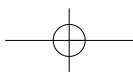
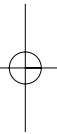
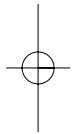
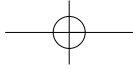


Trace Elements and Heavy Metals In Irish Soils

David McGrath &
Garrett A. Fleming

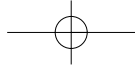
A compilation of existing data with input from the following

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Culleton, Noel
Fay, Deirdre
MacNaeidhe, Fionnan S.
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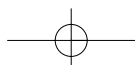
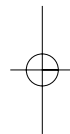
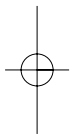


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Trace Elements and Heavy Metals in Irish Soils



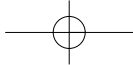
Foreword

This volume consists of a compilation of existing collated information on trace elements/heavy metals in soils, plants and food. Information presented in the past by Johnstown Castle staff that is largely relevant to Ireland is reproduced here. Papers published in scientific journals have not been included although, of course, the information enclosed herein is largely derived from them. Articles were part of the output from an active programme on trace elements/heavy metals that has now all but ended. Much of this information still exists in hard copy but is becoming less easy to access and is in danger of being lost. This information is as relevant today as when it was first compiled. The principle objective in producing this compilation is to ensure that the information is made available to staff of Teagasc and to researchers with an interest in trace elements/heavy metals in an Irish context: it has not been to produce another textbook.

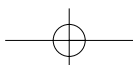
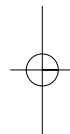
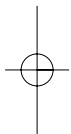
As far as possible original publications have been little modified. It is important to note that Tables are numbered within chapters whereas Figures are numbered consecutively throughout the book. Where changes have been made this has generally been done in order to avoid duplication and to ensure consistency. However, some duplication is considered acceptable in order to increase the value of the volume as a reference. To this end, citations relating to research in Ireland and a subject index have also been included.

Assistance from the following is gratefully acknowledged; R.J. McCormack (data compilation), E. McDonald (map presentation) and Ms S.Lacey and M.Foley (secretarial).

D Mc GRATH
March , 2006



Trace Elements and Heavy Metals in Irish Soils



¹ Trace Elements in Irish Soils - Content and Distribution

During the past century our knowledge of trace elements and their importance in crop and animal nutrition has grown steadily. More recently their role in human nutrition has been increasingly recognised. This chapter outlines the present position regarding the content and distribution of some trace elements in Irish soils. The soil status of the different trace elements is shown in a series of maps but it must be emphasised that the formulation of such maps is an ongoing process subject to continuing review and refinement consequent on emerging research findings. It is most important to interpret the maps correctly. For instance not all farms within areas designated as anomalous will have a particular trace element problem. With the intensity of sampling employed, the maps can only highlight high-risk areas, but they serve to draw attention to the possibility of a particular problem arising.

Certain geochemical and pedological tenets are taken into account when considering the likely status of any particular trace element in soils. The nature of the parent material provides a starting point and is indicative of likely total contents in soils. For instance, it can be reasonably assumed that soils formed from acid igneous rocks will have low

contents of a number of biologically important trace elements because the minerals with which these trace elements are normally associated are not abundant in such rocks. Conversely, soils formed from fine-grained sedimentary rocks such as argillaceous or clayey shales will, on average, have higher contents.

From the point of view of plant nutrition, however, it is not so much the total but the available content which is of greatest importance. Soils may have relatively high total contents yet the amounts available for plant uptake may be quite small. Factors such as soil pH, organic matter content and drainage status all affect the availability of trace elements to plants.

With regard to Irish soils it is necessary to recall that in the majority of cases they were not formed from the weathering of rocks *in situ*, but from glacial and fluvio-glacial deposits of one kind or another. This immediately explains their relatively complex distribution patterns. The nature of the glacial deposits which form the soil parent materials varies both in composition and texture. The former reflects the rock types over which the ice moved, the latter results from the interplay of various factors and events inherent both in the presence and

¹ **Trace Elements in Irish Soils – Content and Distribution** was presented by G.A. Fleming and P. J. Parle at the Symposium Trace Elements in Soils Crops and Animals, page 1-30, Johnstown Castle, March, 1987. The Proceedings of the Symposium were edited by G.A. Fleming and P.J. Parle.

Trace Elements and Heavy Metals in Irish Soils

in the retreat of an ice mass. Glacial deposits vary from coarse-textured sands and gravels which form the parent material of (for example) the Athy soil complex, to the heavy-textured tills from which many soils in the drumlin areas are formed. Fig. 1, adapted from Charlesworth (1963), shows the distribution of some glacial and fluvio-glacial deposits in Ireland. This diagram is useful in providing a rough guide to the location of heavy- and light-textured soils but the precise distribution of different soil types and information on their chemical and physical composition is only known for those counties where a soil survey has been completed.

Soil analysis

The availability of trace elements in soils is assessed by extracting the soils with reagents which purport to indicate their potential for supplying these elements to plants. It cannot be too strongly emphasised that such analyses must be correlated with field response data before they can assume any credibility. Because of the complex nature of Irish soils this presents special problems insofar as extensive field trial data are often necessary in order to achieve acceptable levels of correlation. Excessive extrapolation of soil analysis data is obviously scientifically unsound and can only result in error and confusion.

COBALT

Cobalt in the form of vitamin B12 is required by animals and humans. In plants it does not appear to be required by non-legumes. It is essential for nitrogen fixation by Rhizobium and thus is indirectly required by legumes.

In practical agriculture its importance lies in the ability of different soils to supply sufficient of the element for efficient nitrogen fixation by clovers on the one hand and for ruminant nutrition on the other. In Ireland, soils with inherently low levels of the element are formed mainly from acid igneous rocks, *e.g.* granites and rhyolites, from sedimentary rocks such as sandstones and conglomerates and from metamorphic rocks as typified by quartzites, schists and gneisses. Peat soils are also inherently low in cobalt. Levels of cobalt in limestone soils are very variable depending on the purity of the parent rock. Contents in shale soils range from low to quite high, depending on whether the shales are arenaceous (sandy) or argillaceous (clayey). Cobalt levels in Irish soils formed from a variety of parent materials are shown in Table 1 (Fleming, 1978).



Fig. 1. Glaciations and soil formation

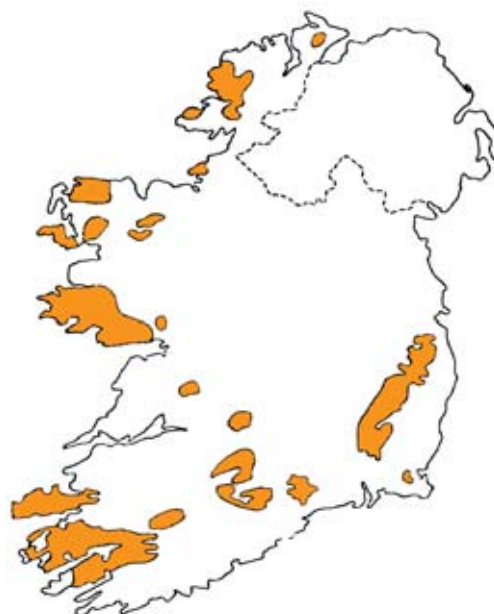


Fig. 2. Soils of low cobalt status

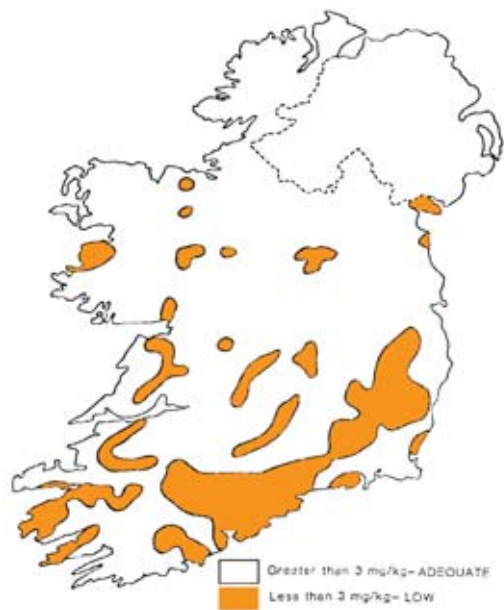


Fig.3. EDTA-soluble copper in soil

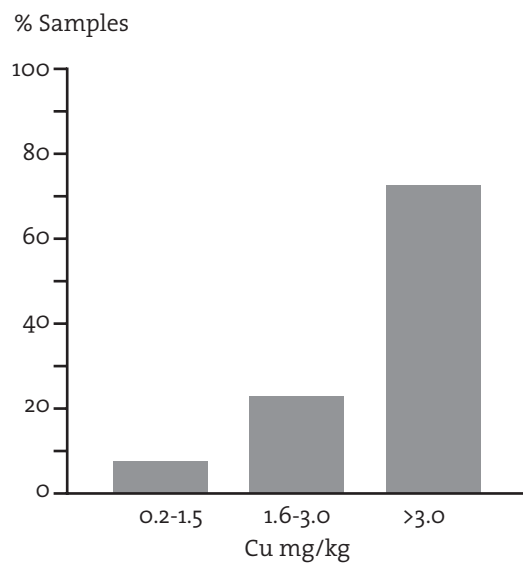


Fig.4. Frequency distribution of EDTA-soluble Cu

Table 1: Cobalt (mg/kg) content of soils formed from different parent materials

Parent material	No. of soils	Range	Mean
Basic igneous	7	6.3 - 17.0	12.8
Mica schist	5	10.4 - 14.2	12.6
Shale	56	1.6 - 18.4	8.2
Limestone	278	1.8 - 17.5	6.0
Sandstone	75	0.5 - 13.8	3.6
Gneiss	6	0.2 - 4.4	2.4
Granite	79	0.3 - 17.5	2.1
Blown sand	19	0.2 - 1.0	0.4

The soil samples were received from agricultural advisers. Sampling depth was 10 cm. Cobalt was extracted from soils with concentrated HCl. Thus the figures are essentially total values.

Distribution of low cobalt soils and the effect of manganese on cobalt availability

Low-cobalt soils (less than 5 mg/kg) have been mapped by Walsh et al. 1952 (Fig. 2). This serves to pinpoint areas where the risk of cobalt deficiency in stock is high. Such maps however do not reveal the true extent of risk areas. There are many soils where total cobalt contents are quite high but where the availability to the pasture is very poor. This is particularly apparent in limestone and shale soils and the factor primarily responsible is the high content of soil manganese (Fleming, 1983). Here we have an excellent example of the interaction in soils of one trace element

with another. Research in Australia highlighted the significance of various forms of manganese dioxide in binding soil cobalt (McKenzie, 1967; Adams et al., 1969).

Manganese dioxide minerals often occur in soils in extremely finely divided forms which results in their absorptive capacity being out of all proportion to their mass content. The crystal structures of these compounds are such that they readily accommodate cobalt ions into very stable structures. In short, the availability of cobalt in high Mn soils is severely restricted even in soils with high total Co contents.

Podzolization strongly influences the content of cobalt in topsoils. During the podzolization process cobalt is leached from surface horizons and deposited in the iron-rich B horizon. Many hill land soils, already inherently low in cobalt, are further depleted

by podzolization. Frequently these soils are overlain by blanket peat and here cobalt deficiency in mountain sheep can be a problem unless remedial measures are adopted. The effect of podzolization on soil cobalt is shown in Table 2 (Finch and Ryan, 1966).

Soil analysis for cobalt

Soil analyses for Co are of little value unless accompanied by parallel analyses for manganese. Only when both analyses are available can one predict the likely herbage content or the benefits which might accrue from applied cobalt. Various extractants have been employed in the estimation of plant-available cobalt. Some such as dilute acetic acid are very useful on acid soils but have in our experience proved of little value on limed soils.

COPPER

Copper is essential for plants, animals and humans. In Ireland, cereal crops are frequently affected by shortage but only rarely does grass respond to copper

supplementation. It is an extremely important element in livestock production.

Areas of low copper status are shown in Fig. 3. Data (Fleming and Parle, 1986) from 10,500 soil samples (0-10 cm depth) were used in compiling this figure. These were obtained by soil extraction with 0.5 M ethylenediaminetetraacetic acid (EDTA). This reagent provides useful correlations between the amounts of Cu extracted and responses in crops such as cereals.

The low copper areas are largely associated with soils formed from granite and sandstone. These rocks are inherently low in copper. Where podzolization occurs, e.g. in many hill land areas, this contributes to further depletion of Cu from surface soil horizons. Figure 3 underestimates the extent of low Cu soils as no samples were available from some midland peats and from west Galway, north-west Mayo, mid and west Donegal and south Kerry. The figure is based on surface soil samples received from agricultural advisers over a ten-year period from 1976 to 1986. The percentage

Table 2: Effect of podzolization on cobalt content of soil

Soil Series	Parent material	Horizon	Co (mg/kg)
Knockaceol (Co. Limerick)	Old Red Sandstone	A ₁	1
		A ₂	1
		B ₂ (ir)	6
		B/C	10

Trace Elements and Heavy Metals in Irish Soils

distribution of three categories is shown in Fig. 4 (Fleming and Parle, 1986). Approximately 8 percent of values are in the category where responses to applied copper in cereals might reasonably be expected. The first and second categories taken together - amounting to some 30 per cent of the total - represent values where copper contents of herbage, though generally adequate for grass growth, may not supply sufficient Cu to herbage to satisfy animal requirements. It must be emphasised that in relation to problems of Cu deficiency in animals, soil Cu figures, though useful, should not be seen as definitive.

Factors affecting the copper content of pastures

Liming Liming reduces available soil Cu. The effect obviously varies between soils but generally it is not large and cannot be compared with, for instance, the effect of lime on manganese.

Pig slurry and sewage sludge Application of pig slurry and some sewage sludges adds copper to soils. Pig slurry contains copper at levels of 600 to 800 mg/kg dry matter (McGrath et al., 1982). Sewage sludges can be very variable in Cu content and values found in Irish sewage sludges ranged from 86 to 5500 mg/kg dry matter (O'Riordan et al., 1986).

The subject of applying copper to land from slurries and sludges has received a great deal

of attention in recent years and an E.E.C. Directive on the use of sewage sludge to land has been drawn up. Copper applied in this way - via soil ingestion - can be hazardous to animals, particularly sheep, unless due precautions are taken.

IODINE

Iodine is required by animals and humans but not by plants. Because of problems with goitre in humans, investigations into the iodine content of some Irish soils were conducted in the 1940's (Shee, 1940; O'Shea, 1946). Goitre was quite severe in parts of south Co. Tipperary and here much research effort was concentrated. Soils from the area formed from limestone, and Old Red Sandstone averaged 3.1 mg/kg I, whereas those from the Spiddal area of Co. Galway, where goitre was not known, averaged 40 mg/kg. In the case of the Galway soils seaweed had been freely used as fertiliser. Subsequent investigations (Anon, 1956) by the Iodine Education Bureau, in collaboration with veterinary practitioners, animal nutritionists and agricultural advisors led to some delineation of iodine deficient areas in Ireland (Fig. 5). The investigations involved the provision of iodized mineral supplements to stock on over three hundred Irish farms and observation of resultant effects on animal health and performance.

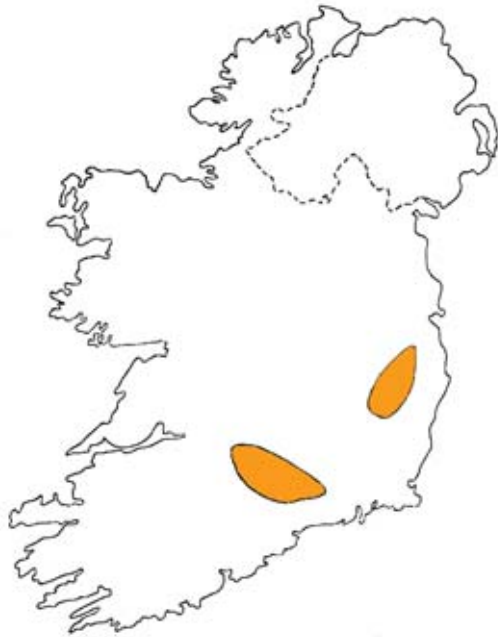


Fig. 5. Soils of low iodine status.



Fig. 6. Soils of high molybdenum status

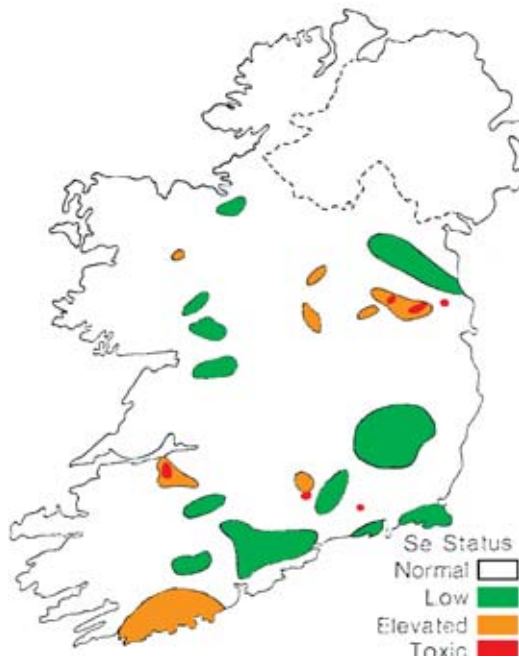


Fig. 7. Selenium in soil

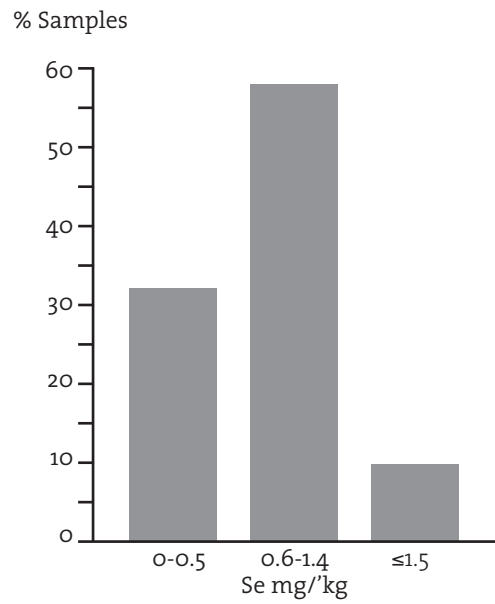


Fig. 8. Frequency distribution of Se in soil

Trace Elements and Heavy Metals in Irish Soils

As iodine is readily leached from soils it is natural to focus on coarse-textured, freely-drained, soils as sources of low iodine. Such soils are frequently associated with glacial and fluvio-glacial deposits as may be found in morainic and outwash plain sands and gravels. It is interesting and probably not coincidental that the areas designated as low in iodine by Shee (1940) and O'Shea (1946) lie on the end moraine of the Midlandian glaciation (Fig.1). Examination of glacial deposit patterns could prove very useful in endeavouring to locate other low iodine soils in Ireland. Where counties have been soil surveyed, information is obviously more precise and the task of identifying low iodine areas should be that much easier.

It is remarkable that since the studies of the 1940s little investigation of iodine in Irish soils has been undertaken. A partial explanation is the fact that human and animal goitre can be prevented by supplying iodine. In practice this is achieved by the use of iodized table salt by humans and by providing iodized salt licks and mineral mixes for animals.

Soil iodine and distance from the sea

It is generally recognised that atmospheric precipitation is the most important source of soil iodine (Fuge and Johnson, 1986). Because of its solubility, iodine is relatively enriched in both surface and sea waters and onshore winds carrying sea spray contribute to the iodine content of soils near coasts. Areas of

iodine deficiency are classically associated with areas remote from the sea but, whereas this may hold for large continental masses, it is not necessarily so for relatively small islands such as Ireland. Fleming (1980) has drawn attention to the importance of soil type in any assessment of iodine in soils. Levels of I in heavy-textured inland soils can be higher than those in light-textured soils closer to the sea. A recent study (McGrath and Fleming, 1988) has borne this out (Table 3).

Soil analysis for iodine

Soil analysis is not a good guide in the assessment of plant-available iodine. Herbage analysis is preferable and even here there may be considerable variation due to soil contamination, plant species and season. The latter may reflect changing amounts of atmospherically-deposited iodine. In the absence of a satisfactory test for plant-available iodine, soil analysis serves as a rough guide in indicating areas of low pasture iodine.

Table 3: Iodine content (mg/kg) of two Wexford soils

Soil Series	Mean distance from sea (km)	Range	* Mean
Screen (Sand)	3.8	2.9 - 6.8	4.8
Clonroche (Loam)	27	6.6 - 24	15.6

*Mean of 18 samples

MOLYBDENUM

Molybdenum is required both by plants and animals. In Ireland, shortage of the element is not a significant problem but on sphagnum peat soils some horticultural crops including swedes, cabbages and onions have responded to molybdenum applications (MacNaeidhe, private communication). Molybdenum deficiency would certainly not be expected on the majority of Irish midland cut-away peats as the high pH condition resulting from underlying calcareous parent materials would ensure that sufficient Mo was present in an available form. Under such conditions the problem is very often one of excess and many of our midland cut-away peats support molybdenum-toxic pastures. These give rise to problems particularly in young cattle when excess molybdenum in the herbage acts as an antagonist, which militates against efficient copper absorption by the animal.

From the soil/plant aspect it is essential to realise that this induced copper deficiency in animals can occur when values for both available soil copper and herbage copper are

relatively high. Soil application of copper is therefore of no value in counteracting the animal problem.

The extent of molybdeniferous soils as presently known is shown in Fig. 6 (Brogan, Fleming and Byrne, 1973). Soils analysing greater than 0.3 mg/kg Mo, extractable by 0.275 ammonium oxalate buffered to pH 3.3, are regarded as molybdeniferous. Whether or not they give rise to Mo-toxic pastures depends on soil factors such as pH, organic matter content and drainage status. Because of the general complexity of Irish soils, not all farms within the shaded areas are molybdeniferous or potentially so whereas, outside the areas mapped, some soils with elevated levels of Mo undoubtedly occur. The figure should be interpreted as indicating high risk areas and analysis of herbage samples is strongly advised to establish both the molybdenum status and the seasonal variation in Mo content.

Soil parent material

As in the case of selenium, the sources of high-molybdenum soils are Carboniferous black shales and limestones. The largest areas with such soil parent materials are found in the midlands but other areas occur in west Co. Limerick and sporadically eastward from there to Clonmel and past. An interesting enclave occurs around Kiltimagh in Co. Mayo where soil and herbage levels can be quite high. Poorly drained soils influenced by local black shale are responsible. Another molybdeniferous area occurs around Ballinamore, Co. Leitrim. Here soils occur which would normally require liming and this presents a special problem. Another area occurs in the Killorglin region of Co. Kerry where many of the soils are poorly drained. Relatively small areas of molybdeniferous soils also occur in soils reclaimed from the sea. The best known are the Wexford and Kilmore "sloblands" but there are similar areas in the Shannon estuary and in the Inishowen peninsula, Co. Donegal.

Soil analyses for molybdenum

Soil analyses for molybdenum are usually carried out using an ammonium oxalate extractant as indicated above. Data need to be interpreted with great care as the effects of organic matter, soil pH and drainage status are very important. Soil analyses can therefore be misleading unless these factors are taken into account. Soil analyses properly interpreted can indicate the potential of a particular soil for producing molybdeniferous

swards but in practice herbage samples taken twice a year in spring and autumn will often yield more valuable information. As in the case of many other soil analyses, values at the extremes of the scale are readily interpreted but for analyses between the extremes due attention must be given to various soil factors as mentioned.

SELENIUM**Selenium toxicity**

Selenium is required by humans and animals but not by plants. Initial interest in selenium in soils centred around its presence in excessive quantities. In the United States large areas were identified where animals suffered from selenium poisoning - known as "alkali disease" or "blind staggers" depending on severity - and similar areas were subsequently discovered in other countries, notably Australia, Canada, China, Ireland, Israel, Mexico and South America.

In Ireland seleniferous soils (Fig 7) are typically low lying, poorly drained, organic matter-rich, and mildly acid to alkaline in reaction (Fleming, 1978). Carboniferous black shales and limestones are the main source of the element. Selenium leached from soil parent materials formed from these rocks reaches depressions filled by river flood plains and old lake-beds, and it is here that the most toxic soils occur. Selenium in these soils ranges from 5 to over 1000 mg/kg but the majority of toxic soils contain between 10

and 50 mg/kg. The soils occur most extensively in Co. Meath and are typically found in relatively small pockets scattered mostly throughout the centre and south east of the county. Sizeable areas of selenium-toxic soils also occur in west Limerick, and smaller areas may be found in south Tipperary, and north Dublin. Because of the sporadic distribution of the soils they are not readily mapped at the scales usually employed. A tentative estimate of their area in the country would be of the order of 1000 hectares. Selenium-toxic soils are also enriched with molybdenum. From the practical farming aspect, seleniferous soils give rise to pastures which when consumed by livestock result in symptoms including loss of hair and cracking of hooves. Horses, cattle and sheep can all be affected. Selenosis

can cause significant ill-thrift but recovery usually occurs when animals are removed to normal pastures.

Other areas exist in the country where the selenium levels are slightly elevated but give rise to no identifiable animal problems. Selenium addition to soils from atmospheric deposition is known. It is alleged that soils on the west coast of Norway have probably been enriched from industrial sources in the U.K. Hill-land areas particularly in the east of Ireland and also peatlands, could well be in receipt of "bonus" selenium in a similar way. Such hill-lands frequently have a skin of peat and, as shown in Table 4 (Fleming and Walsh, 1957), organic matter is capable of retaining selenium.

Table 4: Selenium and organic matter in a seleniferous soil profile

Soil depth (cm)	Organic matter (%)	Se (mg/kg)
0 - 15	31.0	19.6
15 - 30	75.0	175
30 - 50	6.6	6.4
50 - 60	62.6	100
60 - 85	8.0	2.7

Selenium deficiency - low Se soils

Interest in selenium deficiency was triggered in the late 1950's by the discovery that a selenium-containing compound ("Factor 3") was capable of preventing a liver necrosis in rats (Schwartz and Foltz, 1957). This finding led to investigations of certain livestock disorders in many countries and selenium-deficient soils are now widely recognized, e.g. in Australia, New Zealand, the U.S. and China. In Europe, selenium deficiency is especially important in Scandinavia where acid igneous rocks give rise to soils with extremely low levels of the element.

In Ireland, low-selenium soils are known to occur (Fig 7) in parts of Carlow, Wexford, Cork, Tipperary, Waterford and also in light-textured soils formed from clear water limestones in east Galway (Fleming, 1978). However, more intensive sampling is necessary before accurate delineation of low-selenium soil is possible.

Soil analysis for selenium

The occurrence of low-selenium soil, and the incidence of selenium deficiency in livestock must not be equated. The correlation between soil selenium analyses and plant uptake of Se is not good except where soil values are extremely low or very high. Herbage analyses are therefore preferable in endeavouring to identify areas of selenium deficiency in animals but, even here, problems exist as "selenium responsive" diseases of livestock which are conditioned by factors such as the vitamin E content of the diet.

ZINC

Zinc is required by plants, animals and humans. Studies on the zinc content of Irish soils commenced only recently as, in the past, it seemed that zinc deficiency of crops was not a problem here. Some years ago zinc deficiency in onions was reported on peatland (Gallagher, 1969) but this occurred on a site which in the previous year had been heavily fertilised with phosphorus for a celery crop. Phosphorus is an antagonist of zinc in plant nutrition and in areas of the world where zinc-sensitive crops such as maize are grown, this fact is well recognised. In the absence therefore of crop or animal disorders suggestive of zinc deficiency, the element received little attention. In 1984 however, reports on an unidentified disorder in cereals in Co. Louth emerged, and following some preliminary investigations, zinc deficiency was identified as a possible causative factor. Full-scale field trials confirmed this (Mac Naeidhe *et al.*, 1986).

Zinc status of Irish soils

The cereal problem mentioned above occurred principally on hillsides on relatively stony soils, and closer inspection of the area revealed that the soils coincided with morainic deposits associated with the Midlandian glaciation. These particular deposits form part of the (Kells) Re-advance Moraine (Fig. 1). Recognition of this fact provides a directional approach to the search for other possible areas of low-zinc soils.

Examination (Mac Naeidhe *et al.*, 1987) of some 500 soils (0-10 cm depth) from

countrywide sources has revealed a number of areas small in size and rather well scattered (Fig. 9). The largest area occurs in Louth and north Meath. Some of the remaining areas are certainly associated with soils formed from glacial and fluvio-glacial deposits and in this respect the comparison between Figs. 1 and 9 is interesting. More intensive soil sampling will be necessary before the true extent of the association between low-Zn soils and fluvio-glacial deposits can be established. Such an investigation will inevitably be easier in those counties for which a soil survey has been completed.

Zinc availability in soils

The availability of Zn in soils to plants is reduced by liming. Zinc is absorbed by iron and manganese minerals in soils and also by

certain clay minerals. The intensity of absorption by iron minerals increases as pH rises and this in part accounts for its reduced availability.

Under conditions of high soil moisture the availability of zinc is increased. Pore spaces which are normally filled with air are now filled with water giving rise to a scarcity of oxygen. Under such reducing conditions the stability of zinc-binding minerals becomes less.

Potentially zinc deficient soils can be defined as follows;

- 1 Acid leached sandy soils where total Zn levels are low
- 2 High-lime soils where Zn availability is decreased
- 3 Sphagnum peat soils and possibly some cut-away peats underlain by limestone

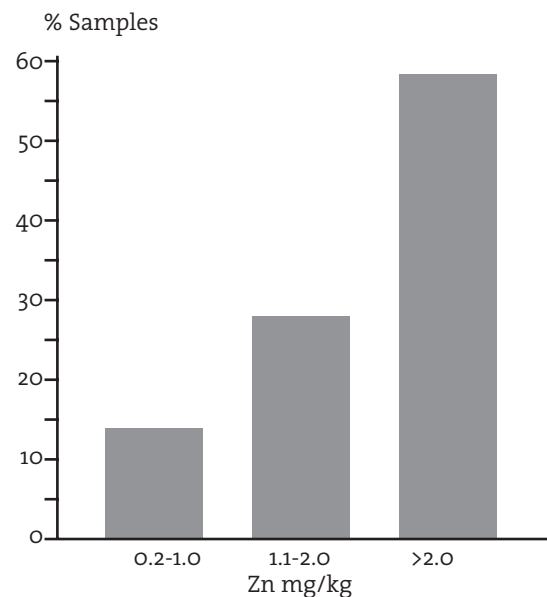
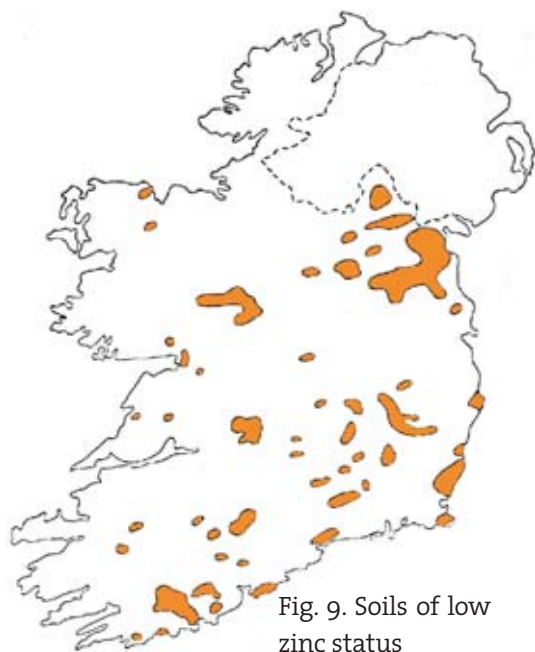


Fig. 10. Frequency distribution of zinc in soil

Trace Elements and Heavy Metals in Irish Soils

Frequency distribution of Zn in Irish soils

The frequency distribution of Zn in Irish soils based on the analysis of the 500 surface soils (0-10 cm depth) is shown in Fig.10. Diethylenetriaminepentaacetic acid (DTPA), the extractant used, is a well-recognised one. Values of 1 mg/kg and less are indicative of deficiency in sensitive crops. Approximately 15 percent of soils fall into the risk area. Obviously more effort needs to be concentrated in tillage areas where cereals will form part of a rotation.

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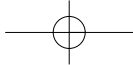
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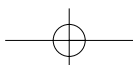
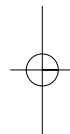
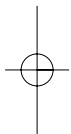
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Trace Elements and Heavy Metals in Irish Soils



Trace Elements in Irish Grassland

Introduction

The elements essential for life are those that cannot be wholly replaced by any other element. If a particular organism does not have a certain minimum supply of an essential element it cannot complete its life cycle. In this respect the trace elements are as important as the major elements - the only difference is that they are required in much lower quantities.

Our very existence depends on the food we eat, on the soil that produces that food, and, ultimately, on the ability of the soils to supply the essential nutrients to sustain life.

Upwards of ninety chemical elements may be found in soils and plants. Many may be quite toxic to animals and humans even at low levels of intake, whereas others are relatively innocuous. The elements are for convenience divided into "major elements" and "trace elements". The dividing line is usually set at 0.1 percent or 1,000 milligrams per kilogram; this is a purely arbitrary limit.

At the present time it is known that plants require nineteen elements for healthy growth, whereas animals require twenty five. The following elements are those required by plants: carbon, hydrogen, oxygen, nitrogen,

calcium, potassium, magnesium, phosphorus, sulphur, boron, chlorine, copper, iron, manganese, molybdenum, zinc, cobalt, silicon and sodium. Cobalt is intimately connected with nitrogen fixation in legumes so a case can be made for its inclusion in the list. Silicon is known to be essential for rice, and sodium is essential for plants adapted to saline environments. These two elements though invariably present in normal herbage species do not appear to be essential for their growth. In the case of animals all the elements listed above - with the exception of boron - are required together with arsenic, chromium, fluorine, iodine, nickel, selenium and vanadium. The soil is an essential medium for the growth of plants and for the breakdown and recycling of organic matter. Changes in soil properties such as variation in pH, redox potential and moisture status can greatly affect the bio-availability and form of the elemental components of the soil. Soil pH values are reasonably stable over the season but they can increase under reducing conditions brought about by water-logging. Low soil pH values can be adjusted to optimum levels for crop production by additions of lime. Metal cations are more active under acid conditions and increases in pH reduce their bio-availability. Conversely, some anions in soil become more available with increases in pH, i.e. molybdate, selenate and chromate.

Trace Elements in Irish Grassland was written by P. J. Parle, N. Culleton and B. Coulter in 1998.

Trace Elements and Heavy Metals in Irish Soils

Elemental uptake by plants is affected by factors controlling (1) the level and chemical form of the element (speciation) in the soil (2) movement of the element to the root (3) absorption of the element into the root and (4) translocation from the root to the plant shoot. In addition to root absorption, plants can also obtain significant amounts of the same elements by leaf absorption and this can be the route of entry by atmospheric pollutants. The readiness of deposited particles to enter through the leaf surface obviously depends on the form of the particular metal. Zinc and cadmium can enter plants more readily through foliar absorption than can lead.

Trace Elements In Soils

Sources of trace elements in soils

Trace elements in soil arise from the following sources;

- Native rocks and minerals from which the soil is formed, i.e. the parent material
- Lime, fertiliser, manures, sewage sludges, pesticides
- Debris from industrial, urban and mining wastes, including fossil fuel combustion
- Atomic weapon testing, sea spray, wind-blown dust, meteoric and volcanic material

Ranges of trace elements in soils

As may be expected, elements vary in concentration in different soils. In the case of the trace elements this variation may often be 100, or even in extreme cases 1,000 fold. Table 1 gives the ranges in content of a number of trace elements in Irish soils, analysed at Johnstown Castle Laboratories. The ranges given are those encountered in non-polluted Irish agricultural soils. Much higher levels may be encountered in the vicinity of ore deposits, or in areas where abnormal soil conditions exist.

Urban soils tend to have much higher concentrations of metal elements than do rural soils. Garden soils, particularly from old gardens, tend to have relatively high metal contents (Purves, 1977).

Extractable trace elements of soils

Because the total content of an element - whether major or trace - is not a good guide to its availability to the growing plant, soils are conventionally extracted with solutions which provide a clearer index of availability. For agricultural purposes this is common practice and for those elements primarily of environmental interest this method can also be employed (Clayton and Tiller, 1979).

Table 1: Ranges of trace elements (total contents) found in Irish non-polluted agricultural soils

Element	Symbol	Range (mg/kg)
Arsenic	As	1 - 20
Boron	B	20 - 100
Cadmium	Cd	0.1 - 1
Chlorine	Cl	30 - 300
Chromium	Cr	5 - 250
Cobalt	Co	1 - 25
Copper	Cu	2 - 100
Fluorine	F	20 - 700
Iodine	I	2 - 10
Lead	Pb	2 - 80
Manganese	Mn	20 - 3000
Mercury	Hg	0.03 - 0.8
Molybdenum	Mo	0.2 - 3
Nickel	Ni	0.5 - 100
Selenium	Se	0.2 - 2
Vanadium	V	20 - 250
Zinc	Zn	10 - 200

The reagents used are relatively mild extractants and they may vary for each element. It is important to realise, that while extractable contents give a better index of availability they are by no means perfect and their ability to predict likely plant contents is dependent on a number of soil factors, e.g. pH, organic matter content and soil texture. Table 2 gives the ranges of extractable trace element in Irish soils. These data have been accumulated over many years.

Trace Elements and Heavy Metals in Irish Soils

Table 2: Ranges of extractable trace elements in non-polluted Irish agricultural soils

Extractant	Element	Content (mg/kg)
Ammonium oxalate -Oxalic acid (pH 3.3)	Molybdenum	0.1 - 1.0
EDTA*(pH 7.0)	Copper	1.0 - 20.0
EDTA(pH 7.0)	Cadmium	0.02 - 0.50
EDTA(pH 7.0)	Zinc	2.0 - 15.0
EDTA(pH 7.0)	Lead	0.5 - 15.0
0.5M Calcium nitrate and 0.2% quinol	Manganese(E.R.)	10 - 600

*Ethylenediaminetetraacetic acid.

Table 3: Ranges of trace elements in Irish pastures (mg/kg in DM) and recommended herbage concentrations to meet animal requirements

Element	Symbol	Herbage content	Animal requirement
Arsenic	As	0.05 - 0.3	-
Boron	B	1 - 20	nil
Cadmium	Cd	0.01 - 0.3	nil
Chromium	Cr	0.1 - 0.3	-
Cobalt	Co	0.03 - 0.2	0.1 - 0.2
Copper	Cu	2 - 15	10 - 20
Fluorine	F	0.5 - 10	-
Iodine	I	0.07 - 0.30	0.5 - 1.0
Iron	Fe	20 - 300	25 - 40
Lead	Pb	0.5 - 20	nil
Manganese	Mn	20 - 300	25 - 300
Mercury	Hg	0.01 - 0.05	nil
Molybdenum	Mo	0.05 - 2	-
Nickel	Ni	0.5 - 3	-
Selenium	Se	0.03 - 0.5	0.08 - 0.2
Vanadium	V	0.05 - 0.5	-
Zinc	Zn	20 - 60	25 - 100

A dash (-) indicates lack of data

Trace Elements in Pasture

The ranges of trace element encountered in Irish pasture herbage are given in Table 3. The requirements in animal diets in so far as they are known are also included. The latter figures can only serve as a general guide as animal requirements vary, both with type and age of animal. In females the requirement during pregnancy and lactation can be higher.

Toxicity

Elements necessary for plant and/or animal health can be present in herbage in toxic amounts and thus cause harm to grazing stock, as can “contaminant” elements, i.e. elements which fulfil no known useful function in plant or animal nutrition. It is not possible to give precise values for toxic elements in herbage as their toxicities may be enhanced or mitigated by the presence of other elements. Frequently the ratios of elements in herbage are more important than their absolute values. A clear distinction must be drawn between toxicity of elements to animals and to plants. Animals may ingest contaminated soil directly or they may consume harmful quantities of toxic elements in material deposited on pastures (McGrath et al., 1982). It is suggested that these routes may be more likely to result in poisoning rather than the consumption of material actually taken up by the plant. With regard to direct plant injury from uptake of elements, i.e. phytotoxicity, various levels

have been quoted but because different plant species vary so much in this respect it is not easy to be specific.

Some figures for phytotoxicity are available for ryegrass and are shown in Table 4. These data were experimentally observed in culture solutions. The figures must be viewed with caution, as phytotoxicity levels in culture solutions may not necessarily be of the same magnitude as those observed in a soil medium. The presence of other ions may produce enhancing or mitigating effects. The data however provide some valuable guidelines. However it is likely that the phytotoxic levels for monocotyledonous plants will vary from those for dicotyledons and that clovers in pastures would be damaged before grasses.

Table 4: Phytotoxicity of elements in ryegrass (mg/kg in DM)

Element	Phytotoxic range
Boron	>190
Cadmium	>100
Chromium	>100
Cobalt	>100
Copper	>20
Fluorine	>50
Manganese	>500
Nickel	>80
Zinc	>400

Trace Elements and Heavy Metals in Irish Soils

Experimentation at Johnstown Castle on the effect of cadmium on perennial ryegrass revealed that loss in yield occurred when cadmium was present in the soil at a level of 16 mg/kg added Cd. No phytotoxic effects could be observed with a level of 8 mg/kg or less of added Cd. Yield losses amounted to around 15 percent. No visual symptoms were apparent on the grass showing yield loss. It is important to appreciate that for a given addition of a phytotoxic agent, the degree of damage produced is dependent on soil texture and phytotoxic damage is more likely on light-textured soils than on heavy-textured soils.

Soil contamination of herbage

It is relatively simple to take an uncontaminated soil sample but it is much more difficult to obtain a soil free herbage sample. Soil contamination of plants can result from (1) trampling by grazing animals, (2) splashing during rain, (3) dust following a prolonged dry period.

The significance of any degree of contamination depends on the element to be determined and its relative amounts in the uncontaminated sample and in the contaminant. In the case of elements with soil/plant content ratios of above 100 especially, due regard must be paid to the possibility of soil contamination when considering the accuracy of analytical results. Cobalt, iron, chromium, vanadium, titanium and iodine fall into this category. Since the

titanium content of plant tissue is minute, the element is frequently used as a tracer for soil contamination in plants.

The role of micronutrients

The micronutrients (essential trace elements) occur and function in low concentrations and should be maintained within narrow limits if the health of plants, humans or animals is to be safeguarded.

The micronutrients are mainly found as constituents of prosthetic groups in metalloproteins and as such are activators of enzyme reactions. They act as catalysts in redox processes by means of electronic transfer, or they assist in enzyme reactions by influencing the molecular configurations of enzymes or substrates.

In plants, the non-metal boron does not act either as a constituent of enzymes nor does it directly play a role in enzyme activities, but instead tends to form cationic complexes. Boric acid reacts with compounds such as sugars, which are found in cell walls. In the following sections, the various micronutrients are dealt with individually with an emphasis on their significance in Irish grassland.

COBALT

The significance of cobalt (Co) in nutrition arises because it is essential for animals rather than for plants. It is especially

important for ruminants as, without Co, rumen bacteria are unable to synthesise the cobalt-containing vitamin B₁₂. In plant nutrition, cobalt does not appear to be necessary for non-legumes but, because it is essential for nitrogen fixation by *Rhizobium*, it is indirectly required by legumes. The requirement by animals for cobalt varies with type of animal and age. Co requirement of common farm ruminants are in decreasing order as follows: weaned lambs > adult sheep > young cattle > mature cattle. Cobalt deficiency is therefore classically associated with sheep but in very deficient soils cattle can be affected. Apart from improvement in thrive following cobalt supplementation, improvement in fertility has also been recorded (Alderman, 1963).

Cobalt content of soils

Soils with inherently low concentration of Co are formed mainly from acid igneous rocks, i.e. granites and rhyolites, from sedimentary rocks such as sandstones and conglomerates and from metamorphic rocks as typified by quartzites, schists and gneisses. Soils formed from limestone vary in Co concentration depending on the purity of the parent rock. Concentrations of Co in soils derived from shales depend on whether the shales are sandy (arenaceous) or clayed (argillaceous). Peats always have low concentrations of cobalt.

Podzolization

Podzolization strongly influences the content of cobalt in top soils. During the podzolization process cobalt is leached from surface horizons and deposited in the iron-rich B horizon. Many hill-land soils, already inherently low in cobalt, are further depleted by podzolization. Frequently these soils are overlain by blanket peat and here cobalt deficiency in mountain sheep can be a problem unless remedial measures are adopted.

Soil drainage

Mobilization of trace elements in soils is affected by a number of factors and in temperate regions drainage can play an important role. This is especially so in the case of cobalt and it is common to find greater quantities of extractable Co in the gleyed horizons of poorly-drained soils than in corresponding depths of well drained soils on the same parent material. Walsh et al. (1956) found that in poorly drained soil, 10 percent of the total Co was extractable with dilute acetic acid, whereas in a well-drained soil on the same parent material only 2.6 percent of the total Co was removed. Such increases in extractable Co are reflected in increased plant uptake from poorly drained soils. Mitchell et al. (1957) compared mixed and pure swards from well and poorly drained Scottish soils and found five to eight times more Co in herbage growing on the poorly drained soils. The explanation for increased availability of cobalt from poorly

drained soils lies in the breakdown or weathering of Fe and Mn oxides with which cobalt is associated. The breakdown occurs readily in the reducing environment associated with poor drainage conditions.

Factors affecting the cobalt status of herbage

A typical example of the effect of one element on another element is the influence of manganese (or more correctly the oxides of manganese) on the availability of soil cobalt. Oxides of Mn carry high negative charges, except under extremely acid conditions, and have large surface areas - out of all proportion to their weight, and, because of the size and charge of the cobalt ion, have very high sorption capacities for the latter. Of the micro-nutrients Co is the most attracted to the surfaces of the Mn oxides and is ultimately trapped in their lattice structures and is thus rendered unavailable to the plant. Under poor drainage conditions the soil pores become filled with water rather than air producing reducing conditions. The stability of the oxides of Mn is thus weakened and the resultant mineral breakdown releases the trapped Co which are then ready available for plant uptake. Liming with its resultant pH increase has the opposite effect.

Species Different grassland species contain varying quantities of cobalt. It is generally assumed that clovers contain more than grasses. Whereas this is true when there is a plentiful supply of Co the reverse may obtain

when Co supply is limiting. Among the grasses themselves, ryegrass (*Lolium* spp.) generally contains more Co than other species such as cocksfoot (*Dactylis*) and timothy (*Phleum*) (Reith and Mitchell, 1964) but differences are often marginal especially when the general level of Co is low (Fleming, 1963). Levels in Irish pastures typically range from 0.02 to 0.11 mg/kg. The desirable level of Co in pasture is 0.1 mg/kg for lambs. Data for the true Co content of herbage are often difficult to obtain as any soil contamination of the herbage exercises a significant effect. Unless Co levels in herbage are accompanied by a statement of the degree of soil contamination they are quite meaningless.

Season Evidence relating to seasonal variation of cobalt in pasture herbage appears contradictory. An autumn increase in the Co content of ryegrass was obtained by Reith and Mitchell (1964). A decrease was recorded by Fleming (1970a) when under conditions of frequent cutting and N application, the Co content of perennial ryegrass ranged from 0.06 mg/kg in spring to 0.03 mg/kg in autumn. Variation in sward management may well explain these diverse findings. In practice the onset of cobalt deficiency in sheep often occurs in late summer or early autumn especially when animals are grazing regrowth material.

Stage of maturity A slight downward trend in the Co content of perennial ryegrasses was observed by Fleming (1970a) but was not as pronounced as in the case of copper. Cobalt

tends to concentrate in the seed heads of grasses and this may account for the relatively small change in content with increasing plant maturity.

Liming Liming decreases Co levels in pastures (Wright and Lawton, 1954; Reith and Mitchell, 1964). Pastures with mixed species often reveal variable levels of Co because of botanical composition changes occurring after liming. Care must therefore be taken to ensure that the sample is representative of the sward. Lower Co contents were found in both ryegrass (especially) and clover following liming but the effect was not as pronounced with mixed species samples (Mitchell, 1957).

Management of cobalt deficient pastures

Application of cobalt salts to soil can be a useful method for raising the Co status of herbage, but the efficiency with which this is accomplished varies widely between soils. On light-textured soils and peats the response in terms of Co uptake by herbage can be quite large but on heavier-textured soils the reverse is usually the case. Whereas soil pH, clay, and organic matter content all play a part in determining the availability of Co to herbage, as already stated, the oxides of manganese are more often the prime regulator of the movement of Co from soil to plant. Research in Australia (Taylor and McKenzie, 1966; McKenzie, 1967, 1970; Adams et al., 1969) leaves little doubt that this is so and that Mn oxides can be regarded as the

primary sink for soil cobalt. Fleming (1983) reported on the relationship between cobalt and manganese in Irish surface soils and soil profiles, and on the effect of the application of cobalt sulphate to Irish soils of differing manganese status (Table 5).

Soil application of cobalt sulphate at a rate of 2 kg/ha is frequently employed, and if the entire grazing area is being treated the financial implications must be considered. In practice, it will probably suffice to treat one third of the area in Year 1, another third in Year 2 and the final third in Year 3. At the end of this period it may be necessary to repeat the cycle. Herbage analyses for Co should be the guide here. Where soil Mn levels are in excess of about 400 mg/kg, the application of cobalt sulphate at 4 kg/ha will probably be effective for one season at most. In these circumstances direct supplementation of animals either by oral dosing, cobalt bullet administration, addition of cobalt to the water supply, use of cobaltized mineral licks or injection with Vitamin B12 must be considered.

Soil analyses for Co are of little value unless accompanied by parallel analyses for manganese. Only when both analyses are available can one predict the likely herbage content or the benefits which might accrue from applied cobalt.

Trace Elements and Heavy Metals in Irish Soils

Table 5: Applied cobalt and cobalt content of grass on soils of differing manganese contents

Soil parameter	Soil 1	Soil 2	Soil 3	Soil 4
pH	6.5	5.5	6.7	6.4
Clay (%)	24	22	11	8
Org. C (%)	3.1	2.0	7.7	1.9
Co (mg/kg)	7.0	6.5	2.5	3.0
Mn (mg/kg)	1167	837	213	70

CoSO ₄ ·7H ₂ O Applied (kg/ha)	Pasture data Co (mg/kg) in grass			
0	0.02	0.03	0.03	0.05
1.32	0.04	0.06	0.11	0.17

Animals at pasture may receive useful amounts of cobalt via soil ingestion. Thus the incidence of cobalt deficiency may be less under high rather than under low stocking rates. Differences in stocking rate may well be a factor in explaining yearly variations in the incidence or severity of cobalt deficiency.

COPPER

Copper (Cu) is essential for both plants and animals. Copper concentrations in soils are greatly affected by soil parent material. Soil parent materials derived from such as sandstones and quartzites are inherently low in Cu. Soil derived from acid igneous rocks as typified by granites and rhyolites generally contain less Cu than more basic rocks like gabbros and basalts. Whereas soils derived from shales vary appreciably in their Cu content, arenaceous (sandy) shales are much

lower in Cu than argillaceous (clayey) shales. Copper contents of limestone depend on the degree of purity of the rock - the purer the limestone the lower the Cu content. Peats generally have a very low Cu status and require the addition of Cu as normal fertiliser practice. Where leaching and podzolization have occurred copper is frequently lost from surface soil horizons. Peaty podzols formed from parent materials low in copper often support pastures with inadequate levels of Cu for optimum animal production.

Copper in Irish soils

The Cu content of Irish soils is usually measured by an extraction technique using EDTA. This extractant is widely used for assessing the soil copper availability from both an agricultural and an environmental point of view Clayton and Tiller (1979).

Brogan, Fleming and Byrne (1973) found that in Irish pasture soils EDTA extractable Cu ranged from 1.3 - 44.4 mg/kg with a mean value of 7.9 mg/kg. In a survey of over 10,000 mineral soil samples Parle and Fleming (1985) obtained a mean value of 6.0 mg/kg in the range 0.2-172 mg/kg. This survey, which was performed on a county basis was also used to generate Fig. 3 (page 7) and delineates areas with low soil Cu values, i.e. <3.0 mg/kg. County values are given here (Table 6) for a subsequent survey (Coulter et al., 1999) and reports mean values for soils received for analysis at Johnstown Castle over a period of 10 years before 1998. A value indicative of adequacy varies depending on whether crop or animal requirements are being investigated. Generally, values of less than 1.5 mg/kg EDTA extractable Cu are insufficient for cereal crops. The exact requirement for grass growth is uncertain, but it is important to realise that though a soil may have sufficient Cu reserves for healthy pasture growth, the levels in the pasture itself may not be adequate for animal needs. Soil values of less than 3 mg/kg Cu are regarded with suspicion in the latter respect. Recommended advisory practice in Scotland is to apply copper to arable and pasture soils when the levels of EDTA-extractable Cu are less than 1 mg/kg and 3 mg/kg, respectively (Berrow and Reeves, 1985).

Copper content of pastures

The levels of Cu in pastures generally vary from 2 to 15 mg/kg, with the range in grasses being much narrower than that in clovers. Lowest values are found in pastures on peatland and on mineral soils formed from such parent materials as sandstones, quartzites and granites. Reclaimed hill-land soils frequently support pastures of low copper status consequent on leaching, podzolization and peat formation.

On mineral soils copper is rarely limiting to the point where actual grass production is affected but on some peats this can occur. Grennan (1966) obtained yield increases in both grass and clover following the application of copper sulphate to Irish peat. These increases were generally greater in the clover component of the sward but in the first year increases in grass production of up to 17 per cent were recorded.

Factors affecting the copper content of pastures

The copper content of pasture is a result of the interplay of a variety of factors including soil parent material, herbage species, stage of maturity, season and nitrogen application.

Trace Elements and Heavy Metals in Irish Soils

Table 6: EDTA - extractable soil copper by county - per cent of samples

County	Samples	Cu (mg/kg)			
		<1.5	1.51-2.50	2.51-3.00	>3.0
Kilkenny	2141	2.6	13.1	10.6	73.7
Carlow	3192	8.6	23.2	13.4	54.8
Waterford	474	1.9	7.2	6.1	84.8
Leitrim	17	5.9	0.0	11.8	84.2
Kerry	306	9.2	17.0	7.2	66.7
Cork	9558	7.6	19.0	11.1	62.4
Clare	84	16.7	22.6	9.5	51.2
Louth	4126	0.4	2.5	3.4	93.8
Wicklow	1623	4.9	19.7	16.0	5.0
Tipperary	3210	2.3	14.4	10.8	72.5
Mayo	206	15.0	10.5	8.7	65.5
Wexford	2065	3.6	15.5	12.9	68.0
Westmeath	474	1.9	7.2	6.1	84.8
Roscommon	154	2.6	9.7	8.4	79.2
Laois	1461	6.4	22.2	12.1	59.3
Sligo	31	9.7	0.0	3.2	87.1
Offaly	1514	4.6	14.1	9.5	71.7
Limerick	789	3.8	7.6	9.6	79.0
Longford	79	0.0	6.3	5.1	88.6
Kildare	2638	1.6	8.6	7.0	82.8
Meath	2055	0.6	2.6	75.0	23.0
Monaghan	39	0	7.0	4.4	92.4
Donegal	717	1.7	1.3	2.4	94.7
Cavan	52	3.8	1.9	0.0	94.2
Dublin	2126	1.1	6.9	4.0	88.1
Total	41183	4.5	14.0	9.5	72.0

Species Variations in uptake by different grass species can be appreciable. Generally Yorkshire Fog (*Holcus lanatus*), rough stalked meadow grass (*Poa trivialis*) and *Agrostis* spp contain higher levels of Cu than does ryegrass (*Lolium perenne*). Ryegrasses, in general, are not particularly rich in Cu and the ploughing up of old pastures and reseeded with ryegrass mixtures can result in a general lowering of the Cu status of the sward. This will be particularly so if the original pasture contained clover.

Stage of maturity Apart from species, stage of growth (Table 7) and season can affect the Cu content of pastures (Fleming, 1965). Assuming an adequate soil supply, the level

of Cu in mature herbage is much lower than in young leafy material. In perennial ryegrass Fleming and Murphy (1968) noted a sharp decrease in Cu content as the grass matured, the levels at senescence being approximately half those at the young leaf stage. In perennial ryegrass cut at approximately the same stage of growth and at several times during the growing season Cu contents ranged from 7 to 15 mg/kg. A similar seasonal pattern was reported by Hemmingway (1962) over the course of four silage cuts but nitrogen application affected actual levels. In the absence of nitrogen (N) Cu levels ranged from 4.5 to 8 mg/kg whereas, in pasture receiving N, Cu ranged from 2 to 4 mg/kg between first and last harvests.

Table 7: Copper contents (mg/kg) of grasses/clovers at different stages of growth

	Cocksfoot	Perennial ryegrass	Rough-stalked meadow grass	Timothy	Red clover	White clover
April 4	12.9	8.3	17.3	9.7	-	8.4
May 3	9.8	7.1	10.4	7.0	10.8	7.9
May 26	6.5	4.2	8.8	6.0	9.2	7.8
June 14	5.2	4.1	7.8	4.5	7.5	8.0
June 28	4.0	3.4	6.1	4.2	8.4	7.8

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Seasonal effect In grazed swards the rise in Cu levels with season does not appear to be as sharp. Here seasonal samples will inevitably contain material at different stages of growth and of changing botanical composition. McGrath (private communication) has noted a slight rise in the Cu content of grazed swards with advance in season but evidence of a decrease in Cu levels in the July-August period was apparent. In general the effect of season is less predictable in grazed swards.

Nitrogen Conflicting results have been obtained on the influence of N on herbage Cu content. Where soil Cu levels are adequate, applications of N can enhance Cu uptake by stimulation of root development, but where soil Cu reserves are low herbage Cu contents

will be depressed due to the dilution effect produced by the extra growth. The effect of N on Cu uptake by a ryegrass sward growing on a soil with adequate Cu levels is shown in Table 8 (Fleming et al., 1988). It is interesting to note that applications of N had a greater effect on Cu uptake than had application of copper.

Lime The addition of lime as ground limestone results in a slight lowering of the Cu status of grasses. In mixed grass/clover swards and assuming an adequate Cu supply, its effect will usually be in the opposite direction insofar as after liming, an increase in the clover content of the pasture can occur. The higher Cu levels in clover will then result in an overall increase in pasture Cu levels.

Table 8 : Effect of nitrogen and copper applications on the copper content of a ryegrass sward

Treatments	N ₀	N ₁	N _i
	Copper content of herbage (mg/kg)		
CuO	9.9	12.2	12.8
Cu 1*	9.4	12.2	14.1
Cu 2*	9.3	12.4	14.8

Cu 1 = 2.5 kg/ha N₁ = 80 units/ha Cu 2 = 5.0 kg/ha units/ha

Raising the copper status of pastures

Although the copper content of pasture is rarely low enough to affect grass growth, the level may sometimes be insufficient to meet the requirements of grazing animals. These requirements vary both with type and age of animal. Cattle require more Cu than sheep and the young bovine requires more than the older animal. For dairy cattle a Cu content of at least 10 mg/kg in herbage dry matter is necessary. In ryegrass pastures this level is frequently not attained.

The application of copper sulphate at sowing time is a reliable and effective method of raising the Cu status of pasture to an acceptable level and its effect is long term. A dressing of 20 kg/ha of copper sulphate is adequate. On established swards it may prove difficult to apply this rate without causing some scorching and half this amount will suffice, albeit for a shorter time. The effect of 20 kg/ha $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ on a newly sown pasture, cut three times during 7 subsequent growing seasons, is shown in Table 9 (Fleming, 1984).

The figures refer to samples taken in autumn on a pure grass sward. Spring samples were generally lower than autumn cut herbage averaging between 2 and 4 mg/kg in control plots and clearly insufficient to meet full animal requirements.

Availability of copper to the animal

It has been estimated that Cu deficiency is the most frequently occurring of the micronutrient deficiencies worldwide (Mills, 1985). Recommended dietary allowances do not accurately relate to the animal's copper requirements on all diets as the bio-availability of copper varies with differing diets and with molybdenum and sulphur contents of the diet (Price, 1989). The bio-availability of Cu from herbage can be less than 3 percent of the total Cu content, whereas the availability of Cu from silage and hay can be of the order to 3 and 7 percent, respectively (Suttle, 1983).

Soil ingestion is a significant factor influencing the Cu status of grazing animals.

Table 9: Effect of copper sulphate application on Cu content of freshly established ryegrass

Copper sulphate	Cu content of ryegrass (mg/kg)						
	Year 1	Year 2	Year 3	Year 4	Year 5	Year 6	Year 7
0	4.0	6.7	5.9	4.0	5.0	6.0	4.8
20 kg/ha	9.7	6.7	11.3	8.6	8.0	10.2	5.7

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It would seem that ingested soil can contribute useful quantities of such micronutrients as cobalt, iodine and selenium (Healy, 1970, 1972), but in the case of copper, availability is reduced. Differences in the Cu status of herds grazing similar pastures may be accounted for in part, at least, by differences in stocking rate and thus in the degree of soil ingestion. The release of Fe from soil in the rumen can inhibit the absorption of Cu by the animal. Contamination of silages with soil, thereby raising their Fe content, can also reduce Cu bio-availability.

The major factors governing soil ingestion under Irish conditions have been identified as stocking rate and rainfall (McGrath et al., 1982). Soil type and herbage on offer appear to be of lesser importance. With regard to the availability of a particular micronutrient however, soil type can never be totally ignored.

MOLYBDENUM

Molybdenum (Mo) is essential for both plants and animals. The primary source of molybdenum in the weathering zone of the soil is the ferromagnesian minerals, with the sulphide molybdenum (MoS_2) common in certain granitoids (Chesworth, 1991). Molybdenum is soluble under a wide range of conditions, and is probably the most mobile of all the metalloid elements. Organic matter seems to act as a concentrating agent since

Mo is enriched in organic sediments. Almost all the excess of Mo in terrestrial rocks is associated with Fe and Mn hydroxides and hydrated oxides (Chesworth, 1991).

Molybdenum in grassland is important from both deficiency and toxicity aspects. Deficiency affects clover establishment by influencing nitrogen fixation, whereas excess molybdenum in pastures can give rise to animal health problems. The importance of molybdenum in influencing nitrogen fixation was recognised many years ago (Bortels, 1930). Practical expression was given to the finding when the use of molybdenized superphosphate permitted the successful establishment of clovers and other pasture legumes in large areas of Australia.

Excess Mo in herbage is a major factor in the incidence of scouring and ill-thrift of cattle and this was revealed by the classical researches of Ferguson and co-workers on the "teart" pastures of Somerset, U.K. (Ferguson et al., 1943; Lewis, 1943, a, b). Molybdenum is now known to interfere with copper metabolism in the ruminant. The practical effect of excess Mo in pasture is to induce a copper deficiency in the animal.

Molybdenum in Irish soils

In Ireland the molybdenum problem is one of excess rather than deficiency. Soils with elevated Mo concentrations occur in the following geochemical situations:

- A Areas where the soil parent material is influenced by or formed from black marine shales of Namurian age (mid-Carboniferous)
- B In areas where the soil parent material is influenced by the Calp limestone (shaley carboniferous limestone)
- C Areas where the soil has been reclaimed from the sea such as the sloblands of Co. Wexford, areas on the Shannon estuary and on the Inishowen peninsula, Co. Donegal
- D An area overlying a mineralised granodiorite of Mace Head, Co. Galway (Talbot and Max, 1984; Talbot and Ryan, 1988, a, b)

The distribution of the areas in Ireland where potentially molybdeniferous soils can occur are shown in Fig. 11 which is an update from 1998 of the earlier map (Fig.6). Obviously not all the pastures in the shaded areas on the figure are molybdeniferous - much will depend on local soil types, soil conditions and farm practices.

Molybdenum in Irish pastures

Pasture responses to applied Mo on mineral soils have not been recorded in Ireland. Molybdenum excess and its associated problems have therefore been the focus of attention. Hypocupraemia in cattle has been the principal syndrome associated with excess Mo, but it also has been suggested that the element is implicated in an osteodystrophic condition in horses (Walsh

and O'Moore, 1953). It should be noted that a large number of stud farms are situated within the potentially molybdeniferous areas.



Fig. 11. Recent assessment of molybdeniferous areas in Ireland

The identification of molybdeniferous pastures in Ireland and the occurrence of hypocupraemia in cattle were reported by Walsh et al. (1951-52) and by Neenan et al. (1956). The levels of Mo found in herbage on which the problems described above were encountered varied from approximately 2 to 25 mg/kg. Levels in clover of up to 50 mg/kg were subsequently observed. In the autumn of 1985 Mo levels of up to 100 mg/kg were

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found in some Irish pastures and were the result of the inordinately wet year.

Factors affecting the copper content of pastures

Soil pH A rise in soil pH increases the availability of soil molybdenum in contrast to most other trace elements. This increase can be quite significant at pH values greater than 6.3. It is generally assumed that an anion exchange mechanism involving the replacement of MoO_4^{2-} by OH^- is involved in the increased Mo availability following a pH rise. Liming of pastures with high levels of available Mo results in undesirably high Mo contents in grasses and clovers and can result in molybdenosis in grazing animals. The effect of as little as 2.5 tonnes/ha of lime on Mo content of a stud farm pasture is shown in Table 10.

Soil moisture status Although liming is generally considered to be the most potent factor in increasing the Mo content of pastures, increases in soil moisture can also have serious effects. Drainage impedance, therefore, becomes very important and its effect in relation to molybdeniferous swards must never be underestimated. Under conditions of impeded drainage reducing soil conditions prevail, and in this regime the iron oxide minerals with which molybdenum is commonly associated, break down and the element is released and becomes available for plant uptake. The effects of increased drainage impedance on Mo levels in a ryegrass sward are illustrated in Table 11 (Fleming, 1973). The data illustrate clearly what is commonly observed in practice, i.e. other factors being equal, the most molybdeniferous swards on a farm will be found in areas with the poorest drainage. Molybdenum availability will, however, also increase even in well-drained soils following an extended wet spell.

Table 10: Effect of lime on the molybdenum content (mg/kg) of a Co. Meath stud farm pasture

Treatment	Soil 1		Soil 2	
	pH	Mo	pH	Mo
Control	5.3	2.8	5.4	4.2
2.5 t /ha	6.0	5.4	6.1	5.5

Table 11: Soil drainage and molybdenum content (mg/kg) of ryegrass

Draina	Soil pH	Org. C (%)	Mo in grass
Good	6.3	3.1	2.2
Imperfect	6.5	3.5	3.1
Poor	6.5	5.0	3.9
Very poor	6.6	7.5	13.0

Table 12: Molybdenum content of some herbage species grown on a high Mo soil

Species	Mo (mg/kg)
White clover	85
Red clover	83
Yorkshire fog	63
Cocksfoot	15
Rough stalked meadow grass	15
Perennial ryegrass	11
Meadow fescue	9
Timothy	7

Herbage species The molybdenum content of herbage species varies considerably. Table 12 gives the Mo values for a range of species grown on a high Mo soil (Ferguson et al., 1943) and shows that clovers are richer in Mo than the grasses. However, on a soil with low Mo the reverse may obtain. The latter situation is probably a reflection of the ability of grass roots to scavenge more effectively than the clover roots. Amongst individual

grasses, Yorkshire fog usually accumulates more Mo than the associated grasses and this seems to obtain both in high Mo soil and in a soil with normal Mo levels.

Nitrogen The application of nitrogenous fertilisers tends to reduce the Mo content of herbage. The dilution produced by extra yields is obviously important but the reduction or even elimination of clover from the sward is also a factor. Different nitrogenous fertilisers are likely to effect greater or lesser reductions in Mo content. For instance calcium ammonium nitrate or urea would reduce Mo content by dilution and clover suppression effects but in the case of sulphate of ammonia other factors come into play. These are (a) the soil acidification resulting from the constant application of this fertiliser and (b) the antagonistic effects on Mo by both the ammonium and sulphate ions. The sulphate ion in particular exerts a significant depressing action on Mo uptake, an effect attributed to competition in the soil solution between the similarly sized and

charged sulphate (SO_4^{2-}) and molybdate (MoO_4^{2-}) ions.

Phosphorus The effects of phosphatic fertilisers on Mo uptake are frequently difficult to interpret as these fertilisers may contain other elements which exert their own effects. Certainly phosphatic compounds free of sulphate increase Mo uptake (Barshad, 1951). Barshad has suggested that the stimulating action of phosphate on Mo may result from the formation of a phosphomolybdate complex readily assimilable by the plant. Walsh et al. (1951-52) observed enhancement of Mo uptake by herbage from Irish soils, following fertilizing with monocalcium phosphate. Some of the most severe cases of molybdenum toxicity in animals were associated with soils which had received basic slag, which can be ascribed to the effect of the basic nature of the material with the resultant decrease in soil acidity following its application. Whereas this may have been so, the phosphate effect per se is very likely a contributory factor. The application of superphosphate will reduce Mo uptake by plants, this effect resulting from the sulphate component in this fertiliser.

Potassium Potassium fertilisers do not seem to exert any significant effect on the uptake of Mo (Fleming, 1980a). If, however, the application of such fertiliser resulted in an increase in the clover content of a sward then levels of Mo would be increased.

Sulphur The depressing action of sulphur in the sulphate form on Mo uptake has already been referred to as an indirect effect following basic slag application. In a field trial from which the data of Table 13 (Fleming, 1977) were taken, the application of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) reduced the Mo content of grass from 18 to 2 mg/kg. Table 13 also shows that sulphate of ammonia also reduced Mo contents in herbage. In both these cases there was an accompanying increase in sulphur content of the herbage. Feeley (1990) also showed the effectiveness of sulphate of ammonia and gypsum in reducing the uptake of Mo herbage grown on midland peat. From the animal health point of view, the use of the above methods to reduce Mo excess in herbage may be questionable because of the accompanying high sulphur intakes can exacerbate the Mo effects on their copper status. The question arises as to whether the decrease in the Mo content of the herbage following sulphate application is offset by the resultant rise in the S content.

Table 13: Effect of sulphate of ammonia and gypsum on the molybdenum and sulphur contents of herbage

Sulphate of ammonia (kg/ha)	Mo (mg/kg)	S (g/kg)	Gypsum (tonnes/ha)	Mo (mg/kg)	S (g/kg)
0	12.0	0.40	0	18.0	0.49
250	6.1	0.49	7.5	9.5	0.53
500	3.9	0.62	15.0	4.0	0.61
1000	3.6	0.59	30.0	2.0	0.68

The Mo and S values are means of 4 cuts.

Management of molybdeniferous pastures

Part of the management of molybdeniferous pastures involves taking the decision to reduce (calculated) lime recommendations. The possible resultant loss in pasture production must be viewed against the problems likely to accrue from molybdenosis in grazing stock. Whereas copper therapy is quite effective, it must be realised that once lime has been applied, the pasture will be rendered potentially more molybdeniferous for many years to come. The position is particularly acute on acid molybdeniferous soils and normally liming above a pH of 6.2 is not advisable. In Ireland many cutaway peat soils are already at a high pH and here especially every effort must be made to discourage clover growth by suitable management practices, e.g. increased use of nitrogen. Overgrazing also must be avoided as this increases soil ingestion. Hay is less toxic than fresh grass of comparable Mo content. This probably results from the fact that the Cu content of hay is more

bioavailable, as is the case with silage. Measures to prevent or reduce the severity on molybdenum-induced copper deficiency can be applied to the animal directly and these include copper injections, copper oxide needles and soluble glass boluses, which release copper at a slow rate in the rumen or by copper supplementation of the diet or of the drinking water (Price, 1989).

SELENIUM

Selenium (Se) is not essential for plant growth but is required for animal and human nutrition. At farm level, problems in animals may arise from either excess or deficiency of Se. Disorders due to Se excess have been known for a long time but those arising from a deficiency of the element have been highlighted only since the late 1950's when the possible essentiality of Se for animals was shown by the researchers Schwartz and Foltz (1957).

Selenium in Irish soils

The early work in Ireland on Se was in relation to toxicity (Walsh et al., 1951; Walsh and Fleming, 1952; Fleming and Walsh, 1957; Fleming, 1962). During this period the general areas where toxicity occurred were delineated. These seleniferous soils are typically low lying, poorly drained and of high pH and organic matter status. The soils have been influenced to a large degree by percolating waters from Se-rich rocks where black shales are the predominant facies. These rocks are Namurian (mid Carboniferous) in age and are enriched in a number of elements including selenium, molybdenum and to a lesser degree copper, cobalt, vanadium and uranium.

Seleniferous areas are not extensive and occur mainly in Counties Limerick, Tipperary and Meath. Some small isolated areas also occur in Counties Dublin, Kilkenny, Carlow, Kildare, Offaly, Westmeath and Mayo. The toxic areas of Co. Meath were known in the last century, through the identification of the toxic element was not and early writings refer to "the poisoned lands of Meath" (Fream, 1890). Seleniferous soils can have selenium values as high as 200 mg/kg and those in excess of 5 mg/kg are considered to be toxic.

Geochemical considerations would suggest that soils of low Se status would be found on soils formed from sandstone, granite, the purer limestone and soils developed on glacial and fluvio-glacial sands and gravels.

Blanket peats of the western seaboard, those on the sandstones of Co. Kerry, on the schists and gneiss of Co. Mayo and on the Dalriadans of Co. Donegal would also be suspect. Soils formed on the granite hills of Wicklow and the Leinster chain may well be the subject of atmospheric fallout mainly from the U.K. Fleming and Parle (unpublished) found 3 mg/kg Se in peat on the top of Mount Leinster. Enrichment from atmospheric deposition is one of the main sources of Se (Haygarth, 1994).

Selenium concentrations in Irish soils (excluding the seleniferous soils) range from 0.15-2.5 mg/kg and having a mean value of the order of 0.8 mg/kg. In a survey of some Irish stud farm soils Parle et al. (1995) found that 90 percent of soils from Tipperary stud farms had values which fell in the range 0.15-0.50 mg/kg. A delineation of the Se status of Irish soils is shown in Fig. 7. However, before a very accurate assessment can be made an intensive sampling scheme would be required.

Selenium in Irish pastures

In non-seleniferous Irish pasture the herbage Se content will generally be in the range 0.02-0.50 mg/kg. A review of the herbage analysed at Johnstown Castle in the period 1986-1995 showed that 76 percent of samples had values of <0.10 mg/kg Se, and 25 percent had values of <0.05 mg/kg.

Factors affecting the selenium content of pastures

Sulphur Because of the chemical similarity of sulphur and selenium it is not unreasonable to expect that the addition of sulphur to soil will affect the uptake of Se by the plant. Ravikovitch and Margolin (1959) reduced the Se content of lucerne from 4.6 to 1.4 mg/kg using gypsum. Superphosphate has also been shown to reduce Se content of grass, resulting from the calcium sulphate component of this fertiliser. The authors, in a field trial reduced the uptake of applied and native Se by the addition of gypsum (Fleming, 1970b).

Nitrogen Applications of high amounts of nitrogen producing large responses in grass growth can reduce the Se content of the grass by a dilution effect.

Lime Liming will increase the availability of soil Se and thus enhance Se uptake by herbage.

Weather conditions Long dry periods in summer can have the effect of increasing soil Se availability by the oxidation of some of the soil Se to the selenate form - a more soluble form of selenium.

Selenium toxicity

Selenium toxicity is usually associated with cattle and horses with the latter being more prone to the disorder. Animals suffering from Se toxicity will lose hair from the body - in the case of horses the mane and tail are

particularly affected - cracking of hooves is common and in severe cases the hooves will slough. Toxicity may be acute or chronic. Acute toxicity or "blind staggers" results from the consumption of plants capable of accumulating large quantities of Se whereas the chronic form (alkali disease) is caused by the prolonged ingestion of fodder containing lower but yet toxic quantities. Selenium-accumulating plants have been reported from the United States and from Australia. In the U.S. certain species of the genus *Astragalus* are among the better known Se accumulators. Amounts of Se in excess of 1000 mg/kg are frequently found in these plants. In Australia a native plant of Queensland *Morinda reticulata* is a selenium accumulator and has caused selenium poisoning in horses. True selenium accumulators are only found where seleniferous soils occur and their presence has been used as an aid in the mapping of such soils.

In Ireland true selenium accumulating plants do not occur and the acute form of poisoning in animals is unknown. The chronic type is known and is prevalent in pastures with Se levels ranging from 3 to 100 mg/kg. The variation in Se content can be quite large and outbreaks of selenium poisoning will depend on the length of time animals spend grazing toxic pastures. Soil ingestion may also contribute to the onset of the disorder.

Where farm size is small as in parts of Co. Limerick, the problem of selenium toxicity is

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serious, as stock must be removed to non-seleniferous pastures when symptoms of poisoning occur. In Co. Meath, Crinion (1980) has recorded a number of instances of selenium poisoning both in cattle and horses but because farm size is generally larger in this part of the country it is easier to take preventive measures. The levels of Se recorded (Fleming and Walsh, 1957) for some typical Irish seleniferous pastures are shown in Table 14.

The identification of seleniferous soils and pastures on a farm is obviously of primary importance and can be achieved by means of soil and/or herbage analysis. Frequently seleniferous pastures occupy only a fraction of the total farm area and in such cases they should be fenced off and, if practicable, used for cereal or sugar beet production. In such cases the dilution effect at mill or factory will be sufficient to remove any possibility of

danger. If this is done it must be realised that tillage operations inevitably lead to increased surface soil aeration with possible oxidation of soil selenium to more available forms. When such land is ultimately returned to grass, hay should be made as its toxicity is less that of fresh grass. Toxicity can decrease with storage but even then forage should be fed only sparingly to stock and should be monitored for selenium content. Selenium values in excess of 5 mg/kg can be toxic to cattle and in the case of the horse values greater than 2 mg/kg should be viewed with extreme caution.

The spreading of river spoil in areas where Se is elevated will result in an increase in soil and herbage Se values. Material dredged from some rivers in Co. Meath has proven deleterious in this regard and the practice is not advisable.

Table 14: Selenium contents of soil and plant material from toxic areas (mg/kg)

Limerick		Tipperary		Meath	
Soil	Herbage	Soil	Herbage	Soil	Herbage
324.0	450.0	3.9	9.8	1.8	10.6
1.7	69.3	9.5	3.5	3.3	19.6
2.9	86.1	1.2	0.9	2.0	13.7
5.5	0.8	-	19.0	2.0	11.1
2.0	7.9	132.0	115.0	-	14.5

Selenium deficiency

The realisation that selenium might be capable of playing an essential role in animal nutrition arose from the work of Schwartz and Foltz (1957) which identified selenium as a component of a preparation capable of preventing liver necrosis in rats. In the USA studies by Muth et al. (1958) indicated that supplementation of the diet of ewes with trace quantities of selenium was effective in preventing prenatal myopathy (muscle wastage) in lambs. Similar studies by a number of workers demonstrated the efficiency of selenium in the prevention of muscular dystrophy or white muscle disease (WMD) in livestock.

It is now recognised that the biochemical functions of selenium are intimately associated with those of vitamin E and the effects of selenium deficiency are often modified by changes in the dietary supply of this vitamin. Both are involved in processes protecting animal cells against oxidative damage to fats and other cellular components. Vitamin E and the selenium-containing enzyme glutathione peroxidase (SeGSHpx) act as antioxidants in destroying peroxides which cause muscle damage. The most commonly recognised clinical syndrome of selenium/vitamin E deficiency in cattle and sheep is a nutritional myopathy. Other selenium-responsive diseases such as "ill thrift" in cattle and reproductive disorders including infertility in ewes and retained placentae in cattle have been widely reported and are described by Levander (1986). There is

also evidence to suggest that "tying up" in horses, which can occur following racing, training or heavy work is associated with low Se values (Cunha, 1991).

The most recent work on Se has been on the non-Se-GSHpx functions and in particular on the important relationships between Se and thyroid hormone metabolism. It has been shown that Se deficiency can increase some indicators of the hypothyroid stress associated with deficiency.

A dietary intake of 0.1 mg/kg Se is quoted by Levander (1986) as being satisfactory in providing a margin of safety against any dietary variable or environmental stresses likely to be encountered by grazing animals. However, requirements are greater when sulphate intakes are high and interfere with the conversion of Se to tissue SeGSHpx in animals (Mayland, 1994). Selenium utilisation varies depending on the form in the feed. The bio-availability of Se in animal by-products (including fish meal) can be as low as 9 percent, whereas that in plant products can be over 80 percent. Oldfield (1997) has reviewed the efficacy of various forms of selenium for livestock.

Increasing an animal's Se status may be accomplished directly by injection or by the use of a selenium heavy pellet or indirectly by means of the soil-plant route. Using the latter method Culleton et al. (1997) maintained blood levels in a dairy herd at similar levels to that of a herd which was supplemented by Se

injection. Attention must be drawn to the fact that under EU regulations the use of Se in fertilisers is not allowed at the present time.

Selenium deficiency in animals has been well characterized, but this is not so in the case of humans. A role for Se in preventing cardiovascular problems has been demonstrated in the Keshan province of China and by Keshan-Beck disease, an endemic osteo-arthritis that occurs in eastern Asia. Both diseases are always located in low-Se eco-environments. There is no doubt that Keshan disease is Se-responsive, however it is clear from epidemiological features that the incidence of the disease suggests an infectious rather than a nutritional cause. It has now been shown that a certain benign human virus, which remains benign in Se-adequate mice become virulent in Se deficient mice (Beck et al., 1994; Beck et al., 1995). This is the first time that it has been shown that host nutritional status can influence the genetic make-up of a pathogen (Levander and Beck, 1996).

Plasma Se and GSHpx activity of people of low Se status in China were increased by supplementation with Se (Xia et al., 1989). In Finland where the incidence of cardiovascular diseases is high, all agricultural multinutrient fertilisers have been supplemented with Se since 1984 in order to increase the Se content of domestic foods and thus raise the population's low Se intake (Eurola et al., 1991).

ZINC

Zinc (Zn) is an essential element for plants, animals and humans. It is a component of many enzymes and it functions as a specific activator in numerous biological reactions.

Zinc in soils

In igneous rocks zinc substitutes for both ferrous iron and for magnesium and therefore it occurs in greater quantities in the more basic rocks. Typical analyses are as follows; basalts 100 mg/kg, diorites and andesites (intermediate basicity) 70 mg/kg, and granites (acidic) 50 mg/kg. In sedimentary rocks it is more abundant in shales than in sandstones or limestone, 90 and 20 mg/kg Zn respectively being typical contents. Zinc exhibits a chalcophylic nature and is frequently found as the sulphide - sphalerite (ZnS). It may also occur as the carbonate ($ZnCO_3$) e.g., in the mineral smithsonite. Zinc from sulphide minerals goes into solution more easily than it does from silicate minerals and during soil formation may be absorbed on to clays, hydrous oxides of aluminium, iron and manganese, and on to organic matter. Montmorillonite is capable of absorbing quite large amounts of zinc.

The concentrations of Zn in soils are a reflection of the composition of the parent material from which the particular soil is derived. In world soils Zn concentrations range from 1.5 to 2000 mg/kg with a mean

value of 59.8 mg/kg (Ure and Berrow, 1982). Zinc values for non-polluted Irish agricultural soils fall within the range 10-200 mg/kg, whereas the EDTA extractable values are generally in the range 2-15 mg/kg with a mean value of the order of 6.5 mg/kg. The distribution of EDTA extractable Zn values below 2.0 mg/kg in Irish soils are shown in Fig. 10 (page 17) and such values must be considered to be suspect. Inherently low levels of Zn can be expected in sandy soils and in coarse-textured glacial deposits. Deficiency of Zn in susceptible crops can be anticipated on such soils.

Some factors affecting zinc availability

Zinc mainly occurs in soil on surfaces of clays, hydrous oxides and organic matter, rather than the soil solution (Armour et al., 1990) but is taken up by plants from soil solution.

pH The availability of soil Zn to plants is less under high pH conditions than under acid conditions and Zn is particularly unavailable when free calcium carbonate is present in the soil. However, plant species may vary in their response to soil pH as shown by Williams (1977) who by decreasing soil pH increased the uptake of Zn by red clover but not that of oats grown on the same soil.

Organic matter Lindsay (1972) concluded that soluble Zn-organic complexes resulting from reactions with organic acids, amino acids or fulvic acids could increase Zn availability and

that insoluble Zn-organic complexes could increase Zn deficiency.

Soil microbial activity can release Zn from relatively unavailable sources and it is known that mycorrhizal plants can absorb more Zn than uninfected plants.

Phosphorus The enhancement of Zn requirements by P has been produced in plants grown in sand and water culture experiments, with very high levels of P supply (Parker, 1993). Lonergan and Webb (1993) stated that it is likely that "P enhanced Zn requirements" are an artefact of glasshouse trials and have little relevance in crop production. However, Zn deficiency has been reported in Ireland in onions grown on sphagnum peat with a high P content, but there was no deficiency at lower P levels (Gallagher, 1969). The levels of Zn in the peat were, no doubt low, and the deficiency may have been a reflection of a dilution effect brought about by a response to phosphorus.

Nitrogen Nitrogen can cure or enhance Zn deficiencies. Where N is limited, an addition will enhance growth; where Zn is adequate Zn concentrations in plants will increase. The addition of high levels of N where Zn is limited will reduce Zn concentrations and can be attributed to a dilution of Zn in the plant due to enhanced growth.

Zinc concentrations in Irish herbage

The Zn requirements of grazing animals are poorly understood and recent data suggest that requirements were formerly over-estimated (White, 1993). A Zn value of 40 mg/kg has been proposed for the diets of calves and dairy cows (NRC, 1988). The typical range for Zn in non-polluted Irish pasture is 20-60 mg/kg with a mean value of about 30 mg/kg, with 25 percent of herbage samples analysed at Johnstown Castle falling below 25 mg/kg the minimum requirement suggested by Rogers et al. (1989) for Irish dairy cattle. In a study of the trace element content of Irish stud farm pastures Parle et al. (1995) found that 30 percent of herbage samples had values of <25 mg/kg on a national basis: on a county basis 80 percent of samples from Co. Tipperary had herbage Zn values of <25 mg/kg.

There appears to be little variation in levels of Zn in Irish pasture herbage over the grazing season, April to October.

Zinc deficiency in Ireland

MacNaeidhe and Fleming (1988) reported a response in spring cereals to foliar sprays of Zn in an area in north-east Co. Louth. The soils where the response was obtained are formed from material deposited by the drumlin readvance moraine. Other areas in the country with soils derived from glacial and fluvio-glacial deposit have also been identified as being low in zinc. Such areas have EDTA extractable values of <2.5 mg/kg Zn.

Manganese

Manganese (Mn) is essential for both plants and animals. McHargue (1923) showed that Mn was essential for the growth of higher plants and Kemmerer et al. (1931) established a role for Mn in animal health. Deficiencies of Mn can occur in cereal and root crops on soils of high pH and high organic matter. Excessive Ca and P in the diet interfere with the absorption of Mn (Welch et al., 1991). People with poor dietary habits can also be at risk where the optimal Mn is not being met (Kies, 1987).

Manganese in soils

Rocks, in general, contain relatively high levels of Mn when compared with values for most trace elements, except iron. Wedepohl (1979) estimated the Mn contents of various rocks as follows: ultra basic 1050, basalts 1300, gabbros 1100-1300, granites 350, rhyolites 620, limestones 550, gneisses and mica schists 600, shales 600, and sandstones 174 mg/kg, respectively, with an overall mean of 733 mg/kg Mn in the upper continental crust.

The concentration of Mn found in soils is a reflection of the levels that occur in their parent materials. The mean Mn content of 8354 world soils was reported as 761 mg/kg by Ure and Berrow (1982) with a range of <1-18,300 mg/kg. The Mn concentration of most Irish soils fall within the range 20-3000 mg/kg. Mn in soil can be divided into two main forms (1) Mn in primary minerals and (2) Mn in secondary minerals, the latter form

being the more important because of its very high surface activity. The Mn oxides in soils have very high sorption ability and they can accumulate ions from the soil solution. The Mn oxides have a particularly strong affinity for Co ions which can render it unavailable to plants (q.v., under cobalt). Manganese content of soils tends to increase with increasing clay content.

Manganese availability

An important soil factor which influences Mn mobility is soil pH, and the application of lime to acid soils will reduce Mn availability. The application of acid forming fertilisers will decrease pH and increase Mn availability (Miner et al., 1986; Conroy, 1961-1962). It has been shown that the amount of Mn solubilized in the rhizosphere is much greater than that in the bulk solution (Godo and Reisenaur, 1980), and the conclusion reached that Mn availability is neither controlled by soil nor by plant characteristics alone but by a combination of effects of soil and plant properties with the interaction of plant roots

with the soil. The plant root can increase Mn availability by exuding organic compounds which can reduce Mn^{4+} oxides. Some forms of organic material such as humic acid can fix Mn whereas organic matter in general can provide an energy source for microbial reductions to occur in soils. The importance of impeded drainage in the mobilization of trace elements in soils is perhaps not fully appreciated and nowhere is the effect more clearly seen than in the case of manganese. Under the reducing conditions resulting from impeded drainage many manganese minerals become unstable with resultant release of Mn^{2+} ions. These are then readily assimilated by plant roots. The effect is illustrated in Table 15 (Mitchell et al., 1957). Manganese deficiency, however, can occur in poorly drained soils and arise from the solubilization during periods of low aeration followed by leaching of Mn^{2+} below the root zone (Robertson and Lucas, 1981). Drying of soil, combined with high temperatures, can affect the availability of Mn, and Mn deficiency in various crops can disappear after heavy rainfall following a dry period.

Table 15: Manganese levels in herbage from well and poorly drained soils

Drainage status	Mn (mg/kg)			
	Mixed herbage	Cocksfoot	Ryegrass	Red clover
Well drained	47	70	62	33
Poorly drained	134	182	92	46

The determination of the easily-reducible soil Mn (calcium nitrate/quinol) gives a good indication of the availability with values below 50 mg/kg, particularly if liming is contemplated.

Manganese in plants

Manganese is present in plants mainly as Mn^{2+} but it can be readily oxidized, and because of this it has a major role in redox processes such as electron transport in photosynthesis and the detoxification of oxygen-free radicals. In Mn deficiency situations because of restriction of photosynthesis, soluble carbohydrates are largely reduced (Romheld and Margehner, 1991).

The critical deficiency concentration of Mn for barley and wheat about 25 mg/kg Mn in mature leaves (Hannam and Ohki, 1988). The critical deficiency concentrations for brassicas and sugar beet are of the order of 35 mg/kg Mn. Manganese deficiency symptoms in cereals appear as greenish grey spots, flecks and stripes (grey speck) on basal leaves whereas dicotyledons develop inter-veinal chlorosis of the less mature leaves. Manganese deficiency in the pea shows up as dark discolouration of the cotyledons (Marsh spot).

MacNaoidhe et al. (1986) obtained severe Mn deficiency in sugar beet growing on a soil with easily reducible (ER) Mn value of 30mg/kg. Mild symptoms were associated with soil ER Mn values of 60-75 mg/kg. The

Mn deficiency symptoms developed when the foliar Mn levels fell below 30 mg/kg.

Manganese concentrations in herbage growing on typical agricultural soils range from 30 to 500 mg/kg, but, because of the influence of soil reaction, values are encountered outside this range. On very acid soils Mn concentrations in herbage can exceed 1000 mg/kg, whereas on alkaline soil herbage values can be below 20 mg/kg Mn. In a 130 km² area sampled at a density of approximately two samples per km². Mn concentrations in herbage ranged from 35 to 1184 mg/kg (Fleming and Parle, 1981). Soil pH values in this area varied between 4.0 and 7.7 and there was a significant relationship between the soil pH and herbage Mn content.

Correction of manganese deficiency in Ireland

Walsh and McDonnell (1956-57:personal communication) showed that fertiliser fortified with manganese sulphate drilled with the crop controlled Mn deficiency in cereals. O'Sullivan (1974) controlled deficiency in cereals by spraying with manganese sulphate and by drilling in manganese sulphate with the NPK compound fertiliser and showed that broadcasting was ineffective. Five sources of manganese were evaluated by MacNaoidhe et al. (1984) on spring barley and winter wheat and by O'Riordan and Codd (1984) on sugar beet. Responses varied in both trials between the sources of Mn and the different soil types.

IODINE

Iodine (I) is not an essential element for plant growth, but is required by humans and animals, and is a component of the thyroid hormones. Iodine deficiency is a primary cause of goitre. The term "goitre" it is suggested can be replaced by the term "iodine-deficiency disorders" as goitre does not adequately represent the current knowledge on the number of conditions occurring as the results of I deficiency (Hetzl, 1983).

Iodine in soil

The geochemistry of iodine is related to its association with biological processes. The I content of soil varies to a large degree, and, in general, soils are richer in I than are their parent rocks. The amount of I in soils depends greatly on their silt and clay content, the organic matter status and on their location. Atmospheric precipitation is by far the most important source of soil iodine (Fuge and Johnson, 1986). A considerable amount of I enters the atmosphere from the oceans and from the burning of fossil fuels. It is estimated that annually up to 400,000 tonnes of I escapes from the surface of the oceans (quoted by Hetzel and Maberly, 1986). The I content of soils near the sea have been shown to be higher than inland soils. This effect is more likely to be seen with the larger land masses, and is not apparent in Ireland (McGrath and Fleming, 1988) or in Britain where Whitehead (1973) found no significant correlation between I and distance from the

sea. Some coastal soils, however, can have elevated I values resulting from the use of seaweeds as fertiliser source.

The total I contents in 8444 world soils range from <0.09 - 210 mg/kg with a mean value of 7.08 mg/kg (Ure and Berrow, 1982). Fuge and Johnson (1986) suggest that a meaningful average for total content of soils lies between 4 and 8 mg/kg. In general the I contents for Irish soils fall within the range 2.3-14.8 mg/kg with a mean value of 6.2 mg/kg. However, McGrath and Fleming (1988) found that the I content of some soils from the Clonroche Series, Co. Wexford, had values in the range 6.3-24.9 mg/kg with a mean value of 16.9 mg/kg.

Areas in south Tipperary, west Wicklow and south Antrim have been associated with I deficiency in humans (Anon, 1956).

The iodine content of herbage

The I content of pasture herbage, in general, falls within the range 0.10-0.35 mg/kg, with the higher values reflecting the amount of clover in the sward. The I content of herbage bears little relationship to the soil content (McGrath and Fleming, 1988). Butler and Johnson (1957) reviewed the concentrations of I in New Zealand grasses and noted that the soil and seasonal effects were subordinate to variational differences.

McGrath and Fleming (1988) obtained no effect from the application of N and lime on

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the I content of herbage on two Co. Wexford soils, whereas Hartmans (1974) obtained decreases in I content of herbage with the application of calcium ammonium sulphate caused by "dilution" as plant growth rate outstripped the uptake of I from the soil. There appears to be little effect of P and K fertilisation on the uptake of iodine. Farmyard manure has been shown to reduce I levels by more than tenfold irrespective of the form of I applied to the soil (Whitehead, 1975). It would be of interest to know what effect cattle slurry might have on the uptake of iodine.

Soil contamination of herbage can give spurious I analytical values and elevated I plant values must be viewed with suspicion unless accompanied by a titanium plant value. The titanium content is an excellent index of soil contamination.

IRON

Iron (Fe) is a major element in geological terms but behaves as an trace metal in nutrition, and is essential for plants and animals. Most of the Fe in the earth's crust is associated with ferromagnesium silicates. Fe concentrations in rocks vary as follows: igneous rocks 5.6 percent, shales 4.7 percent, sandstone 1.0 percent and limestone 0.4 percent. The mean Fe concentration in soils is of the order of 3.5 percent.

Availability of iron in soil

Under oxidizing and neutral pH conditions Fe is immobilised with minimum solubility in the pH range 7.5-8.5. Calcareous soils fall within this pH range and Fe deficiency is common on these soils. Plants require in excess of 0.5mg/l of soluble Fe to supply nutritional needs (Schwal and Lindsay, 1989). Inorganic Fe (III) oxides cannot maintain this level of soluble Fe in soils above pH 5.5-6.0 : therefore, chelation either by natural or synthetic chelates (organic matter) or reduction of Fe^{3+} to Fe^{2+} (for example at high soil moisture content) is necessary to maintain the solubility of Fe in soil above the critical level (Lindsay and Schwal, 1982).

Nutrient interactions can affect the availability of Fe. For example, N fertiliser such as ammonium sulphate can increase availability through its acidifying effect on soil, whereas high soil P levels can reduce Fe solubility by immobilising Fe (Mandel and Halder, 1980). Zinc deficiency increases Fe uptake by plants whilst very high concentrations of Mn and heavy metals can induce Fe deficiency in plants.

Iron in plants

In practical agriculture and horticulture in Ireland Fe levels in mineral soils are such that a deficiency of the element is a rare occurrence except perhaps in ornamental shrubs growing in garden soils with very high pH values, or crops growing on plaggen (man-made) soils in some coastal areas

where these were large additions of calcareous sands. By contrast with the situation on mineral soils, Fe deficiency of grasses, typified by severe chlorosis, can occur on peatland even under acid conditions. O'Toole (1966) observed such chlorosis in several species on blanket peat at pH values as low as 5.0. Chlorosis varied widely between species and even between cultivars of the same species. In five cultivars of perennial ryegrass the incidence ranged from 15 to 33 percent. Red fescue (*Festuca rubra*), bent grass, (*Agrostis tenuis*) and Yorkshire fog appear to be relatively resistant to Fe chlorosis, whereas timothy is quite sensitive. Spraying with ferrous sulphate or Fe-EDTA is effective in the control of Fe chlorosis (Grennan, 1968). Annual dressings of basic slag are also beneficial. The total Fe content of a plant is of no value in assessing the Fe status. Higher Fe contents are often found in chlorotic compared to healthy material. A measure of the active Fe (generally the ferrous (Fe^{2+}) form in plant tissue is a better indication of the Fe status than total Fe. Measurement of peroxidase activity in fresh tissue has, also, proved a rapid and successful method for diagnosing Fe deficiency in grasses (O'Sullivan, 1972).

From the standpoint of animal nutrition the true iron content of herbage may be of limited significance as animal intakes from soil ingestion frequently exceed those from herbage. Typical Fe values in pasture fall within the range 50-200 mg/kg. Where values exceed 200 mg/kg it can be assumed that

high value results from soil contamination of the herbage.

The Sampling of Soils and

Plant Materials For Trace Analysis

The sampling of any biological materials for subsequent trace element analysis presents a variety of problems depending on the nature of the material. Apart from some obvious precautions which must be taken in relation to contamination, many other factors must be considered and these are discussed below.

Soils

The sampling of soils presents a variety of problems depending on soil type, location, drainage, and such factors as a recent application of lime or fertiliser.

Herbage

Different plant species assimilate varying amounts of trace elements. Factors that affect the mineral content of plants are stage of maturity and season. Under grazing conditions it is not possible to separate these two parameters, but data obtained under cutting conditions are relevant when the material is conserved for silage or hay.

Soil contamination

Soil contamination of herbage is one of the hazards encountered when sampling

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herbage, particularly in a sward that is being or has recently been grazed. It becomes very important when the ratio of the level of a particular trace element in the soil compared with its level in the plant is large. The following elements fall into this category: cobalt, iron, aluminium, iodine, chromium and titanium. The last is the best indicator of soil contamination and any herbage sample with a Ti content in excess of 10 mg/kg should render analytical values for the above trace elements invalid.

Field Sampling

Soil

- 1 Obvious differences such as variations in soil type or drainage, *etc.*, in a field should be noted prior to sampling and the field should be sub-divided and sampled accordingly.
- 2 A soil sample should consist of at least 20 cores taken from *ca.* 2 ha areas. The areas should be traversed in a "W" manner avoiding previous lime and fertiliser deposits, cow pads and their regrowths, and areas near gateways, *etc.* Grassland should be sampled to a 10cm depth and tillage land to plough depth (*ca.* 20cm).
- 3 Sampling should not be undertaken following recent applications of lime or fertiliser.
- 4 Where a problem occurs in a field or on a farm, soil samples should be taken from the "good" and "bad" areas for comparison purposes.
- 5 The soil sampler should be clean and a few cores should be taken and discarded before taking each sample.
- 6 The composite soil sample should be placed in a waxed carton or a clear plastic bag and clearly numbered on the outside. Details should be recorded on the proper form before dispatch to the laboratory.

Herbage

- 1 When sampling plant material it is important that the composite sample is representative of the plant population.
- 2 It is important to ensure that the sward is not soil contaminated. Herbage should not be sampled immediately following grazing because of the percentage of stemmy material likely to be present and because the sward will be soil contaminated.
- 3 Herbage should be cut 2.5 cm above soil level with clean clippers and not allowed to come in contact with the soil. Samples should not be taken by plucking.
- 4 The sampling area should be traversed in the same manner as described for soils. About 30 clippings should be taken to give a total of *ca.* 250 g of fresh material.
- 5 Samples should be collected in clear plastic bags, closed and numbered. Paper or plastic labels should not be enclosed with the samples and bags should not be tied with metal ties.
- 6 Samples should be sent to the laboratory without delay with the relevant information. If this is not possible, they

should be stored in large plastic bag under refrigeration.

- 7 Root crops can be forwarded intact to the laboratory and, in the case of large leafed plants such as cabbages, etc. comparative leaves from a number of plants can be bulked. Soil contamination is not as serious a problem with large leafed plants as they can be easily washed.

Time of sampling

Herbage April/ May when there is a large flush of growth is advised. At this period growth may outstrip uptake. The molybdenum concentration in herbage rises in the autumn with increases in soil moisture and a sampling in late September or early October is recommended.

Analysis

Having regard to the factors referred to above the following analyses should be undertaken:

Soil	Total Cobalt, Manganese and Iodine
Soil reserve	EDTA-soluble Copper EDTA-soluble Zinc Water-soluble Boron Easily-reducible Manganese
Plants	Copper, Zinc, Manganese, Molybdenum, Selenium, Boron, and Iron

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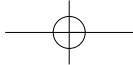
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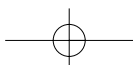
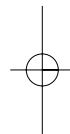
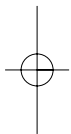
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Trace Elements and Heavy Metals in Irish Soils



Trace Element Deficiencies in Tillage Crops

Introduction

The trace element deficiencies which occur most frequently in tillage crops are boron (B) deficiency in sugar beet and in swedes, manganese (Mn) deficiency in cereals and sugar beet and copper (Cu) and zinc (Zn) deficiency in cereals. Boron is easily leached from soils and is more likely to become deficient in sugar beet and brassica crops than any other trace element but it is applied on a routine basis in compound fertilisers and B deficiency is no less common in sensitive crops. Investigations are at present in progress on Mn in cereals and sugar beet and on Cu and Zn deficiency in cereals. These trials are discussed in this chapter.

Identification of trace element deficiencies

Trace element deficiencies are identified by visual symptoms on plants, by soil analysis and by plant analysis. The relative usefulness of these methods varies between trace element. In some cases there are no visual deficiency symptoms and routine crop examination is of little value. In other cases the trace element content in the soil may be adequate but uptake by the plant may be inhibited. The value of visual symptoms and of plant analysis is often limited by the speed

with which the plant deteriorates before treatment can be implemented.

Visual symptoms

Visual symptoms are useful for the identification of deficiency in cereals and in sugar beet and these crops respond well to foliar sprays. Zn deficient cereal crops also respond well to foliar sprays but it is not yet known if such crops make a full recovery following treatment.

Emergence is sometimes reduced in Zn deficient soils and the reduction in ear numbers can affect the grain yield. In cases of severe Cu deficiency young seedlings begin to die off rapidly as the symptoms appear and spraying must be done quickly to prevent reduction in ear density. Cu deficiency can cause ear sterility or the production of small, shriveled, grain in an otherwise strong and vigorous crop.

¹ **Trace Elements Deficiencies in Tillage Crops** is a composite of the following

- 1 The Proceedings of the Symposium Trace Elements in Soils Crops and Animals, Johnstown Castle, March, 1987. F MacNaoidhe. Edited by G.A. Fleming and P.J. Parle 31 – 42
- 2 Trace Elements in Cereal Crops in Ireland. F.Mac Naoidhe, 1999. The Tillage Farmer 13 - 15
- 3 Boron (Supplied by P. Parle, 1998)

Trace Elements and Heavy Metals in Irish Soils

Soil analysis

Prior knowledge of Cu and Zn deficiency in a cereal crop enables the grower to take preventive action and soil analysis provides this information. Recent investigations have shown that the Mn level in sugar beet foliage increases as the easily reducible (E.R.) Mn level in the soil increases. Further investigations are necessary before these trends are confirmed in other tillage crops but these results indicate that an analysis of the easily reducible (E.R.) Mn content of a soil is useful in predicting manganese deficiency.

The availability of soil Mn and soil Zn is reduced as the soil pH increases and this should be taken into account in the interpretation of soil analytical results. In most soils of pH 7.0 or greater, there is a yield response in cereals to Mn sprays when the E.R. Mn value falls below 50 mg/kg. In sugar beet Mn deficiency symptoms begin to appear at a soil pH of 7.5 - 8.0 when the E.R. Mn level is at 60-75 mg/kg and symptoms are severe when the E.R. Mn level falls below 30 mg/kg.

In cereals Zn deficiency symptoms are severe when the EDTA-extractable levels are less than 1.0 mg/kg and the soil pH is 6.0 - 7.0. At a pH value above 7.0 Zn deficiency symptoms may be severe at soil levels of 1.0 - 1.5 mg/kg. Zn deficiency causes more severe crop injury when the soil phosphorus (P) is high. It is less severe when the soil organic matter is high. For this reason Zn

deficiency occurs most frequently under conditions of intensive tillage. The response to zinc sprays is increased by the application of nitrogen (N) and magnesium (Mg). The analysis of soil samples throughout the country shows that soils which are deficient in Zn are also quite likely to be deficient in Mg. Trials are at present in progress to test the response of cereal crops to combined Zn + Mg treatment.

The availability of soil Cu to the plant is not greatly affected by soil pH or by the presence of high concentrations of other elements. A high organic matter content reduces the availability of copper to the plant because part of the organic fraction forms a strong bond with the Cu ion. In soils with a heavy texture, copper deficiency does not occur unless the EDTA-extractable Cu level in the soil falls below 1.0 mg/kg but in light textured soils copper deficiency may occur at soil levels up to 2.5 mg/kg.

A number of different reagents are used to extract trace elements from soils. These include acids of varying strengths, salt solutions, organic extractants and combinations of all three. The extractants most frequently used in soil laboratories are those which purport to remove from the soil only the chemical form of a trace element which can be used by the plant. Some extractants do this more effectively than others. The extractants used by An Foras Taluntais are closely related to a group of chemicals which are synthesized by the plant

and are active in the transportation of trace elements from the roots to other plant parts. Such extractants provide an excellent estimate of the amount of utilizable trace element in a soil. The value of a given analytical method is measured by the relationship between the soil and plant levels of the trace element and by the response that is obtained from crop treatment following the diagnosis of a deficiency. The accuracy of the analytical methods used at Johnstown Castle is frequently checked in field and laboratory trials.

A number of commercial companies have been providing an analytical service for soils and crops in recent years. These companies use some soil extractants that are different from those used at Johnstown and the results cannot be compared. Attempts have been made in the past at international level to introduce standardised methods for the extraction of different trace elements from soils. These attempts have failed mainly because there are large differences between soil types and between other soil factors. Consequently an extractant that gives a satisfactory result in one country is often found to be unsuitable in another. Chemical extraction of trace elements from soils is a time consuming operation. The use of a single extractant per element reduces the rate at which analytical data is produced. Extractants, which are suitable for the extraction of several trace elements, are continually being developed by An Foras Taluntais. These extractants will hopefully

result in a more rapid turnover of analytical results and will make routine analysis of trace elements more feasible. However, caution is needed to ensure that the precision and reliability of the analytical results is not impaired by the use of multi-element extractants.

Plant analysis Analysis of plant tissue generally provides a useful measurement of the trace element status of plants. However, a proportion of the trace element extracted from plant tissue is in a chemical form that is not readily available for use by the plant and this is not taken into consideration when acid extraction of plant tissue is used in analysis. There is poor translocation of some trace elements from old to young tissue and for this reason young tissue should be used in trace element analysis.

Recent experiments in cereals and in sugar beet have shown that the levels of trace elements in the foliage of these crops change during the growing season. The critical level at which a deficiency occurs also changes with plant age and it is not always possible to give the precise levels at which the deficiency occurs. Mn deficiency is likely to occur in cereals when the level in the foliage falls below 25 mg/kg. In sugar beet, deficiency symptoms begin to develop when the level in the foliage falls below 35 mg/kg. Cu and Zn deficiency are likely to occur in cereals and in sugar beet when the foliar levels fall below 3 mg/kg and 15 mg/kg, respectively.

Prevention of trace element deficiencies

The risk of trace element deficiencies in cereals and in sugar beet is obviously reduced when steps are taken to ensure that there is a good nutrient balance in the soil. Excessive lime application should be avoided. A high soil pH increases the risk of Mn and Zn deficiency. Heavy applications of P can increase risk of Zn deficiency and high N applications increase the risk of Cu deficiency in cereals. A soil analysis should be carried out every 4-5 years to assess the levels of the different trace elements in soils.

Control of trace element deficiencies

Manganese deficiency is effectively controlled by the application of foliar sprays of manganese compounds. Combine drilling of manganese sulphate also gives satisfactory results. Broadcasting of manganese sulphate is not recommended. Spraying with manganese is not recommended unless the soil or the crop is deficient in this element. There is an absence of response to different manganese compounds by healthy crops of cereals and sugar beet. However, the response to Mn sprays increases as the soil Mn level decreases. The response is also better in dry years than in wet years. Seed dressing with manganese oxide increases the Mn level in the foliage. More recent results have shown that the application of this seed dressing can increase the root and sugar yields.

BORON (*Supplied by P Parle, 1998*)

Boron (B) is essential for plant growth and there is some evidence to suggest that it has a role in animal nutrition (Nielsen, 1986). Boron is one of the less abundant elements with an average value of ca. 10 mg/kg in the earth's crust. The B concentration in rocks ranges from 5 mg/kg in basalts to 100 mg/kg in shales. Total B values for Irish soils fall within the range 20-100 mg/kg, however, the total content is of little value for assessing availability. The water-soluble fraction represents the B which is readily available to plants, and this fraction can be quite variable depending on soil texture and reaction. The water-soluble B concentrations in Irish soils normally fall within the range 0.1-4.0 mg/kg with a mean value of the order of 0.75 mg/kg.

Some factors affecting availability

Liming Liming reduces the availability of boron. This reduction in availability following liming arises from several reactions or processes (a) the adsorption of B on freshly precipitated Al (OH)₃, which accounts for most of the B adsorption, (b) the formation of insoluble meta-calcium borates and (c) in the case of peat soils the reduction in availability is ascribed to the formation of boric acid esters with higher alcohols.

Organic matter The greater availability of B in surface soils compared to subsurface soils is related to relative organic matter levels and in humid regions, where soluble salts are leached out, available B is largely held in the

organic matter. Organic matter can assist in reducing B loss from soils and at the same time hold the element in an available form. Although organic matter does influence B availability it is greatly conditioned by such factors as moisture content of soil, the pH status and the degree of decomposition of the organic matter.

Soil moisture Boron availability has been shown to decrease under dry conditions and B deficiency is associated with dry summers. This can partly be explained by the plant's inability to utilise soil boron due to lack of moisture in the root zone. When the surface dries out, roots are forced to explore deeper horizons and B availability has been shown to decrease with depth.

Soil texture It is self evident that there is a greater movement of nutrients in sandy soils than those of heavier texture. Light-textured soils contain less available B than do the heavy-textured soils and B deficiency is more common in them.

Relationships with other elements

Nitrogen Nitrogenous fertilisers as such do not seem to affect B availability but where B soil concentrations are low, the increase in growth resulting from the use of N would predispose towards deficiency.

Trace Element Deficiencies in Cereal Crops In Ireland

This section, pages 74-79 and including Tables 1-3, has been taken from Mac Naeidhe, 1999.

There has been an increase in the use of trace element compounds in cereal crops over the past 15-20 years. The cost of production of cereal crops has been rising rapidly in recent years and the application of trace elements adds to this cost. Because of this it is important to determine if trace element application is beneficial.

The need for trace element application in cereals is conditional on the history of individual fields or farms, on modern fertiliser practices, and on soil type. Trace element deficiencies occur most often in fields, farms or localities with a history of such deficiencies. When there is no history of trace element deficiencies in an area and the crop appears healthy and yields are normal there is no need to apply trace elements.

The importance of trace elements in tillage crops

The incidence of trace element deficiencies in cereal crops has increased greatly in the last 20 years. The reasons for this are as follows:

- 1 The increase in the use of artificial fertilisers and lime has induced trace element deficiencies in some soils and crops.

Trace Elements and Heavy Metals in Irish Soils

- 2 The introduction of high yielding varieties has led to an increased demand for trace elements in crops.
- 3 Improved manufacturing techniques in fertiliser production has led to a removal of trace element and secondary element contaminants in fertiliser and the loss of this source has reduced soil concentrations of some trace elements.
- 4 The use of several trace element containing products such as fertilisers and fungicides has been discontinued and the loss of this source has reduced soil concentrations of trace elements.

progresses northwards to an average of 7 mg/kg in the midlands and 14 mg/kg in the north. Manganese deficiency occurs in mineral soils with a pH of greater than 7.0 and in peat soils with a pH of greater than 6.0. Overliming has in the past been the main cause of manganese deficiency. In the midlands many of the soils have a high pH due to a high calcium carbonate content and manganese deficiency in cereals is common in these soils. Zinc deficiency is most common in soils that are derived from shale. Zinc deficiency cannot be ruled out in the sandy soils in the south of the country and in the shale and granitic soils in the extreme east near the Wicklow-Kildare border.

Trace element and some other mineral deficiencies in cereals - general

The three most common trace element deficiencies in cereals are manganese, copper and zinc. Boron deficiency has not been diagnosed in cereal crops in the field. Iron deficiency has been identified in cereals on raised and blanket bog but is rare in mineral soils. Magnesium and sulphur deficiency have occurred in light sandy soils and in soils with poor structure. Sulphur deficiency has also occurred in cereals in sphagnum peat soils. Copper is low in peat and peaty soils, in granitic soils, and in the light sandy soils in the south.

The soil copper concentrations are low at less than 3 mg/kg (EDTA extract) in the south (Cork, Waterford) and increase as one

Soil analysis

Soil analysis gives a reliable indication of copper and zinc deficiency in cereals. The soil levels of copper at which deficiency occurs depends on the soil type. In light soils copper deficiency is likely to occur at EDTA-extractable levels of less than 2.5 mg/kg but in heavy soils deficiency is not likely to occur until the extractable levels of copper fall below 1.0 mg/kg. Soil analysis does not always give a reliable guideline to deficiency or sufficiency of manganese in the soil. As the pH rises manganese becomes less available to the plant. Thus, increasing the soil pH above 6.0 increases the risk of manganese deficiency when the easily reducible manganese level is less than 50 mg/kg. When the soil pH is greater than 7.0 an E.R. manganese value of

less than 30 mg/kg will probably produce manganese deficiency.

Guideline levels for the different trace elements in soil are given in Table 1.

Diagnosis by plant analysis

Analysis of plant tissue gives the most reliable diagnosis of the deficiency or sufficiency of a trace element. However, there

is increasing evidence that the chemical forms of different trace elements within the plant has an important effect on their availability in the different growth processes. It is also important that the tissue within which a particular trace element is most active should be analysed, i.e. the younger tissue. Analysis of the whole plant may not show deficiency although such a deficiency may be present and may be severe. High and low levels of trace elements in cereal crops are given in Table 2.

Table 1: Levels of trace elements in tillage soils (mg/kg)

Element	High	Normal	Low
Manganese (easily reducible)	350	100 - 200	50
Zinc (EDTA extract)	200	2 - 15	2
Copper (EDTA extract)	30	3 - 10	1.5

Table 2: Levels of trace elements in cereal crops (plant tissue)

	High (mg/kg)	Medium (mg/kg)	Low (mg/kg)
Manganese	380	30 - 200	20
Zinc	230	25 - 150	20
Copper	50	8 - 20	5

Trace Elements and Heavy Metals in Irish Soils

Climate

Copper and manganese deficiencies occur more readily in well drained soils and under dry conditions. In a very dry spring and early summer reports of copper and manganese deficiency are frequent but reports of such deficiencies are few during wet spring periods. Drought induced manganese and copper deficiency is less common in winter- than in spring- cereals because the root system in the former is well developed by late spring when drought is most likely to occur and can absorb these elements from the deeper parts of the soil profile.

Winter cereals will be affected by drought-induced deficiencies in shallow soils. Zinc deficiency is more severe during cold spring weather than in a warm spring. Symptoms of zinc deficiency may disappear with a rise in temperature and may return when the temperature drops. Soil moisture has a strong affect on the availability of trace elements. The foliar concentrations of a number of trace elements in the same soil in a wet and a dry year are shown in Table 3. The soil test concentrations are more or less similar but the foliar concentrations are much higher in

the wetter year due to the high soil moisture. Temperature also affects trace element availability and uptake. Trace element deficiencies are more common during cold periods than during warm wet periods.

Trace element flushes

The amount of available trace elements which are present in a soil is variable. In the autumn and winter period trace element uptake by plants is low. Trace elements are carried in the soil moisture and when the moisture content drops the quantity of available trace elements also decreases. The periods during which trace elements are most available to the plant are described as flush periods. These occur in random fashion when there is an increase in soil temperature or soil moisture. The plant roots can induce increases in the availability of certain trace elements by producing root exudates that cause the trace element to be released in larger quantities from the soil. The root exudates are often released during the period at which the demand for the trace element by the plant is greatest.

Table 3: The effect of rainfall on available trace elements in soils

	Rainfall/Month (May-Sept)	Soil test concentration (mg/l)				Foliar concentration (mg/kg)			
		B	Mn	Cu	Zn	B	Mn	Cu	Zn
1990	6.4	0.91	84	3.7	2.1	34	51	5.1	19
1991	37.4	0.88	91	3.6	2.4	82	111	7.4	27

Trace element uptake

Trace elements are absorbed through the roots of plants by osmotic pressure and are carried up through the xylem tissue in the mass flow. There are negative ionic charges present on the xylem walls and the trace elements are trapped on the xylem walls by these negative charges. Organic carriers that are manufactured within the plant remove the trapped trace elements from the xylem wall and the trace elements are transported in a chelated form. The organic molecule protects the trace element from being trapped or fixed by negative ions.

In recent years a number of commercial trace element compounds have become available for application in cereal crops. These include chelated compounds and special formulations of inorganic compounds. The chelates and inorganic formulations are more soluble in water and are more compatible with other compounds than the untreated inorganic salts. They are less liable to scorch and may be applied in lower volumes of water. Consequently, less tractor journeys to and from the field are necessary. However, the commercial compounds are more expensive than the inorganic salts. Trials over the past 15 years have shown that none of the compounds tested has a clear advantage over the other in terms of yield response.

Control measures

The following control measures are used where different trace element deficiencies occur.

Manganese

- Manganese sulphate 5 kg/ha as a foliar spray
- Manganese chelates as recommended
- Manganese inorganic formulations as recommended

Copper

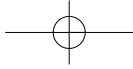
- Copper sulphate 20 kg/ha as a soil dressing
- Copper sulphate 2 kg/ha as a foliar spray. Copper chelates as recommended. Copper inorganic formulations as recommended

Zinc

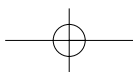
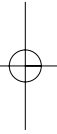
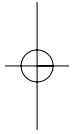
- Zinc sulphate 20 kg/ha soil application (broadcast)
- Zinc sulphate 5 kg/ha foliar spray
- Zinc chelate foliar spray (as recommended)
- Zinc inorganic formulations as recommended

Boron

- Soil application of sodium borate at 35 kg/ha or solubor at 20 kg/ha
- Solubor 2 kg/ha as foliar spray
- Flowable boron applications as recommended by the manufacturers. All spraying operations should be carried out in the late morning or early evening on sunny days to avoid the risk of crop scorch. On dull days spraying may be carried out at any time but application prior to rain should be avoided. The sulphate salts of copper, manganese and zinc should be applied in 450 l/ha water.



Trace Elements and Heavy Metals in Irish Soils



¹Heavy Metals in Soils of Ireland (Southeast)

Summary

The south-eastern region of Ireland representing 22% of the land area of the country was systematically sampled. These soils have now been archived and are available for future analyses as required. Analyses conducted to date, the results of which are discussed here, are for soil parameters pH and organic matter, for major components, aluminium, iron, and for trace elements (heavy metals) arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel, selenium and zinc.

Results have been statistically analysed and frequency distributions have been calculated. Geographic distributions have also been plotted and localised concentrations have been found for most elements. Geochemical factors are considered to be largely responsible for most of these localised concentrations. Aerial deposition of lead and selenium was also indicated.

Overall, little serious contamination of soils, especially caused by man and attributable to toxic elements, was evident. However, 21% of soils breached the provisions of the EU Sewage Sludge Directive for heavy metals in soil.

Introduction

Soils are complex systems with physical, chemical and biological characteristics that vary over time and space. Major components including silicon, aluminum and iron along with oxygen, are responsible for much of the soil matrix. Other major components include but are not confined to manganese, magnesium, potassium, calcium and titanium. A large number of other elements are often described as trace elements when viewed as beneficials and heavy metals when present in amounts considered excessive or when known to be intrinsically hostile to living organisms at any level. The more significant ones number by common consent: cadmium, copper, mercury, nickel, lead and zinc. These elements are listed in the EU sewage sludge directive relating to the use of sewage sludge in agriculture (EEC, 1986), a document that is responsible for almost the totality of legislation relating to soil contamination by heavy metals within the EU. In addition, other elements including especially arsenic, chromium, cobalt and selenium that have comparable environmental impacts are included in a number of national regulations. All these elements have wide industrial usage, all are present in wastes, including fall-out that uses soil as a major sink. All are physiologically active with significant effects on micro-organisms, higher plants and on animals including humans. All have known pathways that

¹**Heavy metals in soils of Ireland (southeast)** was taken from the End of Project Report, No 4268, by D. McGrath and R. J. Mc Cormack, 1999.

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allow for movement to foodstuff and to water. All are toxic in excess and some have been implicated in human illness including carcinomas, hypertension and heart disease.

Information on biologically active inorganic components of soil is relatively haphazard. In the past it tended to be related to individual problems and to baseline surveys. However, a considerable number of countries especially in Europe and in North America have now conducted large sampling programs - often to national level. Surveys have been conducted in England and Wales (McGrath and Loveland, 1992), Scotland (Reeves and Berrow, 1984), Northern Ireland (Cruickshank, 1997), Spain (Tobias *et al.*, 1997), Denmark (Bak *et al.*, 1997), the USA (Holmgren *et al.*, 1993), Florida (Chen *et al.*, 1999) and Belgium (Tack *et al.*, 1997). Some of these studies have accompanied national soil surveys. The information that is generated subsequent to sample acquisition is essential in a number of contexts. These include (a) the fixation of norms in order to sensibly interpret ongoing analyses and (b) the location of areas with abnormally high or low values. In addition, in the Irish context there is a presumption, because of a number of factors including the low degree of past investment in heavy industry, our low usage of sewage sludge in agriculture and our low population density, that our soils, a vital and indispensable link in the food production chain, must be clean. This was considered to be a presumption worthy of confirmation, in the present pollution-

conscious age, as it could not but assist in the marketing of our produce.

Experimental

Soil sampling Soils were taken at fixed locations, two from each 10 x 10 km segment of the National Grid: one location corresponded to each intersection and one to each centrepoint. In order to avoid the problem presented by map corners, each location was moved exactly 1 km to the north and 1 km to the east of the defined position. In the event of it not being possible to take a sample at the sampling position, a default procedure similar to that used in the Geochemical Survey of England and Wales (McGrath and Loveland, 1992) was used. Sampling was next attempted at a point 50m N, then E, S and W in turn with the procedure being repeated at a distance of 100m, 200m and 400m until successful or until a distance of 800 m (in two instances) from the original point was reached. Sites were located using 1:25,000 maps assisted by GPS. At sampling, soil cores were taken to a depth of 10cm at 5m intervals on a grid measuring 20m x 20m and with the center point of the grid at the sample location. Dutch auger was used. Cores (25) were combined: the composite sample weighed about 2 kg. The sample was air-dried at room temperature, sieved to pass a 2mm mesh and stored in an all-glass jar.

Sample digestion for heavy metal analysis

Before analysis samples required digestion. Soil was further ground in a mortar and

pestle to pass a 0.42mm nylon mesh. An aliquot (250 mg) was then placed in a teflon vessel (100 ml capacity) with water (10 ml), HNO₃ (3ml), HF (4ml) and HCl (1ml). It was then subjected to microwave irradiation for 30 minutes in a CEM Digestion System Model MDS 2000. Each set of 12 digests consisted of 10 treatments, a certified reference material CRM 142 R (BCR, 1994) and a reagent blank. Power output was 630 W and maximum pressure was 0.83 MPa. Following cooling, each digest was treated with crystalline H₃BO₃ (2g) to destroy excess HF and made up to 50 ml (53.95g) in a polythene container. Digestions of soil by less severe but established procedures were used for analysis of Hg, Se and As.

Analysis of inorganic components Analysis for Cr, Cu, Pb, Ni, Zn, Al, Fe and Mn were performed using flame atomic absorption. For Al nitrous oxide was used instead of air as oxidant. Cd and Co were estimated by electrothermal atomic absorption. Arsenic (as hydride) and Hg were estimated by cold vapour atomic fluorescence. Selenium was estimated as its DAN complex by fluorimetry. All results were corrected for sample moisture. Organic carbon was estimated by the Walkley Black method (Byrne, 1979).

Results

Sampling In order to ensure a complete and unbiased coverage of the surveyed area, a grid system was adopted. Positions given by

the grid or, in the event of it not being possible to sample at the point, the default position, each provided a sample taken from a 20 x 20m area. Grassland (in the broadest sense ranging from top class sward to heath), tillage, forest and peat were adopted as land use classes suitable for sampling. Areas that failed to provide a sample (9 sites) were largely mountainous but a variety of other causes of failure were encountered. A total of 295 soils were sampled comprising 231 grassland, 30 tillage, 26 forest and 8 peat (Table 1).

Analysis Analysis to date has been completed for a wide range of chemical parameters. These discussed here are confined largely to the potentially toxic inorganic and persistent anthropogenic organics. Inorganics include Cd, Cu, Hg, Ni, Pb, and Zn [all of which are included in the Sewage Sludge Directive as adopted by Ireland (SI 148 of 1998)] and the elements As, Cr, Co and Se that, because of their known impacts, are variously included in a number of national sludge protocols. Because of their known influence on heavy metal occurrence and behaviour, other parameters including pH, organic carbon and total Al, Fe and Mn are also reported. Metals were extracted from soil using hydrofluoric acid which ensured a complete release of all metals. The procedures involved, together with the validation of the results have been discussed in some detail (McGrath, 1998).

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Table 1: Heavy metal concentration (mg/kg DM) in soils by land use

Land use	No	OC g/kg	As	Cd	Cr	Cu	Hg	Ni	Pb	Se	Zn
Pasture	231										
Mean		64.3	15.7	0.52	49.5	18.0	0.11	13.4	30.0	0.77	73.1
SD		56.2	12.9	0.42	19.5	9.5	0.09	9.2	14.1	0.84	32.7
Tillage	30										
Mean		37.0	16.4	0.76	67.6	19.1	0.11	23.3	30.3	0.69	88.6
SD		34.3	10.6	0.71	52.6	8.5	0.05	26.6	14.6	0.24	42.4
Forest	26										
Mean		152.8	12.8	0.29	42.5	8.7	0.15	5.5	38.1	0.87	38.0
SD		111.1	15.5	0.29	24.3	5.9	0.09	5.6	10.8	0.31	25.2
Peat	8										
Mean		437.7	3.1	0.35	6.0	4.9	0.13	4.4	17.6	0.87	26.2
SD		15.9	1.3	0.20	2.0	3.3	0.09	4.2	11.7	0.24	25.2

Archiving

Soils have been stored in all glass bottles and are available for future analysis. This is considered to be a major part of the project. Interest in and the significance of soil components by the element and by their chemical speciation is being continually broadened as environmental imperatives dictate. Elsewhere use is being made of archived samples for new investigations even where they are not always tailor-made for the purpose.

Examination of results - summary statistics

Results were subjected to statistical examination. They are presented firstly by

land use type (Table 1). In addition frequency distribution of all the results are presented as 100, 95, 75, 50, 25, 5 and 0 percentile values (Table 2). Finally, multiple regression analyses using the backward elimination procedure (SAS) has been performed (Table 3) in order to clarify linkages between elements that tend to have similar geological origins or to subsequently develop chemical associations in the soil matrix.

Geographic distribution of elements

Considerable information may be acquired by plotting the geographic distribution of each element. As far as possible, threshold or other value (limit, trigger, cautionary, action) that has acceptance and which has found a

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practical application was used. The most frequently used threshold values are those for Cd, Cu, Hg, Pb, Ni and Zn levels in soils that receive sewage sludge. In this investigation we have used these values to indicate soil levels that are generally taken as being acceptable and have plotted the geographic distribution of values exceeding 75% and 100% of the EU soil value for these elements. These plots are in the End of Project Report which may be obtained from the internet. For As and Co we have taken the 95% percentile value, for Cr the value contained in EU proposals (but which stopped short of Directive status), and for Se a reasonable

precautionary level of 5 mg/ kg (Fleming and Parle, 1987), to serve broadly similar purposes.

Consideration is also given to examining the geographic distribution of four elements Co, Cu, Se and Zn at low levels. The latter elements are essential for animal well being and their impact of deficiency levels are significant in Ireland whereas their impact at toxicity levels, except for Se in Se enriched areas, are generally very minor. Since levels of these elements are low in forest and peat soils, levels in grassland and tillage soils only are considered here.

Table 2: Percentile values

Element	Percentile						
	Max	95	75	50	25	5	Min
Arsenic (mg/kg)	100.2	42.0	16.5	11.9	8.7	4.1	1.1
Cadmium "	3.24	1.48	0.61	0.39	0.24	0.12	0.00
Cobalt "	53.3	20.6	13.5	9.8	5.8	2.2	0.0
Chromium "	322.6	88.5	61.7	47.3	34.4	12.8	3.7
Copper "	72.6	34.2	22.4	14.9	10.1	4.3	1.2
Mercury "	1.05	0.23	0.14	0.09	0.07	0.04	0.2
Lead "	108.5	59.3	34.7	26.5	20.8	14.6	3.7
Nickel "	150.2	29.5	18.5	12.2	5.2	1.1	1.0
Selenium "	9.71	1.59	0.84	0.62	0.46	0.36	0.20
Zinc "	239.5	134.1	68.2	43.7	21.8	18.1	3.3
pH	7.5	7.2	6.6	6.2	5.8	4.1	3.6
Organic carbon (g/kg)	463.4	333.3	72.3	50.2	37.5	22.7	12.0
Aluminium (g/kg)	89.1	77.3	49.2	35.2	21.8	0.9	0.0
Iron (g/kg)	59.4	38.7	27.1	21.0	15.5	7.2	0.5
Manganese (g/kg)	5.97	2.00	1.09	0.69	0.34	0.08	0.01

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Table 3: Significance of regression relationships ($P \leq 0.01$) between heavy metals and major soil parameters in multiple regression relationships in agricultural soils (n = 261)

Metal	Al	Fe	Mn	OC	pH
As	++	++	+++	+++	
Cd	++		+++	++	++
Co		+++	+++		++
Cr	+++	+++			
Cu		+++	+++		
Hg			+++	+++	
Pb			+++		++
Ni		+++			
Se		++	++	+++	
Zn		+++	+++		+++

+++ Significant at $p \leq 0.001$ ++ Significant at $p \leq 0.01$

_ Negative relationship

Discussion

Heavy metals by land use Concentrations of elements in soils (Table 1) generally followed the sequence tillage > pasture > forest > peat. Differences between tillage and pasture, for Ni and Cd for instance, may have been influenced to some extent by geographic location as discussed later. However, low levels of Cu, Ni and Zn found for forest soils and still lower values for peat soils will have resulted in large part from increased mobilisation and leaching as pH decreased.

Contrariwise for some elements, including Hg and Se in both peat and forest soils and for Pb, but not Cd, in forest soils, a slight increase was evident. Increased adsorption by soil

following aerial deposition may have been responsible for this. The situation regarding Pb and Cd is interesting. In some countries a sizeable increase in forest soils for both Pb and Cd especially has been found and is attributed in large part to deposition *via* leaf absorption from smelter and incineration emissions. The increase of lead in forest soil it is suggested, arose from the use of lead in petrol. The impact of Cd emissions is clearly lower here, in the absence of large-scale incineration, than in many other countries.

Levels of elements in soils The frequency distributions of elements in all soils examined together with some relevant parameters, organic carbon, pH and Al, Fe and

Mn are shown in Table 2. No instance of serious pollution except for one soil with elevated Se (9.71 mg/kg) was evident, but many soils (largely forest and peat) had extremely low levels of elements including those essential for plant and animal well being.

When multiple regression analyses were performed on major soil components in agricultural soils (omitting forest and peat soils) many significant relationships between element and soil Fe or Mn were noted (Table 3). Similar type relationships were found for the total soil population. Significant relationships were again found with organic carbon for As, Hg and Se. The positive relationship between Zn or Cd and pH again supports the suggestion that these elements are more prone to retention in soils with higher pHs.

Geographic distribution

Organic carbon and pH There were some regional effects for organic carbon and for pH. Low organic carbon values were most strongly associated with soils of south Kildare (tillage mostly), Laois and south Tipperary. Higher pH values were most frequent in the limestone areas of north Carlow and south Kildare whereas low pHs were most strongly associated with Wicklow.

Sesquioxide elements Mapping of grassland and tillage soils for Al, Fe and Mn showed

approximately similar distribution pattern held for all three metals. High concentration areas coincided with soils of the Clonroche soil series that are known to be rich in these elements.

Arsenic Little has been reported to date on levels of this element in Irish soils. Values now found appear to be higher than the mean of soils worldwide at 11.3 mg/kg (Bowen, 1982). Slightly elevated values here are probably largely due to the association of As with sesquioxides in an area stretching from north Wicklow to east Waterford. These values exceed the 10-40 mg/kg concentration values variously postulated as thresholds (O'Neill, 1990). The maximum value of 100 mg/kg is still far short of the levels associated with areas that have suffered contamination with waste from base metal mining or from arsenical pesticides in the past. Similar to Hg and Se, chemical speciation is important in determining mobility and availability of As. Some clarification of the chemical forms of As in Irish soils and their influence on plant and water appears to be needed.

Cadmium Information on Cd in Irish soils is relatively scarce. It is known that elevated Cd levels of 1-3 mg/kg frequently occur in soils derived from a belt of limestone shale stretching from north Clare to southwest Limerick (McGrath, 1996). A second area with elevated Cd now appears to include north Carlow and south Kildare. Soils with values in excess of 1 mg/kg Cd are generally considered to be polluted. Even on soils with lower (*ca.* 1.0

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mg/kg) Cd levels, grazing livestock have been found to accumulate Cd in kidney and liver and this has led to restriction in the sale of these body organs in Australia and New Zealand (Roberts, Longhurst and Brown, 1994). Elsewhere, concern about the negative environmental effects of the element is also widespread but consequences for human health have not yet been fully clarified. There would appear to be a need to at least determine the impact of soil Cd on levels of the element in food of both plant and animal origin.

Chromium Again, Cr is an element that is associated with Clonroche soil. The levels determined are considered to be innocuous.

Cobalt Cobalt is associated with Fe and Mn in our soils. It is known that uptake of Co by plants is strongly influenced by oxides of Mn, especially, and Fe (Fleming, 1983). The soil test for Co (Coulter *et al.*, 1996) considers both Co and Mn levels in predicting the status of the soil in supplying Co to the grazing animal *via* the plant. The occurrence together of both elements highlights soil ingestion as a source of Co to the animal and begs the question as to how available is Co in this form to the animal.

Copper Only two instances of elevated Cu were found. One of these was from the Avoca area of Wicklow, which is known to have suffered extensive pollution by this element from mining activities in the past.

Mercury Hg in Irish soils was present in small amounts, generally less than 0.09 mg/kg. However, one area with slightly elevated levels, Wicklow, was identified. Such a localised concentration could not have been predicted and indicates the necessity to conduct a base line survey before initiation of any activity that could possibly increase metals in the area in order to forestall the possibility of subsequent, incorrect, assignment of pollution.

Nickel Nickel, similarly to Cd, is associated with limestone soils in north Carlow-south Kildare. Levels are not high except in the context of the limit in the EU Directive. Localised increases in Ni have been found elsewhere in Ireland (McGrath, unpublished, 1998).

Lead It has already been shown that Pb levels in Irish agricultural soils were low - much lower than in an urban area (McGrath, 1995) and this was confirmed by the survey. Nevertheless, concentration effects were still evident. These were associated to an extent with eastern and southern areas. It is not clear to what extent lead in soil is affected by adsorption on sesquioxides or by association with organic matter. The possibility of long-range transport which is known to occur in the south of Norway for Pb (Steinnes *et al.*, 1989) and in Ireland for sulphur (Bowman and McGettigan, 1994) cannot be ruled out.

Selenium Higher levels of Se occur in peaty phases of sedimentary soils in isolated

pockets (Fleming, 1962). Two values in excess of a precautionary level of 5 mg/kg were found in the survey.

Zinc This element like Cu was not found in excess in any area. However values exceeding 75% of the threshold were commonplace.

Lower levels of Co, Cu, Se and Zn

Forest soils and peats which do generally contain exceptionally low levels of Co, Cu and Zn, were excluded and the remainder, numbering 261, were examined for distribution of Co, Cu, Se and Zn at low levels.

Cobalt It is known that some areas, generally with granitic or peaty soils, have low levels of this metal. In the present investigation there seems to be some contradiction between what was expected (Fleming and Parle, 1987) and what was found. Granitic soils of Carlow-west Wicklow and those of west Waterford did not exhibit low Co in the present investigation, whereas soils of east Waterford – south Kilkenny undoubtedly did. This matter should be clarified.

Copper and zinc Prediction of insufficiency of these elements in soil for the satisfying of animal requirements may be made using EDTA extractable Cu and Zn values. Levels considered here are for total soil contents, which is not the same. However, it is probable that areas with very low indigenous soil Cu will tend to produce deficiency problems especially in grazing animals. Pockets of

lowest Cu and Zn were found to coincide in two areas, west Waterford and Offaly.

Selenium Lower levels of Se were evident in counties Kilkenny and Tipperary. It is known (Haygarth, 1994) that soils in coastal areas or close to emission sources are richer in Se than some inland areas and this may account for the phenomenon. However, some coastal, sandy, soils also had low Se. Most of the selenium in soils is unavailable for plant uptake. Total soil Se in the Kilkenny – Tipperary area is high in relation to the threshold value considered liable to lead to deficiency diseases in humans (Tan *et al.*, 1994). Nevertheless without knowledge of chemical speciation, this area must be considered more likely to provide less Se for animals than any other area in the region.

Use of soil for sewage sludge disposal

The provisions of the sewage sludge directive were designed to set specifications for quality. Using this indicator the performance of Irish soils may be viewed (Table 4). A total of 54 agricultural soils, or 21% of those in the region, exceeded the threshold values set for one or more elements. Some areas, and in particular Kildare, were found to have a high proportion of soils that are unsuited to the receipt of sewage sludge (Table 5). Three elements Cd, Ni and Pb exceeded their thresholds much more often than did Cu, Hg or Zn. Higher quality was found for pasture than for tillage soils. Forest soils were affected most by Pb.

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Table 4: No. of sampling sites exceeding threshold for heavy metals by land use

Element	Threshold level (mg/ kg)	Incidence of exceeding threshold level			
		Pasture (n=231)	Tillage (n=30)	Forest (n=26)	Peat (n=8)
Cd	1	21	7	1	0
Cu	50	2	0	0	0
Hg	1	1	0	0	0
Ni	30	10	4	0	0
Pb	50	18	6	6	0
Zn	150	3	1	0	0
By one or more		41	13	7	0

Table 5: Location of soils excluding forest and peat unsuited to receipt of sewage sludge

County	No. of soils analysed	No. with excess heavy metals
Carlow	17	4
Cork	3	0
Kildare	19	12
Kilkenny	40	4
Laois	31	45
Offaly	21	4
Tipperary	40	3
Waterford	29	3
Wexford	50	11
Wicklow	25	9

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¹Guidelines for Environmental Soil (and Herbage) Sampling

Soil sampling

The detail of the procedure adopted is influenced by each situation. The objective is principally to obtain a sample that can be expected to represent accurately the area being sampled. A sample may be a single soil core but is generally a composite core sample: the area covered may extend from what is nominally a point source (typically measuring 2m x 2m or 20m x 20 m) to a large section of a field or even a complete field (2 - 5 ha maximum). Samples should comprise a minimum of 20-25 cores. Point source sampling is generally best suited to surveys where there is a requirement to ascertain (or map) the spatial distribution of soil parameters whereas extensive area sampling is generally used where factual information is required in order to evaluate the agricultural or environmental status of a particular area.

A number of considerations need to be addressed before taking samples. These include the following :

- The known and suspected features including the nature and history of the site, the extent to which it is affected by geochemical or anthropogenic pollution,

and the topographical and land-use features of the area

- Areas and soil depths (or horizons) to be sampled
- Sampling design, viz., whether simple composite sample(s) suffice or whether a systematic (grid) or a more complex random or stratified random sampling program is required
- Choice of sampling equipment

Some procedures used in the past are given as examples.

Samples taken at defined locations in a baseline survey Samples were taken at defined intervals of 10 km on the National Grid. Locations were determined using GPS and field maps. Where practical considerations, generally relating to site access, precluded sampling at the defined position, a default procedure was followed. This involved attempting to sample in sequence at 25m to the E, S, W and N of the defined position and then at 50, 100, 200 and 400m distances until sampling was successful. For each defined position a sample (total weight 2 – 5kg) was obtained using a “Dutch auger”. The sample comprised 25 cores taken to a depth of 10 cm at 5m intervals on a grid that measured 20m x 20m and with the center point of this grid having the defined Irish National Grid co-ordinates.

Guidelines for Environmental, Soil and Herbage Sampling was prepared by D. Mc Grath as part of the Silvermines Investigation in 2001.

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Comprehensive sampling of whole farm

The farm was divided into areas of 2 – 3ha sized units. Smaller enclosures were treated as a single sampling unit. Fields that were non-homogeneous with respect to land use or topography were subdivided. Sampling depth was decreased from the more usual 10 cm to 5 cm in order to facilitate detection of aerial deposits. A composite sample with 100 cores was collected in a bucket sampler adopting a number of random zig-zag patterns across the sampling area. A total of 25 cores is generally adequate but more soil was needed on this occasion.

Smaller-scale baseline surveys The following procedures were adopted in the Silvermines investigation. Soil was sampled to a depth of 10cm at intervals of 400m within an area covering 6.8 km x 4.8 km. In this way 223 positions were sampled from a possible maximum of 234. Sampling was performed to 10cm and 25 cores were collected (from a 20m x 20m area) at each position using a Dutch auger. Herbage were also collected from the same positions in a manner described later.

School playing field Soils were sampled to a depth of 10cm from an area measuring 180 x 72m at intervals of 20m (N/S) and 18m (E/W). At each sampling point, 20 cores were taken from an area of 2m x 2m using a bucket corer.

Sample preparation

Each soil sample is dried at a temperature of

40°C. It is then be manipulated (rolled) gently without crushing stones and passed through a 2mm sieve. Care has to be taken that recovery is high to the point that additional manipulation, including removal of stones, results in no significant extra recovery. Danger of contamination exists where the equipment releases metals that are being analysed (*e.g.* Cu from grinders or sieves or zinc from rubber).

For many analyses it is necessary to further reduce particle size. This may be achieved by grinding in an agate mortar and pestle. Sub-sampling is usually necessary at certain stages and should be done by coning and quartering. Before analysis samples should always be shaken (for at least 30 secs) to counteract the setting effects which can seriously influence results. For accurate analysis moisture determination (which is influenced by carbon content and which varies with atmospheric humidity) should be determined at the same time.

A number of variations are possible, *e.g.* soil may be only partially dried before sieving (for biochemical assessment) or air drying may be undertaken at lower temperatures (for analysis of more labile organic compounds).

Herbage sampling

Sampling for herbage (or other crop) requires the collection of a composite sample of vegetation representative of that in the area. The number of individual samples collected

should be at least 10. Dunged areas should be avoided. Otherwise, representivity and not ease of sampling should be the main consideration.

Herbage preparation

There are divergent views on whether samples should be washed to remove adhering soil particles. Unfortunately results on washed samples may be difficult to interpret – as much as 50% of the contaminant (e.g. Pb) may not be removed (or additional contamination may be introduced (e.g. Cu). We generally shake off adhering soil particles, and perform an additional estimate for Ti (best) or Fe to obtain a measure of the extent of soil contamination (not effective on peats). Herbage is dried at 105°C (40°C where volatile elements such as Se are to be analysed) and sieved to pass a 1 mm mesh.

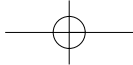
Useful references on sampling

ISO/DIS 10381-5 Soil Quality - Part 5 - Guidance on the Procedure for the Investigation of Urban and Industrial Sites with Regard to Soil Contamination, 35 pp.

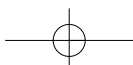
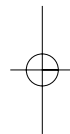
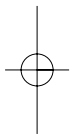
Fortunati, G.U. and Pasturenzi, M. 1994. Quality in soil sampling. *Quimica Analytica* 13 (Suppl 1) S5-S20.

Rubio, R. and Ure, A. M. 1993. Approaches to sampling and sampling pretreatments for metal speciation in soils and sediments. *International Journal of Environmental Analytical Chemistry* 51: 205-217.

Wagner, G. et al., 2001. Comparative Evaluation of European Methods for Sampling and Sample Preparation of Soils. *Sci. Tot. Environ.* 264:1-204.



Trace Elements and Heavy Metals in Irish Soils



¹Soil Survey County Reports - Agronomic Aspects

Introduction

Total trace element content of soil was generally estimated using spectrographic methods. Normal ranges found for some trace elements in Irish soils (total contents) are given in Table 1. Other parameters were generally measured as described by Byrne (1979).

Contents of trace elements in a soil depend largely on the nature and in particular on the mineral composition of the parent material, whereas the distribution within a profile is conditioned by soil forming processes such as weathering, leaching and organic matter accumulation. These processes coupled with such factors as pH, drainage status, and hydrous oxide content affect the availability of trace elements to varying degrees.

Soil Survey County Reports – Agronomic Aspects was compiled from Chapters that were prepared by G.A. Fleming and P.J. Parle for individual County Reports that were produced between 1966 and 1993. These reports should be consulted for accompanying maps and additional soil profile data.

Table1: Normal ranges of some trace elements in Irish soils (total contents)

Element	Symbol	Ranges (mg/kg)	Element	Symbol	Ranges(mg/kg)
Arsenic	As	1 - 50	Lead	Pb	2 - 80
Boron	B	2 - 100	Manganese	Mn	20 - 3000
Cadmium	Cd	0.1 - 1	Mercury	Hg	0.03 - 0.8
Chlorine	Cl	30 - 300	Molybdenum	Mo	0.2 - 3.0
Chromium	Cr	5 - 250	Nicke	Ni	0.5 - 100
Cobalt	Co	1 - 25	Selenium	Se	0.2 - 2.0
Copper	Cu	2 - 100	Silver	Ag	0.01 - 0.5
Fluorine	F	20 - 700	Tin	Sn	1 - 10
Iodine	I	1 - 10	Zinc	Zn	10 - 200

Trace Elements and Heavy Metals in Irish Soils

Several trace elements are known to be important in the nutrition of plants and animals, and the soil is the main source of supply. To date those known to be essential for plant growth are copper, manganese, iron, zinc, molybdenum and boron; under special circumstances and for particular plant species, cobalt and selenium may also be necessary. Those necessary for animals are cobalt, copper, manganese, iron, zinc, molybdenum, selenium and iodine. Soils containing abnormally high levels of certain trace elements occur in various parts of the country. From the animal health point of view, the two most important elements causing toxicity problems are selenium and molybdenum. For general agriculture the availability to the plant of a particular trace element may be more important than the total content in the soil; nevertheless, total soil values can provide considerable guidance in predicting likely toxicities or deficiencies. Although the main factor governing the total content of a trace element in any soil is the nature and in particular the mineral composition of the parent material, the distribution within the profile is conditioned by soil-forming processes such as leaching, weathering and organic matter accumulation. Accurate knowledge of the composition of the parent material and of the soil profile character can provide valuable guidance. Where the parent material is composed of glacial drift of mixed geological origin, the inference is less clear-cut but not necessarily fruitless.

In most cases availability is reduced by an increase in soil pH; this is particularly true of

manganese and to a lesser and varying degree of copper, iron, boron, zinc and cobalt. A major exception is molybdenum, the availability of which is enhanced with an increase in soil pH. Impeded drainage limits soil air, giving rise to reduced forms of some trace elements, particularly iron, cobalt and manganese. The reduced forms of these elements are more soluble than the oxidised forms, and this is reflected in greater uptake by plants. For instance, a well-drained and a poorly drained soil having the same total content of an element like manganese could be expected to have quite different amounts in the available form. Leaching of nutrients in free-draining soils can produce trace element deficiencies. These are referred to as "acquired" to distinguish them from "inherited" deficiencies that result from a shortage of the particular element in the parent material of the soil. Acquired deficiencies commonly arise under a podzolization process in soil development.

The soil values below which deficiencies might be expected to occur are as follows: copper and zinc—1.0 mg/kg (EDTA extractable), molybdenum—0.01 mg/kg (Grigg's reagent), manganese—40 mg/kg (easily reducible) and boron—1.0 mg/l (water soluble). Availability of cobalt is largely dependent on the manganese level in the soil. It must be stressed, however, that these figures can only be regarded as broad guidelines. More precise information for different soils can only be achieved after calibration experiments.

Table 2: Summary of soil analytical methods for trace elements

Element	Extraction method
Boron (B)	Extraction with boiling water
Copper (Cu)	Extraction with 0.05 molar EDTA
Manganese (Mn)	Extraction with a mixture of 0.5 molar calcium nitrate and 0.2% quinol
Molybdenum (Mo)	Extraction with Tamm's Reagent (ammonium oxalate — oxalic acid buffered to pH 3.3)
Zinc (Zn)	Extraction with 0.05 molar EDTA

Cobalt (Co) and manganese (Mn) are extracted with HCl (specific gravity 1.12). Being a very strong extractant this gives values which are practically totals.

Interpretation of trace element analyses

Total levels of trace elements in soils are of limited use in predicting the availability of the elements to growing plants and thus indirectly to the grazing animal. Where total levels are either extremely low or unduly high, it can be reasonably assumed that risks of deficiencies or toxicities are present. In most circumstances it is necessary, that some index of trace-element availability to the plant be known. Such information has been obtained by extracting soils with various solutions, the premise being that these extractants simulate behaviour of the growing plant in terms of nutrient uptake. Because the basic soil chemistry of trace elements differs markedly, different solutions are required in the assessment of availability. Even when this is done, extractants must be calibrated against crop responses in the field and this may often vary for a given crop on

different soils. Table 2 details the different extracting solutions employed at Johnstown Castle.

In the case of cobalt, the total value viewed together with a value for total manganese gives a good indication of the likely cobalt status of herbage. Calibration trials in the field have shown that when total Mn values exceed about 500 mg/kg, cobalt availability to pasture is severely limited.

In the absence of response data from field calibration trials, trace-element analyses cannot provide definite information regarding the occurrence of a crop or animal disorder. They can however be extremely useful in indicating likely problem areas. More intensive follow-up work is then necessary to establish the extent and severity of different disorders. A summary of soil response thresholds for trace element disorders is given in Table 3.

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Table 3: A summary of soil response thresholds for trace element disorders

Element	Content (mg/kg)	Practical agricultural significance
Copper	1.5	Risk of Cu deficiency in cereals if value is below this figure.
Zinc	1.0	Risk of Zn deficiency in cereals and possibly some horticultural crops if value is below this figure.
Molybdenum	0.01	Risk of Mo deficiency in brassicas if value is below this figure.
	0.30	Risk of Mo-induced Cu deficiency especially in young cattle if value exceeds this figure but other factors such as liming, sulphur content of feed and possibly level of soil intake (i.e. stocking rate) are important.
Manganese	40	Possibility of Mn deficiency in cereals and sugar beet if value is below this figure.
Boron	1	Risk of B deficiency in swedes and some horticultural crops – slight risk in sugar beet and oil seed rape if B content is below 1 mg/kg.
Cobalt	5	Risk of cobalt deficiency, especially in lambs, if Co content is below 5mg/kg. For correction of cobalt deficient pastures cobalt sulphate works best when Mn figure is below 400 mg/kg
		Direct Co supplementation of animals is probably best when Mn is 700 mg/kg or higher.

WEXFORD

Analyses for a representative profile of the Macamore Series indicate that the soil is adequately supplied with the biologically important trace elements, with the possible exception of molybdenum. For this element the total figure is recorded as less than 1mg/kg or one part per million (1 ppm) in all horizons, this being the limit of detectability of the spectrographic method employed for analysis. This low level may be adequate, but further work involving availability measurements is necessary before a definite conclusion can be drawn. An interesting feature of the figures for this soil is the lower content of most trace elements in the A0 horizon. Only lead and copper show higher contents in the A1 than in the A2 horizon.

The Screen soil is particularly low in all trace elements and, under an intensified system of agriculture, crop and animal health problems could become serious here. Copper and manganese deficiency in cereals could easily arise unless preventive or remedial measures were adopted. As in the other soils examined the molybdenum content is low. The amount present, however, may be adequate to meet the needs of most crops with the exception of brassicas, which have a particular requirement for this element. Cobalt could not be detected in the A horizon of this soil and was scarcely evident in the B and C horizons. It would be natural, therefore, to assume that cobalt deficiency in stock might easily be a problem. While boron analyses have not been carried out, the general level of

trace elements in the soil is such that boron deficiency might also be a problem in the production of certain crops. This may be also true of zinc.

Analyses for a profile from the Ballindaggan Series indicate that this soil is adequately supplied with trace elements. The manganese, cobalt and copper contents in the surface are such that deficiencies would not ordinarily be expected. From the pedological point of view the soil is also interesting. The tendency for some elements, rubidium, lithium, barium, nickel, zirconium, beryllium, yttrium and molybdenum, to accumulate in the B horizon is apparent. Manganese, on the other hand, tends to fall off here; lead definitely does so. The relatively high manganese and cobalt contents are interesting, and probably reflect little loss of these elements in the course of weathering of the parent material or of the soil itself. In the Clonroche soil, formed from predominantly Ordovician shale drift, the manganese and cobalt contents are also quite high.

The Rathangan soil appears reasonably well supplied with trace elements but the values, in general, are rather lower than those of the Ballindaggan soil. This is not surprising considering the quartzitic influence in the parent material of the former. There is a slight tendency for some elements to increase in the B horizons, notably rubidium, cobalt, nickel and zirconium. The only trace element trouble likely to arise would be cobalt deficiency, particularly where the

quartzitic influence in the drift is more pronounced. However, the poorly-drained nature of the soil would counteract this tendency to some extent, cobalt generally being more available under impeded drainage conditions. The trace element pattern in the soils of the Kiltaly, Old Ross and Clonroche Series has been fully discussed elsewhere (Fleming *et al.*, 1963). Here the most interesting feature is the change in trace element content that occurs with decreasing granitic influence of the parent drift material. In the Kiltaly soil the granite influence is most pronounced, least in the Clonroche, and intermediate in the Old Ross. Likewise the influence of the Ordovician shale is most apparent in the Clonroche soil and least in the Kiltaly and is reflected in the trace element figures for the respective soils. This is particularly well illustrated by the cobalt and nickel figures, which show a steady rise as the effect of the granite declines and that of the shale increases. From the agricultural standpoint, molybdenum, and possibly copper, might be considered low, but the remarks made earlier regarding the former in the Screen soil should be borne in mind. Some determinations of 'available' trace elements as measured by solubility in 2.5 per cent acetic acid were carried out on these three. The amounts of cobalt present in the surface horizons of the soils were as follows: Kiltaly 0.24 mg/kg, Old Ross 0.21 mg/kg, and Clonroche 0.23 mg/kg. An interesting observation here is that the higher total cobalt in the Clonroche soil is not accompanied by higher available figures as is

the case for nickel. Since a level of 0.25 mg/kg of cobalt or over, by this method of estimation, is generally regarded as adequate from the point of view of providing cobalt-sufficient herbage for grazing stock, the available contents could be regarded as reasonably satisfactory. The possibility of cobalt deficiency occurring in stock is more likely, however, in the Kiltaly and Old Ross soils, as acetic acid-soluble cobalt declines in the sub-surface horizons at a greater rate than in the Clonroche soil where it occurs at a fairly uniform level throughout the profile.

LIMERICK

Gleys

Four soils representative of this group, Abbeyfeale, Howardstown, Kilrush and Puckane, were analysed. In these series some of the lowest contents of many trace elements in the profile occur in the surface horizon; this is particularly true of barium, strontium, manganese, chromium, cobalt, nickel, zirconium, vanadium, yttrium and copper. Some of these, most notably manganese, cobalt, and copper, are important in plant and animal nutrition but are not sufficiently low to be suspect for deficiency problems. Both rubidium and lithium, of no known agricultural importance, are low. In the Howardstown profile there is a marked increase of certain elements, notably manganese, chromium, cobalt, nickel, vanadium, yttrium, and titanium, in the lower horizons and principally in the B/C zone. The same

trend, though less pronounced, is apparent in the Abbeyfeale, Kilrush and Puckane profiles. Copper is almost three times higher in the Kilrush than in the Howardstown or Puckane profiles. In the Abbeyfeale profile the organic-rich surface horizon contains 1 mg/kg selenium; no selenium was detected in the lower horizons. Although the level of 1 mg/kg is not considered dangerous, the possibility of somewhat higher levels occurring in isolated pockets must be borne in mind. Silver, which rarely exceeds 1 mg/kg in soils, gives values as high as 5 mg/kg in certain horizons of the Abbeyfeale profile.

From the agricultural point of view there should be no problem due to trace element anomalies on the majority of the gley soils in Limerick.

Podzols

Four series representative of the Podzols in the county, Knockaceol, Knockanimpaha, Knockastanna and Seefin, were analysed.

The general tendency for many of the trace elements to increase in content with increasing depth in the profile, and to accumulate in the region of the B horizon, is a well-known feature of Podzols. This phenomenon is also apparent in the four selected Podzols but is less obvious in the Knockanimpaha and Knockastanna profiles due to the shale in the parent material modifying the rate of profile development. For the same reason, 'total' contents of several trace elements, most notably rubidium,

strontium, manganese, chromium, cobalt, nickel, zirconium and gallium, are much higher throughout these two profiles. For elements such as manganese and cobalt this is highly significant in regard to agriculture. Lead is generally concentrated in the surface horizons in association with the organic matter; this is especially marked in the Knockanimpaha and Seefin profiles. In all but the Seefin profile there is an obvious retention of manganese in the surface horizon even though the overall tendency is for this element to increase in content down the profile.

In these soils generally, important elements such as cobalt, copper, manganese and molybdenum are either extremely deficient in all cases as in the more strongly podzolised Knockaceol and Seefin profiles, or borderline to deficiency level for some and deficient for others as in the Knockanimpaha and Knockastanna profiles. In improving output from these soils, amelioration procedures, including lime and fertiliser treatments, may further accentuate the inherent deficiencies. Intensification of grazing stock would place greater demands on the meagre native supplies of these essential elements. Special attention then would need to be paid to elements such as cobalt, copper, molybdenum and manganese on these degraded soils.

Selenium and molybdenum

The abnormally high selenium levels prevailing in the so-called 'seleniferous' soils

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in County Limerick are the outcome mainly of two factors, one related to the nature of the soils themselves and the other to drainage waters associated with certain geological formations.

The soils concerned are generally low-lying, poorly drained, rich in organic matter and neutral to alkaline in reaction. Many of them have formed in depressions once occupied by lakes mostly of glacial origin. These depressions were filled with sediments eroded from surrounding geological formations, and subsequently several cycles of plant growth and decay resulted in the accumulation of many trace elements, including selenium and molybdenum, in the present organic-rich soils.

The condition also obtains in portions of the river alluvial soils and of the contiguous gley soils which are influenced by the waters of those streams with sources in the region of the geological formations known as the Clare Beds. These beds occur in the scarp of the Upper Carboniferous Shales and Sandstones and extend from Foynes south to Ardagh. The soils so far known to be affected are certain peaty phases of the Drombanny Series, certain localised areas of the Camoge, and to a lesser extent in portions of the Coolalough and Howardstown Series. In this region also the Weichsel Glaciation eroded the Clare Beds and as a result there are limited areas of high-selenium soils within the Ashgrove Complex. Pockets of peat within the limestone drift area around Askeaton have also been found

to have high selenium contents. All lake alluvial soils in County Limerick are not high in selenium and molybdenum—only those where the deposits were associated with certain geological formations, most notably the Clare Beds. The profile described below (Table 4) is very typical of those soils associated with extremely high contents of selenium and molybdenum and of certain other less important trace elements. The selenium, molybdenum and organic carbon contents are shown in Table 5. As the concentrations of selenium and molybdenum normally occurring in soils are less than 1 mg/kg, it is apparent that soils such as this are quite unusual in this respect. In practice the importance of such high figures lies in the fact that pasture herbage and crops grown on these soils will contain amounts of selenium and molybdenum which may be toxic to animals.

Selenium contents of different crops grown on one of these soils are shown in Table 6, and the high content prevailing in most cases is apparent. Selenium contents in the 10 to 50 mg/kg range are common in pasture herbage samples collected in the seleniferous area. Normally the level on selenium occurring in plants seldom exceeds 1 mg/kg. While the information regarding molybdenum levels in pasture herbage and crops is not as great as that on selenium, nevertheless sufficient exists to warrant the assertion that the herbage is potentially dangerous to animals. In pot experiments 40 mg/kg of molybdenum and more have been found in

Table 4: Alluvium derived from Upper Carboniferous Shales and limestone-rich glacial drift

Depth (cm)	Description
0 - 15	Clay loam to loam; dark greyish-brown (10 YR 4/2); weak, fine crumb structure; wet, sticky; gradual, smooth boundary to:
15-23	Clay loam; grades downwards from dark greyish-brown (10 YR 4/2) to almost white (10 YR 8/2); massive structure; wet, plastic; clear, smooth boundary to:
23-30	Peat; very dark grey (10 YR 3/1) to black (10 YR 2/1); weak, coarse crumb structure; friable; diffuse boundary to:12-15 cm depth: Peat; very dark grey (10 YR 3/1); weak, fine crumb structure; friable; abrupt, wavy boundary to:
30-38	Peat; very dark grey (10 YR 3/1); weak, fine crumb structure; friable; abrupt, wavy boundary to:
38-76	Clay; white (10 YR 8/2); massive with tendency towards columnar structure; wet, sticky.

Table 5: Selenium, molybdenum and organic carbon in a typical 'seleniferous' Limerick soil

Depth (cm)	Se (mg/kg)	Mo (mg/kg)	Carbon (%)
0 - 15	34	15	13.7
15 - 23	49	30	6.8
23 - 30	194	70	34.0
30 - 38	220	150	34.5
38 - 76	45	200	2.4

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tall fescue grown on one of these affected soils. In general it can be stated that ingestion of any material containing more than 5 mg/kg (dry weight) of either selenium or molybdenum is potentially dangerous. An accurate estimate of the total area of seleniferous soils in County Limerick was not feasible at the scale of mapping employed or with the knowledge to hand, but it should scarcely exceed 40 ha in all.

The matter of animal health in the seleniferous areas is receiving attention; the

question of human health merits investigation particularly in view of recent findings connecting high selenium intake with increased incidence of dental caries. A re-appraisal of land use generally in these areas is worthy of consideration. Apart from the high molybdenum contents occurring in the seleniferous soils of County Limerick, other areas are affected by high molybdenum unaccompanied by toxic selenium levels. Due to their close similarity in many respects to certain estuarine alluvial soils mapped in County Wexford, the soils of the Shannon

Table 6: Selenium content (mg/kg) of some cultivated crop plants - County Limerick

Material	Se	Material	Se
<i>Mangel, Yellow Globe:</i>		<i>Cabbage:</i>	
Roots	3.2	Stems	37
Leaves	8.3	Leaves	118
<i>Mangel, Red Intermediate:</i>		<i>Apples:</i>	
Roots	1.5	Fruit	0.5
Leaves	7.3	Leaves	1.5
<i>Swedes:</i>		<i>Potato, Arran Victory:</i>	
Roots	5.1	Tubers	9.9
Leaves	31	<i>Potato, Arran Banner:</i>	
<i>Sugar Beet:</i>		Tubers, Sample No. 1	11
Roots	1.5	Tubers, Sample No. 2	1.8
Leaves	12	<i>Oats:</i>	
<i>Carrot:</i>		Grain	20
Roots	4.6	<i>Straw:</i>	
Leaves	12	Sample No. 1	1.8
		Sample No. 2	2.4

Series were immediately suspect. A trace element investigation showed high values for such elements as lead, tin, copper, gallium and molybdenum. Although the molybdenum contents are not nearly so high as those in the seleniferous soils they are potentially toxic. Herbage samples from pastures on these soils had 3 to 6 mg/kg molybdenum, potentially dangerous levels; selenium values (0.14 to 0.18 mg/kg) were in the normal range. Standard measures to improve the output of pastures on these soils, and especially lime and fertiliser treatment, would tend to accentuate the condition: the resulting molybdenum-copper imbalance in the animal's system would adversely affect health and thriftiness. In improving these pastures, therefore, due consideration should be given to the potential molybdenum problem.

CARLOW

The trace element status of a number of soil series in Carlow has been investigated. The analytical data for the profiles examined are all total values. Thus, higher than average values for elements such as tin, and lower than average values for elements such as cobalt, are generally associated with the granitic soils. High molybdenum values are most often associated with limestone-rich parent materials. The relation between shale parent materials and molybdenum content is not so clear; in parts of the country high molybdenum values are found in soils derived from certain carboniferous shales. It is interesting to note that in the Carlow

shales examined, the general level of manganese seems to be lower than in the Wexford shales. Manganese in the Ordovician shale of the Clonroche soil in Wexford reached 7,000 mg/kg, whereas the highest value for any parent material examined in Carlow was 1,500 mg/kg.

In considering the general trace element pattern, the soil series selected for examination represent the most important Great Soil Groups in the county and are grouped accordingly.

Grey Brown Podzolics

In this group of soils the trace element pattern is generally satisfactory. However, molybdenum toxicity may become a problem in the Kellistown Series; in the modal profile the surface soil has 4 ppm of this element and the pH is 5.6. Heavy liming of the soil could enhance the availability of molybdenum, leading to increased levels in the herbage and to molybdenosis in grazing stock. On the other hand, symptoms of molybdenum deficiency in brassica crops have been reported locally.

Distribution of the various elements within the profiles is generally fairly uniform. The biggest exception is the Mortarstown Series where there is a rather well-defined increase of lead, gallium, molybdenum, vanadium, copper, nickel and cobalt, in the B_{2t} relative to the surface horizon. The corresponding clay contents are 23 and 42 per cent for the surface

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and B2t horizons, respectively. In the Paulstown Series the surface horizon has 24 per cent clay and the B2t 43 per cent. Except for copper, nickel and cobalt, there is much less evidence of trace element accumulation in the B horizon.

Brown Earths

The total contents of the trace elements in the soils of this group all fall within normal ranges. However, for some elements there are variations between Series, which largely reflect differences in parent materials. In the Acaun Series manganese occurs at the highest levels for the group. This is probably due to the limestone influence in the parent material of these soils; limestones generally contain more manganese than either granite or sandstones which are the other components of the parent material. Total manganese is lowest in the Keeloge series although falling within the normal range; there is a possibility of manganese deficiency in crops especially after liming of these soils.

The cobalt contents of the upper horizons of the Brown Earths in general tend to be somewhat low, and a deficiency could develop under intensified stocking. The danger of a deficiency is greatest on the Borris Series where levels throughout the profile are rather low.

The distinctly higher tin values apparent in the Ballytarsna and Borris Series are of no importance agriculturally, but they are of

interest geochemically and are most probably related to the granitic parent material. Similar trends appeared in the granitic soils in County Wexford.

Agriculturally the two most salient features of the analyses are: (a) general tendency towards low cobalt levels and (b) the possibility of manganese deficiency in the Keeloge Series.

In general trace elements are fairly uniformly distributed throughout the profile of the Brown Earths. Some notable exceptions are the distinct rise in copper, nickel, cobalt and manganese in the C horizon of the Acaun Series and of copper, nickel and cobalt, and of zinc, nickel and cobalt, respectively, in the sub-surface horizons of the Ballindaggan and Ballytarsna Series.

Brown Podzolics

The trace element figures for the Clonegall Series depart little from normal soil levels. However, total cobalt contents are marginal and a test for available levels would be necessary to ascertain possible deficiencies. There is little evidence of translocation of elements from the A to the B horizon. Gallium, molybdenum, vanadium, copper, nickel, cobalt, chromium and titanium are distinctly higher in the C horizon than in the upper horizons; the reverse is true for manganese.

The main interest in the Kiltyale Series is the

low values for copper, cobalt and manganese. Cobalt deficiency in grazing stock is a distinct probability on these soils. Availability studies would be necessary to determine if crop deficiencies due to copper or manganese shortage are likely. The distribution of trace elements within the profile is generally uniform but there is a noticeable drop in chromium, titanium and manganese in the C horizon. Of particular interest in the shallow variant of the Killealy Series is the accumulation of tin, lead, gallium, copper, chromium and titanium in the surface horizon.

In the Ridge Series the general levels are normal but some points regarding distribution within the profile are worthy of comment. Both cobalt and manganese show a distinct decrease in the Ba horizon; cobalt is highest in the C horizon, and manganese in the A horizon.

In summary, cobalt deficiency would be the most likely trace element problem on these soils except on the Ridge Series where reserves are apparently adequate. Manganese and copper deficiencies may occur sporadically, especially on the Killealy soils.

Podzols

In the Ballinagilky Series cobalt, copper, manganese and molybdenum are low and deficiencies of these elements may be expected, especially in the more organic

surface soils. Cobalt deficiency would be most serious in sheep farming, manganese and copper deficiencies in cereal growing, but copper shortage might be a limiting factor also in clover establishment in pastures. A molybdenum shortage would mostly affect brassica crops.

In the Blackstairs Series general levels of trace elements are rather similar to those of the Ballinagilky Series and here also the agriculturally important elements cobalt, copper, manganese and molybdenum, are all quite low. The most striking difference between these two soils is the generally lower values in the surface horizon and the sharp increase apparent for most elements between the organic surface and the mineral sub-surface horizons of the Blackstairs profile. To allow for an organic matter content in excess of 50 per cent in the surface of the Blackstairs profile, and to provide a more valid comparison, the analytical figures should be expressed on an ash rather than a "whole soil" basis.

The Black Rock Mountain soils derived mainly from shale show some interesting differences from the Ballinagilky and Blackstairs Podzols developed on mainly granitic material; the most obvious differences are in the parent materials or C horizons and to a lesser degree in the B horizons. Molybdenum, vanadium, copper, chromium, and titanium are generally higher, and tin, gallium and zinc lower in corresponding B and C horizons of the Black

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Rock Mountain profile than in either the Ballinagilky or Blackstairs profiles. The surface horizons again are very low in cobalt and manganese. The organic nature of the surface horizon makes interpretation of the copper and molybdenum figures difficult, as in the Blackstairs profile.

Gleys

In both the Ballywilliam and Belmont Series molybdenum, cobalt and manganese are low and deficiencies may arise. Distribution within the profile shows a definite increase particularly of vanadium, zinc, cobalt, chromium and manganese in the lower horizons.

The soils of the Castlecomer and Clowater Series appear to be adequately endowed with trace elements. Copper, zinc and nickel increase with depth in the profile whilst manganese decreases .

The plough layer of the Coolnakisha is particularly low in copper and manganese, and cobalt is marginal in the surface horizon; there is a general increase to satisfactory levels in the lower horizons.

The trace element supply seems quite satisfactory in the Greenane Series but molybdenum and manganese levels tend to be higher than in the other gleys. There is an obvious accumulation of lead, copper, zinc and manganese accompanying the clay accumulation in the B horizon.

The trace element levels in the Moanduff, Newtown and Parknakyle Series in general appear satisfactory except for the rather low copper in the Parknakyle Series. In the Moanduff and to a lesser extent in the Newtown and Parknakyle profiles, elements tend to increase in content with depth, but lead is clearly concentrated in the upper horizons of the Newtown and Parknakyle profiles.

In the Gleys in general, the availability of many elements, including molybdenum, cobalt and manganese, is usually greater under the reducing conditions obtaining in these wet soils. Thus where total values for cobalt and manganese are marginal, deficiencies would be less likely than under free-draining conditions. Conversely, molybdenum levels of 2 and 3 mg/kg, which in freely-drained soils could be disregarded, might conceivably give rise to anomalous levels in herbage, especially when lime is applied.

Regosols (Alluvials)

Trace element levels in these soils are apparently satisfactory and problems from shortage or excess should not arise. Manganese content declines sharply in the lower horizons of the Kilmannock profile which is not surprising in view of the nature of the parent material (coarse calcareous gravels).

Complexes

Athy complex Despite the variable nature of the soils, trace element levels are generally satisfactory and quite uniform throughout the complex. Copper and zinc tend to be concentrated in the upper horizons of the profile in all four component soils.

Broughillstown complex As in the soils of the Athy Complex, the levels for all trace elements are satisfactory. An interesting aside on these soils is that cadmium was detected at a level of around 10 mg/kg in the B horizon of the moderately deep component. This element follows zinc in the geochemical cycle and it is noteworthy that zinc shows comparatively high values in this soil, especially in the B horizon. The zinc levels, however, are well within the normal range for soils and would not be a problem agriculturally.

WESTMEATH

Extractable trace element data on various soils in Co. Westmeath provide a guide to the availability of some nutritionally important trace elements to plants, and indirectly to grazing stock. The soil values below which deficiencies might be expected to occur are as follows: for copper and zinc 1.0 mg/kg, molybdenum 0.01 mg/kg, manganese 40 mg/kg, and cobalt 5.0 mg/kg. It must be stressed, however, that these figures can only be regarded as broad guidelines. More precise information for different soils can only be

achieved after calibration experiments linking extractable levels with plant uptake. Nevertheless, the figures can be used to draw attention to likely anomalous areas and to indicate where corrective measures are advisable.

Rendzinas

Examination of the Burren Series for trace element content showed that this soil is inherently low in cobalt. All other essential trace elements are adequate.

Brown Earths

Two series from this group were examined - Baggotstown and Ladestown. Both are adequately supplied with trace elements, but low cobalt values may be found in herbage as a result of high soil manganese content. High, easily reducible, manganese values found within the Ladestown series could give rise to manganese toxicity at low pHs. One sample within Ladestown had a higher than normal extractable molybdenum.

Grey Brown Podzolics

All the soils examined within this group are adequately supplied with trace elements except the Rathowen series where some low soil cobalt values occur. High easily reducible manganese values found within Elton, Patrickswell and Rathowen Series could give rise to manganese toxicity where pH values are low and also could be reflected by a low

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cobalt herbage content. Higher than normal extractable molybdenum levels are found within Patrickswell and Rathowen which would necessitate care in the application of lime.

Gleys

Mylerstown, Camoge and parts of Street soils are inherently low in cobalt, while low herbage cobalt values may be found in parts of Ballyshear. All other essential trace elements are in adequate supply. Ballyshear has higher than normal extractable molybdenum values which could cause problems with animals.

Regosol

Miltownpass, the one soil classified as being in this group, is inherently low in cobalt, otherwise it has an adequate supply of trace elements.

Lithosol

Knockeyon was the only soil classified as being in the group and examination for trace elements content showed it to be low in cobalt. All other essential trace elements appear adequate.

Soil complexes

Of the soils examined for trace elements in this group Baggotstown - Crush was found to be low in cobalt. Copper deficiency may occur on parts of this complex particularly where

high nitrogen is applied. High easily-reducible soil manganese values from Finnea-Banagher-Athy suggest that low cobalt levels may be found in herbage in areas within this complex.

Peaty Lake Alluvium - Drombanny Series

High selenium values are found within this series which could cause toxicity problems for the grazing animals. Extractable molybdenum levels also tended to be higher than normal.

MEATH

Selenium and molybdenum

Abnormally high levels of selenium occur in certain soils of Co. Meath and are the result mainly of two factors, one related to the nature of the soils themselves and the other to drainage water associated with certain black shales of Namurian age. The soils are generally low lying, poorly drained, rich in organic matter and neutral to alkaline in reaction. Many of them have formed in depressions once occupied by lakes mostly of glacial origin. The depressions were filled with sediment eroded from surrounding Namurian formations. Cycles of plant growth and decay resulted in the accumulation of a range of trace elements, mainly selenium and molybdenum. The situation also obtains in portions of river alluvia. Three soils are known to be affected, the Drombanny and Dunsany series and the Complex mapped as Boyne Alluvium.

The first Irish report of an animal disorder which is now recognised to be selenium toxicity was by Fream (1890) who described the symptoms of animals grazing "the poisoned lands of Meath". Fleming (1962), Kiely and Fleming (1969, 1978) and Crinion (1980) have further delineated the selenium toxic areas of County Meath.

While selenium- toxic levels tend to be confined to organic soils, molybdenum which has the same black shale source, is quite ubiquitous and is found across a wide range of Co. Meath soils at varying levels dependent on the extent of the influence of the black shales on the parent material. The following soils, Baggotstown, Ballincurra, Ladestown, Dunboyne, Dunboyne-gravelly phase, Dunboyne-shaley phase, Elton, Mortarstown, Rathowen, Rathowen-cherty phase, Howardstown, Drombanny, Dunsany, Boyne Alluvium, Glane, Dunboyne-Ashbourne Complex, Dunboyne-Ashbourne shaley phase have been found to be potentially molybdeniferous. Areas within the Ashbourne series and within the Rathowen-associated Complexes could also have elevated molybdenum values depending on the degree of shale influence. It is important, however, to realise that the whole area mapped (Fig 12) is not molybdeniferous but rather that within the area, toxic soils occur leading in turn to an induced copper-deficiency especially in young cattle. Where this occurs or is suspected, advice should be sought before any application of lime. Application of sulphur would also exacerbate

the molybdenum -induced copper deficiency but in practice sulphur is usually not limiting on the heavy-textured soils which are usually those with elevated levels of molybdenum.

With regard to drainage two points must be borne in mind. Poorly drained soils invariably contain more available Mo than their freely drained counterparts and the same can be said with regard to Se. Where arterial drainage in seleniferous or molybdeniferous areas is being carried out, the spreading of spoil may cause a definite hazard in that molybdenum and/or selenium-bearing material may be dredged and subsequently cause problems. Herbage analysis of pastures sown on such material should be sought before animals are allowed to graze on such soil strips.

Cobalt

The high manganese content of most of the County Meath soils will reduce the availability of cobalt to such a degree that the pasture may well have inadequate levels to satisfy animal requirements, particularly those of young lambs. The application of cobalt sulphate to pasture is unlikely to be of benefit for the above reason, except on the following soils: Howardstown, Rathowen, Street, Ashbourne and Slievebeag. Poole *et al.* (1974) have obtained responses to cobalt dosing in Co. Meath on soils which were once considered adequately supplied with cobalt. Cobalt application trials on soils in Co. Meath have shown that very low herbage Co levels

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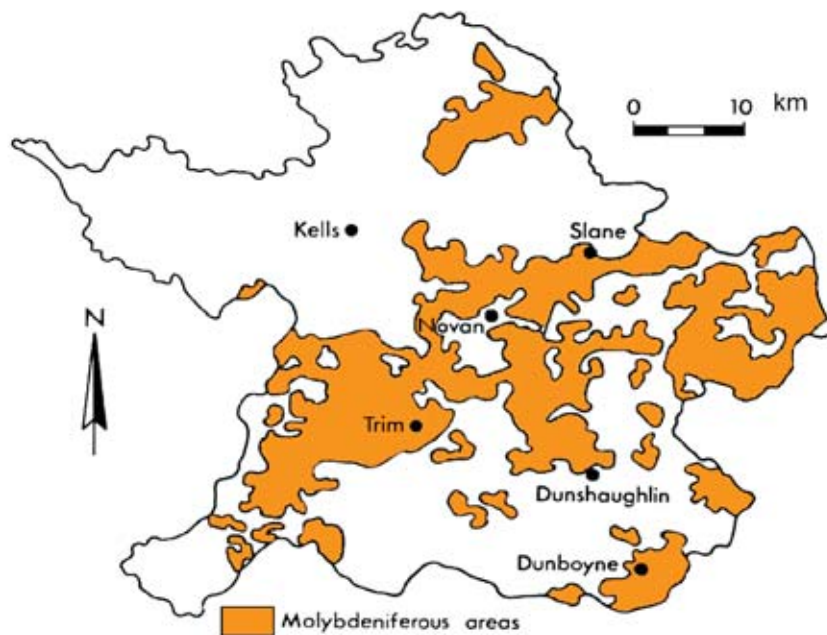


Fig. 12. Molybdeniferous areas in Co. Meath

may be prevalent. In particular, areas around Oldcastle, Headfort and Wilkinstown had quite low levels of Co in the herbage but because of the high soil levels of Mn obtaining, soil application of cobalt-sulphate at normal rates (2 kg per hectare) would have only minimal benefit. In such areas direct treatment of animals is advised.

LAOIS

Total contents

Central Lowland soils including Soil Series Fontstown, Cullahill, Stradbally, Patrickswell

and Knockbeg are formed primarily from calcareous glacial till but with increasing admixtures of sandstone and shale in the sequence as outlined. Increasing shale contents should be reflected in increased trace-element levels in the soils and if the data representing the five soils mentioned are examined in general, trace element levels increase in the sequence Fontstown, Cullahill, Stradbally, Patrickswell and Knockbeg. It must be stressed, however, that with the low intensity of sampling inherent in the survey method, general trends only can be anticipated.

Even though only one peat soil was examined (Banagher) extremely low levels of all trace elements are apparent. This can generally be expected with peats but in the case of some other trace elements such as molybdenum, high levels may be encountered. This will be referred to later.

In the Castlecomer Plateau soils the Ridge Series has higher trace element levels compared with the Abbeyfeale non-Peaty soil.

This is consistent with the higher content of shale in the parent material but equally it must be noted that the Abbeyfeale Undulating Phase has rather higher levels than might be expected. Obviously much more intensive sampling would be necessary to identify fully the effect of parent matter on general soil trace-element content.

In the Clonin soil lead (Pb) levels are slightly high in two of the profiles whereas in one instance a figure of 702 mg/kg was found in an Ap layer. Such a figure is definitely anomalous and some form of contamination or possibly some lead mineralization is responsible.

In the Fontstown Series 220 mg/kg zinc was found in a B2 horizon. This is most probably due to a natural accumulation in such horizons.

A surface soil of one of the Patrickswell profiles contains over 400 mg/kg boron (B)

and this is quite unusual. Such figures could be obtained from fields which had been freshly fertilised with a boronated compound or could be the result of adventitious "contamination" from a tourmaline-containing sandstone. Tourmaline in soils is quite resistant to weathering. It is frequently associated with sandstones which themselves are "residual materials". Some horizons in one of the Knockbeg profiles also show slightly elevated boron levels.

Some low levels of copper (Cu) occur in the Graceswood and Banagher soils. As the former contains glacial sand in the parent material and as the latter is a peat this is not surprising.

There is a considerable variation both in the copper and zinc levels in the River Alluvium Complex. Copper ranges from 9 to 149 mg/kg and zinc from less than 50 to 243 mg/kg. River alluvium would naturally tend to be variable, such variation being dictated by frequency and intensity of flooding.

Pedological considerations

Profile distribution of trace elements in young soils where little profile differentiation has taken place is relatively even. Any variations which may occur usually involve a decrease in content from the parent material upwards. During the various soil-forming processes different trace elements become redistributed in different ways; in a typical podzol many elements will concentrate along

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with clay and iron in the B horizon whereas others such as lead and silver tend to be retained by surface organic matter. In the soils of Co. Laois only two podzols occur, the Conlawn and Rossmore Series, and together they occupy only around 0.6% of the land area of the county. These soils were not analysed for trace element content. Viewing the Grey Brown Podzolic soils which were analysed, some accumulation of trace elements is apparent in B2 and B2t horizons, the most striking examples being copper, zinc, boron and gallium in the Fontstown and Cullahill Series.

The surface accumulation of lead *vis-a-vis* its association with the more organic horizons is apparent in a number of soils, e.g. the Slieve Bloom, Fontstown, Stradbally, Patrickswell and Knockbeg Series.

Available contents

Copper Cu values are reasonable for crop growth in Co. Laois but some very low values occur in the Baunreagh, Slieve Bloom and Graceswood Series.

Zinc A wide range of values occurs and some quite low ones were encountered in the following Series: Baunreagh, Stradbally, Mylerstown, Mountrath, Graceswood and Raheenduff. Unusually high values occur in one soil of the Slieve Bloom Series and in the Banagher peat.

Molybdenum The soils of Co. Laois which are potentially molybdeniferous include the following Series: Fontstown, Stradbally, Mylerstown, Ballyshear, Banagher, Mountrath, River Alluvium Complex, Patrickswell and Knockbeg in the Central Lowlands, and the Ridge, Abbeyfeale, Raheenduff and Ballinakill Series in the Castlecomer Plateau soils. The molybdeniferous soils depicted in Fig. 13 are therefore probably an overestimate and are intended only to indicate general high-risk areas. In practice, farms within the shaded areas should be more thoroughly investigated to establish their molybdenum status.

Boron All soils seem to be adequately supplied with boron but two very high levels (13 mg/kg) occur in one soil in the Slieve Bloom Series and in one in the River Alluvium Complex.

Manganese Two forms of manganese were measured, easily-reducible (ER-Mn) and HCl-soluble Mn. The former is useful in predicting areas of possible Mn deficiency which would be important in cereal and possibly in sugar beet growing. The latter is useful for interpreting soil cobalt values.

Very low ER-Mn values occur in the Slieve Bloom gley soil whereas in the Central Lowlands the Mylerstown, Graceswood and Mountrath soils have low levels. Mn deficiency in cereals has in fact been confirmed on the Mylerstown Series.



Fig. 13. Molybdeniferous soils of County Laois

Cobalt The soils of the Slieve Bloom Series are very low in cobalt, and soils in the Baunreagh and Clonin Series are also low. Where the HCl-soluble Mn is also low, the Co status of pastures on these soils is readily corrected by applying approximately 2 kg cobalt sulphate/ha and the improvement will probably be sustained for about three years. Where HCl-soluble Mn values are in excess of 400-500 mg/kg, however, extra cobalt will be necessary to correct Co deficient pastures. Where Mn values are greater than about 700mg/kg, direct administration to the animal may well be the best option. Cobalt deficiency is primarily a problem of sheep and more particularly lambs. In areas of extreme Co shortage, however, the possibility

of cobalt deficiency in cattle should be considered.

NORTH TIPPERARY

Regosols

Regosols only occupy a total of 0.07% of the land area. The two Series occurring, the Carney and the Milltownpass, occupy only 22 and 129 hectares, respectively. The pH of the Carney soil (Table 7) at 8.0 is high, reflecting the limestone parent material. This is essentially a grassland soil and it may be necessary to fertilise with copper and cobalt to raise the levels of these elements in herbage.

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Table 7: Regosols - trace element content

Soil Series	Soil pH	Available (mg/kg)					Total (mg/kg)	
		B	Cu	Mn	Mo	Zn	Co	Mn
Carney	8.0	1.0	1.2	24	0.07	3.3	2.0	210
Milltownpass	7.4	1.3	0.6	45	0.07	1.2	1.6	160
	6.2	1.3	5.0	250	0.14	3.5	8.4	1050
	6.3	1.5	4.9	35	0.03	0.8	8.4	135

Table 8: Lithosols - trace element content

Soil Series	Soil pH	Available (mg/kg)					Total (mg/kg)	
		B	Cu	Mn	Mo	Zn	Co	Mn
Slievereagh	4.1	2.9	2.8	11	0.14	35	0.8	35
	4.5	1.8	1.8	80	0.14	11	0.8	85

On the Milltownpass soil the pH values are somewhat lower at 6.2-7.4. This soil is also only suitable for pasture. Cobalt and copper contents of herbage will probably be quite low and fertilisation with these elements may well be necessary.

Lithosols

Only one Lithosol, the Slievereagh Series, has been mapped. The area occupied is again very small - only 20 hectares - representing some 0.01% of the total land area.

The pH values of the soil (Table 8) are very low, boron contents are quite normal, copper contents are fairly low and manganese is very low in one sample (11 mg/kg). One high

zinc value occurs and this is out of character with the nature of the parent material - it is possibly a reflection of some zinc mineralisation in the general area or some adventitious contamination. The very low cobalt values are consistent with the nature of the parent material (Old Red Sandstone bedrock).

Brown Earths

The total area occupied by Brown Earth soils is quite small. Those examined for trace element content (Table 9) - Baggotstown, Ballincurra, Ballynalacken and Knocknaske - total less than 5000 hectares and comprise approximately 2.5% of the total land area.

The Baggotstown soil has quite a high pH, and generally trace element levels are adequate. This is fortunate because availability of most trace elements is reduced by high soil pH. Molybdenum is an exception, being more available under alkaline soil conditions. The molybdenum content recorded for Baggotstown averages 0.34 mg/kg and the prevailing alkaline soil conditions might produce herbage with undesirably high Mo levels. When this happens there is danger of an induced copper deficiency in ruminants and copper supplementation will then become necessary. Grassland farmers on this soil should have herbage monitored in spring and autumn for molybdenum content. Cobalt may be low in herbage on this soil as the soil manganese content is high (940 mg/kg). The possibility of cobalt deficiency in sheep should not be overlooked. Copper and zinc

levels appear adequate for cereal growing but with the high soil pH the possibility of manganese deficiency in either cereals or sugar beet is very real.

The Ballinacurra soil pH values are also quite high and variation may be due to recent liming. Trace element levels in general are variable but for cereals, deficiencies of copper, manganese or zinc are a distinct possibility. For grassland, trace element levels are reasonably good but cobalt deficiency in sheep might be a problem and copper levels in pasture should be kept under review.

The Ballynalacken soil occupies a somewhat larger area than either Baggotstown or Ballinacurra. The soil pH is very high at 8.0 so manganese deficiency in cereals or sugar beet is likely. The copper level is quite good but zinc and cobalt contents are marginal.

Table 9 : Brown Earths - trace element content

Soil Series	Soil pH	Available (mg/kg)					Total (mg/kg)	
		B	Cu	Mn	Mo	Zn	Co	Mn
Baggotstown	7.8	1.0	4.6	350	0.36	3.4	7.6	940
	7.8	2.7	2.4	390	0.31	3.0	10.0	965
Ballinacurra	6.5	1.4	1.5	215	0.17	1.4	2.8	400
	7.9	0.7	1.0	45	0.10	0.8	6.8	390
Ballynalacke	8.0	1.3	6.0	55	0.14	1.6	7.6	450
Knockaskeha	6.4	1.4	5.5	45	0.14	0.2	4.8	390
	6.0	1.0	2.3	205	0.14	3.6	2.0	500
	6.0	2.4	7.2	210	-	11.0	6.4	500

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Table 10: Rendzinas - trace element content

Soil Series	Soil pH	Available (mg/kg)					Total (mg/kg)	
		B	Cu	Mn	Mo	Zn	Co	Mn
Burren	6.9	1.3	9.7	500	0.20	4.9	6.4	1500
	6.8	1.7	2.6	250	0.40	2.8	7.2	815
Kilcolgan	7.5	1.6	5.6	440	0.27	6.2	8.0	1130

The pH values of the Knocknaskeha soil are much lower than in the other Brown Earths. There is one very low value for zinc (0.2mg/kg) and this should alert farmers to the possibility of zinc deficiency in cereals, especially barley. From the tillage point of view all other trace element levels appear satisfactory but the possibility of cobalt deficiency in sheep exists.

Rendzinas

Two Rendzinas, the Burren and Kilcolgan Series, were analysed (Table 10). Both Soil Series are very small, comprising 0.17 and 0.03% of the total land area, respectively. The Burren Series extends to 344 hectares and the Kilcolgan Series to only 56 hectares.

The high pH of the Burren soil, coupled with an available molybdenum level of 0.4 mg/kg, may lead to undesirably high levels of molybdenum in herbage. Herbage analysis for molybdenum is advisable for grassland farmers on this soil. The total manganese contents are quite high and cobalt availability will therefore be low. Other trace element levels appear satisfactory.

The Kilcolgan soil may also give rise to herbage with elevated levels of molybdenum, but, as in the case of the Burren soil, cobalt availability will be poor, and thus pose problems in sheep farming.

Grey-Brown Podzolics

The Grey Brown Podzolic soils comprise two Series and occupy approximately one third of the map area. The Elton soil occupies some 10% of the area (approximately 20,000 hectares) and the Patrickswell Series 23% (46,000 hectares).

Soil pH values in the Elton soil are relatively high (Table 11). Trace element levels for arable crops are generally satisfactory but a few low zinc contents are apparent. These may give rise to zinc deficiency in cereals. Copper and manganese levels seem adequate, likewise boron contents. From the grassland point of view, molybdenum levels are satisfactory with just a few exceptions, *i.e.* where the Mo content exceeds 0.3 mg/kg and the soil pH is over 7.0. Cobalt levels are reasonably high but because of the generally high values for manganese (440-1250 mg/kg) cobalt

availability will be poor and, as in the case of other soils, cobalt deficiency may pose a problem in sheep farming.

Twenty-one samples from the Patrickswell Series were taken representing a sampling density of approximately 1 sample per 2000 hectares (Table 11). Soil pH values on the whole are high with only three values less than 6.5. For tillage crops the trace element levels are generally satisfactory. A few low

zinc values occur but there are also two high values which reflect some form of contamination or are possibly related to zinc mineralisation. Available Mn figures are high but, in view of the high pH values obtaining, manganese deficiency may occur in cereals especially in dry years. This possibility should be kept in mind. From the grassland point of view cobalt deficiency in sheep - especially lambs - may be encountered from time to time. As in the case of the Elton soil the total

Table 11: Grey Brown Podzolics – trace element content

Soil Series	Soil pH	Available (mg/kg)					Total (mg/kg)	
		B	Cu	Mn	Mo	Zn	Co	Mn
Elton	6.0	1.0	2.3	430	0.27	2.0	5.2	800
	7.4	1.7	2.2	205	0.14	2.2	9.6	690
	7.3	1.1	2.3	245	0.20	1.4	7.2	625
	7.3	1.2	3.4	110	0.17	0.8	3.2	300
Patrickswell	6.5	0.9	2.6	65	0.07	1.8	8.8	875
	6.9	1.1	3.3	225	0.20	2.4	5.6	675
	6.8	2.7	3.2	390	0.20	2.2	9.2	865
	6.6	1.5	3.8	370	0.20	1.6	7.2	975
	6.1	1.0	4.9	195	0.24	3.0	6.4	440
	6.9	1.3	2.7	225	0.34	1.4	5.6	615
	6.7	2.7	5.9	360	0.24	6.0	7.6	815
	7.2	1.4	2.7	380	0.32	4.8	6.8	840
	6.9	1.5	1.0	195	0.14	11	12	565
	6.1	2.0	1.4	195	0.20	2.6	6.4	450
	7.6	1.5	7.8	340	0.27	4.3	6.8	815
	6.5	0.7	2.8	360	0.27	3.2	14	805
	7.7	1.1	4.7	390	0.17	6.8	7.6	780

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Table 12: Brown Podzolics - trace element content

Soil Series	Soil pH	Available (mg/kg)					Total (mg/kg)	
		B	Cu	Mn	Mo	Zn	Co	Mn
Borrisoleigh	4.6	3.9	2.8	350	0.34	9.2	6.8	890
	5.3	1.6	1.4	70	0.20	3.3	3.6	275
	5.0	2.9	2.2	140	0.20	0.8	12.0	940
	4.3	1.7	3.2	17	0.20	6.0	0.4	85
	6.8	1.3	3.5	65	0.17	1.7	5.2	590
Doonglara	5.0	1.3	2.4	135	0.17	2.9	3.2	340
	6.1	1.9	2.2	70	0.14	2.4	5.2	185

Mn figures are quite high - thus rendering soil Co relatively unavailable. Molybdenum levels are generally satisfactory and although pastures with elevated levels of molybdenum may occur, the area in general is not considered molybdeniferous.

Brown Podzolics

Two Brown Podzolic soils, the Borrisoleigh and Doonglara Series were analysed (Table 12). The Borrisoleigh Series occupies 10.9% of the total land area (21,772 hectares). The Doonglara Series is much less extensive occupying 2314 hectares and representing 1.16% of the total area.

In contrast to the Elton and Patrickswell soils discussed above, the soil pH values of both the Borrisoleigh and Doonglara soils are relatively low. In the case of the Borrisoleigh soil two extremely low values of 4.6 and 4.3 occur. The loss-on-ignition figures from these samples are 24 and 28%, respectively, indicating quite a high organic matter

content. This to some extent explains the low pH values. The Borrisoleigh soils in general need lime and this will have repercussions in terms of reducing trace-element availability especially of manganese and boron. As these soils are primarily suitable for grassland, the addition of copper and cobalt may be necessary. Lime will also be needed for good grassland production and quality. This may have the effect of increasing the molybdenum content of swards and they should therefore be monitored for molybdenum content before and after liming. Liming will reduce cobalt availability and herbage analyses for cobalt are advisable especially if sheep are being grazed.

Podzols Soil Series

Only one Podzol, the Knockaceol Series, was analysed (Table 13). This Series is very small in extent, occupying only 0.04 % of the land area (78 hectares).

Table 13: Podzol - trace element content

Soil Series	Soil pH	Available (mg/kg)					Total (mg/kg)	
		B	Cu	Mn	Mo	Zn	Co	Mn
Knockaceol	6.0	1.3	1.4	180	0.14	3.1	0.8	340

Trace element levels in general are low with copper and cobalt being especially low. These low levels are consistent with the nature of the parent material (Old Red Sandstone). As this soil will in all probability be used for grassland, application of both copper and cobalt is advised as an aid in maintaining good stock health. Application of 10 to 20 kg/ha of copper sulphate and 2 to 3 kg/ha of cobalt sulphate will raise the herbage content of these elements and reduce the possibility of copper and cobalt deficiency in grazing stock.

Gleys

Fourteen Gley soils have been mapped in North Tipperary and 13 of these have been analysed for trace element content (Table 14). Only the Kilgory Series, which occupies but 0.3% of the area (54 hectares), was not analysed.

The Ballyshear soil (0.47% of the total area - 942 hectares) has a relatively high pH and the trace element levels in general are satisfactory. One high figure for copper was recorded (19 mg/kg). There is no immediate explanation for this except that the area may have been used for potato growing in the

past. On analysis, such soils often show a high copper content consequent consequent on applications of the fungicide Bordeaux mixture.

Considerable variation in soil pH is apparent in the Camoge soil. Values range from 5.3 to 7.7 but this may be merely a reflection of liming. Boron, copper and molybdenum contents are satisfactory. A few low values for zinc are apparent (1.6 and 1.8 mg/kg). Values for this element are quite variable with one rather high one occurring (12 mg/kg). Cobalt levels are variable and, as some high manganese values occur, the risk of cobalt deficiency (especially in sheep) exists. Only one sample was analysed from the Coolalough Series. The soil occupies only 0.15% of the total area and covers approximately 300 hectares. Trace element contents are satisfactory but with a soil pH of 7.3 the possibility of manganese deficiency, especially in cereals, must be considered.

Two samples were analysed from the Derrygarreen Series which again is very small, occupying a mere 0.05% of the total area. Here the soil pH is extremely low (4.2) and trace element levels in general are also very low. Obviously this soil needs lime and

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Table 14: Gleys – trace element content

Soil Series	Soil pH	Available (mg/kg)					Total (mg/kg)	
		B	Cu	Mn	Mo	Zn	Co	Mn
Ballyshear	6.5	3.8	19	160	0.07	11.0	5.6	375
	7.2	2.8	5.2	205	-	11.0	9.6	675
Camoge	5.5	1.7	6.2	210	0.17	5.6	6.4	525
	7.7	0.8	2.7	35	0.03	1.6	4.0	125
	7.4	3.7	9.4	60	0.10	2.2	5.6	350
	5.3	3.5	12.0	420	0.17	12	7.2	790
	7.2	7.3	14.0	195	0.55	7.6	7.6	765
	6.0	2.0	3.2	100	0.07	1.8	2.8	460
	6.2	10.0	4.0	75	0.20	2.9	6.0	300
	7.3	2.0	2.9	430	0.10	2.0	8.0	1000
Coolalough	7.3	1.4	4.0	140	0.10	4.6	4.0	400
Derrygarren	4.2	1.9	1.4	5	0.14	1.2	0.2	20
	-	1.6	0.6	25	0.03	0.6	0.2	30
Drombanny	5.8	3.5	6.5	34	0.52	20.0	3.6	100
Feale	4.8	1.0	11	65	0.07	13.0	6.8	200
	7.3	1.8	22	95	0.14	5.0	6.4	275
	5.6	1.6	1.9	165	0.39	0.6	6.8	415
	5.2	1.5	0.8	210	0.10	4.8	4.0	325
Gortaclareen	5.6	1.2	2.5	90	0.70	3.9	2.4	135
Howardstown	5.7	2.1	3.2	90	0.20	3.6	3.2	160
	6.0	1.2	3.0	100	0.07	1.4	3.6	200
	6.9	1.2	3.7	85	0.3	1.4	3.2	175
Kilcommon	6.0	2.2	4.3	85	0.24	1.4	3.6	285
	6.5	1.2	7.6	210	0.14	1.4	4.8	390
	5.3	2.0	2.7	110	0.10	2.8	7.6	360
	5.5	1.8	3.8	85	0.17	4.0	5.6	175
	5.2	0.7	2.3	50	0.10	1.8	8.0	200

Table 14: Gleys – trace element content (continued)

Soil Series	Soil pH	Available (mg/kg)					Total (mg/kg)	
		B	Cu	Mn	Mo	Zn	Co	Mn
Kilcommon (Peaty Phase)	4.8	2.5	8.4	85	0.70	12.0	9.2	175
Mylerstown	7.2	0.5	1.9	150	0.20	0.8	9.6	625
	7.8	0.7	2.1	175	0.10	5.0	7.6	565
	7.5	1.2	6.3	48	0.07	1.0	6.0	260
	7.2	3.3	2.7	140	-	8.4	5.6	590
Puckane	5.8	1.0	3.6	50	0.07	2.8	1.1	85
Puckane (Peaty Phase)	4.8	1.2	1.2	6	0.70	2.5	0.4	30

this will exacerbate trace-element deficiency problems. For crops such as cereals, copper, manganese and zinc supplementation would be necessary and for grassland, cobalt and possibly copper would need to be applied.

The Drombanny soil (513 hectares - 0.26% of land area) is low in manganese and slightly elevated in molybdenum content. Liming of this soil should be accompanied by manganese supplementation for cereals. Grassland would need to be monitored for molybdenum content as liming would increase available soil molybdenum.

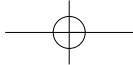
The Feale Series, occupying 2.4% of the area, is variable both in pH and trace-element content. Some liming will be necessary. Cobalt levels are reasonably satisfactory and

there should not be any severe problems from cobalt deficiency.

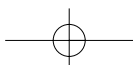
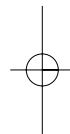
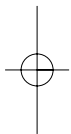
The Gortaclareen soil is similar in extent to the Feale. It too needs lime. As it is primarily a grassland soil, addition of cobalt will probably be necessary for sheep if soil physical conditions are such that sheep farming is practicable.

The Howardstown Series is reasonably well supplied with trace elements. Cobalt will be necessary for sheep farming. This soil is relatively small in extent - 0.95% of the land area or 1902 hectares.

The Kilcommon Series is reasonably extensive, occupying over 12,000 hectares (6.15%) of the total land area. Soil pH values



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Table 15: Peat — trace element content

Soil Series	Soil pH	Available (mg/kg)					Total (mg/kg)	
		B	Cu	Mn	Mo	Zn	Co	Mn
Aughty	4.1	2.5	1.4	6	0.07	1.6	0.8	20

are mostly low and lime application will be necessary. The cobalt status is reasonably good.

The Peaty Phase of the Kilcommon Series is extremely acid and liming is required. Levels of other trace elements are satisfactory for this essentially grassland soil.

The Mylerstown Series (4297 hectares, 2.15% of total area) has a high pH value. Copper and zinc levels are marginal but are probably sufficient for grassland.

The Puckane Series, with the low pH of 5.8, would require lime for barley or sugar beet. For grassland, cobalt would probably be necessary; cobalt sulphate application will give a good response in terms of increasing the cobalt content of herbage.

The Peaty Phase of the Puckane Series is very acid and liming is necessary. The copper level is low and the manganese levels extremely

low. The cobalt content is also very low and application of cobalt sulphate to grassland is advisable. Copper levels in pasture may also be low. After liming, manganese levels in grassland should be monitored.

Seven peat soils have been mapped but only one, the Aughty Series, was analysed for trace elements (Table 15). This Series occupies 0.53% of the land area (1056 hectares). For tillage crops or grassland, liming is required. As expected on a peat soil, levels of most trace elements are low. On grassland, extra cobalt will be required for sheep but cattle may also require supplementation. This soil will respond very well to applied cobalt as the manganese level is very low. Copper levels in pasture are likely to be undesirably low.

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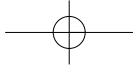
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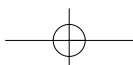
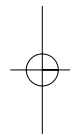
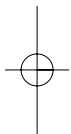
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¹ From Askeaton Investigation

Major and trace elements in soils and plants

The soil is an essential medium for the growth of plants and for the breakdown and recycling of organic matter. Soils are considered the most important environmental compartment functioning as a sink for trace elements (Senesi *et al.*, 1999). Changes in soil properties such as pH, redox potential and moisture status can affect the bio-availability and form of the elemental components of the soil. Soils are reasonably stable but become progressively more acid due to the action of dissolved carbon dioxide. Acidity (low soil pH) can be adjusted to optimum levels for crop production by additions of lime. Metal cations are more active under acid conditions and increases in pH reduce their bio-availability. Conversely anions, for example molybdate, become more available with increase in pH.

Large transfer of elements, including metals, to soil systems will change not only the chemical properties but will also influence the physical and biological properties of the soil. Certain metals, including Cu, Zn and Ni, at moderate levels, are also harmful to micro-organisms and may affect essential soil processes (McGrath, Chaudri and Giller, 1995).

Metal pollution can include two categories of

harmful effects to higher life forms. In the first category the concentration in plant or in the soil could reduce growth of vegetation by phytotoxic effects. Secondly, the concentration present may not affect the growth of vegetation but could constitute a health hazard to those who consume it.

Elemental uptake by plants is influenced by factors controlling (1) the level and chemical form of the element (speciation) in the soil (2) the movement of the element to the root (3) the absorption of the element into the root and (4) the translocation from the root to the plant shoot. In addition to root absorption, plants can also take in significant amounts of the same elements by leaf absorption and this can be the route of entry by atmospheric pollutants. The readiness of deposited particles to enter through the leaf surface obviously depends on the particular metal; for example zinc can enter plants more readily through foliar absorption than can lead or copper (Little, 1973).

Nearly ninety chemical elements may be found in soils and plants. Many may be quite toxic even at low levels of intake, whereas others are relatively innocuous. The elements which are essential for life are those which

From Askeaton Investigation was taken from D. McGrath, O.T. Carton, J.J. Diamond, A.M. O'Sullivan, P.A.M. Rogers P.J. Parle and J.E. Byrne, 2001. Investigations of Animal Health Problems at Askeaton, Co. Limerick. Vol. 3. Soil, Herbage, Feed and Water, EPA, Wexford. 138 pp. This publication relied heavily on an Interim Report prepared in 1995 by P.J. Parle and published by the EPA in 1995.

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cannot be wholly replaced by any other element. If a particular organism does not have a certain minimum supply of an essential element it cannot complete its life cycle. In this respect the trace elements are as important as the major elements - the principal difference is that they are required in much lower quantities. The elements are for convenience divided into major elements and trace elements. The dividing line is usually set at 0.1 percent or 1,000 milligrams per kilogram; this is a purely arbitrary limit.

Ranges of elements in soils

Range of values anticipated for major elements (Table 1) and for trace elements/heavy metals (Table 2) are based on experience of Irish soils by P. Parle (personal communication, 1995) and McGrath and McCormack (1999), Range I and II, respectively. Data on some of these elements in Irish soils is relatively limited. The ranges given are those encountered in Irish agricultural soils. Much higher levels may be encountered in the vicinity of ore deposits (DAFRD, 2000) and in industrial areas. Urban soils tend to have much higher concentrations of metal elements than do rural soils. Garden soils, particularly those from old gardens, tend to have relatively high metal contents (McGrath, 1995).

Extractable trace elements in soils

Total content of an element in soil - whether major or trace - is not a good guide regarding

its availability to the growing plant. Therefore, a range of empirically derived extraction procedures have been developed to simulate the availability of elements to plants. The extraction techniques used for soils employ reagents whose extractable content correlates with the plant-available content of the soil and so can be used to predict plant uptake or the possibility of deficiency or toxicity symptoms occurring in plants or animals. This approach is well established in soil science for predicting the uptake at normal concentrations of essential and potentially toxic elements (Martens and Lindsay, 1990; Risser and Baker, 1990).

The reagents used are relatively mild extractants and they may vary for each element. Extractants are described by Byrne (1979) and estimates are by Parle (personal communication, 1995). It is important to realise that, whereas extractable contents give a better index of availability they are by no means perfect and their ability to predict likely plant contents is dependent on a number of soil factors, e.g. pH, organic matter content and soil texture. Table 3 gives the normal ranges of elements extracted with conventional extractants. These data have been accumulated over many years and represent the position as it is known at present.

From Askeaton Investigation

Table 1: Typical ranges (g/kg) of major elements (total contents) in non-polluted Irish soils

Element	Symbol	Range I	Range II
Aluminium	Al	10.0 - 80.0	7 - 89
Calcium	Ca	5.0 - 30.0	-
Iron	Fe	10.0 - 50.0	3 - 59
Magnesium	Mg	1.0 - 15.0	0.4 - 18
Nitrogen	N	1.0 - 4.0	-
Phosphorus	P	0.2 - 2.0	-
Potassium	K	1.0 - 30.0	3 - 25
Silicon	Si	150 - 400	-
Sodium	Na	0.5 - 15.0	-
Sulphur	S	0.2 - 1.5	-

Table 2: Typical ranges (mg/kg) of trace elements (total contents) in non-polluted Irish soils

Element	Symbol	Range I	Range II
Antimony	Sb	0.2 - 3.0	-
Arsenic	As	1 - 50	3 - 104
Boron	B	20 - 1000	-
Cadmium	Cd	0.1 - 1	0.01 - 3.2
Chlorine	Cl	30 - 300	-
Chromium	Cr	5 - 250	3-323
Cobalt	Co	1 - 25	1-53
Copper	Cu	2 - 100	2 - 73
Fluorine	F	20 - 700	-
Iodine	I	2 - 20	2.5 - 16
Lead	Pb	2 - 80	10 - 100
Manganese	Mn	20 - 3000	20 - 5167
Mercury	Hg	0.03 - 0.8	0.03 - 1.0
Molybdenum	Mo	0.2 - 3	-
Nickel	Ni	0.5 - 100	1 - 150
Selenium	Se	0.2 - 2	0.2 - 9.7
Thallium	Tl	0.1 - 0.5	-
Tin	Sn	1 - 40	-
Uranium	U	1 - 10	-
Vanadium	V	20 - 250	-
Zinc	Zn	10 - 200	4 - 239

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Table 3: Typical ranges of extractable elements in non-polluted Irish agricultural soils

Element	*Extractant	Content (mg/l)
Phosphorus	Acetic acid - sodium acetate	1 - 20
Potassium	Morgan's reagent (pH 4.8)	50 - 300
Magnesium		30 - 400
Sodium	Ammonium acetate	20 - 100
Sulphur	Calcium phosphate	<10.0 - 50
Manganese (easily reducible)	Calcium nitrate and 0.2% Quinol	10 - 600
Copper	EDTA (pH 7.0)	1.0 - 20.0
Zinc		2.0 - 15.0
Molybdenum	Ammonium oxalate/ oxalic acid Tamm's reagent (pH 3.3)	0.1 - 1.0
Boron	Hot water	0.1 - 4.0

Effects of aerial contamination on soil and herbage

In this section types of contamination likely to be experienced on farms, and that may lead to an increase of chemicals (mainly inorganic) in soil and herbage, are considered.

The composition of both soil and herbage can vary quite considerably with the variability of the former being generally much greater than that of the latter. There is no such thing as a standard soil and many soils have an excess or deficiency of one or more elements that are required for good plant growth and animal health.

In suspected soil/herbage contamination cases, especially where animal ill-health or death occurs, at least three scenarios fall

within the remit of the chemist. These comprise (1) events involving emission and deposition, (2) natural (geochemical) pollution or contamination by mining or dumping and (3) direct or induced mineral deficiencies.

Pollution of herbage/soil by aerial deposition

Industry has been and still is responsible for the emission of a wide range of solids and gases (Burton, 1986). The former include largely inert materials from earth-moving activities (quarrying, mining) but may also include mining residues containing heavy metals, or products of incomplete combustion, *e.g.* soot. Gaseous emissions and their products include acid-forming gases, *i.e.*

oxides of sulphur and nitrogen, hydrofluoric acid, hydrochloric acid and ozone. All of the above, at a sufficiently high concentration, can have a visible effect on plants (Guderian, 1977). Most, with the possible exception of nitrogen oxides and ozone, may in practice affect animals and have been implicated in incidents involving farm and wild animals (National Research Council, 1991; Samiullah, 1990).

Smelting and combustion may also cause the volatilisation of some metals especially mercury, cadmium and lead in addition to acid gases. Organic substances, particularly solvents may also be released in variable amounts. Insecticides, especially are continually being implicated in acute toxicity events in underdeveloped countries (Knott and Day, 2000). Immediate effects following explosive dispersion of chemicals and their derivatives as in Bhopal in 1984 and Seveso in 1976 have received widespread publicity, but are of infrequent occurrence. Emissions from discarded solvents and from petroleum refineries have been implicated in reported chronic incidents. When it comes to long-term chronic effects, the list of possible influential emissions lengthens for animals, especially humans, but not to the same extent for plants.

In Ireland a number of proven instances of emissions influencing soil or herbage have been documented. Greatly increased levels of lead in soil have been demonstrated for one mining area (DAFRD, 2000): deposited lead on

herbage has been reported in another (Donovan *et al.*, 1968). Animal deaths had been authenticated in both these areas and were attributed to lead poisoning.

Also in Ireland, significant gaseous emissions have been found for hydrofluoric acid (used for glass-etching) and in earlier years sulphur dioxide generated from pyrites or in superphosphate production. The former constituted a risk to animal health from excess hydrofluoric acid deposited on vegetation. High sulphur dioxide levels associated with the phosphate fertiliser plant is known to have caused considerable damage to vegetation.

Elsewhere, very serious metal emissions tend to be confined to smelters and superphosphate plants. Gaseous emissions are associated with smelters, superphosphate plants and brickworks. This is not a comprehensive list, as even localised industries can cause serious emissions, *i.e.* where mercury is used in gold prospecting.

Emissions tend to leave only a minor impression on soil compared to herbage. Very high sulphate levels have been found in soils (Meshalkina *et al.*, 1996) in affected areas. Sulphuric acid deposition also causes acidification of soils. This can result in leaching of essential elements especially in light textured soils. Very acid soils require amelioration with lime before crops can again be grown. pH elevation also reduces the availability of many trace elements. In parts

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of the US this process has produced crops (for example, alfalfa) containing extremely low levels of manganese. This in turn has resulted in illness and death of ruminants due to manganese deficiency or refinery smoke syndrome as it has been called (Cowgill *et al.*, 1980).

Overall, outside of long established heavy dirty industry, aerial emissions occurring in amount sufficient to influence soil and vegetation are rare. In the experience of Teagasc, chemically measurable effects in recent years have been largely confined to dust or soil from mine workings and to hydrofluoric acid used in glass etching being deposited on herbage. Vegetation is susceptible to large numbers of other effects, physical, climatic, seasonal and disease. Visible symptoms displayed by plants are much more likely to result from these causes than from polluting influences. This is not to deny that emissions do occur – where fuel is burned, sulphur dioxide is formed and metals are volatilised. It is saying that such emissions now generally have little impact on the composition of soil and plants.

Geochemical pollution

Some soils are heavily polluted. In mining areas it is difficult to separate natural (geochemical pollution) from pollution caused by historic mining activities especially in areas that have been naturalised over the years. Some of this pollution is quite extensive but some occurs in small pockets.

Levels of metal, lead, zinc and copper can be sufficiently high to affect animals *via* ingestion of soil but not normally of soil-free herbage. Parts of the country experience low level enrichment of these and other metals in soil. Such areas include parts of Limerick and Clare as well as some Midland counties. A special instance of poisoning results from selenium which has accumulated in small pockets in peaty soils especially in Counties Limerick, Tipperary and Meath. Consumption of herbage grown in these areas can cause sporadic injury and even death to cattle. In these regions, other metals and especially cadmium have also been found at potentially dangerous levels in soil. Frequency of occurrence of any of these pollutants in toxic amounts is not large but effects can be serious. Perhaps a milder but much more extensive level of pollution relates to molybdenum, which is not in itself toxic but which interferes with copper absorption by ruminants, and this will be referred to below.

Mineral deficiency

Trace elements in Irish mineral soils are generally sufficient to sustain grass growth. However, mineral deficiencies may occur on farms and may impinge on animal performance and health. They principally include cobalt, selenium, iodine and copper (Rogers and Keating, 1994). Other soil components interact with these nutrients, at plant or animal level. Interactions include interference by manganese in soil with cobalt uptake by plants and interference by

molybdenum but also zinc, iron and sulphate with absorption of copper by animals from ingested herbage. Many soil nutrients, both major and trace, are relatively permanent although they need replenishment to varying degrees. However, as indicated above, some are especially transitory, *i.e.* iodine, selenium and sulphur.

Whereas many industrial pollutants, and particularly those with major impact, are deposited close to their emission point, many have long range (often transboundary) effects. Some are noxious but others may have a positive effect. Among the former may be listed lead (from petrol additive) mercury and perhaps sulphur. Among the positives may be selenium and iodine. Some would now be tempted to transfer sulphur to the positive list as sulphur deficiency in grassland has been recognised in Ireland for many years (Murphy and Boggan, 1988) and is now regarded as commonplace even in industrialised areas (Bristow and Garwood, 1984).

Askeaton Investigation

The remainder of this chapter deals with analytical result of general interest from the Askeaton Investigation (EPA, 2001). The investigation had been conducted in an attempt to determine reasons for the widely reported increased incidence of ill-health and death in farm animals and humans in the Askeaton area of Co Limerick. The Teagasc contribution dealt largely with soil, herbage,

feed and water. It centered on three farms (one of which was termed a control) and *ca.* 20 additional farms which were subjected to less intensive investigation. It dealt with fluorine and selenium in soils of the area, monitoring of sulphur and selenium in herbage, heavy metals in soils in soils and herbage (Retrospective Study) and follow-up investigation of instances of excess heavy metal in soils and plants.

Soil sampling procedure

Soil sampling procedures vary in respect of a) sampling depth, b) area represented by each sample and c) number of sub-samples in each sample. Despite the variability of published protocols it is the Teagasc view, and one generally held, that the actual procedures used should be tailored to the circumstances of each case.

For agronomic purposes, Johnstown Castle stipulates that (i) samples be taken to a depth of 100 mm; (ii) the maximum area represented by each sample is an area of two to five ha, or one enclosure whichever is the smaller; (iii) at least 20 cores be taken in a W-shaped pattern across each sampled area and combined to constitute a sample. In the present case, the fields were inspected and divided into 2 to 3 ha-sized units before sampling. In 1995 soils were sampled to a depth of 50 mm. At least 100 soil cores were taken from each sampling unit. The primary objective was to obtain evidence of aerial deposition of contaminants. A depth of 50

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mm was the minimum that could be conveniently and accurately sampled. This was the sampling depth used in previous baseline surveys conducted in the area. However, it meant some loss of comparability against standard Johnstown Castle agronomic data on grassland soils. This loss will be more important for pH and extractable phosphorus and potassium than for other soil chemical parameters. pH is normally lower in the 0 to 50 mm horizon than in the 50 to 100 mm horizon. Phosphorus and potassium levels will be higher at 0 to 50 mm, as a consequence of ongoing fertiliser applications, compared with the 0 to 100 mm layer.

Soil analytical methods

Before analysis, soils and sediment were dried at 40°C in a forced draught oven, ground gently, and sieved to pass a 2 mm sieve.

A brief description of the analytical methods used for soils and sediments is given in Appendix 1. In general, extraction and estimation procedures in common use at Johnstown Castle were followed. These approximated to those described by Byrne (1979) with amendments to accommodate newer extraction (*e.g.* microwave) and estimation (*e.g.* electrothermal atomic absorption) techniques.

The accuracy of each method was verified by the use of standard reference materials for

which the accepted values of the analyte concentrations were established either internationally, *i.e.* BCR (EU) or NBS (U.S.) or, in exceptional cases, by in-house studies.

Fluorine in soil

Mean fluorine values for the soils from the Somers, Ryan and Control farms are 984, 675 and 697 mg/kg, respectively. These values are high compared to mean values of 300-400 mg/kg for UK soils (Fuge and Andrews, 1988). No information was available on fluorine levels in Irish soils. Therefore, as part of this investigation, fifteen additional samples were selected at random from soil received for analysis at Johnstown Castle and were analysed. Results are presented in Table 4.

The mean value for soil fluorine was 461 mg/kg which is comparable with reported UK values. However, the levels in the Limerick soils were consistently higher. A further series of fluorine determinations were made from soil archival samples, 4 taken from N, S, E and W of each of the Askeaton Farms. These soils had been sampled in 1979 as part of the Aughinish baseline survey (Fleming and Parle, 1981). They were found to have significantly elevated fluorine levels (Table 5) with means of 760, 578 and 760 mg/kg associated with Somers, Ryan and Control farms, respectively.

From Askeaton Investigation

Table 4: The fluorine content (mg/kg) of Irish soils

County	No. of samples	Fluorine
Tipperary	1	370
Roscommon	1	540
Offaly	2	470, 490
Dublin	1	470
Donegal	1	540
Galway	1	300
Louth	1	310
Waterford	1	250
Wexford	2	300, 280
Mayo	1	680
Limerick	3	680, 700, 540
Mean		461

Table 5: Fluorine content (mg /kg) of soil samples taken in 1979 as part of the Aughinish Baseline Survey

Location and Ident No.	Fluorine
Somers Farm (AAH 277)	640
Near Somers (AAH 272)	620
Near Somers (AAH 276)	980
Near Somers (AAH 285)	800
Mean	760
Ryan Farm (AAH 302)	600
Near Ryan (AAH 205)	490
Near Ryan (AAH 206)	620
Near Ryan (AAH 294)	600
Mean	578
Near Control (AAH 290)	800
Near Control (AAH 291)	800
Near Control (AAH 293)	640
Near Control (AAH 295)	800
Mean	760

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Selenium and fluorine in soil profiles

In order to confirm that the mild enrichment of selenium and fluorine in soils on the Somers farm were not due to aerial deposition, soil on paddock was sampled at various depths from surface to 225 mm (Profile 1) and from surface to 175 mm (Profile 2) - depths roughly equivalent to the plough layer. The results (Table 6) showed no variation with depth indicating that selenium and fluorine did not significantly increase in this soil since it was last tilled.

Herbage - Introduction

Both fodder (silage and hay) and herbage samples were taken for analysis. Even under controlled conditions pasture herbage varies

in mineral content throughout the year. Fertiliser treatment will obviously affect pasture mineral content, but even in the absence of applied fertiliser, season and stage of growth effects combine to alter mineral composition. The magnitude of such changes varies depending on the element. In a study such as the present one where material is comprised of different herbage species at different stages of growth and from diverse pasture management systems, major element composition may vary by as much as twofold between maximum and minimum (Fleming and Murphy, 1968). Trace metal composition can vary even more, especially following contamination of herbage by soil.

Table 6: Selenium and fluorine content (mg/kg) of soil * from the Somers farm

Profile	Depth (mm)	Se	F
1	0 - 12.5	0.60	840
	12.5 - 25	0.60	720
	25 - 50	0.65	790
	50 - 75	0.60	900
	75 - 125	0.60	900
	125 - 175	0.66	900
	175 - 225	0.65	900
2	0 - 12.5	0.55	840
	12.5 - 25	0.50	860
	25 - 50	0.50	820
	50 - 75	0.55	860
	75 - 125	0.55	860
	125 - 175	0.55	860

* two profiles : 1 lower, 2 higher elevation

Ranges of elements in pastures

At the present time it is known that nineteen elements are needed by plants for healthy growth, whereas twenty five are needed by animals. The following elements are those required by plants: carbon, hydrogen, oxygen, nitrogen, calcium, potassium, magnesium, phosphorus, sulphur, boron, chlorine, copper, iron, manganese, molybdenum, zinc, cobalt, silicon and sodium. Cobalt is intimately connected with nitrogen fixation in legumes so a case can be made for its inclusion in the list. Silicon is known to be essential for rice, and sodium is essential for plants adapted to saline environments. These two elements though invariably present in normal herbage species do not appear to be essential for their growth.

In the case of animals all the elements listed above are required together with the

following - arsenic, chromium, fluorine, iodine, nickel, selenium and vanadium. The ranges of the above elements - with the exception of carbon, hydrogen and oxygen - normally found in Irish pasture herbage are shown in Tables 7 (major nutrients) and 8 (trace elements). An estimate of requirement for individual nutrients in herbage is also given (Whitehead, 2000). The latter figures only serve as a general guide as animal requirements vary with animal type, age and stage of development.

Seasonal variation and stage of maturity

Changes in mineral composition of pasture plant will occur over the growing season. The magnitude of those changes will differ with plant species and all the elements will not be affected to the same extent. Management practices will have a major influence on the

Table 7: Typical ranges (g/kg) of major elements in non-polluted Irish pasture and recommended dietary concentrations (g/ kg) for animals (cow, pregnant, non-lactating)

Element	Symbol	Herbage content	Typical concentration	Animal requirement
Calcium	Ca	2.0 - 17.0	6	2.9
Chlorine	Cl	2.0 - 20.0	3.5	2.0
Magnesium	Mg	0.8 - 5.0	2	1.6
Nitrogen	N	10.0 - 50.0	28	19.2
Phosphorus	P	1.0 - 5.0	4	2.3
Potassium	K	8.0 - 40.0	25	6.5
Silicon	Si	1.0 - 2.0	-	-
Sodium	Na	0.1 - 6.0	2.5	1.0
Sulphur	S		3.5	1.6

Trace Elements and Heavy Metals in Irish Soils

variation in content, as will factors such as soil temperature, rainfall and fertiliser applications. Stage of maturity will affect mineral components of pasture plants to a similar extent when dry matter production of the growing plant out-strips uptake of minerals. For pasture species these effects have been described in detail by Fleming and Murphy (1968) and by Fleming (1973).

It is relatively simple to take an uncontaminated soil sample but it is much more difficult to obtain a soil-free herbage sample. Soil contamination of herbage can result from (1) trampling by grazing animals, particularly under intensive grazing (2) splashing caused by rainfall, (3) deposition following a prolonged dry period.

Table 8: Typical ranges and dietary concentration (mg/kg) of trace elements in non - polluted Irish pastures and recommended (cow, pregnant, non-lactating) dietary concentration

	Symbol	Herbage content	Typical conc.	Animal requirement
Antimony	Sb	0.05 - 0.3	-	Nil
Arsenic	As	0.05 - 0.3	-	-
Boron	B	1 - 20	5	Nil
Cadmium	Cd	0.01 - 0.3	-	Nil
Chromium	Cr	0.1 - 0.3	-	-
Cobalt	Co	0.03 - 0.2	0.1	0.10
Copper	Cu	2 - 15	-	10
Fluorine	F	0.5 - 10	9	-
Iodine	I	0.05 - 0.3	-	0.60
Iron	Fe	20 - 300	150	50
Lead	Pb	0.5 - 20	-	Nil
Manganese	Mn	20 - 300	165	40
Mercury	Hg	0.01 - 0.05	-	Nil
Molybdenum	Mo	0.05 - 2	0.9	-
Nickel	Ni	0.5 - 3	-	-
Selenium	Se	0.03 - 0.5	0.05	0.3
Titanium	Ti	1 - 5	-	Nil
Vanadium	V	0.05 - 0.5	-	-
Zinc	Zn	20 - 60	37	40

Degree of contamination by an element will depend not only on the proportion of soil present but also on the ratio of element in soil relative to plant. Certain elements such as Al, Co, Fe,

Cr, V, Ti and F have high (100+) soil/plant ratios and use can be made of these to demonstrate the presence/absence of soil.

Toxicity

A number of elements necessary for plant and/or animal health may be present in herbage in toxic amounts and thus can cause harm to grazing stock. Similar remarks apply to a number of contaminant elements, elements which fulfil no known useful function in plant or animal nutrition. It is not possible to give toxicological data for elements in herbage for a number of reasons including the fact that their toxicities may be enhanced or mitigated by the presence of other elements.

Grass sampling and analysis

Grass was sampled close to ground level using an electric shears, taking care not to include soil, between May 9 and 11, 1995. Sampling locations were analogous to those used for soils. Samples from the one enclosure were bulked to comprise a single plot sample. These were dried at 104°C for general analysis and at 40°C for Se, As and Hg analysis. Procedures generally involved strong acid digestion and estimation by

flame or electrothermal atomic absorption analysis as appropriate (Appendix 2: Byrne 1979).

Sulphur, copper and molybdenum

Sulphur deficiency in grassland in Ireland is associated with light-textured soil low in organic

matter content. Herbage production can be affected, as can quality. Levels of less than 2.0 g/kg are considered to be undesirable especially if the ratio of nitrogen to sulphur in the plant is in excess of fifteen. Low levels of copper do not normally affect grass production in Ireland, particularly on mineral soils, but deficiencies can occur in cereals and root crops and on peatland. Molybdenum deficiency in crops is rare in Ireland except, perhaps, in cauliflower.

The molybdenum requirements of animals are extremely low and can be met by most natural dietary ingredients. Animal disorders arise from a shortage of copper with the young bovine being particularly susceptible. When molybdenum in herbage is in excess, it has the effect of reducing the availability of copper from pasture to the grazing animal. If sulphur levels are also high, the effect can be exacerbated (Suttle, 1978). Levels of molybdenum >3 g/kg must be considered suspect in this regard.

Pasture species vary in copper content. This will be influenced by the copper content of

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the soil, pH of the soil, stage of maturity of pasture, season and management procedures such as fertiliser usage - particularly nitrogen applications. Levels of copper of >10 mg/kg in herbage are desirable for cattle but are rarely attainable in pure ryegrass swards. Old pasture containing clover and plant species will usually have higher levels of copper than the pure ryegrass pastures.

The sources of the Irish high-molybdenum soils are Carboniferous black shales and Calp limestones. The main areas with such soil parent materials are found in the Midlands, Co. Limerick and sporadically eastward from there to Clonmel. Other small areas are scattered throughout the country. An elevated soil pH greatly increases the uptake of molybdenum by plants. The magnitude of the increase varies with species - clover contents being higher than grasses, whereas with grasses Cocksfoot (*Dactylis glomerata*) and Yorkshire fog (*Holcus lanatus*) will absorb more molybdenum than do the ryegrasses. Molybdenum uptake can also be influenced by season, which is mainly a reflection of the moisture status of the soil. Following wet periods there can be up to a fivefold increase in molybdenum content in pasture species.

Elements such as zinc, cadmium and iron can also depress copper absorption by the animal and can reduce plasma copper concentrations when ingested at high dietary levels. Soil ingestion, particularly at high stocking rates and at the end of the grazing season, when

soil moisture is high, can be a major source of metal intake, especially in the case of iron.

Monitoring of farm herbage

Herbage was sampled to ground level on 4 pre-selected paddocks on both Ryan and Somers farms. Sampling was conducted at 4-8 weekly intervals between November 1995 and February 1998. Samples were analysed for nitrogen, sulphur, selenium and molybdenum. Mean results of these analyses are shown in Table 9. Results showed that increases in herbage selenium were unrelated to increases in herbage sulphur. A similar situation has been reported for atmospheric levels of these elements in areas suffering from low levels of pollution. Conversely, a highly significant relationship between the two elements occurred where pollution levels were high and sources numerous (Eldred, 1997). Much of plant sulphur (Whitehead, 2000) and plant selenium (Haygarth *et al.*, 1993) is derived from atmospheric sources. The pattern of the relationship in Askeaton was suggestive of a comparatively small number of weak local sources for both elements for example, households and small industries rather than large industries.

Sulphur and nitrogen Sulphur content of herbage was generally high, averaging about 3.5 g/kg (Table 9). There was little difference on average between mean S levels on Ryan and Somers farms. Individual S values varied with N. However, herbage N and S, for

Table 9: Mean herbage S (g/kg), N (g/kg), Se (mg/kg) and Mo (mg/kg)

	Somers				Ryan			
	S	N	Se	Mo	S	N	Se	Mo
Mean	3.6	37.6	0.14	1.52	3.8	30.9	0.07	1.04
Max	5.20	49.0	0.28	2.34	5.20	52.0	0.15	2.78
Min	2.40	24.6	0.07	0.97	2.40	23.7	0.03	0.52

samples taken on the same occasion from different fields on the same farm varied by as much as two-fold. Winter values tended to be higher than summer values on average. In general the range of values and mean values over time (Table 9) were similar to those encountered in other surveys. There is no evidence of an excess of sulphur in herbage on either farm between November 1995 and February 1998.

Mean sulphur levels (with SD) in the four individual sampled sites were 3.86 (0.77), 3.64 (0.73), 3.68 (0.86) and 3.29 (0.99) g/kg on the Somers farm and 4.04 (0.90), 3.66 (0.75), 3.52 (0.74), 3.97 (0.86) g/kg on the Ryan farm. No statistically significant difference between any site could be demonstrated. On the Somers farm higher values were associated with proximity to the roadway-on the Ryan farm with proximity to the mud flats on the River Deel which bordered the eastern side of the farm.

Selenium Selenium values were generally higher on Somers than on the Ryan farm as

anticipated. Replicate values for either farm at the one time varied considerably-by a factor of as much as five-fold. This finding does not encourage the belief that a single selenium determination for herbage in a paddock can accurately reflect the quantity of selenium available to grazing animals on a farm. In their baseline survey of the Aughinish area, Rogers and Poole (1984) highlighted the variation in herbage selenium within farms and between seasons. Winter values were higher than Summer values which has been previously noted (Haygarth *et al.*, 1993).

Mean selenium levels (with SD) on the four individual sampled sites were 0.079 (0.044), 0.189 (0.076), 0.162 (0.099), and 0.100 (0.093) mg/kg on the Somers farm and 0.066 (0.038), 0.067 (0.045), 0.066 (0.027) and 0.070 (0.035) mg/kg on the Ryan farm. Difference between some of the Somers sites were statistically significant ($P \leq 0.05$) with highest levels on two paddocks that had been found to have higher soil Se. As one unmonitored part of the farm had yet higher values for herbage selenium in unmonitored parts of the farm

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Table 10: Frequency distribution of selenium (mg/kg) in Irish pastures 1986-1993

	0 - 0.05	0.05 - 0.07	0.07 - 0.10	0.10 - 0.15	0.15 - 0.5
%	26.4	32.9	18.0	12.9	9.7

can be assumed. Levels of selenium on all parts of the Ryan farm were generally low with means of 0.06-0.07 mg/kg over the period. Levels during the grazing season were even lower, ranging from 0.04 to 0.06 mg/kg. The values, although decidedly low, are not exceptional when viewed against those for herbage samples received for analysis at Johnston Castle Analytical Laboratories over an 8 year period (Table 10: P. Parle, personal communication, 1995). Price (1989) in Scotland has argued that values of 0.03-0.05 mg/kg selenium in herbage does not necessarily indicate a resultant biochemical (blood enzyme) deficiency not to mention a clinical deficiency.

Molybdenum Molybdenum values again varied to an extent similar to selenium. On both Ryan and Somers farms Mo values were never so high as to present a serious risk of reducing copper availability to a dangerous extent.

Retrospective Study Soils - July 1997

On all but three farms, departures from normality of soil components were relatively small, reflecting probably geochemical influences, and would have had no

toxicological significance for plant or animal. Values for soil pH, and for extractable P, K, Mg, Cu, Zn and Mn were unexceptional, varying from moderately deficient to moderately enriched. Soil pH in particular was generally on the high side reflecting the limestone parent material. The metals, Cu, Mn and Co were present at normal concentrations. F values were higher than those found in most other parts of Ireland: they were similar to those recorded for the Ryan and Control farms in the 1995 investigation but were lower than those on the Somers farm. Ni values were a little on the high side and Cr (with which Ni is generally positively associated) tended to be low. Se and Pb levels were perhaps slightly elevated on average.

Elevated Cd levels were attributed to the proximity of the Clare shale out-crop which runs generally in a north-south direction and crosses the Shannon near Foynes. Cd is now viewed as a negative component of soils and levels in excess of 1 mg/kg are generally taken as indicating contamination. The level of contamination, generally 1-2 mg/kg was mild but widespread, extending to more than half of the soils analysed.

Three soils differed considerably from the norm. One soil had a relatively high level of Se

which could be considered dangerous to grazing animals: very high levels of this element are associated with the peaty phase of alluvial soils occurring in small pockets in a number of areas including south-west Limerick. A second soil had a particularly high level of Pb, approaching 800 mg /kg. Such a level, although exceeding normal background by a factor of about 30 would not normally have a measurable impact on plant or animal within a small area. Zn in a third soil, in particular, was high, nearly 400 mg/kg. At such a level the possibility of inhibition of plant growth arises. From existing information it seems likely that instances of elevated Se and of Zn had a geochemical origin whereas mining on a small scale in the past may have contributed to the presence of elevated Pb.

Retrospective Study Herbage – July 1997

Analyses for herbage N, P, K, Mg, Na, Ca and S (Table 11) indicated a fairly normal range with the occasional high value, for instance for S, being balanced by low values (even to the point of being suggestive of S deficiency). With respect to trace components, Se levels, although normal, included some very low values (*i.e.* 0.03 mg/kg) – values which, although low, are not rare. Two of the manganese values at 8 and 20 mg/kg were exceptionally low, perhaps the lowest recorded at Johnstown for an Irish herbage: these samples come from soils of exceptionally high pH 7.4, which is a feature in the production of Mn deficient herbage. As noted above soils in the area have generally normal, and arguably even slightly elevated, levels of Mn. Zn and Cu levels were unexceptional.

Table 11: Composition (mg/kg DM) of herbages (47) from 21 farms participating in the Retrospective Study, July 1997.

Component	Mean	SD	Min	Max
N (g/kg)	32.0	10.1	12.6	48.8
S (g/kg)	3.0	0.6	1.0	4.7
Cd (mg/kg)	0.16	0.25	0.02	1.66
Cr (mg/kg)	0.37	0.26	0.04	1.10
Cu (mg/kg)	10.1	2.3	5.9	15.2
Mo (mg/kg)	2.2	2.7	0.3	17.0
Ni (mg/kg)	2.27	1.19	0.47	5.74
Pb (mg/kg)	0.64	0.75	0.10	4.00
Se (mg/kg)	0.20	0.71	0.03	4.90
Zn (mg/kg)	40.3	30.3	20.0	236.2
Mn (mg/kg)	146	105	8	517

Trace Elements and Heavy Metals in Irish Soils

However, a number of samples had elevated Mo. This was not unexpected since the area covered overlaps considerably that delineated in 1966 as having elevated environmental levels of this element (Thornton *et al.*, 1966). This suggests the possibility of a more marked elevation of Mo later in the year, since its uptake by plants is strongly influenced by soil moisture.

Values for herbage nitrogen (N), phosphorus (P), potassium (K), magnesium (Mg), sodium (Na) and sulphur (S) were similar to those found for the July sampling. Calcium (Ca) was considerably reduced in November samples, a feature that has been encountered previously at this time of year.

Most selenium values were greater in November than in July, although the high July value for farm 15, silage area at 4.90 mg/kg was reduced to 0.54 mg/kg. Manganese (Mn), zinc (Zn) and copper (Cu) values were similar for both sampling dates. However, molybdenum was on average twice as high in November, averaging 4.3 mg/kg. Three paddocks had molybdenum values exceeding 10 mg/kg whereas an additional 17 herbage had a value of 3.0 or above; this is the level at which interference with copper metabolism in the ruminant may be considered to become significant.

Follow up investigation on three farms

Selenium Farm No. 15, silage area was re-sampled in June of 1998. The field away from

border areas was divided into 8 approximately equal plots of 0.20 ha each. Samples of soils (0-100 mm) and herbage (mature grass for silage) were taken from each plot. The selenium content of soil ranged from 13.5 - 22.5 (mean 17.6; SD 3.8) mg/kg and herbage ranged from 1.20 to 5.40 (mean 2.72; SD 1.4) mg/kg. These values confirmed the belief that selenium toxicity to animals was a possibility when conditions favoured plant uptake of the element. Soil pHs were low 5.3-5.9 (mean 5.5; SD 0.2) which would have militated against the uptake from soil of selenium by herbage.

Zinc and lead Soil samples numbering 11 were taken from 0.30 ha areas on Farm No. 24, silage area. Ground had been tilled since the previously sampling. Analysis of samples confirmed the presence of high soil zinc (221 - 1596; mean 479, SD 405 mg/kg) and lead (93 - 1234; mean 256, SD 329 mg/kg). The area with the highest values was characterised by the presence of darker soil compared to its surrounds. The area most elevated in zinc soil had a higher than normal proportion of the element in plant available form (364 mg/l EDTA extractable) suggesting that it would be phytotoxic especially to newly established plant species.

Lead Soil was obtained from Farm 31, grazing area, subdivided into 7 sections each of ca. 0.15 ha. Soil lead ranged from 176 - 1653 (mean 613; SD 507 mg/kg). It is now known that the site

overlaid a disused lead mine. Whereas grass or other plants would not be expected to suffer growth reduction or to assimilate high quantities of lead, nevertheless the presence of very high amounts in soil could be dangerous to young livestock especially by direct ingestion.

The above investigations confirm earlier elevated measurements on some farms. The conclusion is that there may be a toxicologically (plant or/and animal) significant excess of selenium, zinc and lead on some farms in the Askeaton area with undesirably high molybdenum and cadmium. However, all of these are almost certainly wholly geochemical in origin, with perhaps some input from residues from old mine works.

Metals in potato foliage

Foliage with different degrees of chlorosis was taken from potato plants growing in the area of plots 1-6 on Farm 24. Analysis (Table 12) showed that zinc content increased in parallel with severity of chlorosis observed in plant. More worrying was the elevated cadmium level in all three foliage samples. Lead was also elevated in one sample which also exhibited severe growth retardation. Elevated lead levels which occurred in plants, that also appeared to be desiccated and stunted, could possibly be attributed to soil contamination.

Table 12: Analyses of potato leaves with various degrees of chlorosis/necrosis sampled on Farm 24, June 1998

Leaf colour	N	P	K	Zn	Cu	Pb	Cd
	(g/kg)			(mg/kg)			
Green	57.4	3.0	25.7	130	15.0	0.8	3.4
Green/Yellow	28.8	2.0	26.2	249	11.3	1.8	4.2
Yellow	27.8	1.0	26.0	314	8.9	24.9	3.2

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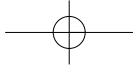
Appendix 1: Analytical methods for soils and sediments

- **Lime requirement** Soil-buffer (pH 5.0) suspension measured with glass electrode
- **Phosphorus** Extracted with Morgan's reagent (acetic acid-sodium acetate buffer pH 4.80)
- **Potassium** Determined colorimetrically, potassium by flamephotometry and by atomic absorption spectrophotometry
- **Magnesium** Determined colorimetrically, potassium by flamephotometry and by atomic absorption spectrophotometry
- **Sodium** Extraction with ammonium acetate and flamephotometry
- **Sulphur** Extraction with Morgan's reagent and nephelometry
- **Manganese(ER)** Extracted with calcium nitrate/quinol reagent and determined by atomic absorption spectrophotometry
- **Copper** Extracted with 0.05 M EDTA (ethylenediamine-tetraacetic acid-disodium salt)
- **Zinc** Extract buffered to pH 7.0 and contents determined by atomic absorption spectrophotometry
- **Arsenic** Extracted by nitric/sulphuric/perchloric acid (triacid) digestion and determined by atomic absorption spectrophotometry using the hydride technique - a modification of the method described by Ihnat and Miller (1977)
- **Cobalt** Extracted with hydrochloric acid sp. gr. 1.12 and contents determined by atomic absorption
- **Manganese (ER)** Determined by spectrophotometry
- **Iodine** Extracted with 2M sodium hydroxide, subjected to digestion with acid and determined by the catalytic reduction of cerium
- **Selenium** Tri-acid digestion and Se complex with 2, 3 diaminonaphthalene and determined fluorimetrically. Modification of the method described by the Analytical Methods Committee (1979)
- **Mercury** Digestion with nitric/sulphuric acid mixture and oxidation with potassium permanganate. Content determined by cold vapour A.A. (Ure and Shand, 1974)
- **Molybdenum** Extraction with Tamm's reagent pH 3.3. Content determined colorimetrically with ammonium thiocyanate
- **Boron** Extraction with hot water and determined colorimetrically

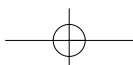
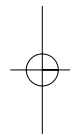
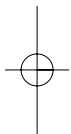
- **Aluminium** Extraction with calcium phosphate and determined by nephelometry
- **Fluorine** Fusion with sodium carbonate. Determined by ion electrode
- **Metals** Total thallium, lead, cadmium, zinc, copper, nickel, antimony, chromium, iron, vanadium, titanium and aluminium were determined by atomic absorption spectrophotometry following dissolution with hydrofluoric/ perchloric acid

Appendix 2 : Analytical methods for plants

- **Calcium** Acid digestion and flame atomic absorption spectrophotometry
- **Magnesium**
- **Copper**
- **Zinc**
- **Manganese**
- **Phosphorus** Acid digestion and Auto-analyser
- **Nitrogen**
- **Potassium** Acid digestion and flamephotometry
- **Sodium**
- **Sulphur** Nephelometry
- **Molybdenum** Acid digestion and colorimetry using dithiol; subsequently electrothermal atomic absorption spectrophotometry
- **Cadmium** Acid digestion and electrothermal atomic absorption spectrophotometry
- **Lead**
- **Nickel**
- **Tin**
- **Thallium**
- **Antimony**
- **Vanadium**
- **Iron** Dissolution with hydrofluoric acid and flame atomic absorption
- **Titanium**
- **Aluminium**
- **Fluorine** Fusion and ion selective electrode
- **Boron** Acid digestion and colorimetry using azomethine-H
- **Selenium** Tri-acid digestion and Se complexed with 2, 3 diamionaphthalene and measured fluorometrically. Modification of method described by the Analytical Methods Committee (1979)
- **Arsenic** Triacid digestion and determined by atomic absorption spectrophotometry using the hydride technique - a modification of the method described by Ihnat and Miller (1977)
- **Mercury** Digestion with nitric/sulphuric acid mixture and oxidation with potassium permanganate. Content determined by cold vapour atomic absorption spectrophotometry (Ure and Shand, 1974)
- **Molybdenum** Extraction with Tamm's reagent pH 3.3. Content determined colorimetrically with ammonium thiocyanate
- **Boron** Extraction with hot water and determined colorimetrically
- **Aluminium** Extraction with calcium phosphate and determined by nephelometry
- **Fluorine** Fusion with sodium carbonate. Determined by ion electrode
- **Thallium** together with total lead, cadmium, zinc, copper, nickel, antimony, chromium, iron, vanadium, titanium and aluminium were determined by atomic absorption spectrophotometry following dissolution with hydrofluoric/perchloric acid



Trace Elements and Heavy Metals in Irish Soils



¹Spatial variability of nutrients and heavy metals on farms

SUMMARY

Variability of heavy metal/trace element amounts in soil and herbage from 3 farms encompassing 26.5, 33.6 and 21.6 ha and in a 230 km² surrounding area, in Co. Limerick, has been estimated. Variability was least in the farm with the greatest soil physical uniformity. It increased in line with increasing sampling area. In soil, the coefficient of variability (COV) was least (*ca.* 10%) for sesquioxide metals, iron and aluminium, and trace elements, chromium and nickel. It was highest where there was evidence of geochemical contamination with cadmium and selenium. In general, COV was highest (*ca.* 20%) for extractable components including copper, zinc and manganese. Regression analysis of elements in soil showed up a number of useful associations particularly for selenium, sulphate sulphur, mercury, cobalt, vanadium and fluorine with soil organic matter. Associations were also found involving fluorine, vanadium and chromium.

Elements in herbage exhibited two types of associations (i) those reckoned to be within the plant and confined mostly to major elements and (ii) those involving metals associated primarily with soil and indicative

of the extent to which herbage was contaminated by soil. Elements that showed lower variability in soil exhibited large variability in herbage. These included iron, aluminium, chromium, vanadium and fluorine, where the cause was attributed to contamination of herbage by soil. It is suggested that iron could be used almost equally as well as titanium as an indicator of the degree to which herbage has been contaminated by soil.

Experimental data used were those that were generated for and included in the Askeaton Animal Health Investigation (EPA, 1995). Also used were data from the same investigation relating to 47 sites from 21 farms in the same locality and also to a 28 month herbage selenium monitoring program.

Two sets of soil results were examined.

Soils

All soils were sampled to a depth of 10 cm. Uniformity in land use and topography were taken into account in the delineation of sampling areas.

- a In March 1995 three farms were divided into sampling areas of 2-3 ha. In practice

¹ **Spatial Variability and of Nutrients and Heavy Metals on Farms** was prepared from an End of Project Report 4610, Soil and Herbage Heavy Metal Trace Element Variability and Relationships at Farm and Regional Level, 2000, D. McGrath, 20pp. The investigation relied heavily on soil and herbage field data from the Askeaton Investigation.

Trace Elements and Heavy Metals in Irish Soils

- individual fields comprised between one and four sampling areas. Cores were obtained at random along 2 zig-zag paths in each paddock. Composite samples each consisting of a minimum of 25 cores were thus obtained from each sampling area. This operation yielded 16, 19 and 15 samples from farms 1, 2 and 3, respectively.
- b. Soil was similarly sampled on representative areas of 2 ha on 21 farms in the Askeaton region in July 1997. Two and occasionally four areas were sampled on each farm and a total of 47 samples were collected.

Herbage

All sites were under permanent pasture and three sets of herbage results were examined:

- a In May 1995 herbage was taken from the areas that had previously been sampled for soil.
- b A herbage sample was obtained from each of the 47 areas at the same time as soil was obtained in July 1997.
- c Sampling was performed at intervals of 4-8 weeks on 4 selected sampling areas on farms 1 and 2 on 17 occasions between December 1995 and March 1997.

On each occasion a sample of herbage was obtained by compositing 20 cuts obtained along a zig-zag line as used in soil sampling.

Sample preparation

Soil was dried at 40°C and sieved to pass a 2mm mesh.

Herbage was dried at 105°C, ground in a hammer mill, and sieved to pass a 1mm mesh.

Analysis

Soil Digestion procedures for total components were generally as described by Byrne (1979) with modifications as described by McGrath (1998) using a HF mixture. For fluorine estimation, fusion with sodium carbonate was performed. For selenium, arsenic and mercury digestion with strong mineral acids was used.

For extractable components a range of extractants (Byrne, 1979) was employed; aqueous sodium acetate at pH 4.8 for phosphorus, potassium and magnesium, water for pH and boron, calcium phosphate for sulphate sulphur, 0.05 M EDTA for copper and zinc, calcium nitrate-quinol for manganese and ammonium oxalate for molybdenum.

For total components, results were corrected for moisture content of soil. Extractable components, were expressed on a soil volume basis and were not corrected for moisture.

Herbage Digestion of herbage was performed using HNO₃ (Byrne, 1979).

Estimates Estimations were generally performed using flame AA. Cadmium was estimated using electrothermal AA. Arsenic and mercury were estimated as hydride and metal, respectively, by AA in the fluorescent mode. Selenium was estimated as its DAN complex by spectrofluorimetry. Iodine was quantified by the catalytic ceric reduction method, phosphate and boron by colorimetry, sulphate sulphur by nephelometry and fluorine using an ion specific electrode.

Data handling used included Excel and SAS procedures.

RESULTS AND DISCUSSION

Soil variability

Variabilities displayed by a wide range of parameters for (1) Farms 1-3 (with 16, 19 and 15 sampling areas) for (2) the combined 50 sampling areas, for (3) 47 locations on 21 farms in the region, and (4) for soils of the southeast of Ireland described previously (McGrath and McCormack, 1999) are shown in Table 1. Farms 1-3 enclosed areas of 26.5, 33.6 and 21.6 ha, respectively. The regional soils were within an overall area of 230 km². In this investigation most consideration was paid to the farm results and less to the regional results for which there are less data. The south-east data are appended only for general comparative purposes. Unsurprisingly, variability increased with increasing area represented, which is considered the norm (McIntyre, 1967).

COVs of 35-55% are typical for extractables from soils from the same landscape where soils are actively managed (Beckett and Webster, 1971). For natural soils, COV values may be closer to 10% as they are for sand, silt and clay and for total components such as are most of the constituents considered in this investigation. It is known that variability increases with increasing geochemical pollution. This was the case on Farm 1 where paddocks had mildly elevated levels of selenium and of some other elements. In the regional soil study one instance of elevated selenium (14.5 mg/kg) one of elevated lead (789 mg/kg) and one with elevated zinc (377 mg/kg) were found. This again resulted in very high variability for these elements in the regional soils. Values greater than 100% for COV are considered indicative of significant skewed distribution which can be attributed to geochemical pollution.

Variability (or COV) was least for pH (Table 1). Assuming that data for soils within a farm can be considered as being from the one population, there is a 95% probability that the COV for any parameter of soil representative of any sampled area will differ from the mean by less than 2 standard deviations (\pm). Thus for Farm 1, with a mean soil pH of 6.62 and a COV of 3.9, pH lies between 6.1 and 7.1, 95% of the time. The essential trueness of this for the farm data was confirmed by inspection of the data.

COVs for a number of metal components tended to be low (COV less than 20%) on all

Trace Elements and Heavy Metals in Irish Soils

Table 1: Mean and variability (as % COV) of heavy metals, etc.

Parameter	Mean for 3 farms	COV			COV Three farms	COV Region	COV Southeast
		Farm 1	Farm 2	Farm 3			
Area	-	26.5ha	33.6ha	21.6ha	-	239km ²	-
pH (water)	6.1	3.9	3.4	2.7	7.0	7.2	9.8
LO ₁	134 g/kg	36.4	17.1	8.9	25.6	35.9	78.8
Extractable							
Phosphorus	6.9 mg/l	31.6	46.5	38.7	47.0	66.0	197.5
Potassium	134 mg/l	20.4	40.4	32.7	32.36	67.2	67.5
Magnesium	190 mg/l	19.0	23.7	16.4	23.2	55.0	60.2
Molybdenum	0.28 mg/l	54.1	34.8	21.1	42.0	-	74.8
Copper	4.7 mg/l	27.5	27.5	27.2	32.2	69.2	71.9
Manganese	309 mg/l	35.6	23.5	38.7	39.4	43.7	65.1
Zinc	5.5 mg/l	26.8	13.2	38.7	23.4	47.2	85.5
Cobalt	18.5 mg/l	12.9	14.4	7.6	15.5	27.5	51.0
Boron	1.03 mg/l	25.0	30.8	22.3	29.7	-	-
Sulphur	17.9 mg/l	26.4	15.5	26.0	36.5	-	-
Total							
Cadmium	0.51 mg/kg	44.6	27.8	19.9	38.5	68.5	81.5
Chromium	50.7 mg/kg	14.6	8.6	14.2	21.9	26.6	39.4
Copper	19.2 mg/kg	223.9	22.4	14.7	25.12	49.0	53.1
Mercury	0.10mg/kg	27.4	18.5	13.3	25.0	-	79.32
Nickel	47.0 mg/kg	13.5	12.0	10.7	14.0	28.9	68.8
Lead	29.0 mg/kg	25.5	39.6	15.0	44.0	153.8	47.0
Zinc	96.3 mg/kg	13.6	23.5	10.9	22.4	41.6	44.8
Arsenic	14.4 mg/kg	19.3	19.3	9.4	18.9	-	82.1
Vanadium	58.8 mg/kg	17.0	14.6	9.4	21.5	-	-
Fluorine	803 mg/kg	16.0	13.2	15.2	23.4	24.3	-
Selenium	0.76 mg/kg	81.0	11.8	11.8	85.1	194.3	73.8
Iodine	7.6 mg/kg	17.4	21.9	20.2	24.3	-	38.5
Iron	22.7 g/kg	8.2	12.2	9.4	12.0	-	38.4
Aluminium	40.5 g/kg	10.8	9.0	7.5	9.6	-	49.3
Titanium	1.02g/kg	27.8	16.5	16.2	21.6	-	57.5
Manganese	562 mg/kg	29.1	24.7	14.5	40.2	-	84.2

three farms. These included the major sesquioxide elements, iron and aluminium. They also included the metals known to be adsorbed on these sesquioxide, i.e. chromium and arsenic. Other elements with low variability included nickel, vanadium, fluorine and cobalt together with selenium on Farms 2 and 3 where there was no evidence of geochemical pollution.

pH is a parameter whose variability is known to be low whereas many soil parameters especially most extractables, including phosphorus and potassium, are usually so large as to render them comparatively useless. Interestingly however, mean COV calculated for phosphorus, potassium and magnesium were very similar to those for mean field values reported for English counties (ADAS, 1995). In the latter instance, mean field size was approximately the same as farm size in the present investigation. However, they were in tillage as compared to grassland in the present investigation.

High COV was evident in instances of geochemical pollution, principally cadmium and selenium on Farm 1. Variability was least on Farm 3 - not surprising in view of the exceptional physical uniformity of soils on this farm (J.J. Diamond, personal communication, 1995).

Regression between soil components

Regression analyses for soil data suggested some interesting relationships between soil

components. Not all the relations that were highly significant over the three farms (Table 2) were significant at individual farm level (results not shown). This was particularly the case when either component had low variability and the data plots tended to cluster. Regional results are also shown for comparative purposes but there are not considered in detail because of the occurrence of geochemical pollution as indicated above. Metal extractability with 0.05 M EDTA was considered to relate significantly to total metal in soil for copper, but not for zinc. These relationships had previously been demonstrated (McGrath, 1996) for a collection of Irish soils.

Some individual relationships, nickel with chromium, selenium with loss on ignition, emerged that were not unexpected. There were also others such as arsenic with lead which is taken to be an example of a fortuitous relationship sometimes thrown up by analysis of data by regression analysis.

Strongly significant relationship on farms between fluorine, vanadium and chromium were found. These three components were also related to the sesquioxide components iron and aluminium although not as strongly.

Metal extractable with 0.05M EDTA was considered to relate significantly to total metal in soil for copper, but not for zinc. These relationships had previously been demonstrated (McGrath, 1996) for a collection of Irish soils.

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Table 2: Some significant regressions (r) between soil constituents

Correlation	3 Farms (n=50)	Region (n=47)
Cu _{EX} - Cu	0.456 ^{xx}	0.773 ^{xx}
Zn _{EX} - Zn	0.204 NS	0.0249 NS
Mn _{EX} - Mn	0.771 ^{xx}	0.752 ^{xx}
Se - LO1	0.638 ^{xx}	0.376 ^{xx}
As - Pb	0.563 ^{xx}	-
Cr - Ni	0.635 ^{xx}	0.422 ^{xx}
F - V	0.576 ^{xx}	-
V - Cr	0.537 ^{xx}	0.053 NS
V - Cr	0.390 ^{xx}	-
Se - S	0.287 ^x	-
Hg - S	0.450 ^{xx}	-
Se - Hg	0.368 ^{xx}	-
Zn - Mn	0.634 ^{xx}	0.091NS
Zn - Pb	0.729 ^{xx}	0.069 NS
Pb - Mn	0.590 ^{xx}	0.003 NS

^{x,xx} significant at $P \leq 0.05$ and 0.01 , respectively.

The highly significant relationships for selenium, sulphur and mercury with loss on ignition (organic matter) were considered indicative of the effect that organic matter has in absorbing and retaining labile elements.

Significance of relationships were generally much less when extended to the greater region (Table 2). The exceptions were between extractable components copper and manganese on total soil element and between nickel and chromium.

Multiple regression analysis using the SAS stepwise procedure for farm soils elicited a large number of very significant relation-

ships (Table 3). These built upon relationships such as those shown in Table 2 by including additional parameters, typically LO1 (loss on ignition), pH, iron, aluminium and manganese. Those with $r^2 \geq 0.60$ are shown in Table 3.

Variability of heavy metals / trace elements in herbages

Variability (Table 4) was in general higher for herbage than for soil. Values for major components which are governed by plant physiological processes tended to be lower than those associated with heavy metals - trace elements which are influenced in some instances by soil levels and in others, as will be described later, by contamination with soil.

Table 3: Multiple regression relationships where $r^2 \geq 0.60$ for soil components using the stepwise procedure (SAS)

Parameter	Regressed on	r
Mn _{EX}	Mn, LO1	0.808
Se	LO1, pH, Mn	0.770
Ni	Cr, Fe, Al, Cr	0.744
Mg _{EX}	Pex, Kex, LO1, Fe	0.695
Cd	pH, LO1, Zn	0.637
V	F, pH	0.603

However, in the case of major nutrients the relatively moderate COVs would be expected to increase where sampling times were not synchronized. Variability for major elements were increased by consideration of the wider area, perhaps reflecting the wider range of management practices in use.

Mean herbage values for a number of elements, those elements taken up by the plant in very small amounts, e.g. chromium, arsenic and selenium, were small and COVs were generally high. For other herbage components contamination of herbage by soil serves to raise both herbage values and COVs to high levels. Among such components may be listed vanadium, fluorine, iron, aluminium, titanium, iodine and manganese.

Regression between herbage components

Correlation analysis performed on herbage from the 3 farms (Table 5) showed strong relationships between a number of

components – aluminium, iron, titanium, vanadium, chromium, lead, iron and iodine. Relationships additional to these were small in number – involving nitrogen, magnesium and potassium and also pairing copper with zinc ($r = 0.725$) and lead with zinc ($r = 0.757$). It is noteworthy that all the elements listed in the correlation matrix are those known to occur in greater quantity in soil than in plant (Healy, 1973; McGrath et al., 1982). Additions to the list of those generally included in this category could be vanadium and fluorine for which little was known previously for Irish soils. The elements above are also those which were found earlier to display higher variability in plants – not surprising since much of the element content arises directly from soil and since soil content may be several orders of magnitude higher than plant level for the element.

Trace Elements and Heavy Metals in Irish Soils

Table 4: Mean and variability (% COV) of heavy metals, trace elements and nutrients in herbage

Element	Mean 3 farms	COV			COV 3 Farms	Cov Region
		Farm 1	Farm 2	Farm 3		
Nitrogen	33.4 g/kg	29.1	24.2	19.1	24.5	31.4
Phosphorus	3.92 g/kg	17.8	16.8	17.4	23.2	18.7
Potassium	28.7 g/kg	6.7	17.4	18.1	18.1	26.4
Magnesium	1.93 g/kg	18.7	14.5	11.3	17.1	17.9
Calcium	6.05 g/kg	15.3	6.1	11.4	20.2	24
Sulphur	3.46 g/kg	32	16.7	20.5	26.2	21.7
Cadmium	0.123 mg/kg	48	29.8	29.9	49.2	150.6
Chromium	0.78 mg/kg	75.7	42.5	42.3	60.4	70.3
Copper	10.0 mg/kg	23.7	17.3	14.5	19.3	22.4
Mercury	0.022 mg/kg	18.7	23.3	15.3	19.1	-
Nickel	2.54 mg/kg	41.1	33.9	22	39.2	52.5
Lead	2.05 mg/kg	44.4	24.6	42.9	47.3	116.8
Zinc	29.6 mg/kg	22.9	18.6	8.8	20.1	75.2
Arsenic	0.49 mg/kg	55.1	54.2	78	70.1	-
Vanadium	2.39 mg/kg	77.7	35.5	62.8	77.1	-
Fluorine	10.2 mg/kg	112.3	52.6	62.3	86.7	-
Selenium	0.086 mg/kg	142.3	28	36.6	138.1	351.6
Molybdenum	1.86 mg/kg	26.7	23.1	48.9	40.5	125.3
Boron	7.76 mg/kg	21.3	21.4	18.4	25.1	-
Iron	33.1 mg/kg	106.2	59.5	76.1	87.2	-
Aluminium	432 mg/kg	118.6	77.8	88.6	101.8	-
Titanium	47.7 mg/kg	95.9	43.8	87.4	80	-
Manganese	171 mg/kg	45.2	48	20.5	64.5	71.9
Iodine	0.236 mg/kg	59.9	73.2	24.4	75.4	-

Table 5: * Relationships (r) between plant constituents for herbage from 3 farms

	Al	Fe	Ti	V	Cr	Pb	F	I
Al	1							
Fe	0.978	1						
Ti	0.869	0.902	1					
V	0.768	0.799	0.892	1				
Cr	0.957	0.951	0.899	0.805	1			
Pb	0.678	0.666	0.748	0.795	0.721	1		
F	0.905	0.925	0.783	0.654	0.876	0.496	1	
I	0.818	0.784	0.722	0.652	0.757	0.613	0.666	1

* r significant at $P \leq 0.01$ for all values

A number of inferences may be drawn from these data: (1) For most heavy metals, values are a reflection of the extent to which herbage is contaminated by soil (2). Titanium content of herbage is generally taken as an index of soil contamination: it appears that other elements, and especially iron, that are more easily determined, may serve almost as well.

Relationships between herbage and soil component levels

In conventional agronomy the inference is that in the food web, nutrients pass from the soil to the plant and then to the animal. As indicated earlier, many elements appear to pass directly from the soil to the animal. However, the orthodox view is clearly correct in respect of some elements such as major nutrients and perhaps copper, zinc and nickel.

In addition to a number of weak relationships involving plant phosphorus, potassium, magnesium with extractable forms in soil (not shown), a number of other relationships were demonstrated (Table 6). Those involving selenium, zinc and lead were due in part to the presence of elevated levels of those elements in at least one soil. It cannot be inferred that uptake plant of the metal had occurred; soil contamination was a more likely cause.

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Table 6: Most significant relationships (r^2) between herbage components and soil factors

Herbage - Soil	Data set	
	3 Farms	47 Paddocks
Se - Se	10.888 ^{xx}	0.967 ^{xx} (0.350 ^{xx})
Mn - Mn _{EX}	0.448 ^{xx}	0.0015 NS
Mn - Mn	0.331 ^{xx}	0.087 (NS)
Zn - Zn	0.448 ^{xx}	0.623 ^{xx} (0.040 NS)
Pb - Pb	0.253 ^{xx}	0.484 ^{xx} (0.050 NS)
Zn - Zn _{EX}	0.113 ^x	0.292 ^{xx}
Mo - Soil pH	0.149 ^{xx}	-

(^t) value obtained when 3 soils variously containing very high levels of selenium (14.5 mg/kg), lead (789 mg/kg) and zinc obtained (377 mg/kg) were omitted from consideration

Of the extractable metals (quantified by procedures that were used originally to predict the uptake of the metal by plant) only manganese in one set of soils and zinc displayed significant relationships. Copper relationships were non-significant. Of the other suspected relationships only molybdenum in plant was correlated (negatively) but weakly with a soil factor – pH. Cadmium failed to show a previously demonstrated (positive) relationship with pH. Iodine was not related to aluminium as might have been anticipated.

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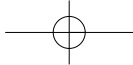
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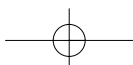
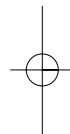
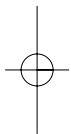
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Trace Elements and Heavy Metals in Irish Soils



¹Soil and Herbage Contamination in a Mining Area (Silvermines)

The objectives of this component of the investigation were:

- To determine heavy metal (lead, zinc, cadmium, copper and arsenic) concentrations in soil, herbage, water, silage and hay samples taken from agricultural lands in the Silvermines area
- To evaluate the severity and extent of environmental pollution

Soils of the Silvermines area are entirely devoted to grassland agriculture, predominantly dairying and dry stock. They have been classified by Finch and Gardiner (1993) in their Soil Survey of Tipperary North Riding. The classification process includes division into soil type and potential for grassland production. Class A soils are potentially the most productive with Class E being the least. A small proportion of soils are assigned to Class V (variable restrictions). The latter generally have severe limitations for production.

In summary, the three soil series, Borrisoleigh, Borrisoleigh-Ballinalackan and Elton comprise more than half of the area selected for chemical examination in this investigation. All these soils are Class A, high yielding with only minor use limitations.

Two soils are designated Class C with wetness a major limitation in both the Knockastanna and Banagher series. Other soils, Class D, E and V, tend to have even more severe restrictions such as susceptibility to flooding, elevation and slope in addition to wetness. They may be suited only to extensive grazing, or to occasional grazing or cutting for hay in summer. Thus the soils in the Silvermines area are, in general, productive but include areas where agricultural use is severely restricted. All soils contain heavy metals in measurable amounts. The heavy metal concentrations of Irish agricultural soils are summarised (McGrath and McCormack, 1999) in Table 1.

Most agricultural soils in Ireland contain about 25 mg/kg of lead, slightly less copper and arsenic, and slightly more zinc. Cadmium is generally less than 1 mg/kg. Of the above, copper and zinc are essential for adequate plant and animal performance.

Lead and cadmium have no beneficial effects but are not toxic at 95 percentile concentrations in soil (Table 1).

Soil and Herbage Contamination in a Mining Area was taken from O.T. Carton, and D. McGrath, 2000. Lead in Soils Herbage, Fodder and Water. The latter was part of the Report Investigation into the Presence and Influence of Lead in the Silvermines Area of Co Tipperary, Dept. of Agriculture, Food and Rural Development 63-74.

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Table 1: Heavy metal concentrations of Irish agricultural soils

Heavy metal	50 Percentile*	95 Percentile
Lead	26.5	59.3
Copper	14.9	34.2
Zinc	43.7	134.1
Arsenic	11.9	42.0
Cadmium	0.39	1.48

*50% and 95% of agricultural soils, respectively, have values less than this

Impact of lead and zinc mining on grassland agriculture

Mining has left a strong imprint on the landscape and soil in many countries. As a consequence, crops including grass, are exposed to elevated amounts of heavy metals. Plant growth may be adversely affected and the quality of the crop for animal and human consumption may be diminished (Davies, 1983).

The situation in Silvermines is not unlike that in parts of the UK (Davies, 1983; Alloway and Davies, 1971) and the US (Levy *et al.*, 1992). In these areas, grassland agriculture is being conducted on soils with highly elevated concentrations of lead and zinc and, in some instances, cadmium and copper. Long after the cessation of mining there have been reports of animal deaths as a consequence of lead poisoning (Alloway and Davies, 1971).

There is a real difficulty in determining the

probable impact of pollution from lead on agriculture. In general, farmers live with the problem by adopting sound husbandry practice, *i.e.* by denying animals access to herbage when it appears to be contaminated. This strategy has been articulated in a number of publications (Davies, 1983; Levy *et al.*, 1992; Anon, 1990) and is based largely on a knowledge of the pathways by which lead travels from soil to animal. A value of 1,000 mg/kg of lead has been suggested as a threshold below which toxicity problems are unlikely to occur in grazing animals (Anon, 1990). This is believed to be a conservative value having regard to the physical and chemical properties of lead in soil and to the amounts required to produce toxic symptoms in cattle (Quarterman, 1986). It should, however, be realised that quantitative data of a dose-response nature (*i.e.* animal health effect at known concentration of lead in soil) is almost entirely non-existent. However, Thornton and Kinniburgh (1977), in a survey

of 11 farms in Derbyshire, demonstrated a broad relationship that showed blood lead of cattle rising from 100 to 300 µg/l as soil concentrations rose from 100-400 to 1,000-2,000 mg/kg.

Lead pollution incidents in Silvermines - 1985

In the aftermath of dust blows early in 1985, Teagasc (An Foras Taluntais and ACOT) personnel visited farms adjacent to the Gortmore TMF on five occasions throughout that year. Eighty-six soil samples and 50 herbage/fodder samples were taken and analysed for lead and occasionally for other metals.

On one farm adjacent to the Gortmore TMF (Tailings Management Facility) evidence for polluting event(s) involving dust blow was obtained. Soil lead concentrations were low for the area and decreased with depth, an indication of aerial deposition. Lead on herbage exceeded 1,000 mg/kg on occasion. Such an amount on forage or fodder would be expected to represent a major risk to cattle or other animals.

Soil lead values ranged from near normal (less than 100 mg/kg) to nearly 20,000 mg/kg in a later survey (November, 1985) of other farms in the Silvermines area. Associated herbage lead concentrations were comparatively modest, rarely exceeding 100 mg/kg and were often less than 10 mg/kg.

In an earlier incident in the West of Ireland (Donovan et al., 1969), 50% of the herbages in an area which was affected by dust from mining activity had lead values in excess of 500 mg/kg.

Scope of the current investigation

The scope of the investigation was to measure the amount of lead and other relevant heavy metals in

- Soils
- Grazed herbage
- Conserved fodder
- Drinking water on farms within the designated study area.

Investigations and Methodology

The investigation included the following stages:

- An exploratory investigation of soils and herbages on two transects, one oriented North-South and one East-West, was conducted first. The survey covered the Gortmore TMF and low-lying adjacent areas (Fig.14).
- A total of 34 soils (0-10 cm samples) and 33 associated herbages (one tailings pond sampling area had no vegetation) were collected at regular intervals of 200 m along each transect. These included 29 soils under grassland agriculture and five from Gortmore TMF. Soils were analysed (McGrath, 1998) for lead, zinc, cadmium, copper, and arsenic. Herbage was analysed for a similar range of heavy metals and also for botanical species composition.

Trace Elements and Heavy Metals in Irish Soils

- An extensive investigation of soil and herbage was conducted in September/October, 1999. The sampled area extended about 3 km north and 2 km south of an east-west line from Silvermines village to Kilnacranra (Fig.14). Samples (to a depth of 0-10 cm) were collected on a grid at intervals of 400 m. A grab sample of herbage, cut to within 50 mm of the soil surface, was taken at each soil sampling point. A total of 223 soils and 218 associated herbage were collected from within an area of 4.0 x 4.8. Analyses were performed on all soils for lead, zinc, copper and cadmium and for pH and loss on ignition (organic matter content). Analyses were performed on 119 of these herbage samples for lead, zinc, copper, and cadmium and for iron (a useful indicator of the extent of contamination of herbage by soil).
 - A total of 51 silages and 23 hays were obtained from 54 farms in the problem area. Samples were analysed for lead, zinc, copper, cadmium, molybdenum and iron.
 - Samples of animal drinking water from farms were collected at functioning outlets. A total of 154 samples were obtained from 93 farms. They were analysed for lead, zinc, cadmium, copper and arsenic. Samples showing high lead and cadmium were re-sampled for repeat analysis.
- All data were analysed using statistical and geostatistical techniques.

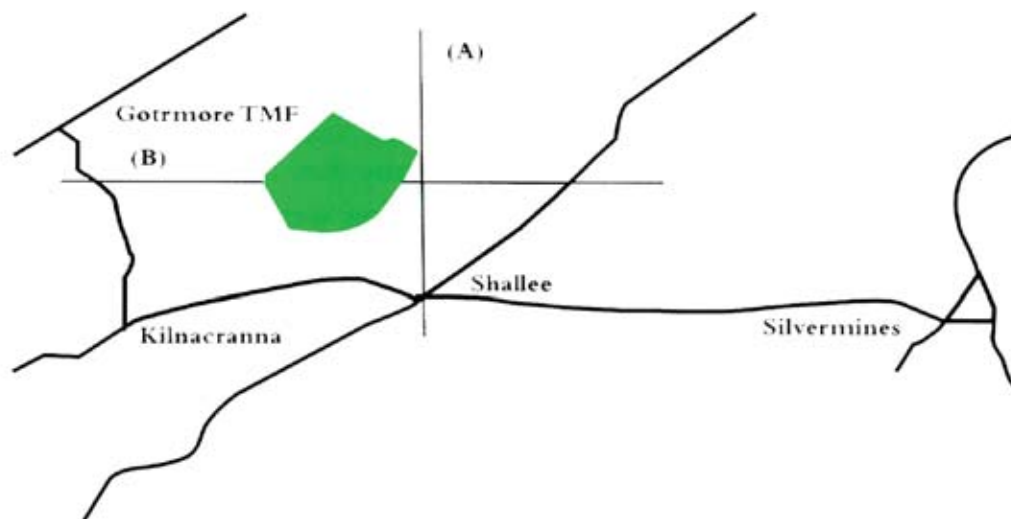


Fig. 14. Location of sampling transects (A) and (B) used in the exploratory investigation

Soil and Herbage Contamination in a Mining Area (Silvermines)

Results and discussion

Exploratory investigation This investigation was performed principally to develop site-specific techniques for sampling and analysis.

Soils The results served to confirm that the average agricultural soil in the surveyed area had significantly elevated lead, zinc, and cadmium content that allowed for the

possibility of at least some impact on crop and animal (Table 2). As expected, concentrations of lead, zinc, cadmium, and arsenic from the Gortmore TMF were very high compared with most agricultural soils (Table 2).

Herbage On the other hand, herbage concentrations of heavy metals were such as to give rise to much less concern (Table 3).

Table 2: Exploratory investigation: mean heavy metal concentrations (mg/kg) in agricultural soils and Gortmore TMF.

Samples(No)	Lead	Zinc	Copper	Cadmium	Arsenic
Agricultural (29)*	1136	836	46.2	2.6	35
Gortmore TMF((5)	8154	7872	150.3	24.8	543

*No. of samples

Table 3: Herbage (mg/kg) from agricultural sites, Gortmore TMF, and comparative values from non-polluted herbage

	Lead	Zinc	Copper	Cadmium	Arsenic
Agricultural (29)*	10.7	84.6	7.9	0.45	0.26
Gortmore TMF (5)*	15.9	127.2	7.1	0.81	0.94
Comparative**	0.6	40.3	10.1	0.16	-

*No. of samples ; **McGrath *et al.*, 2001 for herbages (47) from 21 farms in West Limerick

Trace Elements and Heavy Metals in Irish Soils

Regression analyses indicated that herbage lead, cadmium, copper, and arsenic did increase with soil heavy metal concentrations but relationships were poor. Uptake of these metals into plants is limited in various ways. Thus, the presence of high lead on herbage is indicative of contamination by soil, sediment or dust. On the other hand, the relationship between herbage and soil zinc was highly significant, indicating uptake within the plant rather than on the plant. Herbage samples from the tailings pond consisted largely of *Agrostis*, *Poa* and *Holcus* species. Samples from farmland also contained a high proportion of these species. Only 10 contained more than 5% *Lolium sps* although three of these had

more than 50% *Lolium sps*. *Lolium sps*. tended to be more dominant dominant in more productive pastures.

Extensive investigation

Soils The survey area encompassed five Gortmore TMF sampling sites and 218 others. Of these, 213 were broadly involved in grassland agriculture and yielded a herbage sample; the remaining samples were from mining sites and are not included in the summary. Many of the agricultural samples had very high concentrations of lead and also of other metals (Table 4).

Table 4: Extensive investigation: mean heavy metal concentrations (mg/kg) in agricultural soils and Gortmore TMF

Soils	Lead	Zinc	Copper	Cadmium	Arsenic
Agricultural (213)*	780	365	24.5	1.11	21.9
Gortmore TMF (5)*	11694	7046	395.6	20.21	463.5

*No. of samples.

About one fifth of all soil samples had lead values of 1,000 mg/kg or greater. Soils enriched in

lead were also enriched in zinc. High soil zinc concentrations (approximately 1,000 mg/kg) are known to affect plant growth, including pasture establishment, and to inhibit copper absorption by animals.

Soil cadmium concentrations were elevated (> 1 mg/kg) over an extensive area. This raises concern about the accumulation of the metal in both vegetables and animal liver and kidney. Soil arsenic concentrations were not exceptionally high in the agricultural areas.

Mostly, heavy metal accumulation was associated with either (a) the Gortmore TMF

Soil and Herbage Contamination in a Mining Area (Silvermines)

(b) the Shallee area and (c) the Silvermines river and subsequently the Kilmastulla river into which it flows. This pattern of enrichment was best illustrated by lead (map not shown). It must, however, be borne in mind that the map shows predictive data based on sampling locations separated by 400 m. It was reassuring that, on the five occasions that additional sample(s) were taken from within areas that showed high lead concentrations on mapping, high concentrations were confirmed. Approximately one third of the mapped area showed concentrations exceeding 1,000 mg/kg.

Distribution patterns for the other metals, zinc and cadmium were similar to that for lead except that the southernmost areas appeared to be more depleted of zinc and cadmium. This was attributed to the acidity

of the soil in the southern area as acidity is known to promote leaching of these two metals.

Copper and arsenic again followed the same pattern as lead. However, outside Gortmore TME, copper and arsenic concentrations were not notably elevated compared with unpolluted areas elsewhere.

Soil fertility and the impact of lead

Both acidity, which is corrected by application of calcium carbonate or lime (Table 5), and phosphorus deficiency (Table 6) were more pronounced than normal (Coulter *et al.*, 1999). The effects of this may be much more profound than simply limiting the growth of grass.

Table 5: The percentage distribution of the estimated lime requirements

Lime requirement (t/ha)	0	0.1 - 5.0	5.1 - 10.0	10+
Silvermines farms	3	19	25	53
Co. Tipperary	13	32	35	20

Table 6: The percentage distribution of the soil phosphorus test values for Silvermines soils and soils of Co. Tipperary

	Soil test 0 - 3.0	phosphorus 3.1 - 6.0	levels (mg/l) 6.1 - 10.0	10+
Silvermines farms	41	41	14	4
Co. Tipperary	18	35	24	23

Trace Elements and Heavy Metals in Irish Soils

Firstly, phosphate is known to assist in the formation of more inactive forms of lead in soil (Cotter Howells *et al.*, 1994) thus reducing bio-availability. Secondly, increasing phosphate and calcium in soil will promote uptakes of these nutrients by herbage. Increased concentrations of both calcium and of phosphate in feed are known to reduce the availability of lead to the animal. This nutritive effect is likely to be further aggravated by the high proportion of poorer grasses in pastures as these tend to have lower nutrient concentrations than do productive species.

The fertility status of potassium (not shown) was very similar to normal for soils of Co. Tipperary.

Lead in Silvermines school play area

Following evidence from additional analyses, it emerged that the Silvermines school play area had elevated lead and zinc. Thirty one soil samples (0-10 cm depth) were taken on an 18 m (North-South) x 20 m (East-West) grid from this enclosed area. These samples were analysed for lead, zinc, cadmium and copper.

The pattern for lead was complex with the highest concentrations on the non-tended, westernmost, or left side of the field as viewed from the school. Amounts must give immediate cause for concern, particularly as they relate to a children's play area. This concern is based purely on the magnitude of soil lead concentrations (ranging from

2,300mg/kg to 38,000 mg/kg) approximately and on the fact that they are greatly in excess of values above which, for many countries, action is recommended (Logan *et al.*, 1995). The pattern of concentration for zinc was somewhat similar to that for lead, but with an unrelated accumulation in the south eastern corner. Cadmium as expected reflected zinc. Copper values were markedly elevated at the mid-section of the northern side (the non-tended area).

Herbage

Herbage samples, (115 agricultural and four from Gortmore TMF) from an area West of Kilnacrana to Silvermines, and from 2 km north of the roadway to 400 m South were analysed. The mean herbage lead value was 8.5 mg/kg (Table 7). This was lower than the mean value (15.4 mg/kg) recorded over a three-year period for herbage at the Tara mines TMF in Co. Meath where sheep were grazed with no ill effects (Crilly *et al.*, 1998).

Table 7: Extensive investigation: mean heavy metal concentrations (mg/kg) for herbage from agricultural sites, Gortmore TMF and comparative values from non-polluted herbage.

	Lead	Zinc	Copper	Cadmium
Agricultural sites (115)	8.5	93.3	10.9	0.43
Gortmore TMF (4)	29.2	190.6	8.2	1.03
*Comparative values	0.6	40.3	10.1	0.16

* McGrath *et al.*, 2001 for herbages (47) from 21 farms in West Limerick

Herbage lead is known to arise from physical contamination of the plant surface by soil. The ratio of herbage lead to soil lead should therefore give an indication of the extent to which herbage is contaminated by soil. This value was found to be less than 2% for most herbage in this investigation. This was smaller than expected. It could therefore be misleading to equate high lead animal intakes with high soil lead concentrations.

Herbage lead values contrast with those reported for some herbage samples from the same area examined in 1985 and with those reported for the West of Ireland (Donovan, 1969). Both of these reports clearly identified surface contamination of herbage by dust-blow. Consideration of lead concentrations in herbage samples taken North of the Gortmore TMF, where soil lead concentrations were low, indicated no significant effect from dust blow.

As with soils, mapping of herbage lead showed some interesting features. Highest concentrations tended to occur in very close proximity to a number of waterways

including sections of the Yellow river. It is not clear whether this indicates any ongoing contribution from the waterway other than an inclination to wetness which increases the tendency for grass to become contaminated with soil by grazing animals.

Silage and hay

Silage and hay samples were taken from 54 farms. The range of values for lead and for other metals (Table 8) was not unlike that for metals in herbage (Table 3). Maximum for lead in fodder was 47 mg/kg. About a quarter of farms had silage, or hay with lead content exceeding 20 mg/kg. Metal concentrations were similar for silage and hay with mean lead concentrations of 10.3 and 11.5 mg/kg, respectively (Table 8).

Trace Elements and Heavy Metals in Irish Soils

Table 8 : Mean heavy metal content (mg/kg) of silage and hay samples

	Lead	Zinc	Copper	Cadmium
Silage (51)*	10.3	81.1	14.6	0.36
Hay (23)*	11.5	86.8	6.4	0.36

*No. of samples

Concentrations of lead recorded in the present survey are considered to be below the concentrations that are associated with lead toxicity in animals. However, it should be noted that significant contamination of hay and silage with lead from soil/dust may have a potential for causing lead toxicity.

Water

The standards set in the Drinking Water Regulation (SI 81 of 1988) for lead and cadmium were exceeded in five and three instances, respectively, from a total of 154 water samples analysed. Water contaminated in this way was surface water and mostly from the catchment area of the Yellow River. Repeat sampling and analysis proved positive in all instances.

Content of lead and cadmium in water may rise during the winter period, as a consequence of oxidative changes that occur over the summer months. Nevertheless, on qualitative grounds, it is difficult to see farm water in this area ever presenting a health risk to animals.

Recent outbreak on Farm B

Following the deaths of three calves on one farm in late April 2000 of soil (5), herbage (5), and stream sediment (4) were analysed. Lead was elevated in soil (4,600-8,005 mg/kg; mean 5,827 mg/kg), herbage (52-188 mg/kg; mean 109 mg/kg), and sediment (6,970-15,945 mg/kg; mean 10,655mg/kg).

Extraction trials showed that lead in sediments was largely solubilised (50% or greater) at pH values below 2.0 but was much less soluble at values in excess of 3.0. Similar results were obtained on soils from the area. It is believed that that the lead concentrations in the soil or sediment samples were sufficiently high, and sufficiently bio-available, to account for the animal deaths - although other contributory sources are also possible.

Conclusions

- The extent to which soils of the Silvermines areas contain excessive concentrations of heavy metals, principally lead and zinc, but also cadmium, copper and arsenic has been quantified.

Soil and Herbage Contamination in a Mining Area (Silvermines)

- The quantity of soil lead in about one third of the investigated area indicated a potential risk to grazing animals.
- The quantity of soil lead in the Silvermines school yard gives immediate cause for concern.
- Phosphorus concentrations are low and lime requirements are high for the agricultural soils surveyed compared with the average for Tipperary and nationally.
- The quantity of lead on or in herbage samples indicated no obvious threat to animals.
- Silage and hay samples had lead concentrations similar to grazed herbage and again suggest no obvious threat to animals.
- Drinking water that is available to animals does not appear to be a major provider of lead; only five farm supplies had mildly elevated lead concentrations that exceeded the drinking water standards for humans.
- No significant indication of lead depositions on herbage from dust blow arose during the sampling period.
- Elevated levels of soil cadmium and arsenic were noted particularly in the Gortmore TMF.

Recommendations

- Herd owners should have soil analysed to establish nutrient status and lime requirement. Lime soil to pH 6.5 if necessary. Use adequate phosphate. Apply adequate nitrogen to maintain dense/healthy swards.
- Herd owners should refer to individual farm maps to determine the lead status of their soils.
- Herd owners should ensure that soil is disturbed as little as possible. This means the avoidance of poaching by animals and of damage to sward by machinery.
- Animals should not be allowed to ingest herbage heavily contaminated by soil - whether this material arises as a consequence of poaching, flooding or by wind erosion from tailings pond areas.
- If it is considered necessary to reseed, a part of the area should be tested to ensure that re-growth does occur. Late flowering, preferably diploid ryegrass varieties, should be used to ensure a dense sward.
- Drain sediments should not be spread on pastures.
- The elevated cadmium in soil should be noted in relation to levels of this metal in locally grown vegetables and in animal kidney and liver.

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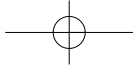
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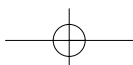
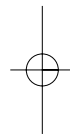
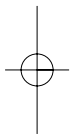
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Trace Elements and Heavy Metals in Irish Soils



¹ Biosolids use in Irish Agriculture

Sewage sludge in Ireland

At the present time approximately 50,000 tonnes of sewage sludge are produced each year in Ireland. About 40% of it is reputedly applied to agricultural land, the bulk of this coming from the new Dublin Bay thermal treatment facility. These values are lower than those predicted by the European Environment Agency in 2001 for Ireland (Table 1).

However, Irish sludge production is known to be increasing and set to increase into the coming decade. Use or recycling of sewage sludge or bio-solids in agriculture is perceived to be its most important destination as is the situation in many other European countries. However, some countries rely heavily on incineration, *e.g.* Germany, France and the Netherlands (where it is the main

destination) and landfill is still noted as an option.

Bio-solids use in agriculture

A bio-solid is a sewage sludge that has been treated for use in agriculture. Some countries have a long tradition of sludge/bio-solids use in agriculture where it was accepted as a source of nutrients for crop production. It is very important to note that the quantity and total nutrient value of Irish bio-solids is almost negligible compared with animal manures. For example, approximately 40 million tonnes (*ca.* 4 million tonnes dry weight) of animal manures are applied to agricultural each year (Brogan *et al.*, 2001: Table 2). Their combined nutrient content (Brogan *et al.*, 2001) is conservatively estimated at 9170 million, assuming 100% nutrient availability. This compares with

¹ **Biosolids Use in Irish Agriculture** by D. McGrath, W. Kato and O. T. Carton, was presented at the Seminar Treating Industrial and Municipal Sludge with Lime on 15th May, 2003 in Carlow. The Seminar was organised by The Institute of Engineers of Ireland.

Table 1: Trends over time in the destination or fate of sludge from Irish treatment plants ('000 dry tonnes). European Environmental Agency (2001)

	1992	1995	1998	2000	2005
Surface waters	14	15	-	-	-
Recycling	4	7	25	65	84
Landfill	16	14	17	35	29
Incineration	-	-	-	-	-
Not specified	3	4	1	-	-
Total	37	40	43	100	113

Recycling = Use in agriculture

Trace Elements and Heavy Metals in Irish Soils

25,000 tonnes of bio-solids with a nutrient value of g1.64 million (Tables 2 and 3). In Ireland, with about 8×10^6 bovines, farm animal waste production dwarfs human waste production.

Although animal manure is highly regarded as cheap and nutritionally attractive fertiliser and recycling to soil is an essential component of animal production systems, its management can sometimes be burdensome and difficult for farmers. Therefore, it should not be surprising that sewage sludge/bio-solids has never had much appeal here as a fertiliser.

Most of the beneficial nutrients in bio-solids derive from food. A very justifiable case can be made for the recycling of organic waste materials derived from food back to food-producing land. It is easy to accept this principle for animal and other agricultural-wastes. However bio-solids contains more, and sometimes much more, than food components. Value to the plant and avoidance of pollution have long been essential features of bio-solids use in agriculture. In the past, organisations like the Environmental Protection Agency (Ireland) and the European Union (EU) have strongly advocated recycling. In introducing proposed

Table 2: Mean quantity (t) of nutrients, from animal wastes and sewage sludge , received by agricultural land in 1998 (Brogan et al., 2001)

	Nitrogen	Phosphorus
Cattle slurry	185,000	28,565
Pig slurry	12,082	3,970
Sewage sludge (25000 t)	1462	480

Table 3: Estimated values of nutrients in animal waste spread on agricultural land in 1998

	Value (€106)
Bovine slurry	162.4
Pig slurry	13.5
Sewage sludge	1.64

changes to the Sewage Sludge Directive the EU (2000) states, *Sludge should be used when there is an agronomic interest for the crops or the quality of the soil can be improved.* In practice, disposal has also been a major objective of sludge use in agriculture and in many instances has been the driving force behind such use. However the prime consideration still needs to be the beneficial, safe and sustainable re-use of sludge.

The value of bio-solid as a fertiliser

Since sludge is mainly of organic origin, it contains nutrients that may be utilised for growth by plants. Nutrients vary considerably even on a dry-weight basis (Table 3) and even more so by wet weight. On average (Table 4: McGrath et al., 2000) a tonne DM of sewage sludge contains approximately 20 kg of phosphorus (P), 60 kg of nitrogen (N) and essentially no potassium (K). Following application to soil, these nutrients become available to plants for the next and for subsequent harvests.

O'Riordan et al. (1987) investigated the availability to plants of nutrients in liquid aerobic and anaerobic sludge. For the first harvest after application mean N availability was about 20-30% of fertiliser N, and P availability was about 70% compared to mineral P fertiliser. These results were from field trials with grass for cutting and with cereals. The results mirror those published in the international literature, having regard to the fact that bio-solids N availability varied from 10-70% of mineral fertiliser. These bio-solids nutrient values were obtained with liquid sludges, that have been superseded largely by lime treated and by thermally dried bio-solids which are much more user friendly. However, the availability to crops of both N and P in the newer bio-solids has been found to be lower than the nutrients in liquid anaerobic sludge or in cattle slurry. Thermally dried sludge is a particularly poor provider of P in the short term as has been noted by Hogan et al. (2001).

Table 4: Nutrient composition of Irish sewage sludges (g/kg DM)

	Nitrogen	Phosphorus	Potassium
Mean	58.5	19.2	4.9
Minimum	32.3	8.7	1.6
Maximum	87.4	37.1	11.7

Trace Elements and Heavy Metals in Irish Soils

On-going experiments, part funded by the Department of the Environment and Local Government, at Johnstown Castle, have indicated that for the first cut following application the nutrients in thermally or lime treated bio-solids are only about 50% as effective as the nutrients in the less highly treated sewage sludge (anaerobically digested) or in cattle slurry. However, over 5 cuts there was little difference in growth response from different organic fertilisers, except thermally dried sludge where nutrient efficiency was still lower.

The challenges for bio-solids use in agriculture

There are a number of significant challenges that must be addressed if agriculture is to remain a significant outlet for bio-solids. Some of the challenges for bio-solids use in agriculture include:

- Poor nutrient availability
- Heavy metal content
- Persistent organic pollutants
- Pathogens

Poor nutrient availability

Crop management considerations favour the use of products that give a predictable response to both N and P. Given the present state of knowledge it is not possible to predict response to any organic fertiliser applied to soil with reasonable certainty. Therefore, reliance on organic manures creates the potential for under- or over- supply of

nutrients. Under-supply results in yield loss (e.g. for early grass) while oversupply may cause loss of quality (e.g. excess N for sugar beet can reduce sugar yields). A safe procedure would be to landspread bio-solids in small quantities and to disregard its capacity to supply nutrients in the short term. However, such a policy would not sit kindly with the concept of beneficial re-use and would be onerous on the biosolids producer. In situations where soil P levels are low (P Index 1 on the Teagasc scale) biosolids could usefully serve to correct the deficiency.

Heavy metals

EU and national legislation has developed in response to phytotoxicity episodes caused by heavy metals in sludge applied to crops in the period prior to 1986. Controlling rates of application of metals has in practice eliminated the heavy metal problem (Table 5). Legislation concerning levels of metal in soil still needs to comply with Irish legislation, which until 2001 was quite stringent, although not as stringent as that in Scandinavian countries. In contrast, EU legislation is moving to further limit metal additions to soil (Table 5).

Despite the absence of heavy industry it cannot be presumed that that Irish sewage sludges have low metal contents. Values have fallen from the high level of twenty years ago (O'Riordan *et al*, 1986). However, a recent survey (McGrath *et al*, 2000) found some elevated values particularly for copper (Table 6).

Table 5: Irish and EU limit values for heavy metals that may be added annually to soil (g/kg/year)

	Ireland	EU		
	2001	1986	Medium term	Long term
Cadmium	50	150	15	6
Chromium	3,500	4,500	-	-
Copper	7,500	12,000	2,400	1,800
Mercury	10	100	15	6
Nickel	3,000	3,000	600	300
Lead	4,000	15,000	1,500	600
Zinc	7,500	30,000	6,000	4,500

¹S. I. 267 of 2001

Table 6: Mean heavy metal composition (mg/kg) of Irish sewage sludges

Metal	O'Riordan (1986)	McGrath et al. (2000)
Cadmium	1	1.5
Chromium	88	36
Copper	493	664
Mercury	-	1.5
Lead	269	123
Nickel	83	53
Zinc	1579	664

Persistent organic pollutants and pathogens

In more recent years the realisation that bio-solids can contain measurable quantities of organic compounds has strongly influenced concerns in relation to sewage sludge impact. These organic compounds had become ubiquitous in bio-solids, albeit mostly at very low levels. "Endocrine disruptive activity" or the ability to interfere with the function of essential hormones has been attributed to them. These compounds are lipophilic and tend to accumulate in fatty tissues (including milk) of animals. Little convincing evidence exists to indicate that any of them have any meaningful effect at normal levels. However, as a precautionary measure, Teagasc has advised against the use of bio-solids in beef and milk enterprises.

In practice bacteria, viruses, helminths, cysts, *etc.*, do not appear to present a significant problem giving rise to few if any reports of food contamination or disease transmission.

Sludge and the agricultural industry

It is unfortunate that association with a range of, high profile, non-desirables (chemicals, disease organisms, and even GMOs) with sludge can easily magnify the effect of any mis-event involving sludge, no matter where it occurs and what the circumstances are. Consumer concerns can increase to the point where commercial damage can result. The size of Irish agri-business is *ca.* 5 billion per annum. The doomsday situation is that this could be put

at risk – perhaps even by an event elsewhere in Europe.

The quantity and value of nutrients in Irish sewage sludges is minuscule compared to the quantity in agricultural wastes (Tables 2 and 3). The national value of the agricultural industry greatly exceeds the value to agriculture of sludge/bio-solids. Actuarial and risk assessment considerations would seem to advise strongly against the use of sludge, especially on animal farms.

The future

From the perspective of bio-solids managers, a less than optimistic outlook for bio-solids use in agriculture has been presented. Aware of this and realising that society requires a range of options for the management of bio-solids including use on land, the following proposal is made. Only dedicated spread lands with select crops (preferably for energy) should be used for bio-solids application. Agricultural land used for food production need not receive bio-solids. This does not reduce the requirement for high grade bio-solids as the transport and use of liquid sludge is widely regarded as being unacceptable. It is important to realise that the land area required to safely assimilate the nutrients available in Irish bio-solids is at a maximum, only 50,000 ha or about 1% of the total land area in use for agriculture in Ireland.

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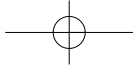
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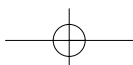
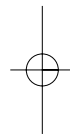
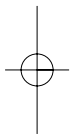
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Trace Elements and Heavy Metals in Irish Soils



¹Trace Element - Heavy Metal Cycling On Grassland

and to analytical data generated by the research and analytical programs at Johnstown Castle Research Centre. Available information is summarised here.

Introduction

The total land area of the Republic of Ireland is 6.89×10^6 ha (Teagasc,1999).The area farmed is comprised of grassland (51.7%), rough grazing in use (6.5%) and tillage (5.9%) with the remainder being accounted for by forestry (ca. 10%), water, peatland, mountain and surfaced area. In 1999 animal numbers were as follows (Teagasc, 1999); cattle 7.5×10^6 , (ca. 33% cows), sheep 8.0×10^6 , pigs 1.79×10^6 and poultry 13.1×10^6 . Total human population numbered 3.70×10^6 . The low population density, the relatively low adoption of traditional heavy industry and the high animal numbers, allied to the processing of agricultural produce, all influence the nature and magnitude of heavy metal inputs and losses from agriculture.

Accessible sources of information for Ireland are relatively limited, being largely confined to published statistical data (Teagasc, 1999)

Heavy metal contents in rocks and soils

The influence of geological factors on the heavy metal composition of Irish soils is recognised as being complex (Fleming *et al.*,1968). The causes of this are the complexity of the bedrock geology and the extent of glacial activity (Collins and Cummins,1996).

Information on heavy metals in representative profiles of soil series is included in a number of soil survey bulletins. Only one database that is representative of a sizeable land area (22% national coverage) exists (Mc Grath, 1998) and mean values from this for soils with different land use are given in Table 1.

¹Trace Element - Heavy Metal Cycling on Grassland, D. Mc Grath, was presented at the AROMIS project meeting on Assessment and Reduction of Heavy Metal Input into Agro-ecosystems, pages 129-136, Rennes 2001.The proceedings of the meeting was edited by H. Eckel, H. Dohler and U. Roth.

Table 1: Mean heavy metal concentrations (mg/kg) in soils (0-100 mm layer) of the south-east in different land use categories

Land use	Number	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Grassland	231	0.52	49.5	18	0.11	13.4	30	73.1
Tillage	30	0.76	67.6	19.1	0.11	23.3	30.3	88.6
Forestry	26	0.29	42.5	8.7	0.15	5.5	38.1	38

Trace Elements and Heavy Metals in Irish Soils

There are indications in these data that soils that are being used for tillage may contain more of some metals. Also, forest soils have much lower levels of most elements probably because leaching is facilitated at the lower pHs found in these soils. However Pb and Hg appear to be enriched in forest soils.

Atmospheric deposition

To date the only processed data appears to be for maximum/minimum concentrations in rainfall, sampled weekly at remote sites, one on the east and one on the west coast (EPA, 2001). Using mean annual precipitation rates, 1,400 mm at both sites, an estimate of potential maximum rates of deposition may be obtained (Table 2). Summated values are certain to be much less than those cited.

Metal deposition is also associated with aerial movement of soil or dust. Mean deposition rate for solids collected at rural sites over the period 1987-1994 was calculated

at 73.4 mg/m²/day (EPA,2001) or 268 kg/ha/per annum.

Inputs related to agriculture

Mineral fertilisers Generally only phosphate-rich fertilisers were found to contain significant amounts of heavy metals. For seven compound fertilisers that were in common use in Ireland in 1998, mean metal content per unit of phosphorus (P) is given in Table 3 (Mc Grath,1998).

Sewage sludge Ireland has had little history of sewage sludge use in agriculture and present usage is estimated at 20-30% of production. However, it is possible that essentially all sewage sludge will in the future be disposed of to soil (not-necessarily being used for agricultural production). In 1998, total sewage sludge production amounted to nearly 40,000 t DM and this has been projected to rise to 130,000 t in the next decade.

Table 2: Deposition of metals in rainfall: potential maximum values (mg/m²/year) from weekly sampling at two sites, 1997-1998

Cd	Cr	Cu	Ni	Pb	Zn
0.58	0.7	12.5	1.6	13.3	235

Table 3: Heavy metals content in Irish fertilisers (mg/kg P) 1998

Cd	Cr	Cu	Ni	Pb	Zn
94	705	264	197	-	2585

Table 4: Mean heavy metal content (mg/kg DM) of Irish sewage sludge

Cd	Cr	Cu	Hg	Ni	Pb Zn
1.52	36.2	664	1.54	52.8	123 664

Table 5: Heavy metal content (mg/kg DM) of spent mushroom compost

Cd	Cr	Cu	Hg	Ni	Pb	Zn
0.47	14	8	0.07	13	17	122

Mean composition of 45 sewage sludges sampled nationwide between 1995 and 1998 is given in Table 4 (McGrath *et al.*, 2000).

Compost Compost generation in Ireland is confined almost entirely to substrate for mushroom production. Spent mushroom compost with an annual production of 120,000 t DM (Maher, personal communication, 2001) constitutes a problem rather than an asset. No information is available on heavy metals in Irish made compost. Data provided (Maher, personal communication, 2001) in Table 5 for similar type material are considered indicative of contents for Irish compost.

Animal manures In Ireland cattle and horses spend much of their time outdoors, sheep most of their time, whereas pigs and poultry spend all their time confined. In all instances waste is returned to the soil. Heavy metal streams may be assessed (a) directly by analysis of faecal waste and (b) indirectly by

analysis of feed including mineral supplement. Quantities and (for b) animal absorption indices also need to be considered. For Ireland, both approaches present problems because of the scarcity of data at this time. An estimate of annual production of waste (Brogan *et al.*, 2001) from different animal populations together with compositional data derived from a small number of samples (Analytical Laboratory, Johnstown Castle, 1998) are shown in Table 6.

Pig slurry, because of the uniformly high additions of Cu and Zn at the fattening stage, generally appears to have elevated levels of these two metals.

Trace Elements and Heavy Metals in Irish Soils

Table 6: Animal wastes (10⁶ t DM) arising in Ireland in 1998 together with some analyses

Waste	Total	Managed	Cd	Cr	Cu	Ni	Pb	Zn
Cattle	9.65	3.71	0.28	4.2	134	9.5	14	385
Sheep	2.03	0.08	-	-	-	-	-	-
Pig	0.16	0.16	-	-	840	-	-	806
Poultry	0.17	0.17	0.87	5.6	18	6.8	2.4	104
Horses	0.22	0.11	-	-	-	-	-	-

Table 7: Mean composition (mg/kg DM) of dairy and abattoir sludges

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Dairy (n=36)	0.53	37.6	110.7	0.2	38.5	41.7	293.8
Abattoir (n=6)	0.74	24.2	177.8	0.12	22.2	66.7	835.2

Agri-industrial wastes Considerable quantities are associated with the processing of dairy and abattoir (mainly beef) wastes. Amounts for Ireland totalled 88,890 t DM for the former and 19,400 t DM for the latter (Brogan *et al.*, 2001). Mean composition is given in Table 7. These wastes are recycled to soil.

Livestock feeds

The heavy metals, Cu and Zn, are included in both feed concentrates (energy rich) and in mineral mixes fed to animals. Both materials contain other heavy metals as indicated in Table 8. Even with the small number of concentrates (four) and mineral mixes (three) variations in "impurities" were found (McGrath *et al.*, 2001).

For Ireland an estimate of Cu and Zn supplied to bovines may be made on the basis of recommended addition in supplementary feed - 450 and 750 mg per diem of Cu and Zn, respectively, for cows and about half this amount for animals being fattened. Where an absorption is assumed (Mertz, 1986) of 5% for Cu and 25% for Zn outputs of 544 and 716 t for Cu and 25% Zn, respectively in faeces may be calculated. For pigs, calculations using animal numbers, levels of mineral supplement in use, together with an assumed absorption of 15% for both metals, indicate a total output of 85 and 109 t of Cu and Zn, respectively, in slurry (B.Lynch, personal communication, 2001).

Table 8: Mean composition (mg/kg) of concentrates and mineral mixes

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Concentrate	0.22	1.7	58	0.02	1.2	3.8	110
Mineral mix	0.81	9.7	4335	-	15.3	8.3	4151

Table 9: Calculated annual metal inputs to Irish soils (g/ha)

Input	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Atmospheric deposition (over estimate)	-5.8	-7	-125		-16	133)	-2,350
Fertiliser	1.2	8.9	3.3	-	2.9	-	32.6
Sludge (1998)	0.02	0.09	0.7	0.02	0.13	0.31	1.7
Added in feed:							
bovines			137.1				284.1
pigs			21.4				27.5

Off takes

True losses include those caused by leaching of metals from soil and also removal and non-return of metals in produce. The latter may be quite significant for Ireland which exports about 90% of its beef and a high proportion of its dairy produce. The calculated quantities of Zn amount to ca 40 t in beef (exported) and to 20 t in milk (total production). Equivalents for Cu are approximately 1-2% of that for zinc in both meat and milk. Data used include export statistics (Teagasc,1999) and reported analytical data for metals in muscle tissue (Mertz, 1986) and in milk (O'Brien *et al.*,1999)

Heavy metal balance

Calculations for heavy metal inputs on the basis of data already considered are given in Table 9. obtained by dividing national usage by the total area under combined managed grassland and tillage (3.968×10^6 ha).

It is clear from the above that animal feed is a much larger source of metals Cu and Zn than fertiliser is now or than sludge may be in the future. Data for deposition must be regarded as provisional at this stage.

Trace Elements and Heavy Metals in Irish Soils

Research

A Cd recovery trial was performed on a cattle grazing trial where phosphorus additions over a 30 year period were 0, 480 and 960 kg P/ha. At the end of the period soil Cd values were 0.23, 0.28 and 0.30 mg/kg for the three treatments, respectively. Calculated Cd recoveries averaged 75% (McGrath, Dowdall and Mc Cormack, 2000).

Requirement for data

Essential requirement must be 1) analytical information, and 2) material quantities involved. For fertilisers, spent mushroom compost and agri-industry wastes, analyses sufficient to evaluate the national picture should be relatively easily performed. A project designed to evaluate nutrients in animal wastes is projected to start in 2002. For atmospheric deposition, scarcity or perhaps absence of data is considered to be a severe limitation. Information is probably even scarcer for heavy metal losses by leaching. Quantitative data for wastes and chemicals should, in general, be available but it may be necessary to go beyond published data in some instances.

Legal regulations

Legislation governing the suitability of soils for receipt of sewage sludge is contained in SI 267 (of 2001). This is the only Irish legislation that is specific in relation to heavy metals and their levels in soil. Legislation prohibiting the use of lead in petrol, and legislation setting

maximum allowable levels of Pb and Cd in drinking water and in food for human consumption will also restrict quantities of heavy metals that are released to the environment. Supplementation of animal feed with some nutrients, including principally Cu and Zn, is also controlled by legislation. Contaminant levels in fertilisers appear to be controlled by voluntary trade agreement. Application to soil of non-agricultural wastes (EPA, 2000), that have some beneficial fertiliser use, is regulated under license by the Environmental Protection Agency.

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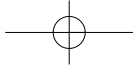
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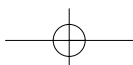
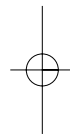
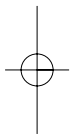
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Trace Elements and Heavy Metals in Irish Soils



¹Heavy Metals in Food

Introduction

Investigations have clearly established that major route of man's exposure to heavy metals is by ingestion. Even in the case of lead where the use of leaded petrol produces ambient lead levels which are generally higher than those of other heavy metal pollutants, direct inhalation contributes less to the total body burden than ingested lead (Hubbard and Lindsay, 1979). The main contributors therefore, to heavy metals in the body are the foods consumed and this applies both to nutrients and to unwanted metals.

This paper summarises some of the more salient points relating to the contents of heavy metals in the main food types. Particular stress is laid on work carried out by An Foras Taluntais in an effort to compile an inventory of research findings in this area. As total metal intake is not always a reliable guide to the quantities of metals metabolised by humans, the question of bio-availability is dealt with briefly. As is normal, in biological processes, the availability of different metals to an organism is conditioned by a variety of factors. In the case of humans, these may be either dietary or metabolic. Because this is so, any serious approach to evaluating the impact of heavy metals on human health must of necessity be an interdisciplinary one.

Vegetables

Heavy metal levels in vegetables from contaminated soils

During investigations in the Clondalkin area an opportunity arose to study heavy metal levels in vegetables from both endogenous and exogenous sources (Fleming and Parle, 1977). Vegetables were obtained from a number of gardens in the area which were contaminated to varying degrees as a result of general industrial and urban pollution, but more specifically with cadmium, copper, lead and zinc. The vegetables were analysed for the above metals using unwashed material. The contents found therefore represented metal levels both in and on the plants i.e. resulting from endogenous plus exogenous sources. To evaluate true uptake, i.e. from purely endogenous sources, soil from one of the gardens, typical of the area was used in a greenhouse pot trial.

Table 1 shows the metal levels found in cabbage, lettuce and onions from the gardens and Table 2 the levels found in the greenhouse experiment. Cabbage, lettuce and onions were Table 2 the levels found in the greenhouse experiment. Cabbage, lettuce and onions were obtained from a reasonably large number of gardens, 18 in the case of cabbage and 12 in the case of both lettuce and onions. Contents are expressed on a dry matter basis.

Heavy Metals in Food was presented by G.A. Fleming at the Conference on Pure Food Production -Implications of Residues and Contaminants. Dublin, 1988, An Foras Taluntais.

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Table 1: Heavy metals levels (mg/kg) – uptake and deposited – in vegetables from contaminated urban soils

Element	Range in soils	Range in vegetables		
		Cabbage (18 samples)	Lettuce (12 samples)	Onion (12 samples)
Cadmium	All < 3	nd – 0.4	nd – 3.3	nd – 0.6
Copper	9 – 240	0.6 – 13	4.4 – 82	1.2 – 14
Lead	17 – 840	1 – 59	2 – 67	0.8 – 12
Zinc	102 – 1125	15 – 72	40 – 188	15 – 65

nd = not detected

Comparing the data from both tables it is evident that cadmium levels in the plants from the pot trial were low and similar to those found in the garden plants.

With copper and lead quite a different picture emerged, levels in the garden vegetables being generally much higher than in those from the greenhouse. In the case of zinc, differences between garden and greenhouse, while present, was not so marked. In general plants absorb zinc from soil much more readily than lead or even copper though

exceptions occur with some copper-accumulating species.

In polluted areas metal content of vegetables are a reflection of plant morphology ; those with a large surface area to mass ratio being capable of capturing atmospherically deposited particulate matter.

In another pot trial using the soil of Table 2 a number of other vegetables were grown and the order of uptake of the four metals determined. Results are shown in Table 3.

Table 2: Heavy metal levels (mg/kg) – uptake only – in vegetables from a contaminated urban soil¹

Element	Content in soil	Cabbage	Lettuce	Onion
Cadmium	4	nd	1.6	0.24
Copper	100	3.5	4.3	1.3
Lead	380	0.19	2.9	0.8
Zinc	360	30	74	34

nd = not detected. ¹means of 5 replications.

Table 3: Order of uptake of some heavy metals from a contaminated soil

Cadmium	Copper	Lead	Zinc
Lettuce	Pea	Lettuce	Lettuce
Onion	Parsley	Turnip	Pea
Beetroot	Lettuce	Radish	Parsley
	Cabbage	Beetroot	Radish
	Carrot	Carrot	Turnip
	Beetroot	Parsley	Onion
	Radish	Onion	Cabbage
	Turnip	Cabbage	Carrot
	Onion	Pea	Beetroot

Some interesting differences are apparent. Highest uptakes of cadmium, lead and zinc were recorded for lettuce. Relatively low levels of all metals were found in onions.

Geo-chemical pollution

Geochemical pollution occurs in soils when the associated bedrock contains elevated levels of one or more metals. Rock weathering results in the release of such metals and their incorporation into derived soils. Such a situation is evident in seleniferous and molybdeniferous soils in Ireland where leaching from black shale bedrock has resulted in the soils acquiring toxic levels of both elements. Normally selenium and molybdenum occur at around 1 mg/kg in soils. In one area in Co. Limerick a soil with a total selenium content of 160 mg/kg and a total molybdenum content of 50 mg/kg was located. A number of vegetables and some cereal crops were grown in this soil in the

greenhouse (Fleming, 1973). Selenium contents (dry matter) ranged from 9 mg/kg in peas to over 200 mg/kg in cress and turnips. Molybdenum contents were lowest in parsnips (3 mg/kg) and highest in cress (407 mg/kg).

In another geochemically polluted area where organic vegetable growing is being practiced, onions contained 4.2 mg/kg Se and potatoes 1.5 mg/kg Se. These levels are not considered very serious in the overall context but a thorough examination of all produce from the area is warranted in order to establish maximum levels which might be expected.

Elevated levels of lead in vegetables from a geochemically polluted area in the west of Ireland have been recorded by Donovan *et al.* (1969) but here as in the case from the Clondalkin area cited above, much of the lead

Trace Elements and Heavy Metals in Irish Soils

has resulted from particulate fallout, in this instance associated with lead mining in the area.

Cereals

Heavy metals in wheat from different locations

Unlike some vegetables where heavy metals levels often reflect exogenous sources, cereal grain contents are of exclusively endogenous origin. Samples of winter wheat from Department of Agriculture trials in several counties were examined for copper, iron, zinc and selenium and the results (dry weight basis - means of two cultivars) are shown in Table 4.

Levels of copper zinc and iron are typical for wheat grown on good soils but the Zn content of the wheat from Co. Meath was slightly low. Copper and iron contents were also rather

low from this area. MacNaeidhe *et al.*(1986) have identified zinc deficiency in cereals in parts of Counties Meath and Louth where the soils have formed from morainic or other glacial deposits. In such instances the coarse texture of the soils can lead to inherently low levels of a number of trace elements.

Perhaps the most interesting figures are those for selenium. These exhibit by far the widest variation in content - almost a sevenfold difference between the highest and the lowest. Elevated levels of selenium in Irish soils are found when the soil parent material contains black shale and/or Calp limestone. This is so in the three areas where the wheat Se is lowest, Balrath, Ballylooby and Backweston. Geochemical considerations can be quite useful in predicting the likely selenium status of plants. Many soils of the classical wheat growing states of the U.S. mid-west have soils which are influenced by Se-rich shales and limestones.

Table 4: Heavy metals (mg/kg) in winter wheat

County	Location	Cu	Zn	Fe	Se
Carlow	Oak Park	5	28	46	0.8
Wicklow	Woodenbridge	4.4	18	39	0.9
Dublin	Lusk/Skerries	4	21	43	0.7
Kildare	Backweston	7.8	30	43	0.23
Tipperary S.R.	Ballylooby	6.6	17	38	0.15
Kilkenny	Gowran	7.7	23	46	0.6
Meath	Balrath	4.7	14	30	0.13
Louth	Ardee	6.7	20	45	0.8

Heavy metals in grain flour and bread

Three varieties of spring wheat front Department of Agriculture trials in Counties Carlow, Louth and Wexford together with their corresponding flour and bread prepared at AFT, Kinsealy, were analysed for copper, zinc, iron and selenium. Results (Fleming et al., 1987) are shown in Fig. 15 and are means of nine values (three varieties x three sites).

The refining process from wheat to flour has resulted in a general loss in heavy metals. Iron levels were reduced by 72 percent, zinc by 72 per cent, copper by 47 per cent but selenium by only 25 per cent. In the corresponding bread samples there was a marked increase in iron and zinc contents-86 and 42 per cent respectively, and smaller increases in the copper and selenium

contents - 5.8 and 17 per cent, respectively. These increases are consistent with the addition of approximately 5 per cent yeast which on analysis contained 400 mg/kg iron, 280 mg/kg zinc, 10 mg/kg copper and 0.14 mg/kg selenium. All figures refer to analyses on a dry weight basis.

It is interesting to compare the iron data with those of Downey (1983). Here flour from six mills and six large bakeries in the Dublin area were collected over a two year period together with sliced white pan bread from a supermarket. The mean iron contents-recalculated to a dry might basis-were 17.3 mg/kg and 16.6 mg/kg from flour and bread, respectively. It is not clear why the iron levels were higher in commercial flour compared with the contents of flour milled at Kinsealy.



Fig. 15 . Copper, zinc, iron and selenium from (wheat) grain. flour, and bread

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The limited data available at this time indicate that the selenium level in flour (mean 0.06 mg/kg Se) is quite low. Mean protein content was 11.5 percent. Barclay and McPherson (1986) examined flour from the U.K. and protein contents of less than 12 per cent averaged 0.046 mg/kg Se. Those with protein contents of between 12 and 14 per cent averaged 0.163 mg/kg Se and those with protein contents greater than 14 per cent averaged 0.327 mg/kg Se. The latter flour was of Canadian origin.

The contribution of cereal products to total dietary selenium intake will obviously vary from country to country but in the U.K. it is reckoned to be of the order of 40 per cent. The reduction in the percentage of Canadian wheat allied to a fall off in actual bread consumption in the UK has inevitably led to a reduction in selenium intake from cereal sources (Barclay and McPherson, 1986). The reported associations between selenium and disorders such as cardiovascular disease and some cancers suggest that more information should be available on the level of selenium in the Irish diet. A thorough appraisal of the selenium content of native and imported Irish wheat is now necessary from a human health point of view. From the animal health aspect, barley needs to be examined.

Seed dressing of cereals

In the past cereal seed was commonly dressed with organic mercurial compounds.

Exact formulations varied between suppliers and amounts applied depended on the type of cereal being dressed. Overall, the final mercury level in seed ranged between 20 and 30 mg/kg Hg. Levels of mercury in harvested grain were extremely low and did not give any cause for concern (M. Lynch/ private communication). However seed dressing with arsenicals is not currently practiced and dithiocarbamates containing manganese, zinc and copper are now used. The metal levels applied are very low and are in no way deleterious

DAIRY PRODUCTS

Because the cow acts as a "biological filter" with respect to heavy metal emanating from feed, milk and milk products are generally considered to be practically free from heavy metal contamination. Processing and packaging processes are not reckoned to add significant amounts though special problems can occur with copper and to a lesser extent with iron. These are discussed below. The pathways of some heavy metals to milk together with estimates of acceptable levels and those normally encountered (I.D.F., 1978; Murphy et al., 1977) are summarised in Table 5. As this table shows, heavy metal contents of milk are very low and not generally considered a problem. In point of fact the low metal levels can present special analytical difficulties and many of these have only recently been overcome.

Table 5: Heavy metals (mg/kg) in milk

Metal	Pathway	Acceptable Level	Normal Level
Cadmium	Fertilisers	0.001	<0.001
	Pesticides		
	Mine spoil pollution		
	Sewage sludge		
Copper	Feed	0.15	0.04 - 0.13
	Milk processing		
	Pig slurry		
Iron	Feed	0.3	0.2 - 0.4
Lead	Feed	0.01	0.002 - 0.01
	Cans (soldered)		
	Mine spoil pollution		
Mercury	Feed	0.001	<0.001
	Drinking water		
	Pharmaceuticals		

Selenium in milk

Selenium is an exception to the general rule insofar as it passes from feed to milk relatively readily. The levels of the element in milk definitely reflect soil and pasture Se levels. Typical values from low Se areas in New Zealand ranged from 0.003 to 0.004 mg/kg (Thompson and Robinson, 1980) whilst values of "less than 0.02 mg/kg" were reported from low Se areas in Oregon (Allaway *et al.*, 1968). These workers recorded values of 0.05 mg/kg from high Se areas of South Dakota. Higher levels ranging from 0.16 to 1.27 mg/kg were noted in "high Se rural areas" in the U.S. (Rosenfeld and Beath, 1964). Little information is available concerning the selenium status of Irish milk but in a

seleniferous area of Co. Meath levels ranging from 0.04 to 0.07 mg/kg Se were found by the author. In this instance cows were confined to seleniferous pasture for a period of 15 weeks. Of potentially greater interest would be the selenium contents of milk from low Se areas in Ireland. To date this information is not available.

Copper and iron in milk and butter

Quite apart from direct toxic effects, heavy metals in food can potentiate secondary effects. Copper and iron in milk and butter illustrate this point. Here levels may be quite low - less than 0.1 mg/kg in the case of copper - yet high enough to catalyse the oxidation of fatty acids and lead to off-flavours in milk

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and milk products. Their effect in this regard has been studied by Murphy *et al.* (1977). Copper is of greater significance than iron as iron bound to proteins is not involved in lipid oxidation. Higher levels of copper were found in winter (November) milk than in sunnier (July) milk from creameries but since little differences were apparent in unprocessed milk, the higher levels of copper were attributed to contamination from processing equipment. The lower volumes of milk processed in winter would obviously favour this. In general levels of copper were not sufficiently high to cause significant oxidative rancidity in butter.

In unprocessed milk highest levels of both copper and iron were found in colostrum and were presumed to have arisen from prepartum accumulation of blood in the mammary gland. With time, levels of both metals decreased but from September to November iron levels rose again. One wonders if this was a reflection of increased soil ingestion by cows at this time of year. In turn this poses the question of possible effects of high stocking rates - with accompanying increases in soil ingestion (Nolan and Black, 1970; McGrath *et al.*, 1982; Fleming, 1986) on iron levels in milk.

Meat And Fish

Heavy metals in meat and fish have not been studied to any great extent in An Foras Taluntais so research data are not available.

Discussion on these foods is therefore confined to some general comments.

Meat

In the case of grazing animals, changes in heavy metal contents of fodder are more strongly reflected in liver and kidney than in muscle tissue. The contribution to human heavy metal body burden from the meat portions most commonly consumed, is therefore not large. Attention must, however, be drawn to possible hazards from liver when this is a constituent of baby foods. The copper levels in fresh liver may reach a few hundred mg/kg consequent on the supplementation of pig rations with copper. Baby - foods containing beef liver can have copper contents as high as 26 mg/kg (Hughes *et al.*, 1960). Careful monitoring of liver-based baby foods for copper - and indeed other heavy metals is therefore necessary. The banning of liver from copper-supplemented pigs in baby foods has actually been advocated (Bories, 1980).

With adults the problem is obviously not quite so important. Liver consumption has been estimated at 1 to 2 per cent of annual meat intake. On this basis increases in copper intake consequent on copper supplementation of pigs would be quite innocuous if liver consumption was distributed evenly throughout the year. In practice this may not necessarily be so and possible transient consequences of copper overloading must not be overlooked (Bories,

1980). Fortunately however, humans possess a powerful homeostatic mechanism, which protects against copper toxicity. The application of sewage sludge to land has given rise to much concern in relation to potential increases in heavy metal levels in crops and thus by extension, in animal products. Some American work has indicated that heavy metals in tissues of cattle grazing pasture on a sludge disposal site had higher levels of zinc and cadmium in kidney than control animals but overall contents were such that high applications of sewage sludge to land were not considered a hazard from either the livestock or human health aspects. No differences were apparent in muscle tissue metal levels (Baxter *et al.*, 1983).

In relation to such studies however, the effect of stocking rate must not be ignored as when stocking rate is high, heavy metal intake is considerably increased through direct ingestion of soil.

In the Irish context heavy metals levels in fish taken from the Irish Sea is of obvious importance. Selenium also accumulates in marine organisms but here its presence may well be beneficial to humans rather than detrimental, depending on dietary intake of the element. The recommended daily intake of selenium for humans appears to be in the 50 to 200 microgram range (Food Nutrition Board, 1980). The average daily intake of selenium is known for many countries (Barclay and McPherson, 1986) but to date this information does not appear to be

available for Ireland. Data on the mineral element composition of Irish foods in general and the contribution of different food types to daily intakes is not readily accessible. In Finland a survey (Koivistoinan, 1980) has provided such data for twenty five elements and a model dealing with a number of heavy metals. Future work in the food science area should include something similar for Ireland.

Lead in the Dublin diet

Few heavy metals have received the attention equal to that accorded to lead. The dispersion of the element into the atmosphere from automobile exhausts has caused considerable worry among urban communities and blood lead levels of urban residents are often elevated compared with rural populations. The lead content of foods in cities is therefore of understandable concern. Murphy (1985) surveyed a variety of foods consumed in the Dublin area for lead content and found that canned foods, fish and some meats had highest level, though some herbs and spices also contained relatively large amounts. A selection from the data is given in Table 6. Some data on vegetables from known polluted areas (P) in Clondalkin, Tallagh and Ballycorus are included.

The data are reassuring in that the contents are-with a few exceptions-well within acceptable levels.

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Table 6: Lead contents of components of Dublin diet (Murphy, 1985)

Food	Lead content (mg/kg) fresh weight)		
	No. of samples	Range	Mean
Fresh	15	0.05-1.6	0.21
Canned meat	100	0.05-2.0	0.28
Fish (fresh, canned)	204	0.05-5.16	0.44
Root vegetables	32	0.02-0.4	0.13
Green vegetables	51	0.02-1.5	0.21
Canned vegetables	169	0.05-2.4	0.28
Root vegetables (P)	17	0.14-7.3	1.4
Green vegetables (P)	62	0.10-21.1	1.1
Fresh fruit	15	0.5-0.4	0.08
Canned fruit	58	0.05-2.1	0.39
Herbs and spices	147	0.05-5.5	0.8
Milk	52	0.01-0.09	0.03
Beverages	340	0.01-0.9	0.05

(P) From known polluted area

Bio-availability of heavy metals from food

Although the intake of micro-nutrients from different foods varies widely, the vital factor from the nutritional point of view concerns their bio-availability.

In the case of cereals the content of phytic acid is extremely important in relation to the bio-availability of both zinc and iron. Phytic acid, the hexaphosphoric ester of inositol (Fig 16) occurs mainly in cereal grain and forms very sparingly soluble salts with a number of divalent cations, e.g., zinc and iron. Its calcium-magnesium salt is known as phytin.

Downey *et al.* (1982) have indicated that the bio-availability of iron and zinc is less from brown than from white bread, because of the greater content of phytin in brown bread.

With milk, there is a lower bio-availability of zinc from bovine than from human milk; this is attributed to the stronger bonding of zinc by colloidal calcium phosphate complexes in the former (Singh *et al.*, 1984). The entry of zinc into calcium phosphate complexes is not really unexpected. The incorporation of guest elements into host minerals is governed to a large extent by the relative sizes and charges

of competing ions. Calcium and zinc ions are similarly sized; the ionic radius of Ca^{2+} is 0.099 nm and that of Zn^{2+} is 0.08 nm.

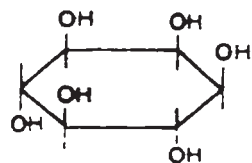
Another compound influencing the bio-availability of zinc from milk is picolinic acid (Hegarty, 1981).

The iron contents of bovine and human milk are similar yet the bio-availability from human milk is greater. This is indicated by the greater resistance to anaemia of breast fed babies compared with bottle fed babies (Hegarty, 1981).

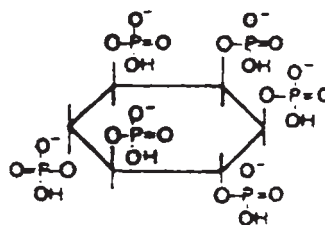
Differences in the bio-availability of lead have been recorded by Sherlock (1987). Tracer experiments with ^{203}Pb have shown that absorption of lead from drinking water is approximately 70 per cent whereas that from beer is only 20 per cent. Although the content of lead in liver and kidney is elevated relative to other body organs its absorption across the gut appears to be very low - of the order of 3

per cent. This is attributed to the strong binding of lead by the proteins in liver and kidney. The absorption of lead then, varies widely with the type of meal being eaten but with conventional meals an absorption of around 5 per cent would appear to be the norm (Sherlock, 1987).

The bio-availability of cadmium is influenced by the levels of iron, zinc and calcium in the diet (Chaney, 1988). When iron is in sufficient supply ferritin, a protein-bound hydrous iron oxide, readily binds cadmium in intestinal cells. When iron is deficient, this mechanism is not nearly as efficient. Increased dietary zinc favours the biosynthesis of the high-cysteine protein metallothionein; this protein then binds cadmium and also zinc. Calcium deficiency increases the ability of the intestine to absorb calcium and this also increases cadmium absorption possibly through competition of the similarly sized calcium and cadmium ions for binding sites.



Myoinositol



Phytic acid

Fig. 16. Myo-inositol and phytic acid

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Tracer studies with Se 75 have shown that the availability of the element to humans is greater from selenomethionine, the major form present in cereals, than from selenite. For chicks the availability of selenium is greater from cereal products than from fish and meat products (Thomson and Robinson, 1980). The low bio-availability of selenium from fish is ascribed to the formation of stable complexes between selenium and heavy metals (Vokal-Borak, 1979). Selenium bio-availability from foods estimated on the basis of animal studies however, may not necessarily reflect the availability to the human.

Information on the bio-availability of heavy metals, and of nutrients in particular, calls into question the value of total levels of elements in the diet. It is clear that these total values are frequently poor indices of bio-availability. It is now time to expand studies on the speciation, or forms of combination, of metals in food products with a view to providing data which will admit of a more meaningful interpretation in relation to their bio-availability. Possibly the best example is that of mercury where the contents of methyl (HgCH₃) and ethyl (HgC₂H₅) mercury are of much greater significance than total mercury level.

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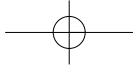
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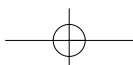
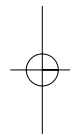
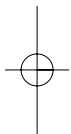
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Figures

Fig.1. Glaciations and soil formations

Fig.2. Soils of low cobalt status

Fig.3. EDTA-soluble copper in soil

Fig.4. Frequency distribution of EDTA-soluble copper

Fig.5. Low iodine soils

Fig.6. Soils of high molybdenum status

Fig.7. Selenium in soil

Fig.8. Frequency distribution of selenium

Fig.9. Soils of low zinc content

Fig.10. Frequency distribution of zinc in soil

Fig.11. Current assessment of molybdeniferous areas in Ireland

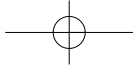
Fig.12. Molybdeniferous areas in Co. Meath

Fig.13. Molybdeniferous soils of Co. Laois

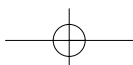
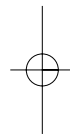
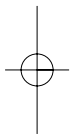
Fig.14. Location of sampling transects (A) and (B) used in the exploratory investigation

Fig.15. Copper, zinc, iron and selenium from grain (wheat), flour and bread

Fig. 16. Myo-inositol and phytic acid

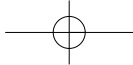


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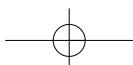
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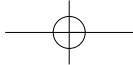
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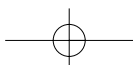
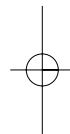
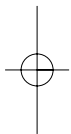
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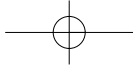
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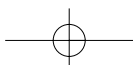
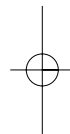
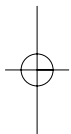


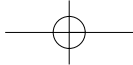
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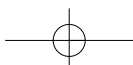
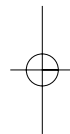
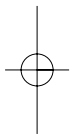


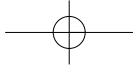
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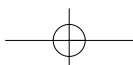
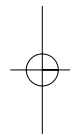
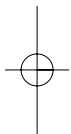


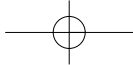
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