

**SOIL AND HERBAGE HEAVY METAL/  
TRACE ELEMENT VARIABILITY  
AND RELATIONSHIPS AT FARM  
AND REGIONAL LEVEL**

**END OF PROJECT REPORT**

**ARMIS 4610**

**Author**

---

D. McGrath

**Johnstown Castle Research Centre  
Wexford**

**August 2000**

ISBN No. 1 841701 16 5



AGRICULTURE AND FOOD DEVELOPMENT AUTHORITY

---

Teagasc, 19 Sandymount Avenue, Ballsbridge, Dublin 4.

# TABLE OF CONTENTS

<b>SUMMARY</b> .....	1
<b>CONCLUSIONS</b> .....	2
<b>INTRODUCTION</b> .....	3
<b>EXPERIMENTAL</b> .....	5
<b>RESULTS AND DISCUSSION</b> .....	8
<b>REFERENCES</b> .....	19

## 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 km<sup>2</sup> surrounding area 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, variability was least (CV 10%) for sesquioxide metals, iron and aluminium, and elements chromium and nickel. It was highest where there was evidence of geochemical contamination with cadmium and selenium. In general, variability was higher (>20% CV) for extractable components including copper, zinc and manganese. Regression analysis of elements in soil showed up a number of useful associations particularly for the volatiles selenium, sulphate sulphur, mercury, cobalt, vanadium and fluorine with soil organic matter. Associations were also found between 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 was 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.
- Long term monitoring of herbage for selenium content highlighted the unreliability of relying on a single determination to characterise the selenium status of pasture.

## CONCLUSIONS

- ① On three farms soil variability, expressed as CV, for a number of soil components including iron, aluminium, nickel, cobalt, chromium, fluorine and vanadium, were close to 10%. This suggested that in situations where geochemical pollution is known to be absent, a single-measurement can give an indicative value for these elements on farm.
- ② For herbage, component variability was generally greater at 20% and often much higher.
- ③ Correlations between soil extractable and total metals were noted for manganese and copper, but not for zinc. A number of other very significant useful soil correlations were noted at farm and regional level, *i.e.* chromium with nickel, selenium with loss on ignition. Clusters of related elements included fluorine – vanadium – chromium and selenium – sulphate sulphur and mercury.
- ④ Two separate types of relationships were found for plants (1) those which we consider to be dependant on plant uptake involving major nutrients and a number involving heavy metals *i.e.* lead with zinc, (2) those involving aluminium, iron, titanium, vanadium, chromium, fluorine, lead and iodine, giving expression to the extent to which herbage was contaminated with soil.
- ⑤ Iron on plant can be taken as a useful indicator of soil contamination, substituting for titanium, where opportune.
- ⑥ Relationships between total soil metal and herbage metal were poor with major significance for zinc and manganese only.
- ⑦ Results from a long term monitoring program on herbage from separate locations on each of two farms indicated high variation between results. It indicated the difficulty of adequately expressing selenium status of a field or farm with a single value for herbage.

## INTRODUCTION

Heavy metal and trace element content of soils and herbage is estimated with least expenditure of effort and cost by taking a representative sample from a defined area, compositing samples and conducting analysis on a suitably prepared sub sample (Voss, 1998). For agricultural purposes this is essentially the only method used. The sampled area is generally 2-5 ha and should at least be visibly uniform and comprise a single land-use class or enclosure. Soil cores generally number 20 – 25. The sampling depth is often 10cm, especially on grassland. (Voss, 1998). However, numerous variants of the above are used (Friesen and Blair, 1984). For herbage sampling there is a singular lack of protocols but operating procedures appear to mirror those in use for soil sampling.

Reliability of estimate is usually expressed as CV (coefficient of variation) or (standard deviation/mean) x100. Variability (bias or uncertainty) in estimates is considered to arise at sampling, sample preparation and analysis stages. Sampling variability is also subdivided into geochemical and sampling components (Ramsey and Argyraki, 1997). In general, geochemical and sampling variabilities are considered to be large and analytical variability small except for some elements such as sulphur by nephelometry (Cameron et al., 1994) and little is known of variability arising during sample preparation.

Variability within discrete or over extended areas following grid sampling has been widely used for precision farming and for landscape studies. Variability within discrete areas following random sampling is generally used to evaluate land contamination. What has been considered much less often is variability between discrete sampling areas in defined geographic areas (*i.e.* at farm level). This is despite the fact that composite sampling resulting in a single value estimate is the commonest sampling procedure in use for agricultural and arguably environmental purposes. Estimates of variability are, of course, not available from analysis of a single composite sample.

Between-field variability for soil extractables, principally phosphorus and potassium, has been considered (Beckett and Webster, 1971 : Cameron et al, 1994). Much less is known for total trace components. In an earlier investigation (McGrath and McCormack, 1999) it was found that some elements of environmental importance tended to have concentrations that were characteristic for the area. These elements included chromium, cadmium, nickel and selenium. It was considered desirable to evaluate the variability of these and other elements in an attempt to maximise the value of analyses particularly those conducted in single or small numbers of soil and herbage at farm level.

In order to quantify variability at farm level, data for soil and herbage available for individual sampling areas of 2 – 3 ha on three farms were evaluated. Data from 2 ha sampling areas from at least two locations on 21 farms in the same locality were evaluated separately. The data comprised a wide range of trace elements and heavy metals. Some major soil components and nutrients were also considered mainly for comparative purposes. It was anticipated that the generalizations made would assist in improving our understanding of chemical relations in at least one geographic area.

In addition data on the variation of selenium content of herbage on two farms over a 28 month period was assessed to evaluate fluctuations in element content.

## 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.

### Soils

Two sets of soil results were examined:

- (a) Three farms were divided into sampling areas of 2 – 3 ha. Cores were obtained at random along two zig-zag paths in each paddock. Composite samples each consisting of a minimum of 25 cores were thus obtained from each sampling area in March 1995. 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 July 1997. Two and occasionally four areas were sampled on each farm and a total of 47 samples were collected.

All soils were sampled to a depth of 10 cm. Uniformity in land use and topography was taken into account in the delineation of sampling areas. On farms, individual fields comprised between one and four sampling areas.

### 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 bicarbonate 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. For extractable components, results were expressed on a soil volume basis and were not corrected for moisture.

*Herbage:* Digestion of herbage was performed using HNO<sub>3</sub> (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 DISCUSSIONS

### Soil variability

Variabilities displayed by a wide range of parameters are shown in Table 1 for the following:

- ① Farms 1 – 3 (with 16, 19 and 15 sampling areas)
- ② The combined 50 sampling areas
- ③ 47 locations on 21 farms in the region, and
- ④ Soils of the southeast of Ireland described previously (McGrath and McCormack, 1999)

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 km<sup>2</sup>.

In this investigation most consideration was paid to the farm results and less to the regional results for which there are less data. The southeast data are appended only for general comparative purposes. Unsurprisingly, variability increased with increasing area represented, which is considered the norm (McIntyre, 1967).

**Table 1: Mean and variability (as % CV) of heavy metals, trace elements and other soil parameters**

Parameters	Mean 3 farms	CV (%)					
		Farm 1	Farm 2	Farm 3	Combined 3 farms	Region	Southeast
Area		26.5ha	33.6ha	21.6ha	-	239km <sup>2</sup>	-
pH (water)	6.10	3.9	3.4	2.7	7.0	7.2	9.8
*LO1	134.00 g/kg	36.4	17.1	8.9	25.6	35.9	78.8
Extractable							
Phosphorus	6.90 mg/l	31.6	46.5	38.7	47.0	66.0	197.5
Potassium	134.00 mg/l	20.4	40.4	32.7	32.6	67.2	67.5
Magnesium	190.00 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	4.70 mg/l	27.5	27.5	27.2	32.2	69.2	71.9
Manganese	309.00 mg/l	35.6	23.5	38.7	39.4	43.7	65.1
Zinc	5.50 mg/l	26.8	13.2	38.7	23.4	47.2	85.5
Cobalt	18.50 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	17.90 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	50.70 mg/kg	14.6	8.6	14.2	21.9	26.6	39.4
Copper	19.20 mg/kg	22.9	22.4	14.7	25.1	49.0	53.1
Mercury	0.10 mg/kg	27.4	18.5	13.3	25.0	-	79.2
Nickel	47.00 mg/kg	13.5	12.0	10.7	14.0	28.9	68.8
Lead	29.00 mg/kg	25.5	39.6	15.0	44.0	153.8	47.0
Zinc	96.30 mg/kg	13.6	23.5	10.9	22.4	41.6	44.8
Arsenic	14.40 mg/kg	19.3	19.3	9.4	18.9	-	82.1
Vanadium	58.80 mg/kg	17.0	14.6	9.4	21.5	-	-
Fluorine	803.00 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	7.60 mg/kg	17.4	21.9	20.2	24.3	-	38.5
Iron	22.70 g/kg	8.2	12.2	9.4	12.0	-38.4	-
Aluminium	40.50 g/kg	10.8	9.0	7.5	9.6	-49.3	-
Titanium	7.02 g/kg	27.8	16.5	16.2	21.6	-	57.5
Manganese	0.56 g/kg	29.1	24.7	14.5	40.2	-	84.2

\* LO1 loss on ignition

CVs 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, CV 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 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 CV are considered indicative of significant skewed distribution which can be attributed to geochemical pollution.

Variability (or CV) 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 CV 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 CV 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.

CVs for a number of metal components tended to be low (CV less than 20%) on all three farms. These included the major sesquioxide elements, iron and aluminium. They also included the metals known to be adsorbed on these sesquioxides, *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 the variability of many soil parameters especially most extractables, including phosphorus and potassium, are usually so large as to render them comparatively meaningless. Interestingly however, mean CV 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 CV 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 (S. Diamond, personal communication, 1995).

## Correlation 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 they are not considered in detail because of the occurrence of geochemical pollution as indicated above.

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.

Some individual relationships, nickel with chromium, selenium with loss on ignition, emerged that were not unexpected. There were also others of which only arsenic with lead is taken as 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.

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 volatile forms of these elements.

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

Correlation	3 Farms (n = 50)	Region (n = 47)
${}^2\text{Cu}_{\text{ex}}$ - Cu	1.456 <sup>xx</sup>	.773 <sup>xx</sup>
${}^2\text{Zn}_{\text{ex}}$ - Zn	.204 NS	.249 NS
${}^2\text{Mn}_{\text{ex}}$ - Mn	.771 <sup>xx</sup>	.752 <sup>xx</sup>
Se - LO1	.638 <sup>xx</sup>	.376 <sup>xx</sup>
As - Pb	.563 <sup>xx</sup>	-
Cr - Ni	.635 <sup>xx</sup>	.422 <sup>xx</sup>
F - V	.576 <sup>xx</sup>	-
V - Cr	.537 <sup>xx</sup>	.053 NS
V - Cr	.390 <sup>xx</sup>	-
Se - S	.287 <sup>x</sup>	-
Hg - S	.450 <sup>xx</sup>	-
Se - Hg	.368 <sup>xx</sup>	-
Zn - Mn	.634 <sup>xx</sup>	.091
Zn - Pb	.729 <sup>xx</sup>	.069 NS
Pb - Mn	.590 <sup>xx</sup>	.003 NS

1, x, xx Significant at  $P \leq 0.05$  and  $0.01$  respectively;  ${}^2\text{Cu}_{\text{ex}}$ ,  ${}^2\text{Zn}_{\text{ex}}$ ,  ${}^2\text{Mn}_{\text{ex}}$  = extractable Cu, Zn and Mn respectively.

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 number of very significant relationships (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  $r^2 > 0.60$  are shown in Table 3.

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

Parameter	Regression on	$r^2$
Mn <sub>ex</sub>	Mn, LO1	0.808
Se	LO1, pH, Mn	0.770
Ni	Cr, Fe, Al, Cr	0.744
Mg <sub>ex</sub>	Pex, Kex, LO1, Fe	0.695
Cd	pH, LO1, Zn	0.637
V	F, pH	0.603

### Variability of heavy metals / trace elements in herbage

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. However, in the case of major nutrients the relatively moderate CVs 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.

**Table 4:** Mean and variability (% CV) of heavy metals - trace elements and nutrients in herbage

Element	Mean 3 farms	CV%				
		Farm 1	Farm 2	Farm 3	Combined 3 farms	Region
Nitrogen	33.40 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	28.70 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	24.0
Sulphur	3.46 g/kg	32.0	16.7	20.5	26.2	21.7
Cadmium	0.12 mg/kg	48.0	29.8	29.9	49.2	150.6
Chromium	0.78 mg/kg	75.7	42.5	42.3	60.4	70.3
Copper	10.00 mg/kg	23.7	17.3	14.5	19.3	22.4
Mercury	0.02 mg/kg	18.7	23.3	15.3	19.1	-
Nickel	2.54 mg/kg	41.1	33.9	22.0	39.2	52.5
Lead	2.05 mg/kg	44.4	24.6	42.9	47.3	116.8
Zinc	29.60 mg/kg	22.9	18.6	8.8	20.1	75.2
Arsenic	0.49 mg/kg	55.1	54.2	78.0	70.1	-
Vanadium	2.39 mg/kg	77.77	35.5	62.8	77.1	-
Fluorine	10.20 mg/kg	112.3	52.6	62.3	86.7	-
Selenium	0.09 mg/kg	142.3	28.0	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	33.10 mg/kg	106.2	59.5	76.1	87.2	-
Aluminium	432.00 mg/kg	118.6	77.8	88.6	101.8	-
Titanium	47.70 mg/kg	95.9	43.8	87.4	80.0	-
Manganese	171.00 mg/kg	45.2	48.0	20.5	64.5	71.9
Iodine	0.24 mg/kg	59.9	73.2	24.4	75.4	-

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

### Correlations 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). Perhaps additions to the list of those generally included in this category are 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.

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 is also more easily determined, may serve as well.

<b>Table 5: <sup>1</sup>Relationships (r) between some plant constituents for herbage from three farms</b>								
	Al	Fe	Ti	V	Cr	Pb	Fl	I
Al	1.00							
Fe	0.978	1.00						
Ti	0.869	0.902	1.00					
V	0.768	0.799	0.892	1.000				
Cr	0.957	0.951	0.899	0.805	1.000			
Pb	0.678	0.666	0.748	0.795	0.721	1.000		
F	0.905	0.925	0.783	0.654	0.876	0.496	1.000	
I	0.818	0.784	0.722	0.652	0.757	0.613	0.666	1.000

<sup>1</sup>r significant at  $P \leq 0.01$  for all values

### **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 and this may show in the relationship between levels in plant and soil.

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 is 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.

<b>Table 6: Most significant relationships (<math>r^2</math>) between herbage components and soil factors</b>		
Element Herbage - Soil	Data Set	
	3 Farms	47 Paddocks
Se - Se	.888 <sup>XX</sup>	.967 <sup>XX1</sup> (.350 <sup>XX</sup> )
Mn - Mn <sub>ex</sub>	.448 <sup>XX</sup>	.0015 NS
Mn - Mn	.331 <sup>XX</sup>	.087 NS
Zn - Zn	.448 <sup>XX</sup>	.623 <sup>XX</sup> (.040 NS)
Pb - Pb	.253 <sup>XX</sup>	.484 <sup>XX</sup> (.050 NS)
Zn - Zn <sub>ex</sub>	.113 <sup>X</sup>	.292 <sup>XX</sup>
Mo - Soil pH	.149 <sup>XX</sup>	-

<sup>1</sup>( ) value obtained when 3 soils containing very high level of selenium (14.5 mg/kg), lead (789 mg/kg) and zinc (377 mg kg<sup>-1</sup>) were omitted from consideration

Of the extractable metals (using procedures that were designed 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)

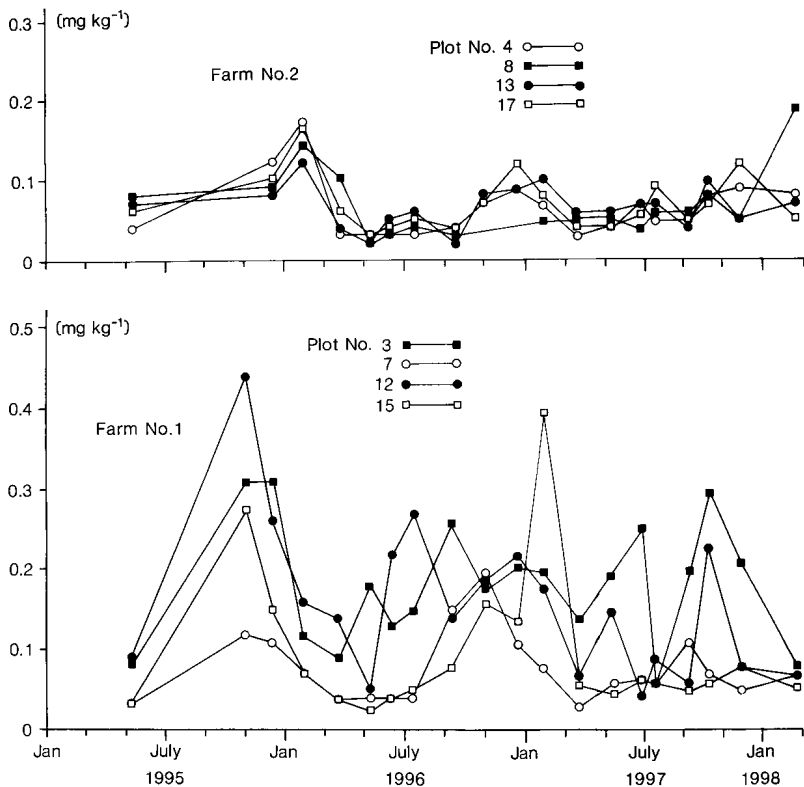
relationship with pH. Iodine was not related to aluminium as might have been anticipated.

### Monitoring of herbage for selenium

Selenium level in herbage was monitored on two farms, four paddocks per farm on 19 occasions between December 1995 and March 1998. The results (Fig 1) show that wide variation existed both spatially (within farms) and temporarily (with time). Conclusions were similar to those previously reported by Haygarth *et al* (1993). The extent of this variation (Table 7) was as large on Farm 2 as on Farm 1 – which had a higher level of selenium particularly in one sampling area. The main conclusion of this experiment is that selenium content of herbage varies to such an extent that estimates on single samples cannot be relied upon to express the selenium status of a pasture.

<b>Table 7: Variation of selenium content (mg/kg) of herbage over space and time on two farms</b>		
	<b>Farm 1</b>	<b>Farm 2</b>
Range of values	0.03 - 0.46	0.02 - 0.170
Range of means	0.075 - 0.28	0.032 - 0.147
Overall mean	0.130	0.068
Mean CV (%)	42.6%	44.6
Plot 1 <b>Mean (mg/kg)</b>	0.081	0.066
2	0.196	0.067
3	0.161	0.066
4	0.101	0.070
Plot 1 <b>CV (%)</b>	54.4	57.1
2	37.4	66.1
3	62.4	41.3
4	91.6	50.0

SEASONAL VARIATION OF SELENIUM IN HERBAGE  
(4 locations per farm)



**Fig 1:** Selenium in herbage (mg/kg) from 4 plots on Farm 1 and on Farm 2.

### Acknowledgements

The author wishes to thank R.F. McCormack for technical assistance, W.E. Murphy who assisted in statistical analysis and V. Staples for diagrams.

## REFERENCES

- ADAS 1995.** A review of spatial variations of nutrients in soils. Winchester, Hants. 68pp.
- Beckett, P.H.T. and Webster, R.** 1971. Soil Variability – A Review, *Soils and Fertilisers*, 34: 1-15.
- Byrne, E.** 1979. *Chemical Analysis of Agricultural Materials*. An Foras Taluntais, Dublin, 194pp.
- Cameron, D., Paterson, J.E. and Hunter, E.A.** 1994. The components of variation associated with sampling soil for the measurement of major and trace nutrients in grazed fields in S.E. Scotland. *Soil Use and Management*. 1011 – 1015.
- EPA, 1995.** Investigation of Animal Health Problems at Askeaton, Co. Limerick. Interim Report.
- Friesen, D.K. and Blair, G.J.** 1984. A comparison of soil sampling procedures used to monitor soil fertility in permanent pasture. *Aust. J. Soil Res.* 22: 81-90.
- Haygarth, P.M., Harrison, A.F. and Jones, K.C.** 1993. Geographic and seasonal variation in deposition of selenium to vegetation. *Environmental Science and Technology*, 27: 2878 – 2884.
- Healy, 1973.** Nutritional aspects of soil ingestion by grazing animals in *Chemistry and Biochemistry of Herbage*. Ed. G.W. Butler and R.W. Bailey. Academic Press: vol 1: 567 – 588.
- McGrath, D.** 1996. Application of single and sequential extraction procedures to polluted and unpolluted soils. *The Science of the Total Environment*, 178: 37-44.
- McGrath, D., Poole, D., Fleming G.A. and Sinnott, J.** 1982. Soil ingestion by grazing sheep. *Irish J. Agric. Res.*, 21: 135-145.

**McGrath, D.** 1998. Use of microwave digestion for estimation of heavy metal content of soils in a geochemical survey. *Talanta*, 46: 439-448.

**McGrath, D. and McCormack, R.J.** 1999. The significance of heavy metal and organic micropollutants in soil. End of Project Report No. 4268.

**McIntyre** 1967. Soil sampling for soil testing. *The Journal of the Australian Institute of Agricultural Science*, 309 – 320.

**Ramsey, M.H. and Argyraki, A.** 1997. Estimation of measurement uncertainty from field sampling: implications for the classification of uncontaminated land. *Science of the Total Environment*: 198: 243-257.

**Voss, R.** 1998. Fertility recommendations: past and present. *Commun. Soil Sci. Plant Anal.* 29: 1429-1440.