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Malcolm Cresser, Ken Killham and Tony Edwards
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Why study soil chemistry?

It doesn't matter who you are or where you are, your very existence and survival depend upon the chemical reactions taking place all the time in soil. Indeed, this book itself owes its existence to the same reactions. The paper originates from trees grown in soil, the ink is from chemicals traceable back to the soil, and the authors are mere links in a complex food chain passing through soil-based cycles. The longevity of their role depends upon soil-derived food and regulation of the composition of the atmosphere by chemical reactions controlling the growth of photosynthesising plants. Of all the scientific disciplines that interact to make up the complex web of environmental science, soil chemistry could therefore be regarded as the most central. It is worth elaborating upon this concept, because any vague and fuzzy images the reader might have of possible applications of soil chemistry should then spring sharply into focus.

Figure 1.1 is an attempt to demonstrate the central role of soil chemistry, and its major interactions with other aspects of science. The outer ring of topics is impressive in its scope, but is by no means exhaustive. We could, for example, include terrestrial and aquatic zoology, since soils affect plants and water quality, and hence animal life. Plants may influence climate on a local scale and, in the long term, on a global scale, so we could add meteorology. Soil chemistry regulates soil fertility, so its links to agriculture and horticulture are obvious. Less obvious perhaps are its links with archaeology, social and economic history, and human geography, which arise as a consequence of the need for sustainable agriculture. We will only consider briefly here the major disciplines included in Fig. 1.1, and leave the reader to ponder over omissions, whether accidental or by design.

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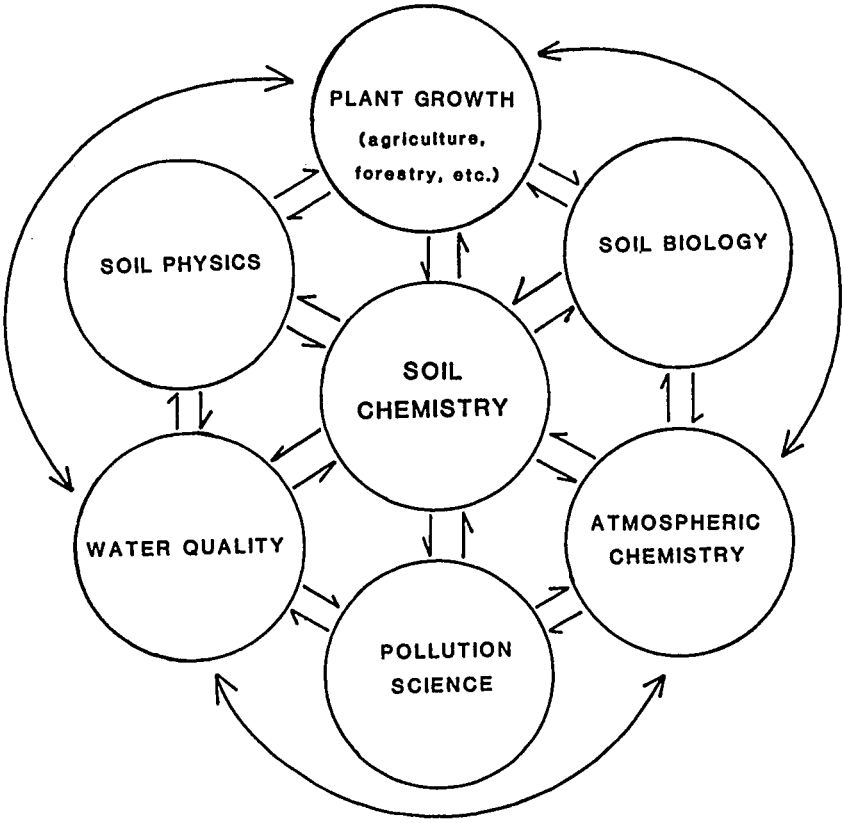
Soil chemistry and plants

Soil chemical properties regulate the availability of essential major elements (nitrogen, phosphorus, sulphur, potassium, calcium and magnesium) and trace elements (boron, copper, iron, manganese, molybdenum and zinc). 'Essential' in this context describes an element which must be present if the plant is to proceed through every physiological stage of its growth cycle. Soil chemical characteristics also govern the availability of elements such as cobalt which may be essential from the viewpoint of animal dietary requirements, and of elements or ionic species such as selenite which may be toxic to higher plants or animals. The regulatory mechanisms involved are discussed in Chapter 4. Soils are also important in restricting undesirable side effects from plant protection chemicals such as selective herbicides, fungicides, molluscicides, etc. (see Chapter 7).

Fig. 1.1 Schematic representation of the interactions between soil chemistry and other branches of soil science and environmental science.



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Plants, in turn, may substantially influence soil physicochemical properties in many ways. The major mechanisms include soil acidification by release of hydrogen ions at the root to compensate for plant uptake of base cations (calcium, potassium, magnesium and sodium), anion uptake, modification of soil moisture content, the effects of organic compound exudation from roots, root respiration, incorporation of plant litter and its subsequent degradation in the soil, and the effects of organic compounds leached from foliage or litter. These and other influences are discussed where appropriate in later chapters.

Soil chemistry and soil biology and biochemistry

As will be seen in Chapters 2–5, the biological population of the soil, especially the microbial population, plays a vital role in the biogeochemical cycling of nutrient elements such as carbon, nitrogen, phosphorus and sulphur, and hence in the regulation of soil fertility. However, the activities of macro- and micro-organisms in soils are themselves regulated by soil chemical properties. The plant species growing in a soil may influence soil biological activity both indirectly, through effects upon soil chemistry, and directly, through the size and biodegradability of the litter load. Soil physical properties, especially drainage status, may also considerably influence biological activity.

Soil chemistry and soil physics

The chemical reactions which occur in soil may have far-reaching effects upon the physical properties of the soil, such as the stability of its structural units, especially in regions with arid climates. In many soils in wetter areas, the particle size distribution, which governs its drainage characteristics, is a function of the chemical weathering of the minerals present in the soil parent material. Soil organic matter also plays an important role in water retention, and in the establishment of stable soil structure, the macropores created facilitating drainage. As will be seen in Chapter 4, soil drainage is crucial if the soil is to remain well aerated and plant growth problems associated with anaerobiosis are to be avoided.

Soil chemistry, geochemistry and soil formation

The chemical nature of the minerals initially present in the rock, till or sediment from which a soil has developed exerts a substantial influence upon the soil chemical properties at any given time in its

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evolution. These properties may, in turn, have a striking effect upon the soil biological activity, and the combined biological and chemical effects govern the type of soil which is formed and the uses to which it may be put. We will return briefly to the subject of soil formation later in this chapter.

Soil chemistry and water chemistry

Except where outcropping rock dominates the landscape, precipitation (rain, sleet, snow, etc.) reaching the soil surface flows through or over soil before reaching groundwater or draining into streams or lakes. During this period of soil–water contact, a range of chemical reactions take place which regulate the chemical composition of the freshwater eventually obtained. Provision of freshwater supplies of adequate quality for an ever-increasing world population is such an important topic that Chapter 6 has been devoted in its entirety to this theme. Solute and suspended solids are transferred by rivers to the oceans, so soil chemical reactions also play a role in marine chemistry.

Precipitation itself contains a significant amount of solute which will also interact with the soil solid components as the water drains through or over soil. The solute may be of natural origins, for example, sea salts from oceanic spray, sulphuric acid from volcanic sulphur dioxide, etc., or it may be a consequence of human activities, i.e. pollution. The extent to which soil modifies the passage of these inputs to waters depends upon the stage of soil evolution. This may be true because the hydrological pathway followed by the water may change with the degree of soil development, or simply because of the changes which occur over decades and centuries in soil physicochemical characteristics.

Soil chemistry and pollution science

The world's soils serve as a depository for vast quantities of pollutants. Sometimes the fate and consequences of individual pollutants become very emotive topics, for example nuclear waste or fallout, acid rain or lead from petrol. Another important source of potential pollution is the spreading of manures and sewage sludge on soil, either for disposal or for their fertiliser effect. Such materials are a major component of the annual phosphorus budget in the UK, for example. The ultimate fate of these pollutants, and of fertilizers and other agrochemicals added to soils, is an increasingly important area of study by soil chemists. Of particular concern is the possibility of toxic

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substances entering the human food chain in unacceptable amounts. Many soils have an extraordinary capacity for rendering pollutants innocuous, but at the present time there is much concern that this capacity is being abused to the extent that critical loads may be exceeded. 'Critical' is the term applied to the annual load of a pollutant at which the normal functioning of the ecosystem breaks down in some way.

Atmospheric pollutants may influence plant growth directly, and thus exert an indirect effect upon soil chemistry, for example by changing the plant litter load or degradability, or the soil moisture content. Forest growth may also influence the efficiency with which atmospheric pollutants are captured.

Soil chemistry as a subdivision of chemistry

From the brief summary above of the role of soil chemistry in the broader context of environmental science, it should be immediately apparent that the subject draws upon knowledge of physical, organic, inorganic and analytical chemistry. Developments in analytical science over the past two to three decades have made a very significant contribution to our understanding of the complex workings of the soil–plant–water ecosystem. However the soil chemist must avoid thinking of soil chemistry in isolation, and requires at least a rudimentary knowledge of the interacting areas included in Fig. 1.1. Thus, although this book is essentially a chemistry text, the authors have attempted throughout to put soil chemistry in a broader sphere of reference. By avoiding making the text unnecessarily complicated, they have also tried to produce a book which will serve as an interesting and readable introduction to this fascinating topic for other types of environmental scientist.

Soil chemistry in history and pre-history

As an experimental science, soil chemistry is quite ancient insofar as manures and primitive liming materials such as shell sands have been employed to improve soil fertility for thousands of years. Although detailed investigation of archaeological agricultural sites is perhaps less glamorous than excavation of dwellings, certainly there is evidence to suggest that the contents of domestic waste pits were distributed over wide areas. To a degree, the interpretation of a wide spread of pottery, tool and shell fragments over field sites must remain

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speculative, although alternative interpretations of such labour-intensive practices are not easy to come by. Certainly it is not difficult to conceive that, following the move from hunting and gathering through slash and burn to more static agricultural areas with identifiable field boundaries, soil infertility problems would soon have arisen, even with primitive, low-yielding cereal varieties. It is a small jump from there to the point at which some early farmer would notice improved growth in the vicinity of animal waste, and perhaps try a few experiments.

Certainly by the birth of Christ, it is possible to find mention of the use of manuring as if it was a long-standing practice (see e.g. Varro's *Res Rusticae*, *ca* 37 BC or Columella's *Res Rustica*, *ca* 60 AD). Purists might argue that this muck-and-magic agriculture should not be described as chemistry. However, it is relevant because tried and tested agricultural practices should have pointed the first true soil chemists in the right direction in the seventeenth century. In fact, the exact opposite happened. Once it was established that a potted plant could increase in weight with nothing apparently added but water, it was erroneously concluded that water was all that the plant required, plant organic components coming from soil organic matter. Thus the manure provided the organic matter in the plant. This misconception is hardly surprising, for it would have required a truly exceptional mind to conceive the idea of fixation of a gaseous component of the air at that stage. It survived for several decades, however, with minor modifications as it was demonstrated that substances such as saltpetre could sometimes dramatically accelerate crop growth. An excellent and concise account of this early work has been presented by Russell (1987) in his celebrated text *Soil Conditions and Plant Growth*. It was not until 1782 that Senebier concluded that fixation of an atmospheric component in the presence of light (i.e. photosynthesis) was the origin of plant organic matter, a hypothesis eventually proved conclusively by de Saussure (1804). De Saussure also demonstrated the importance of soil for supplying nitrogen, potassium and phosphorus to plants, thus sowing the seeds for modern soil chemistry.

Widespread belief in soil humus as the source of plant carbon remained until Liebig in 1840 published a highly critical attack upon the prevalent attitudes and concepts. He stressed the importance not just of photosynthesis, but also of a range of plant nutrients, emphasising that the lack of any one essential nutrient could be sufficient to restrict plant growth. The next major advance came some 37 years later with developments in bacteriology. Schloesing and Muntz (1877) were able

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to demonstrate that ammonium in sewage could be converted to nitrate, after an initial delay, by bacteria, and it was soon shown that the same process occurred in soils. Since that major advance, progress has been slow but steady, with more and more detail being filled in about both the biological and the chemical reactions occurring in soils and the interactions of soils with other ecosystem components. The current state of our knowledge of soil chemistry arising from this progress constitutes the basis of Chapters 2 to 7.

The nature of soil – what it is and what it does

Soil may be defined as material of variable depth with a substantial solids content at the Earth's surface which is undergoing change as a consequence of chemical, physical and biological processes. Thus, towards the bottom of a deep soil pit, material that was not changing with time would be classified as parent material, but not as soil.

Soil essentially consists of three phases, a solid phase, a solution phase and a gas phase. The solid phase usually includes an intimate mixture of mineral material, originating from rock, sediment or till, and organic material arising as a consequence of biological activity. It interacts continuously with the solution phase, which originates from precipitation infiltrating the soil or from rising water or water moving laterally. The chemical composition of the soil solution depends upon the physicochemical characteristics of the soil solids, precipitation solute composition, biological activity within the soil matrix, and to some extent upon contact time. It contains both organic and inorganic components. The gas phase, or soil atmosphere, composition depends upon biological activity also. It may be greatly enriched in carbon dioxide (up to *ca* 3–4%) compared to normal above-ground air (*ca* 0.035%) as a consequence of microbial and root respiration, and relatively depleted in oxygen. Under certain conditions, it may contain significant amounts of gases such as nitrous oxide or ammonia, and even hydrogen sulphide and ethylene. These are discussed fully in Chapter 4.

That the soil fulfills a multiple role in most ecosystems should already be clear from the discussion of the relationship between soil chemistry and other branches of environmental science. It is worth summarising briefly here the major roles, however. Soil provides plants with essential major and minor nutrients, with water and with firm anchorage. It acts as a sink for organic detritus (plant and animal remains and waste products) and for natural and pollution inputs from the atmosphere.

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Unless subjected to excessive pollution stress, it regulates the solute chemistry of freshwaters to make the appropriate environments to support aquatic life. If properly managed, soil continues to fulfill all these roles. Proper management requires an understanding of soil chemistry.

The transition from rock to soil

We are now in a position to consider briefly the processes involved in the transformation from rock to soil. Clearly rock will be subjected to physical weathering as a consequence of the action of wind, rain, frost and rapid temperature changes. Some dissolution may also occur, releasing essential nutrient elements such as calcium, potassium, magnesium and phosphorus and the various trace nutrient elements. However nitrogen, a major nutrient element, is not released in significant amounts by mineral weathering, although small inputs of ammonium- and nitrate-nitrogen occur even in pollution-free rain. The rock surface tends to be colonised therefore by lichens. Lichens consist of algae and fungi living in a mutually beneficial (symbiotic) relationship. The algae can fix atmospheric nitrogen and photosynthesise. They are thus able to provide the organic substrate for the growth of the fungi. The fungi, in turn, speed up the chemical attack of the rock surface by organic acid production, thus providing more nutrients for the algae. In this way a thin soil layer starts to accumulate. The organic matter content starts to build up, increasing the moisture holding capacity of the soil to the point where other species such as mosses may become established. Initially the skeletal soil may be subject to erosion, except in cracks in the rock. Over a long timescale, however, the soil will spread, especially if the soil becomes stabilized by the establishment of vegetation cover. Chemical reactions will penetrate deeper into the rock, as the evolving soil is mixed and remixed by soil biota.

Subsequent soil evolution depends upon a number of factors, the most important being time, precipitation amount and temporal distribution, temperature, topography and aspect. We shall return to the topic of soil formation under diverse climatic conditions where appropriate in Chapters 2–4.

The remit of the soil chemist

Clearly the remit of the soil chemist is very broad. She/he may work in agriculture, forestry or horticulture, or for a water quality

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control authority. Interest may be centred around optimisation of plant growth, provision of adequate grazing, pollutant effects upon crop yields or freshwater quality, or the passage of radioactive fallout into the food chain. These examples should suffice to give some insight into the scope of the subject.

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Inorganic and mineral components of soils

As we saw in Chapter 1, rock plays a vital role in soil formation, whether the soil evolves from solid, outcropping rock weathering *in situ* or from fragments which have broken away from massive outcrops and been transported, often down slope. This movement occurs as a consequence of the action of forces arising from gravity, wind, rain, ice movement or drainage water, either alone or in combination. It may result in a substantial degree of mixing of parent materials. Clearly the origins, and hence the chemical composition, of the parent rock might be expected to influence significantly the chemical and physical properties of the evolving soil at any stage in its development, and this is indeed the case. In the present context we need to consider the properties of rocks insofar as they influence the characteristics of the soils ultimately obtained, and the transformations which rock and rock-derived products undergo over the timescale from seconds to tens of centuries resulting from interactions with water and the soil flora and fauna.

The nature of rocks

It is intuitively obvious that rocks are chemically very stable. If they were not, clearly chemical attack upon rock outcrops would be much more rapid than it is. It follows that the chemical bonding in the macromolecules (minerals) that constitute rocks must produce lattices which are very favourable in energetic terms. Disruption of the lattice, i.e. dissolution, requires a high input of energy to overcome the forces holding the atoms together into well-defined mineral lattices.

The core of our planet exists at very high temperature and pressure. Although never sampled directly, it is thought to have a composition not unlike that of iron meteorites and a mean density of around 11 000 kg m^{-3}, so that it is 11 times more dense than water (Bowen,

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