

Soil Pollution

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B. Yaron R. Calvet R. Prost

Soil Pollution

Processes and Dynamics

With 105 Figures and 46 Tables



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Professor Dr. Bruno Yaron
Agricultural Research Organization
Institute of Soils and Water
The Volcani Center
P.O. Box 6
Bet Dagan 50250, Israel

Professor Dr. Raoul Calvet
Institut National Agronomique
de Paris-Grignon
Science des Sols et Hydrologie
Département Agronomie Environnement
78850 Thiverval-Grignon, France

Dr. René Prost
INRA
Station de Science du Sol
Route de Saint Cyr
78026 Versailles Cedex, France

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Preface

The soil is the medium through which pollutants originating from human activities, both in agriculture and industry, move from the land surfaces to groundwater. Polluting substances are subject to complex physical, chemical and biological transformations during their movement through the soil. Their displacement depends on the transport properties of the water-air-soil system and on the molecular properties of the pollutants. Prediction of soil pollution and restoration of polluted soils requires an understanding of the processes controlling the fate of pollutants in the soil medium and of the dynamics of the contaminants in the unsaturated zone.

Our book was conceived as a basic overview of the processes governing the behavior of pollutants as affected by soil constituents and environmental factors. It was written for the use of specialists working on soil and unsaturated zone pollution and restoration, as well as for graduate students starting research in this field.

Since many specialists working on soil restoration lack a background in soil science or a knowledge of the properties of soil pollutants, we have included this information which forms the first part of the book. In the second part, we discuss the partitioning of pollutants between the aqueous, solid and gaseous phase of the soil medium. The retention, transformation and transport of pollutants in the soils form the third section. Finally, the fourth part, consisting of the last two chapters, deals with models used to predict the behavior of pollutants in soils and the general principles of soil restoration.

The processes involved in the behavior of pollutants in soils have been illustrated from the literature or from our own results in a number of examples. Because of the limited number of cases which could be selected from the vast quantity published, the choice was very difficult and we are convinced that many other research results of equal worth could have been used to illustrate soil pollution processes. We hope, however, that we have succeeded in presenting the reader with a comprehensive, but not exhaustive, review of the current knowledge concerning soil pollution.

This book was prepared as part of the ongoing cooperation of the authors with the ARO, Volcani Center (Bet Dagan, Israel), INA (Paris-Grignon, France) and INRA (Versailles, France). We are grateful to these institutions for their continuous support. Special thanks to Shulamith Gordon and Etta Shur for their untiring assistance in the preparation of the manuscript.

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Bruno Yaron
Raoul Calvet
René Prost

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Part I
The Interacting Materials

CHAPTER 1

The Soil as a Porous Medium

The soil is the upper layer of the unsaturated zone of the earth. Soils are very diverse in composition and behavior. The solid phase consists of mineral particles of various sizes and shapes and organic matter in various stages of degradation. Plant roots and the living soil population complete the system.

In nature, soils are heterogeneous assemblies of materials, forming porous media. The open boundaries between the solid, liquid and gaseous phases lead to a pattern of continuously changing processes of chemical and biological origin, leading to transient soil properties. The porosity of the soil system is controlled mainly by the association of its mineral and organic parts, soil water having a strong effect. However, the reactivity between the solid and liquid phases could, with time, affect even the stability of the porous medium itself and, consequently, change the open boundaries of the reactive phases.

In most natural soils the solid particles tend to be molded into aggregates or peds, either by a shrink-swell phenomenon under wetting and drying-freezing conditions, or by biologically induced molding, due to soil animals, plant roots, and fungi. This situation again affects the porosity of the soil system, with implications for the transport of water, solutes, nonaqueous liquids, and suspended particles in the unsaturated zone from the land surface to the groundwater.

Since both the soil components and the binding agents govern the porous-aggregation status of the soils, a large spatial heterogeneity is found in nature. Figure 1.1 (Tisdale and Oades 1982) illustrates soil aggregation and soil porosity as affected by the soil components and the binding agents. It might be observed that the ratio between open and closed pores is strongly affected by the agents of formation. A functional classification of the soil pores, given by Greenland (1977), may give a general idea of the effect of soil pore dimensions on the water and solute status in the soil medium (Table 1.1).

In general, soil porosity is the limiting factor in defining the ratio between the solid, aqueous and gaseous phases of the soil medium, the water-air ratio at a given time being controlled by the amount of liquid in the system.

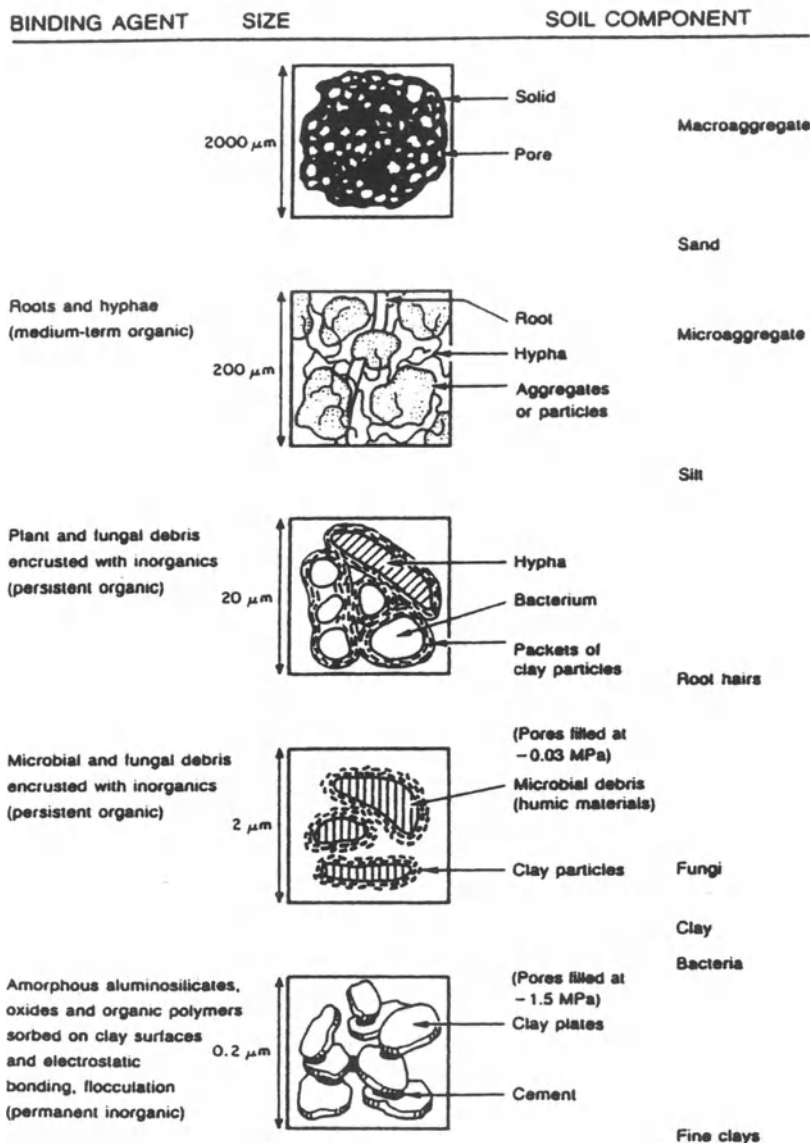


Fig. 1.1. Model of a soil aggregate organization. (Paul and Clark 1989, as adapted from Tisdale and Oades 1982)

1.1 The Solid Phase

From the point of view of potential interactions with various pollutants, the constituents of the soil solid phase should be grouped according to their sur-

Table 1.1. A functional classification of soil pores. (Greenland 1977)

Name	Function	Equivalent cylindral diameter μm
Transmission pores	Air movement and drainage of excess water	> 50
Storage pores	Retention of water against gravity and release to plant roots	0.5–50
Residual pores	Retention and diffusion of ions in solution	< 0.5
Bonding spaces	Support major forces between soil particles	< 0.005

face area. The fate of pollutants is affected by all the components of the soil solid phase. The soil constituents with low surface area could, however, mainly affect the transport of the pollutants as solutes, as immiscible with water liquids, or as vapors. The soil solid phase can also indirectly induce the degradation of the organic pollutants in the soil medium, through its effects on the water/air ratio in the system and, consequently, on the biological activity of the soil. The group of constituents with high surface area controls, besides the transport of pollutants, their retention, and release on and from the soil surface, as well as their surface-induced chemical degradation. It is, therefore, natural that when dealing with the topic of soil pollution, emphasis should be placed on the soil constituents characterized by a large surface area – and these are the clays and clay-organic complexes.

Since our book is addressed not only to soil scientists, but also to a large body of scientists, engineers, and technicians involved in soil pollution problems, we consider it necessary to include a short description of the reactive constituents of the soil.

1.1.1 Clay Materials

The clay materials, which comprise the smallest particles in the soil, are defined as the fraction with particles smaller than a nominal diameter of $2\ \mu\text{m}$. Many clay minerals have layer structures in which the atoms within a layer are strongly bound to each other, the binding between layers being weaker. Due to this situation, each layer can behave as an independent structural unit. We can find several types of layer arrangements which, however, do not greatly differ in free energy. The most common inorganic structural units to be found in soil clays are the silica tetrahedron SiO_4^{4-} and the octahedral complex MX_6^{m-6b} , formed of a metal unit M^{m+} and six anions X^{b-} . Figure 1.2 shows sheet structures formed by the polymerization of the above two structural units.

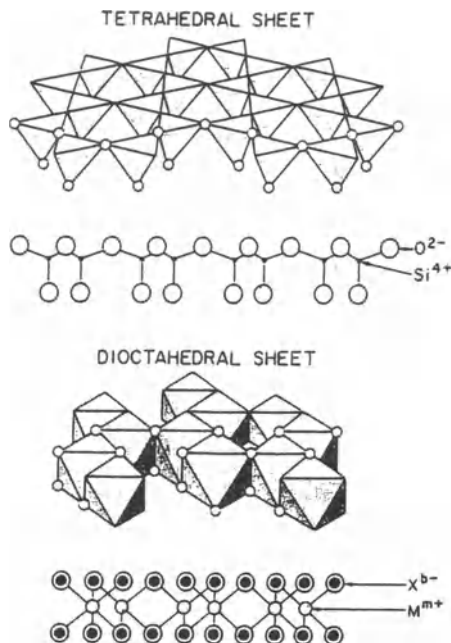


Fig. 1.2. Three layer types of phyllosilicate structure in soil clays. (Sposito 1984)

Brown et al. (1978) emphasized that the architecture of the silicate layer is due simply to the fact that each SiO_4 coordination group shares oxygen atoms with three neighboring SiO_4 groups, to form rings containing six Si and six O atoms, each ring being joined to a neighboring ring through shared oxygen atoms. Brown et al. (1978) showed that the other main structural element in layer silicate is an octahedral sheet that contains cations in MO_6 coordination between two planes of oxygen atoms. They summarized the types of octahedral sheets as follows:

“The anion groups coordinated to the M cations are $(\text{OH})_6$, $(\text{OH})_4\text{O}_2$ or $(\text{OH})_2\text{O}_4$, depending on the structural class of the layer silicate, and as the cation can occupy either four or six of the octahedral interstices, there are six possible types of octahedral sheet, with the following compositions:

Dioctahedral: $\text{Y}_2(\text{OH})_6$; $\text{Y}_2(\text{OH})_4\text{O}_2$; $\text{Y}_2(\text{OH})_2\text{O}_4$
 Trioctahedral: $\text{Y}_3(\text{OH})_6$; $\text{Y}_3(\text{OH})_4\text{O}_2$; $\text{Y}_3(\text{OH})_2\text{O}_4$

- (a) If all the anion groups are OH, the sheet is complete without further coordination of the oxygens; such sheets occur singly, alternating with silicate layers, in the chlorites, and comprise the only structural units in hydroxide minerals such as brucite, $\text{Mg}(\text{OH})_2$ and gibbsite, $\text{Al}(\text{OH})_3$; they are known as hydroxide sheets.
- (b) Octahedral sheets of composition $(\text{OH})_4\text{O}_2$ are present in the kaolinite and serpentine group minerals. One plane of groups is entirely (OH) , the other has the composition $(\text{OH})\text{O}_2$ and the oxygen atoms are shared with tetrahedral Si atoms, forming the apical oxygen atoms of tetrahedral sheet superimposed on the octahedral sheet; this junction represents the ideal structure of the clay mineral kaolinite. Each layer in this group of minerals contains one tetrahedral sheet and one octahedral sheet and the minerals are termed 1:1 layer silicates.

- (c) Octahedral sheets of composition $(\text{OH})_2\text{O}_4$ occur in the mica, vermiculite, smectite, pyrophyllite, and talc minerals. In these, both planes have the composition $(\text{OH})\text{O}_2$ and tetrahedral sheets are superimposed on both sides of the octahedral sheet, one tetrahedral sheet being inverted with respect to the other. The layer unit consists, therefore, of two outer tetrahedral sheets and an inner octahedral sheet, and minerals containing such layers are called 2:1 layer silicates. Because the oxygen atoms in the upper plane of the octahedral sheet are displaced relative to those in the lower plane (by the 'octahedral stagger'), the Si_6O_6 rings of the upper tetrahedral sheet are also displaced with respect to those of the lower tetrahedral sheet.
- (d) The chlorites contain two types of layer, a hydroxide sheet alternating with a 2:1 silicate layer, and they have sometimes been referred to as 2:1:1 or 2:2 minerals.

From these structural considerations, it can be seen that the layer silicates can be represented by ions in tetrahedral and octahedral coordination and that the numbers of such ions bear a relatively simple relationship to the oxygen and hydroxyl construction of the mineral."

In extreme cases, a great number of isomorphic substitutions leads to the formation of amorphous compounds classified under the name of "allophane" substances. These materials are mainly 1:1 phyllosilicates with defects containing Al in both tetrahedral and octahedral sheets. Sometimes, they can also exhibit a tubular morphology (e.g., imogolite).

1.1.2 Minerals Other Than Clays

In addition to the clay minerals (i.e., layer silicates), the clay fraction of the soils ($<2\ \mu\text{m}$) could contain a variety of minerals, e.g., oxide minerals, calcium carbonates, or calcium sulfates, etc. Summarizing the character of the soil metal oxides, Gilkes (1990) states that iron oxides (hematite $\alpha\text{-Fe}_2\text{O}_3$, maghemite $\beta\text{-Fe}_2\text{O}_3$, goethite $\alpha\text{-FeOOH}$, lepidocrocite $\beta\text{-FeOOH}$, etc.) are common constituents of soils, with crystals which vary greatly in size, shape, and surface morphology. The surface of iron oxides in soils is often hydroxylated, either structurally or through hydration of the Fe atoms. The crystals of the aluminum oxides that commonly occur in soils [gibbsite $\text{Al}(\text{OH})_3$, boehmite $\beta\text{-AlOOH}$] are also small, but are often larger than the associated iron oxides. Other oxide minerals are generally less abundant than the Fe and Al oxides but, because of their very small crystal sizes and consequently large surface area, they may significantly influence soil properties. For example, the various Mn oxides that are present in some soils can occur as very small ($\sim 10\ \text{nm}$) structurally disordered crystals. Similarly, titanium oxides in soils (rutile, anatase, TiO_2) and even the rare pyrogenic soil mineral corundum ($\alpha\text{-Al}_2\text{O}_3$) occur within the clay fraction as approximately 30-nm crystals. The ability of Fe and some other metal ions to undergo redox reactions further increases the role of the metal oxide in the activity of the soil solid phase surface.

Many soils formed from the appropriate parent materials contain significant quantities of relatively high-surface, soluble calcium carbonate (CaCO_3) or calcium sulfate (CaSO_4). Some agricultural soils may contain more than 50%

Table 1.2. Definitions of soil organic matter components. (Stevenson 1994)

Term	Definition
Litter	Macroorganic matter (e.g., plant residues) that lies on the soil surface
Light fraction	Undecayed plant and animal tissues and their partial decomposition products that occur within the soil proper and that can be recovered by flotation with a liquid of high density
Soil biomass	Organic matter present as live microbial tissue
Humus	Total of the organic compounds in soil exclusive of undecayed plant and animal tissues, their "partial decomposition" products, and the soil biomass
Soil organic matter	Same as humus
Humic substances	A series of relatively high-molecular-weight, yellow to black colored substances formed by secondary synthesis reactions. The term is used as a generic name to describe the colored material or its fractions obtained on the basis of solubility characteristics. These materials are distinctive to the soil (or sediment) environment in that they are dissimilar to the biopolymers of microorganisms and higher plants (including lignin)
Nonhumic substances	Compounds belonging to known classes of biochemistry, such as amino acids, carbohydrates, fats, waxes, resins, organic acids, etc. Humus probably contains most, if not all, of the biochemical compounds synthesized by living organisms
Humin	The alkali-insoluble fraction of soil organic matter or humus
Humic acid	The dark-colored organic material that can be extracted from soil by dilute alkali and other reagents and that is insoluble in dilute acid
Hymatomelanic acid	Alcohol-soluble portion of humic acid
Fulvic acid fraction	Fraction of soil organic matter that is soluble in both alkali and acid
Generic fulvic acid	Pigmented material in the fulvic acid fraction

CaCO₃ and almost the same percentage could characterize the sulfatic soils from an arid and semiarid region.

It is hard to estimate the contribution of amorphous materials like allophane or imogolite to the surface activity of the soils. The amorphous materials often coat the crystals present in the soils and, therefore, besides their direct contribution, they could alter the surface properties of the crystalline materials in the soil.

1.1.3 Soil Organic Matter

Soil organic matter is defined as the nonliving portion of the soil organic fraction, and it is a heterogeneous mixture of products resulting from microbial and chemical transformation of organic residues. Although the soil organic matter is, in most cases, only a small part of the total soil solid phase, it is of major importance in defining the physical, chemical, and surface properties of the soil material.

The transformed products of the fresh organic debris have the general name of *humus* but, in reality, they may be composed of humic and nonhumic substances. These substances could be amorphous, polymeric, brown-colored

humic substances differentiated on the basis of solubility properties into humic acids, fulvic acids, and humins, and recognizable classes such as polysaccharides, polypeptides, altered lignins, etc., which can be synthesized by microorganisms or arise from modifications of similar compounds. The major components of the soil organic matter and their definitions, summarized by Stevenson (1994), are presented in Table 1.2.

The organic matter extracted from the soils is usually fractionated on the basis of solubility characteristics and the fractions commonly obtained include humic acid (soluble in alkali, insoluble in acid) fulvic acid (soluble in alkali and in acid), hmatomelamic acid (alcohol-soluble part of humic acid), and humin (insoluble in alkali). These dark-colored pigments extracted from the soil are produced as a result of multiple reactions, the major pathway being through condensation reactions involving polyphenols and quinones. According to Stevenson (1994), polyphenols derived from lignin are synthesized by microorganisms and enzymatically converted to quinones, which undergo self-condensation or combine with amino compounds to form N-containing polymers. The number of molecules involved in the process, as well as the number of ways in which they combine, is almost unlimited, which explains the hetero-

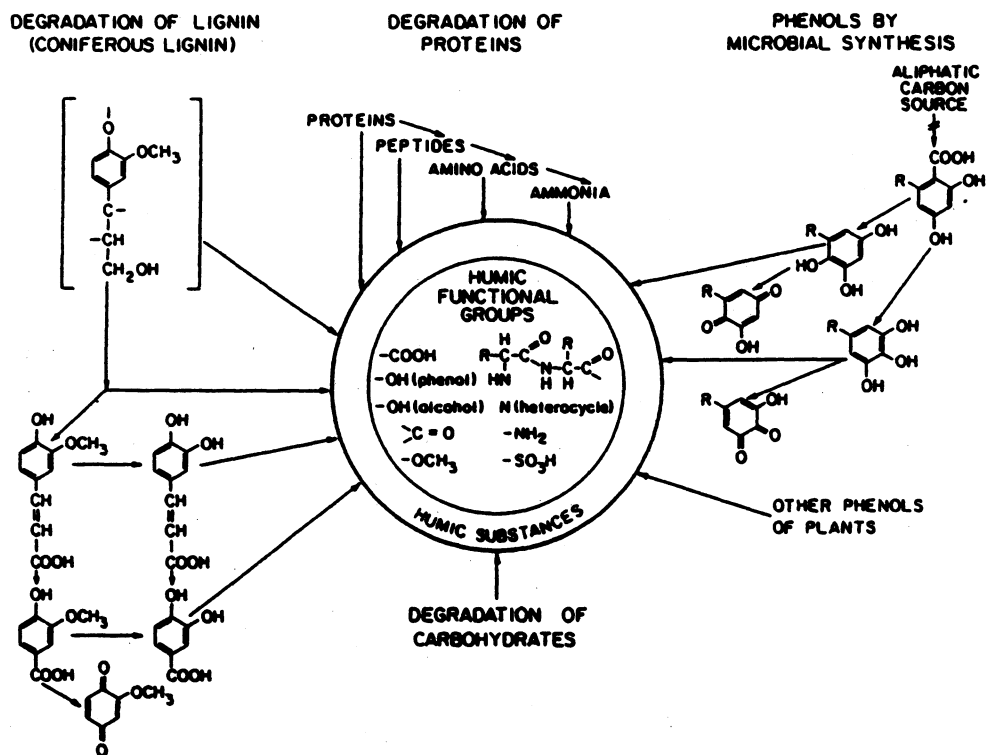


Fig. 1.3. Schematic representation of humic substances in soils and their main components and origins. (Flaig et al. 1975)

geneity of the humic material in any given soil. The structural precursors of humic substances in soils are illustrated in Fig. 1.3.

The major elements in the humic materials are C (50–60%) and O (30–35%). Fulvic acid has lower C but higher O. The percentages of H and N vary between 2 and 6% and that of S from 0 to 2%. The various fractions of the humic substances obtained on a basis of solubility characteristics are part of a heterogeneous mixture of organic molecules which, in different soils and locations, might range in molecular weight from several hundred to several hundred thousands. The average molecular weight range for humic acid is in the order of 10 000–50 000, and a typical fulvic acid will have a molecular weight in the range of 500–7000. The humic fraction of the soil represents a colloidal complex including long-chain molecules or two- or three-dimensional cross-linked molecules whose size and shape in solution are controlled by the pH and the presence of neutral salts. Under neutral or slightly alkaline conditions, the molecules are in an expanded state as a result of the repulsion of the charged acidic groups, whereas at a low pH and high salt concentration, contraction and molecular aggregation occur, due to the charge reduction. These large organic molecules may exhibit hydrophobic properties which govern their interactions with nonionic solutes.

1.1.4 Interactions Between Components of the Solid Phase

The interactions among the various components of the solid phase of the soil strongly affect its surface activity (Wolfe et al. 1990). The surface of the soil solid phase is heterogeneous. It is characterized by multicomponent association among humic substances, clays, metal oxides, CaCO_3 , and other minerals. In some cases, up to 90% of the soil organic matter was found to be associated with the mineral fraction of the soil (Greenland 1965). On the other hand, there is evidence that much of the surface of clay minerals in soils, specifically in the interlayer spaces of smectites, is not covered with organic matter (Ahlrichs 1972). Metal oxides are also likely to coat the external surfaces of clay minerals, and intercalation of oligomeric hydroxyaluminum species with clays has been reported (e.g., Ahlrichs 1972). Cationic aluminum hydroxyoxides, the charge of which is pH-dependent, may coat clay surfaces, thus reducing the contribution of the clay minerals to the soil cation exchange capacity. This phenomenon is more important in acid soils; as the pH increases, the hydroxyaluminum polymers lose their positive charge, and their effect on the CEC is reduced. The coating of clay surfaces with organic matter and with mineral oxides binds or replaces exchangeable cations that are the sites of many surface-enhanced transformations (e.g., Mingelgrin et al. 1977). Coating may also block access to active sites that are not themselves coated.

The most extended interactions between components of the soil solid phase are those between clay minerals and organic matter. As a function of the properties of the organic compounds and of the clay surface, various me-