

# EFFECT OF HEAVY METAL POLLUTION ON PLANTS

*Volume 2*

Metals in the Environment

*Edited by*

N. W. LEPP

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## **Preface**

Trace metals occur as natural constituents of the earth's crust, and are ever present constituents of soils, natural waters and living matter. The biological significance of this disparate assemblage of elements has gradually been uncovered during the twentieth century; the resultant picture is one of ever-increasing complexity. Several of these elements have been demonstrated to be essential to the functions of living organisms, others appear to only interact with living matter in a toxic manner, whilst an ever-decreasing number do not fall conveniently into either category.

When the interactions between trace metals and plants are considered, one must take full account of the known chemical properties of each element. Consideration must be given to differences in chemical reactivity, solubility and to interactions with other inorganic and organic molecules. A clear understanding of the basic chemical properties of an element of interest is an essential pre-requisite to any subsequent consideration of its biological significance. Due consideration to basic chemical considerations is a theme which runs through the collection of chapters in both volumes.

Perhaps the single most important stimulus to the rapid expansion of research in this field has been the great strides made in analytical techniques, particularly during the past decade. In many respects these advances have proceeded more rapidly than our ability to place the resultant data in its proper perspective; each increase in analytical sensitivity or reduction of detection limits has highlighted the inherent problems of sample contamination. In addition, the present dependence of most readily-available techniques on liquid samples results in the production of complex analytical matrices which present analytical problems for several elements. The need to overcome this problem is one area in which future developments will be keenly awaited. A further, more

disturbing aspect of basic analytical procedures is the lack of rigorous verification of individual methodology; many inter-laboratory comparisons often reveal significant discrepancies in analytical precision on the same prepared samples. As analytical data is the core of the majority of research in this field, all workers should pay more than lip service to the validity of their analytical techniques.

Having summarized the inherent problems in this field of study, one must now consider the best way in which the ever-expanding literature on this topic can be treated, to produce a meaningful compendium of information. Any editor is faced with a difficult dichotomy in the organization of the subject matter. It is now conclusively established that the impact of trace metals on plants, in real world situations, is never the result of the effect of a single element. Thus, it could be cogently argued that treatment of individual plant/element responses, relating, in the main, to laboratory or glasshouse studies, is not a particularly valid approach to the topic. Nevertheless, a great deal of valuable information can still be gathered from this approach; the study of elemental interactions is still in a formative stage, with some being well known and clearly understood, whereas others, only recently identified, are still under careful investigation. At present, therefore, the adoption of the 'element in isolation' approach to be found in Volume 1, has been taken as a matter of necessity. Hopefully, in the next decade, this will not be the case, and workers will lean much more towards an interactive approach; but for the present, this compromise situation is the only feasible approach.

The individual elements, explored in Volume 1, illustrate the wide diversity of plant response to trace metals. As technology continues to concentrate previously dispersed and rare elements, removing these from their original matrices and altering their chemical form, great care will have to be taken in interpreting the potential consequences of these steps to living organisms. The information presented here illustrates many interesting facets of the basic interaction. Elements such as copper and zinc, long known as essential to life, are now being joined in this category by nickel. The alarming mobility of cadmium in soils and crops is highlighted, but the other toxic element, lead, is demonstrated to have a much lesser potential impact on crop production. Many elements will need to be exhaustively appraised as new directions in manufacturing industry and energy generation provide the potential to liberate more exotic and little-considered elements into the biosphere. These should be considered now, before problems arise.

One certain aspect of this area is that the consequences of metal

contamination will be with us for a considerable period of time. Thus, the need for more critical identification of potential future problems continues to exist and such studies should place particular emphasis on agriculture and food production. Lessons learnt in the past must be rigorously applied to future research considerations, and areas where the magnitude of potential problems has been overstated must be carefully re-appraised.

The second volume presents a more integrated approach to plant/trace metal interactions, but the majority of evidence presented here requires the sound base of information from individual studies of the 'plant-element' type described in Volume 1.

It is essential that we understand the sources of trace metal additions to our environment, the reaction these have with soils, their biogeochemical cycles, and their consequences for natural and agricultural systems. All these topics have received detailed coverage, and the synthesis of ideas presented will be of considerable relevance to those concerned with the monitoring, regulation and amelioration of trace metal contamination. Practical aspects of reclamation are also emphasized, with full documentation of successful case histories.

Finally, two topics deserved special attention, the tolerance of plants to certain trace metals, and the interaction between trace metals and lower terrestrial plants. Metal tolerance is a phenomenon often noted, but the understanding of the physiological and biochemical aspects of this fascinating aspect of plant metabolism have not progressed apace. Recent advances in our understanding of this biological puzzle are carefully detailed. Lower plants have an interesting interrelationship with trace metals. The infinite capacity of some bryophytes and lichens to sorb trace metals has led to their use as biological monitors for atmospheric metal burdens; the unique lichen symbiosis presents a system in which basic effects of metals on biological systems can be monitored and probed.

In the compilation of a work of this nature, it is inevitable, and indeed desirable, that areas of overlap will occur. The juxtaposition of several points of view in relation to a topic is a valuable part of any critical appraisal; thus no attempt has been made to reconcile any differences of opinion. The authors have been selected for their specialized knowledge of particular fields, and all have contributed to produce an integrated synthesis of the current status of plant/trace metal interactions. I would like to record my pleasure in editing these volumes, and to praise the consistently high standard and informative nature of each contribution. I would also like to thank the authors for their time, effort and ready co-operation in the assembly of this work. It is they, not I, who have translated

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an idea into reality. Finally, I would like to thank my colleagues at Liverpool Polytechnic for their encouragement and advice, and also the publishers for their full and friendly assistance in all stages of the production of these volumes.

NICHOLAS W. LEPP

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## CHAPTER 1

# ***Geochemical Aspects of the Distribution and Forms of Heavy Metals in Soils***

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## 1. INTRODUCTION

The total concentrations of trace metals and metalloids in soils, their chemical forms, mobility and availability to the food chain, provide the basis for a range of problems in crop, animal and human health. Some 15 elements present in rocks and soils, normally in very small amounts, are essential for plant and/or animal nutrition. Boron, copper, iron, manganese, molybdenum, silicon, vanadium and zinc are required by plants; copper, cobalt, iodine, iron, manganese, molybdenum, selenium and zinc by animals. The roles of arsenic, fluorine, nickel, silicon, tin and vanadium have also been established in recent years in animal nutrition. In large concentrations, many of the trace elements/metals may be toxic to plants and/or animals, or may affect the quality of foodstuffs for human consumption. These potentially toxic elements include arsenic, boron, cadmium, copper, fluorine, lead, mercury, molybdenum, nickel, selenium and zinc.

The natural concentration ranges of most trace metals in soils are wide. The main sources are the parent materials from which the soils are derived. These are usually weathered bedrock or overburden transported by wind, water or glaciation, which may be of local or exotic origin. However, man-effected inputs may add to, and at times exceed, those from natural geological sources. The main sources of metal contaminants in soils are from metalliferous mining and smelting activities, other industrial

emissions and effluents, urban development, vehicle emissions, dumped waste materials, contaminated dusts and rainfall, sewage sludge, pig slurry, composted town refuse, fertilizers, soil ameliorants and pesticides.

Both deficiencies and excesses of trace metals may give rise to nutritional or toxicological problems in plants and animals, resulting sometimes in crop failure or death of farm animals. Less severe imbalance may result in a lowering of crop or animal production. Sub-clinical effects, where visual symptoms are absent, may be present but are frequently not recognized. These latter effects are thought to have considerable economic implications, as the land areas involved are likely to be large.

The soil is the primary supplier of trace metals to the soil-plant-animal system and the soil-foodstuff/water-human system. In these systems, the metals and metalloids do not of course occur in isolation, and a number of synergistic and antagonistic interactions are recognized at both deficiency and excess concentrations. These interactions sometimes involve major elements as well as trace metals, as illustrated by the effect of calcium ions on the specific adsorption of cadmium onto root surfaces and the copper-molybdenum-sulphur interrelationship in ruminant nutrition. In this chapter, specific reference will be made to the elements copper, selenium, molybdenum, arsenic, zinc, lead and cadmium which are either of economic significance in the above systems or of concern as environmental pollutants at this present time. These elements will, however, be treated as part of their association with other elements, of both geochemical and industrial origin, and emphasis will be placed on interaction at the soil-plant interface.

Information on the sources of trace metals in soils and plants and on the regional distribution of trace metal problems in agricultural crops and livestock is presented in greater detail in recent reviews by Thornton and Webb (1980a,b).

## 2. SOURCES OF TRACE METALS IN SOILS

Sources of metals in soils may be from natural geological materials or may arise from man's activities. In terms of environmental pollution, it is essential to have reliable data on the naturally occurring amounts of metals present in order to assess the significance of contributions from man and industry. The normal abundance of an element in earth material is commonly referred to by the geochemist as *background*, and for any particular element this value, or range of values, is likely to vary according to the nature of the material (Hawkes and Webb, 1962). The establishment

TABLE 1.1

RANGE AND MEAN CONCENTRATIONS OF SOME METALS AND METALLOIDS IN IGNEOUS AND SEDIMENTARY ROCKS (ppm)

Element	Basaltic igneous	Granitic igneous	Shales and clays	Black shales	Limestones	Sandstones
As	0.2-10 (2.0) <sup>a</sup>	0.2-13.8 (2.0)	— (10)	— (1.7)	0.1-8.1 (1.7)	0.6-9.7 (2.0)
Cd	0.006-0.6 (0.2)	0.003-0.18 (0.15)	0-11 (1.4)	<0.3-8.4 (1.0)	— (0.05)	— (0.05)
Cr	40-600 (220)	2-90 (20)	30-590 (120)	26-1 000 (100)	— (10)	— (35)
Co	24-90 (50)	1-15 (5)	5-25 (20)	7-100 (10)	— (0.1)	— (0.3)
Cu	30-160 (90)	4-30 (15)	18-120 (50)	20-200 (70)	— (4)	— (2)
Hg	0.002-0.5 (0.05)	0.005-0.4 (0.06)	0.005-0.51 (0.09)	0.03-2.8 (2.5)	0.01-0.22 (0.04)	0.001-0.3 (0.05)
Pb	2-18 (6)	6-30 (18)	16-50 (20)	7-150 (30)	— (9)	<1-31 (12)
Mo	0.9-7 (1.5)	1-6 (1.4)	— (2.5)	1-300 (10)	— (0.4)	— (0.2)
Ni	45-410 (140)	2-20 (8)	20-250 (68)	10-500 (50)	— (20)	— (2)
Se	— (0.05)	— (0.05)	— (0.6)	— (0.08)	— (0.05)	— (0.05)
Zn	48-240 (110)	5-140 (40)	18-180 (90)	34-1 500 (100)	— (20)	2-41 (16)

<sup>a</sup> Numbers in parentheses are mean concentrations.Adapted from table compiled by M. Fleischer and H. L. Cannon (Cannon *et al.*, 1978).

of background values for metals in soils and plants has for some time been recognized as part of the geochemist's role in pollution studies (Cannon and Anderson, 1971).

## 2.1. Weathering of Unmineralized Bedrock and Other Parent Materials

The earth's crust is made up of 95% igneous rocks and 5% sedimentary rocks; of the latter about 80% are shales, 15% sandstones and 5% limestones (Mitchell, 1964). However, sediments are more frequent at the surface as they tend to overlie the igneous rocks from which they were derived. The abundance of some metals and metalloids in igneous and sedimentary rocks is shown in Table 1.1.

TABLE 1.2

THE CADMIUM CONTENT (ppm) OF SOME BLACK SHALES IN ENGLAND AND WALES.  
(AFTER HOLMES, 1975)

Formation	Locality	Age	Range	Mean <sup>a</sup>
Lower Worston shale group	Bowland Forest, Lancs	B1-2	<1-32	4.4 (46)
Lower Bowland shale group	Bowland Forest	P1	1-105	16.2 (35)
Lower Bowland shale group	Bowland Forest	P2	1-158	16.5 (20)
Upper Bowland shale group	Bowland Forest	E1	1-219	16.6 (59)
Edale shales	North Derbyshire	E2	1-39	5.2 (48)
Edale shales	North Derbyshire	H1	1-50	6.0 (14)
Edale shales	North Derbyshire	H2	<1-91	14.8 (25)
Edale shales	North Derbyshire	R1	1-32	6.0 (11)
Dove shales	South-west Derbyshire	E2	<1-25	6.5 (45)
Mixon limestone and shales	North Staffordshire	P1-2	<1-65	12.8 (31)
Onecote sandstone and shales	North Staffordshire	P1-2	1-39	9.3 (8)
Onecote sandstone and shales	North Staffordshire	E2	1-2	1.4 (12)
Cracklington formation	Devon/Cornwall	H1	<1-5	1.3 (39)
Cracklington formation	Devon/Cornwall	R1	<1-4	1.7 (55)
Cracklington formation	Devon/Cornwall	R2	<1-3	1.5 (29)
Coal measures	Glamorgan	d5	<1-5	1.0 (9)
Coal measures	Chesterfield	d5	<1-3	1.5 (15)

<sup>a</sup> Number of samples in parentheses.

The degree to which trace elements become available upon the weathering of igneous rocks, depends on the type of minerals in which they are present and the susceptibility of these minerals to weathering. The more biologically important trace metals, including copper, cobalt, manganese and zinc, occur mainly in the more easily weathered constituents of igneous rocks such as augite, hornblende and olivine (Mitchell, 1974). Of the sedimentary rocks, sandstones are composed of minerals that weather with difficulty and usually contain only small amounts of trace metals. Shales, on the other hand, may be of inorganic or organic origin, and usually contain larger amounts of trace metals (Mitchell, 1964). It is seen that black shales in particular are enriched in copper, lead, zinc, molybdenum and mercury (Table 1.1). Detailed studies on cadmium in British black shales showed a wide range of concentrations in those examined ranging up to 219 ppm (Table 1.2; Holmes, 1975).

Soils developed from these parent materials tend to reflect their chemical composition, though pedogenetic processes may modify this relationship. Soils derived from the weathering of coarse-grained materials such as sands and sandstones and from acid igneous rocks such as rhyolites and granites,

tend to contain smaller amounts of nutritionally essential metals, including copper, cobalt and zinc, than do those derived from fine-grained sedimentary rocks such as clays and shales, and from basic igneous rocks. For example, the average copper content of British surface soils has been recorded as 20 ppm (Swaine and Mitchell, 1960). However, the total copper contents of a large number of surface soils from England and Wales (Table 1.3) reflect a wide range, from 2 ppm in soils derived from Pleistocene sands in East Anglia, to 2000 ppm in both alluvial and upland soils in mineralized areas of south-west England. Detailed studies on soils

TABLE 1.3  
THE TOTAL COPPER CONTENTS OF SOILS DEVELOPED FROM A VARIETY OF PARENT MATERIALS IN ENGLAND AND WALES

Geological formation	Cu (ppm)	Geological formation	Cu (ppm)
<i>Recent</i>		Lower Greensand	
Marine silt	9-50 <sup>e</sup>	Hythe Beds	3-13 <sup>e</sup>
(East Anglia)	22 (29)	(Sussex and Hants)	8 (28)
<i>Pleistocene</i>		Sandgate Beds	4-14 <sup>e</sup>
Breckland	2-20	(Sussex and Hants)	9 (26)
(chalk-sand drift)	8 (35)	Folkestone Beds	2-17 <sup>e</sup>
(East Anglia)		(Sussex and Hants)	8 (28)
<i>Tertiary</i>		Weald Clay	
Bagshot Beds	4-37 <sup>e</sup>	(Sussex and Hants)	10-25 <sup>e</sup>
(Dorset)	13 (22)	<i>Jurassic</i>	
<i>Cretaceous</i>		Kimmeridge Clay	9-27 <sup>e</sup>
Chalk	7-28 <sup>e</sup>	(Berks and Oxon)	16 (21)
(Wiltshire)	15 (128)	(south-west England)	11-40 <sup>e</sup>
(Sussex and Hants)	12-17 <sup>e</sup>		18 (30)
	14 (3)	Corrallian Sandstone	5-19 <sup>e</sup>
(Berks and Oxon)	10-17 <sup>e</sup>	(Berks and Oxon)	11 (30)
	13 (7)	Corrallian Limestone	10-25 <sup>e</sup>
Upper Greensand		(Berks and Oxon)	16 (15)
(Sussex and Hants)	10-20 <sup>e</sup>	(south-west England)	11-26 <sup>e</sup>
	14 (8)		17 (11)
(Berks and Oxon)	7-14 <sup>e</sup>	Oxford Clay	
	11 (3)	(Berks and Oxon)	10-26 <sup>e</sup>
(Wilts)	4-18 <sup>e</sup>		20 (12)
	10 (28)	(south-west England)	10-25
Gault			18 (10)
(Sussex and Hants)	10-17 <sup>e</sup>	Cornbrash	14-20 <sup>e</sup>
	13 (9)	(south-west England)	17 (4)
(Berks and Oxon)	14-25 <sup>e</sup>	Lower Lias	30-40 <sup>d</sup>
	19 (6)	(Gloucestershire)	35 (6)

(continued overleaf)

TABLE 1.3—*contd.*

Geological formation	Cu (ppm)	Geological formation	Cu (ppm)
(Somerset)	6–60 <sup>a</sup>	Downton Marls	
	<b>32 (30)</b>	(Herefordshire)	16–60 <sup>d</sup>
<i>Permo-Triassic</i>			<b>30 (56)</b>
Permian Sandstone	5–40 <sup>d</sup>	Raglan Marl	20–40 <sup>d</sup>
(Cumberland)	<b>15 (18)</b>	(Monmouth)	<b>28 (19)</b>
Triassic Sandstone	4–16 <sup>d</sup>	St Maughans Group	10–40 <sup>d</sup>
(Cumberland)	<b>10 (17)</b>	(Monmouth)	<b>21 (4)</b>
Keuper and Bunter		Brownstone	5–30 <sup>d</sup>
Sandstone	10–40 <sup>d</sup>	(Monmouth)	<b>18 (37)</b>
(Lower Severn Valley)	<b>20 (13)</b>	Tintern Sandstone	5–20 <sup>d</sup>
Keuper Marl	10–300 <sup>d</sup>	(Monmouth)	<b>13 (24)</b>
(Lower Severn Valley)	<b>48 (80)</b>	Ditton Sandstone	20–50 <sup>d</sup>
<i>Carboniferous shales</i>		(Hay-on-Wye)	<b>32 (56)</b>
(Staffordshire)	<b>40 (68)<sup>f</sup></b>	<i>Silurian</i>	
<i>Devonian</i>		(Denbigh Upland)	9–90 <sup>b</sup>
Devonian Slates	14–42 <sup>b</sup>		<b>22 (99)</b>
(South Devon)	<b>26 (44)</b>	(Denbigh Moorland)	6–32 <sup>b</sup>
Devonian Sandstones	2–31 <sup>b</sup>		<b>15 (45)</b>
(North Devon)	<b>14 (37)</b>	(Herefordshire)	20–50 <sup>d</sup>
Old Red Sandstone	13–40 <sup>d</sup>		<b>31 (15)</b>
	<b>27 (60)</b>		

Soils contaminated by mining and smelting in the Tamar Valley area of south-west England:

Upland Soils 29–2000<sup>g</sup> ppm Cu

**314 (28)**

Alluvial Soils 35–2000<sup>g</sup> ppm Cu

**620 (12)**

<sup>a</sup> Thornton (1968)

<sup>b</sup> Keeley (1972)

<sup>c</sup> Thomson (1971)

<sup>d</sup> Wood (1975)

Number of samples in parentheses.

Bold type indicates mean value.

<sup>e</sup> Jordan (1975)

<sup>f</sup> Fletcher (1968)

<sup>g</sup> Colbourn *et al.* (1975)

developed from individual beds within selected sandstone formations have shown that the total copper content of the soil is generally lowest on the coarser grained parent materials and that concentrations increase with decreasing grain size (Table 1.4; Wood, 1975).

On the other hand, potentially toxic amounts of trace metals in soils may be derived from naturally occurring metal-rich source rocks (Table 1.5). Nickel-rich soils derived from ultra-basic rocks containing ferro-magnesium minerals in parts of Scotland may lead, under poor drainage



TABLE 1.4  
AVERAGE COPPER CONTENT AND TEXTURE OF SOILS DERIVED FROM  
INDIVIDUAL BEDS OF THE OLD RED SANDSTONE FORMATION (UPPER  
DEVONIAN) IN SOUTH WALES (WOOD, 1975)

Bed	Soil texture			Total Cu (ppm)
	Coarse sand	Fine sand	Silt and clay	
Raglan Marl	14	50	36	28
St Maughans Group	13	60	27	21
Brownstones	66	14	20	18
Tintern Sandstones	51	25	24	13

TABLE 1.5  
TRACE ELEMENTS IN SOILS DERIVED FROM NORMAL AND GEOCHEMICALLY ANOMALOUS  
PARENT MATERIALS

	Normal range in soil (ppm)	Range in metal-rich soils (ppm)	Sources	Possible effects
As	<5-40	up to 2500 up to 250	Mineralization Metamorphosed rocks around Dartmoor	Toxicity in plants and livestock; excess in food crops
Cd	<1-2	up to 800 up to 20	Mineralization Carboniferous black shale	Excess in food crops
Cu	2-60	up to 2000	Mineralization	Toxicity in cereal crops
Mo	<1-5	10-100	Marine black shales of varying age	Molybdenosis or molybdenum-induced hypocuprosis in cattle
Ni	2-100	up to 8000	Ultra-basic rocks in Scotland	Toxicity in cereal and other crops
Pb	10-150	1% or more	Mineralization	Toxicity in livestock; excess in foodstuffs
Se	<1-2	up to 7  up to 500	Marine black shales in England and Wales Namurian shales in Ireland	No effect  Chronic selenosis in horses and cattle
Zn	25-200	1% or more	Mineralization	Toxicity in cereal crops

conditions, to nickel toxicity in cereal and other crops (Mitchell, 1974). Of particular significance to agriculture in Britain, is the observation that excess molybdenum in soils and pastures can give rise to molybdenosis or molybdenum-induced copper deficiency in cattle. Molybdenum toxicity was originally described on calcareous soils containing 20 ppm Mo or more



derived from the Lower Lias formation in Somerset (Ferguson *et al.*, 1943; Lewis, 1943; Le Riche, 1959). At the present time it is recognized that soils containing 5 ppm Mo or more may support herbage containing 2 ppm Mo or more; this may result in loss of production and growth retardation in cattle due to molybdenum-induced copper deficiency. In England and Wales, soils derived from marine black shales of Cambrian, Ordovician, Silurian, Jurassic, Carboniferous, Cretaceous and Recent age usually contain from 1 to 100 ppm Mo compared with the majority of soils developed on other parent materials with less than 2 ppm Mo (Thomson *et al.*, 1972; Thornton and Webb, 1976).

The influence of parent materials on the total content and form of trace metals in soils is modified to varying degrees by soil-forming processes, which may lead to the mobilization and redistribution of elements both within the soil profile and between neighbouring soils (Swaine and Mitchell, 1960; Mitchell, 1964). In the UK and similar temperate areas, most soils are relatively young and the parent material remains the dominant factor. Under tropical climates and on more mature land surfaces, e.g. Australia, weathering processes have been more vigorous or of much greater duration, and relationships between the chemical composition of the original parent materials and the soil may be completely changed by the mobilization and secondary distribution of chemical elements and the formation of secondary minerals.

The processes of gleying, leaching, surface organic matter accumulation and podzolization, together with properties such as reaction (pH) and redox potential ( $E_h$ ), may affect the distribution, the form and the mobility of trace elements in the soil. The mobilization of trace metals by aerobically decomposing plant material has been described by Bloomfield (1969), and it has been shown that mobilization is partly in association with colloidal humidified organic matter, and partly in true solution as complexes that seem to be anionic (Bloomfield *et al.*, 1976). The distribution of trace elements in freely drained and poorly drained Scottish soils has been described by Mitchell (1971). The solubility and mobility of individual metals varies considerably. Iron, manganese, cobalt, cadmium and zinc are relatively mobile compared to lead and molybdenum and are sometimes redistributed in the course of soil formation and maturity. Redistribution of cadmium and zinc in soils derived from Carboniferous marine shale in Derbyshire is shown in Table 1.6. In contrast to lead, both metals have been leached from freely and imperfectly drained soils on hill tops and slopes and accumulated under reducing conditions in the lower horizons of very poorly drained soils at the base of slopes (Marples, 1979).