

# THE SIGNIFICANCE OF HEAVY METAL AND ORGANIC MICROPOLLUTANTS IN SOILS

END OF PROJECT REPORT

ARMIS 4268

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## SUMMARY

The southeastern region of Ireland, representing 22% of the land area of the country, has been systematically sampled. Soils have been analysed for a range of heavy metals and persistent organics. These soils have now been archived and are available for future analyses as required.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, aluminum, iron, and manganese, for trace elements (heavy metals) arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium and zinc and for organics, hexachlorobenzene, hexachloro-cyclohexanes, and for DDT and its metabolites. Other organics, polychlorinated biphenyls and polycyclic aromatic hydrocarbons, were examined in a proportion of soils.

Results have been statistically analysed and frequency distributions have been calculated. Geographic distributions have also been plotted and localized concentrations have been found for most elements. Geochemical factors are considered to be largely responsible for most of these localized concentrations. Aerial deposition of lead and selenium was also indicated. Historic usage of DDT and  $\gamma$ -HCH was detected in soils with different land uses.

Overall, little serious contamination of soils, especially that caused by man, by toxic elements was evident. However, as many as 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 (Al) and iron (Fe) along with oxygen, are responsible for much of the soil matrix. Other major components include but are not confined to manganese (Mn), 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 (Cd), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). 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 (As), chromium (Cr), cobalt (Co) and selenium (Se) 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 use 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 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.

Soils contain about 10% of organic matter in a typical grassland topsoil. This is largely derived from decaying vegetation with significant amounts of animal and microbial biomass. Soil is also the recipient of a large number of synthetic organic compounds. When these display resistance to degradation and when they are biologically active they give rise to concern. Among such may be listed organochlorine insecticides (OCs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs).

Information on biologically active inorganic and organic components in soil is relatively haphazard. In the past it tended to be related to individual investigations 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 (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 allaying of consumer fears.

## **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, than 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. A 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), HNO<sub>3</sub> (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 H<sub>3</sub>BO<sub>3</sub> (2g) to neutralize excess HF and made up to 50 ml (53.95g) in a polythene container. Digestion of soil by less severe but established procedures was conducted for Hg, Se and for As analysis.

### **Analysis of inorganic components:**

Analysis for Cr, Cu, Pb, Ni, Zn, Al, Fe, and Mn was performed using flame atomic absorption. For Fe, 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 fluorescence spectrometry. All results were corrected for sample moisture. Organic carbon was estimated by the Walkley Black method and soil pH in water (1:1) using a calomel electrode (Byrne, 1979).

### **Analysis of organochlorines:**

Mineral soil (30g) or peat (20g) was exhaustively extracted with dichloromethane in a soxhlet extractor. After concentration to

near dryness, the residue was taken up in hexane and passed through a column of activated florisil topped with a layer of  $\text{AgNO}_3$  on silica gel (10%) to remove sulphur compounds and with a layer of anhydrous  $\text{Na}_2\text{SO}_4$ . Organochlorines were removed by elution with 20% dichloromethane in hexane. Eluates were concentrated and finally taken up in hexane (2ml, but a larger volume where the concentration of an organic component exceeded  $0.5 \mu\text{g kg}^{-1}$  in soils). Organochlorine insecticide residues were quantified using an external standard containing generally hexachlorobenzene (HCB),  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  - hexachlorocyclohexane (HCH) and 4,4' -DDE, DDD and DDT. Separations were effected on a DB 608 column (J. and W. Scientific) with dimensions 0.53mm ID x 30m length and film thickness 1.2 $\mu\text{m}$ . Aliquots of 2 $\mu\text{l}$  were injected. Operating parameters were injection temperature 240 $^\circ\text{C}$ , initial temperature 160 $^\circ\text{C}$  for 10 minutes, x 28/min to 200 $^\circ\text{C}$ , 2 min at 200 $^\circ\text{C}$ , x 58/min to 220 $^\circ\text{C}$ , at 220 $^\circ\text{C}$  for 2 min, x 108 to 230 $^\circ\text{C}$ , and finally at 230 $^\circ\text{C}$  for 10 min to clean column. Detector temperature was 375 $^\circ\text{C}$  and flow rate of helium carrier gas 2 ml  $\text{min}^{-1}$ .

For PCB analysis, the purified extract was reprocessed through a similar florisil column and eluted with hexane. An external standard containing six PCB congeners Nos 28, 52, 101, 138, 153 and 180 was employed. Column separation conditions were similar to that used for OCs. After quantification, individual values of the six congeners were summed and a factor of 3.36 was used to convert to total PCBs. The factor used was that generated from using a 1:1:1 mixture of Arochlors 1248, 1254, and 1260, which gives a mixture of congeners not unlike that found in environmental samples.

### **Analysis of PAHs:**

Soil (10g) was extracted (soxhlet) with dichloromethane for 2h. Clean-up was effected on a silica gel column (63-200  $\mu\text{m}$  particle size: deactivated with 12% water). Column was 1 cm in diameter and contained 5g of adsorbent. It was topped with anhydrous sodium sulphate. Elution was with a hexane-dichloromethane (80:20) mix. Eluate (100 ml) was concentrated to 1 ml on the rotary evaporator and then to incipient dryness

under a stream of nitrogen. Residue was taken up in acetonitrile water (1/1:1 ml). It was passed through a nylon filter (pore size 0.45  $\mu\text{m}$ ). Mixtures were separated on a dedicated PAH column (Chromospher PAH:3 $\mu\text{m}$  particle size: dimensions 100 mm x 4.6 mm). An aliquot (20  $\mu\text{l}$ ) was injected, using an autoanalyser, into the chromatograph. A 30 min cycle, comprised of 10 minutes linear gradient from 50 to 100% acetonitrile, 10 minutes at 100% acetonitrile, and a 10 minute equilibration period at 50% aqueous acetonitrile before the next sample injection, was adopted. The flow rate was 1.0 ml min<sup>-1</sup> and column temperature 308C. A standard procedure (Dong et al., 1993) was adopted which optimised the separation of peaks and their visualisation using fluorescence detection. Components (11) were quantified by reference to a standard mix. A CRM supplied by NIST, of which SRM 1647 c is the product currently available, was used.

## **Sampling**

# **RESULTS**

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 gave a sample taken from a 20 x 20m area. Grassland (in the broadest sense ranging from top class sward to heathland), 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 (Fig 1).

## **Analysis - inorganic**

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 guaranteed a complete release of all metals. The procedures involved, together with the validation of the results have been discussed in some detail (McGrath, 1998).

### **Analysis - organic**

Persistent organics include OC pesticides and their breakdown products, PCBs and PAHs. OCs were examined as described earlier using other Irish soils (McGrath, 1996). The components selected for quantification were confined to those most frequently encountered in soil, i.e. 4,4'-DDT and its degradation products, DDD and DDE, together with  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ -HCH and HCB. Total amount of PCB was estimated as described earlier (McGrath, 1995) following quantification of six representative components in a total of 73 soils.

PAHs were quantified in soils from S Waterford and S Wexford (Soils No 1 - 33). This, the first report of PAHs in Irish soils, indicated generally low levels of these compounds, some of which are known carcinogens.

### **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 - gross 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 for heavy metals (Table 2) and for organics (Table 6). 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 the elements. As far as possible, threshold (limit, trigger, cautionary, action) values which have some acceptance and which have found a practical application were 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 in Fig 2 - 14. 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 cautionary level of 5 mg kg<sup>-1</sup> (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 at 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. Finally data for organic contaminants are assessed.

## **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 arisen 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 in forest soils, a slight increase was evident. Aerial deposition may have been responsible for this. The situation regarding Pb and Cd is interesting. In some countries a sizable 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 differences found here between forest soils and agricultural soils arises, it is suggested, from emissions of lead in petrol. The impact of Cd emissions is clearly lower here than in many other countries.

Table 1: Heavy metal concentration in soils by land use.												
			Heavy metal (mg kg <sup>-1</sup> ).									
Land Use	No	Organic carbon g kg <sup>-1</sup>	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Se	Zn
Pasture	(231)											
Mean		73.1	15.7	0.52	10.6	49.5	18.0	0.11	13.4	30.0	0.77	73.1
SD		32.7	12.9	0.42	5.4	19.5	9.5	0.09	9.2	14.1	0.84	32.7
Tillage	(30)											
Mean		37.0	16.4	0.76	13.6	67.6	19.1	0.11	23.3	30.3	0.69	88.6
SD		34.3	10.6	0.71	9.0	52.6	8.5	0.05	26.6	14.6	0.24	42.4
Forest	(26)											
Mean		152.8	12.8	0.29	7.7	42.5	8.7	0.15	5.5	38.1	0.87	38.0
SD		111.1	15.5	0.29	6.5	24.3	5.9	0.09	5.6	10.8	0.31	25.2
Peat	(8)											
Mean		437.7	3.1	0.35	2.4	6.0	4.9	0.13	4.4	17.6	0.87	26.2
SD		15.9	1.3	0.20	0.9	2.0	3.3	0.09	4.2	11.7	0.24	25.2

## 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<sup>-1</sup>) was evident, but many soils (largely forest and peat) had extremely low levels of elements including those essential for plant and animal well being.

**Table 2:** Inorganics: Percentile values

Element	PERCENTILE						
	Max	95	75	50	25	5	Min
Arsenic (mg kg <sup>-1</sup> )	100.2	42.0	16.5	11.9	8.7	4.1	1.1
Cadmium (mg kg <sup>-1</sup> )	3.24	1.48	0.61	0.39	0.24	0.12	0.00
Cobalt (mg kg <sup>-1</sup> )	53.3	20.6	13.5	9.8	5.8	2.2	0.0
Chromium (mg kg <sup>-1</sup> )	322.6	88.5	61.7	47.3	34.4	12.8	3.7
Copper (mg kg <sup>-1</sup> )	72.6	34.2	22.4	14.9	10.1	4.3	1.2
Mercury (mg kg <sup>-1</sup> )	1.05	0.23	0.14	0.09	0.07	0.04	0.2
Lead (mg kg <sup>-1</sup> )	108.5	59.3	34.7	26.5	20.8	14.6	3.7
Nickel (mg kg <sup>-1</sup> )	150.2	29.5	18.5	12.2	5.2	1.1	1.0
Selenium (mg kg <sup>-1</sup> )	9.71	1.59	0.84	0.62	0.46	0.36	0.20
Zinc (mg kg <sup>-1</sup> )	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 <sup>-1</sup> )	463.4	333.3	72.3	50.2	37.5	22.7	12.0
Aluminum (g kg <sup>-1</sup> )	89.1	77.3	49.2	35.2	21.8	0.9	0.0
Iron (g kg <sup>-1</sup> )	59.4	38.7	27.1	21.0	15.5	7.2	0.5
Manganese (g kg <sup>-1</sup> )	5.97	2.00	1.09	0.69	0.34	0.08	0.01

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.

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

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

+++ Significant at  $p < 0.001$

++ Significant at  $p < 0.01$

— Negative relationship

## Geographic distribution of elements

### Sesquioxide elements:

Soils with higher levels of Al, Fe and Mn are indicated in Figs 2, 3 and 4. It can be seen that an approximately similar distribution pattern held for all three metals. High concentration area coincided with soils of the Clonroche soil series which are known to be rich in these elements.

Mapping of grassland and tillage soils showed some regional effects for organic carbon and for pH (not shown). Low organic carbon values were most strongly associated with soils of S Kildare (tillage mostly), Laois and S Tipperary. Higher pH values were most frequent in the limestone areas of N Carlow and S Kildare whereas low pHs were most strongly associated with Wicklow.

## **Trace 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  $11.3 \text{ mg kg}^{-1}$  (Bowen, 1982). Slightly elevated values here are probably largely due to the association of As with sesquioxides in an area stretching from N Wicklow to E Waterford (Fig. 5). These values exceed the 10-40  $\text{mg kg}^{-1}$  concentration values variously postulated as thresholds (O'Neill, 1990). The maximum value of  $100 \text{ mg kg}^{-1}$  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 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  $1\text{-}3 \text{ mg kg}^{-1}$  frequently occur in soils derived from a belt of limestone shale stretching from N Clare to SW Limerick (McGrath, 1996). A second area with elevated Cd now appears to include N Carlow and S Kildare (Fig. 6). Soils with values in excess of  $1 \text{ mg kg}^{-1}$  Cd are generally held to be polluted. Even on soils with lower (ca  $1.0 \text{ mg kg}^{-1}$ ) Cd levels, grazing livestock have been found to accumulate Cd in kidney and liver and this has led to restriction in the scale of these body organs in Australia and New Zealand (Roberts, Longhurst and Brown, 1993). Elsewhere, concern about the negative environmental effects of the element is also widespread but consequences to 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 (Fig. 7). The levels determined are considered to be innocuous.

**Cobalt** Cobalt (Fig 8) 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) and 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 (Fig. 9). 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 (Fig. 10). 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 as with Cd is associated with limestone soils in N Carlow – S Kildare (Fig. 11). Levels are not high except as defined in the EU Directive. Localized 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 (Fig. 12). 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, 1988) 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 cautionary level of 5 mg kg<sup>-1</sup> were found in the survey.

**Zinc** This element like Cu was not found in excess in any area (Fig. 14). 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 (Fig. 15). Granitic soils of Carlow – W Wicklow and those of W Waterford did not exhibit low Co in the present investigation, whereas soils of E Waterford – S 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, W Waterford and in Offaly (Figs 16 and 17).

**Selenium** Lower levels of Se in the survey were evident in counties Kilkenny and Tipperary (Fig. 18). 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 (Fig. 18). 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 compound 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, which were designed to set specifications for soils that may receive sludge, have been widely used as threshold or indicator values of soil 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. 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. When soils are viewed on a county basis (Table 5) it can be seen that, largely because of the presence of Ni and Cd, Kildare behaves worst whereas Wicklow, containing a high number of instances of excess Pb, was only a little more satisfactory.

<b>Table 4:</b> No. of sampling sites exceeding threshold for heavy metals by land use					
		<b>Incidence of exceeding threshold level</b>			
<b>Element</b>	<b>Threshold level (mg kg<sup>-1</sup>)</b>	<b>Pasture (n=231)</b>	<b>Tillage (n=30)</b>	<b>Forest (n=26)</b>	<b>Peat (n=8)</b>
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	250	3	1	0	0
By one or more		41	13	7	0

**Table 5:** Location of soils excluding forest and peat unsuited for 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	4
Offaly	21	4
Tipperary	40	3
Waterford	29	3
Wexford	50	11
Wicklow	25	9

### **Organic micropollutants:**

**Persistent chlorinated organics** Volatile organochlorine compounds (OCs) found in soils world-wide were also detected in most Irish soils (Table 6). Occurrences of  $\gamma$ -HCH (lindane) and DDT (including metabolites) shown in Figs 19 and 20, respectively, indicated the irregular nature of the occurrence of these compounds above background levels near  $0.1$  and  $1.0 \mu\text{g kg}^{-1}$  respectively. Lindane was found in amounts exceeding  $1 \mu\text{g kg}^{-1}$  in 8 tillage, 6 pasture, 3 forest and 4 peats. Lindane is still used in forest planting and one of the forest soils had  $78 \mu\text{g kg}^{-1}$  of lindane: next highest value was  $4 \mu\text{g kg}^{-1}$ . The findings of some excess lindane in virgin bogs even at low levels of  $1\text{-}2 \mu\text{g kg}^{-1}$  would indicate accumulation by adsorption from the atmosphere. DDT above  $5 \mu\text{g kg}^{-1}$  was found in 18 tillage and 8 pasture soils. Highest levels of  $100 \mu\text{g kg}^{-1}$  occurred in soils of both grassland and tillage land use types. A high concentration of DDT enriched soils occurred in W Wexford/S Carlow. The ratio for metabolite DDE to undegraded DDT was generally greater than 1 which would suggest that most of the residues were of considerable age. Levels for PCB in the 73 soils examined were consistently low indicating no serious addition of this material by spillage to soil. The narrow range of values was consistent with adsorption from the atmosphere.

<b>Table 6: Organic contaminants: Percentile values (<math>\mu\text{g kg}^{-1}</math>).</b>							
	<b>PERCENTILE</b>						
	<b>Max</b>	<b>95</b>	<b>75</b>	<b>50</b>	<b>25</b>	<b>5</b>	<b>Min</b>
$\gamma$ -HCH	78.3	1.20	0.40	0.21	0.2	0	0.0
HCB	0.63	0.25	0.10	0.06	0.04	0.0	0.0
$\Sigma$ DDT	101.0	22.0	0.8	0.4	0.2	0.0	0.0
$\Sigma$ PCB	6.8	5.1	3.3	2.5	2.0	1.3	1.2

**PAHs** PAH contents of 33 soils (from S Waterford and Wexford) were determined. Eleven components were quantified. These included anthracene, fluoranthene, pyrene, benz [ $\alpha$ ] anthracene, chrysene, benzo [ $\beta$ ] fluoranthene, benzo [ $\kappa$ ] fluoranthene, benzo [ $\alpha$ ] pyrene, dibenz [ $\alpha,h$ ] anthracene, benzo [ $g,h,i$ ] perylene and indeno [ $1,2,3\text{-cd}$ ] pyrene. Total PAH had a mean value of  $318 \mu\text{g kg}^{-1}$  and varied from a low of  $36 \mu\text{g kg}^{-1}$  to a maximum of  $3120 \mu\text{g kg}^{-1}$ . The former was from a grassland site on a mineral soil; whereas the latter was from under grass in the grounds of an educational establishment in Waterford city. The values obtained were in line with those reported by Jones et al (1989) in agricultural soils in south Wales. Higher values associated with industrialized areas or peats were not found in the present investigation.

Benz [ $\alpha$ ] pyrene is often taken as indicative of carcinogenic PAH level. Amounts of this component in Irish soil were consistently low (generally  $10 \mu\text{g kg}^{-1}$ ) with the city soil being only  $17.7 \mu\text{g kg}^{-1}$ . These were similar to values reported for soil in remoter areas in Wales and were much lower than values associated with industrialized areas.

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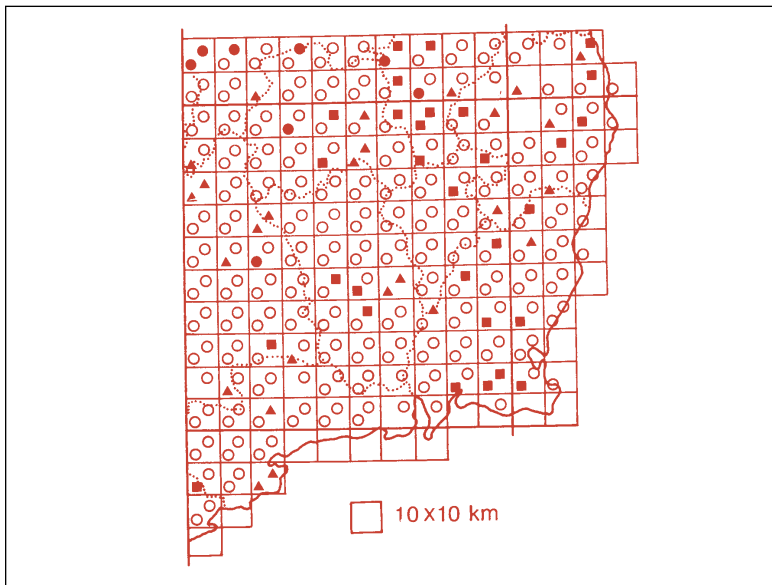
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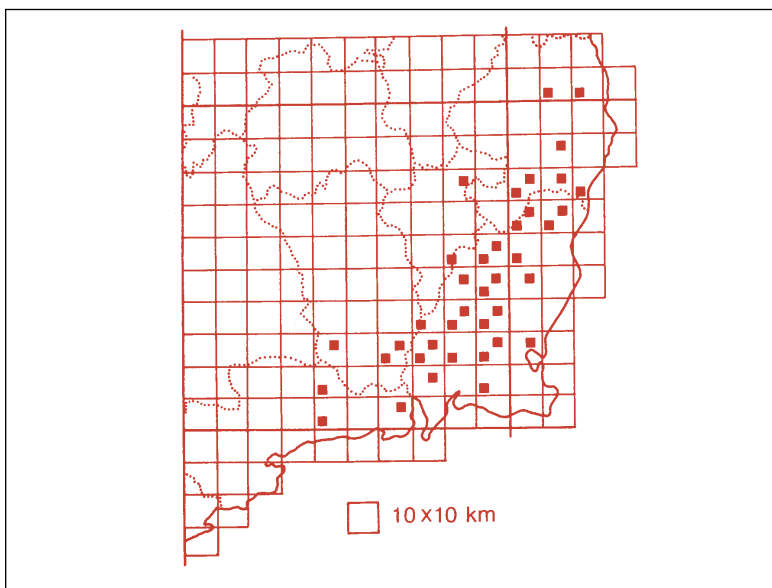
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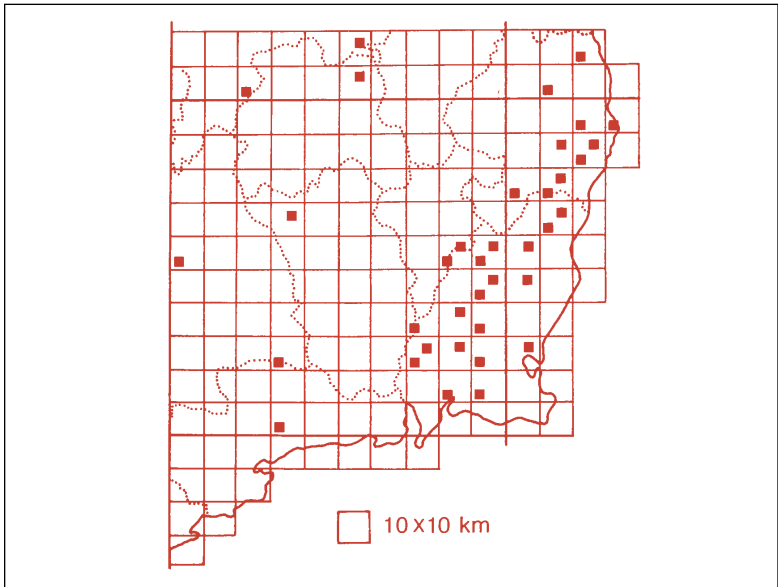


**Fig 1.** Land use at sampling locations; pasture (O), tillage (■), forest (▲) and peat (●).

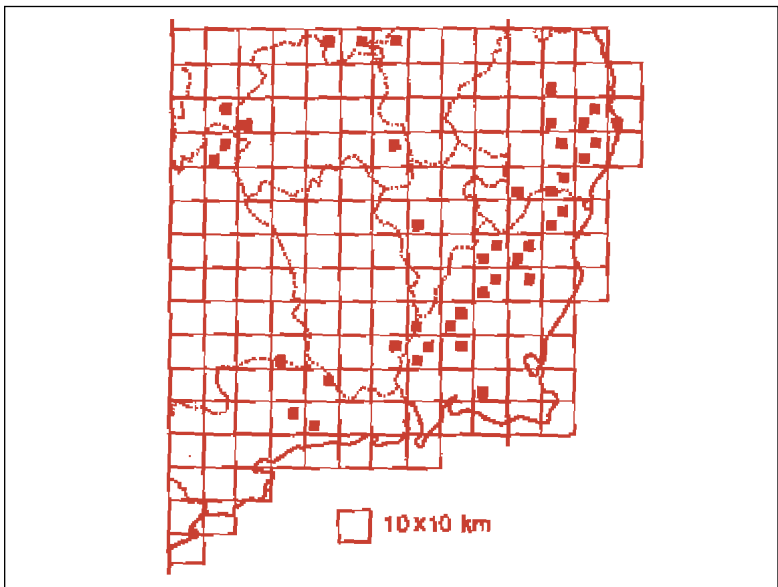


**Fig 2.** Locations showing concentrations of Al in soil of > 60g kg<sup>-1</sup> (■).

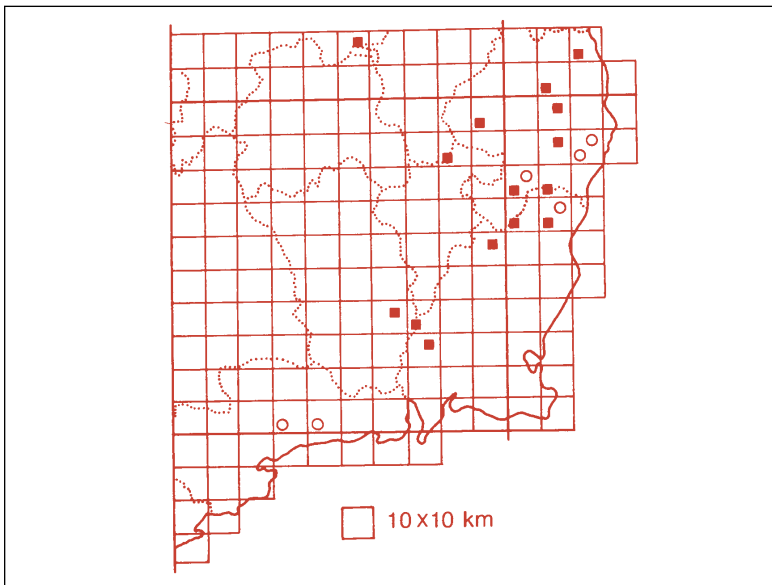




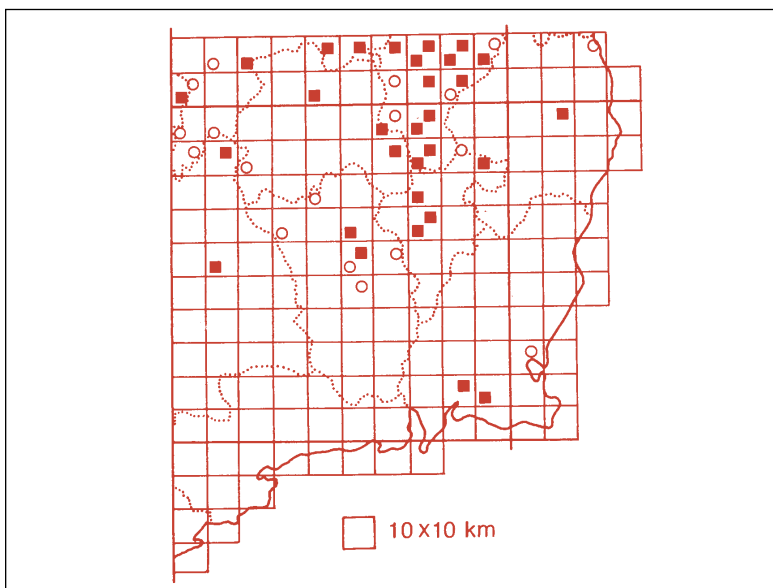
**Fig 3.** Locations showing concentrations of Fe in soil of  $> 35\text{g kg}^{-1}$  (■).



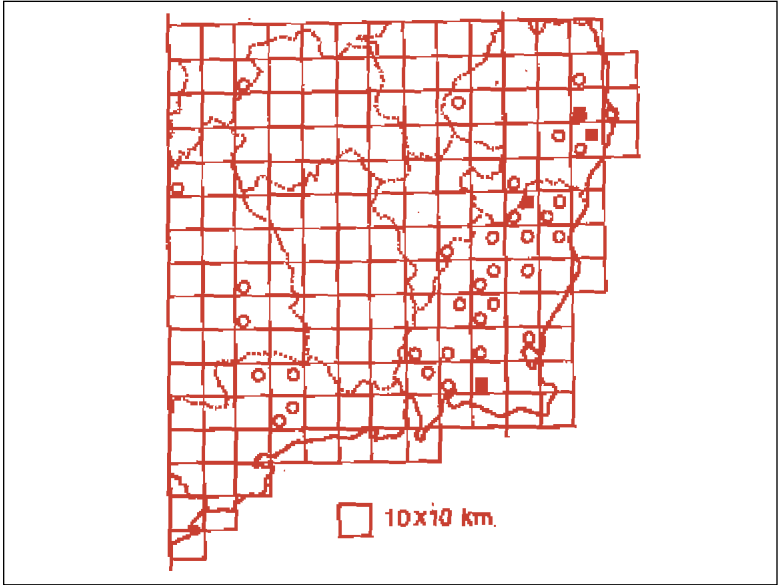
**Fig 4.** Locations showing concentrations of Mn in soil of  $> 1500\text{mg kg}^{-1}$  (■).



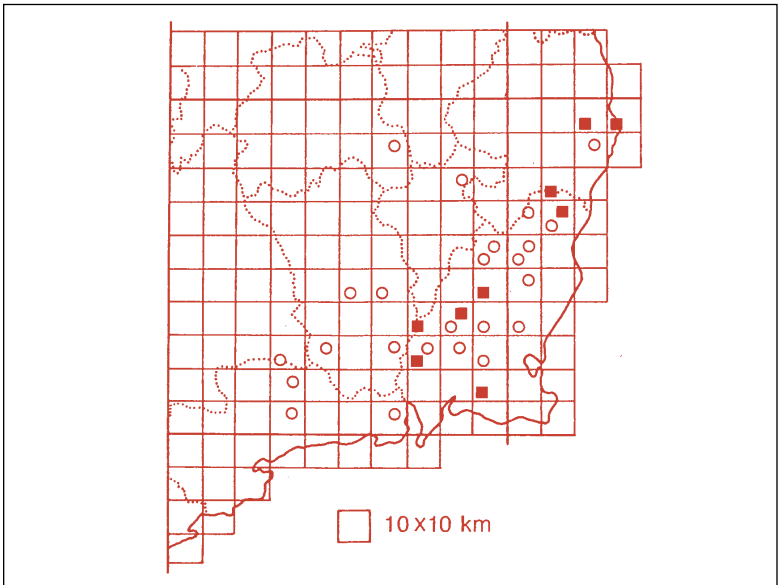
**Fig 5.** Locations showing concentrations of As in soil of 31.5-41.9 (○) and of > 42.0 (■) mg kg<sup>-1</sup>.



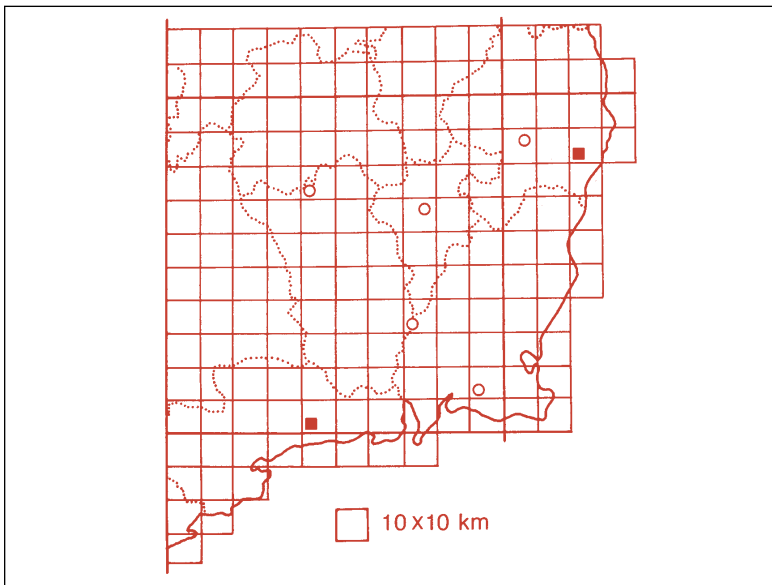
**Fig 6.** Locations showing concentrations of Cd in soil of 0.75-0.99 (○) and of > 1.0 (■) mg kg<sup>-1</sup>.



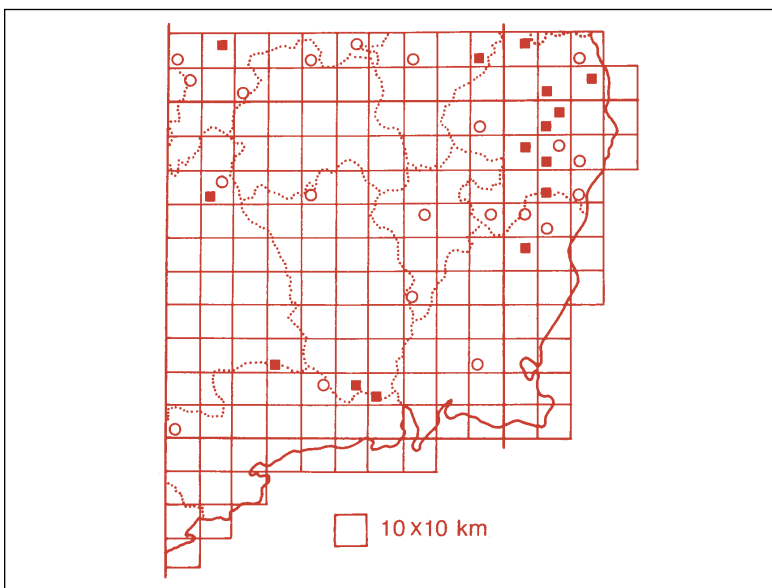
**Fig 7.** Locations showing concentrations of Cr in soil of 75.0 – 99.0 (O) and of > 100.0 (■) mg kg<sup>-1</sup>.



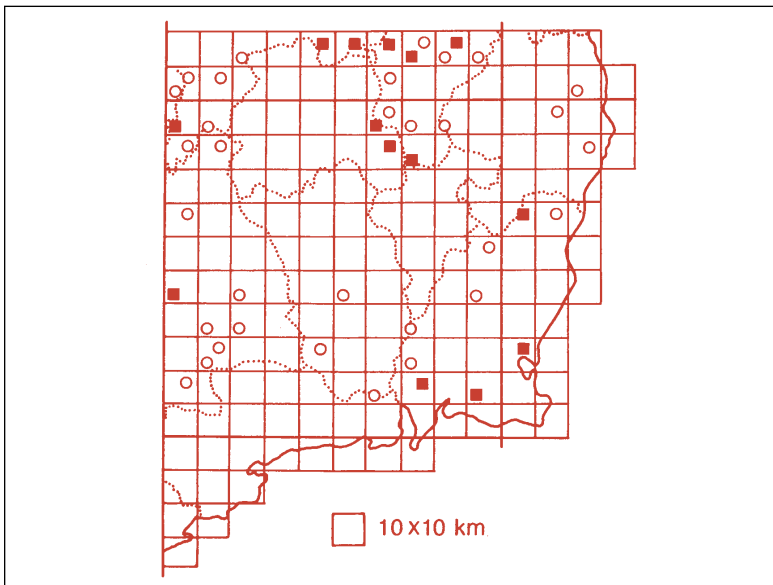
**Fig 8.** Locations showing concentrations of Co in soil of 16.9 – 22.5 (O) and of > 22.6 (■) mg kg<sup>-1</sup>.



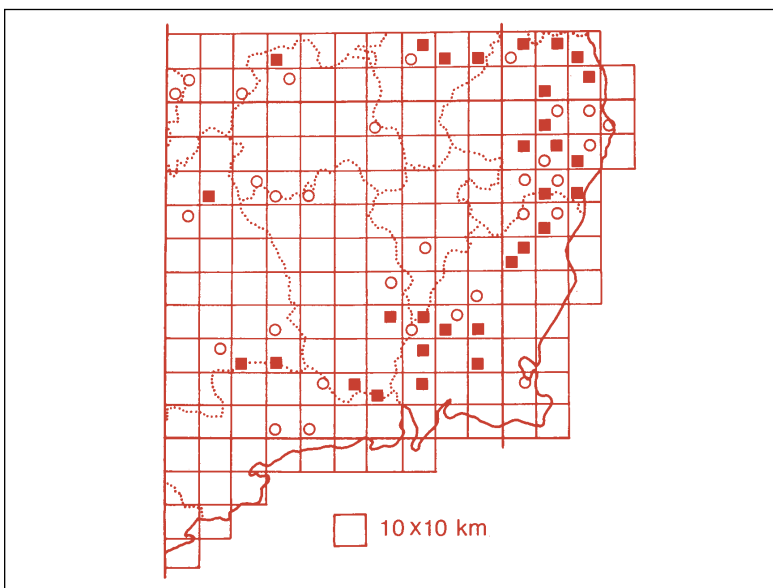
**Fig 9.** Locations showing concentrations of Cu in soil of 37.5 – 49.9 (O) and of > 50.0 (■) mg kg<sup>-1</sup>.



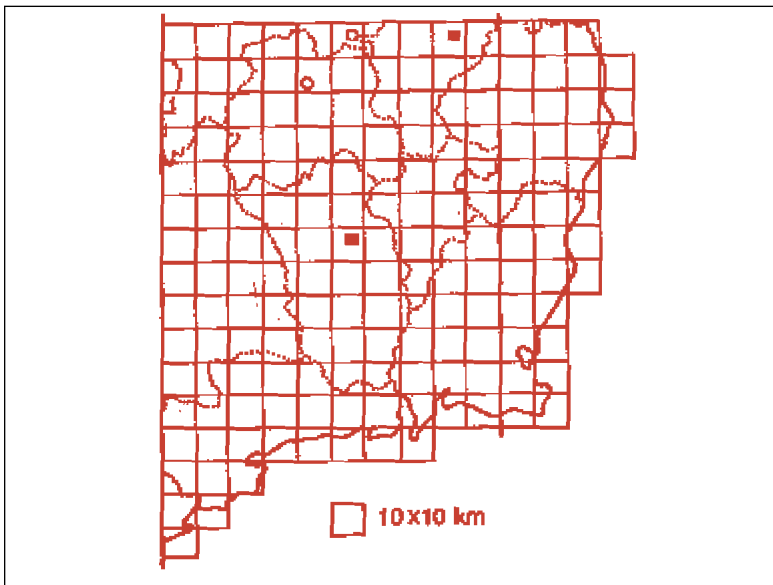
**Fig 10.** Locations showing concentrations of Hg in soil of 0.18 – 0.22 (O) and of > 0.23 (■) mg kg<sup>-1</sup>.



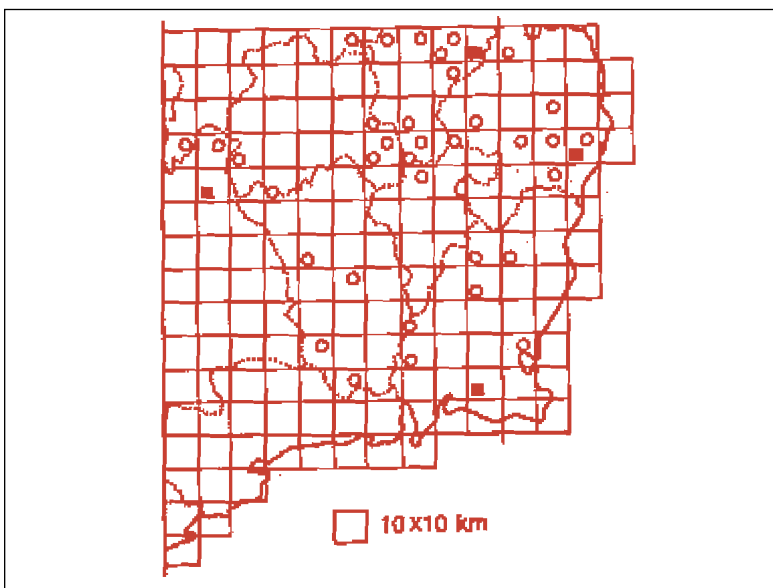
**Fig 11.** Locations showing concentrations of Ni in soil of 22.5 – 29.9 (O) and of > 30.0 (■) mg kg<sup>-1</sup>.



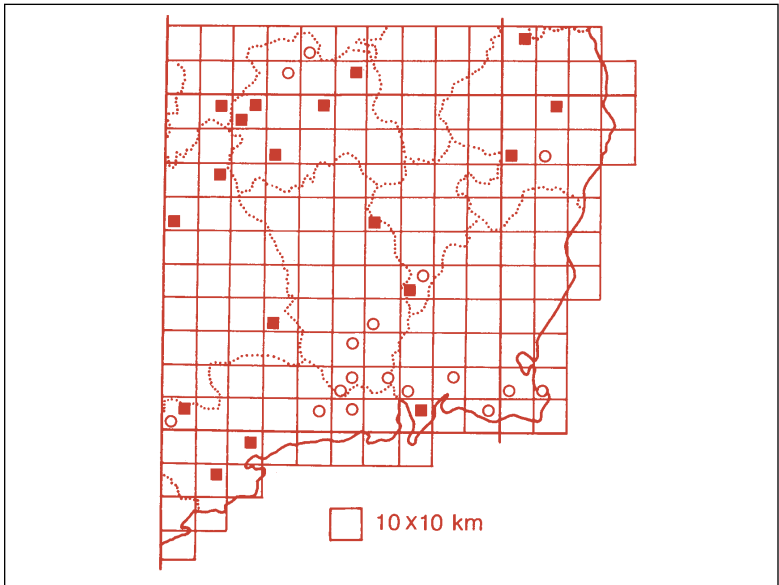
**Fig 12.** Locations showing concentrations of Pb in soil of 37.5 – 49.9 (O) and of > 50.0 (■) mg kg<sup>-1</sup>.



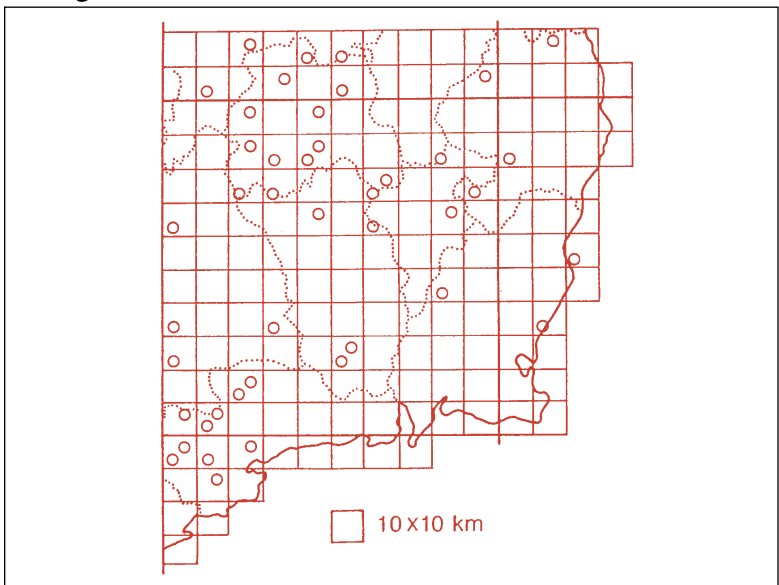
**Fig 13.** Locations showing concentrations of Se in soil of 3.60– 4.99 (O) and of > 5.0 (■) mg kg<sup>-1</sup>.



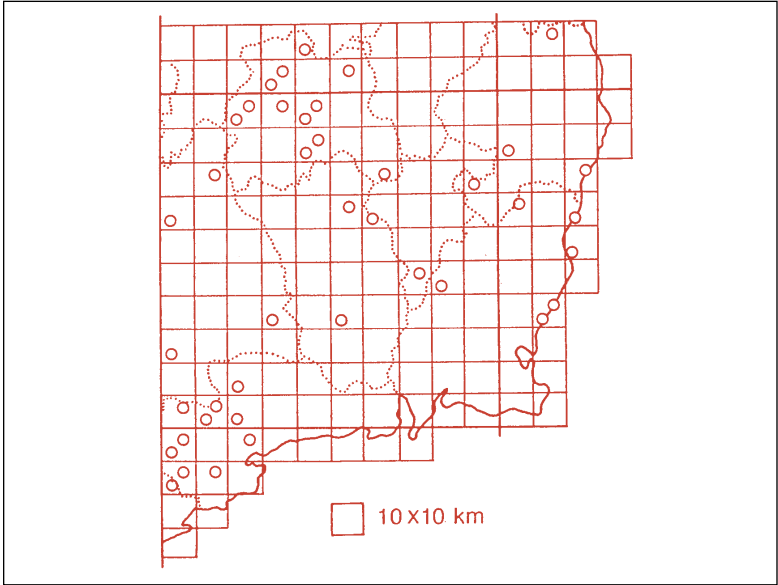
**Fig 14.** Locations showing concentrations of Zn in soil of 112.5 –149.9 (O) and of > 150.0 (■) mg kg<sup>-1</sup>.



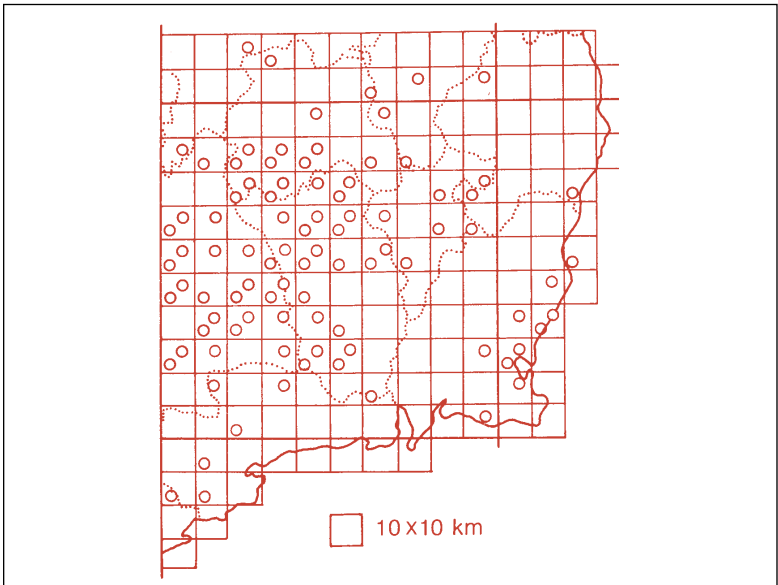
**Fig 15.** Locations showing concentrations of Co of 0 – 3.0 (O) and 3.1 – 5.0 (■)  $\text{mg kg}^{-1}$  for pasture and tillage soils



**Fig 16.** Locations (pasture and tillage only) showing concentrations of Cu in soil of  $< 10 \text{ mg kg}^{-1}$ .

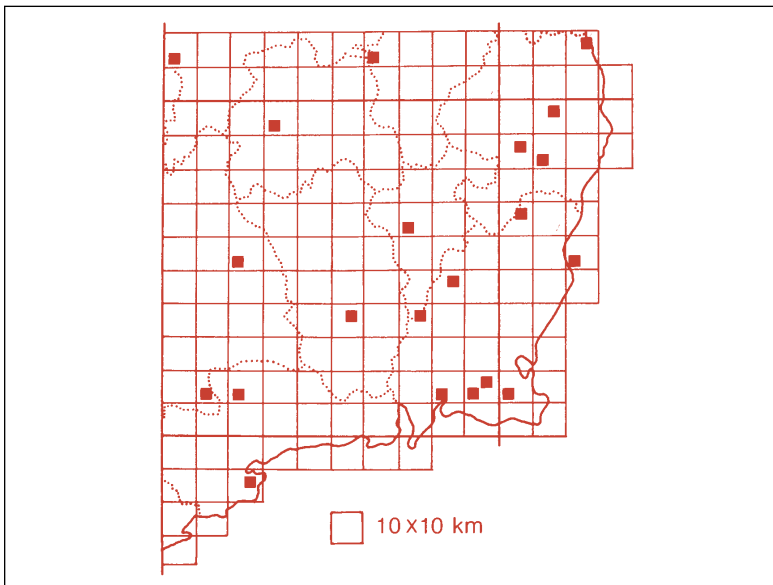


**Fig 17.** Locations (pasture and tillage only) showing concentrations of Zn in soil of  $< 40 \text{ mg kg}^{-1}$ .

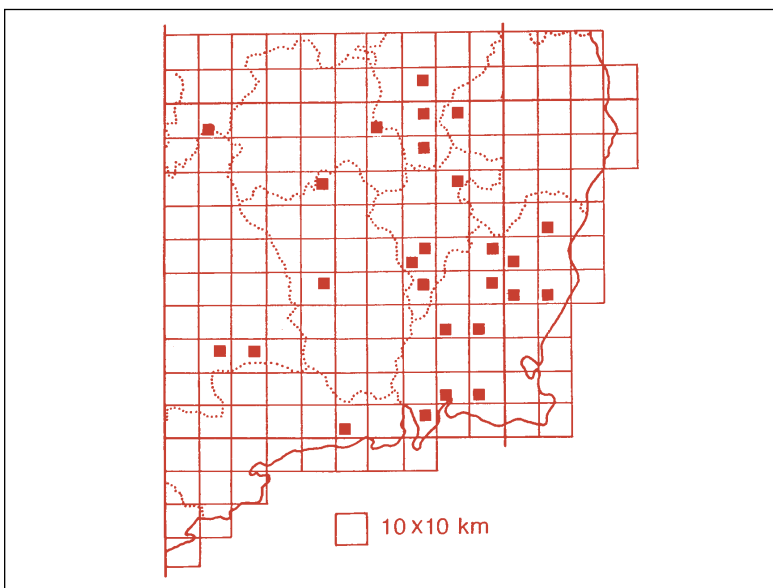


**Fig 18.** Locations (pasture and tillage only) showing concentrations of Se in soil of  $< 0.5 \text{ mg kg}^{-1}$ .





**Fig 19.** Locations showing concentrations of lindane ( $\gamma$ -HCH) in soil of  $> 1 \mu\text{g kg}^{-1}$ .



**Fig 20.** Locations showing concentrations of  $\Sigma\text{DDT}$  (4,4' -DDE + -DDD + -DDT) in soil of  $> 5.0 \mu\text{g kg}^{-1}$ .

# SUMMARY