

Applied Soil Trace Elements

Edited by

Brian E. Davies

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Preface

Until comparatively recently micronutrients and trace elements in the soil-plant system were largely the concern of agriculture or agronomy and were dispatched in their textbooks in a few short pages, probably under the heading 'minor elements'. But in ten or twenty years there has been change and diversification and the subject has become not only a growth point in soil science but also the legitimate concern of ecology, environmental science, geochemistry, and even epidemiology. Underlying this new vigour are several different yet linked developments. First, in agriculture, the use of purer NPK fertilizers and higher yielding plant varieties with increased nutrient demands, the decreasing availability of farmyard manure (rich in trace elements) in areas where mixed farming has given way to intensive arable agriculture, and higher stocking rates in pastoral regions, have combined to increase the demands made on the soil in terms of its ability to supply trace elements to plants. In consequence, deficiency problems have become more common and attempts to solve these problems have necessarily required a better understanding of the soil chemistry of trace elements. Second, the world demand for metal ores has greatly increased and has stimulated the development and use of biogeochemical and pedochemical prospecting methods to discover new sources. Except when they are concentrated locally in ore bodies, trace metals are rare and dispersed and in order to interpret biogeochemical data the geochemist has also needed to learn more of the normal soil and plant chemistry of trace elements. These developments have demanded of the analyst better sensitivity and precision, faster and simpler working. These demands have been met by a variety of new instrumental techniques (and flame absorption must be counted as seminal here) which, in turn, have allowed the soil scientist both to pose and answer new questions. Meanwhile, the 'environmental crisis' has led to a growth of knowledge concerning toxic elements such as cadmium or mercury—curiosities just a couple of decades ago—which accumulate in soils and therefore enter our food chain. Finally, there has been a parallel growth of interest in trace elements in biochemistry and medicine resulting in an increase in the number of elements

regarded as essential and a better understanding of the biochemistry of those which are toxic. This renewed interest has stimulated epidemiologists to involve the environmental geochemistry of trace elements in their investigations.

Fourteen years ago I moved from agriculture to geography and found myself, in a sense, at the crossroads of these trends and it is out of these interdisciplinary experiences that the idea for this book was born. It is about trace elements, both the essential micronutrients and the others: its focus is the soil with a bias to practical rather than theoretical considerations which is how the title *Applied Soil Trace Elements* arose. But individual authors have been free to interpret their terms of reference quite broadly providing they did not entirely forsake the soil: they were not asked to write instructional manuals.

So far as the structure of the book is concerned an overall introduction is provided in Chapter 1. Then, two chapters are devoted to sampling and analysis which comprise the essential foundation for work in the subject. Because soil and environment data tend to be voluminous and relatively imprecise the application of statistical techniques to them is essential for valid interpretations and some commonly used methods are outlined in Chapter 4. Four chapters on selected essential micronutrients follow including sulphur, which, although not strictly a trace element, has been included in view of the increasing problems of sulphur deficiencies in crops in some areas and pollution by SO_x in many others, and the role of sulphur species in the environmental chemistry of many trace elements. Chapter 9 deals with trace elements as pollutants and Chapter 10 is concerned with them in biogeochemical prospecting with a consequential emphasis on wild rather than crop plants. Finally, two chapters describe the geography of trace element problems and are deliberately contrasted. Chapter 11 exemplifies the application of geochemical techniques to agricultural problems in a small island (Great Britain) while Chapter 12 illustrates the problems, and successes, of attempting to synthesize research effort on a continental scale (North America).

It is a pleasure to acknowledge the ready cooperation I received from the individual authors, from the staff of the Aberystwyth Geography Department, especially Miss Bernadette O'Donovan who undertook most of the final typing, and from my wife who displayed great patience whenever I took myself off to my office on Saturdays and Sundays to work on 'the book'.

Aberystwyth

Brian E. Davies

St. David's Day, 1979

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CHAPTER 1

Trace Elements in Rocks, Soils, Plants, and Animals: Introduction

DAVID A. JENKINS AND R. GARETH WYN JONES

I. INTRODUCTION

Life has evolved in, and thus adapted to, the inorganic environment at the earth's surface, the major terrestrial zone of this interaction being the soil. Of the ninety odd elements which comprise the inorganic portion of the soil all but ten usually occur at concentrations of less than 0.1% (i.e., 1000 $\mu\text{g/g}$, mg/kg, g/tonne, or ppm) and are referred to as 'minor' or 'trace' elements. Of these around a dozen have been shown to be essential to life at low concentrations (i.e., 0.1–100 $\mu\text{g/g}$ dry matter: Epstein, 1965) and may thus qualify as 'micronutrients', while a further half dozen or so are required at much higher concentrations (i.e., 1–10 mg/g dry matter: Epstein, 1965) and are referred to as 'macronutrients'. Iron is an interesting anomaly in this respect, being a micronutrient biologically yet a major element geochemically. This distinction between trace element and micronutrient is therefore important particularly in an area bridging geochemistry and biochemistry where even such basic terms as 'mineral' can assume an unfortunate ambiguity. Due to the focal position of soils in the sedimentary geochemical cycle and in most biogeochemical cycles, their trace element content has been under increasing scrutiny by pure and applied geochemists, soil scientists, and agronomists. In this chapter we intend to review briefly the trace element content of soils and the assimilation of trace elements into the biosphere *via* plants. This will provide a background to the more specific aspects discussed in subsequent chapters. The trace element content of soil parent materials will be considered first, then redistribution during pedogenesis, and finally uptake by plants: the overall cycling of trace elements to and at the earth's surface is summarized diagrammatically in Figure 1.1. There exists a number of standard texts and reviews on geochemistry (e.g. Wedepohl, 1969; Krauskopf, 1967), on soils (e.g. Mitchell, 1964; Mortvedt *et al.*, 1972), and the inorganic nutrition of plants (e.g. Hewitt and Smith, 1977; Gauch, 1972), which deal with trace

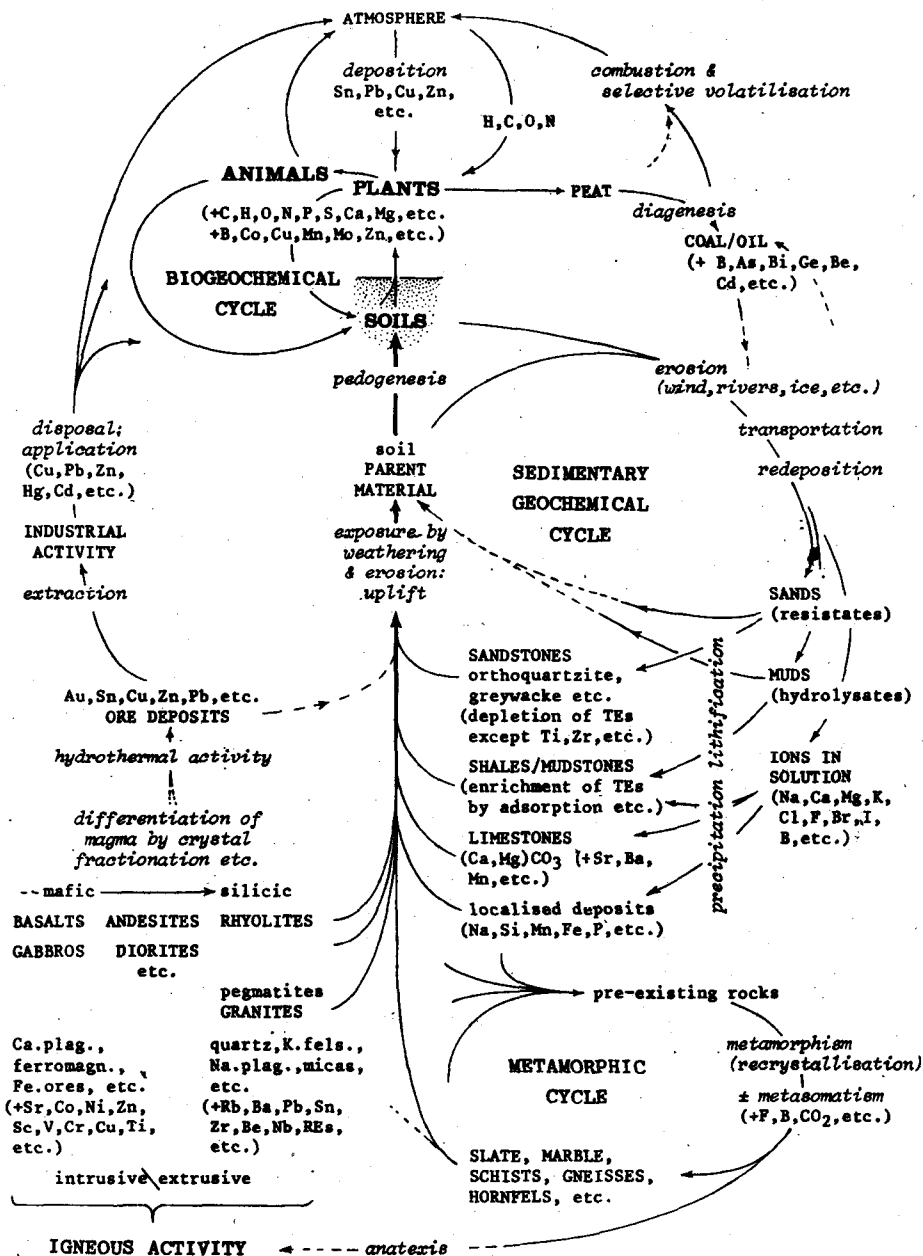


Figure 1.1 A schematic summary of the cycling of elements at the earth's surface

elements in some detail. This brief introduction will therefore be selective rather than comprehensive in approach.

Trace element studies are, by their nature, dependent to a large degree on advances in analytical technique and this subject will be taken up in greater detail in Chapter 2. However, it is worth making the point here that this dependence has had a marked influence on the development of our knowledge. Interest in particular elements waxes and wanes as techniques become available which are of sufficient simplicity and sensitivity to detect the elements at the levels at which they are present in soils and organisms. This was obvious in the initial impetus given by arc spectrography as applied by Goldschmidt (e.g., 1937) to geochemistry in general, and by Mitchell (e.g., 1948) and Vinogradov (1959) to soils in particular. This technique offered the possibility of simultaneous analysis for a number of elements at low concentrations in small solid samples. In contrast, earlier investigations were mostly concerned with individual elements and were inhibited by the excessive time and skill demanded by the wet chemical methods employed. Arc spectrography encompassed most of the elements of relevance in the soil, though unfortunately Zn, B, F, I, and Se were not amenable to routine analysis. The advent of atomic absorption spectroscopy brought a greater precision and sensitivity for selected trace elements, though it necessitated the dissolution of samples, which is inconvenient for studies of trace elements in the solid phase, but on the other hand proves particularly useful for analysis of extracts: our knowledge of Cu, Pb, and in particular Zn expanded rapidly with the advent of this technique. More dramatically, atomic absorption in its various forms provided for the first time a convenient and sufficiently sensitive method to detect and estimate quantitatively Cd and Hg levels in the natural environment; consequently there followed a rapid increase of interest in the potential hazards presented by the toxicity of these elements. X-ray fluorescence spectroscopy is also now being applied on an increasing scale to the study of trace elements in soils and plants.

Mass spectrography operates at concentrations several orders lower than those of other techniques and, in addition, discriminates between individual isotopes (e.g., Ure *et al.*, 1979). Application of this technique could presage a major phase in the development of our knowledge of the trace element content of soils and the biosphere, extending to many elements which lie outside the scope of more conventional techniques (e.g., Be, Ge, In, Sb, Tl): it is not unlikely that the list of essential and toxic elements will increase accordingly. A related but divergent line of development is offered by electron probe microanalysis and ion microprobe mass analysis (Bisdom *et al.*, 1977). These allow the spatial location and mutual association of elements to be studied within organized materials such as soil microfabric and the tissues and structures of organisms as distinct from the average composition of the homogenized materials.

It is desirable that analytical studies should be as objective and catholic as possible. Unfortunately, too many studies have prejudged the functions of trace

elements by being restricted to elements of known importance only, this being particularly true for the micronutrients B, Co, Cu, Mn, Mo, and Zn in soils and plants. Because of the geochemical associations that exist between elements there is then the danger of detecting indirect correlations and of not recognizing them as such. For example, in areas affected by sulphide ore deposits, In, Cd, and Ag may be concentrated to the same degree above normal environmental levels as Zn, Cu, and Pb, but they are not often included in analytical schemes. On the other hand the elements favoured by a particular technique are linked by physical properties not necessarily relating to their geochemical or biochemical behaviour. This is well illustrated by the detailed analytical studies involving Ce, Co, Ba, La, Hf, Ta, Sc, etc., a motley collection but all conveniently estimated by neutron activation analysis. While advantage should obviously be taken of each technical development as it occurs, it is also necessary that an overall balance is retained irrespective of the particular elements in fashion due to the latest advances in analytical techniques.

II. TRACE ELEMENTS IN SOIL PARENT MATERIALS

The trace element content of soil parent material corresponds closely to that of the different contributing rock types. These may be few and readily recognized, or, conversely, diverse and difficult to identify, according to the nature of the superficial deposits from which the soil develops. Among individual rock types the geochemistry of those of igneous origin has received most attention so that the patterns of trace element distribution are now reasonably well understood. This understanding stems from Goldschmidt's (1937) early recognition of the overriding importance of ionic size and charge in relation to the lattice geometry of possible host minerals. It was later refined by taking into account the 'chemical nature' of an element as manifested in the type of bonds formed and quantified in such parameters as electronegativity (e.g., Ringwood, 1955). A more rigorous approach to chemical bonding by application of the Crystal Field Theory and, in the case of sulphide minerals, the Molecular Orbital Theory has subsequently resolved some of the anomalies that were still apparent for the transition elements (Burns, 1970). Further insight has also been gained, for example, from the study of the partition of trace elements between coexisting phenocrysts (e.g. feldspars, pyroxenes) and their matrix in porphyritic extrusive rocks (Jensen, 1973). A selection of current elemental parameters is given in Table 1.1. On this basis it is possible to explain why individual trace elements may or may not be incorporated into particular coordination sites in the common rock forming minerals, and so effectively 'proxy' for the major elements normally occupying these sites. An important generalization that can be made here is that micronutrients such as Co, Mn, Zn, and, to a lesser extent, Cu are associated with the Mg/Fe^{2+} octahedral sites of the relatively unstable ferromagnesian minerals concentrated in mafic igneous rocks.

Table 1.1. Some Ionic Properties of Selected Major and Trace Elements

<i>Z</i>	— Ionic charge
<i>IR</i> (Å)	— Ionic radii for the coordination (<i>C</i>) indicated. (N.B. for Fe and for Co high (H) and low (L) spin values given) (Whittaker and Muntus, 1970)
<i>C</i>	— Observed coordination with respect to O ⁻² (Mason, 1966)
<i>E</i>	— Electronegativity (Pauling, quoted in Krauskopf, 1967)
<i>IP</i>	— Ionic potential (<i>Z</i> / <i>IR</i>)
<i>EHID</i> (Å)	— Effective diameter of hydrated ion in aqueous solution (Klotz, 1950)

	<i>Z</i>	<i>IR</i> (Å)	<i>C</i>	<i>E</i>	<i>IP</i>	<i>EHID</i> (Å)
Cs	+	1.96–1.89	12–10	0.7	0.5	2.5
Rb	+	1.81–1.74	12–10	0.8	0.6	2.5
K	+	1.68–1.59	12–8	0.8	0.6	3
Ba	+2	1.68–1.50	12–8	0.9	1.3	5
Pb	+2	1.57–1.37	—	1.8	1.4	4.5
Sr	+2	1.40–1.33	10–8	1.0	1.5	5
La	+3	1.36–1.26	—	1.1	2.3	9
Sn	+2	1.30	8	1.8	1.5	—
Na	+	1.24–1.10	8–6	0.9	0.9	4.5
Ca	+2	1.20–1.08	8–6	1.0	1.8	6
Mn	+2	1.01–0.75	8–6	1.5	2.0	6
Y	+3	0.98	6	1.2	3.1	—
Cu	+	(0.96)	—	1.9	1.0	—
Zr	+4	0.92	8	1.4	4.3	11
Fe	+2	(H)0.86/0.69(L)	6	1.8	2.6	6
Zn	+2	0.83	6	1.7	2.4	6
Co	+2	(H)0.83/0.73(L)	6	1.7	2.6	6
Sc	+3	0.83	6	1.3	3.7	9
Li	+	0.82	6	1.0	1.2	6
Cu	+2	0.81	6	2.0	2.5	6
Ni	+2	0.77	6	1.7	2.6	6
Mg	+2	0.80	6	1.2	2.5	8
Fe	+3	(H)0.73/0.63(L)	6	1.9	4.4	9
Mo	+4	0.73	—	—	5.5	—
Cr	+3	0.70	6	1.6	4.3	9
Ti	+4	0.69	6	1.5	5.8	—
Ga	+3	0.70–0.55	6–4	1.6	4.9	—
Mn	+4	0.62	6–4	—	6.5	—
Al	+3	0.61–0.47	6–4	1.5	5.6	9
Mo	+6	0.50	4	1.8	12	—
Ge	+4	0.48	4	1.8	8.3	—
V	+5	0.44	4	—	11	—
Cr	+6	0.38	4	—	16	—
Be	+2	0.35	4	1.5	5.7	8
Si	+4	0.34	4	1.8	12	—
P	+5	0.25	4	2.1	20	—
S	+6	0.20	4	—	30	—
B	+3	0.20–0.10	4–3	2.0	20	—

Conversely, other trace elements are effectively misfits by virtue of an unacceptable combination of their ionic size, charge, and chemical nature. Such elements tend to concentrate in the magma until the solubility of a specific accessory mineral is exceeded. When precipitation occurs this may be at an early stage of crystallization with the uniform dispersal of mineral grains throughout the body of the rock: the trace element distribution is then relatively homogeneous throughout the rock except at the level of the mineral microfabric (e.g., Zr in zircon). Alternatively, the element may persist within the magma to the final stages of differentiation and then be loosely absorbed at lattice surfaces along intergranular boundaries, although such a distribution has yet to be substantiated fully. By contrast, the element may be concentrated in, for example, pegmatite deposits and so achieve a heterogeneous pattern of distribution of low background levels with highly localized concentrations which, as ore deposits, may form the basis for commercial exploitation. Of major importance in this respect is the behaviour of sulphur which may separate from the magma as a distinct phase taking with it 'chalcophile' elements such as Ag, Cd, Mo, Pb, Zn, and, in particular, Cu whose distribution in igneous rocks can be dominated by this factor. Again, it has been suggested (Krauskopf, 1972) that the resulting sulphides may either be disseminated through the body of the rock as submicroscopic interstitial granules, or concentrated in separate ore deposits. On a global scale the distribution and concentration of major ore deposits is now explicable by 'plate tectonics' in terms of both converging and diverging plate margins (e.g., Rona, 1973).

Although the average values for igneous rocks are predictable, local peculiarities can extend the ranges about these averages. This can be of significance in any detailed study of trace element distribution in the derived soils. For example, median concentrations for Ordovician igneous rocks in Snowdonia, Wales (Table 1.2), follow the predicted pattern with higher concentrations of Co, Cu, Cr, Mn, Ni, Sc, Sr, Ti, and V in the mafic rocks and of Ba, Rb, Y, Zr, in the silicic rocks. However, the ranges for such elements as Ba and Cu reveal distinct anomalies: on closer inspection these are explicable in terms of K-enrichment (+ Ba) in certain dolerites, and sulphide mineralization (+ Cu) in certain rhyolites. Other minor differences within rocks of the same general group (e.g. rhyolites) can be detected between extrusive and pyroclastic varieties and between different volcanic centres (Jenkins, 1964). It is therefore always advisable to temper predictions of trace element status based on general theory with considerations of petrography where such details are available.

The sedimentary cycle produces a diversity of rock types reflecting the variety of physical and chemical processes involved. However, many of these rock types, although of interest geochemically, are relatively rare and localized in their occurrence (e.g. evaporites, ironstones). Sedimentary rocks as a whole are dominated by the fine grained mudstones and shales, and the trace element composition of these argillaceous rocks therefore tends, with the important