List of Acronyms and Abbreviations

2,4-D 2,4-dichlorophenoxyacetic acid
BIO soil biomass
CGS centimetre-gram-second
CI Colour Index
COM chemically stabilized organic matter
CP cross-polarization
C–P–OM clay–polyvalent metal–organic matter
DMSO dimethyl sulphoxide
DOSY diffusion-ordered spectroscopy
DPD diffusion pressure deficit
DPM decomposable plant material
DTG differential thermogravimetry
EDTA ethylenediaminetetraacetic acid
FA fulvic acid
FC field capacity
FYM farmyard manure
HA humic acid
IR infrared
LGS Lower Greensand
MAS magic angle spinning
meq milliequivalent
NMR nuclear magnetic resonance
PBC potential buffering capacity
PD potential difference
PL lower plastic limit
POM physically stabilized organic matter
ppm parts per million
PTFE polytetrafluoroethylene (trade name Teflon)
Q/I quantity–intensity
RPM resistant plant material
SOM soil organic matter
TDR time-domain reflectometry
VA vesicular-arbuscular
VCL virgin compression line

Editorial Introduction to Volume II

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Introduction

Soil science is a relatively young science that has developed out of the application of geology, chemistry, physics and biology, to the complex entity called soil. As indicated in the Overview to these volumes, the earliest studies on soil as an entity took place in the mid-19th century when seminal works on soil in relation to the underlying geology and a soil's ability to nourish plants were published, for example, by Liebig (1847) and others (see Overview to the Four Volumes). However, after these studies on soil per se in the 19th and early 20th centuries, scientists specializing in physics, chemistry and mineralogy began to examine components from soils, such as clay minerals and organic matter. The results of these studies helped to explain the complex behaviour that the more generalist 'soil scientists' had observed earlier. However, as Thomas wrote in 1977, our understanding of ion exchange in soils, where the exchangers are complex mixtures of clay minerals, oxides and organic matter, has not kept pace with the work on purer exchange materials. ... The progress made in the past has depended on solid experimental data and it is evident that additional advances will not occur until we obtain such data on soils themselves.

Because for many years chemistry, physics and biology were the three major subdisciplines of soil science, the bulk of the past literature falls within the scope of this volume, which has made the selection of papers very difficult. Nevertheless, the papers selected here are intended to show how studies on the properties and behaviour of soil components, often in purified forms, progressed in tandem with studies on whole soils sampled from a range of environments. Hypotheses to describe soil properties and behaviour were developed and tested by experiment, leading gradually to an accepted core of knowledge about many soil processes in general, and about the behaviour of some soils in particular. More descriptive work focused on soil biology, supplemented in some cases by chemical and physical analyses. Many examples occur of scientists coming to similar conclusions independently, and also through collaboration, locally and internationally. Inevitably, there are also examples where early insights were either ignored or overlooked so
that a new generation of researchers ‘rediscovered the wheel’, usually with a recurrent period of 25 years or so.

**Soil Physics**

A prominent topic for research in soil physics has been soil structure – its creation naturally or through human intervention, its stability and its influence on such diverse processes as water infiltration, water storage and retention, water movement and drainage, gas exchange, the resistance of soil to root penetration, and a soil’s workability with tillage implements and its ability to withstand shearing and compressive forces. Soil has structures that are unique to it. Dexter (1988, this volume) defined soil structure as ‘the spatial heterogeneity of the different components or properties of soil’; in other words ‘spatial heterogeneity = spatial variability = structure’ (cf. Nikiforoff (1941) and Brewer and Sleeman (1960), Volume 1). Many would question the utility of such a broad definition, preferring to recognize the aggregation of primary soil particles and organic matter as the basis of structure, which can be described in terms of (i) the arrangement of the primary particles into aggregates or pedds, and (ii) the size, shape and arrangement of the aggregates and voids or pore spaces that separate particles and aggregates (see Soil Morphology and Micromorphology, Volume 1).

The water-stability of soil aggregates has received much attention because of its importance to agricultural and engineering uses of soil. The determining factors are complex, involving an integration of mineralogy, physicochemical reactions at interfaces, organic compounds and the activity of soil organisms, but the paper by Tisdall and Oades (1982, this volume) gave an excellent exposition of the state of knowledge up to 1982. This knowledge was reinforced by Dexter’s (1988) wide-ranging review not only of the creation and stabilization of soil structure, but also of techniques for measuring structure and its effects on infiltration, evaporation, soil workability and the mechanical strength of soils.

In England, Lawes et al (1882) made some of the earliest observations of the effect of structure on the movement of water and dissolved solutes using the Rothamsted drain gauges. They found that some of the drainage from these undisturbed soil monoliths appeared to move rapidly through large pores, bypassing the network of fine pores inside aggregates. However, these observations in the late 19th century were ignored or overlooked by physicists and chemists in other parts of the world who studied the movement of water and air through soils. Although the work of French engineer Darcy (1856) on liquid sewage flow through sand beds was acknowledged, researchers such as Green and Ampt (1911, this volume) and Richards (1931, this volume) were preoccupied with the capillary flow of water and air. They conducted their experiments on artificial media such as columns of glass beads or sand particles of uniform size, or narrow, repacked columns of finely sieved, dry soil.

The picture that emerged from these studies on homogeneous (in terms of pore size distribution) media was one of water moving vertically through a dry soil behind a uniform wetting front, at the boundary of which there was a sharp change from near-saturated to dry soil. Although this behaviour was a reasonable representation of water flow in a sandy, poorly aggregated soil, it was at odds with Lawes’ observations of the Rothamsted drain gauges and those of others who examined water flow, often traced by dissolved dyes, in soils in the field (Bouma, 1981, Volume 1; Beven and Germann, 1982; White, 1985). Flury et al (1994, this volume) also give examples of preferential or bypass flow behaviour.

Richards (1931, this volume), following the work of others such as Buckingham (1907) and Gardner and Widstoe (1921), demonstrated the relationship between capillary conductivity and capillary potential in repacked soil, and introduced the concept of a continuity equation to describe water movement in unsaturated soil. Subsequently, solutions of Gardner’s (1960, this volume) radial diffusion equation were helpful in quantifying the rate of water movement to the root of a plant experiencing a varying inspirational demand. On similar lines, Philip (1957, this volume) developed a mathematical expression for water infiltration, introducing a new term, sorptivity, to describe what he referred to as ‘the capillary uptake or removal of water’.

The early efforts to model water flow (and associated solute transport) on the basis of assumed physical mechanisms led to an exponential growth of theoretical and experimental papers based on the Richards equation for water flow and the convection–dispersion equation for solute transport. Much of this early work was carried out in a laboratory on columns of sand or sieved soil that were packed to give as uniform a porous medium as possible (see review by Biggar and Nielsen, 1967). The mathematical description of water flow through unsaturated soil was more complicated than for saturated soil because the hydraulic conductivity \( K \) was non-linearly dependent on the soil’s volumetric water content \( \theta \), Van Genuchten (1980, this volume) and others solved this problem by deriving \( K \) as a function of the matric potential \( \psi_m \), given that the relationship between \( \theta \) and \( \psi_m \) could be measured experimentally or modelled.

Nevertheless, extreme lateral and vertical variability in the hydraulic properties of soils in the field (Biggar and Nielsen, 1976), together with the transient nature of water movement under natural conditions, created great difficulties for deterministic modelling: so much so that alternative approaches that involved stochastic functions of key parameters were attempted (Dagan and Bresler, 1979). Then Jury (1982, this volume), starting from the premise that ‘the many causes of spatial variability of water and solute transport render measurement of the hydraulic and retention parameters of a field soil all but impossible’, proposed that the travel times for solute molecules through an undisturbed soil were a stochastic function of solute input at the surface, this function being a characteristic of the soil profile to the depth of observation. Thus was born the transfer function model of solute transport, which spawned a new stream of theoretical and experimental studies (e.g. Jury et al, 1986; White et al, 1998).
As important as the advances in the study of soil water dynamics were the efforts to improve the method of measuring $\theta$ on a field scale: the traditional gravimetric method, based on destructive sampling of a measured volume of soil, gave point measurements that were time-consuming and therefore costly. Topp et al (1980, this volume), following Davis and Annan (1977), demonstrated a reliable method based on measuring a soil's dielectric constant, which is primarily a function of $\theta$. The method, known as time-domain reflectometry, together with a companion method based on frequency modulation (using a capacitance probe), are now widely used for repeated in situ measurements of $\theta$ in field soils.

**Soil Chemistry, Mineralogy and Interfacial Reactions**

Way's (1852) experiments on cation exchange are some of the earliest studies in soil chemistry (Thomas, 1977). They are an appropriate starting point for the present selection of papers because they introduce many investigations on exchange materials in soil, the complexities of multivalent ion exchange and the mysteries of soil acidity. There was a confluence of investigations into the nature of soil chemical reactions and the physical and chemical properties of soil minerals, especially those of the colloidal or clay fraction, somewhat arbitrarily defined as being <2µm equivalent spherical diameter. Nevertheless, streams in this confluence have separated from time to time, no more so than in the first 30 to 40 years of the 20th century.

On the one hand, Mattson (1929, this volume) asserted that 'the mineral fraction of the soil colloidal material . . . is composed mainly of the hydrated oxides of silicon, aluminium and iron together with certain proportions of alkaline and alkaline earth bases. This material exists (as) a gel which is mixed with, and coats the coarser particles of silt, sand and gravel.' On the other hand, about this time scientists in the United States Geological Survey were identifying the crystalline structure of pure clay minerals, which was first confirmed for clay minerals separated from soil by Hendricks and Fry (1930). Subsequently, Marshall (1937, this volume) reported that the cation exchange capacity of clays of the 2:1 silicon (Si) to aluminium (Al) type originated from the substitution of Al$^3+$ for Si$^4+$ in the Si layers (sheets), and Mg$^{2+}$ for Al$^{3+}$ in the Al layers (sheets) – so-called isomorphic substitution. Hendricks and Alexander (1939, this volume) summarized the various methods for identifying clay mineral structure and composition, including elemental analysis, X-ray diffraction and differential thermal analysis, acknowledging also that oxides and hydrous oxides of iron (Fe) and Al were also common in the clay fraction, as well as some quartz and calcium carbonate.

For the next few decades, Mattson's view of the amphoteric gel nature of the clay fraction was supplanted by the crystalline clay mineral view, which was used to interpret cation exchange and the reactions that produced 'acid clays' and 'sodic' and 'black alkali soils'. Concomitantly, theories were developed to explain the interactions between clay particles in suspension, which had a profound bearing on our understanding, for example, of soil swelling and shrinking in response to changes in $\theta$, and the differential leaching of cations and anions. Whereas Mattson had favoured the Donnan theory of electrolyte behaviour in the presence of a homogeneous, fixed, space charge, Bolt and Pech (1953, this volume) found that the Gouy theory better described cation and anion distribution in dilute clay suspensions in which the space charge was decidedly non-homogeneous.

Bolt (1997, this volume) noted that soil pH and soil acidity were a 'central issue' attracting much attention from soil scientists in the 1920s and 1930s. Certainly, there was a preoccupation with the measurement of soil pH either in a suspension or its equilibrium dialysate, and with the potentiometric titration of clay suspensions. From such titrations, Bradfield (1923) concluded that an acid clay behaved as a weak acid of comparable strength to acetic acid, a concept disproved by Schofield (1949, this volume), who showed that an illicic clay had a constant negative charge (due to isomorphic substitutions) between pH 2.5 and pH 5, and developed a variable, additional negative charge at a pH > 6. Schofield (1949) concluded that the buffering of an acid-washed clay at pH < 6 could be attributed to the stepwise neutralization of exchangeable Al(OH)$_3^+$ ions. This interpretation was subsequently refined and expanded by Coleman, Rich and many co-workers in the US, who found that naturally acid clays contained a mixture of exchangeable and non-exchangeable (polymerized) Al, the latter being formed by the hydrolysis of Al$^3+$ (Thomas, 1977).

As results accumulated for a variety of soil types, especially for highly weathered soils from tropical and sub-tropical regions (e.g. Gillman and Uehara, 1980), the occurrence of pH-dependent charge in clay-fraction minerals was more widely recognized, and Mattson's ideas on amphoteric colloidal behaviour became fashionable again. For example, Farmer et al (1980, this volume) identified minerals such as protoimogolite and imogolite, which have a net positive charge at pH < 6, in the B horizon of podzols. Variably charged allophane was found in soils of volcanic origin, and many studies were made of the structure of hydrous oxides of Fe and Al (the sesquioxides) and reactions at their surfaces involving various ionic species in solution (e.g. Hingston et al, 1972). This information was relevant to the formation and stability of soil structure and the retention of organic and inorganic anions and cations, the latter topics spawning an especially large volume of literature (White, 1980). Instead of focusing on structure and function, Sposito (1983, this volume) presented a general framework for the reactions of cations and anions at oxide surfaces in terms of chemical thermodynamics, rather than postulating a hypothesis concerning the molecular nature of the surface complex.

Complex formation has also been an important topic in the study of soil organic matter (SOM) and the behaviour of organic components. Organic materials - dead plant roots, litter and animal debris - deposited on and in the soil are the substrate for a diversity of soil organisms (see Soil Biology, this volume), and in the process of decomposition these residues become humified. Sutton and Sposito (2005, this volume) describe humic substances as 'refractory, dark-coloured,
heterogeneous organic compounds, the age of which can range from a few weeks to thousands of years. This refractoriness, heterogeneity and the propensity for some of these materials to be strongly adsorbed by soil minerals have created huge difficulties in their chemical identification and the interpretation of their properties. A standard procedure, after the removal of macro-fragments, has been to separate 'humic fractions' according to their solubility in alkali and acid solutions, producing the operationally defined fractions fulvic acid, humic acid and humins (Konovalova and Bel'chikova, 1960). Studies on these fractions have been important for interpreting metal cation complexation and its effect on the plant availability of micronutrient metals, the potential toxicity of trace elements, and the leaching of metals (Schnitzer, 1969, this volume). Despite the application of various sophisticated analytical tools, the structure of humic substances remains a controversial subject, as demonstrated by the recent review by Sutton and Sposito (2005).

Others have eschewed the difficulties of studying the chemical structure of organic matter, turning their attention instead to investigating the dynamics of SOM and carbon (C) turnover in soil. For example, Jenkinson and Rayner (1977, this volume), building on concepts introduced by Jenny et al (1949, Volume 3), used data from long-term field experiments at Rothamsted to develop and test a model of C turnover involving simple assumptions about the rate of decomposition of organic inputs, the microbial biomass and humified SOM components. This model has proved to be a powerful tool for simulating C turnover in a range of soils and environments, and was the precursor of other popular models, e.g. the CENTURY model of Parton et al (1988).

Assessing the availability of essential nutrients to plants has been a major topic of investigation for more than 100 years, especially for phosphorus (P), starting with the use of dilute extractants such as dilute citric acid, designed to mimic the action of plant roots. Such methods are still widely used today, but often without acknowledgement of the original publication (e.g. Lemercier et al, 2008). Schofield (1955) attempted to rationalize soil testing for P by proposing that the chemical potential of calcium phosphate could be used as an index of availability (see Volume 3), an idea that led to the quantity-intensity (Q/I) concept for characterizing the labile fractions of such nutrients as P and potassium (K) (Beckett, 1964, this volume). The Q/I concept was based on the premise that the concentration of a nutrient ion in the soil solution was in reversible equilibrium with an adsorbed phase; but it did not directly account for variations in an ion's rate of diffusion to an absorbing plant root. Nye (1966, this volume) was one of the first to develop a rigorous theoretical analysis of this process that was subsequently tested in many experimental situations.

Application of the concept of solute diffusion in response to a concentration gradient was also important in elucidating the complex behaviour occurring at phase boundaries, as in sediment–water interfaces in flooded and waterlogged soils. Bouldin (1968, this volume) was one of the first to explore theoretically for such systems the relevance of several models of oxygen diffusion from an aerobic to anaerobic zone, and the converse diffusion of a soluble reductant such as Fe²⁺. Ponnamperruma (1972) focused on reactions that affected nutrient availability in submerged soils and sediments, making the startling claim that such materials cover 72 per cent of the Earth's surface. Together with others, such as Patrick and Mahapatra (1968), Ponnamperruma's work complemented the extensive studies of fertilizer reactions in terrestrial soils, which were pioneered by scientists such as Lindsay, Moreno, Taylor and others at the Tennessee Valley Authority in the US (Huffman, 1962; Lindsay, 1979).

Soil Biology

The number and diversity of organisms in soil are enormous; so much so that Wallwork (1976) was prompted to write 'the soil is teeming with life. It is a world of darkness, of caverns, tunnels and crevices, inhabited by a bizarre assortment of living creatures.' Early research on soil organisms focused on the identification of groups of organisms and their functions, especially with respect to the nutrition of plants. For example, the earliest work on soil microorganisms evolved from Pasteur's pioneering research in the 19th century on 'germ theory', expanded by Beijerinck who studied viruses and nitrogen (N) fixation (Chung and Ferris, 1996) and Winogradsky who studied nitrification and N fixation (Waksman, 1946). Subsequent studies focused on the functions of other specialist groups, such as the actinomycetes (Waksman and Curtiss, 1916, this volume), and the effect of environmental conditions on the activities of specialist groups, such as the ammonifying and nitrifying microorganisms (Alexander, 1964).

Since that time, many different strands of research have been followed both in the study of individual groups of organisms and in the interactions between groups, now known as the science of soil ecology (e.g. Bardgett, 2005); similarly in the study of interactions between soil organisms and plant roots, which range from associative to symbiotic to parasitic to pathogenic. The increase in the number of microorganisms in soil close to a plant root, an effect known as the 'rhizosphere effect' (Clark, 1949, this volume), is universal, having been observed even in soils in Antarctica (Bunt and Rovira, 1955). Whereas there is no dispute over this enhancement effect, primarily caused by the availability of substrates for microorganisms through the 'sloughing off' of root material and organic secretions, there has been controversy over the stimulation afforded to specific organisms or groups of organisms. For example, contrary to earlier reports (Starkey, 1958), Döbereiner (1961, this volume) identified greater numbers of free-living, N-fixing organisms of the genus *Beijerinckia* in the rhizosphere of sugar cane than in non-rhizosphere soil, an observation subsequently confirmed more widely for other members of the *Gramineae*.

Many studies have been made of the symbiotic relationship between legumes and *Rhizobium* bacteria (Nutman, 1965) and between mycorrhizal fungi and plant
roots (Nicholson, 1967), and the possible stimulatory effect of microorganisms and their metabolic products ('biostimulants') on plant growth (Welbaum et al., 2004). Furthermore, soil scientists have capitalized on the ability of soil organisms to adapt to consuming foreign molecules as substrate for growth, which has provided a basis for bioremediation of soil contaminated with recalcitrant pesticides and hydrocarbons (see Soil Degradation Control, Remediation and Reclamation in Volume 3).

Identifying and enumerating the many species of soil microorganisms have presented great problems for microbiologists; so much so that alternative approaches have been developed, such as measuring the activity of functional groups of organisms under optimal conditions in the laboratory. For example, the amount of nitrate produced during a few hours' incubation has been used as a measure of the number of nitrifying organisms present in a soil (Schmidt and Belser, 1982), and an enzyme assay has been used to estimate the activity of denitrifying organisms (Burford and Brenner, 1975). Jenkinson and Powleson (1976, this volume) used an indirect approach to measure the amount of microbial biomass, relying on the enhanced rate of respiration observed when fumigated soil is incubated under favourable conditions. This method has been widely used for comparing the microbiological activity of soils from various environments and under different management. More recently, molecular genetic techniques using DNA and stable isotope probes have been used to identify soil microbial groups (Pankhurst et al., 1996).

The early work of Darwin (1881) in the 19th century (see Overview to the Four Volumes) was followed by many studies on the diversity of soil animals that live on and in the soil, and their effects on soil properties (Hole, 1981, this volume). Yet others, such as Nye (1955, this volume), studied the specific effects of termites and earthworms on soil formation in West Africa. Because soil animals play an important part in the functioning of ecosystems, they have attracted more attention from ecologists and zoologists than soil scientists who have focused predominantly on disturbed agricultural systems.

### How Far Have We Come?

Based on more than 100 years of research, we now have a detailed knowledge of soil physical, chemical, mineralogical and biological properties and processes. Much of the work of the past 30 years has involved translating this knowledge into empirical or deterministic-mechanistic or stochastic models of soil processes as a means of confirming current understanding, and indicating the need to refine existing knowledge or to make new discoveries. A major emphasis now is on the relationships between properties and processes and the scale at which observations are made, which is especially challenging for a medium as diverse and spatially variable as soil. Table 1 shows the key developments in soil physics, chemistry, mineralogy and biology and the relevance of papers reprinted in this volume.

### Table 1 Key development phases in soil physics, chemistry, mineralogy and biology and the papers presented in this volume

<table>
<thead>
<tr>
<th>Period</th>
<th>Main developments</th>
<th>Representative papers in this volume</th>
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<tr>
<td>Pre-1880</td>
<td>Concept of soil as a medium for plant growth</td>
<td>Green and Ampt (1911), Waksman and Curtis (1916)</td>
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<tr>
<td>1880–1920</td>
<td>Study of soil physical properties and water movement; early studies on soil organisms and first descriptions</td>
<td>Mattson (1929), Richards (1931), Marshall (1937), Hendricks and Alexander (1939), Clark (1949)</td>
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<tr>
<td>1991–present</td>
<td>Modelling of soil processes, soil ecosystems, physicochemical effects; non-linear dynamics and scaling theory</td>
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### References


Further Reading (by Theme and in Chronological Order)

Soil physics


**Soil biology**


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**Soil mineralogy**


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**Soil chemical, physical and biological interfacial reactions**


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**Soil chemistry**


