
The Chemistry of Soil Processes

Edited by

D. J. Greenland

and

M. H. B. Hayes

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Foreword

Professor Maurice Stacey, CBE, FRS, DSc

Much was known about soils and about procedures for their management for the production of crops long before the approaches used in modern scientific investigations were established. This of course is not surprising because mankind has always been remarkably aware of the importance of conserving his natural resources and of means of utilizing these for his advantage. But, because of the scientific advances which continue to improve the expectancy and the material quality of life, the demands for food and fibre by a rapidly increasing world population have led to considerable interest in studies of the soil as a natural body, and as a medium to support the growth of plants. Both approaches to the study of the soil have contributed significantly to our understanding of the composition and properties of soils, and to progress in other areas of science during the past 150 years or so. It is now true to say that the advances made by soil and plant scientists, together with the appropriate contributions from various sections of the chemical and engineering industries, have provided the knowledge and technology to secure the world's supply of agricultural produce for the immediate future. There must still be concern, however, for the longer term while the present trend of an increasing world population continues.

We have every reason to be confident that scientists who are concerned with soil will be able to face the challenges of the future. The easiest problems have already been solved, but several highly complex questions must be answered before it will be possible to predict accurately the reactivity of any soil under particular sets of circumstances. Such predictions must await detailed information about the structures of the soil colloidal constituents, about the associations which exist between these constituents, and about the nature of the surfaces which they expose for interactions with the soil solution.

Progress in establishing the structures of soil components has awaited the development of appropriate scientific theory and instrumentation. We are aware of the remarkable contribution which X-ray diffraction has made during the past half century to establishing the structures of clays and of the extent to which this procedure is now being used in order to study complex soil-clay and -oxide structures. At this time too instrumentation and techniques

which have revolutionized the approach to research in organic chemistry are being widely applied to investigations of the structures of soil organic colloids. A technology which employs powerful nuclear magnetic spectroscopy, microinfrared spectrophotometry, and the combination of gas-liquid chromatography and mass spectrometry is helping to unravel the component molecules of the complex soil organic polymer structures. The task of determining the properties of the reactive surfaces of soils will be made much easier when these structures and the nature and composition of soil amorphous oxide materials are known.

Chemistry is of course fundamental to investigations of soil components and soil processes. Several chemists have devoted their interests to studies with soils and many of these have made outstanding contributions to soil science. Most of them have enjoyed the familiarity with other disciplines which they needed in order to contribute to the field. The same is true for the contributions by several scientists who trained as biologists. However, Soil Science has now evolved as a discipline in its own right to produce a new 'breed' of highly versatile scientist.

This book and its companion volume provide the kind of stimulus which is needed for the continued advancement of Soil Science. The advanced and intelligent undergraduate will find in both volumes numerous opportunities to make relevant to his soils interests his earlier courses in the basic sciences. For the research student and his more established colleagues the two books will provide a stimulus for new ideas and new approaches to their research.

Some may regret that the complete works were not prepared by fewer authors who could at all times adhere more closely to a highly unified approach to the different topics considered. But whereas it is reasonable to expect that two or three highly competent analytical, organic or physical chemists might together be able to prepare fairly comprehensive treatises in their areas, such would not be possible in the field of Soil Science. However, *The Chemistry of Soil Constituents*, and *The Chemistry of Soil Processes* may well stimulate some persons to improve on them. If so their future contribution will be highly valued, and the task will have been made much easier because of the combined efforts of the contributors to the present series.

Preface

Since the beginning of this century the application of chemical fertilizers has increased many fold, and the production of soil-applied pesticides has become a new major industry during the past twenty five years. Fertilizers and pesticides are not the only chemicals added to the soil, because by accident or design many other compounds which enter the environment end up in the soil. The world population, increasing at a conservative estimate of 2 per cent per annum, doubles in less than thirty five years. The soil has to produce the bulk of the food and fibre to sustain this growing population.

If the soil is to continue to be both the source of our foodstuffs and the 'sink' for many of our wastes, it is obviously desirable that we understand its complex chemistry.

Much scientific endeavour is being directed to this end. This has resulted during the past few decades in a large volume of published literature, including several books concerned with the chemistry of the mineral and organic components of soils, or with certain chemical processes in soils. No recent book has, however, attempted to produce a coherent account of soil chemistry as a whole, suitable for students of both environmental chemistry and soil science, and for the wide range of research and other scientists who are interested in the chemistry of soils. The original intention of the editors of the present book was to attempt to fill this gap. Because of the very diverse topics involved it was felt that it would have to be written by several authors if it was to be appropriately authoritative.

The chemistry of soils falls naturally into two parts, the chemistry of the various soil components, and the chemistry of soil processes. At first it was intended that these, the static and dynamic aspects of soils, should form two parts of a single volume. However, to deal with the topics involved at the intended level would have produced an unwieldy volume, and so two companion volumes are being issued, *The Chemistry of Soil Constituents* and *The Chemistry of Soil Processes*.

The opening chapter of the companion volume provides a short historical outline of the development of soil science. This deals briefly with the evolution of soil chemistry and pedology, and with the development of soil mineralogy, soil physics and soil biology—disciplines which are essential for integrated studies of soils and soil processes. It also refers to some of the processes which weather rocks, transform plant and animal residues, and

lead to the formation of soil constituents. Several systems exist for classifying the major soil types of the world according to their origins, and the most common of the names used to indicate the same soil types are introduced. The two chapters which follow deal with the inorganic and organic components of soils, respectively. Although the chemical structures of the major inorganic components are now reasonably well known, the same is not true of the organic (or humic) materials in soils. The relevant chapter presents an account of what has been experimentally established regarding the constitution of the peculiarly intractable complex of organic compounds found in soils.

Chemical processes in soils are largely determined by reactions at the surfaces of the soil colloids. The final three chapters of the companion volume are therefore concerned with the nature and extent of the surfaces of soil colloids, their electrical characteristics, and the ways in which ions and water are held and arranged at the surfaces.

This volume is intended to describe the chemistry of several of the important processes which take place in the soil. These are discussed in detail in the appropriate chapters which include treatments of precipitation and of ion-exchange reactions, adsorption and the formation of complexes, and of oxidation and reduction. The manuscripts do not, however, adhere exclusively to chemical processes. In contexts of soil as a medium for plant growth or as a 'sink' for waste products, it is not realistic to separate purely chemical from physical and biological processes. Thus the initial chapter attempts to summarize the properties of soils which are relevant to plant growth, to detoxification, and to transport processes within the soil profile, and it tries to relate the development of specific features of soils to the chemical processes operating on them.

Mass flow and diffusion, discussed fully in Chapter 2, controls the transport of molecules and of ions to plant roots, and to adsorption, exchange or deposition sites in the soil profile, or to drainage waters or the atmosphere. Such transport processes are strongly influenced by the extents of aggregation of soil components and by the nature of the aggregates; hence the important concepts of soil structure are summarized in Chapter 1. Similarly, the soil composition and structure determine the aeration and water-holding capacity of the soil, and these properties in turn influence the types, numbers, and activities of the organisms of one kind or another which inhabit it. The diversity and magnitude of the soil flora and fauna are introduced in the first chapter, and frequent mention is made of their activities throughout the volume.

Inevitably, in order to discuss the different topics in some depth it has been necessary to assume that the readership will have a significant knowledge of chemistry and an introductory knowledge of soil science. It is hoped that this book, like its companion volume, will be of use to students of soil

science and environmental chemistry, as well as to those who are involved in research related to the soil.

The editors are grateful for the collaboration and patience of those who have contributed, for the encouragement of the publishers and their tolerance of delays, and for the permission which many authors and publishers have given for material to be reproduced. Special acknowledgements of the latter are made in the text.

We have endeavoured to adhere to SI units throughout. The Ångström has been reluctantly abandoned in favour of the nanometre, but we have found it necessary to retain the terms 'equivalent' and 'milliequivalent', since there is no suitable alternative for expressing the retention of ions per unit weight or unit area of a soil colloid.

D. J. GREENLAND
M. H. B. HAYES

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CHAPTER 1

Soil processes

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1.1 INTRODUCTION

This volume is concerned with the chemistry of soil processes. These are rather arbitrarily divided and discussed in the first part of this book in terms of mass flow and diffusion, precipitation, cation, anion and ligand exchange, adsorption, translocation of metals, and oxidation and reduction. The way in

which these processes operate to determine the fate of different substances added to soils is described in the remaining part of the book. In this initial chapter an attempt is made to show how the individual chemical processes described later combine with physical and biological processes to give soils their ability to support plant life, and to accept the detritus of the world and to convert it to harmless constituents of the soil mass.

1.2 AGGREGATION AND POROSITY AND THEIR IMPORTANCE TO SOIL PROCESSES

The soil allows a great range of chemical processes to occur only because it provides a unique porous environment, including some regions where soil solution and microorganisms are at rest, and slow reactions can occur, and some where rapid flow and removal of products can occur. Physically it is also unique, in that it is normally sufficiently flexible and porous to allow plant roots and soil animals to penetrate it easily, while at the same time providing a firm anchorage for plants.

1.2.1 Pore Sizes and Transport Processes

Typical distributions of the pore space in soils are illustrated in Figure 1.1. The tremendous range of pore sizes includes some extremely fine, or

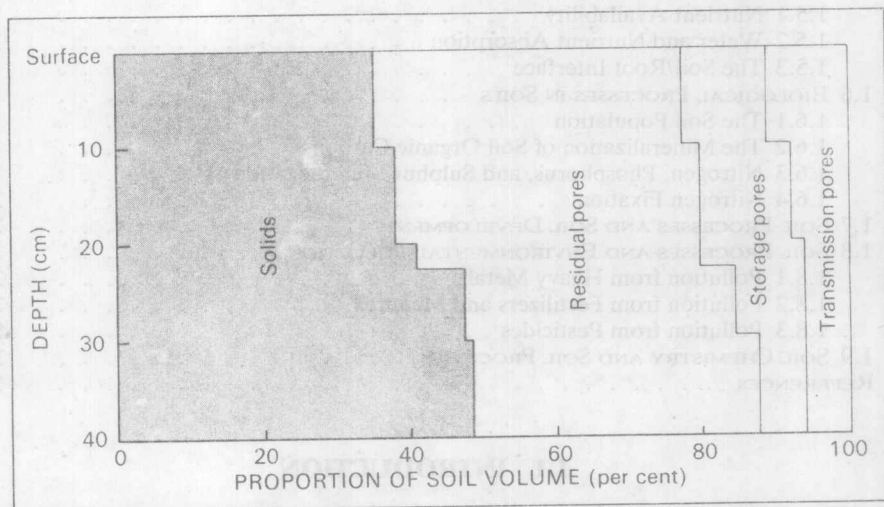


Figure 1.1 Proportion of soil volume in a typical heavy clay occupied by solids, residual, storage, and transmission pores. Residual pores are almost always water filled. Storage pores may be water or air filled. Transmission pores are air filled unless the soil is water saturated

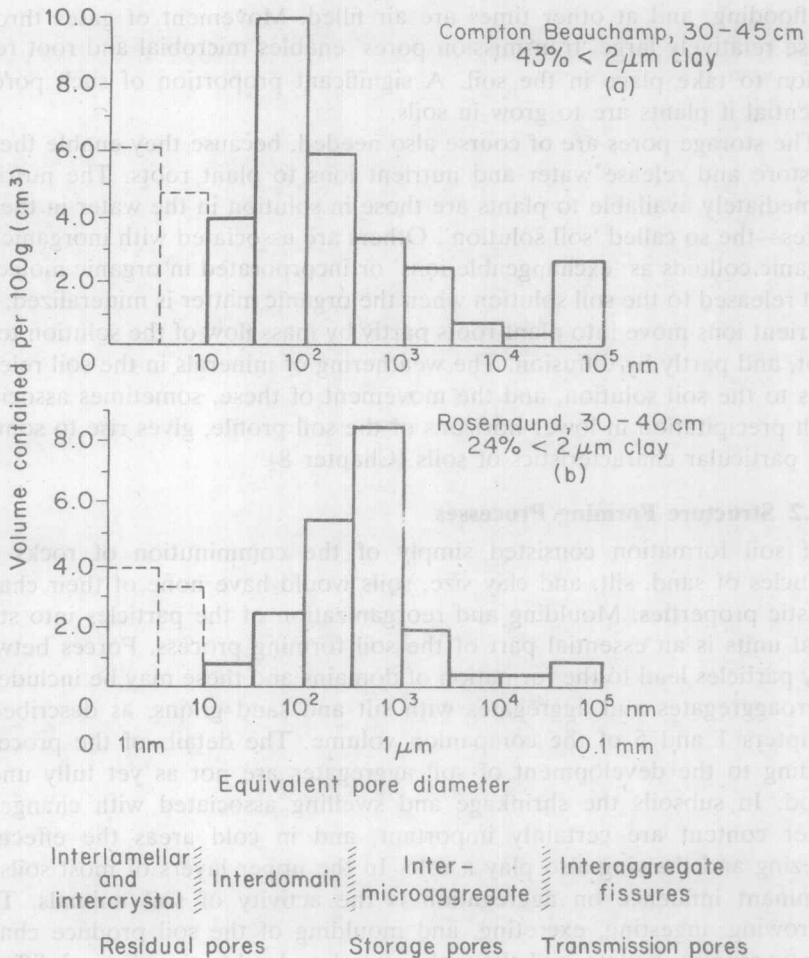


Figure 1.2 Pore size distributions in aggregates from (a) a clay and (b) a loam soil. Transmission pores are mostly formed between aggregates and there are few such pores within aggregates. Broken line lines show porosity determined by nitrogen sorption. Remainder determined by mercury intrusion. (Unpublished data of Lawrence, Payne and Greenland)

residual, pores (smaller than about 500 nm equivalent diameter) which retain water against both drainage and the suction exerted by plant roots, some between 500 nm and 50 μm (storage pores) which retain water against gravity, but allow it to move to roots, and some larger than 50 μm which are unable to retain water against gravity, and so allow soils to drain after rain

or flooding, and at other times are air filled. Movement of gases through these relatively large 'transmission pores' enables microbial and root respiration to take place in the soil. A significant proportion of such pores is essential if plants are to grow in soils.

The storage pores are of course also needed, because they enable the soil to store and release water and nutrient ions to plant roots. The nutrients immediately available to plants are those in solution in the water in the soil pores—the so called 'soil solution'. Others are associated with inorganic and organic colloids as 'exchangeable ions' or incorporated in organic molecules and released to the soil solution when the organic matter is mineralized. The nutrient ions move into plant roots partly by mass flow of the solution to the root, and partly by diffusion. The weathering of minerals in the soil releases ions to the soil solution, and the movement of these, sometimes associated with precipitation in lower horizons of the soil profile, gives rise to some of the particular characteristics of soils (Chapter 8).

1.2.2 Structure Forming Processes

If soil formation consisted simply of the comminution of rocks into particles of sand, silt, and clay size, soils would have none of their characteristic properties. Moulding and reorganization of the particles into structural units is an essential part of the soil forming process. Forces between clay particles lead to the formation of domains and these may be included in microaggregates and aggregates with silt and sand grains, as described in Chapters 1 and 5 of the companion volume. The details of the processes leading to the development of soil aggregates are not as yet fully understood. In subsoils the shrinkage and swelling associated with changes in water content are certainly important, and in cold areas the effects of freezing and thawing also play a role. In the upper layers of most soils the dominant influence on aggregation is the activity of soil animals. Their burrowing, ingesting, excreting, and moulding of the soil produce characteristic crumbs, pellets, and channels, and often lead to the physical differentiation of the surface soil from the subsoil, where they are less active.

The aggregates or 'peds' produced by the physical and biological pressures developed in the soil give rise to very specific structural characteristics, differing markedly between different major soil groups. These characteristics are described fully by Butler (1955), Brewer (1964), and others.

For present purposes it is the pores between the structural units, rather than the peds or aggregates themselves, which are of greatest interest. The range of pore sizes, their continuity, and tortuosity determine the extent to which gases and the soil solution move in the soil, and so to a large extent, many of the processes which occur in the soil (Figure 1.2). Flow and diffusion of water and ions in soil systems is therefore described in Chapter 2. The movement of air and water in soils is complicated by the fact that the

proportion of the large transmission pores is easily reduced by compactive stress (Greenland, 1977). The continuity and tortuosity are also easily changed.

Soil cultivation is conducted to break clods into smaller aggregates, and so create more of the large interaggregate pores in the surface soil. The increase in the number of fissures and transmission pores improves the opportunity for seedlings to emerge and young roots to develop. Properly timed cultivations also kill weeds, and this can be the most important effect of ploughing and harrowing soils. Sometimes 'plough pans' are formed by repeated shearing of the soil at a fixed depth during cultivation (Figure 1.3b). The pan breaks the continuity of pores leading from the surface, and may cause water to collect in the surface soil, inducing anaerobic conditions and so having a deleterious effect on crop production.

1.2.3 Structural Stability

The low bulk densities of soils immediately after tillage tend to be temporary, and the soil gradually slumps to a more compact mass during succeeding months. The rate at which the open structure collapses depends on the stress to which the soil is subjected, and the stability of the soil aggregates, which in turn depends on the forces acting between the soil particles.

When distances of separation between particle surfaces are of the order of only 1 nm or less, water-electrolyte interactions described in Chapter 5 of the companion volume, allied to Van der Waals forces (e.g. Adams and Israelachvili, 1978) give rise to strong interparticle bonding. Only when diffuse electrical double layers are formed do the repulsive forces between the particles outweigh the attraction. Consequently clay particles tend to associate in groups or domains in which the individual crystals lie close and parallel to each other. These domains usually consist of relatively few clay particles and have dimensions of the order of 1 to 5 μm (Quirk, 1978). Within domains the clay particles are separated by only a few layers of water molecules, and the forces between the clay particles are sufficient, provided the system remains flocculated, for the domain to be a permanently stable entity in the soil. The strength with which water is held within the domain is sufficient to prevent its removal in any circumstances likely to arise in the soil.

Between domains, and so within microaggregates, pores of the order of 0.1 to 1 μm diameter may arise. The suction needed to drain these is of the order of 2.5 to 0.5 MPa or 25 to 5 atmospheres. In soils they lose water only in intensely dry conditions. When water has been removed from all pores in which it is retained by a suction of less than about 1.5 MPa or 15 atmospheres, most plants reach the stage of permanent wilting from which they cannot recover. The reason is partly the high strength of retention, and

partly the slow rate at which water can move in such narrow capillaries. Transfer within the soil in the vapour phase is also slow. The relative humidity in the soil atmosphere when permanent wilting of plants occurs and water is held at 15 atmospheres (pores larger than $0.2\text{ }\mu\text{m}$ equivalent diameter drained) is as high as 98.8% (Table 1.1). Thus for all soils where plants are growing the relative humidity in the soil is normally greater than

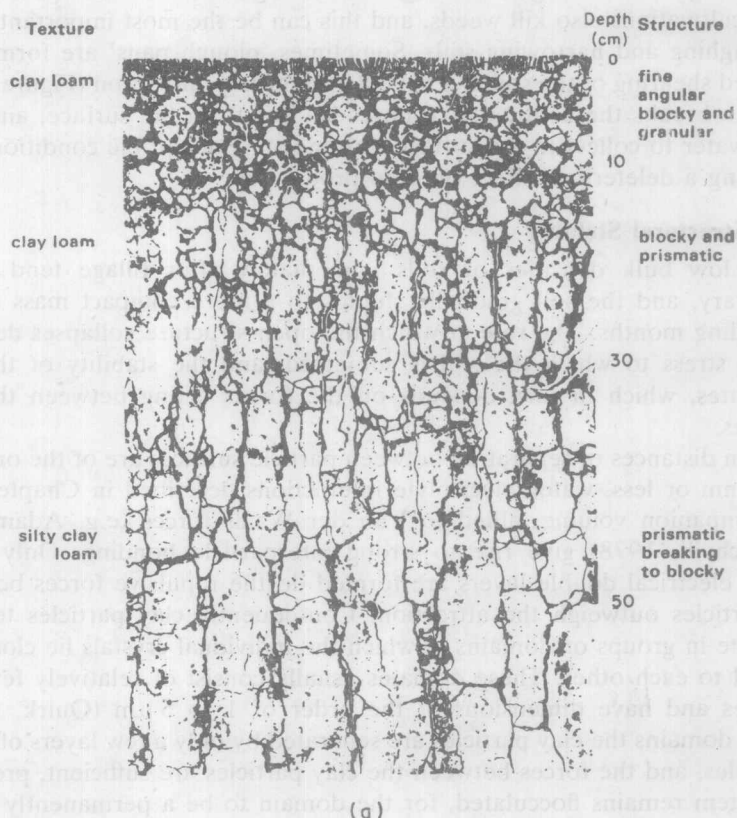


Figure 1.3 Illustrations of structural characteristics of two English arable soils:

(a) Typical chalky clay with very stable structure under arable cultivation. Flow of air and water occurs through the extensive fissures and transmission pores.

(b) A typical non-calcareous clay profile, which is badly drained because fissures and transmission pores are blocked by mud which has flowed from the upper part of the profile. The soil has slaked and formed a platy layer at 20–25 cm due to ploughing and wetness.

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