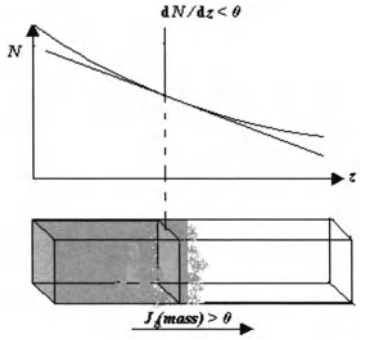


Fig. 63. Flux of particles down a concentration gradient (Atkins, 1978)

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, η 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 ϕ 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, $D^a{}_g$ *the* binary diffusion coefficient of the vapour in air, and ξ_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.

Chapter 9

Pollutants' alteration, transformation, and initiation of chemical changes within the soil.

In a highly complicated system of different phases, such as soil subsurface, penetrating substances will go through a myriad of chemical, physical, and biological processes that will determine their fate, besides controlling the degree of their toxicity to the environment. Such subsurface processes are broadly classified into the following groups:

A. Physical processes (processes related to chemical mobility)

B. Chemical processes

C. Biological processes

9.1 Processes related to chemical mobility

These include process in which no net chemical change occurs. They normally affect physical conditions that control phase distribution of the substance i.e. its association with aqueous or solid phases under given environmental conditions. It is due to this that these processes are collectively known as ***distribution processes***. Distribution processes include processes such as advection dispersion and volatilisation. They include besides the processes discussed in the foregoing chapter (chapter 8) all those processes that may affect the ***mobility*** of a substance in the subsurface environment. Of these, the following are most prominent.

- Immiscible phase separation

- Acid-base equilibrium
- Precipitation-dissolution reactions

a) Immiscible phase separation

Depending on their miscibility in water, fluids or gases will separate forming an independent layer in a multi - component system. An example may be given by NAPL's, separating to form a floating layer on the surface of underground water (LNAPL) or sinking to form a deposit on an impermeable bed at the base of the aquifer (DNAPL).

b) Acid-base equilibrium

The Brønstead- Lawry theory defines an acid as any substance that can give or donate a proton. Likewise, the theory defines a base as a substance, ready to accept a proton. Following examples provide illustration of both definitions:

1) Ionisation of hydrochloric acid:

HCl° (neutral) $\leftrightarrows H^{+} + Cl^{-}$

2) Ionisation of sulphuric acid

$H_2SO_4^{\circ}$ (neutral) $\leftrightarrows 2H^{+} + SO_4^{2-}$

3) Ionisation of carbonic acid

$H_2CO_3^{\circ}$ (neutral) $\leftrightarrows H^{+} + HCO_3^{-}$

All three reactions are reversible. In reaction 1 (ionisation of hydrochloric acid), the acid completely dissociates to give a proton (H^{+}) and an anion (Cl^{-}), ready in the reverse reaction to recombine with the proton, restoring the original structure of the acid. In this case, Cl^{-} may be called a base according to the definition. In reaction 2, the same happens as in reaction 1 and here also SO_4^{2-} (the sulphate group) plays its role as a base that may restore the acid on recombining with the released protons. Reaction 3 (carbonic acid), though principally the same as the others, shows a basic difference in that the acid does not completely dissociate like

the two other cases. It partially dissociates so that on reaching equilibrium, a fragment of the original neutral species (HCO_3^-) remains unionised in the aqueous solution. Such acids, incapable of complete dissociation in one step are generally known as weak acids, while acids completely dissociating in one stage are known as strong acids. Aqueous solutions of weak acids have pH-values ranging from 4-6, while those of strong acids possess pH-values lower than 4.

Bases may also be classified, on the same grounds, into weak and strong bases. Thus, bases like NaOH or Ca OH, capable of complete dissociation to give a cation and an anion (see equation) are also known as strong bases.

$$Na\ OH^{\circ}\ (neutral) \leftrightarrows Na^+ + OH^-$$

The hydroxyl ion in the last equation might also combine with a proton to form water, thus emphasising its role as a base. Contrary to sodium, potassium, or calcium hydroxides, bases like Fe $(OH)_3$ and Al $(OH)_3$ are described as weak bases because they do not further ionise in water. This may be illustrated by the dissociation of the mineral jarosite, which generally dissolves in water to form ferric oxyhydroxide and K^+, producing a considerable acidity, according to the following equation:

$$KFe_3(SO_4)_2 + 3H_2O \leftrightarrows K^+ + 3Fe(OH)_3\ (ppt) + 2SO_4^{2-} + 3H^+$$

Thus, the mineral is seen here to be a salt of a strong acid (H_2SO_4) and a very weak base Fe $(OH)_3$, which forms a precipitate that almost does not ionise.

Acid-base equilibria in a subsurface environment control the prevailing pH-values and hence the stability and solubility of the substances present. This plays a principle role in determining mobility, fate, and toxicity of the penetrating pollutants.

Buffering capacity:

If a strong acid or base is added to a solution the pH of the solution changes, according to whether H^+ is removed or released in the solution. Some solutions, however, resist changes in their pH upon the addition of small amounts of acid or alkali. Such solutions are called buffer solutions or simply buffers and the degree of resistance to change is called buffering capacity.

To understand this, let us consider the following example of equilibrium between a weak acid (acetic acid) and its Sodium salt (sodium acetate):

$$CH_3\,COOH \leftrightarrows CH_3COO^- + H^+ \qquad \text{(i)}$$

$$CH_3COONa \leftrightarrows CH_3COO^- + Na^+ \qquad \text{(ii)}$$

If to a solution of acetic acid and sodium acetate a slight amount of HCL is added, the hydrogen ions from hydrochloric acid will combine with a portion of the acetate ions to form unionised acetic acid, which is anyway a weak acid i.e. slightly dissociates. The removal of the added hydrogen ions to form acetic acid means that they will not affect or change the hydrogen ion concentration of the solution and thus will not change its pH.

Similarly if OH^- ions are introduced by the addition of a small amount of an alkali, the OH^- will combine with the hydrogen ions resulting from the dissociation of acetic acid to form water. Removal of H^+ in this way will disturb the equilibrium in equation (i), enhancing the acetic acid to increasing dissociation in order to restore the equilibrium. Thus, the pH of the solution will practically remain unchanged. Other weak acids and their salts (e.g. carbonic acid) will also display the same pattern of behaviour of retaining their pH after addition of small amounts of strong acids or bases. The best examples of these are seawater and other brines containing carbonic acid and its salts, which may resist change of its pH on being exposed to small spills of strong acids or bases. The reaction in this case would be controlled by the following equilibrium:

$$CO_2\,(aq) + H_2O \rightarrow \underset{\textit{Carbonic acid}}{H_2CO_3} \leftrightarrows \underset{\textit{bicarbonate}}{HCO_3^-} + H^+ \leftrightarrows \underset{\textit{carbonate}}{CO_3^-} + 2H^+$$

On attaining equilibrium, the concentration of H^+ remains constant. If the solution is exposed to a strong acid, the concentration of H^+ increases leading to a shift of the equilibrium to the left forming unionised carbonic acid, upon which the excess H^+ ions will be removed keeping the pH of the solution practically unchanged. If OH^- ions are added to the solution by the introduction of a strong base, they combine with H^+ to produce water keeping the pH of the solution at its initial value. The buffer capacity however depends on the initial concentration of carbonates

and bicarbonates; since an exhaustion of these will stop the formation of carbonic acid, thus allow an increase of the hydrogen ion concentration, and consequently lead to a lower pH-value.

c) Dissolution-precipitation reactions:

Solubility and precipitation are perhaps the most characteristic phase distribution processes, that take place in the soil environment; for in dissolution there would be a transition from a gaseous or a solid phase into an aquatic one and if at any time precipitation occurs, it will follow just the opposite way. Thus, dissolution obviously induces an increase in mobility, while precipitation inhibits the same.

Solubility of a substance in the soil environment depends on the nature of the substance as well as on physical parameters such as temperature, pressure, pH, and Eh (redox potential). As for the nature of the contaminant substance, we find that organic toxic substances are less soluble than inorganic salts. This is naturally to be expected due to the hydrophobic character of non-polar substances. Another factor determining solubility in water would be the already existing concentration of the same substance in solution and how far it is from the equilibrium concentration at a given temperature. This is manly controlled by the solubility product, which is an expression of the maximum amount of a substance that will dissolve in a solution at a given temperature and pressure. Precipitation occurs when the value of the solubility product is exceeded. In aquatic systems, this may occur due to change of equilibrium conditions such as temperature, pressure, pH, or Eh, making the boundary separating distribution processes from processes encompassing chemical change to fade.

9.2 Chemical transformation processes

In fact, chemical transformation processes and distribution arrangements that may affect the chemical mobility of a substance are complementary in nature. They normally go hand in hand with one or the other implementing the advent of

its successor. Non-the less, the two groups of processes are completely different in their mode of action. While, as said before, distribution processes mainly affect the mode of association of a given substance, chemical transformation will in the first place change the chemical structure of the substance, bringing about a net chemical change. Both may happen parallel and it is rarely observed in the soil environment, that one of them occurs without the other following on its heels. This may be illustrated by the case of precipitation, which - as mentioned above - is one of the most typical examples of phase distribution. PERELMAN, 1967 classified processes of metal precipitation from natural waters into the following types which include a great deal of transformation going hand in hand with the processes affecting mobility and phase distribution.

1. Oxidation type:

An example is the precipitation of iron and manganese oxides by the oxidation of reducing waters.

2.Reducing type:

Examples are given by the precipitation of U, V, Cu, Se, and Ag as metals or lower valency oxides by the reduction of oxidising waters. This is usually caused by encounter with organic matter or by mixing with reducing waters or gases.

3. Reducing sulphide type

Sulphate waters carrying ions of Cu, Ag, Zn, Pb, Hg, Ni, Co, As, or Mo may be reduced to precipitate sulphides of these metals. This occurs usually by the action of sulphate-reducing bacteria or on encounter with organic matter.

4. Sulphate and carbonate type:

Alkali metals such as Ba, Sr, and Ca may be precipitated as carbonates following a shift in equilibrium relations. Griffith et al, 1976 have reported about Pb-precipitation from landfill leachates as carbonates.

5. Alkaline type:

Percolation of acidic solutions into carbonates and silicates as well as their encounter with alkaline solutions lead to precipitation of metals like Ca, Mg, Sr, Mn, Fe, Cu, Zn, Pb, and Cd.

6. Adsorption type

This type encompasses all transition metals, which are susceptible to adsorption on clays and other particulate substances.

7. Oxidation – reduction type:

Mobility of trace metals in aquatic solutions is largely influenced by the redox status of their envirnment, even though they generally are not directly involved in oxidation – reduction reactions. Figure 65 shows the stability relations in the system $Zn + S + CO_2 + H_2O$.

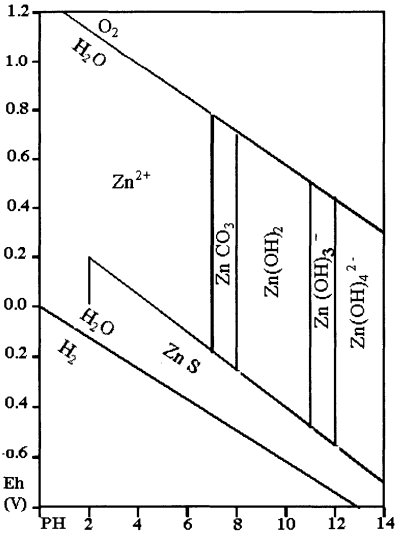


Fig. 65 Stability relations in the system $Zn + S + CO_2 + H_2O$

In this system , three solid phases (Precipitates) are possible: the sulphide, carbonate, and hydroxide of zinc. Under reducing conditions, sulphide and hydroxide are the stable phases at high ph-values. At lower pH-values, however, the hydroxide dissolves and only the sulphide is precipitated.

Oxidising conditions induce precipitation of amorphous iron and manganese oxihydrides, that later as adsorbents tremendously affect the mobility of trace metals in the solution. Reducing conditions induce the reduction of Mn^{+4} to Mn^{+2} and Fe^{+3} to Fe^{+2} thereby solubilising their associated and adsorbed trace metals. Figure 66 summarizes the redox chemistry of iron and manganese.

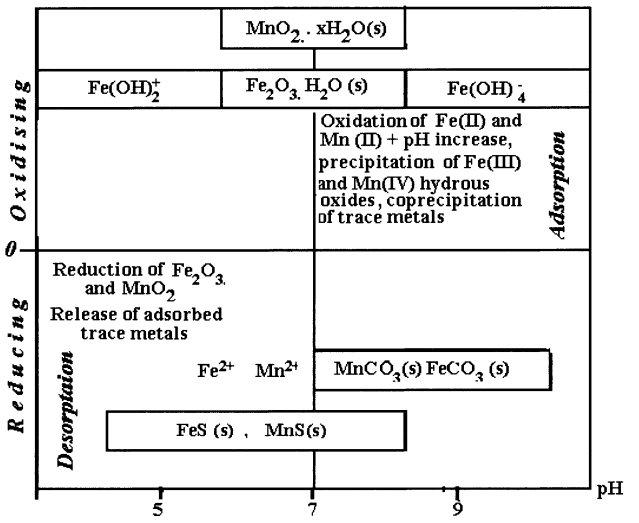


Fig. 66 . Schematic representation of the redox chemistry of iron and manganese

8. Complex formation and chelation:

Most trace elements exist in water as hydrated ions rather than free ones. In the course of hydration, water due to its polar character and the unsatisfied charges on both hydrogen and oxygen, orient its molecules such that oxygen points to the cation while hydrogen points away from it (see figure 67). The water molecules, thus connecting themselves to the cation form a hydration shell, around the cation,

producing a species known as cation aquocomplex (copper aquocomplex in figure 67). Each of the water molecules will be called a ligand and as it is seen here, ligands are not attached to the cation through electron sharing, but rather due to electrostatic forces arising from pairs of electrons that exclusively belong to the cation. The so formed species may further be associated to anions that would form an additional sphere at the outer surface of the water shell, forming what is known as ***an outer-sphere complex***. Anions in the outer sphere complex are associated to the cation by long-range electrostatic forces; their association is not strong enough to displace any of the water molecules in immediate contact with the cation.

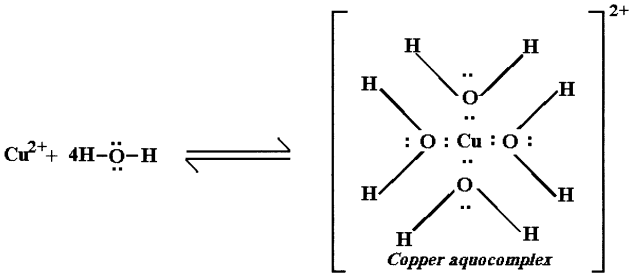


Fig. 67 . Formation of copper aquocomlex

A classical example of the formation of outer-sphere complexes is given by the formation of complex cobalt chlorides. Cobalt forms a simple ionic chloride $CoCl_3$, in which three electrons are transferred from a cobalt atom to chlorine atoms. In the presence of ammonia [NH_3 (aq)], however, this cobalt (III) chloride can form a series of distinct compounds, having up to six ammonia molecules as ligands surrounding the cobalt cation [(Co $(NH_3)_6$] Cl_3, as shown in figure 68.

A ligand is defined as a species capable of donating an electron pair to a central metal ion at a particular site in a geometrical structure. Therefore, a ligand is essentially considered as a Lewis base and the metal ion as a Lewis acid. If a ligand is capable of donating a single electron pair, as in ammonia, it is called a ***unidentate*** (single toothed) ligand. Some ligands however are capable of donating more

than a single electron pair, to different sites in the geometrical structure of a complex ion. These are called ***multidentate ligands***. Most inorganic ligands are unidentate, while multidentate ligands are normally organic ones.

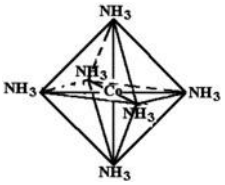


Fig. 68 . octahedral coordination of cobalt with ammonia to form$[Co(NH_3)_6]^{3+}$

Humic acids are multidentate ligands, forming cage structures around metal ions when they associate with their complexes (see fig 23). When bonding between a metal and a multidentate ligand results in such ring or cage structures, the process is called ***chelation,*** the species produced, a chelate, and the multidentate ligand is a chelating agent. The expression chelate is derived from the Greek word ***"Chela"*** meaning a crab's claw.

Complex formation in aquatic systems renders metals less bioavailable for organisms. It also influences the adsorption of metals on colloid substances and may increase the solubility of minerals. Solutions with high ionic strengths are favourable media for the formation of complexes, the stability of which will be directly proportional to the cation charge and inversely proportional to its radius.

Hydrolysis:

As discussed in 1.2 under chemical weathering, hydrolysis is a pure chemical process during which a proper chemical reaction takes place between water and another substance, to produce or consume a proton (H^+) or an electron (OH^-). A

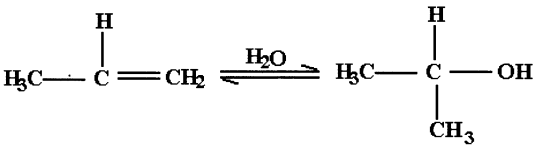
typical example was given by the reaction of the mineral albite with slightly acidic water to produce kaolinite (see equation 1.2).

Organic pollutants percolating through the soil environment may be chemically transformed by hydrolysis, either through water addition to the molecule, or though replacement of some functional groups by water. Examples of replacement reactions may be given by the replacement of halide ions in alkyl halides to form alcohol:

$$RX + H_2O \leftrightarrows R\text{-}OH + HX$$

R = alkyl group, X= halide.

Hydrolysis reactions taking place by addition of water molecules normally proceed more readily than those taking place by replacement. An example of these may be given by the addition of water to alkenes to form alcohol:



Propene ***Isopropanol***

9.3 Biodegradation and biologically supported transformations

As mentioned before (see section 3.2), organisms (soil biota) form a very important integrative constituent of soil and as such, they play a decisive role in determining the fate of foreign substances added deliberately or accidentally to the soil body. They normally respond to the addition of xenobiotics by initiating two main types of reactions: ***a) Primary metabolic reactions*** (also known as phase I biotransformation), during which the foreign substance is rendered more soluble in water by addition or exposure of functional groups on it …and

b) Secondary metabolic reactions (phase II biotransformation), through which the products of primary reactions are conjugated with endogenous groups to facilitate their excretion. On passing into solution, the foreign substance will be capable

of penetrating the organism with rates, which are specific for organisms and their anatomical and biological peculiarities. In case of high rates of penetration i.e. if a foreign substance enters the organism more quickly than it can be eliminated, it accumulates in some of its organs, and if the substance is toxic, this goes on until a toxic concentration is reached. At normal rates of penetration secondary metabolic transforms will lead, by conjugation with endogenous compounds, to the formation of substances that may be used as energy sources by the organism or to ones that are easily eliminated by excretion. Figure 68 explains this in a schematic way.

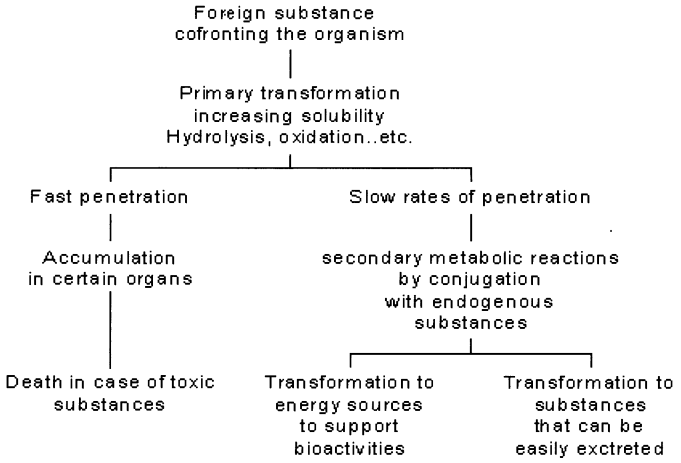


Fig. 69 . Schematic representation of the response of soil biota to foreign substances

From this schematic representation, it becomes clear that the level of metabolism is a principal factor in determining the persistence or degradation of the foreign substance in the soil and thus forms one of the important conditions under which biodegradation succeeds.

As it may be expected, the activation of these reactions requires a high energy demand or at least a source of catalysis to secure their advancement. This catalysis is supplied in organisms by ***enzymes***. These catalytically active high molecular weight proteins enable the activation of biological transformations of substances

into energetic sources or easily eliminated chemicals. In order to understand the fundamental action of enzymes in biologically assisted transformations in soil, an outline of the chemical processes involved in enzymatic actions will be shortly explained.

9.4 Enzymatic transformations –A primer on enzymes, their types and mode of action

Enzymes take their specific names from that of the substrate (the substance they help to change) by adding the suffix "ase" to the name of this substance e.g. proteinase, lipase, etc. According to the type of chemical reactions, in which they are usually involved, enzymes are classified into six main groups. Namely, the ***hydrolases,*** those that assist hydrolysis; the ***transferases***, those that help transfer a certain group to another substrate, not usually water; the ***oxidoreductases,*** those that transfer hydrogen or electrons between two substrates, the ***lyases*** those that remove groups from their substrates, the ***ligases (synthases)*** those that catalyse the joining of two molecules (i.e. synthesise a C—C bond) at the cost of chemical energy, and the ***isomerases,*** which are enzymes that catalyse intramolecular rearrangements. Each of the six groups is further classified into sub groups as seen in figure 70.

An enzyme generally consists of two fragments, a protein portion, forming a colloidal carrier and a non protein fragment made of a simple, well defined compound which, unlike the protein portion can be dialysed and is largely stable to heat. The non-protein fragment is known as the ***prosthetic group***, if it is tightly attached to the colloidal carrier and as the ***coenzyme***, if it is loosely attached to the same.

The catalytic activity of enzymes and specifically the special groups upon which this activity depends are subjects of intensive research; for in many cases these groups are not completely well known. In some cases –SH groups play the major role; in some others metals bound to the protein may be the principal factors of catalysis. However, for most enzymes the catalytic activity may be traced to the

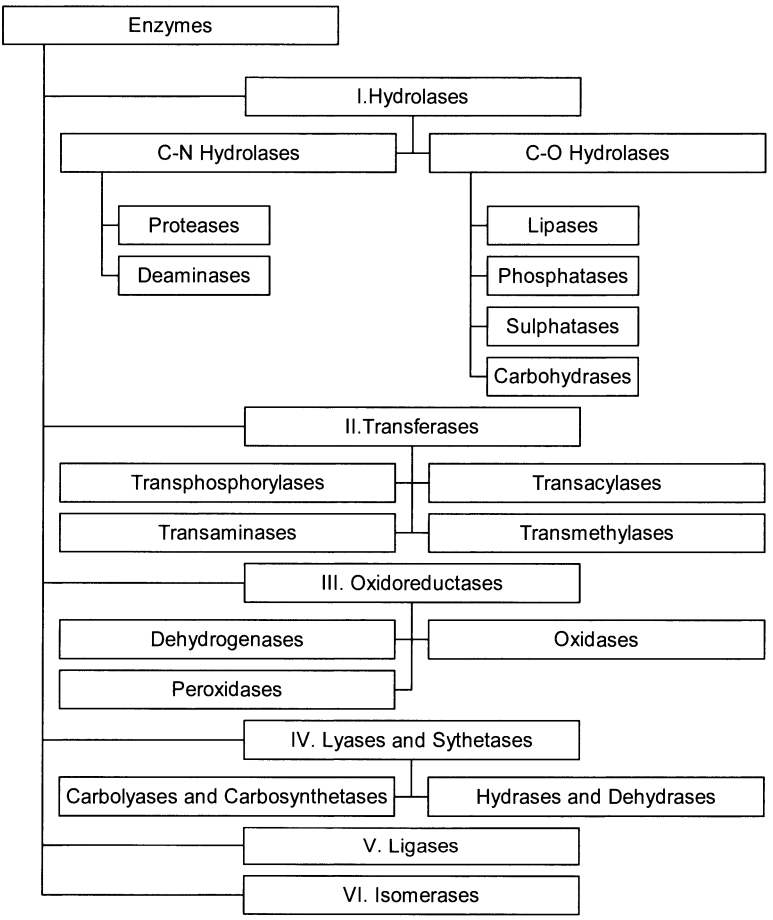


Fig. 70 An outline of enzymes classification

non-protein fragment and may be dependent on certain substances without the presence of which the catalytic activity cannot function. These are called ***cofactors***

I. The Hydrolases

These form about one third of the known enzymes and act mainly on peptides, ester, glycosidic, amide, and similar bonds. They catalyse the hydrolysis of their substrates and may further be classified into C–N and C–O hydrolases according to the type of bond, which may be attacked under their support.

1. C–N - Hydrolases, Specific for the hydrolysis of C–N bond, the C–N hydrolases may be classified according to the C–N bond they hydrolyse into ***proteases*** and ***deaminases.***

a) Proteases. Are those Hydrolases that help degrade proteins (see figure 17 – breakdown series of the proteins) by hydrolysing the internal peptide bonds along the chain linking the individual amino acids in the protein molecule:

$$-CO-NH- + H_2O \rightarrow -COOH + H_2N$$

Normally, proteases are differentiated into the ***proteinases*** that cleave high molecular-weight proteins into simpler compounds (polypeptides), and the ***peptidases*** that further degrade the polypeptides resulting from protein degradation by prteinases.

Proteins $\xrightarrow{Proteinases}$ **Polypeptides** $\xrightarrow{Peptidases}$ **Simpler compounds** *(see figure 16)*

b) Deaminases: These C–N Hydrolases catalyse the hydrolysis of certain types of carbon – nitrogen bond. The most important of them are ***urease*** and ***arginase***. Urease assists the hydrolysis of urea into ammonia and carbon dioxide according to the equation:

$$O=C(NH_2)(NH_2) + H_2O \xrightarrow{Urease} CO_2 + 2NH_2$$

It occurs in Soya beans, watermelon, moulds, and bacteria. Arginase is principally found in animal liver. It helps splitting arginine (a compound of proteins) into ornithine (α, δ - diaminovaleric acid) and urea. Ornithine in the liver of birds removes the toxic benzoic acid in the form of its dibenzyl derivative.

2.C– O - Hydrolases: C–O hydrolases catalyse the hydrolysis of natural esters. Depending upon the type of their substrates, they may be classified into various groups the most important of which are:

a) ***Lipases:*** These are capable of hydrolysing fats. Lipases of vegetable origin are known as ***phytolipases***. An example of them is castor lipase which is found in the seeds of *recinus communis*

b) ***Phosphatases:*** These C-O hydrolases are capable of catalysing the hydrolysis of phosphoric ester groups. They occur in almost all living cells and their catalytic activity is pH-dependent.

c) ***Sulphatases:*** These are capable of hydrolysing natural sulphuric esters e.g. phenyl sulphuric acid.

d) ***Carbohydrases:*** As it is clear from their name, this group of hydrolases is capable of degrading simple sugars as well as transforming polysaccharides into simple ones. A prominent example of them is ***cellulase,*** which degrades cellulose and is only found in bacteria, fungi, and in the digestive juices of certain snails and worms.

The role of hydrolases in pesticide degradation:

Hydrolases, whether they are specialised on the C–N or the C–O bond, are capable, with their various groups and individual enzymes, of degrading many pesticides containing ester, amide or phosphate linkages as explained in the foregoing section. Examples of such pesticides are various. To mention few of them, one

may consider the group of organophosphorus pesticides, the carbamate insecticides, or the urea and carbamate herbicides.

Detoxification of malathion (see table 17 and figure 71) by the action of a C–O hydrolase (carboxylesterase) provides an example for the degradation of an organophosphorus pesticide through cleaving a carboxylethyl linkage.

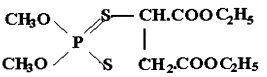


Fig. 71 Malathion

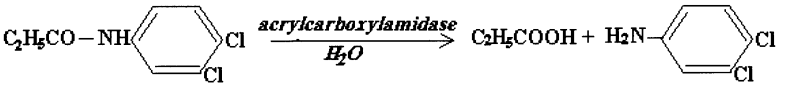
Hydrolysis of the carboxylethyl linkage follows the following reaction path:

$$R{-}COO{-}C_2H_5 \xrightarrow[H_2O]{\textit{Hydrolase (Carboxylesterase)}} R{-}COOH + C_2H_5OH$$

The low toxicity of malathion for some higher animals may be due to the efficiency of this process (Hassall, 1982).

Organochlorine herbicides such as esters of 2,4-D (figure 39 b) are also degraded through the catalytic action of carboxylesterase. After penetrating into the weed, the esters are hydrolysed to release the biologically active dichlorophenoxyacetic acid.

Propanil — an organochlorine herbicide, derived from aniline (figure 40 a), was found to be hydrolysed by the action of a C–N hydrolase (aryl carboxylamidase), found in rice plants (Yih et al, 1968) to produce dichloroaniline.



Propanil *Dichloroaniline*

These were just few examples of the enzymatic degradation of some insecticides and herbicides by the action of hydrolases. The interested reader is referred to (HASSALL, 1982) for a detailed treatment of this theme.

II. The Transferases:

Transferases derive their individual names from that of the transferred group, either with the prefix "trans" and suffix "ase," or followed by "transferase." So one finds names like:

Trans-phosphoryl-ase, trans-acyl-ase, or dihydroxyacetone transferase. Following groups are the most important among the transferases.

1.Transphosphorylases

As mentioned before, some enzymes need to fulfil their action of transforming their substrates into other chemical constitution the assistance of a third substance, normally called the cofactor. Cofactors are usually phosphate esters of sugars or of compounds between sugars and nitrogen-containing bases. A good examples of such cofactors is adenosine triphosphate ATP), formed from the base adenine (figure 72 a), the sugar ribose (figure 72 b) and three phosphate groups.

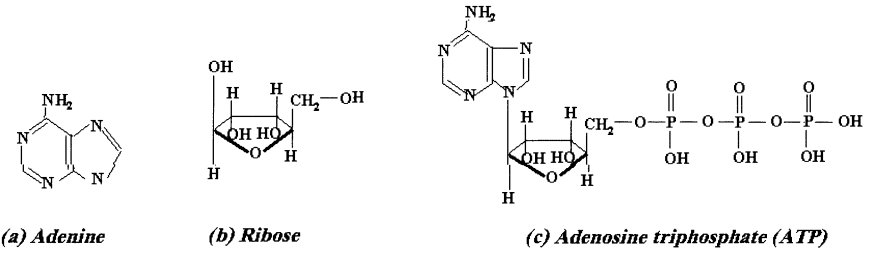


Fig. 72 Constitution of adenosine triphosphate (ATP)

Transphosphorylases, being one of those enzymes that need a cofactor to carry out their task, which is adding phosphate groups to their substrate, use ATP as a source for the required phosphate groups

2. Transacylases

Acyl groups (from *acidum* = acid) are groups of general formula, RCO where R is an alkyl group. They may be viewed as fatty acids (R–COOH), lacking a hydroxyl group (OH^-). Examples are ***acetyl*** (CH_3CO), ***formyl*** (H–CO),etc. En-

zymes, capable of transferring an acyl group from a donor to an acceptor molecule are known as transacylases. These have a loosely attached non-protein fragment functioning as a coenzyme that cleaves the acyl bond in an intermediate step followed by its transfer to the acceptor group. An example can be given by the transfer of an acetyl group (CH_3CO) attached to a molecule X (donor) to another molecule Y (acceptor). Such a process proceeds along the following reaction path:

$$\text{Acetyl} - X + \overline{\text{CoA}}, \quad -SH \longrightarrow \text{Acyl}-S-\overline{\text{CoA}}, \quad +XH$$

$$\text{Acetyl}-S-\overline{\text{CoA}}, \quad + \text{YH} \longrightarrow \text{Acyl}-Y \quad + \overline{\text{CoA}}, \quad -SH$$

($\overline{\text{CoA}}$, = Coenzyme A without –SH group)

Coenzyme A — a coenzyme of transacylases, made of adenine, ribose, phosphate, pantothenic acid, and cysteine plays a decisive role in all biochemical acylations; especially the oxidative degradation of carbohydrates and fats. It also forms a key substance in the conversion of carbohydrates into fatty acids.

3. Transaminases

These enzymes effect a reciprocal process of amination — deamination between keto-acids (mainly pyruvic acid – figure 73 a) and glutamic acid (figure 73) without incurring the presence of free ammonia. In this reciprocal reaction, known as transamination, L-glutamic acid functions as a nitrogen-carrier in the synthesis of amino acids in animal organisms.

In plants, the same role is played by L-aspartic acid. Pyruvic acid, which plays a key role in transamination, is sometimes produced by the degradation of aliphatic herbicides such as dalapon (figure 45).

d) Transmethylases

Like the other transferases, transmethylases transfer a group (in this case methyl) from a donor molecule to an acceptor.

The role of transferases in the degradation of pesticides and other contaminants.

Among the transferases, the system known as glutathione-S-transferase (GST) plays an important role in the detoxification of contaminants by catalysing the conjugation of the endogenous substance (GSH) to an electrophilic site on the intruding xenobiotic material. Glutathione (GSH) is a tripeptide, formed by combination of the three amino acids glycine, cysteine, and glutamic acid as shown in figure 73.

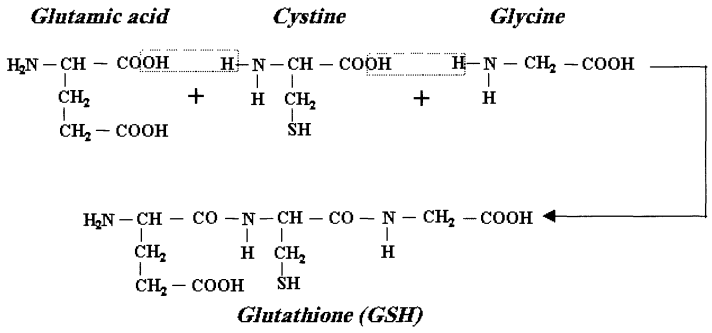


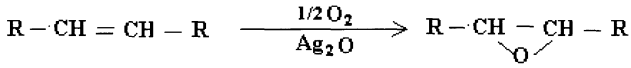
Figure 73 Formation of glutathione

Catalysis of glutathione conjugation on xenobiotics by GST takes place generally on substrates sharing three common features: They must be hydrophobic to some degree, they must contain an electrophilic carbon atom, and they must react nonenzymatically with glutathione at some measurable rate. (T. J. Rees, 1993)

Of the several known glutathione-S- transferases, the following three groups were considered by (HASSALL, 1982) as being among the most important:

a) Glutathione-S-epoxide transferases:

Alkylene oxides or epoxides are groups formed by the oxidation of olefins as shown in the following equation:



Epoxides may be formed during phase I biotransformation as intermediate stages in the degradation of numerous unsaturated compounds. A subsequent opening of the ring by conjugation of an endogenous substance on the epoxide leads in most cases to the formation of substances less harmful to life. This may be illustrated by the GST catalysed glutathione conjugation on the intermediate epoxide of allyl phenyl ether (a substance used in polymer synthesis - see figure 74). In this reaction, glutathione conjugation on the substrate leads to opening of the epoxide ring and formation of a glutathione complex with the detoxified original substance as shown in figure 74.

With benzene rings this reaction precedes more readily if the ring contains chlorine atoms and that is why they may be of great help in degrading organochlorine epoxides, used as pesticides, such as dieldrin (figure 35b) and heptachlor epoxide (figure 35 c).

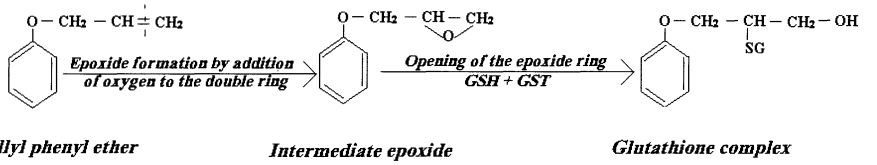


Fig. 74 . Degradation of allyl phenyl ether by Glutathione (GSH)

b) Glutathione –S-aryl transferases

This group effects mainly the elimination of hydrogen halides from their substrates. They are most effective in detoxification of organochlorine pesticides (e.g. triazine derivatives). The chemical mechanism according to which such reaction occurs may be illustrated by the following example (figure 75) of eliminating a hydrogen halide group from a molecule of the herbicide atrazine (figure 43 b).

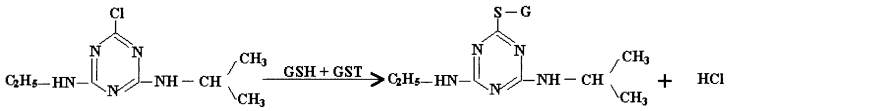


Fig . 75 . Elimination of a hydrogen halide from atrazine by GSH

Various organophosphorus pesticides are also degraded by chemical reactions comprising glutathione conjugation. An example of this is the degradation of the pesticide diazinon, which is strongly adsorbed onto soils. Diazinon is used to control pests that have become resistant to organochlorine compounds. Its cleavage by GST follows the following pathway (Shishido et al, 1972):

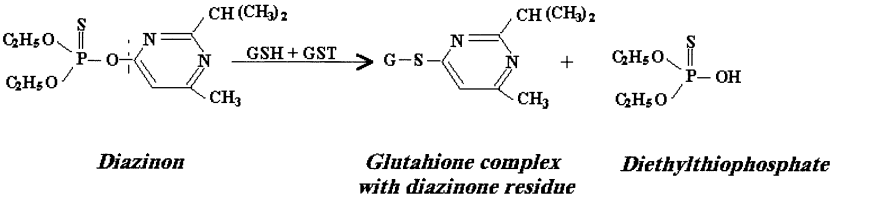


Fig. 76. Cleavage of Diazinon by GSH

c) Glutathione – S – alkyl transferases:

Being capable of reacting with alkyl halides, these enzymes were found effective in removing methyl groups from organophosphorus insecticides, that contain the $CH_3 - O - P$ group. They are less effective in removing ethyl and larger alkyl groups. This may be illustrated by the demethylation of parathion (table 17) as shown in figure 77.

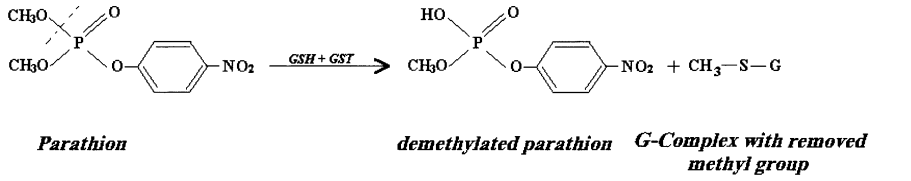


Fig. 77 Demethylation of parathion by GSH

Non-enzymatic glutathione conjugation

Substrates susceptible to glutathione conjugation – as stated before – must be in a position to react nonenzymatically with glutathione (GSH) at some measurable rate. It seems that even in absence of GTS this type of reaction plays an important role in the detoxification of some aromatic pesticides. An example may be given by the degradation of the herbicide propachlor, during which the glutathione is conjugated to an electrophilic site with the elimination of a hydrogen halide to form a complex that subsequently decomposes to an N-acetyl cysteine derivative known as mercapturic acid. The polarity induced by the insertion of COOH group makes such a compound more soluble and hence easy to be excreted in urine or faeces. Figure 78 shows the pathway of such a process. Glutathione levels in soil biota are accordingly used some times as biomarkers in soils i.e. substances that may indicate the level of pollution by relating this to the degree of stress incurred in the organisms. In addition, metabolites such as mercapturic acid may be used for the same purpose.

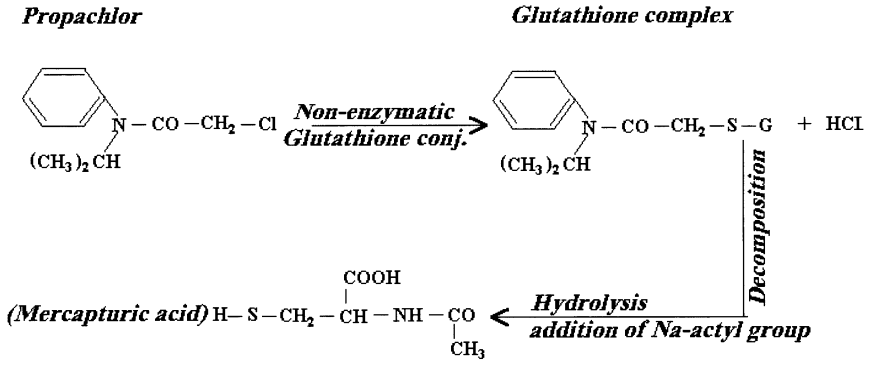


Fig.78 Nonenzymatic propachlor degradation by glutathione

III. The Oxidoreductases

These are enzymes capable of transferring hydrogen or electrons between substrates. They are of three types, the dehydrogenases, the oxidases, and the peroxidases. While dehydrogenases mainly transport hydrogen or electrons to acceptor

enzymes or to oxygen to produce H_2O_2, the oxidases react directly with oxygen to give water. The peroxidases, however, catalyse the decomposition of hydrogen peroxide, which has a toxic effect, into oxygen and water.

a) Dehydrogenases:

The catalytic activity of dehydrogenases is characterised by the transfer of two hydrogen atoms from one organic donor to an organic acceptor. This may be schematically represented –as shown in the following two equations in which the enzyme is represented by the box with the letter D.

$$XH_2 + \boxed{D} \longrightarrow X + \boxed{D}\text{-}H_2$$

$$\boxed{D}\text{-}H_2 + Y \longrightarrow \boxed{D} + YH_2$$

As shown by the equations, two atoms of hydrogen were transferred from the donor X to the acceptor Y, while the enzyme as a catalyst was recovered unchanged at the end of the process.

b) Oxidases

This group of enzymes, also known as aerobic electron transferases, help complete reduction of oxygen into water. They thus differ from the majority of dehydrogenases, which carry the reduction of oxygen only to the peroxide stage. They are metalloprotein compounds carrying heavy metals and are accordingly classified into cytochrome oxidases (Fe-proteins), and cuproprotein oxidase.

c) Peroxidases

These are, as mentioned before, enzymes that attack hydrogen peroxide; they are present in animal organs and most plants and are made of iron porphyrin compounds. Peroxidases catalyse reactions between hydrogen peroxide and other substances according to the equation:

$$XH_2 + H_2O_2 \xrightarrow{\textit{Peroxidase}} X + 2H_2O$$

A similar catalytic function is exerted by ***catalases***, which are also found in almost all animal organs, cells and tissue fluids as well as plant tissues. They effect

the decomposition of the cell toxin, hydrogen peroxide, into water and oxygen according to the equation:

$$2\,H_2O_2 \xrightarrow{Catalase} 2H_2O + O_2$$

The role of oxidoreductases in soil formation and biodegradation of contaminants

Decay of plant debris and other natural organic matter forms one of the main sources of soil humus; among other processes involved in this process biodegradation of lignin holds a central position. This degradation process is initiated by several oxidoreductases excreted by white rot fungi. Examples of such enzymes are haem-containing peroxidases, lignin peroxidase (L.P), manganese dependant peroxidase (Mn P) as well as copper containing phenol oxidase, laccase (Camarero et al, 1999)

Further research revealed that lignin-degrading enzymes, excreted by white rot fungi, are also capable of oxidising high-molecular-weight polycyclic aromatic hydrocarbons (PAH); this directed attention to them as potential agents for bioremediation of contaminated soils (Michiel et al, 1998).

Various oxidases use nicotinamide adenine dinucleotide (NAD) or its phosphate derivative nicotinamide adenine dinucleotide phosphate (NADP) as coenzyme. NADP-dependent reactions were found, as it will be shown in the following examples, to be important for the biochemical degradation of many insecticides.

a) Hydroxylation of carbaryl:

Carbaryl (figure 79), a carbamate insecticide, which is used to control pests mainly on maize and soybeans may suffer ring hydroxylation by NADP assisted oxidases to give a mixture of 4-hydroxy and 5-hydroxy carbaryl as shown in figure 79.

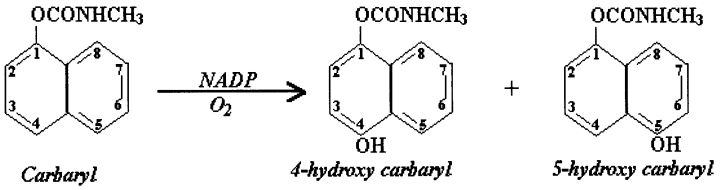


Fig. 79. Ring hydroxylation of carbaryl

b) O-dealkylation of methoxychlor:

Methoxychlor (figure 80) is a minor organochlorine insecticide similar to DDT, yet differing in that it has p, p′ - dimethoxy groups instead of chlorine atoms. It can be easily dealkylated by NADP-dependent enzymatic reactions to produce the polar compound demethyl methoxychlor that can undergo further conjugations, facilitating its removal from animal bodies.

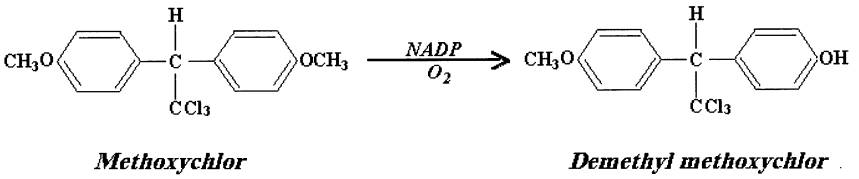


Fig.80. O-dealkylation of methoxychlor

In his book on the chemistry of pesticides, Kenneth Hassall (Hassall, 1982) quotes the eminent toxicologist Barnes with the words that *"if methoxychlor had been marketed instead of the slightly cheaper DDT, the persistence of organochlorine insecticides may never have been regarded as a factor of major ecological importance"*.

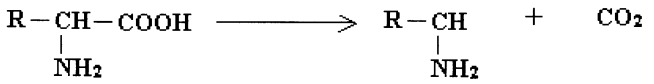
IV. The Lyases:

This group helps mainly the cleavage of a C–C bond. They are subdivided according to the bond they split into the carbolyases and the dehydrases.

a) Carbolyases: an important member of this group is α-carboxylase (pyruvate decarboxylase). It splits pyruvic acid into acetaldehyde and carbon dioxide according to the equation:

Pyruvic acid *Acetaldehyde*

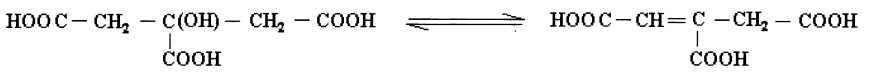
Another important member of the group is amino acid decarboxylase that occurs in microorganisms, in higher animals, and in many plant tissues. It plays a key role in the putrefaction of proteins by catalysing the anaerobic decarboxylation of amino acids into amines and carbon dioxide according to the equation:



Amino acid *Amine*

b) Dehydrases

This group catalyses the elimination of water. It plays an important role in citric acid cycle. Its function may be illustrated by the action of the enzyme ***aconitase*** (citric-isocitric isomerase) that helps changing citric acid into cis-aconitic acid according to the equation:



Citric acid ***cis-aconitic acid***

V. The Ligases

Ligases (Synthases) catalyse the linking of two molecules; they are sometimes classified according to the type of bond formed under their catalytic action. Thus, we may have carbon-sulphur bond forming, carbon oxygen bond forming, or carbon-carbon forming ligases.

VI. The isomerases

This class of enzymes catalyse intramolecular rearrangements. An example may be given by D-arabinose isomerase, an enzyme that catalyses the intramolecular rearrangement of D-arabinose to give D-ribulose.

9.5 Transformations assisted by bacterial action

In the foregoing sections, it was shown that soil organisms assisted by their natural metabolic processes create an environment in soil that allows the whole system to develop and to avoid conditions that would bring it to collapse. It should, however, be reminded that the main target of all metabolic processes is to secure the energy required for an organism to continue its life activities. Energy production in plants is reached through a complex of light-assisted biochemical processes known collectively as photosynthesis. In animals, cleavage (mostly oxidation) of complex organic material fulfils the same purpose; the whole process –in this case- is known under the collective name chemosynthesis.

Bacteria and other low organisms use both processes, yet some bacteria are also capable of energy production through chemical transformation of inorganic material and thus play a role in determining the fate of inorganic pollutants in soil.

Changes in the soil environment by bacterial action are brought about mainly by organisms, known as the lithotrophs (Rock eaters). The Russian microbiologist Sergei Winogradsky, who first described them in 1885, gave them this name. As the name indicates, they are capable of covering their need of energy by oxidising

soil inorganic compounds. This process may be pure chemotrophic as explained before, or it may be a phototrophic one, using visible light as a source of energy. Fig. 81 summarises these relations.

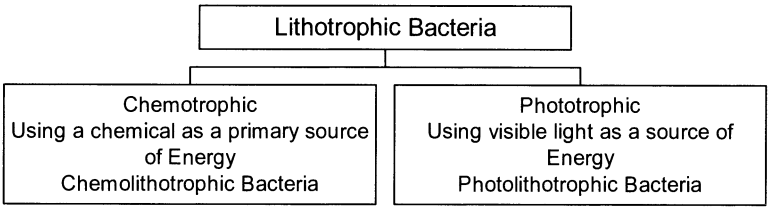


Fig. 81 . Classification of lithotrophic bacteria according to their energy sources

The major groups of lithotrophic bacteria, playing principle roles in modifying the soil environment, are the following:

a) Sulphur bacteria
b) Iron oxidising bacteria
c) Nitrifying bacteria
d) Hydrogen oxidising bacteria
e) Methane bacteria

a) Sulphur bacteria

The natural ecological community of sulphur bacteria is generally known under the collective term *sulfuretum,* coined by Baath-Becking in 1925.

A sulfuretum exists normally in oxygen-deficient environments and may even flourish under extreme conditions such as in the case of the highly alkaline sediments of Wadi Natrun in North-western Egypt (Trüper, 1982). Organisms living in such a community must not essentially follow the same trophic mode– some may be chemotrophic, while others could be phototrophic. As examples of both types, we may mention the following:

1.Photolithotrophic sulphur oxidising bacteria:

A good example of these is provided by the so-called *thiospirills that* belong to the family *Rhodospirillaceae*. They embrace two subgroups of which the first uses

H_2S or S as proton donor in photosynthesis, while the other uses H_2 derived from the breakdown of organic substances such as fatty acids, for the same. To differentiate between them, the first group is called the group of *thiorhodaceans* while the second is known as the group of *athiorhodaceans*.

2. Chemolithotrophic sulphur oxidising bacteria:

Two prominent examples represent this group — *Beggiatoa sp.*, and the oftenmentioned *thiobacillus denitrificans.* Beggiatoa has a peculiar thread like appearance and is always in a continuous state of worm-like motion (see Fig.82)

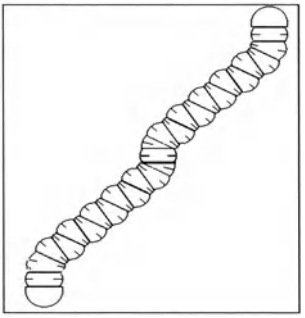


Fig. 82 . Beggiatoa

Sulphur organisms of the beggiatoa species use both Hydrogen Sulphide and elemental sulphur (S^0) for their chemotrophic oxidation processes according to the following equations:

$$H_2S + 2\,O_2 \longrightarrow SO_4^{-2} + 2H^+$$

$$S^0 + 2\,H_2O \longrightarrow SO_4^{-2} + 4H^+$$

Thiobacillus denitrificans is capable of oxidizing hydrogen sulphide, using nitrate $(NO_3)^-$ as an oxidizing agent instead of oxygen. As a result of this process, molecular nitrogen (N_2) and sulphuric acid (H_2SO_4) are released.

Some bacteria species are also capable of reducing sulphate to produce sulphide under anaerobic conditions; of these we may mention *desulfovibrio sp.* And *Desulfotomaculum sp.* Sulphite reduction to sulphide is carried out by the anaerobic bacterium *Clostridium pasteurianum* (Trüper, 1982)

b) Nitrifying bacteria

These widely distributed bacteria, represented by two groups living in a symbiotic community – the nitrite bacteria (e.g. *nitrosomonas europaea*), and the nitrate bacteria (e.g. *nitrobacter agile, nitrobacter winogradskyi)* are very important soil dwellers that cause important chemical changes in the soil environment. The first group changes NH_4^+ (ammonium) into NO_2^- (nitrite), while the second group oxidises nitrite further into nitrate (NO_3^-), according to the following reactions:

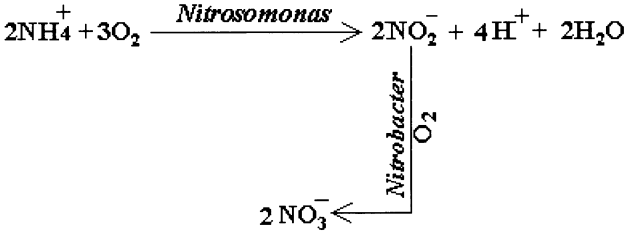


Fig. 83 .The combined work of nitrosomonas and nitrobacter

Nitrosomonas europaea was first discovered and described by Winogradsky in 1890. It flourishes under aerobic conditions in arable soils, where ammonia (NH_3), resulting from the breakdown of organic substances, is continuously oxidised to nitrite $(NO_2)^-$ according to the equation:

$$2NH_3 + 3O_2 \longrightarrow 2HNO_2 + 2H_2O$$

The energy set free in this reaction supplies the major part of energetic requirements for chemosynthesis of carbon dioxide by this group of bacteria.

c) Iron oxidising bacteria

Many species, belonging to the order *Caulobacterials* possess the capacity of oxidising Fe (II) into Fe (III), whereby the oxidation product will be stored in their mucous cells, giving them the characteristic rusty brown colour of Fe (III)-OH. This may in some cases supply an explanation for the appearance of rusty horizons (patches) in soils and marine sediments, inhabited by bacterial colonies such as *gallionella ferroginea* or *siderocapsa treubii*. The first of these, flourishes near iron rich springs, and may also grow in shallow marine environments.

d) Methane oxidising bacteria.

It seems that anaerobic methane oxidation goes hand in hand with sulphate reduction; for it was postulated by many authors that methanogenic bacteria (e.g. *Scarina methanica*) may be producing and oxidising methane at the same time. *Scarina methanica* uses carbon dioxide as a proton acceptor to change alcohols to methane according to the equation:

$$2CH_3CH_2OH + CO_2 \longrightarrow CH_4 + 2CH_3COOH$$

Acetate, produced in this reaction, allows and supports the growth of sulphate reducing bacteria, which may, in turn, assist the anaerobic oxidation of methane into carbon dioxide and water.

e) Hydrogen bacteria

This group, assisted by the catalytic effect of the enzyme hydrogenase, is capable of oxidising molecular hydrogen into water. *Hydrogenomonas* – a species belonging to the family *Nitrobacteriaceae* is capable of oxidising molecular hydrogen to produce water according to the equation:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Part 3

Monitoring of soil pollution

Monitoring is the regular surveillance and quantification of the amount of pollution present in a given location of soil. It should be carried out in a way that enables the detection of spatial as well as time variations in the concentration of pollutants at the site of investigation. Monitoring should provide information on the following:

- Nature of the pollutants, their quantities, sources and distribution
- Effect of the pollutants.
- Concentration patterns, pedological changes and their causes
- Possibility and feasibility of remediation.

It may be carried out using physical, chemical, or biological methods.

Chapter 10

Monitoring and monitoring plans

Before setting up any monitoring plans, complete information about the investigation site should be carefully collected and analysed. This saves a great deal of effort and financial costs and allows a suitable selection of the monitoring technical installations. Important information about the site should include geological, pedological, hydro-geological, and historical data about land use in the area. Geological and hydro-geological information can be taken from geological maps or from information supplied by the local geological survey. For pedological information, soil maps or individual field investigations are normally used.

The main step after collecting and analysing the available information is to determine the main objectives of monitoring, providing careful answers for the following questions:

a) *Is the main objective of the monitoring project to detect the presence or absence of a given contaminant? If yes, this will be a detecting monitoring (see below)*

b) *Is it known that the site is already contaminated with the alleged pollutant where in this case the main objective of the plan would be to determine the extent of contamination? If yes, this will be an assessment monitoring (see below)*

c) *Is the objective of the plan to evaluate the feasibility and required financial burden for remediation of a pre-investigated area? If yes, (one speaks here of performance monitoring)*

d) *Will the monitoring process be a part of a follow up plan to evaluate the success of remediation efforts? If yes, a research monitoring (see below) will be the main activity*

Each of the above-mentioned questions delivers an answer that helps selecting the method of monitoring and consequently the technical installations required for the project. This allows a proper planning and assessment of the financial burden in advance. In fact, each of the above mentioned criteria serve to limit the choice of the monitoring technique planned for the site under investigation. All techniques and possibilities have in common that the preliminary steps follow a general strategy starting with site characterisation followed by determining the objectives of monitoring and finally determining the techniques and field measurements suitable for the objectives and type of monitoring to be conducted – in short the proposal of a sampling and monitoring plan.

An integrated monitoring plan comprises generally the following essential parts:

- Site characterisation
- Data acquisition
- Data quality control
- Interpretation
- Reporting

10.1 Site characterisation:

Collecting all available data about the site of interest should precede all fieldwork in a monitoring project. This includes reviewing all published information about geomorphic and pedological characteristics of the area. If no maps are

available, the area should be mapped, using any of the known standard techniques, whereby the following types of maps should be obtained.

a) Base map: A base map helps characterising the morphology of the site and shows the runoff conditions including water bodies that might be influencing hydrologic flows in the site. In a later stage, all sampling stations should be plotted on the base map. If biological monitoring is also planned, the stands of all trees and plant communities used for measurements are to be marked.

b) Geologic map: Since soil types are normally related to the bedrock and the weathering processes that produced them, a geologic map of the area, detailing the main rock types, is either to be prepared or obtained from the local geological survey authority. Such maps provide valuable information about the soil chemistry and the background concentration of heavy metals in the unsaturated zone of groundwater. It also helps determining the potential for flow, adsorption, and retainment of pollutants in the soil material at the site of investigation.

c) Hydrologic maps, which are based on the interpretation of all geologic information about the area supply information on ground water relations such as availability of ground water, the depth to the water table and the direction of groundwater flow.

Normally, a geologist is in a position to read all required information about subsurface flow characteristics in the area using such maps. Hydrologic maps can be obtained from the local geological survey, other wise test bore holes coupled with careful observation of available wells in the locality may help delineating the hydrologic conditions in the site of investigation to a fair degree.

d) Overburden (Soil material) maps: Pedological maps or soil maps provide information on soil types prevailing in the area according to one of the pedological classification systems mentioned in part 1 of this book. They provide a means of interpreting any differences in the soil chemistry of the area and help understanding any inconsistency in chemical characteristics at different parts of the investigation site. Such inconsistency may result due to the existence of different soil types

at the site of investigation. Soil maps obtained from the local survey authorities include normally useful information on soil texture, soil depth, as well as soil chemistry data such as heavy metals, pH, and CEC-values.

Beside geographic and geologic characterisation of the site, any available information about historical conditions of the site may be of great help in later evaluation of the data obtained. This includes photographs, maps, and any published or unpublished data about earlier land use activities.

10.2 Data acquisition

Following the preliminary preparation and characterisation of the area, the principal step in a monitoring plan comprising data acquisition and generation should be started. This stage includes the preparation of a sampling plan and determination of the chemical and physical characterisation of the problem. Fig 84 shows in a schematic way, the relations connecting all those processes required for data acquisition and generation. Two main steps are essential for this aim — the preparation of a sampling plan and planning of all chemical and physical investigations that will form the framework of data collection.

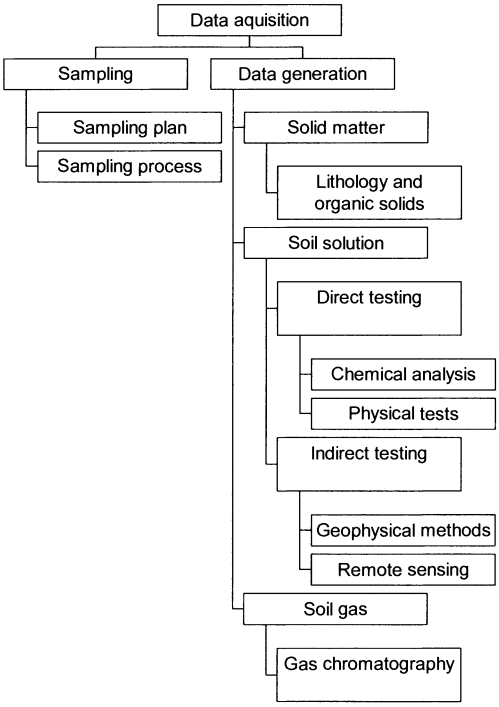


Fig. 84 The main steps in soil monitoring

10.2.1 Sampling – Planning and realisation:

In all types of monitoring mentioned above sampling forms the principal chain in all processes needed for the delineation and characterisation of the environmental quality parameters of the area under investigation. It helps locating the site(s) of contamination and provides information on time and spatial patterns related to the distribution of pollutants.

Location of sample points

In designing a sampling plan the location of sampling points will largely depend upon the purpose of monitoring as well as on the topography and geological conditions of the area. A detection monitoring plan or an assessment monitoring

plan for example imply a dense net work of sampling stations that are more or less systematically distributed over the whole area of investigation, while evaluation monitoring will require a concentration of sampling stations in the neighbourhood of the pollution sites. It must also be emphasised that a good knowledge of the geology and hydrology of the area is very decisive for the selection of the sampling locations.

Spatial patterns of sampling follow two fundamental types that form the basis for all types mentioned by different authors (see for example Boulding1995). These are the simple rectilinear grid type and the traverse type, both of which were originally developed and used by exploration geochemists.

In the first type (grid pattern) a rectilinear grid of samples is taken at equal intervals along evenly spaced lines (systematic, Fig.84). Another variation of this type is to take random samples within every block of the grid (random, Fig. 85).

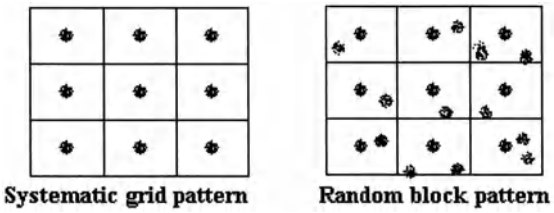


Fig. 85 Rectilinear grid patterns of sampling

In traverse line sampling, points are selected on a traverse following topographic, geological or geophysical data. Decisive for the direction and density of sample points are environmental and geochemical data known about the area. Samples along a traverse may also be taken systematically (at equal intervals) or at random distances. However, rectilinear grid patterns of sampling are more popular because of the ease in laying out the fieldwork and in plotting the data. The reliability of samples as representatives for the environmental conditions in the investigated area depends principally on factors like frequency of sampling, technical procedures of sample collection, objective and technical errors of the

operator as well as storing, handling and treatment of samples in the course of their collection and transport to the laboratory.

Generally, however sampling points should be concentrated around hot spots i.e. around spots, where contamination is expected or near areas that are suspected of being contaminated.

10.2.2 Sampling procedures

a) Sampling solid soil matter

Soil samples are taken either at fixed depths or separately from each pedogenic horizon, if detailed work is intended. Following depths are recommended by the UN/ECE ICP Forests programme (UN/ECE ICP Forests, 1994): 0–5 cm, 5–10 cm, 10–20cm and 40–80 cm. Samples from shallow depths (up to 30 or 60 cm) are collected from small pits. Deeper samples are normally collected using a soil auger. Simple soil augers (Fig. 86) were found satisfactory in sampling depths from 1 to 2 meters.

Fig 86 A simple soil auger

Simple soil augers are normally used to sample loamy soil. For stony soils, especially if deep samples are to be collected, light power augers are recommended.

Peat samples are collected using box-type samplers or by means of special augurs such as the Hillier peat borer (Fig.87).

Fig.87 . Hilliers Peat borer

Undisturbed soil samples can be obtained by using a piston sampler or may be taken from a soil pit dug near to the plot.

b) Sampling soil solution

For monitoring purposes, soil water can be sampled by using either zero-tension lysimeters or suction samplers. A lysimeter is a device permanently installed in the soil to sample soil water periodically. According to the principle underlying flow of water into the lysimeters two types of lysimeter are known:

i) The zero tension lysimeter, which is designed to sample soil water as it moves through saturated soil. It consists of a cylinder placed below an undisturbed core of soil, which has been originally removed by a piston sampler. Two flexible connections are attached to tubes at the soil surface. One of the connected tubes serves as an air let tube, while the other may be attached to a vacuum pump for collecting the samples (see fig. 88)

Zero tension lysimeters were found useful in monitoring soil water during and after in situ remediation. This helps a monitoring of water variability.

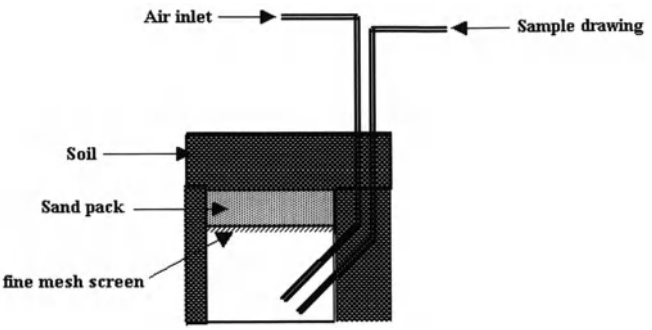


Fig. 88 . Structure of a simple zero tension lysimeter (After Thompson and Scharf, 1994)

ii) Suction lysimeter (Fig. 89): This is a device used to sample soil water in unsaturated soils. A source of constant vacuum draws the water into the lysimeter through a porous membrane. Water samples are brought to the surface by suction through a tube dipping deep into the device.

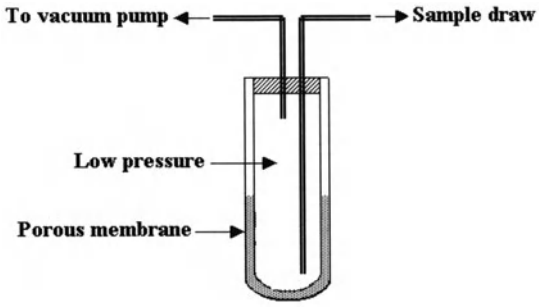


Fig. 89 A suction lysimeter

c) Sampling soil air

Although soil gas investigation may be helpful in monitoring various environmental parameters, it is best used to investigate pollution by highly volatile hydrocarbons such as benzene, toluene. It is also useful for detecting contamination by chlorinated solvents and other organic pollutants.

Soil gas sampling can either be done by simple methods such as air extraction from holes bored with an auger using a manual suction pump, or by relatively advanced methods, where soil air is sucked through a probe rammed in the soil to a depth of about 1m, by pumps mounted on a vehicle equipped with proper analytical facilities. In case manual pumps are used, the collected samples should be stored in airtight stainless steal or glass containers before being sent to the laboratory.

Another method of soil gas sampling, which is relatively new, is the so-called passive sampling. This technique, which is principally used for detecting volatile organic matter, uses an activated charcoal rod buried in the soil as an in situ adsorbent for VOC's. After few days or weeks the charcoal rod is retrieved and analysed by gas chromatography or any other suitable analytical method.

10.3 Field and laboratory investigations

Test methods of the collected samples whether solids, liquids or gases will depend upon the purpose of monitoring as well as the degree of precision aimed. Screening or field methods will some times suffice for a first assessment of the degree of contamination. In other cases however, detailed laboratory tests are required to determine the next steps required for the project.

10.2.2.1 Investigation of solid matter:

The sampling personnel normally screen the lithology of soil in the field by visual assessment. This is a relatively easy task that can be carried out by workers who have got some training in geology. In case more detailed information are required and if grains cannot be identified using a pocket lens, a microscopic examination in the laboratory may be carried out by a geologist. XRD (X-ray Diffraction) analysis may in some cases be required. The presence of certain contaminants can also be ascertained in the field by visual assessment. Examples of theses contaminants are oil, tar and other coloured materials. For oil, however the method of UV-fluorescence that has been successfully used in oil exploration is now in wide use.

If field assessment for organic material does not supply sufficient information, laboratory investigation using I.R (Infra Red Spectroscopy), G.C (Gas Chromatography) or any other method is carried out in the laboratory.

Bulk chemical analysis of the soil matter is very efficient in determining pollution by heavy metals. This may be carried out by Atomic Absorption Spectroscopy (AAS) or by any other suitable method.

10.3.1 Investigation of soil solution

A) Direct methods: Samples collected in the field by the previously mentioned methods should be analysed immediately after being brought to the laboratory. The time between sample collection and investigation should always be kept at minimum. Physical parameters such as pH, Eh and salinity are to be determined at the beginning. Determination of metal contents is normally preceded by adding acid to the samples (0.5 ml conc. HNO_3) to ensure desorption of metals from the walls of the storage bottles. If samples are collected by lysimeters, filtering might not be needed because the porous membranes or the sand pack in case of ZTL act themselves as filters.

The concentrations detected, may however be misleading due to the fact that the samples collected by the previous sampling methods originate normally from the coarse and medium pores of the soil, which often have concentrations deviating from those in the finer pores. Also the possibility that the samples may be collected from depths, where the soil solution is not so much affected by the plume can form a source of error. In order to ascertain better quality of data, soil samples from different depths and locations may be centrifuged in the laboratory. The collected soil solution can be analysed to supply a control for the data gained from analysing lysimeter samples.

B) Indirect methods: Indirect methods that may provide data bout soil solution without disturbing the surface of the soil include surface geophysical methods as well as remote sensing techniques. Both make use of measuring variations in physical parameters such as gravity, electrical conductance or Earth magnetic

fields. Remote sensing methods depend upon measuring the response to specific parts in the electro magnetic spectra such as gamma rays, visible light or micro-waves.

1. Surface geophysical methods:

Inorganic plumes are oft detected and mapped using the property that ions present in leachates are capable of increasing the specific conductivity of soil solution. The classical methods, which have been successfully used in this category, are those depending on measurements of Resistivity or self-potential properties of the soil. However, electrical geophysical methods used in environmental research depend upon measuring variations of two parameters, which are crucial for the conductance of electric current within earth materials. These are the Resistivity and the conductivity.

Resistivity, which is the reciprocal of conductivity of any material is defined as the electrical resistance of a cylinder of this material, having a unit length and a cross sectional area of unity. It controls the amount of electric current that can pass through the material and can be determined by the following equation:

$$R = \frac{\rho S}{l}$$

Where R = the resistance, l = the length, S= the cross sectional area and ρ is the Resistivity. The unit of Resistivity is the ohmmeter or ohm-centimetre. Conductivity for a continuous medium is given by $1/\rho$ and its unit is siemens/m or mho/m.

In Earth materials the porosity and the chemical constitution of the fluids filling the pores are the primary factors determining the Resistivity of the rock or soil body. Due to this, the salinity of soil fluids play the principal role in determining the conductivity of electric current within the soil at shallow depths. Making use of this important fact, the distribution of resistivity at shallow depths of the soil is determined by surface measurements and the so gained results are used to locate contaminant plumes at the site of investigation. This is done in the field by the transmission of direct electric current through the soil, followed by measurement

of the induced potential. Two pairs of electrodes are used at the surface. One pair of electrodes (current electrodes, A and B in figure 90) is used for introducing current into the soil while the other pair (potential electrodes, C and D in figure90) is for measuring the potential associated with the current.

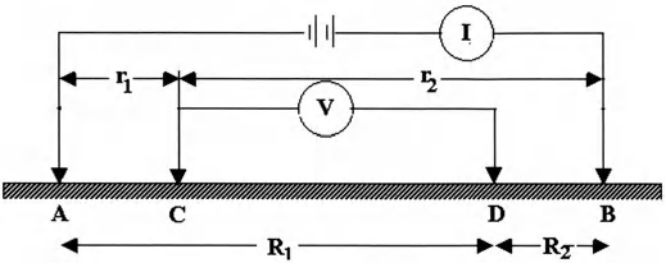


Fig. 90 Arrangement of the electrodes for resistivity measurements in The field (after DOBRIN & SAVIT, 1988)

The potential at point C is given by:

$$V_C = \frac{I\rho}{2\pi}\left(\frac{1}{r_1} - \frac{1}{r_2}\right)$$

Where r_1 = the distance between potential electrode C and current electrode A, and r_2 is the distance between B & C.

The potential at point D is given by the equation:

$$V_D = \frac{I\rho}{2\pi}\left(\frac{1}{R_1} - \frac{1}{R_2}\right)$$

R_1 = the distance from D to A, whereas R_2 = the distance from D to B. In both cases the resistivity ρ can be calculated from the equation since V is known from measurements.

2. Remote sensing methods: Remote sensing is the term used to describe methods of obtaining information about an object with a sensor, which is physically separated from the object. Sensors may be mounted on a variety of platforms ranging from ground-based tripods to aircrafts and balloons. Mostly, however, aircrafts equipped with photographic devices are used.

The majority of remote sensing methods make use of measuring the response to specific parts of the electromagnetic spectrum such as gamma rays, Infra red, visible light, microwaves or radio waves. They also make use of measuring changes in potential fields that may indicate anomalies of the subsurface such as gravity and Earth's magnetic field. Very good results have been achieved in locating buried waste and determining the depth to ground water by Ground Penetrating Radar waves (GPR). This technique (GPR) has also been successfully used for measurement of organic pollutants in ground water. It makes use of measuring the degree of depression of the capillary zone resulting from the presence of hydrocar bon films on the surface of water table – a property, which was already mentioned on page 138 of this book (see for e.g. OLHOEFT, 1986)

10.4 Monitoring of ground water flows

As it was mentioned before, pollutants infiltrating the soil may be transported or absorbed on grain surfaces in the vadose zone. They may also penetrate the substrate to join the saturated zone where they are further transported and spread on a wide scale. Study of the dynamic properties of ground water and the mechanisms of flow may be very important in planning and designing of remediation projects. A monitoring of the velocities and directions of flow is thus an essential part of the whole monitoring plan. To understand the dynamics of ground water, a characterisation of the levels of water concentrations and the extent of change in their dynamic properties according to the prevailing geologic conditions should be shortly explained.

The different zones of ground water:

Ground water is concentrated under the surface in two main zones representing two different concentration (or pressure) conditions. Starting from the surface, the vadose zone is that column reaching down to the water table. It is also known as the aerated zone or the unsaturated zone, despite the fact that it may, under some

conditions, be intermittently saturated. Its description as aerated refers to the fact that the hygroscopic waters collecting here create an environment having a pressure less than that of the atmospheric air. At the base of the vadose zone there is a region, where the water rising by capillary pressure from the water table, forms a fringe, the height of which depends on the pore sizes of the sediments. Following the principles of capillary rise the fringe reaches maximum width at lowest pore size in the aquifer. It may however collapse through contamination with non-aqueous phase liquids as already mentioned in chapter 8. The capillary fringe forms a transition zone between the permanently saturated phreatic zone and the vadose zone. The water table (the upper layer of the saturated zone) forms the base of the capillary fringe. (fig.91 shows, in a schematic way, the distribution of ground water zones in a hypothetical aquifer.

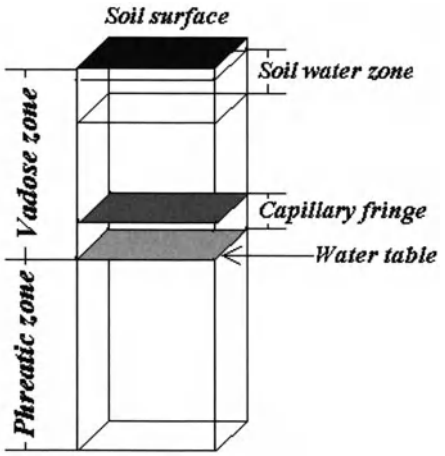


Fig. 91 Schematic representation of ground water zones in a hypothetical profile

Monitoring flow directions:

Flow directions may be roughly deduced from the topography of the site or by consulting a hydrogeologic map, however for accuracy on a local scale this is done by systematic measurements of the water table height above a standard level

(normally sea level) and plotting the results on a base map depicting the distribution of hydrologic heads. For this purpose observation wells reaching below the water table are drilled at several (as many as possible) locations of the investigation site. They should be cased with tubes of equal diameters ($\approx 4''$). Measurements of the depth to the water table are systematically performed at equal periods and the height above sea level is calculated. Location of the test wells depends on two conditions, without which erroneous results could be achieved. These are:

a) All test holes should be sunk to a depth that does not go beyond the same aquifer.

b) They should possess a good hydraulic conductance relative to each other

Fulfilment of the first condition requires a fundamental knowledge of subsurface geology in the area, so that all observation holes should be drilled at depths and positions that remain within the boundaries of the same aquifer.

However, to be sure of a good hydraulic conductance among the test wells, pumping experiments are required. Hölting (1980) quotes Nattermann (1962) with an empirical rule for experiments needed to determine the suitability of a site as a systematic measuring station for water level monitoring. According to this rule, good hydraulic conductance is proven in a test well if the following relation would have a numerical value higher than 0.0115.

$$\varepsilon = \frac{2}{t}\left(\frac{h_1 - h_2}{h_1 + h_2}\right)$$

Where: h_1 = drop of the water table level by pumping relative to the original stand.

h_2 = recovery of the water level after time t

t = time in minutes

To illustrate this, following example may be considered:

In a pump experiment the water table level dropped by 45-cm. After 5 minutes, however, back flow caused the level to rebound to a level, 28 cm higher than the lowest level reached by pumping. Is the site suitable for being chosen as a water table monitoring station?

h_1 (level drop) = 45 cm

h_2 (recovery) = 28 cm in t = 5 minutes

Therefore, ε = (2/5) [(45-28)/ (45+28)] = 0.093, which is higher than 0.0115

i.e. the site is suitable as a monitoring station for water height measurements. It possesses a good hydrologic conductance within the aquifer. Data collected over a long time are later used to plot water table maps, upon which potentiometric contours are drawn to depict the directions of ground water flows. These are generally perpendicular to the contour lines. In the section, dealing with modelling of soil pollution (page), techniques for the construction of potentiometric maps will be introduced.

Monitoring hydraulic heads:

The purpose of measuring the height of water table in different observation wells is not only useful to determine directions of flow, but can also supply information to be used in Darcy's equation to determine many other parameters, such as the velocity of ground water flow, the transport of contaminants in ground water or the time required for a given amount of contaminants to reach a certain point in the area.

Practically the hydraulic head in an observation well is measured by subtracting the depth to the water table at the observation well from the topographic height of its casing top above datum level (normally sea level). So (in Fig 92) if the top of the casing of an observation well lies at a height of 87.0 m above sea level and the depth to the water table measured from the top of the casing is 6.0 meters, its hydraulic head would have a height h_1 = 87.0 – 6.0 = 81.0 m. In the chapter dealing with modelling of soil pollution the use of such data will be discussed with some more elaboration.

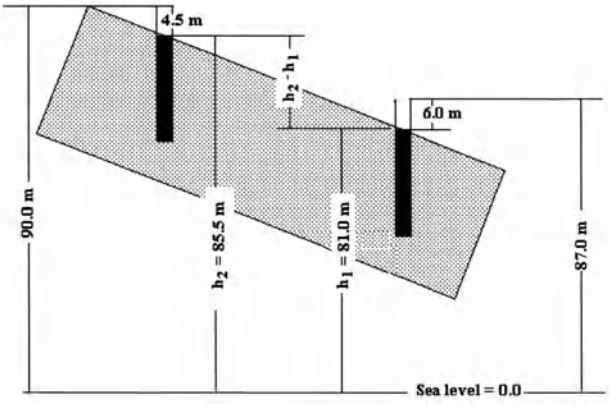


Fig. 92 Monitoring of hydraulic heads in two wells

Measuring hydraulic heads in the vadose zone

Hydraulic heads in the vadose zone are measured using a tensiometer. This is made of a porous cup attached at its upper end to a PVC tube on which a transducer or a common pressure gauge is attached (see. Fig 93) The cup and PVC tubing, which is sealed at the top, are filled with degassed water and brought into the soil at the depth required. Through the porous cup hydraulic contact between the soil water and the tensiometer is established. It reaches dynamic equilibrium when flows in both directions have come to equilibrium.

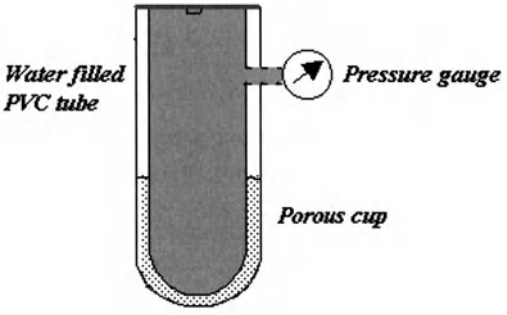


Fig. 93 Tensiometer

Tensiometer readings give the so-called tensiometer potential (ψ_t), which is related to the degree of saturation of the soil. Its value by full soil saturation (where no exchange between the soil and the instrument takes place) is equal to 0 i.e. zero flux. Normally tensiometers of different lengths are buried at specific depths, where potentiometer potential gradients can be read.

Chapter 11

Biological Monitoring

Every plant and every living organism inhabiting a part of the terrestrial environment is, in a way or another, a product of this environment. It reflects the natural conditions prevailing, whether in a chemical or a physical sense. Especially plants have in environmental geochemistry as well as in exploration geochemistry proved to be excellent indicators of the chemical conditions prevailing in their substrates – a property which is now finding wide application in soil monitoring. One should, however, mention that observations associating plant species to chemical conditions in landscapes are not just modern pieces of wisdom that grew with the wide development of environmental science. Old miners in Europe and else where have always known of the indicative character of certain plant species for buried ore deposits. BROOKS (1979) reports about the use of *Lychnis alpina* by Scandinavian miners searching for copper in medieval times. Also, in south Tunisia and in Sinai (Egypt) nomadic tribes have always been using plants as indicators for saline substrates. In middle Anatolia (Turkey), inhabitants identify saline substrates through small shrubs of "saltwort – *salsola nitraria*", known there as the "red *kursalik",* due to its beautiful pink colour. These observations are now classified and critically investigated in the discipline of geobotanics.

MARTIN & COUGHTREY (1982) classify indicator plant species into two main groups: universal indicators, which exclusively grow on soils having high concentrations of the metal indicated by them and local indicators, which are associated

with metal-bearing substrates in certain geographical areas but which also grow elsewhere in non mineralised areas. This means that the most useful types of these, are the universal indicators. However, this classification is not so rigid as it may appear on the face of it. Some universal indicators may occasionally grow in areas having low concentrations of the metal characterising their typical substrates. An example of this may be given by *Crotalaria Cobaltica*, which is otherwise considered as a universal indicator for cobalt. In their book published in 1982, MARTIN & COUGHTREY include a list of plant indicators together with their specific metals.

Plants indicate the condition of their substrates through two properties: geographical distribution or formation of certain assemblages; and the appearance of abnormal morphological changes, due to stress or metabolic problems resulting from metal uptake. Some shrubs, growing on raised reefs in North Luzon (Philippines) are miniature forms of their species growing elsewhere. This is a typical symptom known as dwarfism. Other symptoms of disturbed metabolism may include gigantism, chlorosis of the leaves, distortion of fruits or change of flower colours.

For environmental studies, however, all parts of a plant are considered in the monitoring process. This is especially the case with leaves, which are capable of supplying wide information not only about the chemical constitution of the soil, but also about any atmospheric wet or dry deposits that might be affecting the ecosystem (fig. 94).

Dry deposits may accumulate on the surfaces of leaves leading to interactions with the tissues, or simply to changes of the chemical environment on theses surfaces. They may fall through the canopy to join the soil environment. Wet deposits on the leaves may disturb their gaseous interactions with the atmosphere (fig. 94) or even stop it, thus leading to changes that may appear as pathological symptoms. Wet depositions may also directly attack the surfaces of the leaves causing serious changes (acidic rain). A part of the wet deposits, however, may be transported to the soil by stem flows or by falling directly on the soil surface.

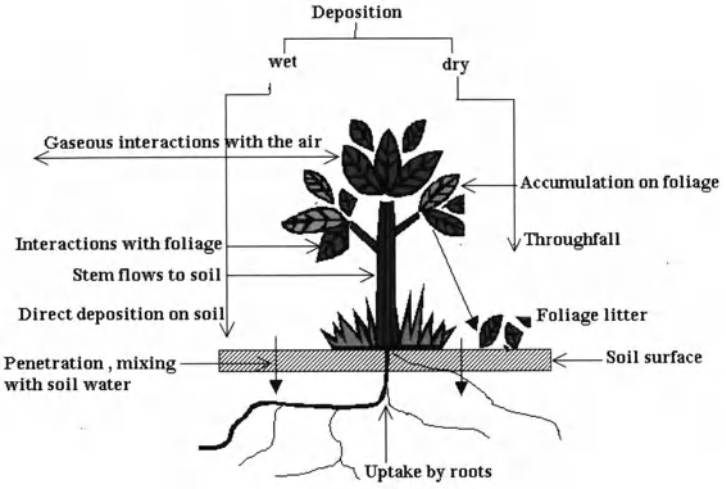


Fig. 94 Interactions between vegetation, soil and atmosphere

The directly deposited material on soil surface (throughfall) together with the material formerly accumulated on leaves surfaces provide the major part of contribution to the soil environment. This occurs through washing of the litter material by percolating surface waters and penetration of the resulting solutions into the vadose zone.

11. 1 Planning and implementation of biological monitoring:

Planning of biological monitoring should start at an early stage of the monitoring project. It forms an integrated part of the plan starting as early as the stage of site characterisation. Preparation of site maps should include besides soil, geologic and hydrologic maps, separate maps showing the distribution of plant communities, tree stands, and maps showing the distribution of vegetation showing any peculiar morphologic changes. Field and laboratory works should include the following:

11.2 Foliage sampling and investigation

Foliage should be sampled, for monitoring purposes, yearly at fixed periods. For example foliage of deciduous species is sampled in late summer, while that of evergreens is normally sampled at the dormant times. In selecting sample trees, one should take those trees that are in the vicinity of the locations where soil samples were taken (provided that their roots were not damaged during soil sampling). The trees should be representing the dominant species on the plot. Their number must be covering and representing the area of investigation. It should not be less than 10% of the number of predominant species.

For all foliage samples, the leaves should be representing the current year or the last three years in case of pine. They should be collected from the upper third of the tree. Topmost leaves, however, are normally not selected

11.3 Chemical investigation of foliage

After the samples are collected and brought to the laboratory, they should be prepared for chemical analysis. Normally it is not necessary to wash them, but in case they were collected in an area of high air pollution a systematic washing may be recommended. Later, they should be dried in an oven at 80°C for 24 hours and then ground to obtain a homogeneous powder.

For the chemical analysis itself, samples of the powder are digested either by wet digestion methods or using dry digestion techniques. If wet digestion methods are selected, the samples would be digested by hot mineral acids or by a mixture of acid and an oxidising agent such as hydrogen peroxide.

In dry digestion methods, dry ashing of the samples takes place in an oven at high temperature (500 –600°C) followed by dissolution in water or dilute acids.

The analytical techniques may depend upon the elements to be determined and measured; yet for most metals atomic absorption methods were found very useful.

It was, also, found that X-ray fluorescence methods are helpful in determining the concentrations of metals and non-metals down to fluorine. This method has the

benefit of not requiring digestion, since the measurements are done on compacted vegetal powder.

11.4 Sampling and investigation of litterfall

Sampling and analysis of shed foliage (litterfall) can provide useful information about the concentrations of nutrients and pollutants in the vegetation brought about by uptake from the soil or resulting from atmospheric deposition.

Litterfall sampling is carried out monthly or at fixed periods to ensure registration of any temporal changes. This is done by distributing litter sacks on the plot at a depth of about 0.5m under the trees to secure collecting the litter before it is blown away by wind.. Litterfall sacks should be made of inert material. Their placement in the ditches should be in such a position that they do not touch the ground. This secures that soil humidity would not mix with the collected material – a process which might accelerate decomposition.

After drying the samples at 40°C, chemical analyses are carried out similar to the analysis of foliage material. Results from both processes are later compared to deduce any conclusions about the nutrition status and transport of contaminants.

Throughfall samples can also be collected in association with litter samples and analysed in the same way.

Part 4

Modelling of soil pollution

"Nature is essentially simple; therefore we should not introduce more hypotheses than are sufficient and necessary for the explanation of observed facts". These words, which were written by Sir Isaac Newton in his *Principia* about 275 years ago, represent, according to the science theoretician GERALD HOLTON (1988), a rule of simplicity and *verae causae* (real causes), that should never be forgotten when treating natural phenomena in a scientific way. Not only Newton, and not only Holton propagate this principle of simplicity. Einstein himself was a great adherent of it. Remember his equation: $E = m\ c^2$. How elegant and how simple does it appear, and yet how deep and pervasive its influence on the development of modern Science was!

Scientists call such an equation a mathematical model of the relation between energy and matter. It summarises the results of centuries of observations and experimentation, and simplifies them in this general mathematical expression. So do all models, whether mathematical as this equation or of any of the other types, which will be explained below. They are necessarily simplifications of reality.

Chapter 12

Models and their construction

A model is formally defined as an object or concept designed according to a structural, functional or logical analogy to a corresponding origin in the real world. It is mainly used to solve a problem or find an answer for which a solution or answer, under the prevailing conditions, through direct operation on the origin, is unfeasible, difficult or impossible. Mathematical models like the previously mentioned equation of Einstein are logical constructions based on the essential quantitative or geometrical relations connecting the basic parameters of the original substrate, so that it allows an access to general information, explanation or prediction of behavioural or evolutionary patterns of the investigated object or phenomenon. Such patterns may serve as bases for work hypotheses, theories or laws, describing or controlling the investigated problem. Thus; we may conclude that models are abstractions of real systems. They may be mathematical or descriptive (geometrical). They may, or may not, be accurate or inaccurate, depending on the information used in their construction.

Soil in the course of material addition or subtraction can be considered as a system reacting to perturbation. This system is a composite one, embracing many closely related subsystems, each of which is aware of the perturbation and reacts in a way to resist any changes resulting thereof. Such reactions can be modelled and the results may, in case of accuracy, be used for predictions of behavioral patterns that may issue under similar conditions. Take, for example, the soil solution, the goal of which is to uphold the chemical equilibrium and thus maintain the conditions

required for a balanced soil environment. In this system serious changes of hydrogen ion concentrations (pH), may lead to far reaching disturbances that could lead to a collapse of the system performance as a whole. Following the onset of such concentration changes, the soil solution system resists the perturbation by rearranging its chemical environment to restore the original pH-values. Such rearrangements (generally known as buffer- reactions), which were already explained in chapter 8, can be mathematically modelled so that future developments, under similar conditions, may be predicted. Another example can be given by the behaviour of soil organisms towards xenobiotic substances. As it was mentioned before (Chapter 9), organisms try at the beginning to digest or detoxify the added material in order to keep the system at balanced conditions. This may go up to a certain degree, yet overworking the system by more perturbations may eventually lead to complete collapse of the system and only external effort in the form of remediation measures can bring it back to its original conditions. Experimental studies on this phenomenon followed by mathematical treatment of the results may lead to the development of generalised formulations that enable predictions and facilitate the planning of remediation measures. Such formulations, based on field observations or experimental work, are nothing but abstract models, treating individual parts of the whole system. From this, we may conclude that modelling in the soil environment can encompass many aspects such as reaction kinetics, biochemistry of the soil environment, or the physical and chemical properties of mineral matter. Each of these modelling studies provides vital information not only for understanding the conditions under which the system may collapse (e.g. strong pollution), but also for its remediation, if required.

12.1 Types of models

It is very difficult to suggest a general classification for models, which may be valid for all cases, yet for our purpose i.e. the classification of models describing relations pertaining to soil pollution we may adopt a simple scheme of model clas-

sification. According to this scheme, we may, for problems related to soil pollution, use either natural analogue models or mathematical models, describing in mathematical terms the dynamic conditions pertaining to the whole soil system. The latter may be deterministic (analytical as in the examples, mentioned above) or they may be stochastic, i.e. using parameters of probabilistic nature.

1. Space analogue models:

It is needless to repeat here that the most important models in this category are maps and other graphical representations as those mentioned in the section dealing with site characterization. Maps (topographical, geological, pedological, or hydrological) are space analogues of the site under investigation. They are not only important for site characterization but they also supply the information required for prediction through mathematical analysis (mathematical modelling). They are of great importance in planning sample collection, understanding flow relations or later designing remediation measures. The base (topographic) map provides the fundamental construction for all subsequent models. Through contour lines (lines of equal elevations) a model representing a two dimensional view of the topography is constructed. It is, however, useful to see this within the framework of the whole region of which the study area forms a small part. This allows understanding the physical conditions of the area in an integrated view of the topographic, geologic and hydrologic conditions prevailing in the region. Fig 96 shows the relation between the contour map and the topography of a hilly area characterized by a ridge extending in a North-South direction (Fig 95). The study area lies at the foot of the northern end of the ridge. Out of this block view of the whole region, a detailed view (Close up) of the study area is constructed to illustrate the local topography (Fig96).

To complete the model a profile representing a stratigraphic section (a diagram, showing the spatial distribution of the different lithologic units in the subsurface) is constructed. This allows a better understanding of the results of soil chemical analyses, since the soil characterising the area is a product of their weathering (see Figs.97 and 98).

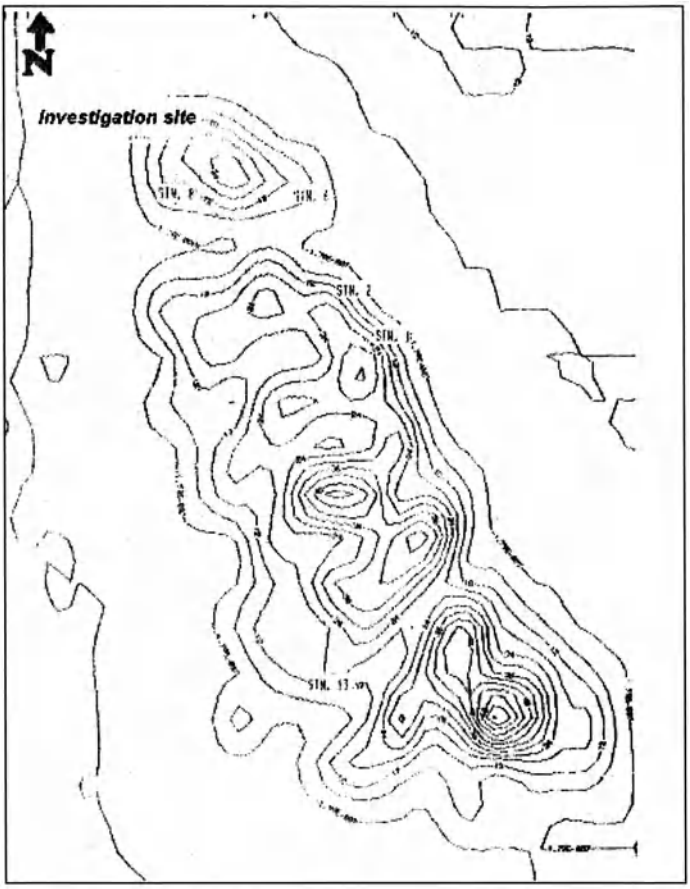


Fig. 95 Topographic (contour) map of the region where the area of investigation lies

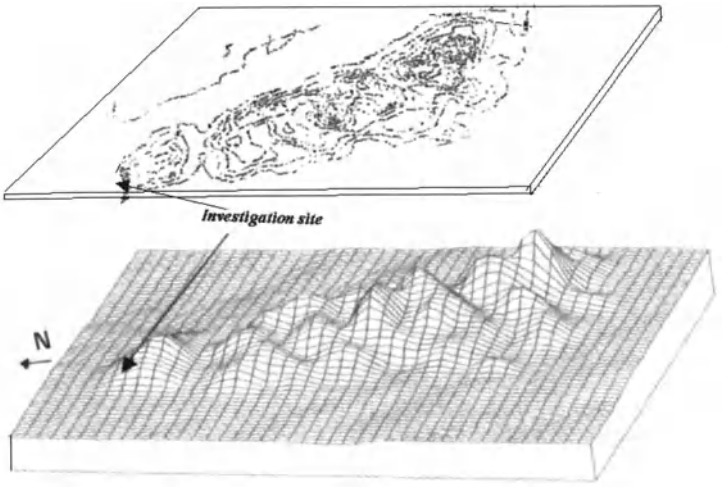


Fig. 96 The relation between contours and real topography of the region in the above example

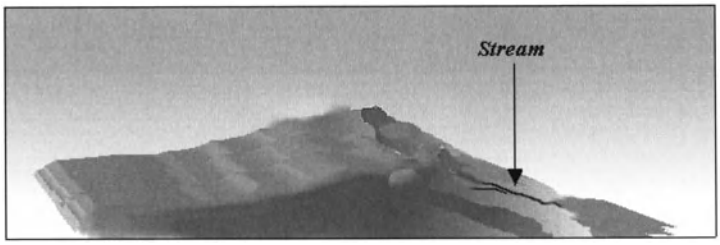


Fig. 97 Local topography of the site

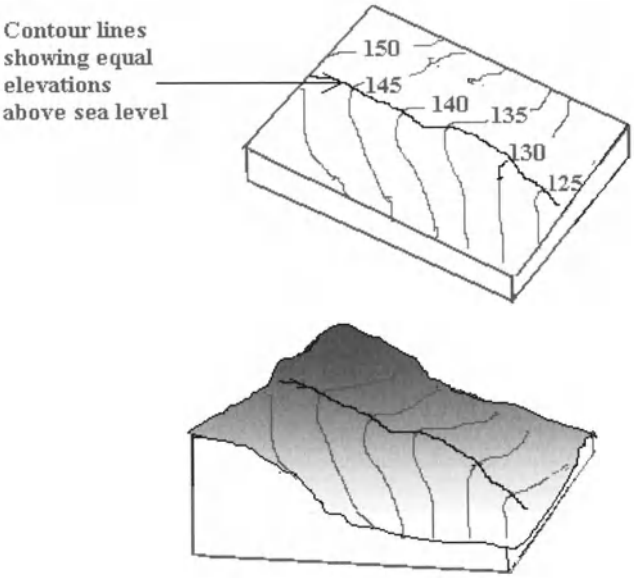


Fig. 98 A block diagram showing a close up of the topography at the streambed together with the original contour map to show the relation between both.

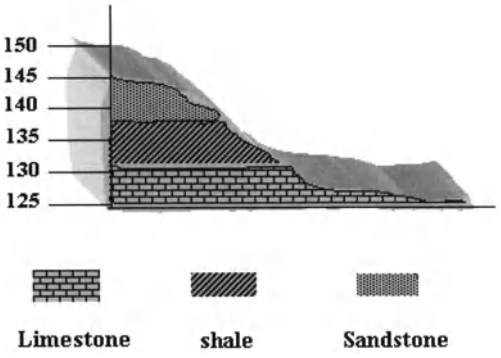


Fig. 99 A stratigraphic profile showing the main lithologic units forming the substrate

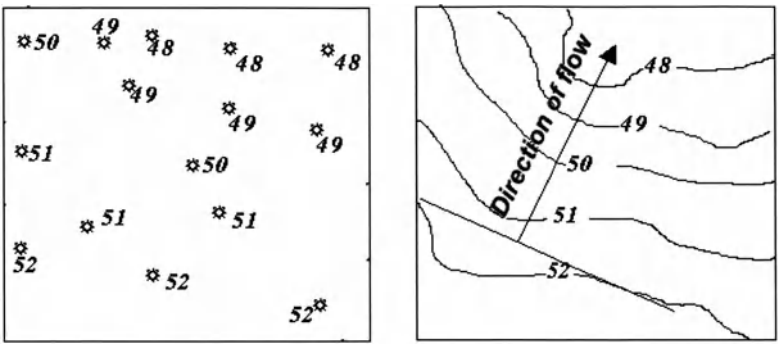
Modelling of fluid transport in soil:

One of the rules for constructing useful models is to define the objects of modelling together with the characterising parameters in order to deliver a clear-cut imagery of the problem to be solved. So speaking about fluid transport in this section requires a definition of the fluids meant and the parameters defining its dynamic evolution and flowage in the soil medium. Soil fluids may include natural fluids (ground water) or any contaminants infiltrating the soil either as separate fluids or as solutions in the ground water. In general however a model dealing with fluid transport in soil should have the following objectives:

a) Depicting the direction of flow in a spatial sense
b) Depicting the feasibility and velocity of flow in distance per unit time.
c) Depicting the amount of flow in quantity per unit time.

Determining the direction of flow and construction of potentiometric maps

Water level measurements as explained in section 3 deliver the basic material for constructing water table isopotentiometric maps, out of which the general direction of underground water flow may be determined. Basically an isopotentiometric map is constructed by plotting the measurements from monitoring wells on the base map and connecting points with equal values of water level heights above sea level (or any standard datum) to form contours (isopotential lines) of the same. In an aquifer of isotropic nature, the direction of ground water flow is perpendicular to the isopotential lines.



a) Base map showing postions of observation wells and the levels of groundwater measured in them

b) Potentiometric map. The contour lines connect observation wells of similar ground water levels

Fig. 100 Data collected from level measurements plotted on a base map (a) , together with the corresponding potentiometric map (b).

Fig. 100 gives an example of such maps and shows the relation between the data registered at the observation wells and the general direction of ground water flow. The map in fig 100 b represents a graphical model of the flow relations in the area, which can be considered as a spatial analogue model. In constructing the potentiometric map, various hypothetical observation wells (fig.100 a) supply enough data for the geometrical construction of the model, but what about the case when in real life considerably lower number of observation wells is available? This leads to the question about the least number of observation wells required to draw a potentiometric map. In fact one can use as low a number of wells as three, out of which a rough delineation of the isopotential lines by geometrical extrapolation may be done. The extrapolated relations should always be compared with the subsurface geology and corrected, if required, to suite the real conditions prevailing in the area. This method of extrapolation is generally known as the method of hydrologic triangle. To explain it, following example may be considered:

The positions of three observation wells A, B and C (fig. 101) are plotted on the base map. Heights of the water table above standard datum are given as A= 51.8, B = 41 and C = 47.3 as shown in Fig; 101. It is required to roughly depict the direction of groundwater flow by geometrical extrapolation on the base map.

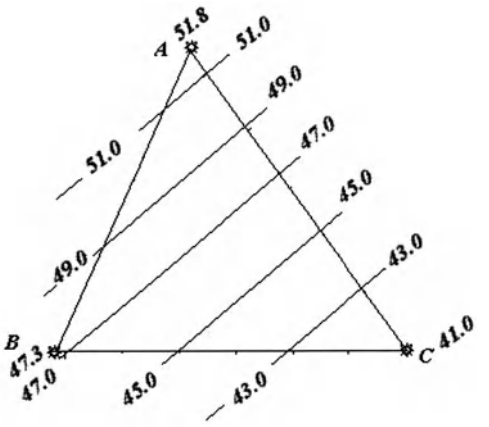


Fig. 101 Extrapolation of the contours for determining the flow direction using data from the three observation wells – hydrologic triangle method

Fig.101 shows the method of extrapolation, using data from the three observation wells. A triangle connecting the positions of the three wells is constructed. The distance between the point of highest potential and the one of lowest potential is divided to scale and the calculated potentials are plotted on the line AB. The same is done with the line BC connecting the lowest and middle potential points. Eventually straight lines are drawn connecting equal potentials on both lines. These represent the equipotential lines, perpendicular to which the general direction of flow (NW to SE) is likely to lie in case of isotropy. These conditions, however, are restricted as, mentioned before, to aquifers of isotropic nature. In case of anisotropy resulting from structural conditions of the aquifer, complications may make corrections essential. Modification methods can be designed using instructions from a standard manual of hydrogeology.

Mathematical modelling of fluid flows in soil:

Mathematical models, as mentioned before, are either analytical ones i.e. made of equations having unique solutions or stochastic ones in which for every input there are a range of possible outputs, reflecting randomness or uncertainty. Problems related to soil pollution can be seen as potential objects for both modelling approaches. However only deterministic models will be dealt with in the present book.

Models dealing with natural phenomena are mostly describing the behaviour of a segment or a subsystem of nature. In dealing with fluid movements in soil, it is clear that we are dealing here with the subsystem comprising the aquifer and the fluids percolating within. Any change or perturbation in the parameters characterising one of the two elements of the system, will have a response shown by a change in the behaviour of the system as a whole. For example an increase or decrease of the pore space or a change in its geometry will result in a change of the flow speed or the quantity of fluid passed or retained. Also a change of the properties of the fluid such as density or viscosity will produce a change in the systems behaviour. Not only the parameters characterising the system elements in this narrow sense are important, but also universal parameters belonging to the system Earth, as a whole will play an important role in determining the behaviour of this subsystem. The most prominent of these are the forces resulting from Earth's gravity and attraction between material bodies. In the following, a short account of the forces acting on the system aquifer/ groundwater will be given.

Forces acting on this system can be viewed as belonging to two main classes:

- Flow-retarding forces and
- Flow-accelerating Forces

Flow-retarding forces are those forces resulting from the attraction of water to the surfaces of solids in the substrate. In this group, forces resulting from attraction by adsorption or capillary action (matric suction), and forces resulting from osmotic attraction (osmotic suction) are most relevant.

Flow accelerating forces are mainly those ones resulting from gravitational attraction towards the centre of the Earth. They are summed up in the so-called gravitational potential. Some other universal forces may be affecting the system, yet their effects are not relevant for practical purposes. The above-mentioned forces, which may be called the system forces, are integral parts of the system producing potentials that may be summarised as follows:

P_m = attraction potentials (known as matric potential)

P_o = potential resulting from attraction of solute ions to water molecules (known as osmotic potential)

P_g = potential resulting from gravity attraction (known as gravitational potential)

The total potential of the system is calculated by algebraically summing up all these potentials. Assigning negative signs to the retarding forces (P_m and P_o) we get the following equation:

$$\mathbf{P_{total} = P_g - P_o - P_m}$$

This means that P_{total} will have a positive value if and only if

$$\mathbf{P_g > P_o + P_m}$$

Out of this result it is clear that flow can only occur if the gravitational potential is higher than all retardative ones.

Darcy's Law – the principal mathematical model of ground water flow

Henry Darcy (1803 – 1858) – a French engineer- was the first to construct a mathematical model for fluid flows in porous media, connecting all parameters of the system in an analytical equation. Through a series of experiments, He could find the following relations:

In a porous medium, Q (total flow rate, standing for the total discharge of fluid/ unit time; cm^3/ second) is directly proportional to:

A, the cross sectional area in cm^2

ρ, density of fluid , g /cm^3

$h_2 - h_1$, the head loss (difference between hydraulic heads in two points ,up and down stream)

It was also found that Q is inversely proportional to:

l, length of the flow path, cm

η, dynamic fluid viscosity (mP. s)

Writing this in mathematical shorthand, gives the following relation:

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

Where K is a proportionality constant (the permeability constant/ hydraulic conductivity), which was found to be dependent on the hydraulic properties of the medium and its lithology. This shows that all parameters describing the two main elements of the system (fluid / porous medium or fluid/soil) are connected in an analytical relation that allows calculation of different values, which might be required in solving problems arising from soil pollution.

For water (η and ρ =1), Darcy's low takes the following form:

$$Q = \frac{AHK}{l},$$

which can be written : $Q = K\,.\,A.\,H/l,$

Where $H = h_2 - h_1$ (head loss) =difference between hydraulic heads in two wells, up and down stream (see fig 102)

H/l is defined as the hydraulic gradient and is dimensionless since h_2, h_1 and *l* have all length dimensions (m).

Putting J = H/*l*, and rearranging in the last equation, we get:

$$K = \frac{Q}{A.J}, \text{ or } Q = K.\,A.\,J$$

Now *Q* has the dimensions $m^3\,.\,s^{-1}$ and *A* is in m^2 , so we get for *K* the dimensions:

$$m^3\,.\,s^{-1}\,.\,m^{-2} = m.s^{-1} \text{ (distance / unit time)}$$

Physically, these are velocity dimensions and give the hydraulic conductivity of the medium in distance per unit time. Hydraulic conductivity values are specific for different lithologic units. They can be determined in the laboratory for samples

taken from the aquifer or found by reference to standard manuals where K-values for different geologic materials are tabulated. Table 26 is an example showing hydraulic conductivity of some selected sediments.

Sediment	K ($m.s^{-1}$)
Gravel	$10^{-1} - 10^{-2}$
Coarse sand	About 10^{-3}
Medium sand	$10^{-3} - 10^{-4}$
Fine sand	$10^{-4} - 10^{-5}$
Sandy silt	$10^{-5} - 10^{-7}$
Silty clay	$10^{-6} - 10^{-9}$
Clay	$< 10^{-9}$

Table 26 Permeability constants for some selected sediments

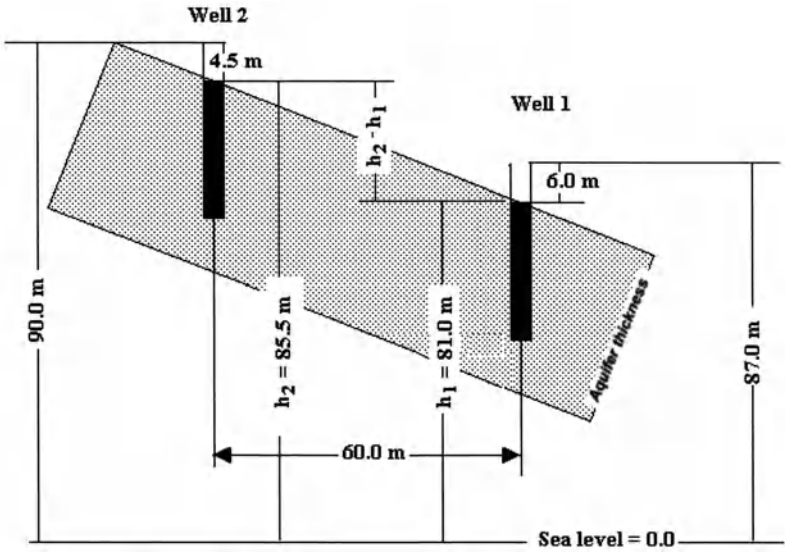


Fig.102 Schematic representation of the sand stone aquifer discussed in the example

Computations based on aquifer model

In fig 102 a sand stone aquifer is represented by the inclined rectangle. Two wells (well 1 and well 2 in the figure) are drilled 60 m apart. The top casings lie at 87 m above sea level for well 1 and 90 m above sea level for well 2. Systematic measurement of water table levels showed that the depth to water table in well 1 makes an average of 6 meter. In well 2 the average depth lies by 4.5 m.

To apply Darcy's mathematical model (Darcy's law) to this aquifer, we may find K from the tables (see table 26), yet the most difficult problem in this case is to find A the cross sectional area perpendicular to the direction of flow (see fig103). This problem can be solved, by applying one of the following methods:

a) Drilling of inspection wells to determine the dimensions of the aquifer, which is very expensive and time consuming or

b) Determining the thickness of the aquifer by computation from the geological map, which is a good method for achieving an approximate result. On a local level as the one discussed here, this method is safe enough to provide satisfactory results. It needs however some training in geological computations.

For the example discussed, if the thickness of the sand stone bed (aquifer) was 12 meters and if it was extending for 600 meters in the breadth, the cross sectional area (A) perpendicular to the direction of flow would be 12 x 600 = 7200 m^2 (see Figure 103)

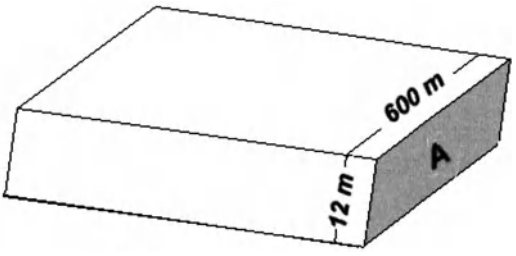


Fig.103 Aquifer dimensions – flow front is represented by the area A, perpendicular to the axis of flow

So the computation would continue as follows:

$Q = K \times J \times A$

$K = 10^{-4}$ meter/second $= 10^{-4} \times 60 \times 60 \times 24 = 8.64$ meters/ day.

$J = (85.5\ m - 81\ m) / 60\ m = 0.075$ (dimensionless)

Therefore: $Q = 8.64\ m.day^{-1} \times 0.075 \times 7200\ m^2 = 4{,}665.6\ m^3$ / day.

This means that the total flow rate (volumetric flow rate) in this sand stone aquifer amounts to about 4,666 cubic meter / day.

Another way of dealing with this model in case of investigating pollution problems may be that of using results of the chemical analysis of water samples taken during monitoring works as follows:

Geochemical dimension of the model

If at the beginning of computations in the example mentioned above, a polluting source was found to lie uphill somewhere in the vicinity of well 2 and if chemical analysis has shown an average concentration of 32 ppm of the pollutant in the ground water. The concentration of the contaminant found by chemical analysis can be mathematically expressed as:

C (Concentration) = (rate of release of the contaminant to ground water) / total flow rate, or $C = R_c / Q$.

If it is known that the rate of release of the contaminant to the ground water was 150 kg /day, then the concentration 32 ppm ($0.032\ kg / m^3$) = 150 / Q

Then, $Q = 150 / 0.032 = 4673\ m^3$ / day

Putting this in Darcy's equation: Q = K. J. A, we get,

$4673 = 8.64 \times 0.075 \times A$,

Then $A = 4673 / (8.64 \times 0.075) = 7211\ m^2$, which is almost the same value for the cross sectional area as calculated from the geologic map.

On the other hand calculating the cross sectional area from the geologic map, helps calculating the rate of contaminant release by using the concentration, known from the results of chemical analysis.

As shown here, the flexibility of this model allows calculating various factors that might be required for solving problems arising from soil pollution and might supply vital information for designing remediation measures. Such information includes the area of contaminated surface, the breadth and dimensions of plumes as well as the rate of volumetric water flow through the aquifer per unit time.

The effective velocity (interstitial velocity) of flow

The flux of water (q) is defined as the flow through a unit cross sectional area perpendicular to a line representing the axis of pathway. It may be calculated from the Darcy's equation by taking A = 1; accordingly, the flux in the foregoing example may be calculated in the following way:

If Q = KJA, then q = KJ (since A = 1; lower case q is used here to differentiate the flux from the total volumetric discharge Q).

This gives a value for q = 8.64 x 0.075 = 0.648

In case the whole pore space was full, the flux (q) would be related to the effective velocity of flow (interstitial velocity) v by the relation: $q = v.\ \varphi$, where φ is the porosity of the aquifer.

Assuming the porosity in the sand stone aquifer was 0.35, the effective velocity of flow in the foregoing example would be calculated in the following manner:

The effective velocity of flow (v) = $q / \varphi = 0.648 / 0.35 = 1.85$ m/day.

This means that despite the huge volume of water flowing through the total volume of the aquifer the front is moving very slowly with a velocity of 1.85 m per day. To reach a point 500 m away from the source of pollution, it needs 270.27 days (500 / 1.85) – about 9 months.

The above-mentioned relations can be used in different ways to calculate aquifer parameters according to the available information. For example, if Q and A are known, then dividing Q / A gives q, which again may be used to calculate other unknowns, if required.

The foregoing discussion however shows that the model as demonstrated here is subject to several constraints, which may be summarised in the following:

a) Full homogeneity of lithologic, hydraulic and tectonic properties throughout the aquifer (isotropy) is assumed.

b) The model is one-dimensional depending on computations that deal with discrete points lying on a one-dimensional axis.

As for homogeneity and isotropic character of the aquifer, the problem cannot be easily solved and unless careful tectonic and petrographic analyses are done, the results of computations remain approximate, if not erroneous, in complicated cases. However the problem of space dimensions may be mathematically treated, especially that several computer programs are now offered that make it possible to deal with complicated computations in relatively short times.

To start with, let us take the case of hydraulic gradient discussed in the foregoing Example. We have here two discrete points representing two wells. These two points have only reference positions along the axis of flow *l.* In the Cartesian plane they may have the coordinates x_1 and x_2; h_1 and h_2 – the corresponding heads at the two points may as well be represented by y_1 and y_2 (see fig104)

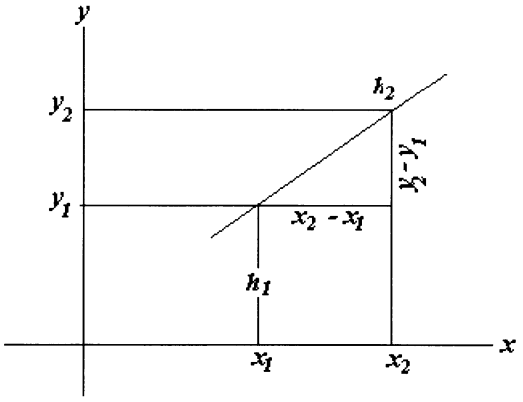


Fig. 104 The relation between hydraulic head and the coordinates on the axis of flow

Accordingly, the head loss $h_2 - h_1$ can be given by $y_2 - y_1$ and the hydraulic gradient J would be given by $(y_2 - y_1) / (x_2 - x_1)$.

If for any point between x_1 and x_2 , there exists a relation that allows the calculation of y , when x is known, one says that y is a function of x or $y = f(x)$, meaning

that y depends on the independent variable x. The function $y = f(x)$ is also said to be one dimensional because y depends on one single variable. If the function $y = f(x)$ holds, i.e. is represented by points, all over the range $x_1y_1 — x_2y_2$, we say that the function is continuous . It is also said to be differentiable i.e. one can find everywhere on the curve, representing the function, the slope of the tangent to the curve, known as the derivative or the rate of change of the dependent variable with respect to any change of the independent one. In our case, this is dy /dx = rate of change of h by changing *l.* This is written dy /dx or y' or f' (x) and is simply known as the first derivative of the function. Higher derivatives may be obtained by further differentiation. Notations such as d^2y / dx^2, $f''(x)$, y'' or y''' are usually used to characterise derivatives of orders higher than one.

Returning to our original problem of the relation between the hydraulic head h and the distance between two points or their coordinates on a given axis (here *x*), we state (without proof) that the relation, that allows calculating h (y) on any point of the x-axis was found to be any relation satisfying the equation.

$d^2 x / d y^2 = 0$. This is a differential equation (known as the Laplace's equation), the solution of which gives another equation - the one regulating the relation between y and *x*. An example may be given by the equation: $y = 5x - 17$, $dh/dl = 5$ and $d^2h / d l^2 = 0$. So, this equation may be a possible expression of the relation between h and *l*. We observe here that h is calculated with respect to one variable only (*l*) i.e. the relation is one-dimensional, and is represented by a straight line equation.

The Continuous one-dimensional Darcy's Model

It has been shown that the hydraulic head is connected to the coordinate on the horizontal axis with a continuous function, the first derivative of which equals $J = dy / dx$ or specifically dh / dx ; since we are dealing with the head loss rather than with the total change in h , dh / dx will take a negative sign , becoming $- dh / dx$., using this new relation in Darcy's law gives:

$$Q = -K\frac{dh}{dx}A$$

The interstitial velocity will be

$v = -\frac{K}{\varphi}\frac{dh}{dx}$, where φ is the porosity ; since v = KJ / φ.

The two dimensional Darcy's model

Suppose that hydraulic heads in two wells A and B lying at a distance x from each other were connected by a mathematical relation that allows the calculation of the hydraulic heads at any point on the line AB and suppose that a third well C lying at a distance Y from the line AB (see fig 104) was found not to obey this relation and that it was found that the hydraulic head here was depending upon both distances X and Y, meaning that h is not only a function of X but a function of X and Y – some thing that we may write in mathematical form as h = f(X, Y).

A function of two variables is said to be a two-dimensional function It can have a derivative with respect to any of the variables calculated under the assumption that the other variable remains constant. Such a derivative is known as a partial derivative. In the present case the partial derivative of h with respect to Y may be denoted by ∂ h / ∂ Y (i.e. the rate of change of h with respect to Y, so long X remains constant), while the derivative with respect to X is written as ∂ h / ∂ X, also meaning the rate of change of h with respect to X, so long Y remains constant. These two derivatives represent the coordinates of a two-dimensional vector (H_x, h_y), commonly known as the gradient of the function y = f *(x, y)* and is denoted by the symbol $\nabla(h_X, h_Y)$, or simply ∇ h (read del h).

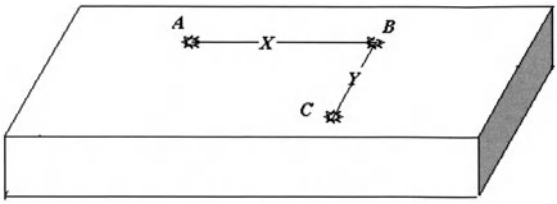


Fig.104 Two-dimensional relation of h with respect to x and y

Accordingly, the equation q = -KJ may be written as q = K(-∇ h) or q = -K∇h

Analogous to the case of the one-dimensional Darcy's model, we state here without proof that in any two dimensional region of an isotropic aquifer of homogeneous conductivity, if the head function h is continuous and depends on two variables x and y, the equation describing the function will be one that fulfils the relation:

$$\partial^2 h / \partial x^2 + \partial^2 h / \partial y^2 = 0$$

This is a second-degree differential equation (including second derivatives), known as the two-dimensional Laplace equation. The solution of this equation is unfortunately, not so easy like the first-degree equation of the last section. For the solution we need additional information about at least two points within the domain of the function. These additional pieces of information are known as the boundary conditions. In practical work solutions at different boundary conditions are found using special computer programs (simulation programs) and the results are tabulated for use under different conditions. This technique of modelling is known as the simulation technique.

The three dimensional case

Analogous to the derivation of the two dimensional case, if h was dependant on three variables x, y and z, we would be confronted with a three-dimensional function denoted by h = *f* (x,y,z). As in the case of the two-dimensional function this one (if continuous) would deliver partial derivatives with respect to x, y and z. the vector having these coordinates (∂h / ∂x , ∂h / ∂y , ∂h / ∂z) is known as the gradi-

ent of the function and is denoted by ∇h (read del h). Some times it is denoted by: grad. h. The equation giving h at any point of the region where the function is continuous is also subject to the condition:

$$\partial^2 h / \partial x^2 + \partial^2 h / \partial y^2 + \partial^2 h / \partial z^2 = 0,$$

which is the three-dimensional Laplace equation.

Simulation solutions are also carried out using special computer programs.

Flows in the vadose zone

We have so far discussed water flows in the saturated zone using Darcy's law. Application of the derived relations to the unsaturated zone (vadose zone) was found to be dependent upon the degree of saturation according to the following relations:

$$v = \left[\left(\frac{s - s_0}{1 - s_0} \right)^a \frac{d_e^2}{c} \frac{\varphi^3}{(1-\varphi)^2} \frac{g}{\eta} \right] grad.h ,$$

$$K(\Theta) = k \left(\frac{s - s_0}{1 - s_0} \right) = k \left(\frac{\Theta - \Theta_0}{n - \Theta_0} \right)^a$$

Whereby: v = interstitial velocity

S_0 and Θ_0 represent the rest saturation and rest water content at which the hydraulic conductivity = 0.

a = an exponent which is commonly taken as 3

d_e = effective grain size

c = a conditional factor depending on the geometry of grains

φ = the porosity

g = gravitational acceleration.

η = dynamic viscosity of the water

grad = del operator of the vector

$K(\Theta)$ = unsaturated hydraulic conductivityΘ = total potential.

Part 5

Soil Remediation

Remediation is the logical consequence drawn from the results of sampling, monitoring and model construction, if pollution at a risk level, that requires intervention was ascertained in the area of investigation. Its goal is, in the first place, to bring a polluted soil to a sustainable environmental condition, at which the risk arising from toxic pollutants is reduced to a minimum. Remediation techniques may be applied to the soil in place (*in situ)* or to the soil after being transported to special facilities. It may be mainly done by applying physical and chemical methods, or may be carried out using bioremediation methods, yet in all cases and under all conditions, remediation is the last step in a soil conservation plan, based on systematic diagnostic efforts including monitoring and modelling of the actual soil condition. A successful remediation plan should make use of all observations and results of the three diagnostic steps: sampling, monitoring and model construction as it was repeatedly mentioned before.

Chapter 13

Planning and realisation of Soil remediation

A successful remediation plan has to be based on the information gained during the preliminary diagnostic works, which are done before taking the decision to start a remediation project. The following check list should be worked out and carefully studied before starting with the actual design of the technical work.

1) What are the types and chemical nature of the pollutants determined at the site?

a) Organics b) Inorganic substances

2) What are the Dimensions and scale of pollution?

a) Is the pollution localised?

b) Is it of the dispersed type?

c) How urgent is the remediation plan?

3) What is the risk level?

a) Low risk level

b) Medium level

c) High risk level

4) Which technical measures are thought to be most suitable for carrying out this project?

a) In place (*In situ)*?

b) Ex-situ? And if yes, should the soil be transported to a special facility? Should the remediation be carried out in a prepared bed system, or in tank?

5) Are there any financial restrictions on choosing the technical method of remediation?

6) Which method is technically suitable and financially fitting in the economic framework of the project?

Categories of pollutants:

In fact a pollutant can be any environmentally harmful substance that is accidentally or on purpose transported to the soil. Yet for the sake of planning, a common rather simplified classification that enables selection of the suitable remediation method may be sought. The following check list helps to limit the uncountable substances that may pollute the soil into few categories, having similar chemical and physical properties, and in most cases having comparable degrees of response to a given remediation process.

- Are the pollutants in the present case chemically characterised and identified? If yes, are they solids, NAPL's or leachates?
- Are they organics or non-organics? If organic, are they aliphatics or aromatics? If aromatics are they halogenated
- How high (low) are their molecular weights? (From the tables)
- Are they volatile or of low volatility?
- Are they (for organics) polar or non-polar? What is their degree of solubility (high, low)
- Is their any information about their biodegradability?
- If inorganic, of which category are they: metals, metal cations, waste - acids and alkalis? Are they easily oxidisable compounds? Are there any inorganic cyanides?

The careful workout of this check list as we will see later is a very important step on the right way to select the appropriate method of remediation. Other factors

such as the scale of pollution and financial restrictions may impose revision of the decisions taken at this stage.

Scale of pollution

Results of sampling and chemical investigation supply enough information about the spatial dimensions of the pollution case, which is supposed to be treated. Pollution cases may according to their spatial dimensions be classified into the following two main types:

1.Localised pollution cases:

These are cases resulting from spill accidents, where materials spilled are known and the risk is at minimum when quick measures are taken. In these cases, remediation is mostly carried out in situ. Material safety data sheets supply information on the pollutant or the hazardous material forming the spill, so that immediate actions can be taken. One speaks also of localised pollution when the source of pollution is known such as leaking tanks, landfills or old industrial facilities. In such cases pollution would be spreading from the source in a flow pattern, which is more or less localised, and showing concentrations that decrease with increasing distance from the source of pollution. The flow pattern and rate of decrease of contaminant's concentration with increasing distance from the source can be characterised by careful sampling, investigation and mapping of the results.

2.Diffused pollution cases

Pollutants entering the soil will try to spread in both horizontal and vertical directions, whereby the dimensions of transport and diffusion will depend upon the saturation of the soil and upon its hydraulic and lithological character. When pollutants reach to the ground water its further transport will as it was said before depend upon the lithological character of the aquifer. Some aquifers due to this property may be selective in transporting material reaching the saturated zone. As an example one may consider the case of nitrates reaching the saturated zone in a fine-grained lime stone aquifer (micrite, chalk). In this environment, the nitrates can persist for very long times and can attain very high concentrations by accumu-

lation. They are safe of being denitrified by dentrification bacteria, simply because the fine-grained chalk has very small pore sizes. These impede penetration of such microorganisms into the aquifer. The same phenomenon is also responsible for the accumulation of many substances in the ground water. Such contaminants, which have been seeping and accumulating in soil over long periods form immense scale of pollution that may be extending over huge spatial dimensions. Accumulation of same scales may also occur when materials that were bound by complex formation on humic substances are released due to change of the chemical environment, and then dispersed within the soil. Such cases of wide spatial dimensions, which are not localised or characterised by a source and flow patterns are normally described as diffuse cases of pollution. Their characterisation, mapping and remediation needs more detailed planning and technical installations than localised cases.

3.Risk level

Risk levels of contaminants should be determined according to the information collected on the chemical and physical properties of the potentially toxic material and its degree of dispersion in the area of investigation. Information on bioavailability and mobility of the material may indicate a low risk level if the toxic material is in an immobile form, or a non bio-available form with no impact on the environmental conditions. However, continuous monitoring is important in such cases, where no immediate risk exists, yet possible problems are expected on change of the chemical or physical conditions. In cases where immediate risk exists such as after spill accidents or the discovery of old toxic deposits resulting from old landfills, military or industrial sites measures for remediation should be started or carried out within short times.

4. Remediation technologies.

According to the scale of pollution, the risk level and the financial and time constraints on the remediation project, treatment of the soil may take place immediately in place *(in situ)* or the soil may be transported to special facilities where remediation may be carried out in special reactors or vessels, that are specially de-

signed for this purpose *(in tank method)*. An example of this process is the washing of heavily polluted soils in special tanks. The polluted soil may also be transported and spread on a surface prepared to prevent the spread of contamination in lateral and vertical directions. Beds prepared in this way form the so-called prepared beds upon which the remediation process will take place. This method is especially suitable for soils contaminated by oil products. Generally speaking, however, four classes of remediation technologies are known. These are:

- Chemical and physical methods
- Biological methods
- Fixation methods (also storing and immobilisation)
- Thermal destruction methods.

Following diagram (Fig. 105) shows the main types of remediation technologies in a schematic way.

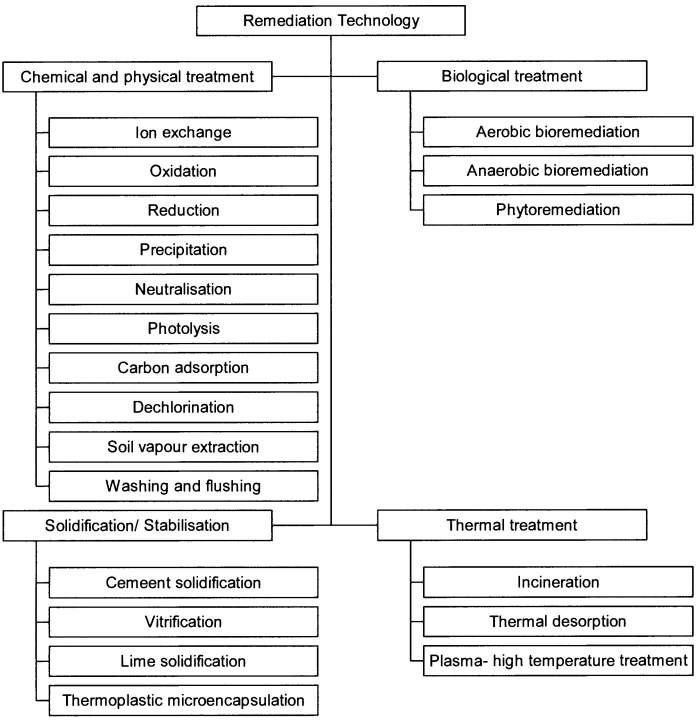


Fig. 105 Common remediation technologies

Some of the above mentioned methods may require specific technical installations (tanks and prepared beds), others may be suitable for use in place (in situ) still others may be suitable for all three operational modes of remediation. The following table(table 27) shows roughly the specific mode or modes suitable for each of the above-mentioned techniques.

Operational mode (s)	Suitable remediation technique
In situ	Soil vacuum extraction (SVE), Soil flushing.
In situ or in prepared beds	Carbon adsorption, Ion exchange.
In situ or in tank	Thermal stripping, dechlorination, Cement solidification, Vitrification, Lime solidification Thermoplastic microencapsulation.
All (In situ, in tank or in bed)	Neutralisation, Oxidation, Bioremediation (all methods).
In prepared bed	Photolysis.
In prepared bed or in tank	Precipitation, Reduction, Carbon adsorption, Ion exchange.
In Tank	Pyrolysis, Infrared, Rotary kiln, Fluidised bed, Soil washing.

Table 27 The different operational modes with their corresponding remediation techniques based on (BOULDING, 1995)

From the table one can clearly see that technologies like vacuum extraction and soil flushing are mainly done in situ, while bioremediation methods are all suitable for all operational modes. This factor plays a role in the financial planning of the remediation project that should be taken into account. The main decisive role, however, is played by the effectiveness of the method to the type of pollution encountered. In the following each of the above-mentioned technology will be shortly described.

1.Chemical and physical remedial techniques:

The aim of all chemical and physical methods of remediation is to change the chemical environment in a way that transport of toxic substances to other elements of the soil system is prevented. Exampl4es here can be given by transport to plants; to ground water; or to soil organisms). Such preventive measures may include decreasing mobility, change of chemical constitution or any of the factors, on which it has been elaborated in chapter 8. Chemical and physical methods of remediation include the following:

a) Oxidation

Oxidation is a common highly effective remediation technology for soils contaminated by toxic organic chemicals and cyanides. Oxidising agents used in this technology include a wide range of substances among which the most common are hydrogen peroxide, ozone and potassium permanganate. All three methods are according to EPA[4] of high treatment efficiency, reaching over 90% at short times in many cases. For example efficiency reaches. >90% for unsaturated aliphatic compounds such as trichlorethylene (TCE) as well as for aromatic compounds such as Benzene.

The reaction, if hydrogen peroxide is the oxidising agent used, takes place according to the following equation:

$$3H_2O_2 + C_2HCl_3\,(TCE) \rightarrow 2CO_2{+}2H_2O + 3HCl$$

Ozone destruction of toxic contaminants takes place in the following manner:

$$O_3{+}H_2O + C_2HCl_3 \rightarrow 2CO_2 + 3HCl$$

Still using the same example i.e. oxidation of trichlorethylene, the reaction, if potassium permanganate ($KMnO_4$) was used, takes the following path:

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2KCl + HCl$$

Oxidation technology has been successfully used for in situ remedy at source areas as well as for flume treatment. It is mostly used for benzene, ethylbenzene, toluene and xylene (BTEX) as well as for PAH's, phenols and alkenes.

b) Ion exchange and precipitation

Soil components with high CEC values are capable of binding positively charged organic chemicals and metals in a way that makes them chemically immobile and thus reduce the risk imposed by them on the soil environment. Addition of soil conditioners such as synthetic resins zeolites or clays may help increasing the CEC characteristics of the soil and thus enhance the binding of positively charged contaminants on the negative functional groups of the soil matter.

[4] EPA 542-N-00-006, September 2000. Issue No. 37

c) Photolysis

Photolytic degradation technology depends upon degrading the organic contaminants with Ultraviolet radiation. This may be carried out using artificial UV light or just by exposing the soil to sunlight, which may be sufficient for degrading shallow soil contaminants. This process can be carried out in situ or in prepared bed. However, deeply contaminated soils must be excavated and transported to special facilities, where the process would be carried out in special tanks. A combination of Photolytic degradation and bioremediation may be achieved by adding micro-organisms and nutrients to the soil after the photolytic treatment.

d) Adsorption on granulated active carbon (GAC)

This technology depends upon the tendency of most organic compounds to adsorb on the surface of activated carbon. Adsorption tendency increases with the molecular weight boiling point of the organic material. Thus we find that the technology of adsorption on granular activated carbon (GAC) is best suitable for volatile organic compounds; hydrocarbons of high molecular weights; halogenated volatile organic compounds(VOC) and their halogenated forms; as well as some explosives and pesticides.

Remediation through adsorption on activated carbon is a method that can be carried out in the liquid phase as in treatment of ground water or in the gas phase as in treating off-gases from soil vapour extraction remediation methods. As a matter of fact one of the earliest applications of this method was the use of (GAC) in adsorbing military gases by gas masks in the first world war.. Adsorption on activated carbon is a process carried out ex-situ in special tanks or in prepared beds. It is principally used to treat toxic gases, solvents and organically based odours. However, impregnation of activated carbon with additional chemicals may be helpful in controlling some inorganic contaminants such as hydrogen sulphide, mercury or radon.

e) Reductive dechlorination

Reductive dechlorination is a quite effective technology with the help of which chlorine in polychlorinated organic compounds can be removed or substituted . It

is mostly used to treat volatile chlorinated compounds by passing the heated gases containing the contaminants through layers of noble metal catalysts , triggering off a reductive reaction that destroys the halogen bond. An example of this may be given by the change of trichlorethylene into ethane.

Reductive dechlorination of organic compounds may also be accomplished by redox active soil components such as iron oxides or Fe (II) bearing clays. This is a low cost technology having a good effectiveness.

Reductive microbial dechlorination (KLASSON et. al, 1996) is a method combining the benefits of biotechnology with the known abiotic methods of dechlorination, by adding micro-organisms to the prepared beds where the remediation takes place. These (micro -organisms) enhance the process of dechlorination.

f) Soil vapour extraction (SVE)

Soil vapour extraction is a popular technology for remediation of soils. It is a relatively simple process to remove volatile and easily evaporated organic contaminants within the vadose zone i.e. contaminants persisting or accumulated above the ground water table. Technical processes of these technology comprise injecting clean air into the unsaturated zone to effect a separation of organic vapours from the soil solution by partitioning between the soil solution and the soil air. The vapours joining the soil air are then removed via vacuum extraction wells.

Figure 106 shows a schematic view of an SVE- arrangement.

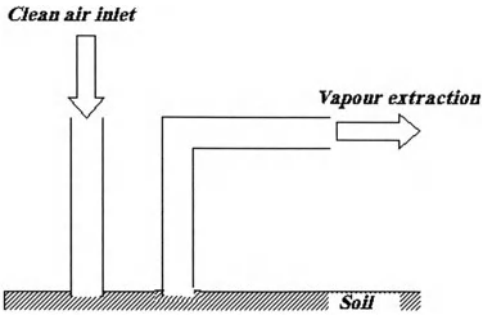


Fig. 106 .A schematic diagram to explain the technical arrangements required for soil vapour extraction (SVE)

It is needless to say that the effectiveness of soil vapour extraction will depend principally on the degree of water saturation in the treated soil as well as on the physical and chemical properties of the extracted contaminant such as vapour pressure and volatility.

Vapour extracted by this method may be further treated by carbon adsorption or any other suitable method that may help to dispose of the toxic gases collected.

To enhance the extraction in this technology, heated air or steam may be injected into the soil. Reports on using steam at sites of defunct gas stations show high efficiency performance at a reasonable low cost. Adding an air sparging system to the technical installations of SVE makes this technology also suitable for removing contaminants from the saturated zone.

g) Soil washing

In this technology polluted water is scrubbed by water and mechanical agitation to remove the hazardous contaminants or reduce their volume. It makes use of the selective binding of contaminants to fine material (silt and clay) rather than to coarse soil material such as sand and gravel. Adding chemical additives or surfactants to the water may enhance this process. After separating the two soil fractions, fine material carrying the major part of contaminants is further treated by other methods of remediation to get rid of the separated contaminants (see figure 107), while the coarse material if cleaned up may be returned to the plot.

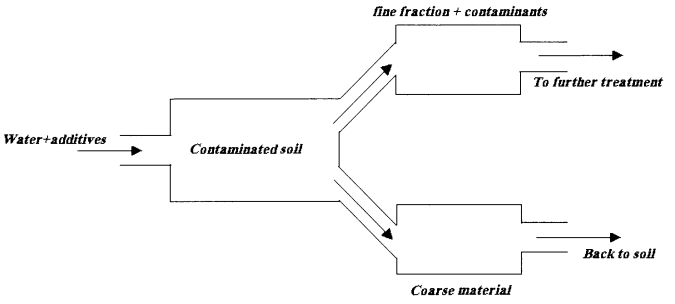


Fig. 107 . Schematic diagram showing the different steps in soil washing

Soil washing belongs to the category of **volume reduction techniques** in which the contaminants are concentrated in a relatively small mass of material. It is used to treat soils contaminated by a wide range of contaminants ranging from metals to oil products and pesticides.

h) Soil flushing

Soil flushing is a remediation method used for in situ treatment of inorganic and organic contaminants. Known sometimes as the cosolvent flushing method, this technique depends upon injecting a solvent mixture such as water and alcohol or surfactants into the vadose or saturated zone. The leachate i.e. the solvent with leached contaminants is drawn from recovery wells to be treated above ground or be disposed of. Flushing technique is used mainly to treat soils contaminated by inorganics including radioactive contaminants. It may also be used to treat VOC's, SVOC's, pesticides and fuel remnants. It must, however be mentioned that flushing may not be effective for soils with low permeability. Also the costs for above-ground treatment of the leachates may raise the financial burden of the remediation project. Fig. 108 is a diagrammatic Illustration of the process.

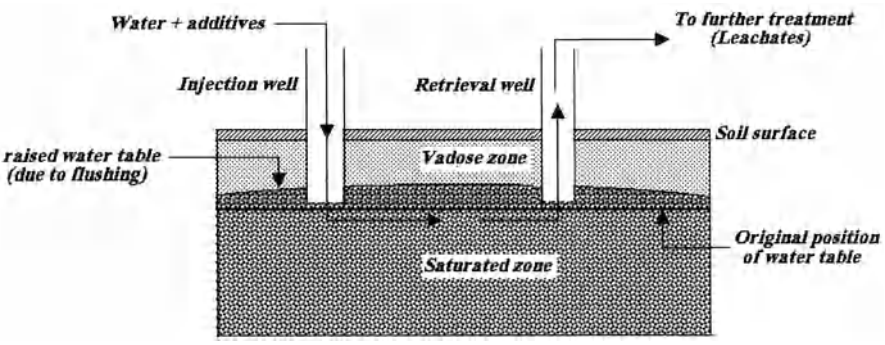


Fig. 108 .Diagrammatic illustration of soil flushing techniques

2. Biological treatment (Bioremediation)

Biological treatment of contaminated soils is a remedial technique making use of naturally occurring micro-organisms in the soil, that , are capable of degrading toxic materials , while carrying out their daily biological activities. Examples of such organisms may be given by bacteria or yeast. As explained before, some bacteria are capable of digesting a wide range of organic contaminants that other wise are very difficult to separate or degrade by any of the known technical methods.
It is an easy and effective method resulting in changing organic contaminants such as fuels or other oil products into carbon dioxide and water. However, the time required for complete remediation will depend upon whether the process is carried out in situ or in special facilities, where excavated soil material is transported. Ex situ technologies are normally faster and more effective than in situ processes.

a) In situ bioremediation techniques

In situ bioremediation techniques is mainly used to treat non halogenated semi volatile organics such as diesel fuel and heavy oils beside other materials that are susceptible to metabolism by micro-organisms. This technique -some times known as aerobic bioremediation- is accomplished by introducing oxygen and nutrients to the soil in order to enhance biodegradation of the contaminants. Two technical methods are used to create the suitable life conditions for the micro-organisms. These are:

1) **Bioventing** In this method atmospheric air is injected through special wells into the soil above the water table i.e. in the vadose zone, to supply the oxygen required for the micro-organisms.

2) peroxide injection: Here oxygen is introduced in a liquid form through injection of hydrogen peroxide into the soil. However this method is only applied to sites, where the ground water is already contaminated, in order to avoid unknown consequences resulting from contamination of the ground water by this chemical in areas of limited pollution.

b) Ex situ bio remedial methods

Ex situ bio remedial methods i.e. those methods carried out away from the pollution site are normally faster than the in situ methods. They are applicable for a wider range of contaminants, yet they are more expensive and may in some cases need pre treatment as well as post treatment measures in order to achieve highest Effectiveness. According to whether the treatment takes place in special tanks or in prepared beds , ex situ bio remediation comprises two main technologies – slurry phase treatment and solid phase remediation.

1) Slurry phase treatment: In this technology the polluted soil is excavated and transported to special facilities, where, it is mixed with water in special tanks (bio reactors). Oxygen and nutrients are later added, and the so formed mixture is thoroughly mixed to form a thin slur. Temperature, nutrients and oxygen concentrations are controlled so that the organisms may have the best conditions to sustain their bioactivities leading to the degradation of the pollutants.

2) Solid phase treatment : Here the polluted soil is treated above the ground in prepared beds. Despite the benefit of being less expensive than the slurry bed treatment, it is not so effective and needs more time and space to prepare the beds. Three main techniques are commonly used to carry out this remediation method – land farming, soil biopiles and composting.

a) Land farming:

The soil is excavated and spread on a pad with a built in system for collecting any possible leachates seepage. The so-formed bed is regularly mixed and turned over in order to facilitate aeration and enhance biological activity in the bed. Nutrients are added if required, since lack of nutrients and oxygen may lead to retardation of the bio degradation processes.

b) Soil biopiles The excavated soil is heaped in piles of several meters height. To enhance degradation activities by the microorganisms, air is blown through the pile. If required, nutrients are also added. Due to emissions from the piles, the whole process is sometimes carried out in inclusions that control any volatile contaminants.

c) Composting

Composting is an aerobic process during which organic matter is decomposed by microorganisms producing heat, carbon dioxide, water vapour and humus.

In the composting technique, biodegradable waste or contaminated soil is mixed with bulking materials such as straw to facilitate circulation of air and water required for the biological activities of the microorganisms. Nutrients are also added if required. Biodegradation of the waste or contaminants takes place some times in **static piles composting heaps,** where the soil is heaped in piles, that are periodically aerated with blowers or vacuum pumps. It may also be carried out in **mechanically agitated special tanks,** where aeration takes place through agitation.. Another technique through which composting may be carried out is the one known as **window composting**. In this technique soil is spread in long piles , exposed to atmospheric air and photolytic effects of sun light. Organic matter degradation by micro-organisms takes place in these heaps assisted by atmospheric oxygen and humidity.

Figure 109 shows in a schematic way the most common processes in biological treatment of polluted soils and the relations that connect them. Metabolic processes and enzymatic reactions were already explained in chapter 9.

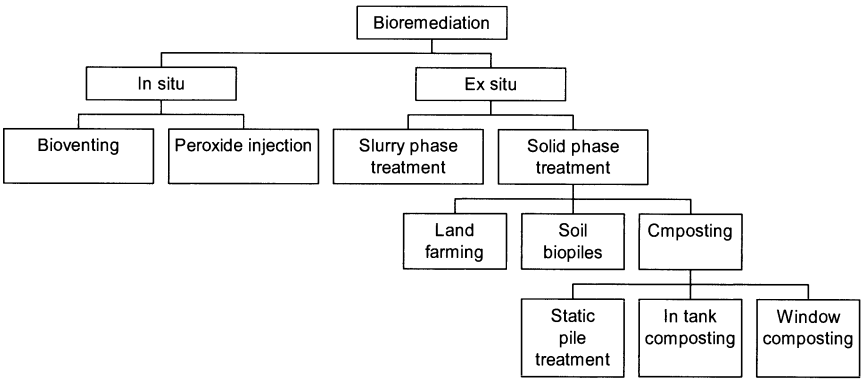


Fig. 109A schematic diagram showing the different technologies of bioremediation

Phytoremediation (Vegetation-assisted bioremediation)

Phytoremediation is a passive technology of soil remediation which has been gaining increasing popularity in the last decades. It depends on using plants (phyto) to remove, break down or stabilize contaminants in moderately shallow polluted sites. In such sites metals are stabilised or removed from the soil when taken up by the plants. Phyto remediation functions through different biological functions, depending upon the chemistry and nature of the soil pollutants.

Plants remove metal contaminants from the soil by two main processes, known as phytoextraction and rhizofilteration:

a) Phytoextraction (phytoaccumulation): Plants absorb metals from the soil by means of their roots and transport them to other plant parts, where they may be accumulated. Accordingly plants known to possess the ability of absorbing metals are chosen and grown on soils contaminated by metals or their salts. After sometime the plants are harvested and are either incinerated or recycled by composting or any other suitable method.

b) Rhizofilteration:

Rhizofilteration is a process through which a well developed root system is used as a filter for metals. This process takes place more readily in water than in soil and that is why it is mainly used to extract metals or radioactive matter from water. Other than in the phytoextraction process, here only the roots, where the metal accumulation has taken place, are harvested and disposed of. Two main steps are characteristic for this method, first the plants are grown in green houses until the root system is well developed and then replacing the water in the tanks, where the plants are grown by the contaminated water. The plants then take up the water and the contaminants along with it.

In case of treating soils contaminated with organic substances, four processes have been observed:

a) Phytodegradation
b) Enhanced rhizosphere biodegradation
c) Organic pumps
d) Phytovolatilisation

a) Phytodegradation

In this process plants are capable to degrade or break down organic contaminants. This occurs mainly through enzymatic reactions. Some of these reactions were explained in length in chapter 9 of this book.

b) Enhanced rhizosphere biodegradation

In this process plants work hand in hand with soil microorganisms in order to breakdown organic pollutants. Microorganisms carrying out biodegradation of the polluting material are supported by the root system (rhizosphere) that produces nutrients (e.g. alcohols, sugars) needed for the energy requirements of the organisms. This cooperative process keeps the microorganisms at a level sufficient for them to carry out their life activities and secure a continuous degradation of the toxic contaminants.

c) Organic pumps

Some trees (e.g. Poplar trees, cotton woods) are capable of pulling out big volumes of underground water, so that they may be compared with pumps continuously pumping water out of the soil. This action decreases the tendency of contaminants to penetrate the saturated zone and reach the ground water.

d) Phytovolatilisation

This occurs mainly in trees taking up a great deal of water containing organic contaminants. The contaminants may evaporate or leave the plant system via evapotranspiration.

Figure 110 shows in a schematic way the different processes observed in phytoremediation and the relations between them.

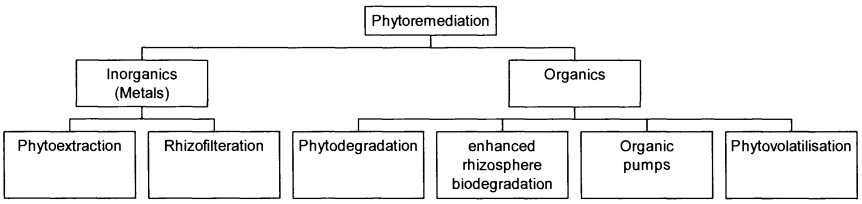


Fig. 110 . Summary of the different phytoremediation processes

3. Solidification / stabilisation methods

This is a group of technologies aiming at immobilising or stabilising contaminants in the soil and preventing them from entering the environment either by enclosing them into a solid mass or converting them to the least soluble , mobile or toxic form. Various technologies are known that secure safe performance of these processes. The following are the most successful among them.

a) Bitumen- based solidification

In this technology, the contaminated material is embedded in molten bitumen and left to cool and solidify. The contaminants thus encapsulated in the molten bituminous mass are changed to an immobile form that cannot enter the environment.

b) Encapsulation in thermoplastic materials

Thermoplastic materials (e.g. Modified sulphur cement) are molten and mixed with the contaminated material in special tanks and vigorously mixed to form a homogenous slurry fluid. After cooling the resulting solid may safely be disposed of.

c) Polyethylene extrusion

The contaminated soil is mixed with polyethylene binders, heated and then left to cool. The resulting solid may be disposed of or used in other ways.

d) Pozzolan / Portland cement

Pozzolanic-based materials (e.g. fly ash, kiln dust, pumice) are mixed with the contaminated matter in presence of water and alkali additives. At this environment heavy metals may precipitate out of the slurry. The rest mass solidifies enclosing the remaining organic contaminants.

e) Vitrification

In this process the contaminated soil is encapsulated into a monolithic mass of glass. Vitrification may be carried out in situ or ex situ. Introducing graphite electrodes into the soil and heating it electrically by powerful generators to temperatures between 1600-1800 °C perform in situ Vitrification. At these temperatures the soil melts and forms a glass block on cooling. Organic contaminants are pyrolysed and reduced to gases during the melting process, while heavy metals remain enclosed in the stabilised glass mass. This method has also been successfully used in treating soils contaminated by radioactive materials.

Vitrification may also be done in special appliances where contaminated soil would be molten in presence of borosilicate and soda lime to form a solid glass block.

4. Thermal treatment

Volatilisation and destruction of contaminants by thermal treatment is a very effective technique . It is achieved by heating the contaminated soil in kilns to temperatures between 400 and 700 °C, followed by further treatment of the kiln off gas at higher temperatures(800- 1200°C) to secure total oxidation of the organic volatile matter. Thermal treatment comprises various technologies, the most important of which are :

a)Incineration

In this technology Contaminants are combusted at high temperatures (970°C – 1200 °C) . It is particularly effective for halogenated and other refractory organic pollutants. Properly operated incinerators may be of very high destruction and re-

moval efficiency (DRE) reaching to as much as 99.9999 %, which is normally required for PCB's and dioxins.

b) Thermal desorption

This is the process by which organic contaminants are volatilised under controlled conditions by heating the contaminated soil to temperatures up to 600°C.Under these conditions, contaminants of low boiling points vaporise to be afterwards collected and further treated. Other than incineration, this technology aims to physically separate the contaminants from the soil.(Fig.111)

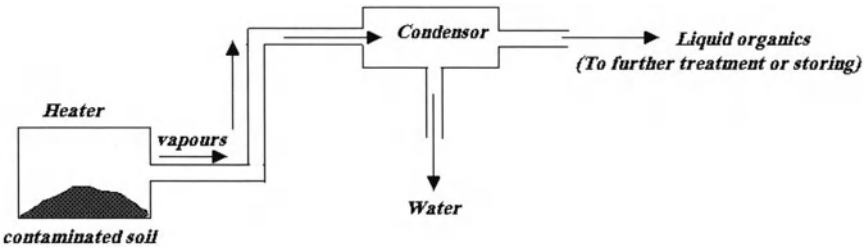


Fig. 111 Schematic diagram of a Thermal desorption system

c) Plasma high-temperature metals recovery:

At high temperature (plasma activated) metal fumes are purged, and later recovered and recycled. This is suitable for soil as well as for ground water.

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