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THE DISTRIBUTION OF SELENIUM IN SOME SOILS DEVELOPED ON SILURIAN, CARBONIFEROUS AND CRETACEOUS SYSTEMS IN ENGLAND AND WALES.

A thesis presented by

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ABSTRACT.

The distribution of selenium in soils developed on geochemically contrasting parent materials in three areas of England and Wales has been studied in relation to soil properties. The mean content of selenium in soils developed on four beds of the Lower Greensand formation in Surrey and Sussex was low (0.14 $\mu g\ g^{-1}$), but was significantly higher on the more ferruginous soils of the Sandgate beds than on the soils of the Hythe, Bargate and Folkestone beds.

The selenium content of soils developed on Carboniferous rocks in Staffordshire and Derbyshire was found to depend principally on the nature of the parent material. Within each profile the distribution of selenium was related to that of iron and organic matter.

Sixty seven percent of the variation in the selenium content of horizons from thirty seven soil profiles representing nine soil series which were developed on parent materials derived from Silurian rocks in Clwyd was explained by the content of organic matter (loss of weight on ignition) and 0.1M potassium pyrophosphate extractable iron. The distribution of selenium in these soils is related to that of these two parameters, and is exemplified by its accumulation in the O and Bs horizons of stagnopodzols. It is proposed that selenium is retained in the soil against the processes of weathering primarily by its adsorption as selenite on ferric, and possibly aluminium, oxides, and by its involvement in the organic cycle. Thus topsoils typically contained ten times the selenium content of the parent rocks.

The problems of adapting established soil selenium fractionation techniques, based on the solubility of selenium species in various chemical extractants, to be compatible with selenium determination by hydride generation and inductively coupled plasma emmision spectrometry are discussed.

The results of the work are discussed in relation to the geographical distribution of potential selenium deficiencies in livestock in England and Wales.

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CHAPTER 1. INTRODUCTION.

1.1. Background to the study.

Problems resulting from selenium (Se) deficiency in livestock have been recognised in Britain for several years, and some of the earliest work in the field, undertaken in Scotland, linked areas where potential and actual deficiencies occurred to areas with soils developed from specific geological formations (Sharman, 1960; Blaxter, 1963). However, more recently the occurrence of white muscle disease, a Se deficiency dis order, has been on the increase (Anderson et al., 1976). These workers postulated that the timing of this increase could be due to the introduction of modern farming practices which tended to produce combined deficiencies of the inter-related Se and vitamin E at the end of the winter feeding period.

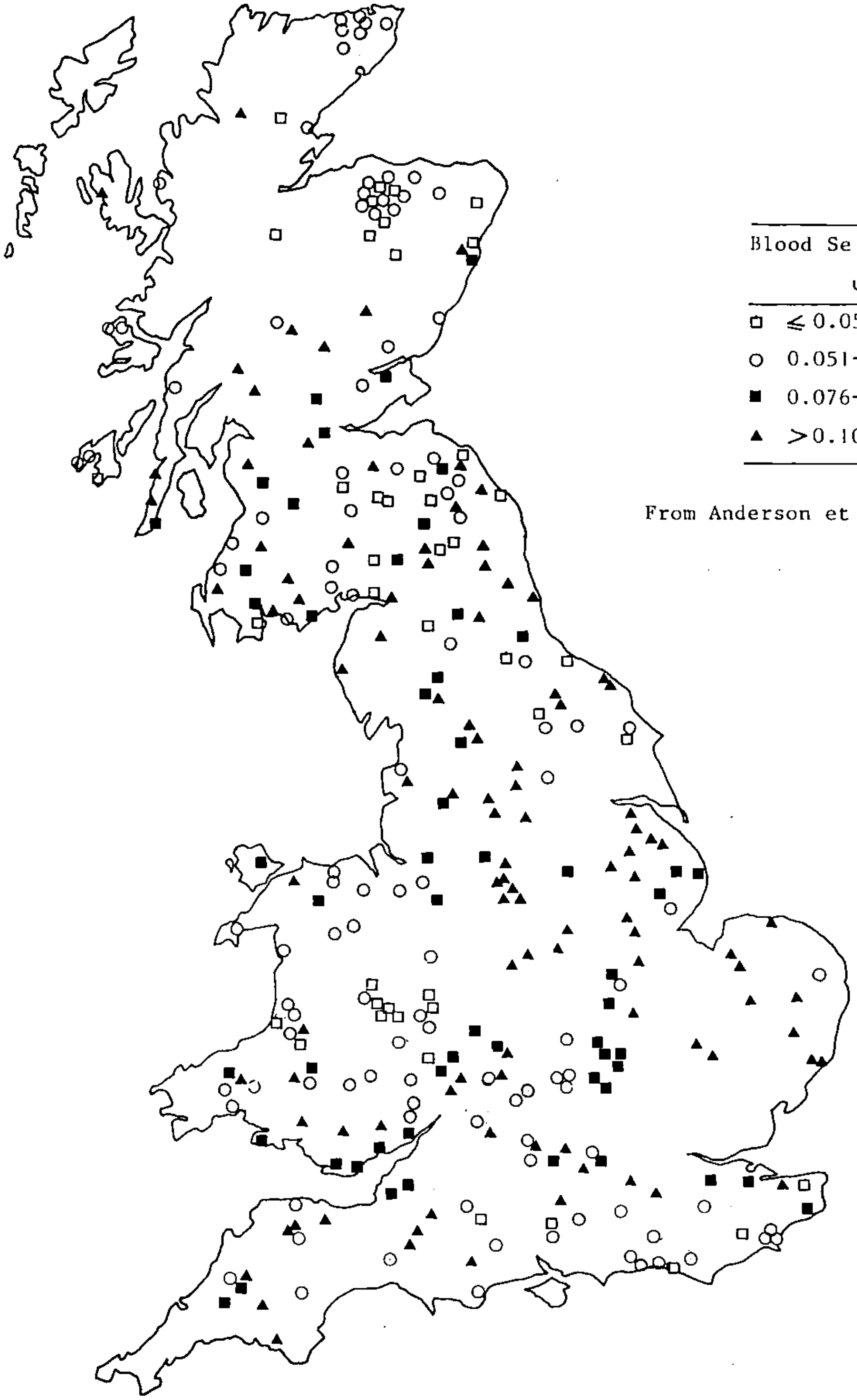
These findings have focused the attention of much current research towards the problems and aetiology of livestock Se deficiencies. In addition to the actual clinical manifestations of deficiency, such as white muscle disease in cattle and lambs, and retained placenta in cattle (Rickaby, 1980), there may be sub-clinical effects of deficiency such that the administration of Se to livestock results in a response, perhaps in the form of a liveweight gain. Thus areas of potential Se deficiency have in the past been identified by monitoring such responses to administered Se (Hartley, 1960; Blaxter, 1963). The combined problems of sub-clinical and clinical Se deficiencies could be of considerable economic importance to British agriculture, although no overall estimates of the scale of this have been made. Clearly the identification of areas where deficiencies might exist could be of great benefit.

In the absence of any alternative comprehensive information for Britain, Anderson et al. (1979) undertook a survey of the biological Se status of sheep flocks in Britain. This they estimated by the assay of the blood erythrocyte glutathione peroxidase activity (see section 2.1.) of sheep which had previously spent at least two months grazing without supplementary feeds. As such they were able to assume that the Se status of the sheep derived solely from the grazings, and hence the survey purported to give indirectly an indication of the distribution of Se in herbage. From the survey of 329 flocks they suggested that "47% of farms were probably unable to provide grazing livestock with sufficient Se to maintain blood levels of greater than 0.075 μg ml^{-1}" a figure which was considered to be indicative of potential deficiencies. The distribution and mean blood concentration of these flocks is given in Figure 1.1.

Anderson et al. (1979) concluded that in a setting where home grown feeds are comprising an increased proportion of livestock rations, their findings might be causally related to an increased occurrence of white muscle disease and other Se-responsive dissorders. Some measure of the extent of the problem in Britain had therefore been established. It may also be of interest to note here that the average human dietary intake of Se in Britain is known to be low (60 μg day^{-1}), compared to those in Canada and the U.S.A., and to the U.S. National Research Councils recommended daily intake of 60-100 μg (Thorn et al., 1978). This low value was thought to be related to the relatively low Se content of British soils, in view of the fact that some 50% of food consumption is home grown.

Work in the Applied Geochemistry Research Group was begun in the mid-1970's to establish if there is a geochemical basis for Se deficiency in Britain. This is a relationship which has been established in other areas of the world, noteably in the U.S.A., New Zealand and Australia (section 2.9.2.), and is also thought to be important in Scotland (Blaxter, 1963). Because of the lack of suitable analytical techniques at the time, Se was not included in the Wolfson Geochemical Atlas of England and Wales (Webb et al., 1978), which was based on the concentration of elements in stream sediments, and therefore no extensive geochemical information on Se existed. A survey of topsoil Se concentrations in England and Wales was therefore undertaken (Thornton et al., in press) which has demonstrated that broad relationships do exist between the Se content of the soil and the lithology of the parent material and these will be detailed later (section 2.9.3.).

The preliminary brief for this project was to determine in more detail the distribution and forms of Se in soils in England and Wales, and its



	Blood Se concentration ug/ml	Proposed significance
□	≤ 0.05	Deficient.
○	0.051-0.075	Low marginal.
■	0.076-0.10	Marginal.
▲	>0.10	Adequate

From Anderson et al. (1979)

Figure 1.1. The geographical distribution of 329 sheep flocks in Britain according to their biological selenium status.

uptake by pasture herbage. This was considered important as previous work has shown that patterns of low Se concentrations in herbage, and livestock Se deficiencies, which could be related to the geology of the parent material might be modified by the effects of soil profile development (Kubota et al., 1967; Watkinson, 1962). Although several workers have investigated the distribution of Se in various soil types and also the factors which affect this distribution (Wells, 1967; Levesque, 1974a; Koljonen, 1975), no such work has been carried out on British soils. It was felt that this project might most profitably begin by investigating the effects of soil processes and differences in soil formation, on the distribution of Se in the soil profile; whilst at the same time attempting to gain an appreciation of the magnitude and nature of the differences is soil Se content imparted by variations in the nature of the soil parent material. Later work might then investigate the influence of these relationships on the uptake of Se by pasture herbage.

1.2. Work plan and presentation of thesis.

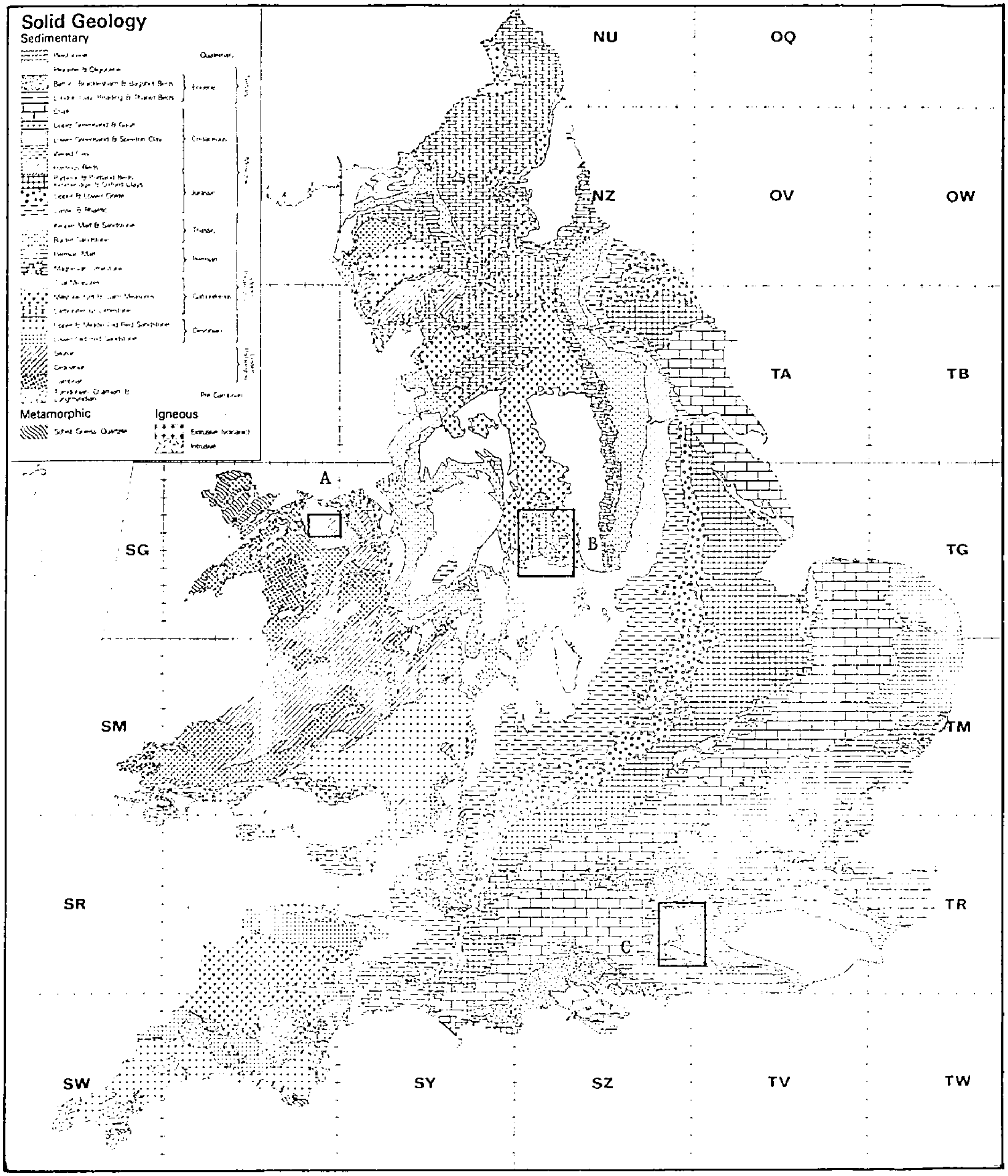
For the first stage of the work three areas were chosen in England and Wales which contained soils expected, or known on the basis of the above information to contain low, high and moderate levels of Se respectively. These, as depicted in Figure 1.2., were:

i. An area of the west Weald in Surrey and Sussex where soils were developed on the outcrop of the four beds of the Lower Greensand formation.

ii. An area in N.E. Staffordshire and S.W. Derbyshire where soils were developed on parent materials derived from a range of Carboniferous rocks, including some marine black shales known to contain high levels of Se (Webb et al., 1966).

iii. An area around the village of Llansannan in Clwyd, the soils of which were developed on relatively uniform parent materials originating from Silurian rocks.

Different patterns of work were utilised in each area, and these will



A. Llansannan area. B. S.W. Derbyshire and N.E. Staffordshire C. West Weald.

Figure 1.2. Location of study areas in England and Wales in relation to the outcrop of the major geological formations.

be described in detail in the relevant sections. Briefly, however, sampling in the first area, reported in Chapter 4, aimed to test if there were differences between the Se content of topsoils on four similar geological formations, whilst at the same time studying the distribution of Se in some podzolic soils typical of the area. The work in area ii above, is described in Chapter 5, and investigated the distribution of Se in sequences of predominantly poorly drained soils developed on several parent materials of varied but generally high Se content. The uniformity of the parent material in the Llansannan area (iii above) allowed a study of the effects of different soil forming environments on soil profile Se distribution, without the complication of variations derived from those of the parent material. This was achieved by the detailed sampling of profiles from several varied soil mapping units, the results being reported in Chapter 6.

The soil properties which were studied were chosen from the literature as being those which had previously been implicated in influencing the chemistry and distribution of Se in soils. The techniques used and the reasons for their selection are given in Chapter 3. This follows a review of previous work pertaining to Se in the environment, with particular reference to soils and the problems of Se deficiency in livestock which forms Chapter 2.

It was intended that later work would investigate in more detail the forms of Se in the soil and the uptake of Se by pasture herbage. The rationale for the scheme of this work is discussed at the begining of Chapter 7, in the light of the results of the preliminary work reported in Chapters 4,5 and 6. The final Chapter of the thesis draws together the findings of the project, which are discussed in terms of the occurrence of Se responsive diseases in Britain.

CHAPTER 2. SELENIUM IN SOILS, PLANTS AND ANIMALS WITH PARTICULAR REFERENCE TO PROBLEMS OF SELENIUM DEFICIENCY.

2.1. Selenium and animal health.

Extensive studies concerning Se in the soil - plant - animal system have primarily been undertaken because of the importance of the element in animal nutrition; conditions of both toxicity and deficiency in livestock are encountered and in terms of the dietary levels of Se involved the difference between the two conditions can be small. Levels of 5.0 μg Se g^{-1} d.m. in vegetation consumed by livestock over several weeks can lead to problems of toxicity (Lakin, 1972); whilst concentrations less than 0.1 μg g^{-1} can give rise to deficiency problems (Ehlig et al., 1968).

Livestock disease syndromes such as "alkali disease" and "blind staggers" had been recognised in areas of central and western U.S.A. since the 1850's. These conditions could be associated with particular areas of land, and in some instances were known as alkali disease because alkalis or mineral salts in the soils or vegetation on which the animals were grazing were thought to be the cause of the problem. Often the problem was associated with the occurrence of species of Milk Vetch (Astragalus spp.) in the vegetation (Rosenfeld and Beath, 1964). However, not until the 1930's was Se toxicity conclusively implicated as the cause of the disease (Robinson, 1933). Subsequently the high concentrations of Se responsible for these problems were linked to the occurrence of specific Se-rich geological formations, mainly of Cretaceous age, and also to the accumulation of the element from the soil by species of Astragalus and some other native plants (Beath et al., 1935). Thereafter, problems of Se toxicity, related to the incidence of seleniferous soils, have been recognised throughout the world but are generally limited to areas underlain by specific geological formations (Table 2.1.).

In 1957 Se was found to be an essential micronutrient for animals, when it was discovered that inorganic Se salts were effective in protecting rats against necrotic liver degeneration (Schwartz and Foltz, 1957). Subsequently Se was found to be necessary to many

Country.	Area.	Parent material.
U.S.A.	Wyoming	Cretaceous shale.
	South Dakota.	Cretaceous shale.
	Colorado.	Triassic sandstone.
	Utah.	Jurrasic shales and sandstones.
Canada.	Alberta. Saskatchewan. Manitoba.	Cretaceous shales.
Colombia.	....	Black slate alluvium.
Eire	Meath. Tipperary. Limerick.	Carboniferous shales and limestones.
South Africa.	....	Triassic shales and sandstones (Karoo system).
Australia.	Queensland.	Cretaceous shales and limestones
U.K.	....	Carboniferous shales.
U.S.S.R.	....	Jurrasic sandstone.
Mexico.	....	Alluvium from mine tips.
Israel	....	Cretaceous limestones and shales.
Puerto Rico	....	Cretaceous pyritiferous shales.

Table 2.1. Parent materials of selenium-toxic and seleniferous soils. (after Fleming, 1980).

animals and significantly Muth et al. (1958) found that supplementation of Se to ewes protected lambs against White Muscle Disease (W.M.D.). Other manifestations of dietary Se deficiency in livestock include; W.M.D. in cattle, sheep, pigs and poultry; Mulbery Heart Disease in pigs; and general conditions of ill-thrift in cattle and sheep (Anderson, 1979). Requirements of Se relate to those of vitamin E, such that in some cases diseases can be treated by the increased intake of Se and/or vitamin E. Also the requirement of Se is increased if the intake of dietary polyunsaturated fatty acids increases (Diplock, 1981). The biochemistry of this process is summarised in Figure 2.1. Lipid peroxides, which if allowed to accumulate in the cell can cause membrane disruption and ultimately cell death, are formed by the oxidation of polyunsaturated fatty acids, a process which can be inhibited by vitamin E. The enzyme glutathione peroxidase, of which Se forms an integral part, catalyses the elimination of lipid peroxides from the cell by their reduction to alcohols (Anderson, 1979). A more detailed description of the biochemistry of Se and its possible interaction with other trace elements is given by Diplock (1981), and Judson and Obst (1975) have reviewed the broader issues concerning Se deficiencies in livestock.

Only recently have the possible effects of Se deficiency in man been identified, not ably as a cardiomyopathy called "Keshan Disease" in the Peoples Republic of China. As with the occurrence of deficiencies in livestock its incidence has been linked with areas where specific soils are found in a broad belt across the country. As yet, however, it is not known whether Se deficiency is the sole cause of the condition. Diplock (1981) has detailed the present knowledge on Keshan Disease, and other effects of dietary Se deficiency in humans.

2.2. The geochemistry of selenium and its occurrence in rocks.

The similarity in the ionic radii of Se and S (Se^{2-} = 2.0Å, S^{2-} = 1.85 Å) influences much of the chemistry of Se, which is thus often found associated with S-bearing compounds in both plants and animals, and in the geochemical cycle. In a crystalising magma, Se as selenide separates out along with sulphides, neither being an essential constituent of the rock forming silicate minerals. Consequently the Se content

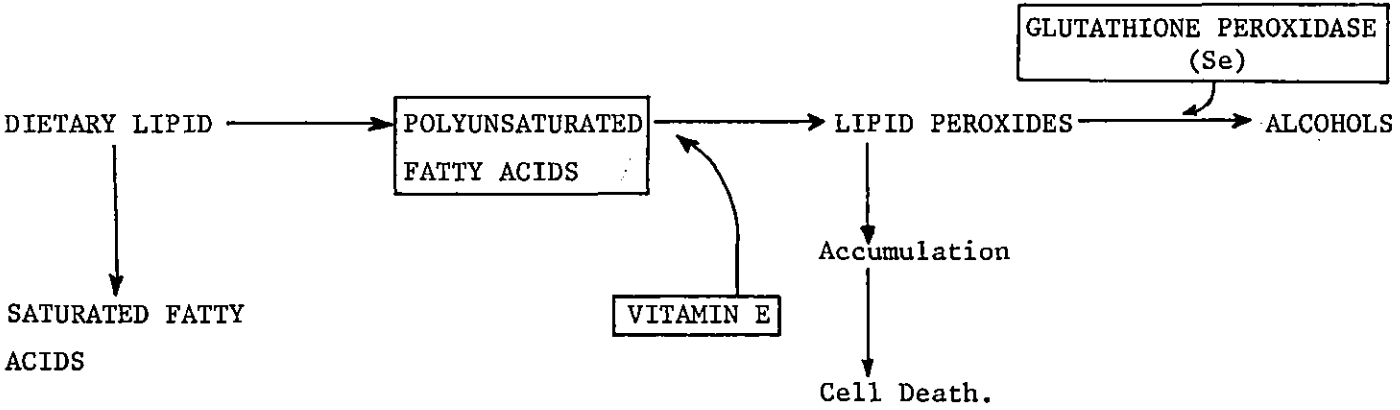


Figure 2.1. The interrelationship between Se, vitamin E and polyunsaturated fatty acids in livestock metabolism (after Anderson, 1979).

of igneous rocks is generally low; Goldschmidt (1954) estimated a mean Se content of 0.09 $\mu g\ g^{-1}$ based upon an average Se:S ratio of 1:6000 in igneous rocks. Conversely sulphide minerals tend to be enriched in Se, although rarely in concentrations of greater than a few hundred $\mu g\ g^{-1}$ (Lakin and Davidson, 1967). Excepting its concentration in sulphide minerals, Se is well dispersed throughout the earth's crust and is rarely found in concentrations above a few $\mu g\ g^{-1}$. Dispersion is thought to result primarily from the evolution of Se, again along with S, as a volatile during volcanism, a process which is estimated to have added 0.1 g Se cm^{-2} to the earths surface (Goldschmidt, 1954).

In oxidative weathering processes Se acts as a resistate, whereas S is oxidised to sulphate and is consequently removed in aqueous solution (Lakin, 1972). Selenium therefore accumulates in sedimentary, rather than igneous rocks, and particularly in oxidates such as vanadium-uranium ores and hydrolisates such as shales. Shales, and particularly those rich in organic matter (black shales), predominate in a list of those parent materials which give rise to seleniferous soils (Table 2.1.). In their review, Lakin and Davidson (1967) summised that an average Se concentration in shales would be 0.6 $\mu g\ g^{-1}$, although some Wyoming black shales contained as much as 227 $\mu g\ g^{-1}$ Se.

In the "classic" area of seleniferous soils in the western U.S.A. enrichment of the Cretaceous shales is thought to have occurred by the release of volatile Se by volcanism and by the dispersion, through weathering, of Se which was separated with sulphides in contemporary magmatic activity (Lakin, 1962). In the British Isles the only recorded occurrence of soils supporting seleniferous vegetation is in the counties of Limerick, Tipperary and Meath in Eire, the source of the Se having been traced to Carboniferous black shales and limestones (Walsh et al., 1951). Prompted by these findings Webb et al. (1966) located non toxic seleniferous soils in the United Kingdom, again associated with black shales of the Namurian and Visean of the Carboniferous in Derbyshire. Black shales elsewhere in the U.K. also commonly contain higher than average amounts of Se (Thomson, 1971).

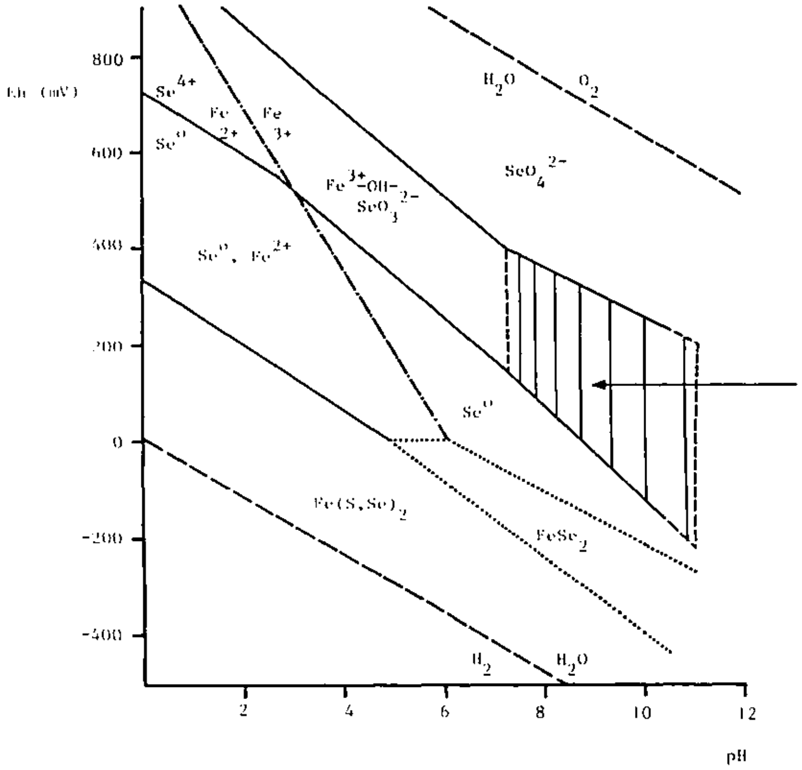
Although the incidence of Se in the parent rocks of seleniferous soils has been widely studied and documented (Rosenfeld and Beath, 1964; Lakin, 1962), much less information is available concerning its distribution in rocks containing normal levels of Se; this applies especially to the British Isles. In this respect, shales can be expected to give rise to soils which provide adequate levels of Se in crops, in the majority of their outcrops.

Sandstones and carbonate rocks usually contain lower levels of Se than shales, although this amount can be very variable, often depending on the amount of carbonaceous material or seleniferous pyrite in the formation. Estimates of the mean Se contents for sandstones and carbonate rocks are in the region of 0.05 and 0.08 $\mu g\ g^{-1}$ respectively (Turekian and Wedepohl, 1961). The Se content of metamorphic rocks is also variable and generally reflects that of the sediments and rocks from which they are formed (Koljonen, 1973).

2.3. The forms and chemistry of selenium in the soil.

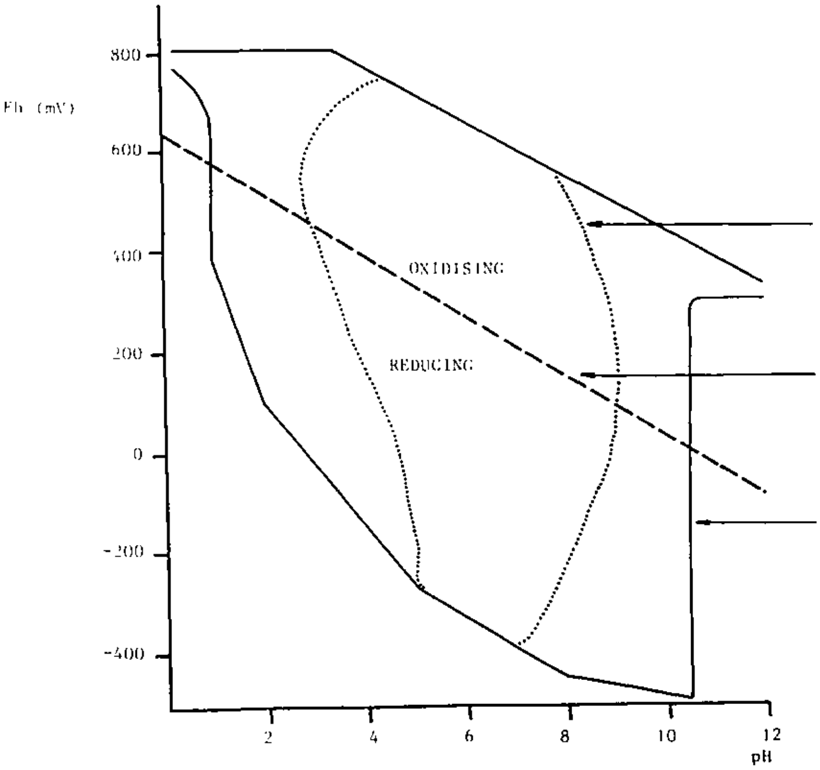
Selenium in soils is thought to exist in several forms dependant upon the nature of the conditions existing within it; these forms include selenides (Se^{2-}), elemental selenium (Se^{o}), selenites (Se^{4+}), selenates (Se^{6+}) and organic forms. The actual Se species which exist in any one soil depend largely on the pH and the redox conditions which prevail. Thus various workers have constructed solubility field diagrams for Se (Geering et al., 1968; Lakin and Davidson, 1967; Howard, 1977) such as that depicted in Figure 2.2., which also demonstrates the relationship between the forms of Se and the limits of the natural environment and soils in terms of Eh and pH.

Selenites are considered to be the most prevalent Se species in acid to neutral well drained soils, and are thus the most important source of Se for plants in these soils. It has been clearly established that the concentration of selenite in solution, and hence its availability to plants, is primarily controlled by its association with ferric oxides, as a selenite - ferric oxide adsorption complex (Geering et al., 1968; Howard, 1977; Hamdy and Gissel-Nielsen, 1977). Hingston et al. (1968) suggested specific adsorption as the mechanism of this process when the adsorbing surface is goethite. The equilibrium solubility of selenite



Progressive decomposition of the Fe-OH-SeO_3 2- adsorption complex.

Figure 2.2.a. Solubility field diagram for selenium, in relation to its association with Fe. (Based on Howard, 1977)



Eh/pH limits of soils (Baas Becking et al., 1960)

Pearsall's dividing line for oxidising and reducing soils (Pearsall 1938)

Eh/pH limits of the natural environment (Baas Becking et al., 1960)

Figure 2.2.b. Limits of Eh and pH of soil systems and the natural environment.

in association with a ferric oxide - selenite adsorption complex increases with pH up to approximately pH 8, when the complexes begin to decompose and the equilibrium solubility then increases more rapidly with pH such that there is almost complete desorption at pH 11 (Allaway et al., 1967; Figure 2.2.). The increase of selenite in solution decreases the Eh of the selenite - selenate couple so that the formation of selenate in alkaline soils is favoured by the breakdown of the adsorption complex. Adsorption of selenites on hydrous ferric oxide at pH 8 and below may remove more than 95% of the ion from solution, the effect of lowered selenite concentrations being to broaden the range of redox potentials over which selenite will exist in solution (Howard, 1977).

Hamdy and Gissel-Nielsen (1977) investigated selenite adsorption by several soil clay minerals and also ferric oxide, but concluded that the latter is the more effective adsorber, partly because the rates of adsorption are much quicker. Both aluminium oxides and silicon species have also been implicated in selenite adsorption in soils (John et al., 1976).

Nye and Peterson (1975) demonstrated, by electrophoretic techniques, the presence of selenate in an alkaline toxic seleniferous soil from the U.S.A. and it is widely considered that the presence of soluble selenate in such soils leads to the increased availability of Se to plants. In contrast, the above workers found that in an acid Irish seleniferous soil, selenite was the main soluble form. Examination of Figure 2.2. shows that selenate should only occur in well aerated alkaline soils, but in pure systems the rates of conversion between selenite and selenate are slow (Rosenfeld and Beath, 1964). Howard (1977) suggested that oxidation of selenite to selenate would not occur readily in normal surface oxidising conditions. However, several species of bacteria and fungi have been shown to be capable of enacting the oxidation of elemental Se to selenite or selenate (Lipman and Waksman, 1923; Sapozhnikov, 1937; Bird et al., 1948; Sarathchandra and Watkinson, 1981). Also Geering et al. (1968) demonstrated that the oxidation of selemental Se to selenite in the soil could proceed by both organic and inorganic pathways. Once present in the soil, selenate is not retained by colloids and being water soluble is easily leached out of the soil. Consequently accumulation of selenate may only be expected to take place in arid alkaline conditions, such as those which prevail in the western U.S.A. where toxic soils are widespread (Rosenfeld and Beath, 1964).

Microorganisms have been shown to be capable of reducing both selenite and selenate to elemental Se, although most of the evidence is for reactions in pure culture and the relevance to soil conditions is not clear (Peterson et al., 1981). The solubility field diagram (Figure 2.2.) suggests that reduction of selenite to elemental Se should proceed readily in acid predominantly reducing soils. Subsequently, elemental Se is relatively stable in water in equilibrium with air (Allaway et al., 1967), although the actual quantities present in soils are unknown, and it may only exist as a transitory constituent before reduction to selenide (Allaway et al., 1967). Cary et al. (1967) found that reduction to elemental Se or selenide is responsible for the immobilisation of selenite added to a soil, since these forms are insoluble and therefore not available to the plant.

Fleming (1980) suggested that selenides, which are largely insoluble, do occur in soils of the semi-arid regions in association with pyrite where weathering is not greatly advanced. The low solubility of selenides may lead to their persistence in agricultural soils. It is conceivable that in very acid reducing conditions selenides could be formed by reduction of elemental Se (Figure 2.2.), and Watkinson (1962) suggested that ferrous selenide may occur in some acid podzolic soils in New Zealand. It seems quite probable, considering the close association between selenite and ferric iron, that on reduction of these species, ferrous selenide would form, although the solubility of ferrous iron in acid conditions may lead to losses of Fe from the soil whilst selenide being insoluble would persist. Geering et al. (1968) also imply that other selenides such as Cu_2Se may form.

Little is known of the organic forms of Se in the soil, despite the fact that several workers have demonstrated associations between Se and organic matter in the soil (Wells, 1967; Levesque, 1974a; Koljonen, 1975) and that Se can accumulate in organic soils (Fleming and Walsh, 1957), although the mechanism by which this occurs has yet to be elucidated. Water soluble Se can contain a portion in organic combination but it is unclear if this may be available to the plant.

Nye and Peterson (1975) demonstrated that some Se was linked to the organic fraction of a water soluble soil extract; whilst the work of Levesque (1974b) suggested that associations between Se and organic acids may require chelation with ferric iron, and that these complexes could play a role in the mobilisation of Se in the soil profile.

Even though evidence exists for the presence of some or all of these Se species in certain soils, little information is available on the relative abundance of each in any particular soil environment, and especially on the persistance and stability of the elemental and selenide forms. Much obviously depends on the rates of conversion from one form to another, but again the information here is scant, especially regarding the action of microorganisms in catalysing reactions which in pure systems appear to be slow. Cary et al. (1967) have investigated, by chemical fractionation, the residual forms of ^{75}Se remaining in the soil after soil ammendment with Se containing ^{75}Se and plant uptake studies, however the relevance of their results to naturally occurring Se in the soil is not known (see section 7.4.).

2.4. The uptake of selenium by plants.

Investigations regarding the mechanisms of Se uptake and assimilation by plants are not within the scope of this work, and to this extent it seems unnecessary to review the topic in detail here. Aspects of Se uptake and metabolism by plants have been recently fully reviewed by Peterson et al. (1981) and forms the basis of the summary below.

Both selenite and selenate may be assimilated by plants, yet Se has not been shown to be essential for plant growth. In terms of comparing the effects of soil additions of Se on plant uptake, the application of selenate results in higher plant uptake than when selenite is added. However, this difference may be largely attributable to the removal of selenite from solution by adsorption processes in the soil. Culture solution techniques eliminate these complications; however, the results of comparisons so obtained have been in disagreement. More recent work suggests that the uptake of selenate is more rapid than that of selenite; further, studies with excised barley roots have demonstrated that the mechanism of absorption is active in the case of selenate, but not so totally for selenite. Although some selenite may enter the root by diffusion it appears that it must be oxidised to either selenate or another form before being transported through the plant, as very little selenite has been identified in plant xylem exudates.

Information on the precise biochemical pathways of Se in the plant is patchy, but it appears that the end product of Se assimilation, during which Se is necessarily reduced to the Se^{2-} oxidation state, are predominantly seleno-amino acids. In normal non-accumulating pasture plants these are selenomethionine, Se-methylselenomethionine, selenocystine and selenocysteic acid etc. In accumulator species, selenolipids and a seleno sugar have also been identified.

Selenosis of plants occurs when non-accumulator species assimilate high concentrations of Se, in which case the high proportion of seleno-amino acids, which substitute for their S analogues in proteins, has deleterious effects. It is supposed that accumulator species can accumulate high levels of Se without harm by synthesising and storing non-protein amino acids or cystathionine Se-methylcysteine, and therefore excluding Se from the functional enzyme systems.

2.5. Variations in the accumulation of selenium by pasture species.

Variations in the ability of common pasture species to accumulate Se from soils containing low or normal levels of Se have been demonstrated by several workers. The most striking manifestation of these differences is that grass species commonly contain more Se than clovers, and some other legumes, grown on the same medium. Thus in a New Zealand pasture Trifolium repens contained less Se than Dactylis glomerata, Lolium perenne and Agrostis tenuis respectively (Davies and Watkinson, 1966); further, A. tenuis contained more Se than T. repens after selenite had been added to the soil (Watkinson and Davies, 1967). Similar, proportionately lower, Se levels in clover were noted by Hupkens and Tetley (1970) when selenite was applied to a peat soil, and when on a normal mineral soil the source of Se was that contained in sheep dung which was considered to be in a colloidal form (Peterson and Butler, 1966). Lessard et al. (1968) found significant differences between the Se content of six pasture species grown on an untreated soil; the only legume (Lotus corniculatus) contained the least Se. They also concluded that although the uptake of Se by particular species did vary throughout the season, the differences in a mixed sward were not great enough to warrant considering changes in harvest time in order to optimise the Se content of the cut herbage.

It would appear that exceptions to the above observations are firstly that alfalfa (Medicago sativa) accumulates more Se than certain common grass species (Kubota et al., 1967; Walker, 1971), and secondly that the relationship may be reversed for clovers when excess Se, or readily available forms such as selenate are added to the soil (Fleming, 1962; Ehlig et al., 1968).

As a result of these relationships it has been postulated that in a marginally deficient pasture, a change to a more clover dominant sward could lead to Se deficiencies in livestock (Ehlig et al., 1968). To this extent it has frequently been observed that outbreaks of W.M.D. in lambs in areas of Australia and New Zealand, tended to occur in spring on pastures dominated by clover (Gardiner, 1969). In summary it is apparent that changes in sward species composition on a low Se soil will not significantly effect the Se content of the sward, unless large changes in the proportion of clovers takes place.

No specific Se tolerant or accumulating flora has been found associated with seleniferous soils in the British Isles (Fleming and Walsh, 1957; Nye and Peterson, 1975); the ability of various classes of such plants to accumulate Se has been extensively reviewed by Rosenfeld and Beath (1964).

In most pasture species the roots accumulate more Se than the tops, with differences of up to 23 times, although it seems that more Se will be transported to the stem and other above ground parts if selenate rather than selenite is the source of Se (Johnson et al., 1967). On low Se soils young plant growth often contains higher levels of Se which are, however, apparently diluted when plant growth takes place (Beeson, 1961; Ehlig et al., 1968). Otherwise there has been little work reported which compares the effects of stage of growth, the age of sward, or the portion of the plant being harvested, on the Se content of the livestock diet.

2.6. The effects of fertilizer additions on the uptake of selenium by plants.

As with the comparison of Se uptake by different plant species, much of the work concerning the effects of other fertilizer additions to soils has been undertaken where Se was also added to the soil, and therefore application of the results to normal situations may only be of modest value.

2.6.1. Liming and pH.

Considering the effect of raised pH on increasing the concentration of selenite in the soil when in equilibrium with a ferric oxide - selenite adsorption complex (section 2.3.), and also that at higher soil pH soluble selenates might form (Figure 2.2.), it might be expected that liming and raising the pH of the soil could result in the increased solubility, and therefore plant uptake, of Se. However, Gupta and Winter (1975) found that liming produced no significant effect on the uptake of native Se by pasture on an acid (pH 6.6) soil supporting low Se vegetation (less than 0.043 $\mu g\ g^{-1}$) on Prince Edward Island, Canada. Alternatively in two separate studies involving additions of selenite to soils, plant uptake has been shown to be greater on limed soils at higher pH; in both cases there was also a texture effect, in that the heavier soils retained more Se than the lighter soils presumably because of their greater adsorption capacity (Cary and Allaway, 1969; Gissel-Nielsen, 1971a). Although the evidence is not extensive it appears that the real effects of increasing soil pH on the uptake of Se by plants on normal or low Se soils are small, and certainly so in terms of increasing the pasture Se content.

2.6.2. Sulphur.

The effects of sulphate on plant uptake of Se have been more widely studied, initiated primarily by the chemical similarity between Se and S. Initial interest in sulphate centred upon the possibility of reducing the uptake of Se on seleniferous soils. In the U.S.A. this was not found to be beneficial, primarily because the soils already contained high levels of gypsum (Frank and Painter, 1939). However, nutrient solution studies demonstrated that sulphate depressed Se uptake when selenate, but not selenite was the source of Se (Hurd-Karrer, 1938). This effect has subsequently been proved to be successful in supressing Se uptake from toxic soils elsewhere (Ravikovitch and Margolin, 1959; Fleming, 1980; Williams and Thornton, 1972).

The possible effects of S additions to soils sustaining vegetation potentially deficient in Se is perhaps of greater concern, especially in regions where S fertilisation is common practice. In Great Britain this practice is rare, however, the application of some fertilizers, noteably superphosphate and sulphate of ammonia, necessarily involves the addition of sulphate to the soil. There is much qualitative evidence that S additions, as superphosphate, can reduce plant Se levels. Walker (1971) reports that farmers in Central Alberta suspected that S fertilisation increased the incidence of W.M.D., however, trials showed that although sulphate fertilisation did decrease plant Se levels, the effect was only significant where this had increased plant growth. Similar dilution effects were observed in New Zealand soils when the addition of superphosphate was compared with that of mono-calcium phosphate (no sulphur) (Davies and Watkinson, 1966).

Cary and Gissel-Nielsen (1973) demonstrated that sulphate additions had only small effects on the solubility of soil selenate and negligible effects on that of selenite, thus assuming that any change in plant uptake due to sulphate addition was due to competetive interaction during plant absorption. It may therefore be concluded that although competition at the plant root may decrease the uptake of Se, the primary effects are of growth stimulation and dilution of the Se content of the plant, especially when selenite is the main available form of Se.

An alternative Se - S interaction also exists as there is some evidence that increased dietary S levels may inhibit the biological availability of Se (Westerman and Robbins, 1974).

2.6.3. Phosphorus.

Carter et al. (1972) found that phosphate additions increased plant Se contents of plants grown on six out of fourteen soils, for both native and added Se; they considered that the effect might be sufficient to induce adequate levels of Se in marginal pastures. Phosphate also increased the uptake of native Se by alfalfa, but at the same time reduced the uptake by lettuce (Levesque, 1974b). Other work with N, P, S and Se additions to soils has shown that the effects of phosphate depended upon the level and interaction with other nutrients (Gissel-Nielsen, 1974). Fleming (1980) proposed that phosphate may act in two ways to increase the availability of Se; firstly in that both phosphate and selenite may be involved in exchange reactions with oxide surfaces, thus addition of phosphate may induce higher solution concentrations of Se; or secondly that phosphate may increase the Se uptake by promoting the growth or roots and thus increasing the plant's capacity for uptake. However, Cary and Gissel-Nielsen (1973) shed doubt on the validity of the first proposal by finding that the addition of phosphate did not increase the solubility, in dilute $CaCl_2$, of added selenite. In the case of superphosphate applications, the effects of phosphate may be masked by those of the sulphate.

2.6.4. Nitrogen.

Little is known of the effects of nitrogenous substances on the uptake of Se by plants. Cary and Gissel-Nielsen (1973) noted that N application may reduce the uptake of Se but that this is probably due to competetive uptake at the plant root, rather than an effect on the solubility of Se in the soil. Fleming (1980) notes that any effects of N application when using sulphate of ammonia can be complicated by the presence of the sulphate ion.

2.6.5. The selenium content of fertilizers.

Phosphatic fertilizers may contain Se, since phosphatic rocks can contain up to tens of $\mu g\ g^{-1}$ Se, and the sulphuric acid used in the manufacture of superphosphate may contain Se in the same order (Lakin and Davidson, 1967). Normal superphosphate can contain about 60% of the Se in the raw material rock phosphate, or some 40% in the case of concentrated superphosphate, the main control on the Se content of the end product being the Se content of the phosphate rock (Robbins and Carter, 1970). The effects of Se added in this way on plant Se concentrations are, however, probably negligible unless the initial phosphates were very seleniferous (Robbins and Carter, 1970; Gissel-Nielsen, 1971b). The concentration of Se in some common Danish fertilizers, which are probably comparable to those in use in the British Isles, are given in Table 2.2. It is conceivable that long term additions of some fertilizers may increase the total Se content of the soil.

2.7. Losses of volatile selenium products from soils.

In some situations volatilisation is thought to be responsible for the loss of significant quantities of Se from soils, which may to some extent be augmented by volatilisation from higher plants. The evolution of volatiles from soils is thought to be an entirely microbial process (Abu Erreish et al., 1968; Doran and Alexander, 1976), and several strains of fungi and bacteria have been shown to be capable of synthesising volatile Se compounds from either inorganic Se salts or organoselenium compounds (Fleming and Alexander, 1972; Cox and Alexander, 1974; Barkes and Fleming, 1974). Dimethylselenide is considered to be the primary volatile product (Francis et al., 1974) but dimethylselenone, dimethylselenide and hydrogen selenide have also been identified (Reamer and Zoller, 1980; Doran and Alexander, 1976); the form evolved depending upon the substrate for the synthesis.

The process is dependant upon many factors, but perhaps the most important is the availability of a suitable substrate; thus the availability of water soluble Se influences the rate of methylation (Abu Erreish et al, 1968; Zieve and Peterson, 1981) and it is therefore expected that alkaline soils, having an appreciable content of selenate, are most susceptable to volatile losses (Hamdy and Gissel-Nielsen, 1976a). Losses may be much less important on more acid soils where selenite or more reduced insoluble species predominate. Other factors influencing the process are those affecting microbial activity such as temperature,

Fertilizer.	Number of samples analysed.	Se content ($\mu g\ g^{-1}$).
Superphosphate	8	4.2 - 8.0
PK.	12	3.6 - 5.5
NPK (Based on sulphuric acid)	7	1.1 - 4.0
NPK (Based on nitric acid).	8	0.021 - 0.19
Lime.	3	0.033 - 0.037

Table 2.2. Selenium content of some typical Danish fertilizers (Gissel-Nielsen, 1971b).

moisture status and the availability of organic matter for use as an energy source (Abu Erreish et al., 1968; Doran and Alexander, 1976; Zieve and Peterson, 1981). In respect of the latter, Hamdy and Gissel-Nielsen (1976a) found that wetting and drying cycles, which were thought to advance the decomposition of organic matter, raised the levels of volatilised Se. Zieve and Peterson (1981) found that more Se was evolved from a soil collected in the spring than in those collected in other seasons, and related this to an increase in the microbial population during this season, implicating seasonal differences in volatilisation in the field.

Less is known of volatilisation of Se by higher plants, but the primary Se accumulators defined by Rosenfeld and Beath (1964) have been known to give off a garlic-like odour, thought to be due to volatile Se compounds. Lewis et al. (1976) found that an accumulator (Astragalus spp.) and alfalfa both produced volatile Se compounds, predominantly from the foliage; the evolution by alfalfa was linked to the plant Se content and the stage of growth.

2.8. Atmospheric cycling of selenium.

On the basis of their experiments, Zieve and Peterson (1981) estimated that the rate of Se volatilisation from soil could vary between 18 and 128 $\mu g\ m^{-2}\ yr^{-1}$ depending on the season. As the soil tested contained quite high levels of total Se (5.0 $\mu g\ g^{-1}$) and was alkaline (pH = 7.4), these might be overestimates for most "normal" British soils, but they do allow for comparison with other environmental Se fluxes. Therefore these volatile losses can be compared with a grass crop of average Se concentration of 0.1 $\mu g\ g^{-1}$, yielding 500 Kg $ha^{-1}\ yr^{-1}$ which removes 5 $\mu g\ m^{-2}\ yr^{-1}$ Se; or a Kale crop (yielding 7400 Kg $ha^{-1}\ yr^{-1}$) which would remove 100 $\mu g\ m^{-2}\ yr^{-1}$ Se (Cawse, 1980).

In comparison with these values, Cawse (1980) monitored the quantities of Se deposited from the atmosphere in the U.K. The average deposition rate for seven sites was 430 $\mu g\ m^{-2}\ yr^{-1}$ Se, which is within the range of 150-750 $\mu g\ m^{-2}\ yr^{-1}$ Se calculated by Ronneau and Haliet (1981) on the basis of extrapolating known S and Se fluxes over Belgium to the rest of

Europe using estimated european S fluxes. Cawse (1980) also noted that the amount of Se deposited (including both wet and dry deposition) was broadly related to rainfall, and that the deposition was greater in winter than in summer, although he felt that this was due to fossil fuel burning which would be greater in winter. Fossil fuels are known to be an important source of anthropogenic Se emmisions (Hashimoto et al., 1970). In contrast, Kubota et al. (1975) cite that the soluble Se in rainfall from one site in Denmark contributes 172 $\mu g\ m^{-2}\ yr^{-1}$ and that the greatest deposition was in the summer period; this they related to increased biological activity due to higher temperatures. None of this work, however, allows for comparison of the relative contributions of natural low temperature emmisions, volcanic emmisions and industrial and other anthropogenic emmisions, although Kubota et al. (1975) noted that the concentration of Se in rainfall in the U.S.A. was highest near to industrial centres.

On investigating the Se content of humic topsoils of Norwegian forest soils, Lag and Steinnes (1977) found that values were strongly correlated with annual precipitation, and thus concluded that airborne supply of the element to the soils was important. Furthermore the accumulation of Se was not particularly related to the greater accumulation of organic matter under higher precipitation. They postulated a marine source of Se since the soil Se concentration was also correlated with the soil content of iodine and bromine, and related to the distance of the soil from the coast. It was appreciated, however, that natural terrestrial outputs (both biological and volcanic) could also make contributions to the airborne supply of Se.

It would seem that anthropogenic emmisions of Se have only a relatively short residence time in the atmosphere, similar to that of water, thus suggesting that such emmisions are quickly rained-out of the atmosphere (MacKenzie et al., 1971). This observation is possibly supported by the data of Weiss et al. (1971) which demonstrate that the S:Se ratio of Greenland ice has increased over a 250 yr period, which they related to increased fossil fuel burning and a greater stability of atmospheric SO_2 compared to similar Se species. They assumed that background Se levels over this period could be related to biological emmisions which would be more constant.

It is probable that in the U.K., with its small land area and high urban and industrial populations, that the majority of atmospheric Se would be anthropogenic. There may be seasonal fluctuations in the total atmospheric land deposition but it appears that this will depend upon location. In proximity to urban and industrial centres fossil fuel burning especially would be greater in winter, therefore increasing emmisions. Away from such centres values may be higher in summer when biological emmisions are greater. Seasonal variations in rainfall may also influence this pattern.

The information presented here suggests that atmospheric inputs to land (mean of 430 $\mu g\ m^{-2}\ yr^{-1}$) probably exceed losses by cropping (perhaps up to 100 $\mu g\ m^{-2}\ yr^{-1}$) and volatilisation (mean of 73 $\mu g\ m^{-2}\ yr^{-1}$). Additionally based on information in Table 2.2. an annual addition of 300 $Kg\ ha^{-1}$ of superphosphate (i.e. 80 $Kg\ ha^{-1}$ P_2O_5) containing 6.0 $\mu g\ g^{-1}$ Se might add a further 180 $\mu g\ m^{-2}\ yr^{-1}$ Se (assuming that the Se content of other fertilizers is minimal). Unfortunately, because of a lack of available information, losses by leaching are difficult to assess. However, MacKenzie et al. (1980) have assesed that globally some 182 x 10^8 $g\ yr^{-1}$ Se are carried by rivers in soluble and suspended forms, which amounts to losses of 136 $\mu g\ m^{-2}\ yr^{-1}$ Se if this is all derived from the land surface. As a very rough estimate therefore it appears that Se additions to land (atmospheric and fertilizer) at approximately 510 $\mu g\ m^{-2}\ yr^{-1}$ may easily exceed the outputs (volatile, cropping and ?leaching) at approximately 209 $\mu g\ m^{-2}\ yr^{-1}$. However, this difference (301 $\mu g\ m^{-2}\ yr^{-1}$ Se) would only increase the total Se content of the soil by around 0.04% per annum (based on a soil containing 0.5 $\mu g\ g^{-1}$ total Se, with a bulk density of 1.5 $g\ cm^{-3}$, and being incorporated to a depth of 1 m.).

2.9. Selenium distribution in soils.

2.9.1. In relation to toxicity problems.

The majority of the early work concerning the distribution of Se in soils centred upon those soils producing toxic vegetation, the vast majority of which were derived from shales, and frequently those shales containing appreciable quantities of organic material (section 2.2., Table 2.1.). Toxic soils have been identified in many coutries. The toxicity of a soil is not, however, related solely to the total content of Se in the soil, but also to the form which the Se takes. From the evidence presented in sections 2.3. and 2.4. it may be summised that toxic Se levels in plants will occur on soils in which the soluble selenate ion is prevalent, that is in predominantly alkaline soils. This in fact conforms with the nature of most toxic seleniferous soils (Rosenfeld and Beath, 1964).

In the classic area of seleniferous soils in the Great Plains of the U.S.A. the soil parent materials are shales enriched in Se, it is thought by selenisation of the surrounding land mass by Cretaceous volcanic activity during the deposition of the sediments. Their occurance and formation has been reviewed by Rosenfeld and Beath (1964), but in short the soils have developed in-situ in an arid or semi-arid climate, and are predominantly alkaline in reaction, often containing free calcium carbonate. The low rainfall (less than 20 inches per annum) results in minimal leaching of the soluble selenate, although it is possible for soluble Se salts (predominantly selenate) to be redeposited due to evapouration of surface waters. Wide variations in soil Se content are often encountered over small distances, and have been related to the outcrop of different strata of the relevant rocks, thus stressing the importance of parent material in influencing the Se content of the soil.

On studying several seleniferous soil profiles in this region, Olson et al. (1942) found that where plant Se concentrations and presumably also the water soluble Se content was highest, the amount of Se increases with depth in the soil, evidently due to some degree of leaching of selenate. However, when the rainfall increases slightly in a similar environment lateral leaching of selenates, and their subsequent depostion in basins or low lying lacustrine deposits, has been observed (Lakin and Davidson, 1967).

The toxicity of these Great Plains soils, in terms of the vegetation which they support, is significantly enhanced by the presence of selenium accumulator species such as <u>Astragalus spp</u>. (section 2.4.) which can contain up to thousands of $\mu g\ g^{-1}$ Se (Rosenfeld and Beath, 1964). The occurrence of these plants has in fact been used to determine the distribution of seleniferous soils in the area.

Toxic seleniferous soils found in Canada, South America and Israel are similar in nature to those of the U.S.A. (Lakin, 1962). In contrast the Irish seleniferous soils in counties Meath, Tipperary and Limerick were formed under humid conditions, in low lying areas and are consequently rich in organic matter. The high Se concentrations derive from the leaching of Se, by alkaline ground waters percolating from the surrounding Se-rich limestones and shales of the Carboniferous Pendleside and Yoredale series'. These rocks contain up to 28.5 $\mu g\ g^{-1}$ Se (Fleming and Walsh, 1957), values which are comparable to those of the parent materials of the toxic soils of the U.S.A. Atkinson (1967), considered that Se in these rocks was related to pyrite and carbonaceous material, there being a relationship between their Se and S contents. In comparison to those of the soils in the U.S.A. soil concentrations of Se are much higher, up to 1200 $\mu g\ g^{-1}$, and have been linked to the concentration of organic material in each horizon (Table 2.3.). Although the soils are alkaline in reaction, the proportion of water soluble Se is relatively low at between 1 and 3% of the total, compared to values of up to 62.5% in soils from the U.S.A. (Rosenfeld and Beath, 1964). Herbage in Eire has been found to contain up to 450 $\mu g\ g^{-1}$ Se despite the absence of a specific seleniferous flora. Webb et al. (1966) investigated soils on the comparative shale formations in England and Wales and located seleniferous soils which occupied similar low lying poorly drained sites, however, no selenium toxic vegetation was identified. This they related to the acidity of the soils and the consequent lower solubility of Se, thus stressing the importance of the alkalinity imparted by the limestone facies in the case of the soils in Eire.

Low herbage Se concentrations have also been noted on seleniferous lateritic soils, this being explained by the almost total adsorption of Se on ferric oxides. The more ferruginous horizons also contained the more Se (Lakin and Davidson, 1967).

Depth (ins)	pH	Organic matter (%)	Se $\mu g\ g^{-1}$
0 - 4.5	6.5	33.0	37.1
4.5 - 6	7.3	22.1	24.1
6 - 10	6.6	61.4	105.4
10 - 20	8.1	4.5	13.5
20 - 28	7.5	5.7	22.5
28 - 36	7.3	10.4	23.6
36 - 37	7.4	26.4	33.7

Table 2.3. Distribution of Se in a soil profile supporting Se-toxic vegetation from Co. Limerick, Eire, in relation to pH and organic matter content. (Fleming and Walsh, 1957).

2.9.2. In relation to deficiency problems.

Despite the wealth of research and information on the subject, toxic seleniferous soils are not particularly abundant in global terms, although they are widespread (Lakin, 1972). The problems of soils producing vegetation potentially deficient in Se are much more critical, and such soils may be significantly more prolific, although information on these and "normal" soils is not as extensive.

Swaine (1955) reviewed all the available world data up to 1955 and concluded that the Se content of most soils was between 0.1 and 2.0 $\mu g\ g^{-1}$. The results from recent surveys, given in Table 2.4., confirm this range and would suggest a mean soil Se concentration of 0.5 $\mu g\ g^{-1}$ as a reasonable world estimate. Obviously the majority of this work has been involved with those soils providing less than adequate supplies of Se for plant uptake and livestock consumption. Some of the earliest work in this field was undertaken in New Zealand, where it was found that sheep responded to Se supplementation in 43% of the South Island and 14% of the North Island (Hartley, 1961). Watkinson (1962) related this pattern to differences in the soils which are a primary factor influencing the the incidence of a Se response. Most of the responses occurred on sandy and silty soils, which are not extensive on the North Island where more intense weathering has produced predominantly clayey soils. Watkinson then confirmed these observations by comparing the Fe:Se ratio of New Zealand zonal soils. The ratio was found to increase in the more highly weathered members of the sequence. It was thought that as weathering increases, selenides in the parent material are oxidised to selenites which are consequently retained by ferric oxides in the soil, some Fe is also lost from the soils due to leaching of soluble ferrous forms. Conversely where weathering proceeds more slowly, little Fe is released from the silicates to form the oxides on which the selenite could be retained. The selenites form because the oxidation of selenides in non silicate phases takes place more readily, and thus Se tends to be lost from the soils. Later, Andrews et al. (1968), reviewed that problems of Se deficiency were noteable on soils developed from granites, rhyollitic pumice and coastal sands. It was considered that soils containing less than 0.45 $\mu g\ g^{-1}$ Se might produce vegetation giving rise to deficiencies; this compares to a mean Se concentration of 0.6 $\mu g\ g^{-1}$ for New Zealand soils (Wells, 1967). Soils with higher

Source.	Region.	Type of soil.	Range $\mu g\ g^{-1}$	Mean value.	Number of samples.
Swaine (1955).	World.	Estimate for all soils.	0.1 - 2.0	--	--
Vinogradov (1959).	Russia.	--	less than 0.01	--	--
Wells (1967).	New Zealand.	All soils.	--	0.60	64
Lindberg and Bingefors (1970).	Sweden.	Representative soils.	0.16 - 0.98	0.38	24 (8 sites).
Tsuge and Terrade (in Wells, 1967).	Japan.	--	--	0.71	--
Misra and Tripathi (1972).	India.	Five typical soil types.	0.158 - 0.710	0.46	106
Bisbjerg (1972).	Denmark.	--	0.20 - 1.44	0.57	11
Lag and Steinnes (1977).	Norway:	Humus layers of podzolics.			
	i. Nord-Trondelag.		0.08 - 1.7	0.63	122
	ii. S.E. Norway.		0.07 - 1.35	0.42	177
Whitby et al. (1978).	Canada (Ontario).	--	0.18 - 1.03	0.40	--
Levesque (1974a).	Canada.	Potentially Se deficient soils.	0.43 - 2.09	--	54
Koljonen (1975).	Finland.	Podzolic topsoils.	0.09 - 0.4	0.21	8
Archer (1980).	Wales and E. Midlands, U.K.	--	0.2 - 1.8	0.60	114

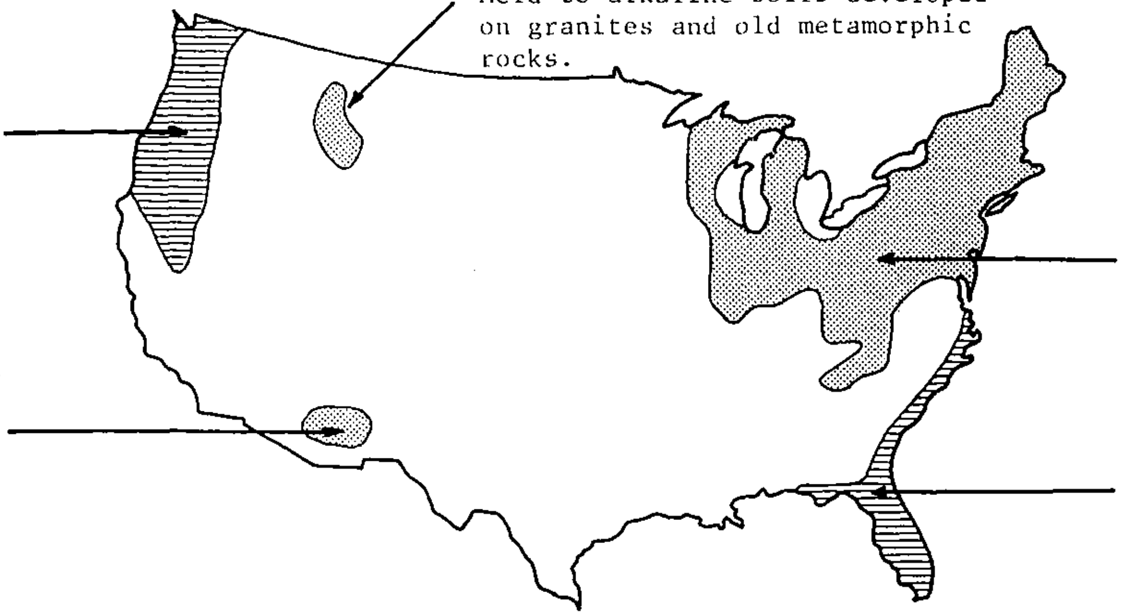
Table 2.4. Reported concentrations of selenium in world soils.

Se concentrations on which a response to Se supplementation took place were often acid and organic (Watkinson, 1962).

In the U.S.A. surveys of herbage Se concentrations were used as a means of locating potentially deficient areas. Kubota et al. (1967), in a nationwide survey, sampled alfalfa and extrapolated the information to areas not covered on the basis of soil and soil parent material maps. They were able to delineate three main areas of potential deficiency which were closely related to the geology of the soil parent material. There were, however, modifications to this pattern due to the effect of soil profile development upon the availability of Se (Figure 2.3.).

It is clear from the above information that Se deficiencies often occur on soils developed from igneous rocks, and this is also confirmed by the work of Sharman (1960) in Scotland who found that occurrences of enzootic muscular dystrophy in calves which could be treated by Se or vitamin E administration, were not only related to soils developed from granites but also from Old Red Sandstone and Carboniferous sandstones. Later Blaxter (1963) reported that sheep in the same areas responded to Se supplementation. Similarly Gardiner (1969) reports that metamorphosed pre-Cambrian rocks and Archaen granites are often the parent materials of soils on which outbreaks of W.M.D. are widespread in Western Australia. This information is summarised in Table 2.5. which clearly demonstrates that igneous rocks and predominantly arenaceous sedimentary rocks may give rise to selenium deficient soils. This is in accord with the observations reported in section 2.2. that Se separates from silicate bearing rocks during igneous activity. In contrast volcanic ashes, and soils developed from them normally contain higher levels of Se (Lakin and Davidson, 1967; Wells, 1967).

As noted by Kubota et al. (1967), any basic relationship between parent material type and soil and plant levels of Se can be modified by other factors. Gardiner and Gorman (1963) found that rainfall affected plant Se levels in Western Australia such that they were lowest near to the coast where the rainfall was greater, probably due to increased leaching of the soils. This interestingly contrasts with the effects of rainfall on the Se content of humic soils in Norway reported by Lag and Steinnes (1977) and discussed in section 2.8. Additionally plant



Plants with very low concentrations of Se: Soils developed from recent volcanic deposits.

Plants with low concentrations of Se: Acid to alkaline soils developed on granites and old metamorphic rocks.

Plants with low concentrations of Se: Predominantly acid soils from pre-cretaceous sedimentary parent materials.

Plants with low concentrations of Se: Alkaline soils developed from low Se tertiary volcanic rocks.

Plants with very low concentrations of Se: Acid and poorly drained soils developed from coastal deposits from a highly weathered land mass.

NOTE Areas of low plant concentrations had more than 80% of plants with less than 0.1 ug g^{-1} Se

Areas of very low plant Se concentrations had more than 80% of plants with less than 0.05 ug g^{-1} Se.

Figure 2.3. Distribution of potentially selenium deficient areas in the U.S.A. (Kubota et al., 1967)

Country.	Parent material.
New Zealand.	Granites. Rhyollitic pumice. Coastal sands.
Scotland.	Granites. Old Red Sandstone. Carboniferous sandstones.
Australia (western).	Pre-Cambrian metamorphics. Archaen granites.
U.S.A.	Recent volcanic rocks. Pre-Cretaceous sedimentary rocks. Weathered coastal deposits- Granites and metamorphics.

Table 2.5. Parent materials of soils giving rise to selenium deficiency problems (after Fleming, 1980).

Se levels were higher on heavier textured soils. In Saskatchewan, Canada, Doyle and Fletcher (1977) established that both the Se content of wheat plants and of the C horizon of the soil on which they grew were related to the nature of the parent material. Median differences between parent materials were significant, however, there was a poor correlation between plant Se and C horizon concentrations within each parent material group, which was explained by differences in soil pH, drainage and secondary iron oxide content affecting the availability of the Se in the soil. Despite the similarity in the C horizon Se concentration of two soils developed on different alluvial parent materials in British Colombia, herbage concentrations were much higher on a carbonated orthic gleysol than on an orthic grey luvisol (Van Ryswyck et al., 1976). This was related to differences in soil type, and primarily to the reduced availability of Se in the more acid Ap horizon of the luvisol; differences in soil organic matter, moisture regime and pH were also implicated.

More detailed studies of the distribution of Se in soil profiles have been undertaken. In a qualitative appraisal of Se distribution in representative New Zealand soils, Wells (1967) found that topsoils (mean Se content of 0.6 $\mu g\ g^{-1}$) were generally more enriched in Se than the parent materials from which they were formed (mean content of 0.42 $\mu g\ g^{-1}$). The Se content of very immature AC type soils was directly dependant upon the Se content of the parent rock. Where weathering had lead to a more distinct profile development Se was retained against the processes of leaching by the products of mineral weathering, clays and hydrous oxides of Fe. Therefore clay rich B horizons and Fe rich horizons of podzols were characteristically more enriched in Se. Additionally, dependant upon the degree of weathering, podzolisation acted to reduce the amount of Se in the elluvial horizon, although even in the absense of ferric Fe, the elluvial horizon of gleyed podzols retained Se against leaching. Gleying apparently had little effect on the amount of Se present; Se also accumulated in zones of organic enrichment. All these processes interacted with the nature of the parent material in influencing the Se content of the topsoil.

Koljonen (1975) found similar patterns of Se distribution in podzols, which predominate in Finland, and due to their low pH he assumed that Se would probably occur as the elemental or selenite form, the latter in association with ferric oxides. In a more detailed study of the factors governing the distribution of Se in Canadian soil profiles, Levesque (1974a) found that the most important factors were the Se content of the parent material and the organic carbon content of the topsoil. However, the profile distribution of Se was closely correlated with both organic carbon and the reactive forms of Fe and Al (extracted by oxalate), and thus he summised that Se was associated with organic matter in upper horizons and with Fe in the subsoil, this being most pronounced in the case of podzols.

In addition Se accumulated in soils relative to the parent material levels, and he postulated that Se accumulation in the B horizon compared to the A was largely the result of downward migration, in which organic matter - Fe(or Al) complexes might be implicated. Further work, using gel filtration techniques to separate alkaline soluble soil Se components on the basis of molecular weight, suggested that a proportion of the selenite added to a soil ultimately became incorporated in organic matter - Se, or organic matter - Fe - Se complexes (Levesque, 1974b). In contrast to Wells (1967), Levesque suggested that clay content had no influence on Se distribution.

In summary therefore, the primary factor influencing the Se content of soils is the nature of the parent material, with granites and coarse grained sandstones most likely to give rise to soils with very low levels of Se. The processes of soil formation may influence this relationship by redistributing Se through the soil profile. The lowest availability of Se is likely to be encountered in acid soils occurring in humid areas. Little is known of how these processes influence the distribution of Se in British soils; and perhaps more importantly in this respect, little work has been undertaken to elucidate the nature of the distribution and availability of Se under predominantly reducing conditions in gleyed soils.

2.9.3. In soils in England and Wales.

The most comprehensive information available on the Se content of soils in England and Wales is that of Thornton et al. (in press), who related the Se content of topsoils to the lithology of the parent material for some 517 soil samples (Table 2.6.). The mean Se concentration of all the soils (0.48 $\mu g\ g^{-1}$) is comparable to those of other world soils presented in Table 2.4., but is lower than the median Se content of soils from a more restricted area in the east Midlands and Wales of 0.60 $\mu g\ g^{-1}$ (Archer, 1980). Selenium concentrations in soils located on chalk, limestone, sands and sandstones (0.33, 0.38 and 0.36 $\mu g\ g^{-1}$ respectively) were lower than those developed on finer argillaceous lithologies (clay, mudstone and shales, mean 0.47 $\mu g\ g^{-1}$). This conforms with reports that the Se concentrations are higher in shales than in sandstones and carbonate rocks (section 2.2.). However, considering the fact that Se is usually concentrated in soils relative to their parent materials (Levesque, 1974a; Wells, 1967) it would appear that a proposed mean Se content for shales of 0.60 $\mu g\ g^{-1}$ (Turekian and Wedepohl, 1961) is an overestimate for argillaceous rocks in England and Wales when compared to a mean content of 0.47 $\mu g\ g^{-1}$ Se for soils developed from such rocks. Considering the fact that many seleniferous rocks are shales, it is possible that previous estimates of mean Se contents for shales were unreasonably weighted by inclusion of data from Se rich rocks. The inclusion of data from soils derived from black shales, which are often enriched in Se, might explain the higher mean Se content of soils developed from shales (0.64 $\mu g\ g^{-1}$) compared to clays and mudstones (0.43 and 0.45 $\mu g\ g^{-1}$ respectively) in this work (Table 2.6.).

The high mean Se concentrations in soils from areas underlain by mineralised rocks presumably derive from the dispersion of Se which was formerly concentrated with sulphides (section 2.2.), rather than from the granites and shales themselves.

Thornton et al. (in press) therefore considered that the nature of the parent material was an important factor in determining the Se status of soils in England and Wales. It might be noted that, excluding peats and soils from mineralised areas, the mean soil Se concentration is 0.41 $\mu g\ g^{-1}$ which is less than the value of 0.45 $\mu g\ g^{-1}$, below which Watkinson (1962) reported a frequent response to Se supplementation in sheep grazing on such land in New Zealand. Although this information may not be directly applicable to the situation in England and Wales, it must be viewed in light of the work

Parent material.	Number of samples.	Se (range)	Se(mean)
		µg g^{-1}	
Chalk.	41	0.11 - 1.43	0.33
Limestone.	25	0.13 - 0.86	0.38
Sandstone.	190	0.01 - 2.11	0.36
Clay.	134	0.08 - 2.91	0.43
Mudstone.	43	0.09 - 1.59	0.45
Shale.	38	0.25 - 1.07	0.64
Mineralised granite and shale.	16	0.71 - 4.66	1.14
Peat.	30	0.47 - 2.11	1.20
ALL SOILS.	517	0.01 - 4.66	0.48

Table 2.6. Concentrations of "total" selenium in some surface soils (0-15 cms) in England and Wales (Thornton et al., in press).

of Anderson et al. (1979) who, by assesment of the biological Se status of sheep, demonstrated that some 40% of farms were unable to provide grazing sheep with sufficient Se in England and Wales; this will be discussed in more detail later.

CHAPTER 3. SAMPLE PREPARATION AND ANALYSIS.

3.1. Sample preparation.

The following techniques were used for all samples collected in the field. Sampling schemes varied between field areas and are discussed in the relevant section, however, after collection all samples were placed in Kraft paper bags for return to the laboratory.

3.1.1. Soils.

All soils were air dried at less than 25°C, then lightly ground to break up the aggregates. The less than 2 mm material was separated by sieving and representative sub-samples were ground to less than 0.5 mm and less than 80 mesh (less than 200 μm) as required. All samples were subsequently stored in paper bags in a cool dry place. Drying and storage at room temperature were adopted so as to reduce the risk of loss of Se by volatilisation from the samples, which would be promoted by warm and humid conditions (Hamdy and Gissel-Nielsen, 1976a; Zieve and Peterson, 1981).

3.1.2. Rocks.

All samples, being relatively soft, were crushed by hand in a pestle and mortar, and then representative sub-samples were ground to less than 80 mesh before analysis.

3.1.3. Herbage.

All herbage was washed immediately on return to the laboratory by rinsing several times in de-ionised water. As much moisture as possible was removed by shaking, and drying with paper towels before the samples were dried for 48 hrs in a drying cabinet with circulating air at 20°C. The dried herbage was then milled in a Christy and Norris mill designed to reduce the risk of trace element contamination. Prepared samples were stored in paper bags in a cool dry place, and were analysed within 14 days of collection.

3.2. Analytical techniques.

For the survey work which was undertaken in the three field areas described in Chapters 4,5 and 6, the same suite of parameters was measured in the analysis of all the soil samples. In general these were soil chemical criteria which, from the evidence presented in past work on Se in soils, were considered to influence the distribution of Se in soils. Thus Fe has often been implicated in this respect (Geering et al., 1968; Cary and Allaway, 1969; Howard, 1977), and hydrous ferric oxides are known to be capable of Se adsorption (Hingston, et al., 1968; Hamdy and Gissel-Nielsen, 1977) and also to be a factor related to both the magnitude of Se adsorption by soils (John et al., 1976) and its concentration in horizons of soil profiles (Levesque, 1974a). Similarly, evidence exists for the adsorption of Se by oxides of aluminium in the soil (Levesque, 1974a; John et al., 1976; Rajan, 1979). For both Fe and Al therefore two techniques were adopted, a nitric acid extraction, representing "total" Fe and Al (Fe_t and Al_t), and Fe and Al extracted by 0.1M potassium pyrophosphate (Fe_p and Al_p) representing "active" hydrous oxides.

Selenium has been shown to be associated with organic matter in the soil, especially in toxic soils in Eire (Fleming and Walsh, 1957; Table 2.3.); and is also thought to be involved in an organic cycle (Shrift, 1964). Levesque (1974b) considered that organic complexes may have a role in the redistribution of Se in soil profiles. Consequently a measure of the organic matter content of the soil, percentage loss on ignition, was adopted.

The oxidation state of the Se in the soil is known to be influenced by changes in the pH and redox potential (Geering et al., 1968; Howard, 1977) and toxicity problems in soils have been linked to the predominance of the soluble selenate anion in alkaline conditions (Olson et al., 1942; Fleming and Walsh, 1957). Measurement of pH is a routine proceedure, and in this study was determined for soil in solution with both water (pH_w) and 0.1M $CaCl_2$ (pH_{Ca}). Subsequent data analysis (Chapter 6) showed that when correlated with other soil parameters measured in this study there was no discernable difference in effect between these two measures of pH, and so pH_w was later chosen as the sole parameter. Estimation of the soil redox potential is a more complex problem; Keeley (1973) considered that field determinations of redox potential were unreliable and at best provided only a semi-quantitative estimate. For the purpose of this study it was decided not to measure Eh quantitatively, as it was felt that careful recording of soil characteristics such as colour, mottling and moisture status, when used in conjunction with information from other sources (Baas-Becking et al., 1960; Pearsall, 1938) would provide useful information on the soil redox potential. Such criteria provide an indication of the effects of oxidation and reduction in the soil over the whole year, whereas Eh measurement by platinum electrode, or other similar methods, is specific to the conditions prevailing at the time of measurement.

Manganese oxides are also capable of trace element adsorption in the soil (Jenne, 1979), and as their occurrence depends upon, and to some extent determined the redox potential of the soil, it was decided that the Se content of the soil might be influenced by that of Mn, although no specific evidence for this exists. Manganese was therefore determined as that extracted by hot nitric acid, representing "total" Mn (Mn_t). Total Ca and Mg were also determined in hot nitric acid extracts as representing other major soil cations (Ca_t and Mg_t).

In these preliminary studies one possible omission from the suite of analyses was the clay content of the soil. Wells (1967) considered that Se tended to be concentrated in horizons of clay and ferric oxide enrichment. However, it has been shown that hydrous ferric oxide fixes Se more readily than several soil clay minerals (Hamdy and Gissel-Nielsen, 1977), and also that the clay content of the soil has little or no influence on the distribution of Se in horizons of Canadian soil profiles (Levesque, 1974a). So the clay content of the soil was not determined, it being considered that the major role of clays in the soil chemistry of Se is probably as a site for the precipitation of oxides of Mn, Fe and Al which themselves would be more important in the adsorption and retention of Se in the soil. Rough field determinations of texture were, however, taken to provide some information on the relative texture of the soils.

Outlines of the analytical techniques used, and the reasons for their selection, are given below.

3.2.1. Total selenium (Se_t).

The technique used, apart from small differences in the digestion proceedure, was the same for soils, rocks and herbage, and follows that of Pahlavanpour et al. (1980). Briefly, Se is solubilised by digestion of the fine ground, or milled, material using a mixture of nitric and perchloric acids under a controlled temperature regime which reduces the risk of loss of Se from the samples by volatilisation. Determination of Se in solution proceeds by its reduction to hydrogen selenide with alkaline sodium tetrahydroborate. The hydrogen selenide is then carried by argon gas to an inductively coupled plasma source for determination by emission spectrometry (using A.R.L. 64000C machine). Traces of Cu in solution interfere with the production of hydrogen selenide and so prior to the reduction stage Se is separated from solution by co-precipitation with lanthanum hydroxide. The precipitate is dissolved in 5M HCl and potassium bromide added to ensure the reduction of Se^{6+} to the 4+ oxidation state, thus enabling its efficient reduction to hydrogen selenide.

The advantages of this method are a capability to handle large batches of samples, a detection limit (c. 1 $\mu g\ ml^{-1}$) comparable to that of an atomic adsorption - hydride system, linear calibration up to 1000 $ng\ ml^{-1}$, and ease of execution compared to the previously used flourescence methods (Pahlavanpour et al., 1980). All results are reported in μg Se g^{-1} of air dry, less than 2 mm soil or rock; or $\mu g\ g^{-1}$ herbage D.M.

3.2.2. Pyrophosphate extractable Fe and Al (Fe_p and Al_p).

0.1M potassium pyrophosphate was chosen as an extractant for free amorphous Fe and Al oxides. Bascombe (1968) reported that this extractant peptised fine amorphous particles without serious attack on silicates, and that this fraction, because of its large surface area, would have a great effect on soil properties. It therefore gives good extraction of amorphous "gel" hydrous oxides of Fe, organic complexes of Fe, and was thought to give good extraction of organic complexes of Al. Other commonly used extractants such as acid oxalate and dithionite are considered to extract in turn, aged amorphous hydrous oxides and crystaline oxides, which do not make as great a contribution to the reactive surface area of the soil. With relevance to the work in Chapter 6, Ball and Beaumont (1972) demonstrated that there was little attack by this extractant on constituents of Silurian shales from north Wales. It has been thought more recently that pyrophosphate is actually specific for organic complexes of Fe, whereas it has a slightly broader action for Al compounds (McKeague et al, 1971). However, as pyrophosphate extraction is used to monitor redistribution of Fe and Al in soil profiles (Avery, 1980), and considering reported relationships between Se and organic matter, pyrophosphate was considered to be the most suitable single extractant to use in this study as an estimate of "active" Fe and Al oxides.

The method used follows that of Avery and Bascombe (1974) and involves shaking of soil and 0.1M potassium pyrophosphate solution at a 1:100 weight to volume ratio for 16 hrs, followed by centrifugation to produce a clear solution in which Fe and Al are determined by atomic adsorption spectrophotometry (using a Perkin Elmer 403). Results for Fe_p and Al_p are reported as the percentage of the air dry, less than 2 mm fraction of the soil.

3.2.3. Nitric acid digestion for Fe, Al, Mn, Ca and Mg in soils and rocks (Fe_t, Al_t, Mn_t, Ca_t and Mg_t).

Estimates of the total soil and rock content of Fe, Al, Mn, Ca and Mg were made using attack on fine ground material (less than 80 mesh) with 70% nitric acid at 105°C for one hour, followed by analysis for all elements by atomic adsorption spectrophotometry (Perkin Elmer 403). This attack is completely effective for solubilising constituents of clay minerals. For other rock forming minerals the attack may be virtually complete (feldspars and olivine), partial (e.g. about 50% for pyroxine, biotite and amphibole), or negligeable (quartz). Results for the above parameters are expressed as a percentage of the air dry, less than 2 mm soil or rock, with the exception of results for Mn_t which are given in μg Mn g^{-1} soil or rock.

3.2.4. pH in water (pH_w).

The method used is that given in Avery and Bascombe (1974), where the pH of a 1:2.5 ratio - less than 2 mm, air dry soil and water suspension is determined using a pH electrode and meter.

3.2.5. Estimate of the organic matter content by loss of weight on ignition (L.O.I.).

Many methods are available for the estimation of the organic matter or organic carbon content of the soil (Hesse, 1971), but for the purposes of this work estimation by the loss of weight on ignition was considered to provide a convenient and rapid technique for dealing with the number of samples involved. The technique adopted is that of Avery and Bascombe (1974) where the loss of weight of an oven dry (105°C) sample is estimated after ignition at 375°C for 16 hrs, and was chosen in preference to ignition at 850°C as errors due to the loss of structural waters from clays are minimised (Ball, 1964). As none of the soils studied were calcareous, weight loss due to the destruction of carbonates was considered to be unimportant, however, it was recognised that this technique destroys elemental carbon in addition to organic forms.

An opportunity arose to calibrate the method against one for the determination of organic carbon. This method involved the destruction of carbonates by reaction of the sample with 25% H_3PO_4 for 30 mins in a 100 ml vaccine bottle. The CO_2 produced is flushed out of the bottle with a stream of air before digestion of carbon,with a mixture of chromium trioxide in 80% HNO_3 and saturated phosphorous pentoxide in concentrated H_2SO_4, takes place in the sealed bottle, at 105°C for 1 hr. The concentration of CO_2 evolved is subsequently determined by gas chromatography (Lovell, 1979).

Twenty six samples, representing a range of organic matter contents, in soils from the Llansannan study area, were analysed by both methods and the results are given in Figure 3.1. There is good linear correlation ($r=0.999^{***}$) between the two determinations which can be described by the following regression equation:

Organic carbon (%) = 0.415 L.O.I. (%) - 0.364.

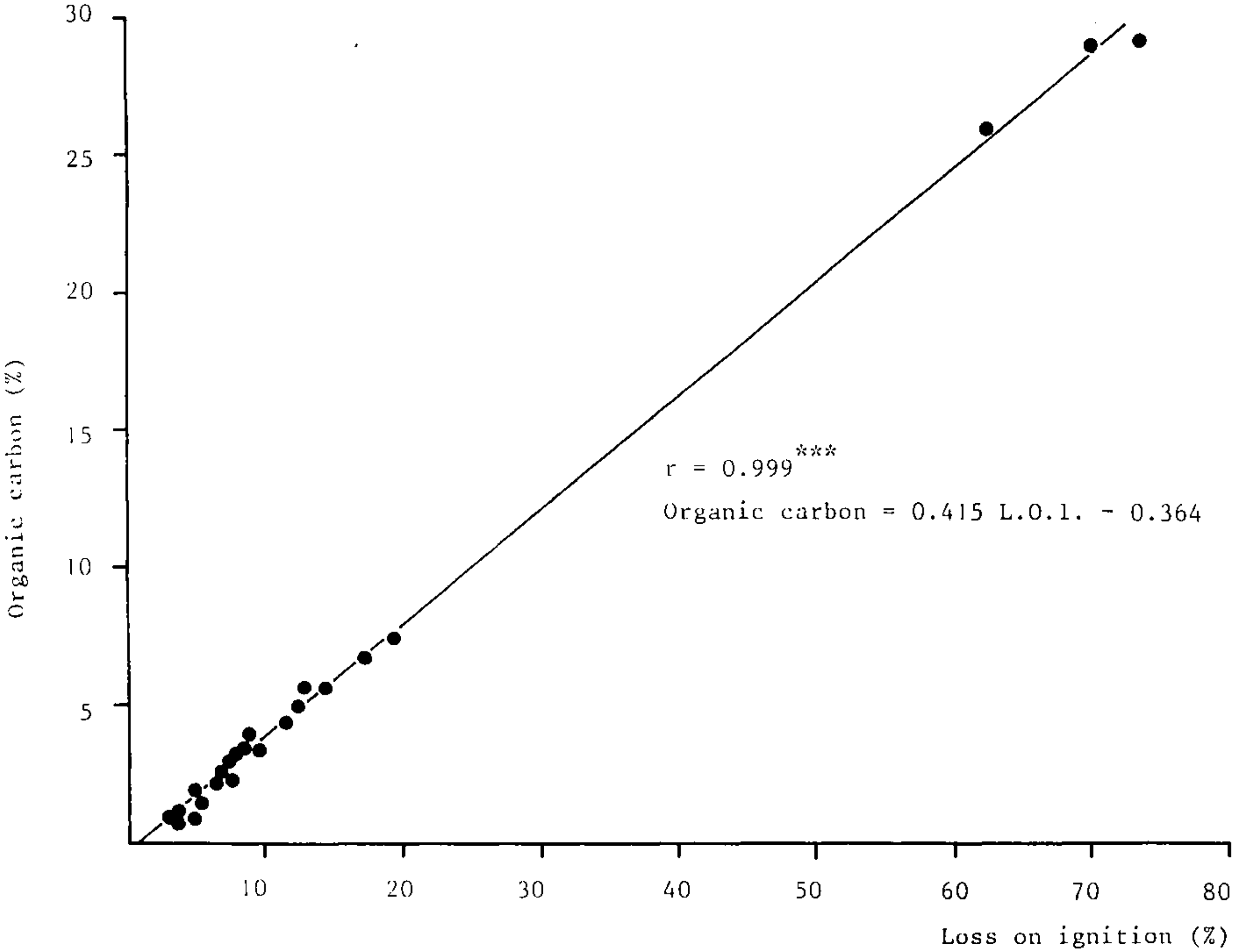


Figure 3.1. Relationship between the organic carbon content and the loss of weight on ignition (L.O.I.) for twenty six soil horizons from the Llansannan area.

This equation compares closely with an equation derived by Ball (1964) for a set of soils from north Snowdonia:

Organic carbon (%) = 0.458 L.O.I. (%) - 0.4

As the relationship between L.O.I. and organic carbon was linear no attempt was made to convert L.O.I. values to percentage organic carbon during the study.

3.2.6. Size fraction separation.

This was an additional technique used in a limited number of soil profiles for the assesment of the contribution of fine and coarse material to the total Se content of the soil.

A representative sample of less than 2 mm, air dry soil was placed in a beaker for 24 hrs with 50 ml, 10% ammonia solution to aid in the dispersion of the clay fraction. The contents of the beaker were transferred to an evapourating basin through a 63 µm seive using a rubber pestle and water to aid the breakdown of aggregates. The contents of the seive were also transferred to an evapourating basin and both the fine (less than 63 µm) and coarse (greater than 63 µm) fractions were dried in a drying cabinet at 20°C. Both fractions were then ground to less than 80 mesh.

3.3. Analytical quality control.

3.3.1. Determination by atomic adsorption and inductively coupled plasma.

The following quality control proceedures were used to assess the accuracy and precision of the results:

i. The use of machine calibrators to monitor machine performance. These were prepared using B.D.H. standard solutions and were made up in a matrix solution similar to that of the samples. They were distributed systematically within, and made up to 10% of the batch.

ii. The use of duplicate analysis of samples to monitor within batch precision (i.e. the reproducibility of the results). In each batch 10% of the samples were analysed in duplicate, and included randomly within the batch. Precision (P) is a function of the coefficient of variation (CV) such that for a normal distribution:

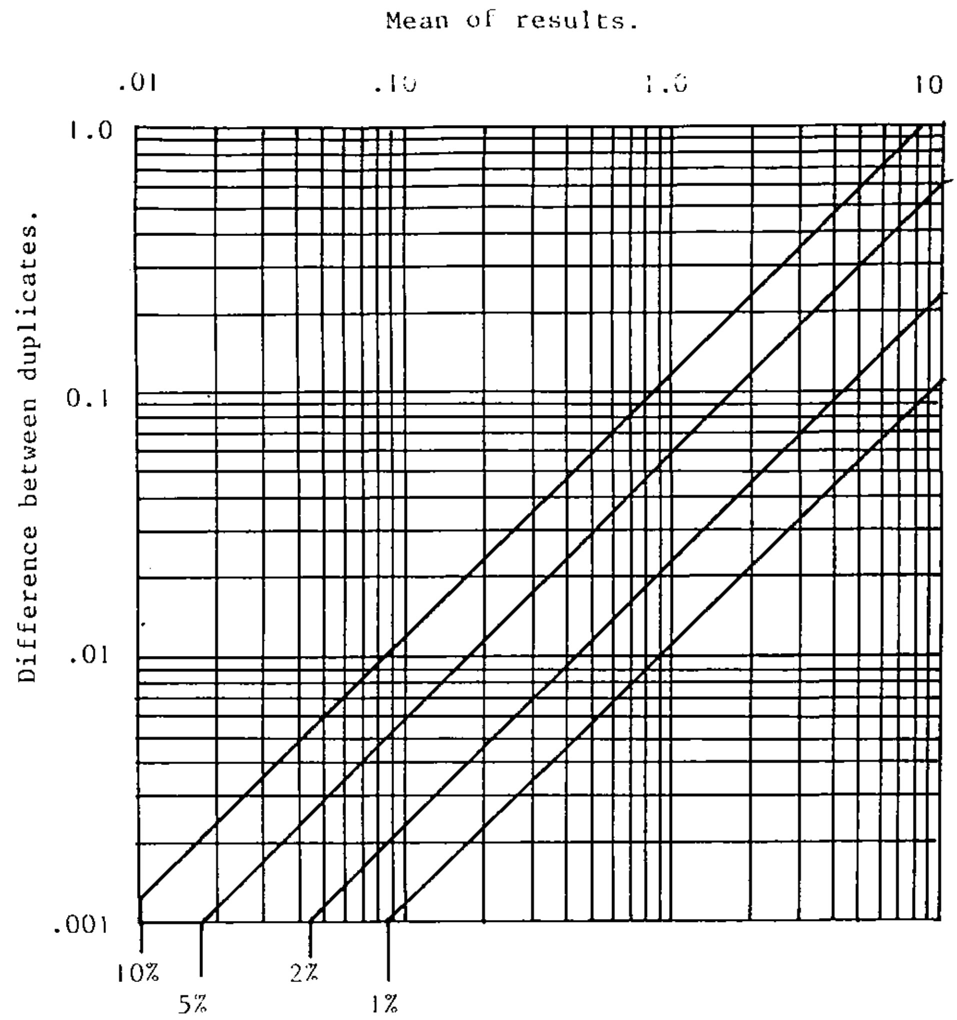
P = F x CV, where F is the confidence limit and is equal to 1 (65%), 2 (95%), etc.

In these analyses F=2 and therefore P = 2 x 100 and so 95% of results fall between 100± P%. This was estimated by the use of precision control charts (Figure 3.2.), 90% of the points plotted on this chart will fall below the diagonal appropriate to the precision at the 95% confidence limit (Thompson and Howarth, 1972).

The results of any one batch of analyses were accepted if the precision was less than, or equal to 10%. Samples were analysed in batches of between 50 and 150 samples, and all the samples within the batch were randomised to ensure that no machine bias would affect any systematic increase or decrease in values obtained in a certain sampling pattern.

iii. The use of departmental standard reference materials, included in each batch to control the between batch bias and the overall bias of results throughout the period of the work. These were again included randomly and made up to 5% of each batch. When available two such reference materials were used to represent high and low value samples. Control charts show the accepted value for each reference material and the range and mean of measured values. Two such charts are shown in Figure 3.3. for reference materials "Weald Loam" and "Lower Lias " which were used during Se analysis of soils and rocks, and represented soils containing low and high concentrations respectively when compared to normally expected values. Mean Se contents were 0.22 $\mu g\ g^{-1}$ for Weald Loam and 0.79 $\mu g\ g^{-1}$ for Lower Lias .

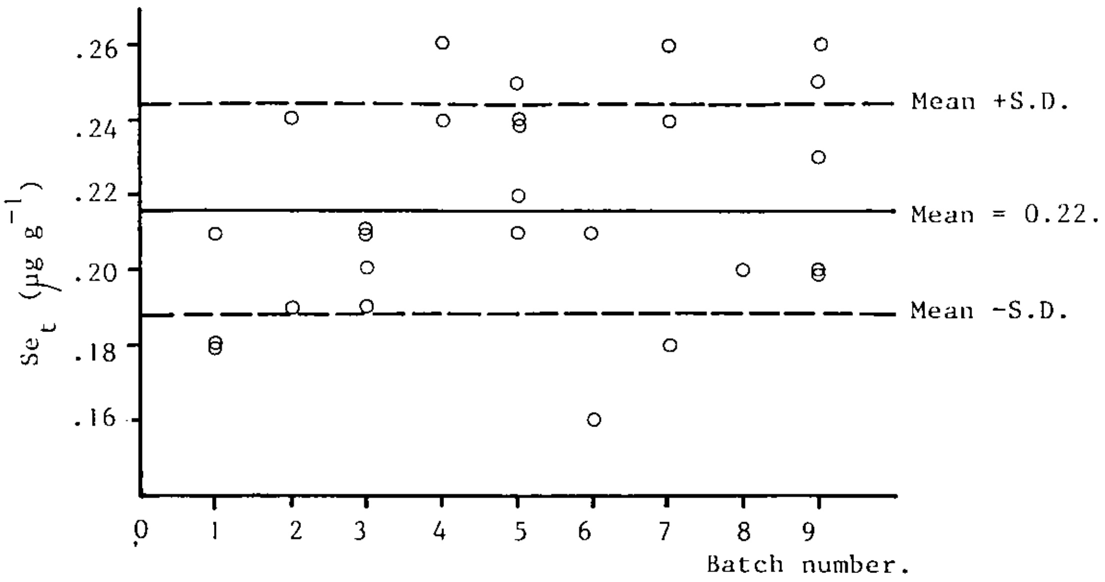
iv. The use of reagent blanks to assess background concentrations and possible contamination errors.



In a set of duplicate measurement on many samples, 90% of the points will fall below the diagonal appropriate to the precision of the measurements at the 95% confidence limits.

Figure 3.2. Example precision control chart used in analytical quality control.

a. Reference material "Weald Loam":



b. Reference material "Lower Lias":

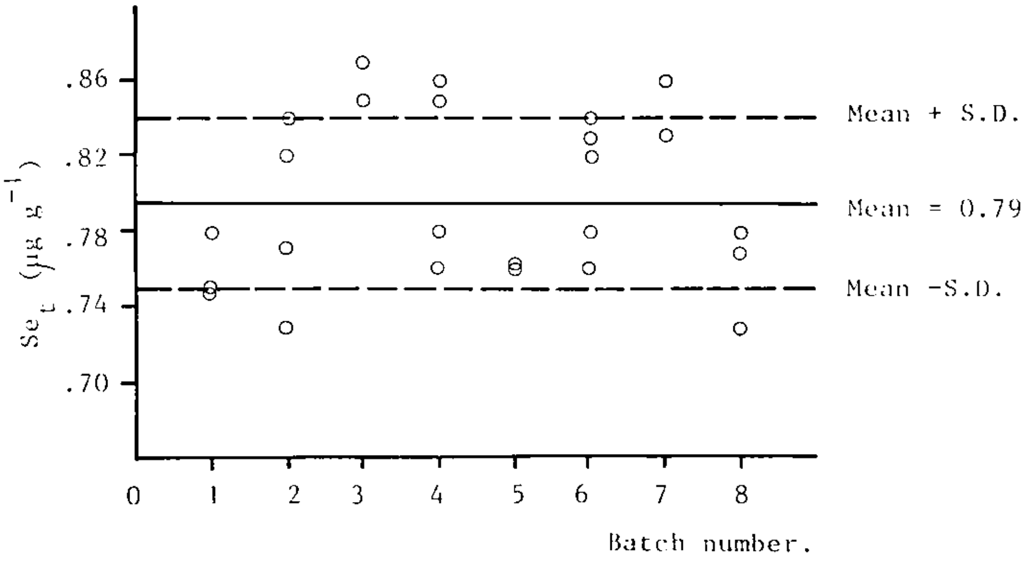


Figure 3.3. Control charts for reference materials used in the analysis of Se_t in soils and rocks.

3.3.2. Determination of pH.

Machine calibrators took the form of standard buffer solutions used to monitor the variations in machine performance. No reagent blanks could be used. Duplicate analyses and a reference material were also included. Batches were normally of 50 samples.

3.3.3. Determination of loss of weight on ignition.

The method used did not allow for the use of machine calibrators or blanks (section 3.2.5.). Duplicate analyses and a reference material were included in each batch which normally contained some 40 samples.

CHAPTER 4. SOILS DEVELOPED ON THE LOWER GREENSAND OF THE WEST WEALD.

4.1. Introduction.

The rocks and soils of the Lower Greensand are known to be inherantly poor in many trace elements, and occurrences of Cu and Mg deficiencies have been reported (Wood, 1975; Jordan, 1975). Considering both these observations, and also those of Blaxter (1963) who demonstrated a response to Se administration in sheep from farms with soils developed from arenaceous parent materials in Scotland, it was considered that soils of the Lower Greensand would provide an example of soils low in Se. The work of Thornton et al. (in press) on British topsoils which is reported in Chapter 2, has already demonstrated that the Se content of soils derived from sandstone (mean=0.38 $\mu g\ g^{-1}$, range=0.01 - 2.11 $\mu g\ g^{-1}$, n=190) is less than that of soils from most other parent materials (mean for all soils=0.48 $\mu g\ g^{-1}$). The sandstone of the Lower Greensand consists of four distinct beds and this study aimed to test, on a more local scale, the existance of a broad relationship between the nature of the soil parent material and the Se content of the soil such as has been reported in other countries (see section 2.9.2.).

Much of the land underlain by the Lower Greensand has been colonised by heath type vegetation, where podzolic soils are commonly developed on these freely draining parent materials. It was considered that the clear redistribution of soil constituents, and especially of sesquioxides and organic matter, in such soils may influence both the distribution and content of Se in their profiles. Additionally, therefore, several podzolic soils were examined in order to investigate such phenomena. Agriculturally this may be important when reclaiming the heathland to productive use; many of the soils of the Lower Greensand now under cultivation having been reclaimed from heathland in the past.

4.1.1. Geology.

The following solid formations are present in the west Weald:

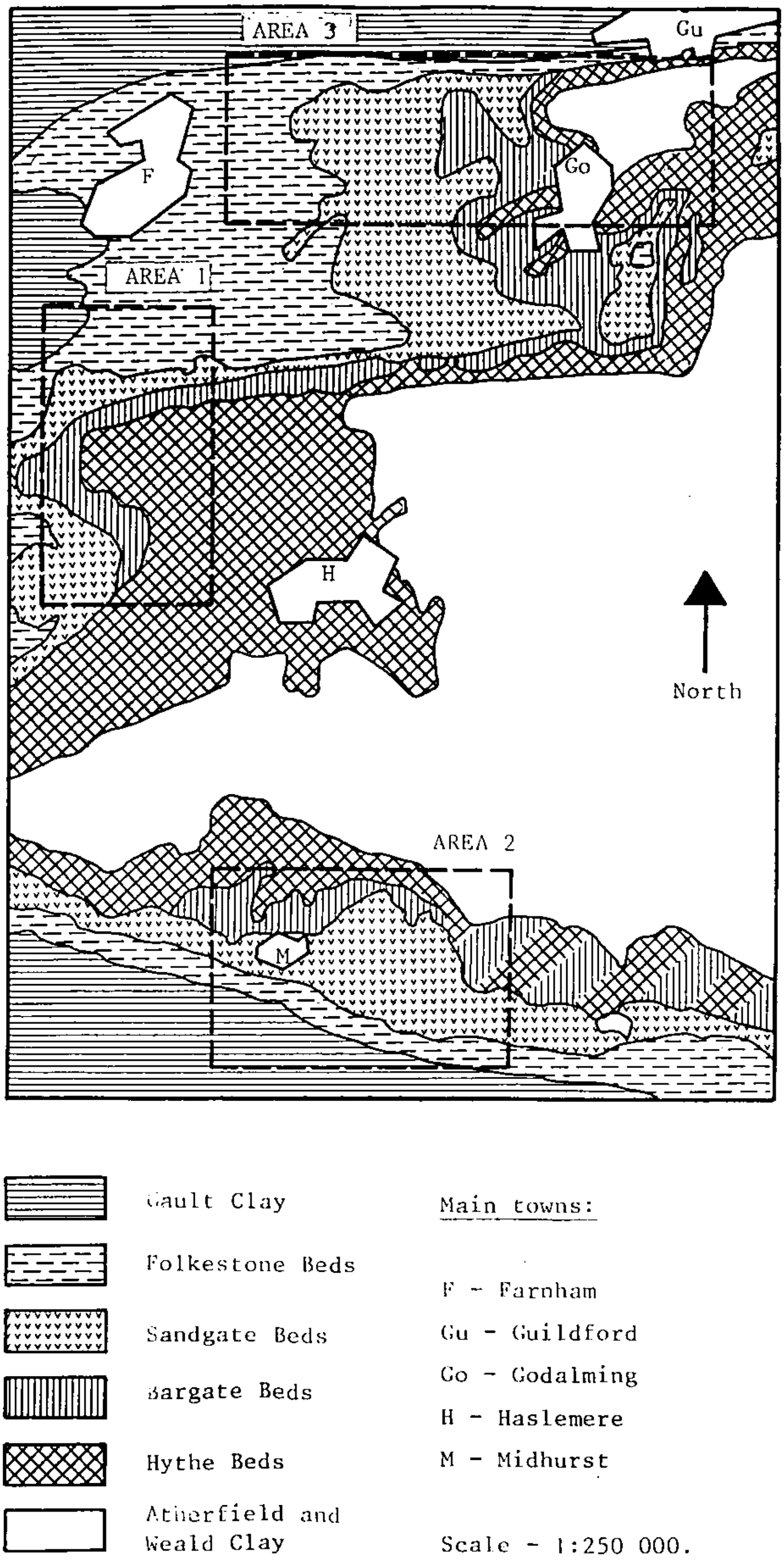
	Chalk.		
	Gault Clay.		
	Lower Greensand,		
		Folkestone beds:	sand.
		Sandgate beds:	clayey sand and iron sand.
		Bargate beds:	sand, calcareous and siliceous sandstone.
Cretaceous		Hythe beds:	sand, siliceous sandstone and chert bands.
		Atherfield clay:	clay and sand.
	Wealden,		
		Weald Clay:	clay and silty mudstone with subsidiary beds of sand, limestone and ironstone.

This study has been concerned with those soils developed on outcrops of the four sandstone beds of the Lower Greensand; the occurrence of these beds in relation to the three sampling areas is shown in Figure 4.1. The geology of the west Weald has been described in detail by Thurrell et al. (1968) and Gallois (1965).

The Lower Greensand formation is predominantly arenaceous but also contains significant small amounts of silty and argillaceous material, in addition to chert, ironstone and calcareous deposits. The formation derives its name from the greenish colour of the fresh rocks, which is due to the presence of glauconite (a dioctahedral iron rich mica); on exposure glauconite is oxidised to limonite, which gives a yellow or reddish brown staining.

The outcrop of the Lower Greensand in the south east of England encircles the outcrop of the older Atherfield clay and the Wealden rocks, and is most extensive in the region of the west Weald. The oldest sandstone beds of the formation are the Hythe beds, which in this region are made up of fine grained glauconitic sands and sandstones. The sands are hardened in the upper part of the formation to beds of compact, non calcareous sandstone, which may be cherty. At approximately 300 ft the beds are at their thickest near Farnham in the north west, and thin towards Midhurst in the south west where they

Figure 4.1. Location of the three sampling areas in relation to the occurrence of the beds of the Lower Greensand.



amount to some 200 ft.

The Bargate beds are discontinuous throughout the Weald but in this region are present to the north of the area around Godalming, Farnham and Haslemere, and also immediately surrounding Midhurst to the south. They consist of glauconitic sands and calcareous sands of variable grade and also include some calcareous doggers, chert and cherty sandstone.

The succeeding Sandgate beds comprise both fine and poorly graded sands which locally include glauconite, limonite, sandy ironstones and clay. In addition, to the south around Midhurst occur the Selham Ironshott Sands which are a loamy sand containing limonite grains.

The Folkestone beds in this region are clearly differentiated into an upper group of coarse sands, including quartz, lydite and ironstone pebbles, and a lower group which consists of fine quartz sand with occasional ill-graded facies; thus they predominantly consist of poorly consolidated quartzose sands. The Lower Greensand is then overlain by the Gault Clay and the Chalk.

Recent and drift deposits in the area consist mainly of head, river gravels and alluvium, which are all of local origin; none of them are, however, extensive and the soils of the area are characteristically formed from the sandstones themselves.

4.1.2. Soils, climate and land use.

The rocks of the Hythe beds, being sandy and largely resistant to weathering, produce a significant upland which in parts presents a well-marked escarpment overlooking the broad lowlands of the Weald Clay. This can be seen in the vicinities of Blackdown, near Haslemere, and at Telegraph Hill to the south which rise to 280 m and 208 m respectively. At the foot of the Hythe dip slope the Bargate and Sandgate beds form a vale over which the Folkestone beds rise in a low escarpment, towards the foot of the Chalk downs.

Soils developed on the outcrop of the Lower Greensand are characteristically coarse textured and well drained; variations in soil type are due largely to differences in the lithology of the parent material.

Detailed surveys of the soils of the Lower Greensand have to date only been undertaken in Kent (Fordham and Green, 1973; Green and Fordham, 1973) however, the occurrence of soils in the west Weald has been extrapolated from such information by McRae and Burnham (1975); they differ from those in Kent by being generally less fertile due to a lesser frequency of loamy drift cover and calcareous facies within the beds.

The sandstone facies of the Hythe and Folkestone beds give rise to a soil association of podzols, brown earths and brown sands. The coarser, most leached soils in general have been colonised by heath and woodland, which has resulted in the podzolisation and further impoverishment of the soils. Such soils are represented primarily by the humo-ferric podzols of the Hothfield series, but there are occurrences of cherty humo-ferric podzols of the Southampton series developed on the sandy flint gravel overlying some of the Folkestone beds. Agricultural soils on such parent materials will be predominantly sandy brown earths of the Bearsted series. Often on Hythe beds these soils may grade into brown earths with signs of podzolisation and true brown podzolic soils (unnamed). Occasionally within this association, on less sandy facies and where there is a thin drift cover, coarse loamy and loamy argillic brown earths of the Barming and Stone Street series occur.

Such finer textured Barming and Stone Street soils comprise the main soils of an association which is developed mainly on the outcrop of the Bargate and Sandgate beds. Within this association are also minor occurrences of Bearsted and Hothfield series soils on the coarser outcrops. This association produces land of mixed quality, with the deeper soils on more level ground being used for intensive agriculture and horticulture. In contrast to the former association the frequency of heath and woodland is less marked. However, soils under such vegetation, although of inherant low fertility, are capable of a good response to applied fertilizers when reclaimed and brought into cultivation. The former association gives rise to an area mainly of heath and woodland with infrequent occurrences of poor quality agricultural land on the acid brown earths. The predominant soil series of the west Weald are summarised in Table 4.1.

Table 4.1. A summary of the main soil series which occur on the Lower Greensand of the west Weald.

Soil series.	Soil Group/Subgroup.	Occurrence.
Bearsted.	Sandy brown earth.	Agricultural areas on sandy facies of Folkestone and Hythe beds. Coarser facies of Sandgate and Bargate beds.
Hothfield.	Humo-ferric podzols.	Heathland on sandy facies of Folkestone and Hythe beds. Less frequently on coarse facies of Sandgate and Bargate.
Southampton.	Cherty humo-ferric podzols.	Infrequent, on sandy flint gravel over Folkestone beds.
Barming.	Coarse loamy and loamy argillic brown earths.	Mainly on the outcrop of Bargate and Sandgate beds. Less frequently on finer facies of Folkestone and Hythe beds, or where there is a thin drift cover.
Stone Street.	Argillic brown earths.	
Unnamed.	Brown podzolic soils.	Sandstone facies of Hythe beds.

Mixed farming and forestry are the main agriculture-related industries of the area. The natural tendency for the heathland to be colonised by trees and shrubs has been used to advantage in the planting of stands of conifers. Arable cultivations are more widespread on the better soils of the Bargate and Sandgate beds. There has been and still continues to be reclamation of podzolised heath soils, which commonly involves amelioration with large amounts of organic matter, lime and other fertlizers.

The presence of glauconite in many of these soils is believed to ensure a relatively high fertility, especially in respect to potassium. Jordan (1975) has noted that reclamation, involving liming, of strongly leached podzolic soils could possibly lead to induced deficiencies of Mn and Zn; also low total concentrations of Cu and Mg in the soils can cause deficiencies of these trace elements in cereals, and potatoes respectively, especially after liming.

4.2. Sampling and analysis.

Topsoil samples were collected in December, 1979 and January, 1980. The bulked topsoil sample at each sampling site consisted of between ten and fifteen single, 0-15 cms auger samples which were taken in a "W" transect over an area of rough ly 50 m x 50 m. All the samples were taken from sites on agricultural land under permanent pasture or arable ley which were shown to be free from drift on the drift geology map (it was recognised that this did not preclude the presence of thin drift coverings).

Within the region of the west Weald three small sampling areas were selected which represented the northern arm, southern arm and westmost portion of the outcrop of the Lower Greensand (Figure 4.1.). In each area five samples were taken from each of the four constituent arenaceous beds of the Lower Greensand, giving a total of 60 samples.

Soil profiles were sampled by digging a profile pit and collecting material from a cleaned face with a small trowel. Both topsoil and profile samples were analysed for the following parameters as given in section 3.2: pH_W, pH_{Ca}, Se_t, Fe_t, Al_t, Mn_t, Ca_t, Mg_t, Fe_p, Al_p and L.O.I.

The topsoil sampling scheme as outlined above was adopted so that a comparison could be made both of soils from the four beds and from different outcrops of the Lower Greensand within the region.

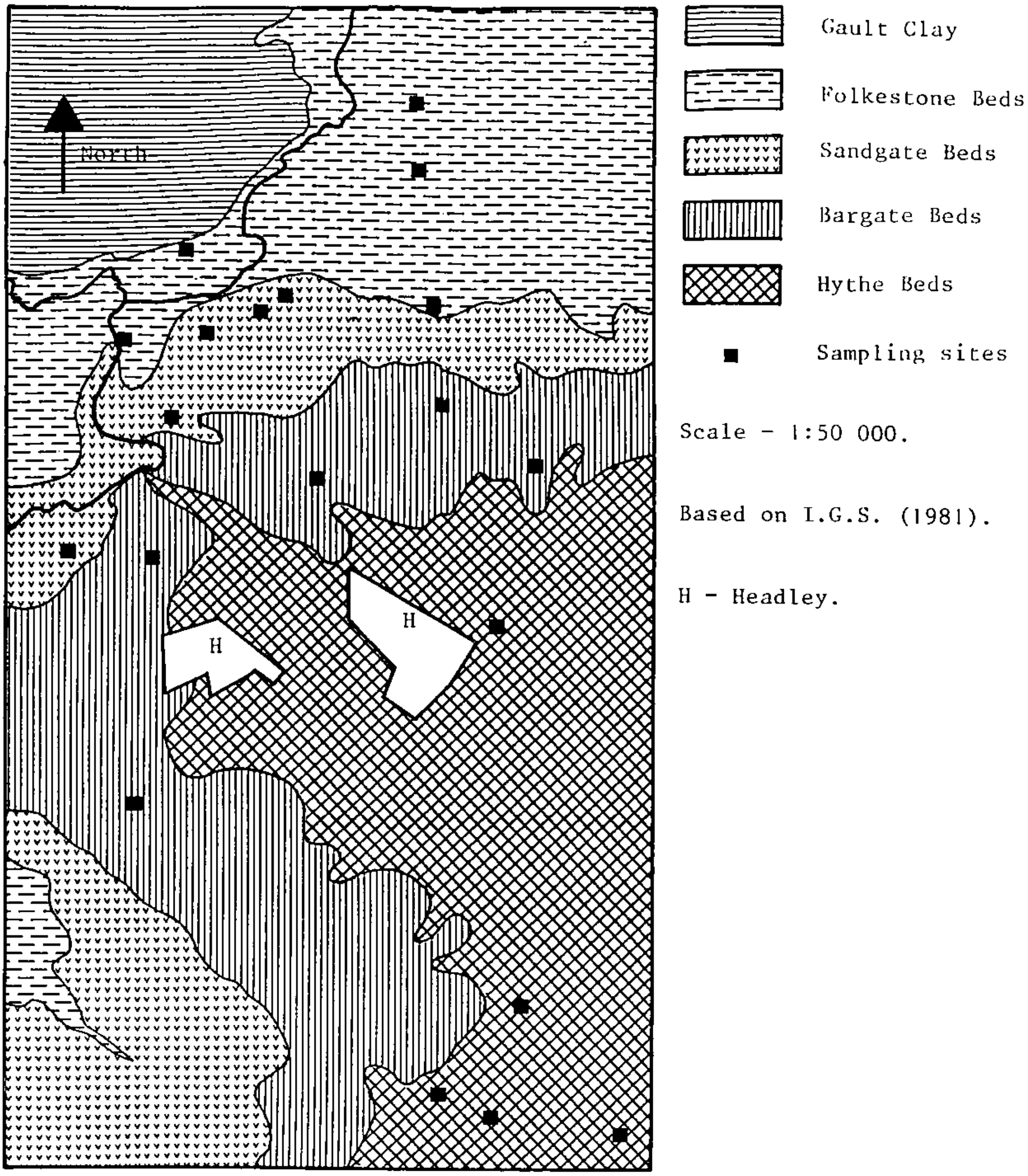
4.3. Results and discussion.

4.3.1. Topsoil sampling.

The position of all sampling sites in the three areas, in relation to the outcrop of the beds of the Lower Greensand, is shown in Figures 4.2., 4.3. and 4.4. Analytical results for Se_t and other parameters are given in Appendix 2.1.1. The Se_t concentrations are low (mean = 0.14 $\mu g\ g^{-1}$, range = 0.06 - 0.26 $\mu g\ g^{-1}$, n = 60) compared to both the overall mean soil Se concentration (0.48 $\mu g\ g^{-1}$) and the mean Se concentration for soils developed on sandstones (0.36 $\mu g\ g^{-1}$) which are reported in section 2.9.3. for British soils. Similarly, Wood (1975) reported that concentrations of Cu, Co, Mn and Zn in soils were significantly lower on the Lower Greensand than in sandstone derived soils from Britain; also Jordan (1975) reported that sediments in streams draining the Lower Greensand contained very low concentrations of Mn, Zn, Cu and Mg.

The mean Se_t concentration of those soils developed on the Sandgate beds (0.19 $\mu g\ g^{-1}$) is significantly higher than that of any of the three remaining beds (overall mean = 0.13 $\mu g\ g^{-1}$, Table 4.2.). Similarly Fe_t and Al_t concentrations are higher in the soils from the Sandgate beds. In contrast, there is no significant difference between the mean Se_t concentrations for the soils of each sampling area. When all parameters are considered for the three areas, only the higher mean Fe_t concentration for area 3 (1.87%) is significant, means for area 1 and area 2 being 1.05% and 0.99% respectively (Table 4.3.).

The mean concentrations of Fe_t and Se_t for each bed in each area show that soils on the Sandgate beds contain consistantly higher concentrations compared to the three remaining beds, with those soils on the Bargate beds being generally more Fe_t and Se_t rich than those on the Folkestone and Hythe beds (Table 4.4.). It can also be seen that

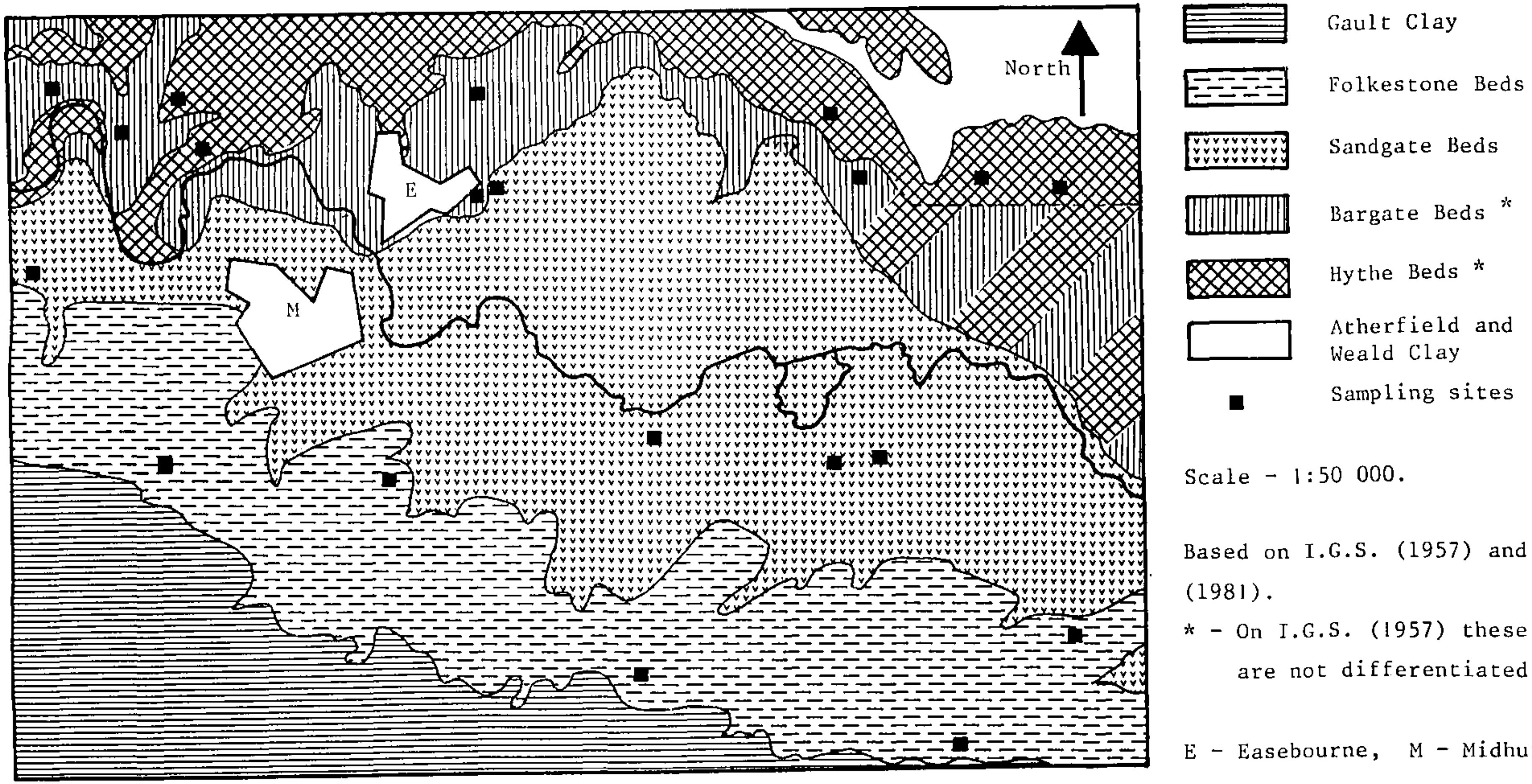


Scale - 1:50 000.

Based on I.G.S. (1981).

H - Headley.

Figure 4.2. Area 1: relation of sampling sites to the outcrop of the Lower Greensand.



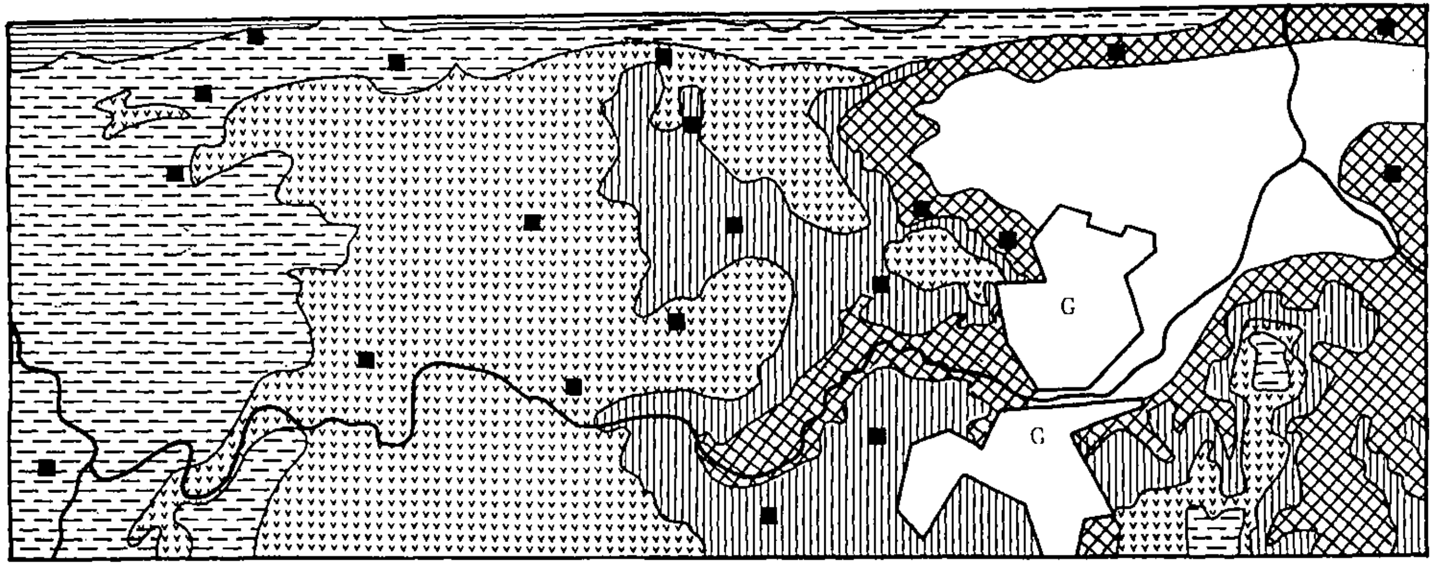
Scale - 1:50 000.

Based on I.G.S. (1957) and I.G.S. (1981).

* - On I.G.S. (1957) these two beds are not differentiated.

E - Easebourne, M - Midhurst.

Figure 4.3. Area 2: relation of sampling sites to the outcrop of the Lower Greensand.



▤ Gault Clay

▭ Folkestone Beds

▨ Sandgate Beds

▥ Bargate Beds

▦ Hythe Beds

☐ Atherfield and Weald Clay.

■ Sampling sites.

Scale - 1:75 000.

G - Godalming.

North.

Based on I.G.S. (1976).

Figure 4.4. Area 3: relation of sampling sites to the outcrop of the Lower Greensand.

Table 4.2. Mean soil concentrations of nine variables for each of the four beds of the Lower Greensand.

Variable.	Hythe.	Bargate.	Sandgate.	Folkestone.
pH_w	6.30^a	6.30^a	6.60^a	6.30^a
Se_t	0.12^a	0.13^a	0.19^b	0.13^a
Fe_p	0.09^a	0.09^a	0.11^a	0.11^a
Mn_t	353^a	534^a	360^a	162^b
Fe_t	0.93^a	1.23^a	2.10^b	0.96^a
Al_t	0.22^a	0.25^{ab}	0.32^b	0.19^a
Ca_t	0.18^a	0.23^a	0.17^a	0.34^a
Mg_t	0.030^a	0.036^a	0.035^a	0.028^a
L.O.I.	3.31^a	3.23^a	3.59^a	4.79^b

Means in the same row with the same super-script letters are not significantly different (at $p < 0.05$).

Table 4.3. Mean soil concentrations of nine variables for each of the three sampling areas on the Lower Greensand.

Variable.	Area 1.	Area 2.	Area 3.
pH_w	6.18^a	6.36^a	6.57^a
Se_t	0.13^a	0.15^a	0.14^a
Fe_p	0.09^a	0.12^a	0.09^a
Mn_t	300^a	308^a	447^a
Fe_t	1.05^a	0.99^a	1.87^b
Al_t	0.21^a	0.25^a	0.27^a
Ca_t	0.15^a	0.24^a	0.29^a
Mg_t	0.026^a	0.033^a	0.039^a
L.O.I.	3.43^a	4.05^a	3.71^a

Means in the same row with the same superscript letters are not significantly different (at $p = 0.05$).

Table 4.4. Mean Se_t and Fe_t concentrations for soils from each bed and each area of the Lower Greensand.

Area.	Element.	Bed				Area Mean (n=20)
		Folkestone.	Sandgate.	Bargate.	Hythe.	
Area 1.	Se_t	0.10	0.18	0.12	0.12	0.13
	Fe_t	0.96	1.68	0.98	0.58	1.05
Area 2.	Se_t	0.15	0.20	0.14	0.13	0.16
	Fe_t	0.52	1.91	0.86	0.70	0.99
Area 3.	Se_t	0.13	0.20	0.15	0.10	0.15
	Fe_t	1.39	2.72	1.87	1.50	1.87
Bed Mean (n=15)	Se_t	0.13	0.19	0.13	0.12	0.14*
	Fe_t	0.96	2.10	1.23	0.92	1.30*

All means are for n = 5.

* Overall mean for all samples (n = 60).

the higher Fe_t concentrations for area 3 apply to each bed of that area. Also although the differences are not significant, there is a tendency for mean concentrations of all the trace elements studied, with the exception of Se, that is Fe, Al, Mn, Ca and Mg to be higher in area 3 (Table 4.3.).

Soils developed on the Folkestone beds have a significantly higher organic matter (L.O.I.) content than those on the other beds (Table 4.2.). This is perhaps best explained by the greater proportion of samples which were taken from permanent pasture, as opposed to arable leys, on the Folkestone beds; thirteen of the fifteen samples were taken from permanent pasture, as compared to seven, nine and six on the Sandgate, Bargate and Hythe beds respectively. It would be expected that topsoils under permanent pasture are more humose than those under arable cultivation. These proportions of soils under permanent and temporary grass are not necessarily representative of the actual proportions which exist on each of the four beds, however, it has been noted that arable cropping is more widespread on soils of the Bargate and Sandgate beds (Thurrell et al., 1968). Despite the reported associations between organic matter accumulation and the accumulation of Se (see section 2.3.), the Se_t concentration of the soils on the Folkestone beds are not correspondingly elevated.

As no other trends are apparent in the data, it would appear possible that the reason for the higher mean Se_t concentrations of the soils from Sandgate beds is due to the higher Fe and possibly Al contents; especially as both these elements have been shown by other workers to play important roles in the chemistry of Se in the soil, predominantly in providing a site for selenite adsorption (Geering et al., 1968; John et al., 1976; Howard, 1977). However, if such a relationship exists it is complicated by the fact that the higher mean Fe_t concentrations of the soils from area 3 are not complemented by a significantly higher mean Se_t concentration. Wood (1975) suggested that the source of several trace elements, including Fe, in the soils of this area was their parent material; if this relationship holds for Se then it is possible that on deposition of the sediments, the input of Se was independent of that of Fe. Such a possibility was postulated by Fletcher (1968) in the formation of Se rich Carboniferous rocks in Derbyshire. It is not feasible, without examination of the actual parent materials, to draw any firm conclusions on this idea.

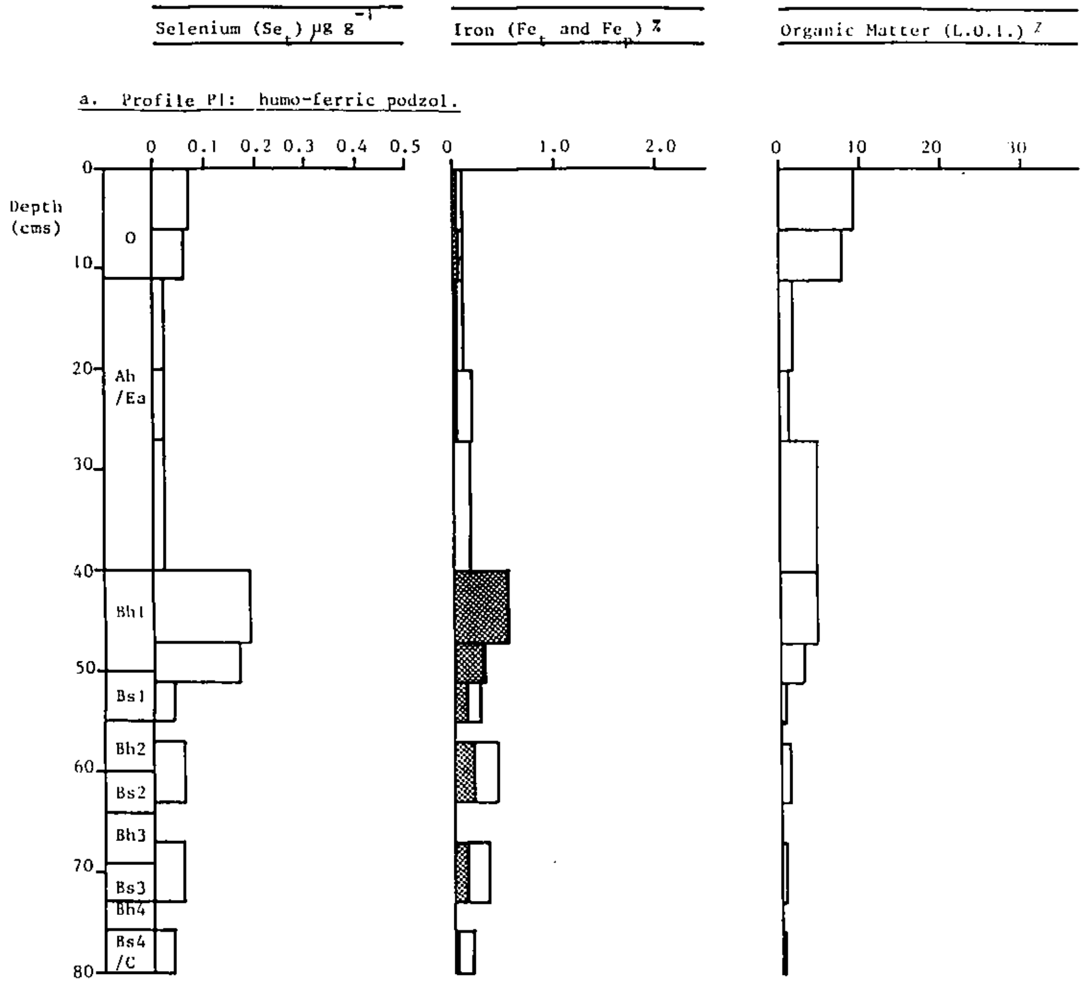
It is also conceivable that much of the Se in these soils has been derived from additions of fertilizers, manures and other ameliorants which have been added to the soils in the course of cultivations. This becomes more pertinent when it is considered that the processes of leaching and podzolisation, which are dominant in the soils under the semi-natural vegetation of the area, result in a substantial impoverishment of the Se content of the soil (see section 4.3.2.). Inputs of such as superphosphate and sulphate of ammonia often contain significant amounts of Se (section 2.6.5.), and it has been shown that rainfall can contribute a small but identifiable input of Se to the soil (Cawse, 1980). In relation to such inputs, the quantities of Fe and Al in the soil, which are implicated in the adsorption and retention of Se in the soil, would be important. It would be expected that the more Fe and Al rich soils would retain more Se against leaching losses, as adsorbed species.

4.3.2. Podzol profiles.

The five profiles presented here are all developed under either the characteristc heathland or coniferous woodland of the area, which occur primarily on the outcrops of the Hythe and Folkestone beds (profile and site descriptions are given in Appendix 1.1.). Such land accounts for approximately 30% of the total area in the three sampling areas, so although they are not of direct importance to agriculture these soils constitute an important proportion of the soils of the region. The five differing soils were chosen to represent the variations in soil type which may be encountered on the heathland developed on the Lower Greensand. Data for these soils is given in Appendix 2.1.2. and profile diagrams, showing the distribution of Se_t, Fe_t, Fe_p and L.O.I. are presented in Figure 4.5.

The distribution of Se_t between the characteristic horizons of these five profiles is essentially similar, and is perhaps best described by first considering profile P2. The Se_t has accumulated, relative to the rest of the profile, in both the O and Bs/Bh horizons. This distribution, when the other data presented are considered, can be seen to correspond to an accumulation of organic matter (represented by L.O.I.) in the O horizon, and to an accumulation of Fe and Al in

a. Profile P1: humo-ferric podzol.



b. Profile P2: humo-ferric podzol.

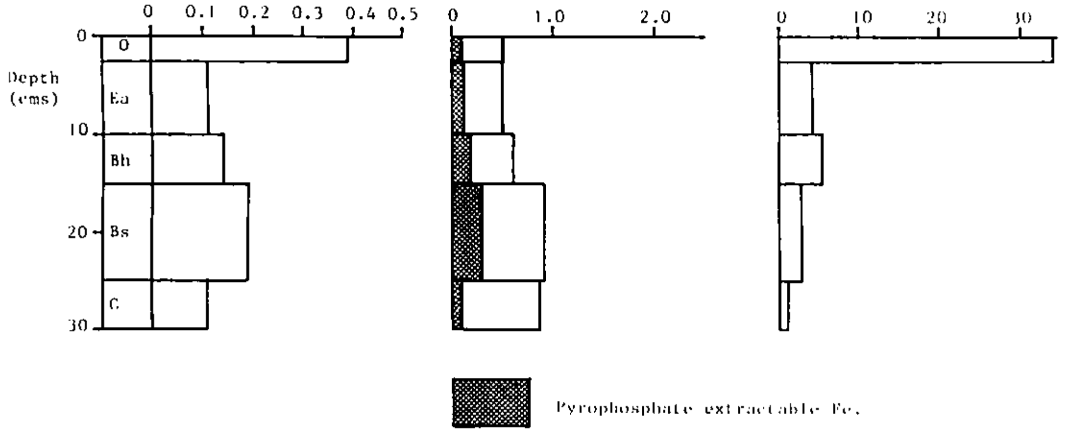
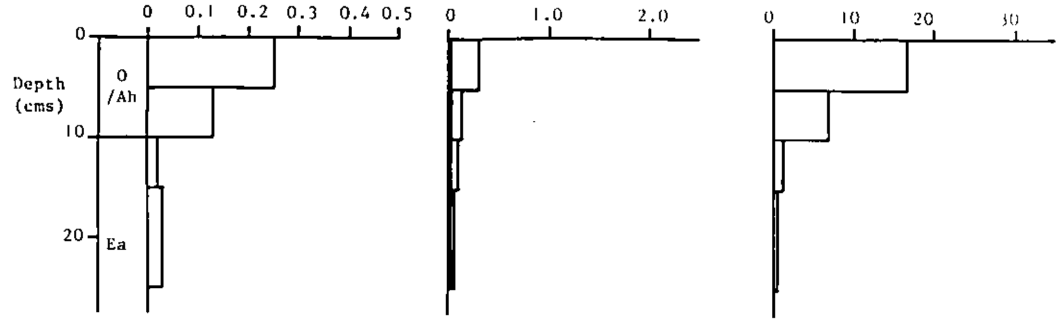


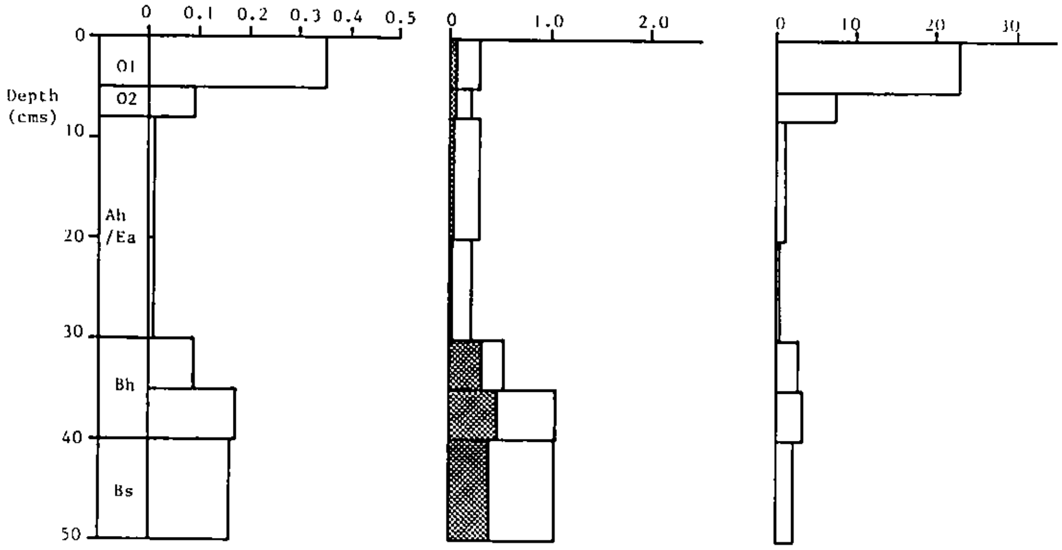
Figure 4.5. Distribution of Se_t, Fe_t, Fe_p and organic matter (L.O.I.) in podzolic soil profiles from the west Weald.

Selenium (Se_t) µg g^{-1} Iron (Fe_t and Fe_p) % Organic matter (L.O.I.) %

c. Profile P3: humo-ferric podzol?



d. Profile P4: humo-ferric podzol.



e. Profile P5: Humus ironpan stagnopodzol.

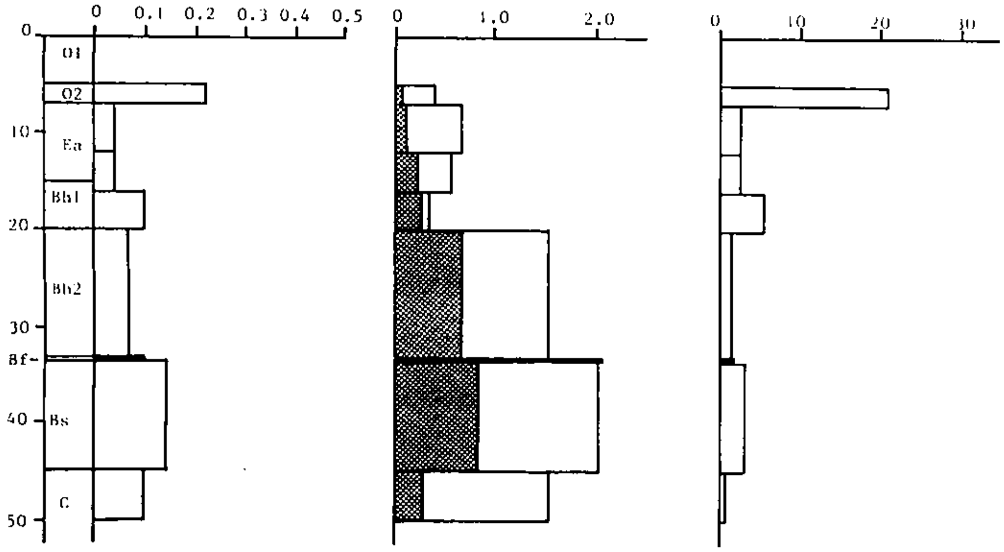


Figure 4.5. (Continued).

the Bs/Bh horizons. This basic pattern of Se distribution in podzols has also been reported for examples from New Zealand, Canada and Finland (Wells, 1967; Levesque, 1974a; Koljonen, 1975). It would seem probable that in the O horizon, Se is present both as a constituent of decomposing plant remains, where it would occur primarily in seleno-forms of the sulphur amino acids (Peterson and Butler, 1962), and also in combination with organic colloids in the humified fraction. Combination with humic acids, which are predominantly negatively charged, would require the presence of a multi-valent cation, such as Fe or Al, to act as a bridge with the negatively charged selenite ion; such a complex has been postulated by Levesque (1974b). However, despite a relative accumulation of Se in the organic topsoils of these soils, when compared with other organic soils the Se concentrations (mean = 0.22 $\mu g\ g^{-1}$) are very low (the mean Se concentration of organic soils in a survey of British soils (Thornton et al., in press) was 1.20 $\mu g\ g^{-1}$, n = 30) reflecting the poor supply of the element from a parent material which is inherantly low in Se.

Below the organic topsoil the distribution of Se closely follows that of the Fe_t in the profile, and more closely that of Fe_p. Consequently the leached, colloid poor, eluvial Ea horizon contains little Se; this relationship is more accute in profiles P1, P3 and P4, whose Ea horizons also contain less Fe and Al than that of profile P2. The relatively high organic matter (L.O.I.) content of the Ea horizon sample from profile P2 suggests that there is some accumulation of organic material in this horizon, and it is possible that a poorly defined Ah horizon exists towards the top of the Ea, material from which has been incorporated in the sample. Such a horizon exists in profiles P1, P3 and P4, and their Se_t content is probably associated with the organic matter.

Beneath the Ea horizon is the illuvial zone, and both the Bh and the subordinate Bs horizons are enriched in Se. For all the profiles examined the most Se rich horizon is that with the highest Fe_t content, for profile P2 this relates to the Bs horizon, since in this profile there is clear differentiation of the Bs and Bh horizons, being horizons of greatest Fe and organic matter accumulation respectively. In profiles P1 and P4, however, the greatest accumulation of organic material and Fe occurs in the same horizon, which is also the horizon of greatest Se accumulation. It is also noticeable that in these two profiles the

Fe_p:Fe_t ratio of the illuvial horizon is greater, approaching unity in both cases. In these instances therefore, it is almost certain that the Fe with which the Se is associated , probably as a selenite - ferric oxide adsorption complex, is present as an organic complex or has been precipitated from such a complex and is represented by that Fe which is extracted by potassium pyrophosphate (Bascombe, 1968). This observation, however, sheds little light on the mode of redistribution of the Se within the soil. It is thought that Fe is mobilised as a ferrous iron - organic complex, and as such would not be expected to be associated with Se, as the ferrous ion has not been demonstrated to have any affinity for the selenite ion. Levesque (1974a) postulated that, because of the association of Se, organic matter and the reactive forms of Fe and Al in spodic horizons, it was possible that organic matter - Fe or Al complexes could be implicated in the migration of Se. It is conceivable that as Fe is reduced and mobilised, selenite is released into solution and then leached down the profile to be adsorbed on ferric oxides which have been precipitated in the Bs and Bh horizons; but unlikely that Se is mobilised in the form of an organic - Fe or Al - Se complex. The formation and transport of the soluble selenate anion would not be possible in the acid conditions which are found in these soils, where the pH was never more than 4.75 (see Figure 2.2.).

As there is a close relationship between the distribution of Fe and Al in these profiles it is not possible to say whether the Se is preferentially associated with either element, and indeed, as peaks in the Al concentration coincide with those of Fe, Al could also be implicated in influencing Se distribution. John et al. (1976) found that free forms of Al were important in the adsorption of selenite by some New Zealand soils, but noted that Se apparantly has a stronger affinity for ferric oxides. Thus in this situation, considering the lower concentrations of Al_p compared to Fe_p, it is possible that Fe is more important in determining the Se distribution.

Much of the evidence presented here, and elsewhere, points to the cycling of Se within the soil (Shrift, 1964; Koljonen, 1975). Plant uptake of Se, probably as soluble selenite, and the subsequent build up of old plant material at the surface, results in the accumulation of Se in the organic topsoil. Selenite would be brought into solution when ferric iron, with which it is associated, is reduced and mobilised; such processes can take place from the base of the O horizon, from the Ea, or even within the Bh and Bs horizons themselves. Small concentrations of selenite would innevitably exist in solution, in equilibrium with the adsorbed phases on the soil colloids.

In these sandy soils leaching has been intense and the Ea horizon contains less Se than the C horizon at depth; this is in contrast to the podzols studied by Levesque (1974a) where the Se concentrations in the two horizons were comparable. The soils are also much depleted of bases (represented by Ca_t and Mg_t, see Appendix 2.1.2.). Profile P3 demonstrates the extreme leaching which may be encoutered in the soils of this area. Below a thin peaty topsoil, and an indistinct Ah horizon, is a deep Ea horizon, which although only sampled to 25 cms, was found to continue to more than 90 cms depth. In these five profiles the base of the Ea horizon varied between 10 and more than 90 cms. Thus reclamation of these soils to agricultural use could lead to the production of a varied topsoil, dependant very much on the depth of ploughing. Although the organic topsoils contain relatively high concentrations of Se_t, this would be diluted by mixing with the Ea which is impoverished with respect to Se_t. Subsequent liming of these acid soils would lead to more favourable alkaline conditions in which humification and mineralisation of organic matter would proceed more quickly, and some loss of Se bound in organic combination would ensue. In the case of the shallower soils ploughing would result in the mixture of Bh and Bs horizons also, which would increase both the Se content of the topsoil, and its content of colloidal sesquioxides which would be important in the retention of the Se in the soil.

4.4. Conclusions.

Consistent with their low content of other trace elements, this work has shown that the Se content of the soils developed on the arenaceous beds of the Lower Greensand is low (mean = 0.14 $\mu g\ g^{-1}$). Whether such soils might produce vegetation which is deficient in Se (normally considered to be less than 0.01 $\mu g\ g^{-1}$ d.m. (Rickaby, 1980)) is difficult to say without further study of the actual pasture herbage Se content. However, Watkinson (1962) demonstrated a frequent response to Se administration in animals grazing pasture on soils containing less than 0.45 μg Se g^{-1} in New Zealand; and it has also been stated that where rocks low in Se decompose to form soils under humid or dry conditions, the plants growing on them are likely to contain insufficient Se to protect livestock from Se deficiency, and that this is more probable the more acid the soil (Allaway, 1971). Using these criteria and considering that the soils tend towards being acidic (mean pH_W = 6.35), it is possible that Se deficiency could be a problem in this area. This said, however, it must be noted that the occurrence of livestock rearing in this area is not widespread, and that the occurrence of Se deficiency in livestock will also depend on the relative consumption of local-grown and imported feeds.

In agreement with the work of Wells (1967) this study has shown that podzolisation can result in the significant depletion of Se from the topsoil, which is especially prominent when the inherant concentration of Se in the parent material is already low. It has also been said that podzolisation and acidity of soils will lead to potentially more Se deficient soils (Koljonen, 1975). This observation prompted the concept that a large part of the Se content of the cultivated soils on the Lower Greensand, which may have been previously leached and podzolised, could be derived from outside sources and not neccessarily purely from the parent material.

The work has shown that there is a significant difference between the Se content of soils derived from the Sandgate beds and that of those on the other three beds, and this has been related to the higher Fe and Al contents of these soils because of the important role played by these elements in the chemistry of Se in the soil (section 2.3.). This has not, however, been taken to be conclusive evidence that the differences in the Se content of the soils are due to differences in the Se content of the parent materials, which in turn is related to the Fe and Al contents. The reason for the lack of higher Se concentrations in the uniformly more ferruginous soils of area 3 on the northern outcrop of the Lower Greensand is unclear, and the problem requires further investigation involving the sampling of the parent materials themselves.

Relationships between soil series and the Se content of the soil would have to be qualified by reference to specific parent materials. Thus although soils on all soil series common to the area are low in Se, those of the Barming and Stone Street series developed on the Sandgate beds will contain marginally higher Se_t concentrations.

CHAPTER 5. SOILS DEVELOPED ON THE CARBONIFEROUS SYSTEM IN N.E. STAFFORDSHIRE AND S.W. DERBYSHIRE.

5.1. Introduction.

Geochemical interest in this area began in the 1960's when it was found that anomalously high molybdenum concentrations in the soils and herbage were inducing the widespread occurrences of hypocuprosis in grazing livestock (Webb et al., 1968). The source of the Mo was traced to Carboniferous marine black shales. Following findings in Ireland that such Mo-rich black shales were also enriched in Se, the rocks, soils and herbage of the area were analysed for Se and it was found that the same associations existed (Fletcher, 1968). This was reported as the first recorded occurrence of seleniferous soils in the U.K.; these were primarily waterlogged soils in low lying sites, having Se concentrations between 1.5 and 7.0 μg Se ml^{-1} (Webb et al., 1966). Thornton (1968) reported that suspected cases of Se toxicity in livestock have been encountered in the area, but that the problem was not thought to be serious.

The area was chosen for the present study because of the occurrence of soils high in Se; the aim of the work being to assess how the Se distribution in soils may be affected by development on parent materials rich in Se, and also to see if the variability in the Se content of the various local parent materials was reflected in the Se content of the largely poorly drained soils of the area.

Two transects have been sampled, the first is at Bent Farm, Tissington, Derbyshire and is of soils developed on a hillside which is underlain by marine black shales; the second is in the locality of Mixon and Butterton Moor in N.E. Staffordshire and covers soils developed on several contrasting parent materials (Figure 5.1.).

5.1.1. Geology.

The geology of the area, with particular reference to the formation of the marine black shales, has been reviewed fully by Fletcher (1968). The geology of the region is depicted in Figure 5.1. and the stratigraphy

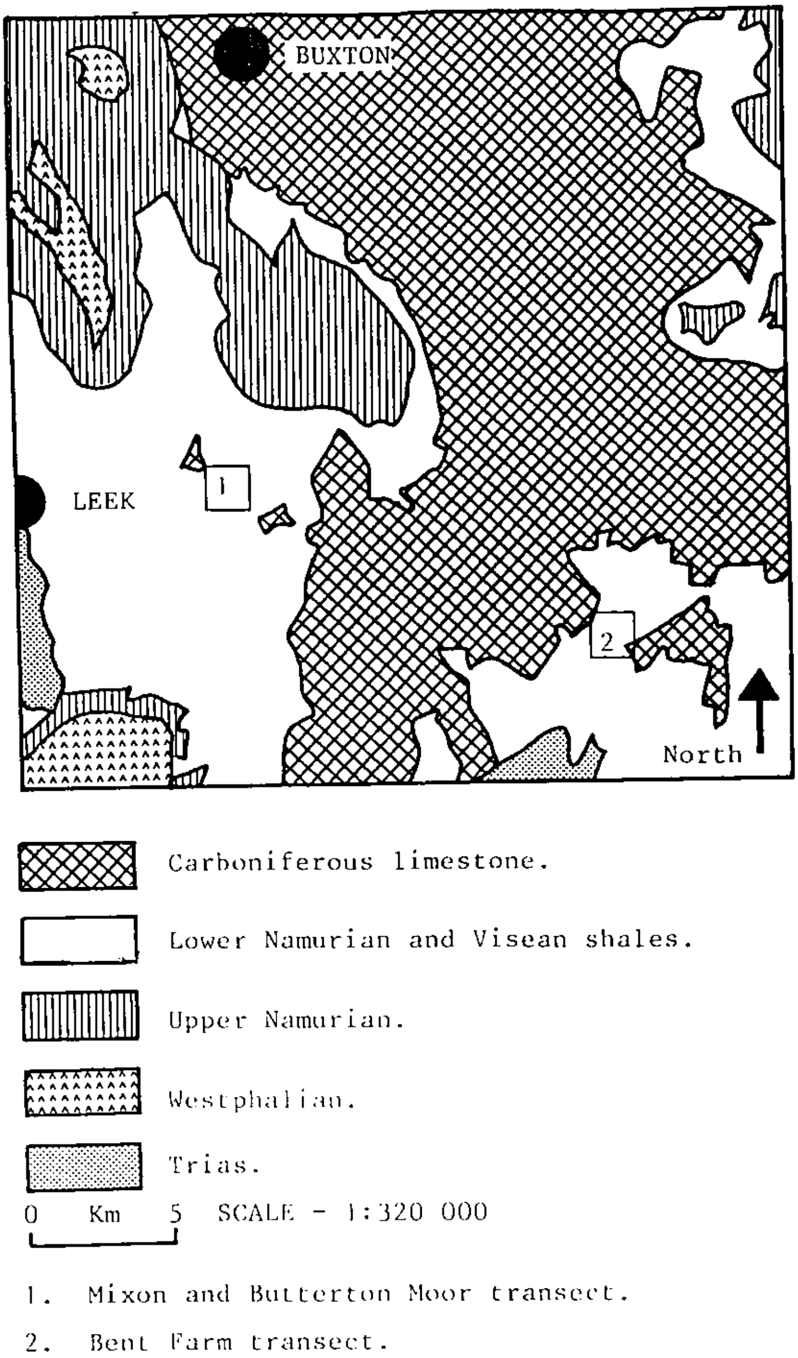


Figure 5.1. Location of sampling transects in relation to a generalised geology of S.W. Derbyshire and N.E. Staffordshire (After Fletcher, 1968)

summarised in Table 5.1.

The oldest formations represented in the area are of Visean age, deposited in the marine environment of the region at the time. They comprise both argillaceous basin sediments and also impure limestones deposited in the basin and at the margins of the Derbyshire massif. During the same period more pure limestones were deposited on the actual limestone massif.

The succession of Namurian sedimentation has been zoned on the basis of goniatite faunal bands in the shale horizons and was split into three main phases in N.E. Staffordshire (Table 5.1.). The first phase (zone E2) comprises shales, deposited in the acid and anaerobic bottom waters, interbedded with calcareous intrabasinal turbidites. During the second phase (zones E2-lower R1) shales were interbedded with quartzitic turbidites which thin towards the north east away from their source. Finally in the third phase (zones upper R1-R2) as the basin infilled, coarse arkosic sediments were transported from the north, the grit bands in the phase thinning and disappearing to the south. Later, fluvial sediments covered the basin and adjoining massif, suitable conditions were therefore established for the sedimentation of the succeeding Westphalian formations in which shales alternate with sandstones and associated coal seams, being deposited in marginal marine environments. The trend towards a terrestrial environment, begun in the Namurian, continued until the basin was infilled towards the end of the Carboniferous period.

In respect of the occurrence of the marine black shales, Fletcher (1968) divided the Namurian into; the lower Namurian of predominantly marine shales (zones E1-lower R1), and the upper Namurian mainly comprising sandstones interbedded with shales (upper R1-R2). The Mo and Se rich shales occurring in the Visean and the lower Namurian.

No younger formations are represented in the area until those of the Quaternary. During the last glaciation the area was generally free from ice, however, older drift of the penultimate Pennine glaciation occurs occasionally, mainly to the south. The periglacial environment, contemporary with the last glaciation, affected the N.E. Staffordshire hills and the limestone plateau. Many of the

	Formation.		Zone.	Local Mixon and Butterton formation.
Upper Carboniferous:	Westphalian (Coal Measures).			
	Namurian (Millstone Grit):	Upper	R2	Manifold formation.
			R1	
		Lower	H E2 E1	Gun Hill Siltstone formation.
Lower Carboniferous:	Visean (Top of Carboniferous limestone)		P	Onecote Sandstone formation.
				Mixon Limestones and Shales formation.

Table 5.1. The stratigraphy of the Carboniferous system in N.E. Staffordshire and S.W. Derbyshire. (after Fletcher, 1968).

valleys contain head, of variable thickness, developed from the local sediments. Recent deposits of alluvium in stream valleys are often indistinguishable from the adjacent head deposits. On the limestone there is a covering of a silty deposit thought to be a mixture of local limestone residue and loessial material which is probably derived from the surrounding Namurian.

5.1.2. Trace element content of the rocks.

Fletcher (1968) found the lower Namurian and Visean shales to be enriched in many trace elements, but not ably in Mo, Se, As, Cu and V. These shales were approximately eight times more enriched in Se than the younger upper Namurian and Westphalian shales, the higher Fe_2O_3 concentrations in the latter being consistent with deposition in an aerobic near shore environment. Examination of detailed sections showed that the distribution of Se in the shale facies closely follows that of Mo, but occasionally Se enrichment occurred when the Mo concentrations were low, probably reflecting differences in supply of the elements on formation of the shales. The enrichment of Mo and Se was thought to occur in acid, stagnant bottom waters either by sorption on organic matter, or in association with iron sulphides (Fletcher, 1968). In contrast the greyer shales in the succession, representing more aerated near shore waters, contained lower concentrations of all the trace elements.

Fletcher (1968) provides no values for Se in the corresponding sandstones and limestones, but in parallel with values for the other trace elements, concentrations might be expected to be low; except perhaps in the argillaceous limestones of the Visean where there was moderate enrichment of Mo and other trace elements. Such rocks occur mainly in the Onecote area and are not widespread elsewhere.

The distribution of Mo and Se in these rocks is essentially similar to that in the Namurian Clare shales in Eire which are known to give rise to soils supporting Se-toxic vegetation (Fleming and Walsh, 1957; Webb and Atkinson, 1965). However, in Eire the impoverished horizons of the grit-shale facies are absent.

5.1.3. Soils, climate and land use.

The area is exposed to the prevailing west winds and as a result is wet and cold throughout the year. Rainfall in the area of Onecote (Mixon and Butterton Moor transect), at between 1016 and 1143 mm per year, is greater than around Bent Farm which receives around 825 to 890 mm per year, nearly two thirds of this falling between July and January (Hollis, 1975).

The monthly mean temperatures at Buxton, which are probably representative of the whole area range between 1.9°C in January and 14.3°C in July. At Onecote monthly mean rainfall exceeds potential evapo-transpiration for all but one month of the year, the annual excess of rainfall over evapo-transpiration being about 650 mm. Lower rainfall and possibly higher temperatures mean that the excess will be less at Bent Farm. As a result of this, the predominantly heavy textured soils developed upon Visean and Namurian rocks are generally poorly drained, although drainage may be locally improved when more sandy facies give rise to a lighter textured parent material. Occasionally extreme leaching may lead to podzolisation on the coarser textured parent materials.

Hollis (1975) has described the soils of the Onecote district, and his classification has been extrapolated to the soils developed on similar parent materials at Bent Farm. The whole of the area is under permanent grass, rough grazing or open moorland, and the small farms, which average about 50 acres (20 ha), concentrate mainly on dairying with some livestock rearing and fattening. The severe climate provides only a short growing season of around 220 days, which combined with the heavy rainfall results in a relatively poor quality pasture, and low stocking rates.

5.2. Sampling and analysis.

The sampling was undertaken in late February, 1980. At each site on a transect the soil profile was sampled and a bulked sample of the top-soil taken.

Profile samples were taken with an auger at intervals of 15 cms depth. Bulked topsoil samples comprised five, 0-15 cms topsoil samples taken with an auger; the samples being collected at 10 m intervals along the strike of the slope. Brief profile descriptions and site descriptions are given in Appendix 1.2.

Each soil sample was analysed for the following parameters as described in section 3.2.: Se_t, Fe_t, Al_t, Mn_t, Ca_t, Mg_t, Fe_p, Al_p, pH_w and L.O.I. Some soil samples were separated into two size fractions (0.063-2 mm and less than 0.063 mm), details of the technique are given in section 3.2.6.

5.3. Mixon and Butterton Moor transect.

5.3.1. Introduction.

This was a broad transect, covering approximately 1500 m, which was chosen to encompass the differing soil series and parent materials in the area. The position of the profile sites on the transect in relation to the local topography is shown in Figure 5.2.

Three geological formations are covered by the transect; as described by Hollis (1975) they are:

Mixon Limestones and Shales - zone P of the Visean - which are a succession of thick black marine shales with thin limestone partings.

Onecote Sandstone formation - zone P of the Visean - consisting of thinly interbedded shales and sandstones, the latter having a calcareous matrix.

Gun Hill Siltstone formation - zone E2 of the Namurian - made up of clay and silty shales with well graded calcareous siltstones and mudstones.

The majority of the Onecote Sandstone formation is covered by a head

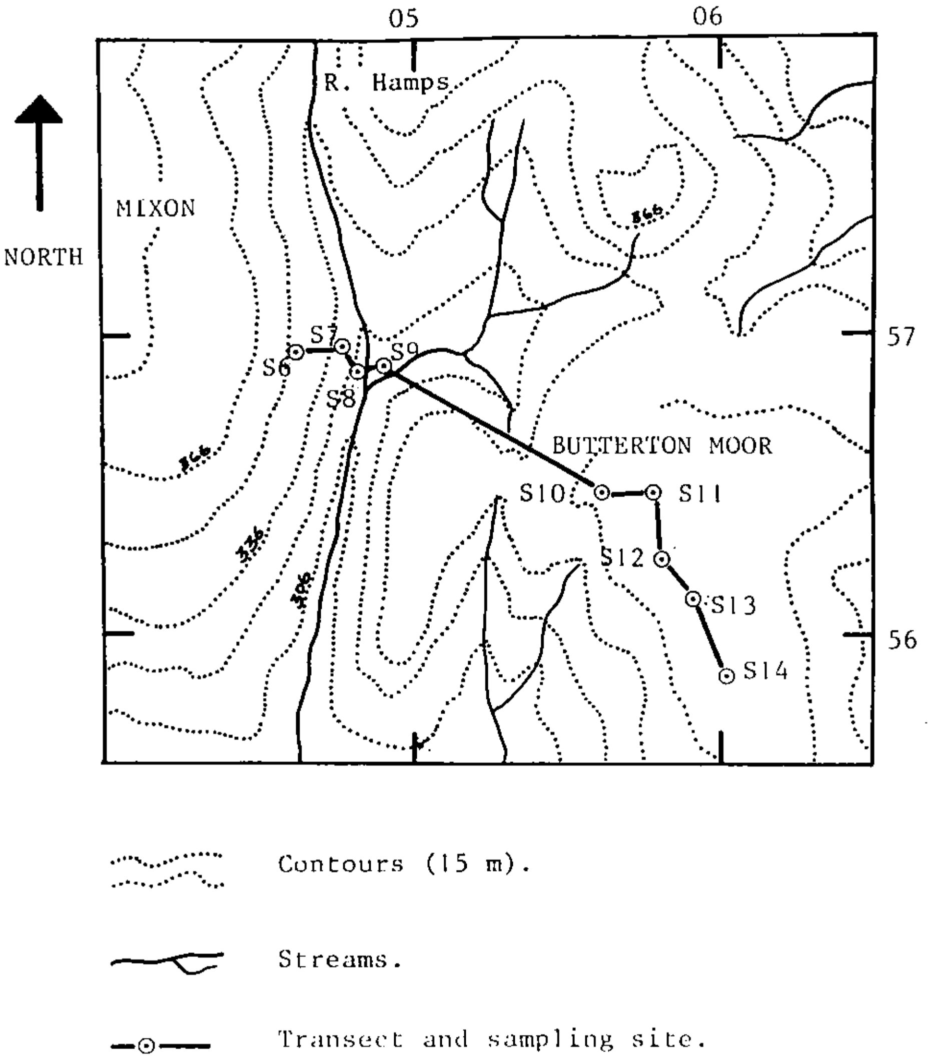


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Figure 5.2. Location of the Mixon and Butterton Moor transect in relation to local topography and drainage.

deposit and so mixing of the various facies may have occurred. However, it is likely that the head is locally derived and thus reflects the underlying solid geology, especially on the gentler slopes. Sandy lenses are often present where sandier strata have been weathered and not incorporated into the matrix.

Fletcher (1968) analysed rock samples from a detailed section near Onecote and found that the dark shales in zones E1-E2 contained between 0.2 and 34.0 μg Se g^{-1}. One sample from the Visean contained 12.0 μg Se g^{-1}. The corresponding grey shale facies were not analysed for Se but may be expected to be low in Se on the evidence of their very low Mo concentrations. The Se content of the parent materials of the area can therefore be expected to vary considerably, and this may be reflected in the soils.

The profile and site descriptions are given in Appendix 1.2. Briefly, profiles S6 and S7 have been classified as pelo-stagnogley soils of the Dale series being developed upon the Mixon Limestones and Shales. Profile S8 is probably developed upon alluvium or head which has accumulated alongside the stream, downslope from profiles S6 and S7. Such soils were not classified by Hollis (1975) but this is probably an alluvial gley soil. The Onecote series (cambic stagnohumic gley soils) is represented by profile S10 which is derived from the Gun Hill Siltstone formation. The remaining four profiles, S11 to S14, are all formed on head deposits derived from the Onecote Sandstone Formation and have been classified as cambic stagnohumic gley soils of the slightly better drained Wilcocks series. Profile S14, however, shows signs of leaching and may be transitional to the typical humus-iron podzols of the Anglezarke series.

In addition to taking bulked topsoil samples and profile samples at each of the eight sites mentioned above, a bulked topsoil sample was taken on a soil of the Ticknall series (cambic stagnogley soils) at Mixon mines farm (grid reference SK 049 570). This soil (S9) is probably developed on silty shales and siltstone of the Gun Hill Siltstone formation.

5.3.2. Results and discussion.

The data for the bulked topsoil samples (Table 5.2.) display a tendency for the more poorly drained soils of the Dale and Onecote series (S6, S7 and S10), which are obviously developed from the more finely grained parent materials, to contain more Se_t (mean = 3.28 μg g^{-1}) than those better drained soils of the Wilcocks series which are developed on the Onecote Sandstone formation (mean = 1.08 μg g^{-1}). The soils on the Mixon Limestones and Shales (S6, S7 and S8) also contain higher concentrations of Fe_t and Mn_t than the other soils. Despite having a higher Se_t content, the Fe_t and Mn_t concentrations of the soil at S10 are more comparable with the soils of the Wilcocks series and Ticknall series.

Evidence from the geological map (I.G.S., 1978) and the soil map (Hollis, 1975) suggests that the soils at S9 and S10 are both derived from the Gun Hill Siltstone formation; however, these data demonstrated a noticeable difference between the Se_t concentrations of the two topsoils. Considering the distance between the two sites (c. 850 m) this may not be unusual as Fletcher (1968) has shown that the trace element content of facies within the same formation can vary considerably.

Some of the above findings can be explained by considering the data for the eight profiles, which are given in Table 5.3. Profile diagrams, showing the distribution of Se_t, Fe_t, Fe_p and L.O.I. with depth, are given in Figure 5.3. It can be seen that relatively small differences in the topsoil Se_t content between soils can mask much larger differences in the subsoil content, as exemplified by the data for profile S10.

With the exception of soil S11 there is good agreement between the data for the bulked topsoil samples and the single (0-15 cms) samples from the profiles; and so it may be assumed that the profiles are reasonably representative of the soils in their locality. There is no obvious reason for the anomalously high single topsoil Se_t value at S11, however, the Fe_t content is also comparatively higher (2.01% compared to 0.62%); this will be discussed later.

The most noticeable feature of the Se_t distribution in profiles S6 and S7 of the Dale series is its increase with depth. This trend is also apparent

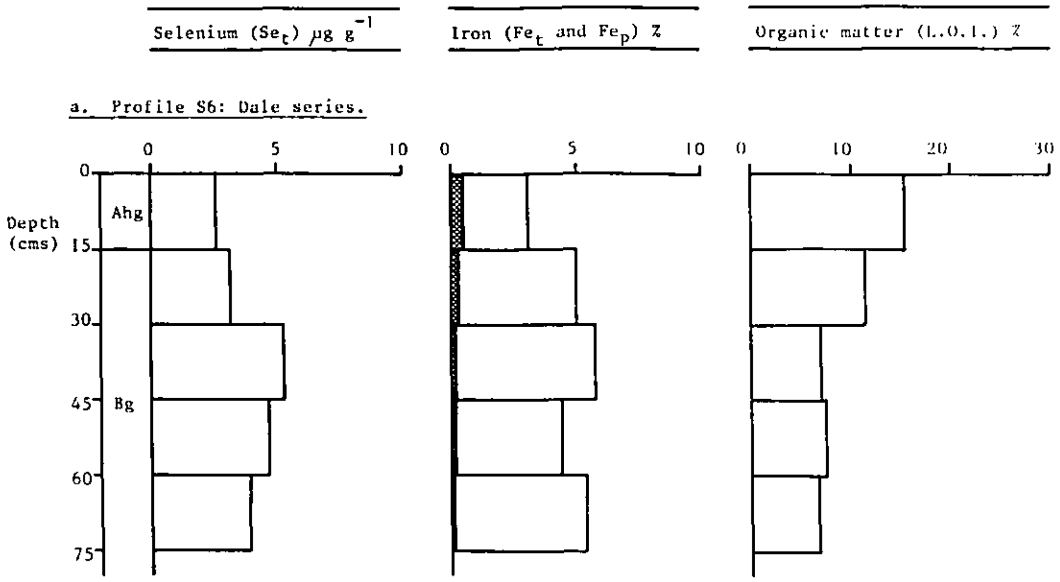
Profile No.	Soil series	Sample No.	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
S6	DALE	2111	5.45	4.95	2.95	0.58	0.12	480	3.60	1.47	0.65	0.08	17.83
S7	DALE	2121	5.00	4.09	4.09	0.74	0.12	536	4.94	1.04	0.36	0.04	14.39
S8	UNNAMED ALLUVIAL GLEY	2122	4.50	3.80	3.89	1.04	0.13	680	3.31	0.80	0.18	0.04	13.92
S9	TICKNALL	2127	4.80	4.25	0.83	0.28	0.07	156	1.25	0.60	0.21	0.02	8.83
S10	ONECOTE	2134	5.50	5.00	2.81	0.26	0.18	60	0.57	1.04	0.52	0.04	17.35
S11	WILCOCKS	2135	5.90	5.30	0.94	0.29	0.13	88	0.62	0.61	0.38	0.04	14.55
S12	WILCOCKS	2145	5.25	4.95	1.14	0.36	0.12	128	0.86	0.52	0.36	0.03	12.51
S13	WILCOCKS	2151	5.15	4.60	1.24	0.51	0.08	172	1.56	0.80	0.38	0.04	13.33
S14	WILCOCKS/ANGLEZARKE	2157	5.10	4.50	1.01	0.48	0.23	56	0.70	0.39	0.50	0.02	28.04

Table 5.2. Mixon and Butterton Moor transect, analytical results for bulked (0-15 cms) topsoil samples.

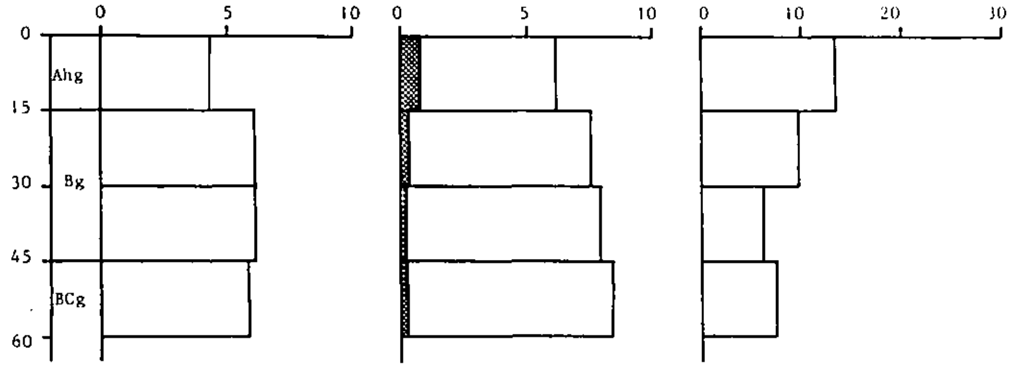
Table 5.3. Mixon and Butterton Moor transect, analytical results for profile samples S6-S14

Profile No	Soil series	Sample No.	Depth (cms)	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
S6	DALE	2112	0-15	5.70	5.15	2.60	0.42	0.10	280	3.12	1.32	0.58	0.071	15.59
		2113	15-30	5.90	5.15	3.12	0.26	0.09	316	4.88	1.36	0.54	0.055	11.81
		2114	30-45	5.80	5.05	5.18	0.10	0.05	472	5.64	1.10	0.36	0.047	7.20
		2115	45-60	5.75	5.00	4.65	0.10	0.05	240	4.40	1.06	0.36	0.051	7.64
		2116	60-75	5.70	5.10	3.95	0.08	0.05	310	5.33	1.12	0.41	0.051	6.77
S7	DALE	2117	0-15	5.05	4.35	4.39	0.80	0.10	620	6.20	1.08	0.35	0.059	13.42
		2118	15-30	5.05	4.60	6.23	0.34	0.06	680	7.52	1.02	0.32	0.047	9.04
		2119	30-45	5.50	4.65	6.23	0.22	0.04	1056	7.92	0.90	0.30	0.038	6.03
		2120	45-60	5.50	4.75	5.95	0.26	0.05	300	8.40	0.94	0.34	0.047	7.54
S8	UNNAMED ALLUVIAL GLEY	2123	0-15	4.35	3.60	3.65	1.22	0.13	380	3.28	0.72	0.10	0.040	13.78
		2124	15-30	4.50	3.70	3.41	0.78	0.11	1106	3.50	0.72	0.19	0.036	8.91
		2125	30-45	5.00	4.15	2.30	0.64	0.09	1012	3.36	0.80	0.25	0.044	8.27
		2126	45-60	5.10	4.35	1.87	0.52	0.08	896	3.88	0.84	0.32	0.044	8.11
S10	ONECOTE	2128	0-15	4.85	4.30	2.75	0.44	0.20	48	0.82	1.00	0.44	0.024	16.04
		2129	15-30	4.40	3.70	7.74	1.00	0.24	8	2.81	1.12	0.11	0.028	8.21
		2130	30-45	4.40	3.60	12.80	1.36	0.24	12	3.61	1.08	0.11	0.024	8.99
		2131	45-60	4.25	3.45	19.60	1.40	0.26	12	4.36	1.08	0.09	0.020	9.21
		2132	60-75	4.40	3.60	17.40	1.40	0.26	88	4.72	1.04	0.09	0.020	8.82
		2133	75-90	4.25	3.45	22.00	1.24	0.25	24	4.76	1.00	0.09	0.020	8.82
S11	WILCOCKS	2136	0-15	5.90	5.20	3.06	0.36	0.10	62	2.01	0.76	0.32	0.034	10.28
		2137	15 30	5.70	5.10	1.09	0.12	0.09	32	0.66	0.64	0.21	0.036	6.39
		2138	30-45	5.85	5.15	1.55	0.18	0.10	36	2.24	1.12	0.11	0.024	5.08
		2139	45-60	5.50	4.80	1.65	0.14	0.10	32	1.82	1.00	0.20	0.072	5.05
S12	WILCOCKS	2140	0-15	5.80	5.60	1.35	0.44	0.13	184	1.50	0.76	0.50	0.044	13.75
		2141	15-30	6.10	5.50	1.74	0.34	0.11	56	2.78	0.84	0.26	0.024	5.28
		2142	30-45	5.80	5.00	1.95	0.37	0.15	28	1.92	0.92	0.21	0.028	5.49
		2143	45-60	5.90	5.20	1.78	0.40	0.16	36	1.92	0.92	0.26	0.020	6.41
		2144	60-75	5.80	5.10	1.47	0.26	0.15	28	1.45	0.96	0.21	0.028	4.89
S13	WILCOCKS	2146	0-15	5.90	5.20	0.95	0.50	0.08	216	1.93	1.00	0.52	0.040	14.71
		2147	15-30	6.05	5.70	0.47	0.14	0.04	60	2.62	0.92	0.29	0.048	5.47
		2148	30-45	6.20	5.40	0.84	0.06	0.03	204	3.98	1.36	0.32	0.320	4.76
		2149	45-60	6.30	5.50	0.88	0.08	0.02	336	3.50	1.28	0.40	0.096	5.84
		2150	60-75	6.25	5.60	0.69	0.04	0.02	548	3.26	1.20	0.46	0.068	6.05
S14	WILCOCKS/ANGLEZARKE	2152	0-15	5.30	4.90	1.10	0.26	0.18	56	0.36	0.29	0.53	0.012	26.57
		2153	15-30	4.65	3.75	0.23	0.10	0.05	8	1.05	0.22	0.04	0.001	1.95
		2154	30-45	4.60	3.90	0.21	0.08	0.04	4	0.91	0.26	0.01	0.008	1.38
		2155	45-60	4.50	3.80	0.37	0.08	0.05	8	0.57	0.76	0.04	0.001	2.18
		2156	60-75	5.65	3.80	0.22	0.08	0.05	12	0.73	0.28	0.30	0.001	2.18

a. Profile S6: Dale series.



b. Profile S7: Dale series.



c. Profile S8: Unnamed alluvial gley soil.

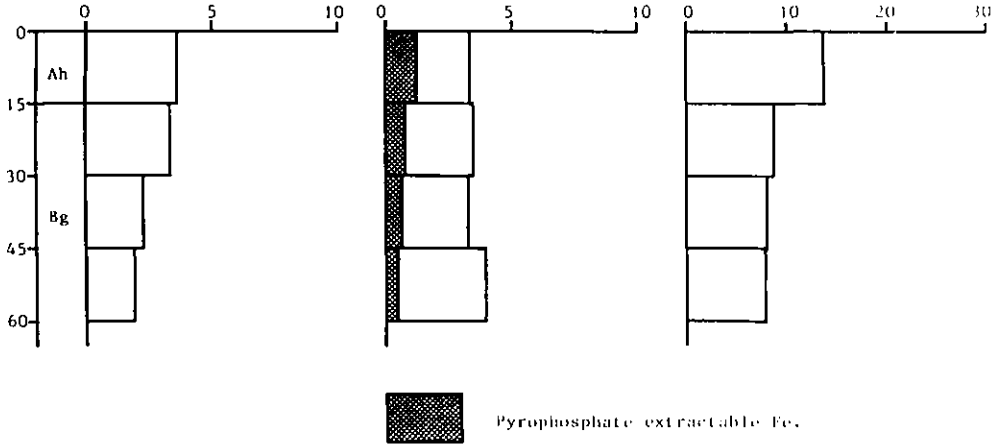
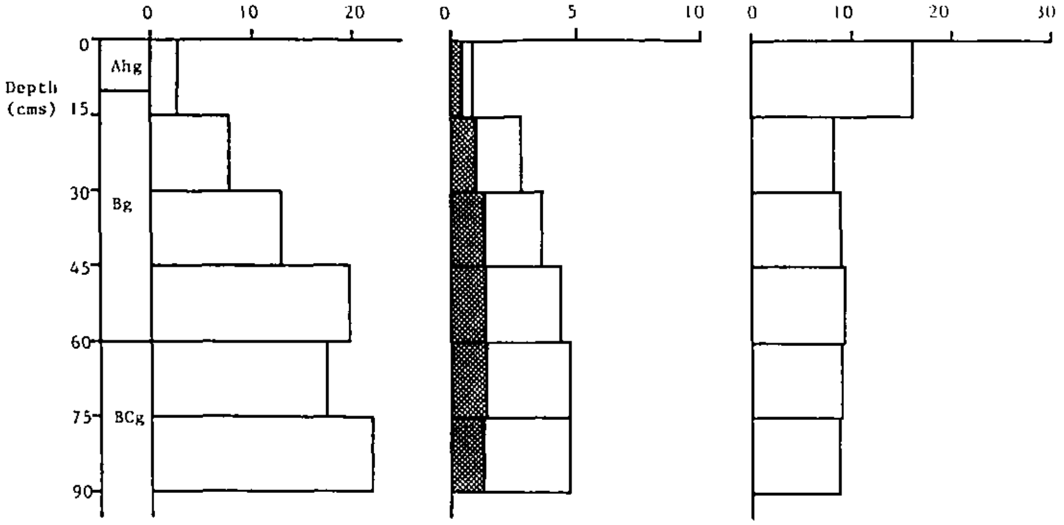


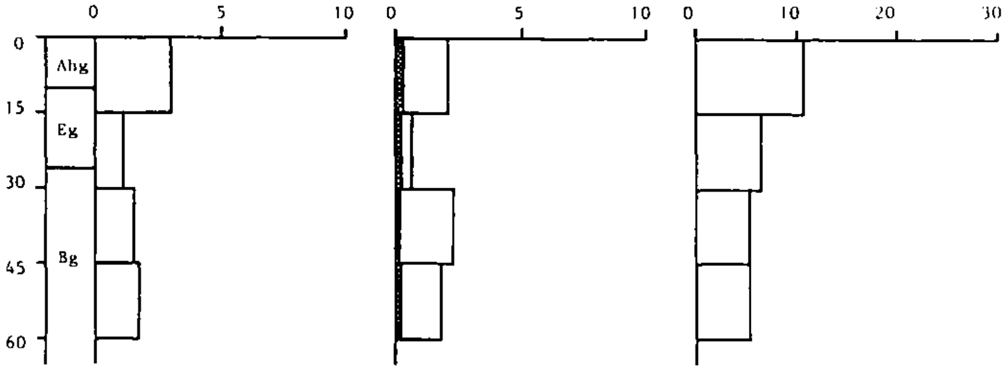
Figure 5.3. Distribution of Se_t, Fe_t, Fe_p and organic matter (L.O.I.) in eight soil profiles on the Mixon and Butterton Moor transect.

Selenium (Se_t) µg g^{-1} | Iron (Fe_t and Fe_p) % | Organic matter (L.O.I.) %

d. Profile S10: Onecote series.



e. Profile S11: Wilcocks series.



f. Profile S12: Wilcocks series.

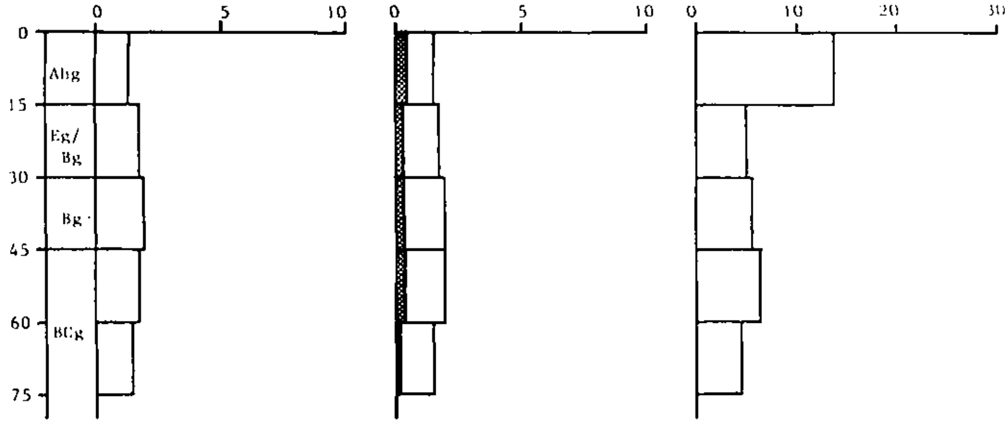
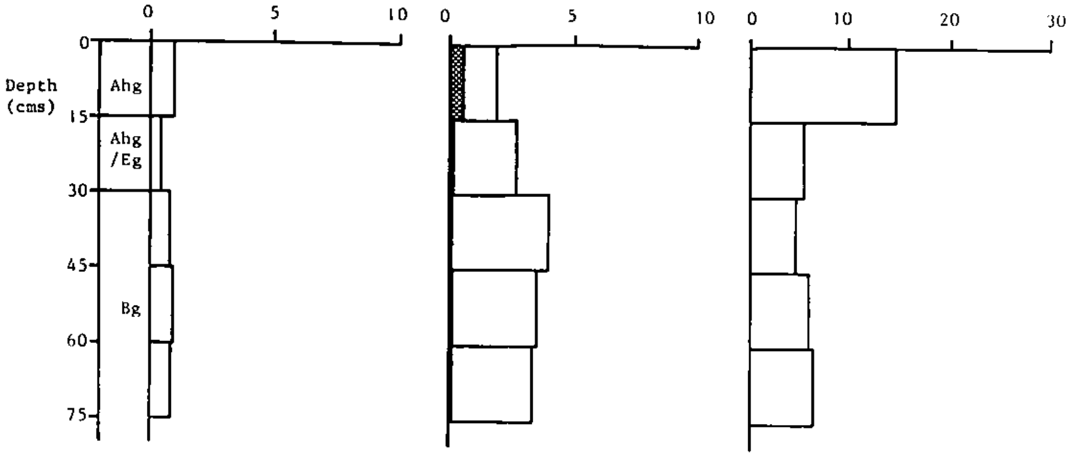


Figure 5.3. (Continued).

Selenium (Se_t) $\mu g\ g^{-1}$ | Iron (Fe_t and Fe_p) % | Organic matter (L.O.I.) %

g. Profile S13: Wilcocks series.



h. Profile S14: Wilcocks series.

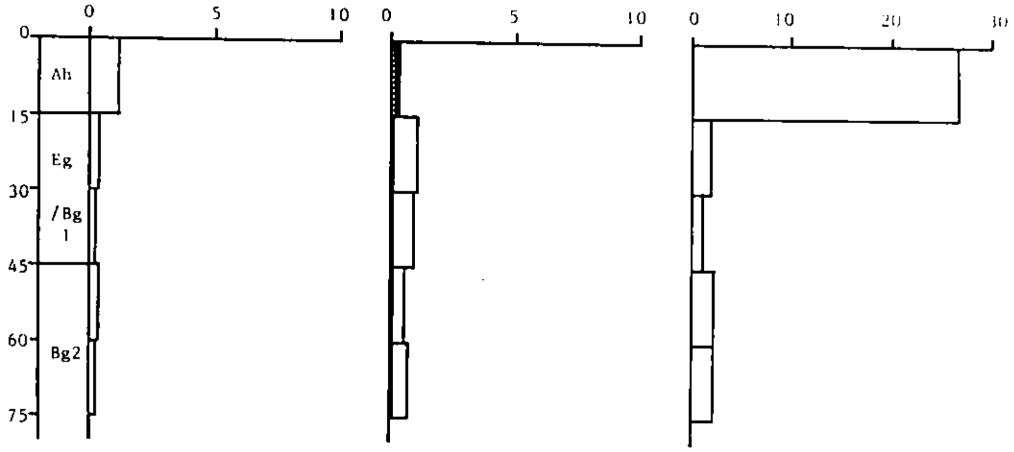


Figure 5.3. (Continued).

in profile S10 and in some of the soils developed from similar parent materials at Bent Farm (Figure 5.9.). The trend in the Dale series is paralleled by an increase in Fe_t with depth; there is, however, a poor correlation with Fe_p. In these gleyed soils the concentration of Fe_p tends to decrease down the profile. Bascombe (1968) showed that this was a common relationship in waterlogged soils and suggested that it was due to the "ageing" of precipitated iron oxides to a well ordered crystaline form in gleyed horizons. Such aged crystaline oxides are not peptised and extracted by 0.1M potassium pyrophosphate.

A feature of both these profiles, and most of the other profiles on the transect, is a lack of a relationship between the Se_t and organic matter (L.O.I.) content. This is unusual considering the well documented relationship between the Se and organic matter in soils (Fleming and Walsh, 1957; Levesque, 1974a). In fact the organic-rich topsoil is relatively depleted of Se compared to the rest of the profile. This may be due to rapid leaching of the element from the surface after decomposition of organic material, or to low uptake of Se by herbage from the soil. The latter would be the case if the Se in the rooting zone was relatively unavailable for plant uptake.

In profile S6 the Mn_t values vary with those of Fe_t, whereas in profile S7 there is a peak in Mn_t content between 45 and 60 cms in the Bg horizon; this is probably due to the precipitation of Mn in favourable oxidising conditions. Hollis (1975) noted that manganiferrous concretions are frequently present in soils of the Dale series. Analysis of the two separated size fractions for this soil (Table 5.4.) showed that the sand fraction from between 45 and 60 cms contained 1.22% Mn_t compared to 0.22% Mn_t in the silt and clay fraction, which would be consistent with the presence of manganiferrous concretions.

Although there are no data available for the distribution of clay in these soils, Hollis (1975) notes that there is a tendency for the clay content to increase with depth in the profile, and field texture determinations would tend to confirm this in the case of these two soils. Clay will innevitably play some role in the distribution of Se, however, considering the relatively poor adsorption of Se by clays compared to that by ferric oxides (Hamdy and Gissel-Nielsen, 1977), and that the main function of clay in this respect is as a site for the precipitation

		Depth	Fine fraction (less than 63 um)			Coarse fraction (63um - 2 mm)		
Profile.	Sample No.	(cms)	Se_t	Fe_t	Mn_t	Se_t	Fe_t	Mn_t
S3	2086	0-15	3.98	2.54	316	11.4	8.40	936
	2087	15-30	4.23	2.45	280	10.8	3.42	428
	2088	30-45	4.44	1.56	144	5.20	1.29	136
	2089	45-60	5.06	1.34	80	9.14	1.70	52
S4	2117	0-15	4.06	5.59	1400	10.0	16.5	1980
	2118	15-30	5.82	7.59	600	14.7	16.3	1900
	2119	30-45	ND	8.11	1020	12.1	15.0	3850
	2120	45-60	6.60	8.03	2190	13.8	16.5	12200
S10	2128	0-15	2.37	1.58	36	3.09	8.48	48
	2129	15-30	7.74	2.76	12	27.7	8.46	16
	2130	30-45	12.0	4.17	12	20.0	8.52	20
	2131	45-60	21.1	6.44	16	31.0	9.90	16
	2132	60-75	14.8	5.06	16	11.6	9.13	24

ND - Not Determined.

Table 5.4. Se_t, Fe_t and Mn_t concentrations in two size fractions of three soil profiles.

of Fe and Al oxides (Jenne, 1977), then the possibity of there being a proportional relationship between the clay content and the Se_t concentration of the soil is unlikely.

Analysis of the two size separations of the less than 2 mm soil for each sample of the profile (S10) shows that the Se_t content of both fractions is largely related to the Fe_t content (Figure 5.4.). The plot of Se_t against Fe_t for these two fractions plus that of the whole less than 2 mm soil shows that Se_t values are approximately the same as for the silt and clay fraction. This is consistent with the soil containing very little coarse material, which would be expected from the field texture determinations. Considering the presence of ochreous mottles throughout the profile, the high Fe content of the sand size fraction suggests that it consists predominantly of ferric oxide concretions; which are also enriched in Se but contribute little to the total Se content of the soil. Fletcher (1968) found a similarly high Fe content in the coarser fractions of poorly drained soils from the same region.

In contrast to the soils of the Dale series the Se_t content of the alluvial soil at S8 decreases with depth, and this trend apparently varies in parallel with decreasing Fe_p and L.O.I. contents, rather than that of Fe_t. So although both soils are gleys and have the same characteristic distribution of Fe_p, the distribution of Se_t is markedly different. However, in profile S8, apart from the difference between the 0-15 cms and the 15-30 cms samples, the decrease in L.O.I. is not large, and so the relationship with Fe_p may be the more pertinent. This therefore suggests a different mode of occurrence of the Se in the soils of the Dale series upslope and this gleyed alluvial soil.

Being at the base of the slope this soil will probably be in receipt of drainage waters moving downslope from the soils of the Dale series; but also, being in close proximity to the stream, no doubt groundwaters will be moving laterally through the soil. The relatively high content of Fe_p in the soil at depth, suggests that such waters are sufficiently aerated to produce the fresh precipitation of ferric oxides; any Se transported to the soil from upslope may then be adsorbed on these colloids. At the same time any Se released from the adsorption complex by either exchange reactions or the reduction of ferric iron

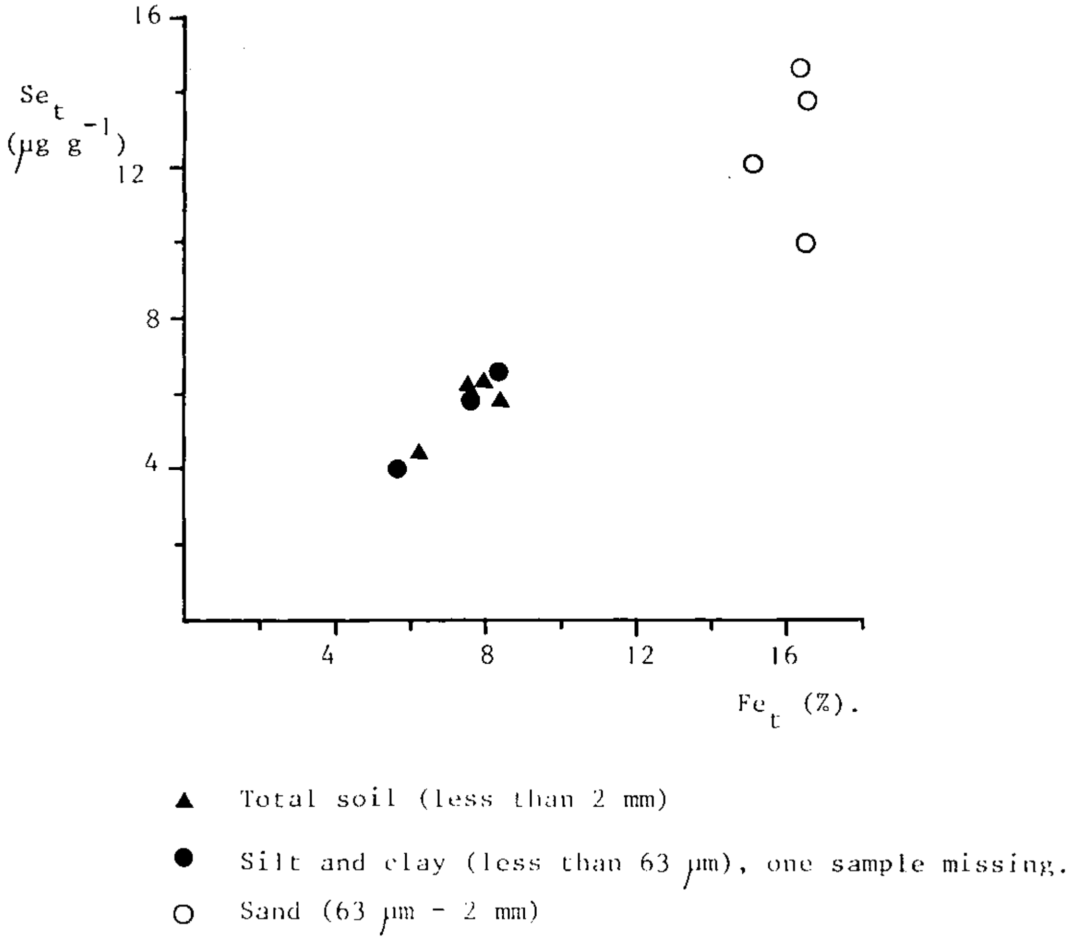


Figure 5.4. Relationship between Se_t and Fe_t for total soil, sand and silt and clay fractions. Profile S7: Dale series.

to the soluble ferrous form may be leached laterally away from the profile by the groundwaters associated with the stream. The process is not absolutely clear but it may be considered that due to the location of the soil at the base of the slope, and adjacent to the stream, the environment of changing redox conditions and leaching is more dynamic than in the soils of the Dale series upslope.

The soil of the Onecote series at site S10 demonstrated the most striking increase in Se_t content with depth of all the profiles on the transect; this increase apparently varies not only with the Fe_t content but also with the Fe_p content of the soil. The pattern of distribution of Fe_p is the reverse of that encountered in the other gleyed soils of the area, the highest concentrations being found in the Bg and BCg horizons at depth. It is noticeable that despite the high concentrations of Se_t in this profile, the Fe_t concentrations are within the range encountered in the other soils of the area. As this soil occupies a fairly level site towards the top of a gentle slope there is little evidence that the site is in receipt of Se transported in drainage waters. It seems probable that the source of the majority of the Se is a parent material which is significantly enriched in Se compared to its neighbours. Figure 5.5. shows that the mean Se_t:Fe_t ratio for profile S10 is much higher than that of the remaining soils on this transect, all of which tend to lie about the same regression line. Profile S10 is therefore more enriched in Se, relative to its Fe_t content, than the other soils. Fletcher (1968) found that there was no overall relationship between the Fe and Se content of the shales of the region, which he supposed was due to differences in the modes of supply of the elements during the formation of the rocks.

In spite of the general trend in these waterlogged soils that the topsoil is relatively depleted in Se, there appears to be an exaggerated difference between the topsoil and subsoil Se_t content in profile S10. Considering the more organic rich topsoils of the Onecote series this may be all the more unusual. Hollis (1975) however, makes special mention of the fact that the soils of the Onecote series in the vicinity of Fairview Farm have a tendency to take on the characteristics of the soils of the Ipstones series, which occur where silty head covers the clay shales of the Gun Hill Siltstone

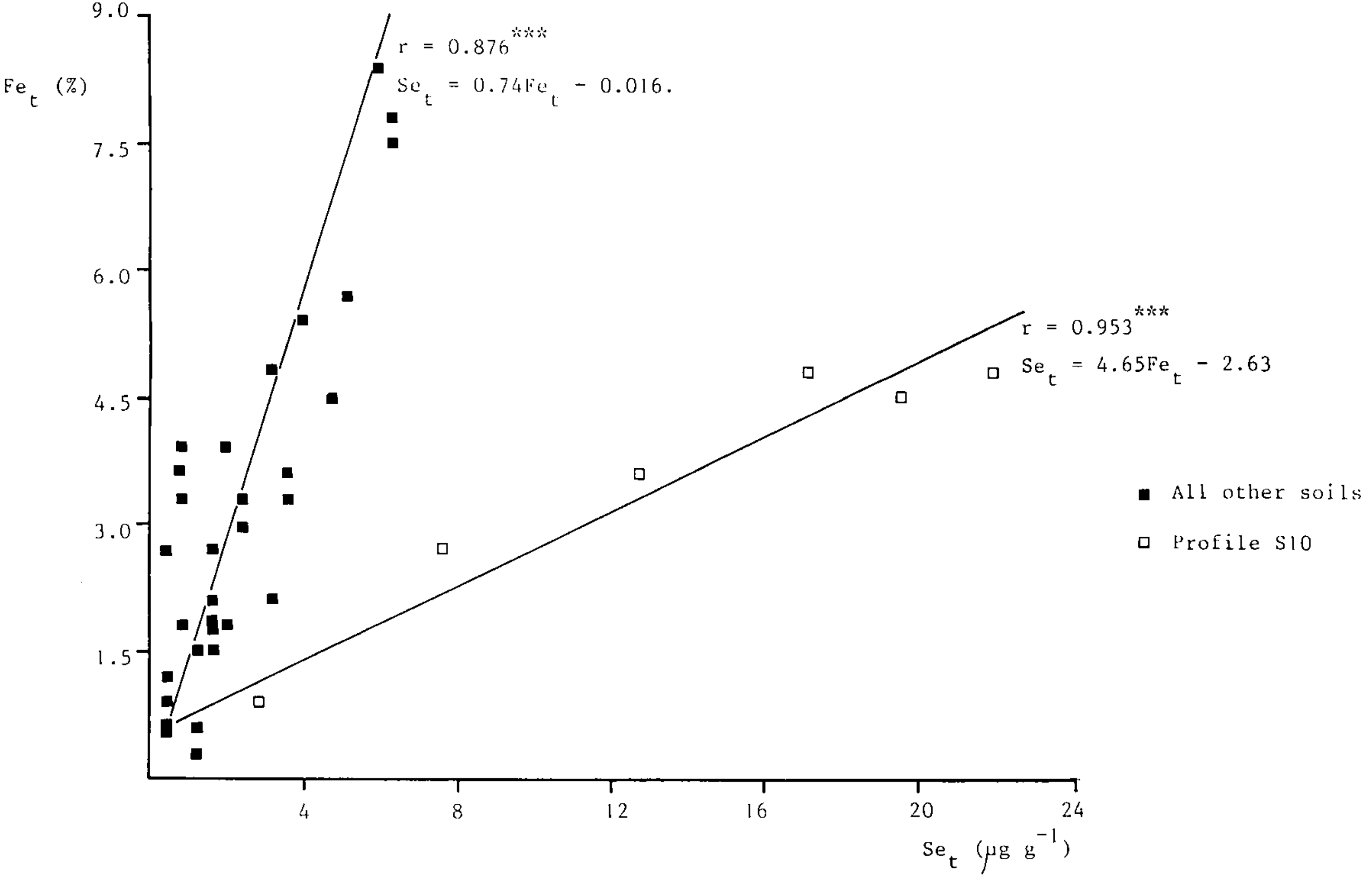


Figure 5.5. Relationship between Fe$_t$ and Se$_t$ for horizons of all soils on the Mixon and Butterton Moor transect.

formation. This soil is very near to the boundary of the Onecote and Wilcocks series, the latter being formed on the head derived from the Onecote Sandstone and Shales, it would seem probable, therefore, that the relatively low Se_t concentration of the topsoil of profile S10 is due to an inclusion of a thin covering of this head. The lower Se_t and Fe_t concentrations of the soils of the Wilcocks series suggests that this head would contain less Se and Fe than the material of the Gun Hill Siltstone formation.

The Fe_p values in profile S10, especially at depth, are appreciably greater then those of the other soils on this transect. This anomaly is difficult to explain; especially considering that there was very little ochreous mottling in the heavily gleyed BCg horizon. One reason may be differences in the susceptability to weathering of the two parent material types thought to be present in this profile. Despite the strong correlation between the Se_t and Fe_p contents of soil horizons from the Llansannan area which has been demonstrated (section 6.4.), it would seem more likely that in the case of these soils the Se_t in the profile is not specifically related to the Fe_p content. Analysis of the sand size fraction (Table 5.4.) shows an enrichment of both Fe_t and Se_t relative to the silt and clay fraction. As with the soils of the Dale series this probably represents the presence of ferruginous concretions; which have been shown to exist in the soils of the Onecote series (Hollis, 1975). The Fe in these concretions would be largely crystaline; yet it obviously has an associated Se_t content, which is of the same order as that in the fine fraction, where much of the more amorphous "fresh" iron oxides will occur (Figure 5.6.). This plot of the Fe_t and Se_t concentrations of the separated size fractions shows that there is a linear trend between the two parameters, with the exception perhaps of the samples from the top and bottom of the profile. The low Se concentration of the sand size fraction of these two samples is difficult to explain. In the topsoil where there is less intense gleying the formation of ferruginous concretions is unlikely.

In the absence in this study of a method by which to determine the relative contributions to the total soil Se of either Se in association with ferric oxides, or Se in more reduced forms such as elemental

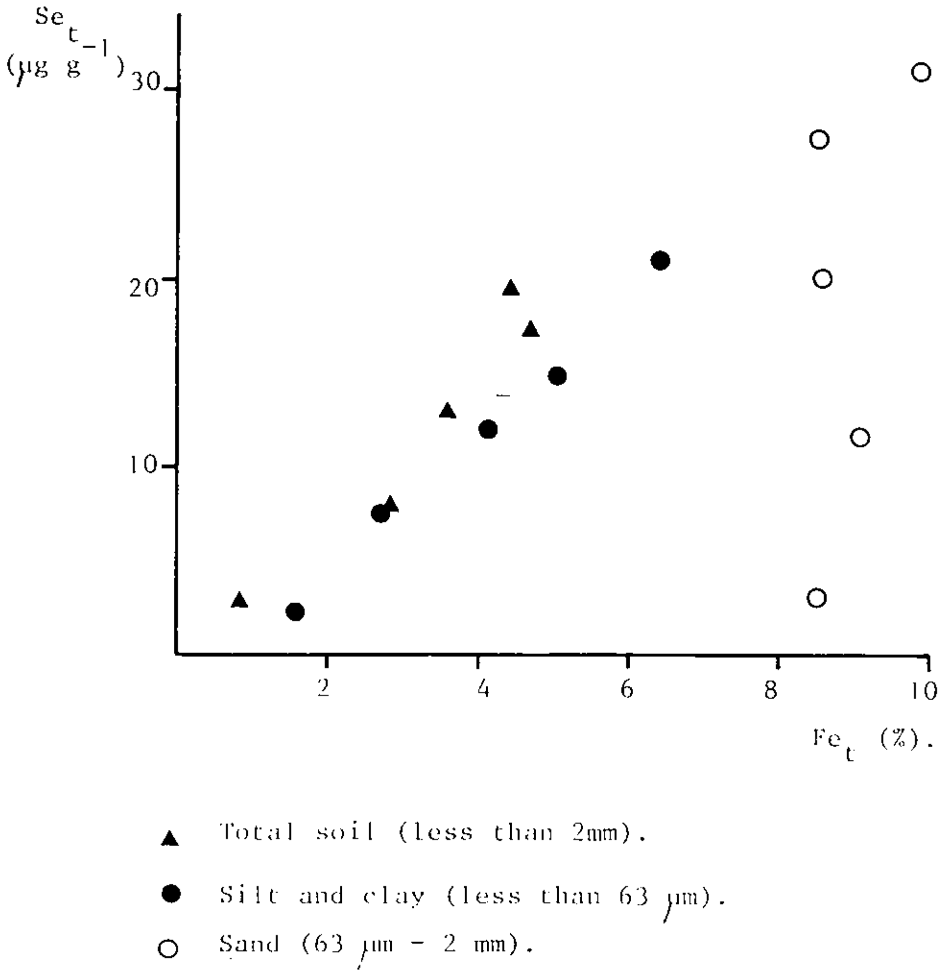


Figure 5.6. Relationship between Se_t and Fe_t for total soil, sand, and silt and clay fractions. Profile S10: Onecote series.

Se (Se^o) or selenides (Se^{2-}) it is difficult to be specific about the relative importance of either fraction. Howard (1977) considers that in the redox conditions prevalent in the presence of reduced ferrous iron, Se would take the form of either of these species, dependant on the extent of the reducing conditions; and that in both oxidising and reducing environments the distribution and forms of Se are controlled by that of Fe.

Profiles S11, S12 and S13 of the Wilcocks series again demonstrate a broad relationship between the Fe_t and Se_t in the soil (Figure 5.3.). In all cases the distribtution of Fe_p is characteristic of gleying, as its concentration decreases with depth. Only for profile S11 do the analytical values confirm the presence of a characteristic Eg horizon, where the concentrations of Fe_t, Fe_p, Se_t and Al_t in the soil at the 15-30 cms depth are less than those of the horizon above and below. Evidence for the presence of such a horizon in S12 and S13 may be masked by the presence of material from other horizons in the relevant sample, as Eg horizons in the Wilcocks series are often thin and weakly defined. The pH of these profiles is generally higher than in those already discussed, which is consistent with the observation of Hollis (1975) that profiles developed on drift material tend to be more alkaline, probably due to the mixing of more calcareous facies with those of the siltstone and other strata.

One anomaly in the results is the large discrepancy between the 0-15 cms profile sample and the bulked topsoil sample at site S11 (Tables 5.2 and 5.3.). Considering the relationship between Se_t and Fe_t so far discussed, this can be explained in part by the significantly higher Fe_t content of the single topsoil sample (2.01% compared to 0.62%), the ratio of Se_t:Fe_t in both samples being equal (1.5). It is difficult to explain the source of the higher Se_t and Fe_t concentrations but local contamination by enriched drift material is possible (c.f. the situation at profile S10).

There is no appreciable accumulation of Se_t with depth in these profiles and the concentration in the topsoil is a reasonable estimate of the Se concentration of the rest of the profile. Although shale fragments were present in the profiles there is no evidence to suggest that these may be significantly enriched or depleted in Se relative to the rest of the solum. The presence of a leached Ea horizon in these lighter textured soils is indicative of enhanced leaching of the soil, which has probably meant a constant redistribution of Se between the organic phase in the topsoil and adsorbed phases on ferric oxides, and reduced forms at depth. Although leaching will have resulted in the loss of some Se from the soil, the generally lower Se_t concentrations are due in most part to the lower Se content of the parent material from which they were derived, compared to that of the Dale and Onecote series. Fletcher (1968) demonstrated that the coarser lithologies in general contained lower concentrations of trace elements.

The profile at site S14 represents a similar yet more advanced situation where an even coarser textured soil has been heavily leached, resulting in the formation of a more acid profile which is relatively depleted of Se. This relationship coupled with the enrichment of the peaty topsoil in Se_t is characteristic of podzolisation as demonstrated elsewhere in this study (sections 4.3.2. and 6.4.1.). Again the sandy rocks giving rise to this soil were probably inherantly low in Se compared to the surrounding lithologies on which the soils of the Onecote and Wilcocks series are developed.

5.4. Bent Farm transect.

5.4.1. Introduction.

This transect covers a sequence of soils developed on a single slope which is underlain by Se-rich black shales of Namurian age. The situation of the transect in relation to local topography and drainage is depicted in Figure 5.7. The land is used for grazing as permanent pasture, and high Mo concentrations in the herbage have lead to problems of Mo induced Cu deficiency in grazing livestock. Considering the relationship between Mo and Se in this type of parent material (Fletcher, 1968), it would be expected that the soils and parent material were also enriched in Se.

Classification of the soils is complicated, as the characteristics change considerably over a small distance. Poorly drained soils

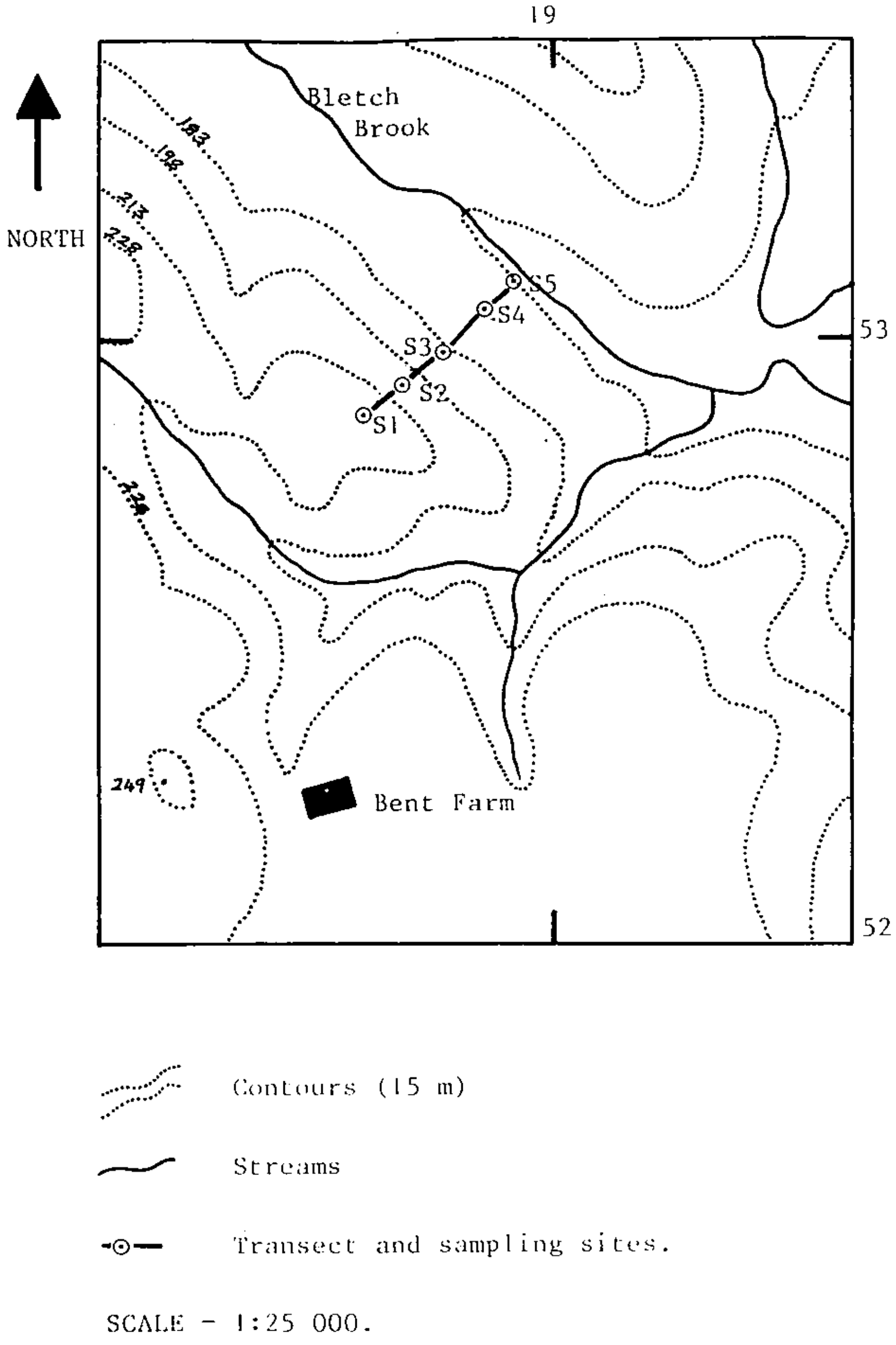


Figure 5.7. Location of the Bent Farm transect in relation to local topography and drainage.

at the crest of the slope, probably belonging to the pelo-stagnogley soils of the Dale series, give way as the slope becomes steeper to better drained soils of the Alton series (typical non calcareous pelosols). The soil at site S2 is probably an intergrade between the soils of the Dale and Alton series, being relatively freely drained yet showing signs of strong gleying at depth; whilst at site S3 a shallow well drained soil containing many black shale fragments has been classified as a soil of the Alton series (steep phase). Towards the base of the slope, as the gradient decreases, the soils become poorly drained again; the presence of a relatively humose topsoil in the profile at site S4 places the soil in the Onecote series (cambic stagnohumic gley soils).

Adjacent to Bletch Brook is an area of very poorly drained soils which at the time of sampling had water lying on the surface. These soils are developed on recent alluvium with perhaps some mixing of head deposits at the base of the slope. Although an odour of sulphide was evident on sampling, the soil is not sufficiently acid to be considered to have a sulphuric horizon (Avery, 1980) and so has been classified as a typical humic-alluvial gley soil. Such soils were unnamed by Hollis (1975). The presence of sulphur-rich horizons would however, be consistent with a soil recieving drainage waters from surrounding pyrite-rich rocks and soils.

Site and profile descriptions for the five profiles are given in Appendix 1.2.2. Additionally, samples of shale were taken from a small outcrop in the vicinity of site S3 which have also been analysed for Se, and a bulk stream sediment sample was taken from along the stream at its intersection with the transect.

5.4.2. Results and discussion.

The data for the bulked topsoil samples are broadly comparable with the corresponding topsoil values for the profiles (Tables 5.5. and 5.6.); the exception is at site S3 where the bulked topsoil Se_t concentration is lower than that of the profile, despite values for the other parameters being similar. The general trend in the bulked topsoil data is for the topsoil Se_t concentrations to increase

Profile No.	Soil series	Sample No	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
S1	DALE	2079	5.10	4.70	1.73	0.42	0.11	340	2.12	1.00	0.36	0.088	12.27
S2	DALE/ALTON	2085	5.50	5.10	2.99	0.49	0.12	480	2.60	0.92	0.42	0.075	12.65
S3	ALTON	2090	5.40	4.90	4.25	0.66	0.14	492	3.00	0.96	0.36	0.075	10.83
S4	ONECOTE	2094	5.60	4.80	5.60	0.34	0.11	640	3.22	1.62	0.62	0.127	14.27
S5	UNNAMED	2095	4.30	4.00	20.90	0.23	0.17	300	3.64	0.72	0.55	0.123	55.11
STREAM SEDIMENT		2101	ND	ND	6.38	ND	ND	1696	8.40	1.06	0.76	0.155	10.41

Table 5.5. Bent Farm transect, analytical results for bulked (0-15 cms) topsoil samples.

Profile No.	Soil series	Sample No.	Depth (cms)	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
S1	DALE	2075	0-15	5.05	4.55	1.92	0.44	0.13	650	2.36	1.07	0.20	0.041	11.58
		2076	15-30	5.00	4.50	2.30	0.28	0.12	1880	3.76	1.00	0.19	0.101	7.19
		2077	30-45	5.00	4.40	3.29	0.22	0.11	1040	3.12	0.10	0.19	0.101	6.66
		2078	45-60	4.45	4.30	2.51	0.10	0.11	840	3.72	1.18	0.21	0.131	5.19
S2	DALE/ALTON	2080	0-15	5.85	5.20	3.56	0.48	0.10	412	2.28	0.84	0.43	0.067	11.22
		2081	15-30	5.50	4.80	4.16	0.48	0.11	308	2.52	0.92	0.33	0.071	8.75
		2082	30-45	5.05	4.50	6.34	0.50	0.14	276	2.58	0.88	0.23	0.057	6.59
		2083	45-60	5.10	4.40	8.40	0.42	0.13	312	2.84	0.86	0.22	0.059	5.97
		2084	60-75	5.20	4.40	10.40	0.28	0.14	272	3.54	0.88	0.21	0.059	4.30
S3	ALTON	2086	0-15	5.40	4.80	7.10	0.66	0.14	392	3.48	0.96	0.58	0.071	11.28
		2087	15-30	6.20	5.50	6.43	0.64	0.16	344	2.80	0.96	0.41	0.059	9.14
		2088	30-45	5.20	4.40	5.26	0.48	0.15	98	1.72	0.75	0.21	0.041	6.60
		2089	45-60	4.85	4.00	8.00	0.36	0.12	88	1.70	0.64	0.13	0.028	5.36
S4	ONECOTE	2091	0-15	5.30	4.70	5.01	0.36	0.11	228	1.50	1.72	0.55	0.123	15.16
		2092	15-30	5.10	4.55	5.29	0.24	0.13	96	1.16	1.62	0.40	0.107	9.75
		2093	30-45	5.15	4.30	7.20	0.16	0.12	464	1.60	1.32	0.22	0.119	4.70
S5	UNNAMED	2095	0-15	4.30	4.00	20.90	0.23	0.17	300	3.64	0.72	0.80	0.085	55.11
		2096	15-30	4.70	4.30	40.00	1.56	0.26	66	2.50	0.90	0.70	0.097	43.92
		2097	30-45	4.70	4.30	77.00	1.16	0.14	64	2.80	1.20	0.72	0.127	28.52
		2098	45-60	4.90	4.55	82.00	0.44	0.11	52	2.36	1.20	0.49	0.127	13.49
		2099	60-75	4.80	4.55	79.00	0.70	0.21	88	4.60	1.36	0.45	0.123	14.77
		2100	75-90	5.10	4.75	93.00	0.58	0.16	136	5.28	1.88	0.54	0.143	15.06

Table 5.6. Bent Farm transect, analytical results for profile samples S1-S5.

downslope, in parallel with an increase in the Fe_t concentration, and with the exception of site S5, in Mn_t. The concentration of Fe_p is highest in the better drained soils at sites S2 and S3. As both Fe and Mn may be mobile in their reduced forms it is possible that these trends are due to the successive enrichment of downslope soils by drainage waters enriched in these metals and derived from waterlogged horizons of soils upslope. It is possible that Se mobilisation and redeposition occurs by a related process.

The plot of Se_t against Fe_t for these five soils is linear for soils S1 to S4 (Figure 5.8.), which suggests a similarity in the mode of occurrence of the Se_t in all the soils; site S5 is considerably enriched in Se_t relative to its Fe_t content. Although some mottling was apparent in the topsoils at sites S1 to S4 it would be expected that these topsoils were well aerated and that the Se occurred primarily as selenite adsorbed on ferric oxides. In contrast at site S5, at the time of sampling the soil was completely waterlogged, and the Se would probably be largely in reduced forms, such as elemental Se or selenides.

The stream sediment sample, although rich in both Fe_t and Mn_t due to secondary precipitation, has a relatively low Se_t content. The shale sample taken from near to the soil at site S3 was composed of dark grey and black unweathered fragments and rust coloured fragments, the latter being considered to have been weathered to a greater extent and a portion of the iron content having been oxidised to the ferric form. The sample was separated on this basis and the data is given in Table 5.7.

The profile of the Dale series at site S1 shows a similar distribution of Se_t to the profiles of the same soil series on the Mixon and Butterton Moor transect, with the Fe_t concentrations increasing with depth (Figure 5.9.). In this case there is a maximum between 30 and 45 cms before the concentration decreases slightly below 45 cms. In common with soil S7 (section 5.3.2.) the observed presence of manganiferrous concretions in the Bg horizon is confirmed by the higher Mn_t concentrations in the sample from the top of the horizon (Table 5.6.).

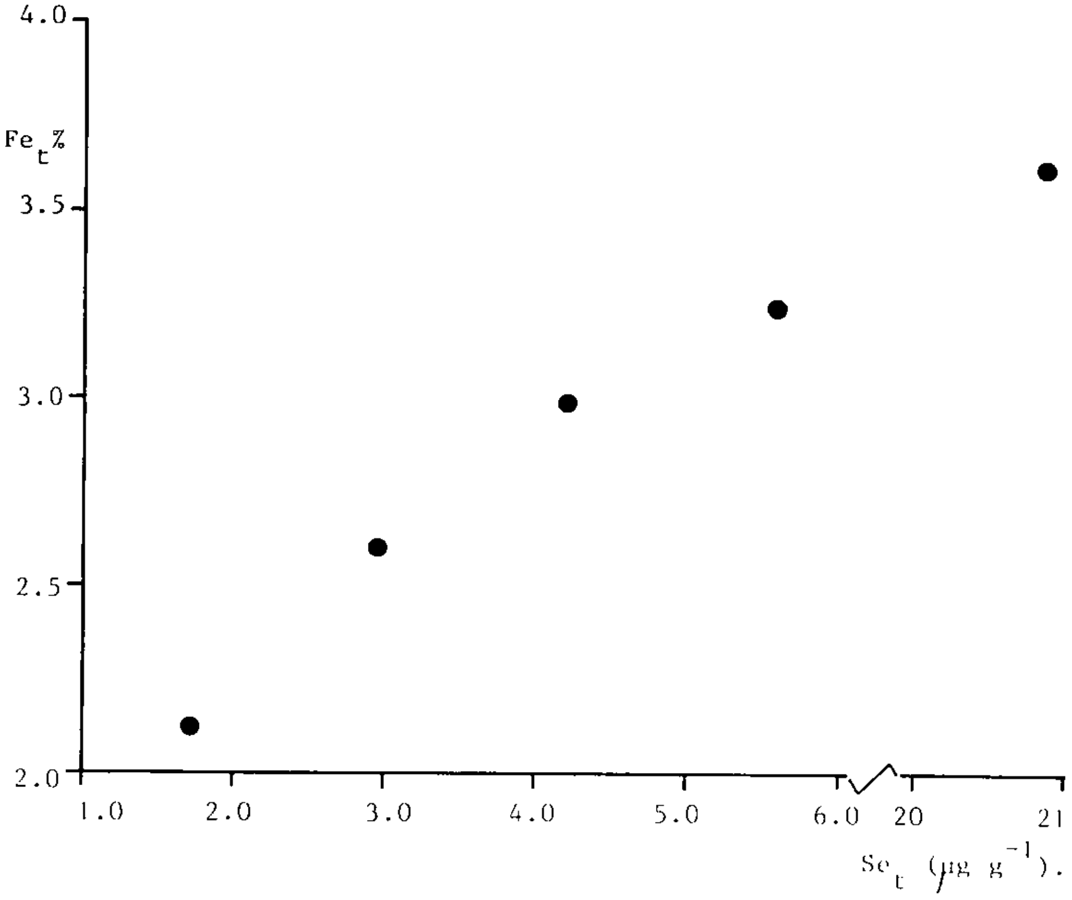


Figure 5.8. Relationship between Se$_t$ and Fe$_t$ for Bent Farm bulked topsoil samples.

Sample.	Se_t	Mn_t	Fe_t
BF 1, "unweathered".	23.2	44	2.90
BF 2, "weathered".	9.9	52	1.32

Table 5.7. Se_t, Mn_t and Fe_t content of shale samples from Bent Farm.

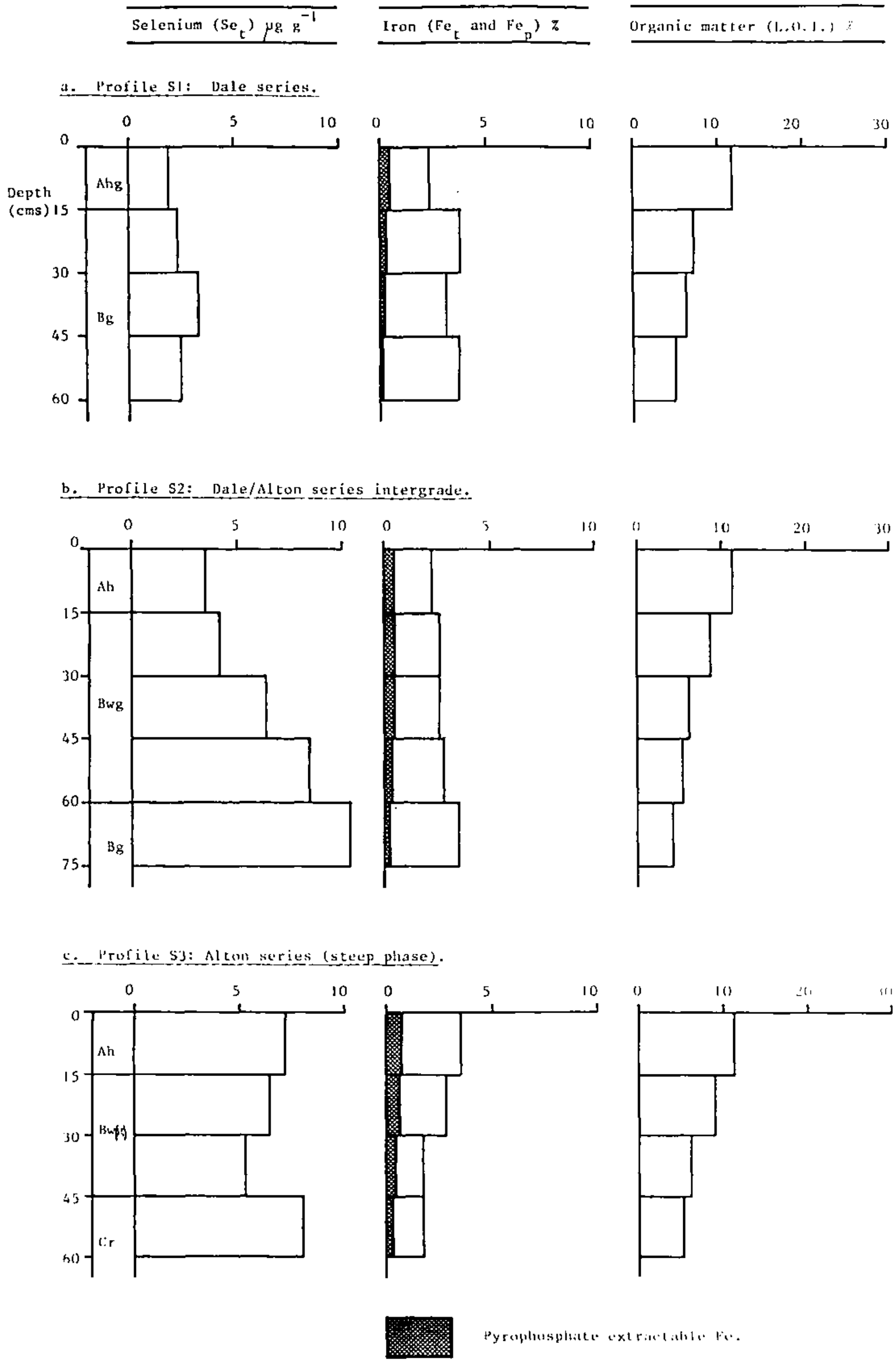
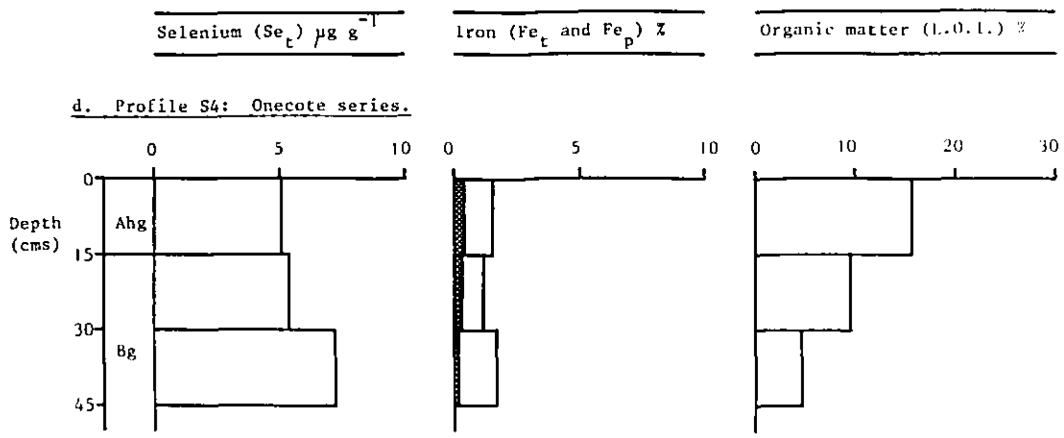


Figure 5.9. Distribution of Se_t, Fe_t, Fe_p and organic matter (L.O.I.) in five soil profiles on the Bent Farm transect.

d. Profile S4: Onecote series.



e. Profile S5: Unnamed, typical humic alluvial gley soil.

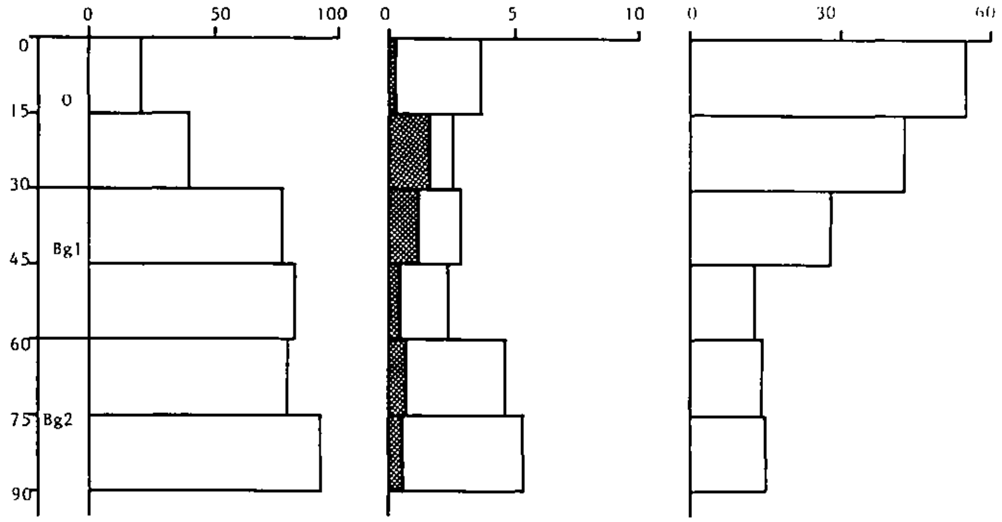


Figure 6.9. (Continued).

Concentrations of Se_t in this profile are lower than in those further down slope, so it is possible that this soil is developed on a different parent material, possibly a different shale facies outcroppin at the top of the slope, or residual drift material remaining in the more level ground.

Profile S2 is predominantly freely drained in the top 45 cms, although some ochreous mottling indicative of gleying is evident; thus Fe_p values are relatively uniform at the top of the profile (Figure 5.9.). There is a sharp increase in the Se_t content with depth, which is difficult to explain in terms of the other data presented. However, the increasing frequency of shale fragments down the profile suggests that much of the total Se_t content of the soil may be present in these shale fragments. If the concentration of Se_t in the dark shale sampled near to site S3 (23.2 $\mu g\ g^{-1}$) is consistent with that of the shale underlying most of the slope then this would be possible; an increase in the shale content would increase the Se_t content of the soil. The Alton series soil at site S3 is well drained and on a steeper portion of the slope, and although similar in morphology to profile S2, especially in the well drained topsoil, the distribution of Se_t is markedly different (Figure 5.9.). Down to 45 cms the Se_t content decreases in parallel with a decrease in the Fe_t concentration. There were also unweathered shale fragments in the soil but these were predominantly in the Cr horizon between 45 and 60 cms. Analysis of the sand, and silt and clay size fractions shows that unlike the soils of the Dale and Onecote series, the Se_t enriched sand fraction makes a larger contribution to the total Se_t content of the soil (Tables 5.4. and 5.6.). However, excepting the topsoil the sand fraction is not significantly enriched in Fe_t compared to the silt and clay fraction. Certainly in the Cr horizon most of the sand fraction will consist of shale material which is relatively unweathered. Thus considering the high Se_t content of the shale samples taken from the slope, it seems probable that the inclusion of shale in the profile is making a significant contribution to the total soil Se_t, both at site S3 and probably at site S2 where the fequency of shale fragments increased down the profile.

Towards the surface in both of these profiles (S2 and S3), where the soil is well aerated, it may be expected that the Se is associated with ferric oxides and organic complexes. The plot of Fe_t against Se_t for the separated size fractions of the Alton series soil (S3) (Figure 5.10) exhibits no linearity in the relationship between the two parameters, which provides evidence for a different mode of occurrence of Se in these better drained soils.

The soil of the Onecote series at site S4 is more poorly drained than the soils of the Dale series at S1 and S2 which has resulted in a greater accumulation of organic matter (L.O.I.) at the surface (Figure 5.9.). Considering the well documented associations between organic matter and Se (section 2.3.) this may in part explain the higher concentrations of Se_t. Being towards the base of the slope this soil occupies a receiving site for drainage waters from upslope which may contain Se and so contribute to the Se content of the soil. Only the top of the profile has been sampled, but the pattern of distribution of Se_t is apparently for an increase with depth.

The most striking feature of these data at Bent Farm are the extremely high Se_t concentrations found in the soil profile at site S5 (Figure 5.9.). A mean profile Se_t concentration of 65.0 $\mu g\ g^{-1}$ is approximately 130 times greater than the mean Se content of some British soils given by Thornton et al. (in press) of 0.48 $\mu g\ g^{-1}$. It also represents an appreciable enrichment compared to the other soils on this transect. The high Se_t concentrations can perhaps be explained by its accumulation in this low lying site from drainage waters carying Se which has been mobilised from the soils upslope. As such the soil is similar to the soils in Eire which were found by Fleming and Walsh (1957) to be enriched in Se. These were soils occupying "flush" low lying sites receiving drainage waters from surrounding rocks and soils which contained quite high levels of Se. Common to such soils in Eire was a relationship between their organic matter content and the distribution of Se (Table 2.3.). Such a relationship is not apparent in profile S5; in fact the more Se-rich horizons are those towards the base of the profile which, although high in organic matter (L.O.I.) relative to the soils on the slope above, are depleted in organic matter in relation to the surface horizons of the soil (Figure 5.9.). The accumulation is more apparently linked, again, to that of Fe_t.

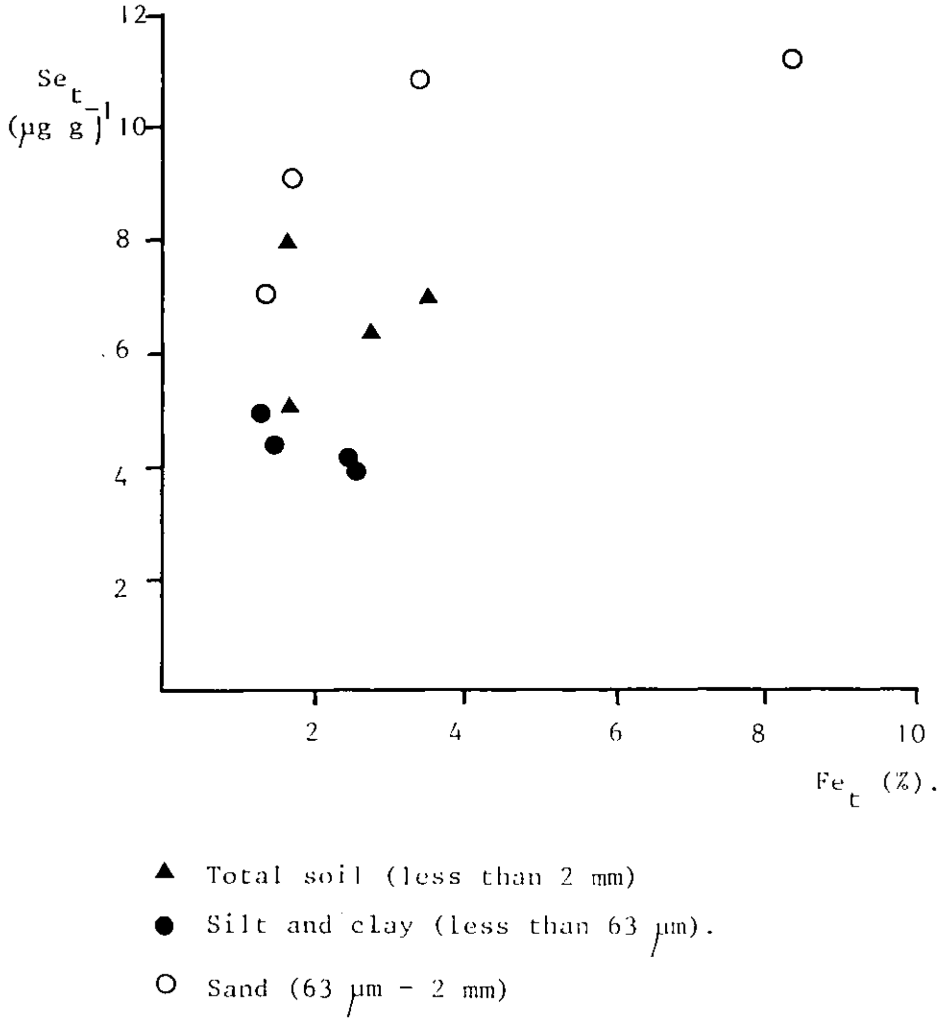


Figure 5.10. Relationship between Se_t and Fe_t for total soil, sand, and silt and clay fractions. Profile S3: Alton series.

Relatively high Fe_t and Mn_t values for the 0-15 cms sample may be anomalous as ferric oxide patches were associated with stagnant surface water lying above this soil. Oxidising conditions causing the precipitation of ferric species might also be expected to cause the precipitation of MnO_2 from reduced, soluble species. The more organic surface horizons contain relatively high concentrations of Fe_p, consistent with the presence of ferric oxides in complexes with organic matter (Bascombe, 1968), and it is possible that much of the Se here is associated with this Fe. Selenium may also be present in unmineralised plant remains; or in reduced forms such as Se^o and selenides in the reduced portions of the soil which are characterised by the grey colours attributable to ferrous Fe. Ochreous mottling, indicative of ferric oxides, occurs to a depth of 60 cms which is designated the base of the Bg1 horizon. In this horizon reducing conditions may cause the reduction of Se to the elemental form, after the Fe is reduced to ferrous iron (see Figure 2.2.). Flushes of oxygenated water which may cause the oxidation of ferrous to ferric iron and the precipitation of mottles of ferric oxides could be responsible for the oxidation of elemental Se back to selenite, although Geering et al. (1968) have shown that this reaction takes place relatively slowly. Most selenite produced would presumably be adsorbed onto the surfaces of the ferric oxides. This horizon therefore probably contains Se as both selenite and elemental Se dependant upon the redox poise in its locality.

Below 60 cms in the Bg2 horizon the ochreous colours of ferric oxides are absent, and it may be assumed that the majority of the Fe is in the reduced ferrous form. A sulphide odour was detected when the lower horizons were sampled, and it is probable that ferrous sulphides are present. In such sulphide rich conditions Howard (1977) suggests that Se would be further reduced, from the elmental form, to the selenide ion (Se^{2-}) which may be present substituted for S in pyritic material, and represented by the formula; $Fe(S_2, Se_2)$, and as such the Se is again associated with the Fe in the soil (Figure 2.2.). The absence of oxygenated waters in this zone means that the acidity produced by the oxidation of sulphide to sulphate is absent, which would be one of the criteria for a sulphuric horizon (Avery, 1980). However, the evidence suggests that this horizon has formed due to the enrichment of the soil by waters draining from pyritic soils and parent materials upslope.

5.5. Conclusions.

The levels of Se in these soils (mean 3.39 $\mu g\ g^{-1}$, range 0.83 - 20.9 $\mu g\ g^{-1}$, n = 16 for bulked topsoil samples) are distinctly higher than those reported in section 2.9.3. for soils from England and Wales, where the mean Se concentration was 0.48 $\mu g\ g^{-1}$, and 0.67 $\mu g\ g^{-1}$ for shale derived soils. Subsoils concentrations were often much higher. This is obviously a reflection of the influence of parent materials which are considerably enriched in Se.

The presence or absence of mottling and the colours associated with gleying have been used to qualitatively assess the redox conditions of the soils; the presence of such colours is largely attributable to the ferric and ferrous species of Fe respectively. The poise of the couple between these two forms of Fe is important in governing the overall redox potential of the soil. Thus it has been postulated that in surface horizons, where waterlogging is less frequent and little Fe is in the ferrous form, the Se would be present as the selenite oxy-anion, adsorbed on the surface of ferric oxides (Howard, 1977). As the Fe is reduced to the ferrous form, Howard has demonstrated that the selenite would be reduced first to elemental Se, and then as the redox potential becomes more negative, to the selenide ion which he thought would be associated with ferrous sulphide. Watkinson (1962) thought that this form of Se existed in soils in New Zealand. Thus it would appear that in both oxidising and reducing conditions in the soil, Se will be associated with Fe, the only exception being in the case of elemental Se. The quantities of elemental Se present in the soils are difficult to assess, its reoxidation has been shown to proceed only slowly, although microbial action may modify this process (Geering et al., 1968). As elemental Se is insoluble and ferrous Fe soluble in acid conditions, it might be expected that under such conditions leaching would produce areas of enrichment of Se relative to the Fe content. The data presented shows no such horizons, suggesting either that leaching is not extensive or that most of the Se occurs as selenide in the presence of ferrous Fe.

It is possible that this clear relationship between Se_t and Fe_t is masking a connection between Se and organic matter, especially towards the top of the profiles, possibly because Se in combination with organic matter can be present as an organic - Fe - Se complex (Levesque, 1974b), but also because small amounts of Se incorporated in plants may be readily leached from the surface when the plant material is mineralised.

Elemental Se and selenides are largely insoluble, and therefore not available for plant uptake (Cary et al., 1967), whilst selenite can be utilised by plants. However, the adsorption of selenite on ferric oxides results in low solution concentrations and thus low plant availability. The combination of these two factors will result in low availability of Se in these soils, despite the high total concentrations of the element.

In the better drained soils developed on the same parent materials there is also an increase in the concentration of Se with depth. In similar soils in Eire, Atkinson (1967) related this purely to the enhancement of lower horizons due to leaching from the surface. However, the evidence for these soils suggests that as well as the accumulation of selenite on ferric oxides at depth, there is relative enrichment of the soil from Se contained in unweathered shale fragments. Selenium in this form would not contribute to the plant available fraction.

The information from the soils at Bent Farm suggests that as well as leaching of Se and Fe down the profile there is lateral movement of these elements in soils on the slope resulting in the accumulation of the elements in the soils on the more level ground at the base of the slope. However, unlike the similar situation in Eire where the soils are alkaline in reaction, the acidity of these soils would make the possibility of high plant concentrations and toxicity in livestock unlikely. It is possible that locally the formation of these Se rich soils might coincide with the occurrence of thin calcareous facies, producing soils of more alkaline reaction, but such occurrences would be scarce and difficult to predict.

The distribution of Se in the soils of the Mixon and Butterton Moor transect demonstrates the variability of the Se content of the soils of the area, and that this variation is due to differences in soil parent materials. Generally the soils on the finer grained parent materials contain the higher concentrations of Se. However, the classification of the soils of the area is based on the lithology of the parent material, and not all of the finer grained parent materials will be enriched in Se to the same extent (Fletcher, 1968). Thus soils of one series may have widely differing Se concentrations. In parallel with the possible occurrence of molybdeniferrous soils, soils high in Se will predominantly be found derived from clay shales and silty shales with siltstones of the Mixon Limestones and Shales formation, and the Gun Hill Siltstones respectively. No specific soil series will contain uniformly high or low concentrations of Se. The lower Se concentrations in the soils of the coarser grained parent materials (e.g. Wilcocks series) is probably due to a combination of inherantly low Se contents, and hightened leaching due to the more permeable nature of the solum.

Whilst considering the data from these soils, drawbacks in the method of sampling have been evident. The use of an auger for taking bulked topsoil samples is both quick and convenient, however, its use in the sampling of profiles, although quick, can lead to misrepresentation. It is only possible to easily sample at one depth interval down the profile (in this case 15 cms), and this may result in the inclusion of material from more than one horizon in a single sample. So although samples taken in this way can be instructive in recognising overall trends, chemical and physical changes in the soil which are attributable to the conditions prevalent in a particular horizon can be masked. As, for example, in the case of the weakly defined Eg horizons of the Wilcocks series. Thus in an initial study of the distribution of Se in the soils of an area, or soil series, a more discrete sampling technique should be adopted. This wiil be discussed in the following chapter.

CHAPTER 6. SOILS DEVELOPED FROM SILURIAN ROCKS IN THE LLANSANNAN AREA OF CLWYD.

6.1. Introduction.

It has been shown in the preceeding chapters that the Se content of the soil can be influenced by the nature of its parent material, and consistent with this in section 2.9.3. it was demonstrated that the Se content of the soil could differ widely when the soils were derived from different lithologies. The work in Chapter 5, covering soils developed from predominantly argillaceous rocks of Carboniferous age, also demonstrated appreciable differences in the Se content of soils from similar lithologies within a resticted area; and to a lesser extent it was apparent in south east England (Chapter 4) that quite small differences in the nature of the sandstones of the Lower Greensand could result in significant but small variations in the Se content of the soils so derived.

Combined with variation in soil Se content due to the influence of the parent material, it has been shown that processes of soil development can influence the distribution of the element both vertically within the soil profile, as exemplified by the podzols developed on the rocks of the Lower Greensand (section 4.3.2.), and also laterally, as evidenced by the accumulation of Se in profile S5 at Bent Farm in Derbyshire (section 5.4.2.). It was therefore sought to extend this work in order to better identify the effects of soil formation and development on the distribution of Se within the soil.

The study area for this work was in north Wales, predominantly in Clwyd, around the town of Llansannan, and covers some 180 Km^2 (Figure 6.1.). It was chosen because of the uniformity of the soil parent material throughout the area, and the fact that the distribution of the relatively diverse soil types is governed largely by topography and land use (Ball, 1960). It is thus possible to study the effects of differing soil forming environments on the distribution of Se, and to make comparisons between the varied soil types. The soils of the area have been clearly classified and documented by Ball (1960), and this information has been used as a basis for estimating

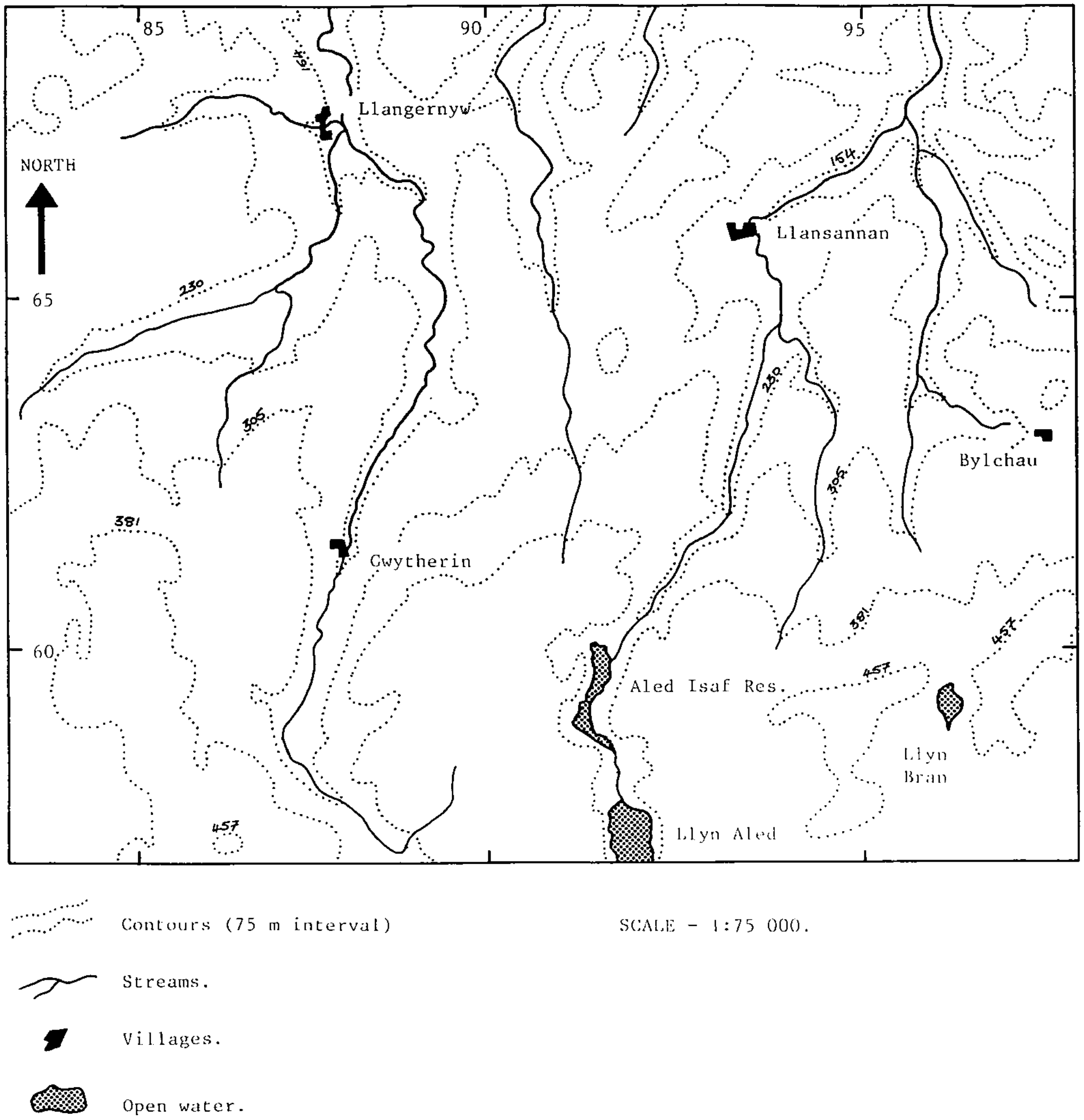


Figure 6.1. Topography, drainage and settlements in the Llansannan area.

the extent of the differences in soil Se content and distribution between the main soil series of the area. Despite the variety of soil types, the soils are predominantly acid and fine textured and therefore can not be taken as being representative of British soils in general. However, they demonstrate characteristics of many British upland soils, and most especially of those in mid and north Wales where similar rock types are found (Avery et al., 1975).

Profile pits were dug to cover the number of common soil series in the area, whilst at the same time sampling each soil with sufficient care to allow all the characteristic horizons to be sampled. This, it was estimated, would reduce the risk of mixing of horizons and lack of definition in results which was found to be a problem in the use of an auger for sampling as in the work reported in Chapter 5. However, although sufficient profiles were sampled to cover all soil mapping units and the major variants therein, any attempts to take into account the geographical variation within each soil series was not possible because of the time which would have been involved in doing so. One assumption made in this work therefore, is that of the uniformity of the composition of the parent material. In order to make some estimation of this uniformity a number of solid rock samples were taken from within the study area, and analysed for their Se content. Keeley (1973) working in the same region, noted that there was little variation in the rock content of several trace elements (Co, Cu, Mn and Fe).

6.1.1. Soil parent materials.

a. Geology and stratigraphy.

The following summary of the geology of the study area is taken from Ball (1960) and Smith and George (1961).

The whole of the study area is underlain by Lower Palaeozoic, Silurian rocks, which in north Wales form a thick series of non-calcareous marine sediments. The Silurian has been divided into three series which are recognised by their characteristic fossil graptolyte contents;

Silurian.
- Ludlow series:
  - (Upper Ludlow rocks are not present in the area.)
  - Elwy Group.
  - Upper Nantglyn Flags.
- Wenlock series:
  - Lower Nantglyn Flags.
  - Denbigh Grits Group.
- Valentian series.

However, only lower Ludlow and Wenlock rocks are represented in the study area. Lithologically both these series are members of the same broad facies which comprises mudstones and shales alternating with flags, sandstones and grits. Structurally the rocks form a syncline pitching to the E.N.E. along the flanks of which the older Wenlock rocks are exposed, thus outcropping towards the S.W. of the study area (Figure 6.2.). Within this outcrop the older Denbigh Grits group, of well cleaved flags and shales interbedded with a dominant development of greywackes, forms well marked scarp features. The greywackes being a poorly sorted, deep water deposit of mixed sand, silt and clay. These are succeeeded by the lower and upper Nantglyn Flags group which spans the boundary between the Wenlock and Ludlow series. These rocks are composed of laminated and ribbon banded alternations of mudstones, muddy siltstones and calcareous siltstones. The youngest rocks represented in the area are those of the Elwy group which are coarser facies consisting of silty and striped mudstones with subordinate sandstones. The outcrop of the Ludlow rocks is the most extensive in the study area.

As a result of later Silurian earth movements a block pattern of faulting with broad symetrical folding was produced, which was later enhanced by minor folds during post-Carboniferous earth movements. This has resulted in an irregular and fragmented outcrop of the various facies throughout the study area.

Drift cover in the area is quite extensive being predominantly a

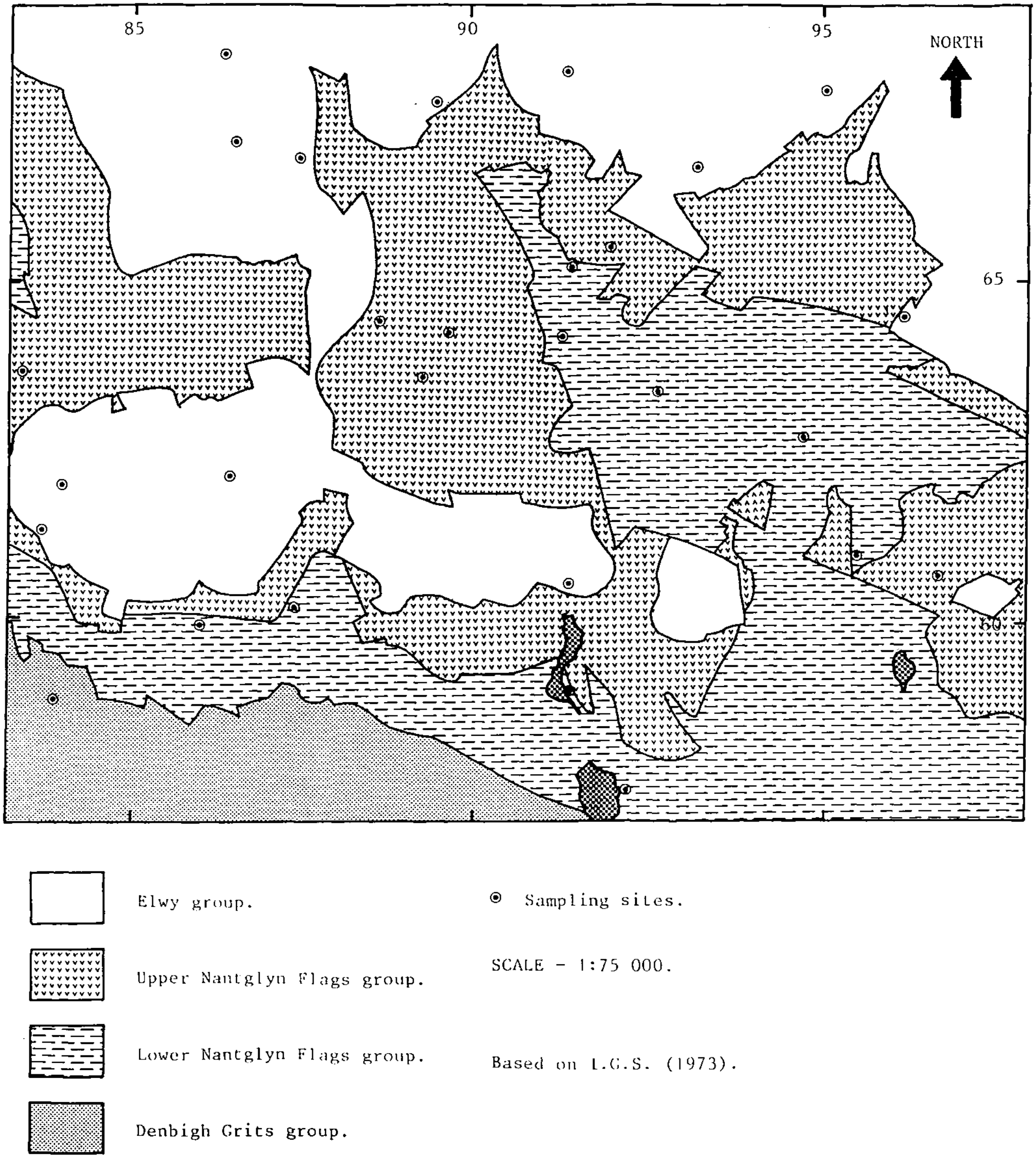


Figure 6.2. Location of solid rock sampling sites in relation to the outcrop of geological formations in the Llansannan area.

till produced by the local Pleistocene, north Wales ice, and can be up to 37 m thick. The till consists of a boulder clay which is grey brown in colour and generally a rubbly and incoherant silty clay loam. It derives from the Ludlow and Wenlock rocks only and is therefore difficult to distinguish from the in-situ weathering products of the rocks themselves (Boswell, 1949; Ball, 1960). Other recent deposits include valley and river deposits of sands and gravels, again being developed mainly from the local Silurian rocks and the drift so derived.

b. Mineralogy and composition.

There is little available information on the composition of the rocks within the study area covered by this work, however, Boswell (1949) gives the chemical composition of comparable rocks (mainly flags) from the nearby Clwydian range as: 65% SiO_2, 18% Al_2O_3, 7% Fe_2O_3, 0.3% CaO, 2.3% MgO and 4% loss on ignition at 950°C. He also noted the commoner heavy minerals of the local Silurian flags and sandstones to be micas, chlorite, epidote-zoisite, tourmaline, garnet, rutile, zircon and iron ores. In agreement with this, dioctahedral illite and iron rich chlorite have been quoted as being the dominant clay minerals in Silurian sediments in Wales, being complimented mainly by quartz (Evans and Adams, 1975a). On studying similar rocks in mid Wales, Adams et al. (1971) found that the main change on weathering was the decomposition of the chlorite component, and that since diagenetic chlorite acted as a rock cement, this lead to a textural degradation of the material.

Smithson (1953) undertook a more local study of the heavy mineral assembleges in soils, concluding that limonite, ilmenite, magnetite, leucoxene and large flakes of chlorite were most common in those soils developed from lower Palaeozoic shales, and that the most probable source of the limonite was easily weathered pyrite which was relatively abundant in some of the rocks.

Unfortunately this information sheds little light on the mode of occurrence of Se within these rocks. However, the pyrite noted by Smithson could be implicated as a possible source (Koljonen, 1974;

Rosenfeld and Beath, 1974; Atkinson, 1967), otherwise an association with any carbonaceous phase, of which little is known in these rocks, is the most probable.

6.1.2. Soils, climate and land use.

The soils of the area have been described in detail by Ball (1960) and the information which follows is derived mainly from that source; however, his classification of soils and their horizons has been modified to comply with that currently in use by the Soil Survey of England and Wales (Avery, 1980).

Because of the relative uniformity of the parent material which underlies the soils of this area the distribution of soil types is governed largely by topography, and in respect of this the area can be split into two topographical units; the upland and the moorland. The upland occupies the north of the area and lies between about 135 m in the north and 310 m to the south where it borders the moorland. It consists of hill blocks, with the more resistant grits and sandstones outcropping near the hill tops, separated by many steep sided narrow valleys. Pleistocene glaciation smoothed the outline of the hills and deposited the extensive locally derived drift, so that the only widespread rocky areas are those of the coarser facies mentioned above, the shales and mudstones being more easily weathered.

The moorland averages between 340 and 400 m with a high point within the study area of 518 m, and is formed of smooth contoured, rolling moorland. It is characterised by a flora of Heather (Calluna vulgaris), or Moor Matt Grass (Nardus stricta) where the Heather has been cleared in the past.

Rainfall over the area increases to the south, away from the coast, as the elevation increases. Thus from being approximately 1025 mm per year in the N.E. corner of the study area it increases to a maximum of about 1280 mm per year at Llyn Aled on the moorland (Figure 6.1.). Mean monthly temperatures decrease away from the coast and with altitude, such that the number of days with a minimum temperature below $0^{o}C$ increases from about 31 at the coast to 50 on the moorland. Frosts are more frequent in the east than the west. Lower mean temperatures on the moorland therefore result in lower evapo-transpiration and therefore a greater excess of rainfall than on the upland.

The most widespread soils on the upland are the silty loam to loam, typical brown earths of the Denbigh series which are acid and of low base status, having a typical horizon sequence of A, AB, B, BC. (Table 6.1.). This soil series is probably the most frequently occurring soil in the non mountainous areas of Wales. The soils are derived from the drift from the Silurian rocks, and the series has been divided into phases which cover the variations in the thickness of the drift, and topographical location. Normal phase soils occur on thick deposits of drift on gently sloping ground where unweathered drift material does not occur within c. 90 cms of the surface; they are primarily found below an altitude of 185 m. The percentage saturation of their good base exchange capacity depends upon the fertilizer history, but these soils generally occur in low rainfall areas where leaching is not as extensive as in the upland phase.

Upland phase soils are found on more elevated sites,usually between 230 and 310 m, and normally overly shales and mudstones. The soils are between 30 and 90 cms deep and have a higher stone content than the soils of the normal phase; otherwise the two phases are similar, those of the upland being perhaps more acid, which is typical of a lower level of fertility resulting from more rapid leaching in a looser and more stony soil situated where the rainfall is higher.

The shallow phase soils are found in hummocky terrain, associated with the normal phase soils, when the drift cover has been affected by erosion. Thus they are shallow soils, the C horizon lying between 30 and 60 cms, and typically have an horizon sequence of A, AB, BC, the BC being composed of only slightly weathered drift.

Soils of the steep phase occupy the steep slopes of the upland which are either wooded or bracken covered, and are developed on colluvium. A thin O horizon, predominantly of leaf litter, merges with a thin A

Soil mapping unit.	Soil subgroup.	Frequency (%).
Denbigh.	Typical acid brown earth.	53
Powys.	Brown rankers and humic rankers.	12
Sannan.	Stagnogleyic brown earths.	11
Cegin.	Cambic stagnogley soils.	1.4
Aled.	Typical brown alluvial soils.	3
Eriviat.	Typical acid brown earths.	1.3
Manod.	Typical brown podzolic soils.	4.7
Hiraethog.	Ferric stagnopodzols and ironpan stagnopodzols.	4.2
Ithel.	Humic brown podzolic soils.	0.8
Ynys.	Cambic stagnohumic gley soils.	7.3
Caron.	Raw peat soils.	1.6

Table 6.1. The frequency of occurrence of the soil mapping units found within the Llansannan study area (Based on Ball, 1960).

horizon which is typically a dark brown gritty loam, high in organic matter. The B is of a similar texture but brownish yellow in colour and merges with the C horizon after about 30 cms. Because of steepness the land is of little agricultural value. The two latter phases are much less widespread than the two former.

Powys series soils are predominantly brown rankers with some humic rankers occurring within the map unit, and are located on the hills of the upland, typically in broken country where the drift cover is thin and rock outcrops at or near to the surface; the soils are therefore developed either from post glacial weathering products or from a thin drift cover. They are shallow acid soils of low base status, profile drainage being excessive due to the open and stony nature of the solum. A dark grey brown silty loam to loam A horizon of about 10 cms thickness merges with a similar AB horizon of lower organic matter content which at about 20 cms passes into shattered rock with warmer coloured material between the fragments. At higher altitudes the increase in precipitation leads to the development of a more distinct B horizon due to the increased vertical leaching of the sesquioxides, and as such the soils often merge with those of the Manod series (see below). Occasionally under heath type vegetation the development of a thin peaty topsoil places the soils within the Hiraethog map unit.

Stagnogleyic brown earths of the Sannan series occupy uniform, gentle slopes and level ground in the upland, where run off is fairly good but profile drainage is imperfect, their parent material being drift derived from the Silurian rocks. In similar situations with more restricted drainage cambic stagnogley soils of the Cegin series, or occasionally at higher altitudes, soils of the Ynys series are found. Thus Sannan series soils are often found downslope of soils of the Denbigh series. Mottling along root channels in the typically grey brown silty loam Ah or Ah(g) horizon becomes more frequent in the B(g), and at perhaps 30 cms depth there is a sharp boundary to a more heavily gleyed Bg horizon, in which light grey and grey brown colours predominate. The grey Cg horizon is normally less stony than the C horizon of the better drained Denbigh series soils, the more moist conditions resulting in the greater weathering of the stones. The position of the boundary between perfect and imperfectly drained soils is largely determined by the presence of faults in the underlying rocks which affect the disposition of the underlying strata in relation to the angle of joints and bedding.

Soils of the Aled series (typical brown alluvial soils) occupy only a small portion of the land area in this study (Table 6.1.) and are developed from alluvium derived from the local Silurian rocks. They therefore occur on narrow, level areas of land adjacent to the rivers. Typically upper horizons have a silty loam texture, and below this is a gravel horizon containing little fine material which is developed from a coarser alluvial deposit than that of the topsoil. Because of the variations in the alluvial parent material these soils are varied in morphology and classification of horizons is often difficult. However, in general the profile drainage is good and these soils are often under arable rotation, being easily worked.

Typical brown podzolic soils of the Manod series are found on cultivated land with gentle to moderate slope and adjacent to the moorland above about 300 m. The soils are thus bounded at the lower altitudes by the soils of the Denbigh series. The parent material is the drift derived from the Silurian rocks, although often this was thin and none now remains below the soil. In this respect therefore, the soils are related to those of the upland phase of the Denbigh series. Profiles are normally free to very freely drained but occasionally imperfect subsoil drainage occurs. Manod series soils can therefore be considered as an extension of the Denbigh series where increased leaching has resulted in sesquioxide movement and the formation of a Bs horizon.

Ball considered Manod series soils to be a component of the moorland fringe (Figure 6.3.), passing at higher altitudes to the stagnopodzols of the Hiraethog series; which in turn are associated with soils of the Ynys and Caron series in a topographical sequence on the moorland. Hiraethog soils are found on moderate slopes, and on more gentle slopes where there is little or no drift cover. The series was not mapped in detail and the map unit therefore represents significant variations in soil type. The majority of the soils are ironpan stagnopodzols which have an accumulation of organic matter overlying a gleyed elluvial

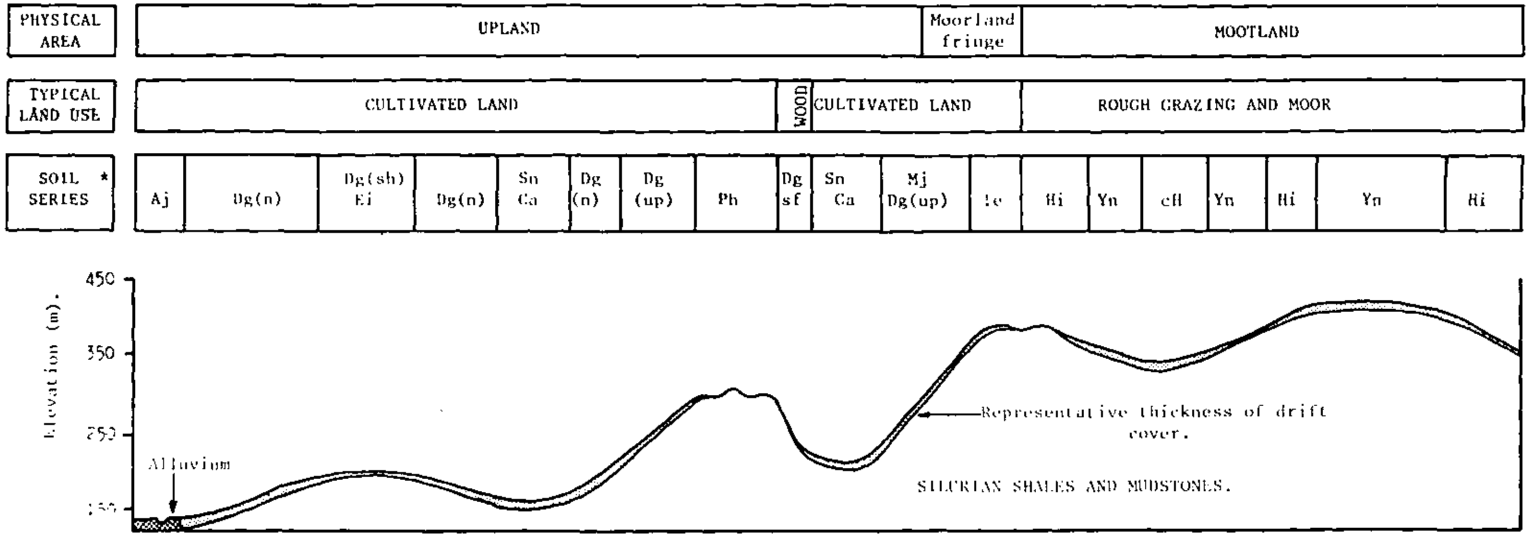
Figure 6.3. Relationship between topography, land use and the occurrence of soil series in the Llansannan area. (After Ball, 1960).

KEY TO SOIL SERIES*:

Dg - Denbigh: (n) - normal phase.
(sh) - shallow phase.
(sf) - steep phase.
(up) - upland phase.
Aj - Aled.
Ei - Eriviat.

Sn - Sannan.
Ca - Cegin.
Ph - Powys.
Mj - Manod.
Ie - Ithel.
Hi - Hiraethog.

Yn - Ynys.
cH - Caron.



horizon (Eag) below which a thin ironpan (Bf) has developed causing the restricted drainage in the upper horizons. Below the pan is a relatively well drained clay to clay loam Bs horizon which is often enriched in clay material;this horizon gives way to a paler BC horizon which may occasionally be more grey in colour due to restricted drainage. Hiraethog soils are commonly found under heather (Calluna vulgaris) but this has often been cleared resulting in the predominance of moor mat grass (Nardus stricta). A common variant within the map unit has no ironpan development. These are ferric stagnopodzols and have more recently been classified elsewhere as soils of the Hafren series (Lea, 1975).

When the Hiraethog series has been reclaimed, usually on the moorland fringe, humic brown podzolic soils of the Ithel series are found. Cultivation and faunal activity in the less acid, limed soil mixes the Hiraethog O, Eag and Bf horizons, thus producing a humic dark brown Ahp horizon containing bleached sand and stones. Below the Ahp are the Bs and BC horizons which are similar to those of the Hiraethog series. In appearance the profile is often similar to that of the Manod series.

Cambic stagnohumic gley soils of the Ynys series are found on the moorland where the slope is more gentle, and are underlain by drift. Profile drainage only really occurs through fissures and old root channels, the soil and parent material being relatively impermeable with the majority of water moving over the surface of the soil. Surface wetness and acidity have resulted in the accumulation of an O horizon, of up to 40 cms; this is underlain by a silty clay loam, dark grey brown to brown, Ag horizon. Prism faces of the predominantly light brownish grey Bg horizon are coated in a dark humic material washed down from above. The Bg passes into a stony and structureless CG horizon of gritty clay loam texture. Vegetation is predominantly Nardus stricta with lesser amounts of other species such as Molinia caerulea. Raw peat soils of the Caron series are perhaps best considered as extreme examples of the Ynys series, occurring where the lack of drainage from level and basin sites has resulted in the accumulation of greater amounts of peat. The mineral matter beneath the very acid peat has the appearance of the Bg and CG horizons of the Ynys series. Vegetation on the peats is poor and little grazed, consisting of Deer Grass, Cotton Grass, mosses and occasional heath.

On both the upland and the moorland therefore, each soil series may be found to merge into one or more other series, the changes depending on gradual changes of altitude, topography and drift cover, and occasionally abrupt changes in land use; the latter being the only instance where clear boundaries between soil series may be found. This relationship, between the occurrence of soil series and other factors such as topography, has been represented in Figure 6.3. Table 6.1. gives the approximate extent of the various soil mapping units within the study area, and their geographical distribution has been depicted in Figure 6.4.

Farms in the region are normally small, those of less than 20 ha being in the majority. Cattle rearing and milk production are the most important practices on the better land of the upland, with sheep rearing becoming more important towards, and onto, the moorland. Some of the better land is down to arable rotation but the majority at any one time, perhaps 90%, is under permanent or temporary grass. The high unreclaimed moorland is primarily used as rough grazing for sheep. There is little woodland in the area, but just outside the study area on the moorland at Clocaenog the Forestry Commision have extensive plantations.

6.2. Sampling and analysis.

The thirty seven soil profiles were sampled in May, 1980 and were all taken from grazing land which was either upland permanent pasture of rough grazing on the moorland. The profiles were sampled by digging a profile pit and collecting material from the representative horizons from a cleaned face using a small trowel. Most soils were sampled to the depth of the C horizon, or the underlying parent material. Brief profile descriptions were taken in the field and concentrated mainly on those characteristics which could be of value in later interpretations of the chemical data. Thus moist colours and the nature of mottles were noted as an aid to assesment of the

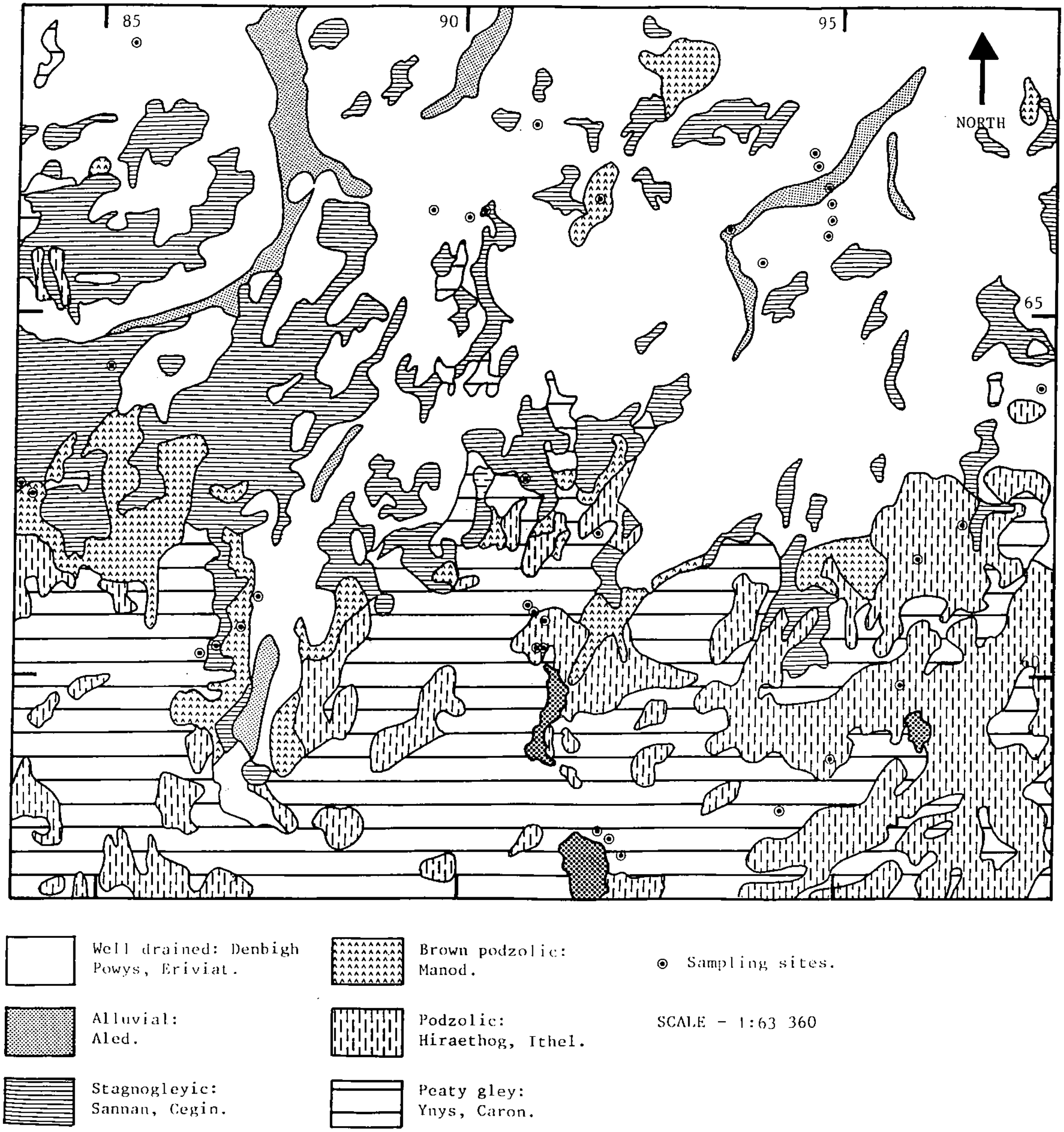


Figure 6.4. Location of soil profile sampling sites in relation to the occurrence of soil types in the Llansannan area

drainage status of the soil. Root depth, the nature and content of stones and rough texture determinations were also recorded. The identification of horizons was finalised after the results of laboratory analyses were known. Profile descriptions for the soil profiles are given in Appendix 1.3. All the samples were analysed for the following parameters as given in section 3.2.: pH_w, pH_{Ca}, Se_t, Fe_p, Al_p, Fe_t, Al_t, Mn_t, Ca_t, Mg_t and L.O.I.

Rock samples were taken from exposures found near to roadsides, which included road cuttings, stream banks, quarries and natural exposures. Each sample was taken from a fresh face produced with a hammer and was analysed for Se_t by the same method as used for soil analysis after the rocks had been crushed and ground to less than 80 mesh.

6.3. Results of solid geology sampling.

Rock samples from the study area were collected, and analysed for their Se_t content, in order to assess the uniformity of the Se content of the soil parent materials in the study area. Twenty eight samples were taken from surface exposures, the location of which, in relation to the occurrence of the main formations in the area, is given in Figure 6.2. Carefull classification of the rock types has not been made, but each sample has been placed within a formation on the evidence of the solid geology map (I.G.S., 1973). Due to extensive folding and faulting of the strata within the area many of the beds are disturbed and have not been clearly differentiated. The Se_t concentrations of the rocks are given in Table 6.2.

The mean Se_t concentration of the rocks is 0.048 $\mu g\ g^{-1}$ (standard deviation = 0.041, median = 0.037, n = 28), this value is low compared to the value of 0.6 $\mu g\ g^{-1}$ quoted by Lakin and Davidson (1967) as a mean Se concentration for shales, however, it must be remembered that many shales are greatly enriched in Se compared to the majority of the sedimentary rocks (see section 2.2.; Rosenfeld and Beath, 1964). Otherwise little comparable data is available for the Se content of rocks in Britain. The range of concentrations encoutered in these

Formation.	Sample number.	Grid reference.	Se_t.
Elwy group.	2502	913 682	0.015
	2504	835 612	0.012
	2507	863 622	0.023
	2509	839 620	0.014
	2510	872 668	0.034
	2511	861 682	0.029
	2512	893 675	0.029
	2513	932 666	0.021
	2514	949 677	0.055
	2521	913 604	0.058
	2525	863 670	0.013
	2527	960 643	0.081
Upper Nantglyn Flags group.	2500	894 645	0.034
	2508	833 637	0.057
	2515	943 659	0.044
	2517	891 634	0.038
	2526	885 645	0.035
	2528	966 606	0.095
Lower Nantglyn Flags group.	2501	922 575	0.052
	2503	858 599	0.024
	2506	872 601	0.079
	2518	911 641	0.208
	2519	913 650	0.043
	2520	926 634	0.063
	2522	912 589	0.005
	2523	954 609	0.110
	2524	948 628	0.046
Denbigh Grits group.	2505	837 588	0.018

Table 6.2. Selenium concentrations in solid geology samples from the Llansannan area.

rocks was therefore quite narrow (0.005 to 0.208 $\mu g\ g^{-1}$) with only two samples having Se_t concentrations greater than 0.1 $\mu g\ g^{-1}$. Analysis of variance ($p = 0.05$) shows that there is no significant difference between the mean Se_t concentration of rocks from any of the formations sampled.

The mean Se_t concentration of all the soils sampled in the study area (section 6.4.) was 0.55 $\mu g\ g^{-1}$, and the mean topsoil Se_t content of the non peaty topsoils was 0.46 $\mu g\ g^{-1}$ ($n = 25$); these values therefore represent approximately a ten times enrichment of the soil compared to the concentration of the underlying solid rocks. Similar enrichment of the topsoil, compared to the C horizon, was noted by Levesque (1974a) for some Canadian soils; and Koljonen (1975), investigating podzolic soils from Finland, reported enrichment factors of 2.3 to 23 for B horizons compared to the parent material. These values obviously demonstrate the appreciable persistance of Se against losses due to weathering in soil formation.

The behaviour of Se in these Welsh soils contrasts with that of other trace elements; Keeley (1973) found that the soils of the same area tended to be depleted in Cu, Co, Mn and Fe relative to the underlying Silurian rocks. In soils of the Denbigh series from an area to the east of Llansannan, rock and topsoil mean concentrations of Fe, Zn, Mg, Co and Mn were found to be of the same order, whilst Cu and Ca were approximately 2 and 3 times respectively more concentrated in the rocks than in the topsoils, and Pb was roughly 2 times more concentrated in the topsoils (Gardener, 1980). Keeley (1973) also found that there was little variation in the trace element (Cu, Co, Mn and Fe) content of rock samples from the area.

6.4. Soil profile sampling.

6.4.1. Observations on soil profile selenium distribution.

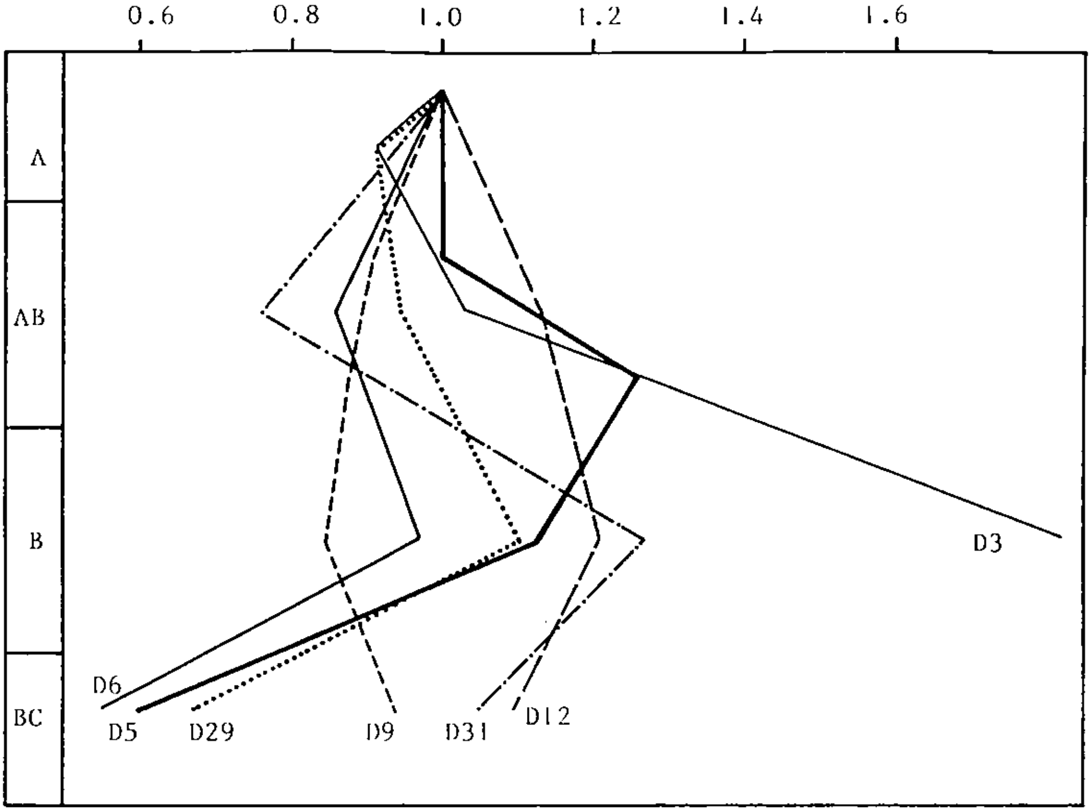
The location of the soil profile sampling sites in relation to the occurrence of the major soil types is given in Figure 6.4. These soils represent the most frequently occurring soil series in the area as given in Table 6.1. In most cases several soils have been sampled from within the same map unit in order to cover the variations in soil morphology which may be encountered within that unit. The soils have been categorised on the basis of the map unit from which they were sampled, and were classified initially on the basis of their profile morphology; the results of subsequent analysis may place a soil within a different series, and this is discussed later. Observations on the Se distribution in these soils, based on the analytical data presented in Appendix 2.2. are given in the following sections.

a. Denbigh series.

Soils of the Denbigh map unit are represented by profile numbers D3, D5, D6, D9, D12, D29 and D31. There is little change in Se_t concentration with depth in these soils, with the exception of profile D3. However, the small variations which are perceptable conform to a basic pattern as demonstrated in Figure 6.5. which shows the Se_t concentration of each horizon as a function of the Se_t concentration of the respective topsoil (A horizon) for each profile. Working down the profile from the A horizon the Se_t concentration decreases into the AB horizon after which there is enrichment of the B horizon relative to both the AB and BC horizons. Such trends are most apparent in profiles D3, D6, D29 and D31. Profile D5 is unusual in that the relative accumulation of Se_t occurs in the base of the AB horizon rather than in the B. Profiles D9, D12 and D29 exhibit the least variation with depth, as demonstrated in Figure 6.6.a. for profile D9.

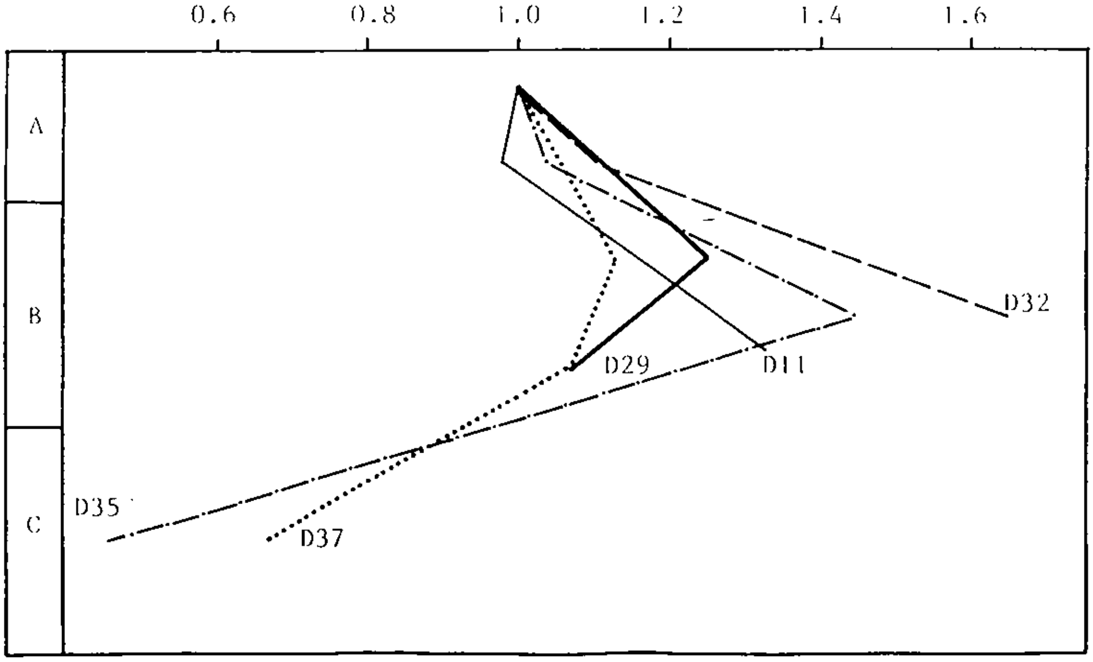
When the Se_t distribution in these soils is compared with the rest of the measured parameters (Appendix 2.2.) it can be seen that in general the accumulation of Se_t in the B horizon is paralleled by an increase in the concentration of Fe_p; this is demonstrated in Figure 6.6.b. for profile D31. Correlation analysis also shows that there are good correlations between Se_t and Al_p ($r = 0,698^{***}$) and Fe_t ($r = 0.602^{***}$) as well as with Fe_p ($r = 0.703^{***}$). Correlation with Al_t was however, poor ($r = 0.183$). Slightly elevated Se_t concentrations in the A horizon compared to the AB horizon are not clearly related to higher Fe_p concentrations (see Figure 6.6.b. for profile D31), but it seems probable that there is an association with organic matter which is obviously more abundant in the topsoil, and is reflected in the higher loss on ignition values for the A horizons compared to the

a. Denbigh series



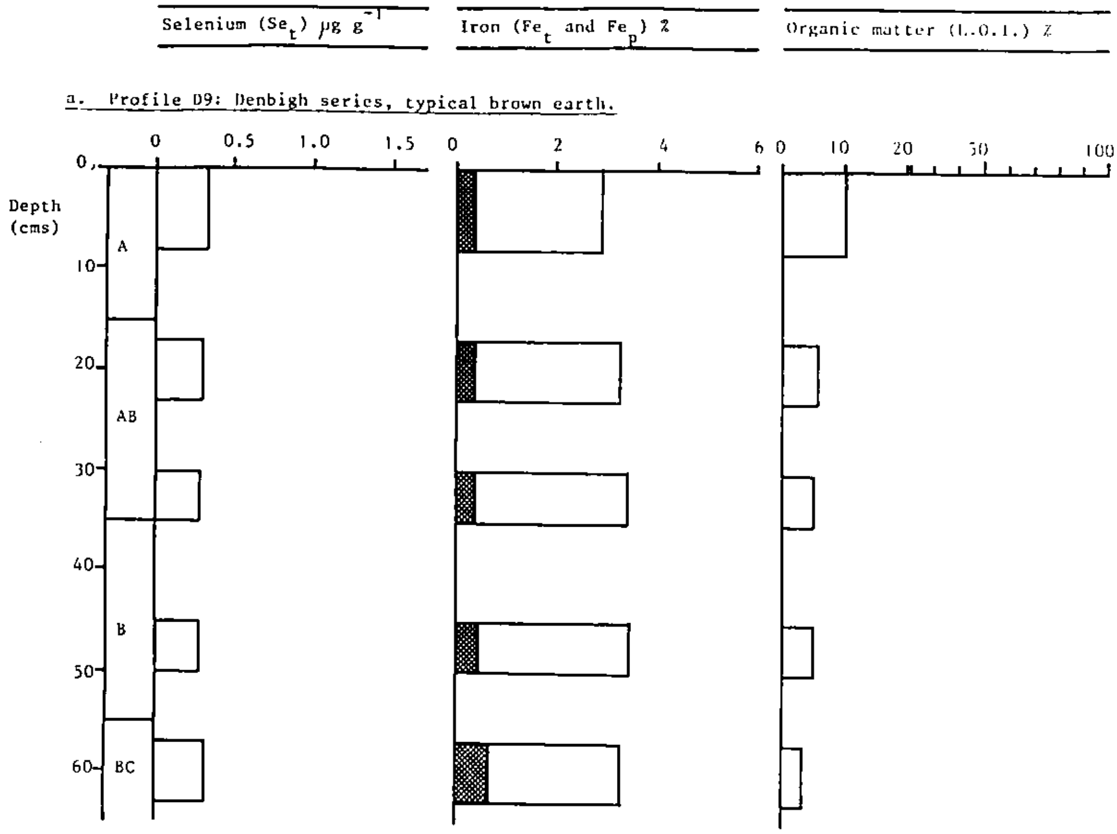
Horizontal scale = horizon Se_t concentration/A horizon concentration.

b. Powys series.



Hoizontal scale = horizon Se_t concentration/A horizon concentration.

Figure 6.5. Relative Se_t concentrations in typical horizons of soil series in the Llansannan area.



a. Profile D9: Denbigh series, typical brown earth.

b. Profile D31: Denbigh series, typical brown earth

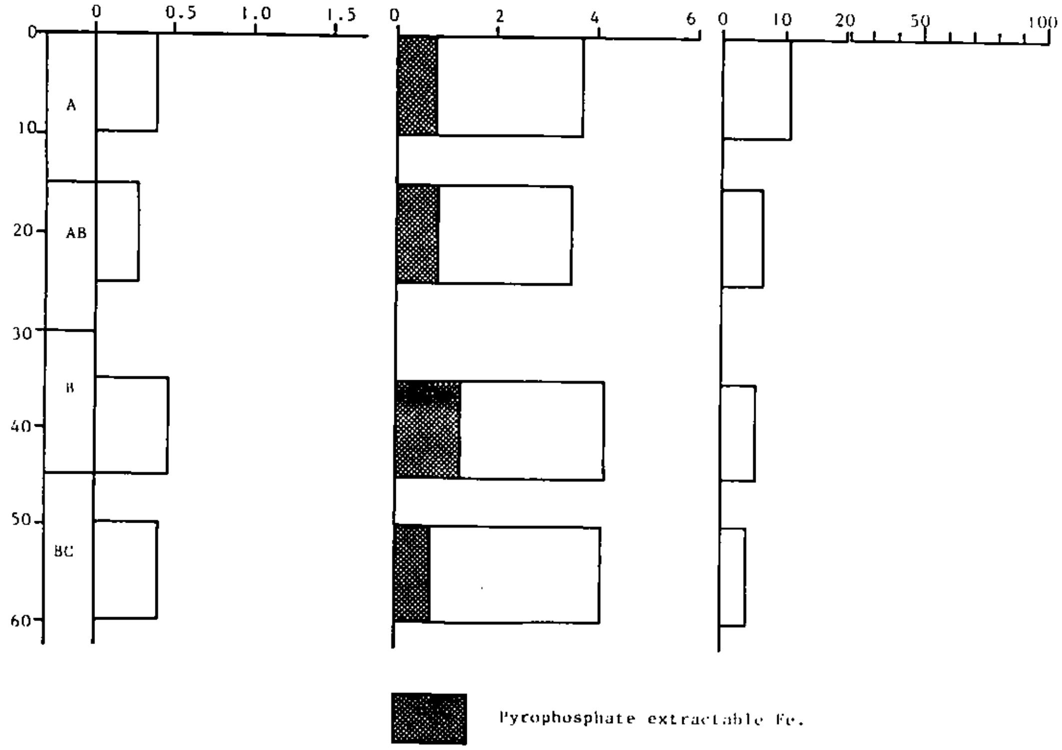
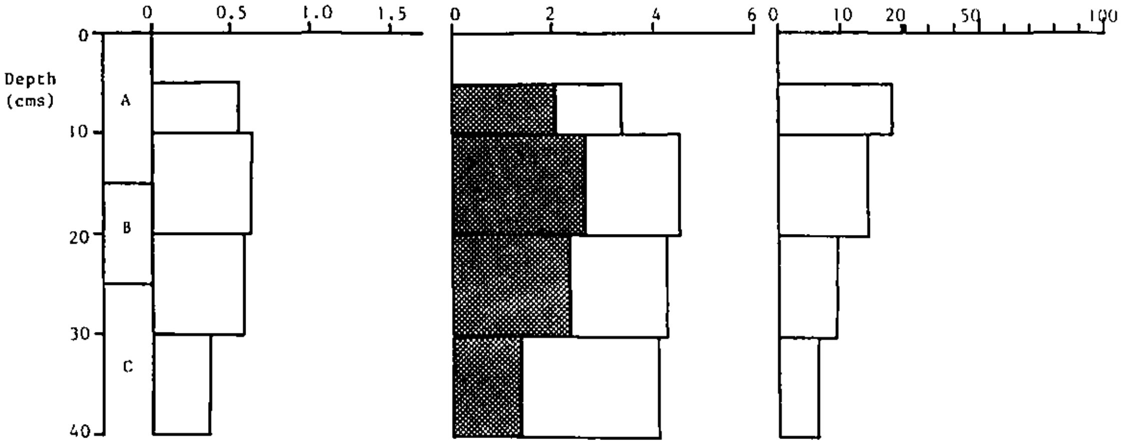


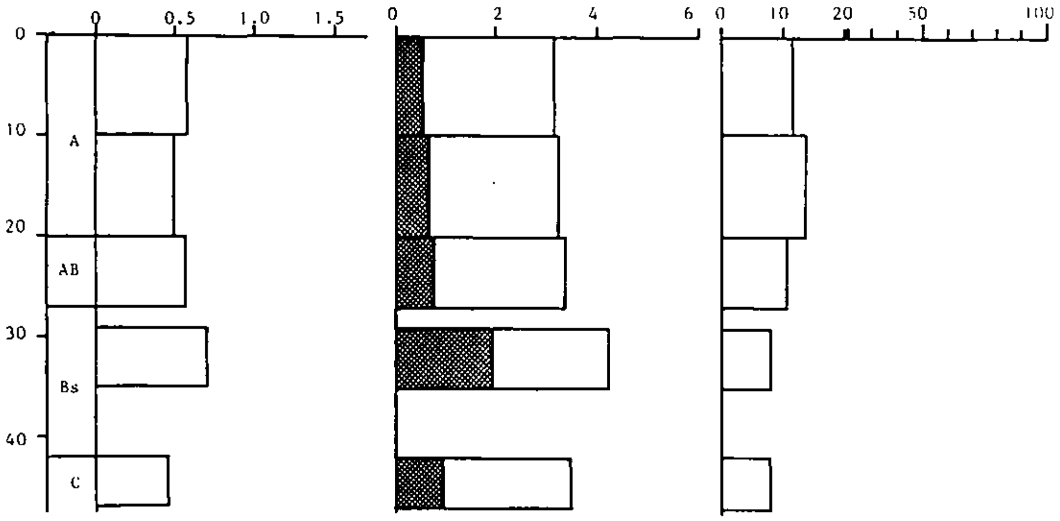
Figure 6.6. Distribution of Se_t, Fe_t, Fe_p and organic matter (L.O.I.) in twelve representative soil profiles from the Llansannan area.

Selenium (Se_t) µg g^{-1} | Iron (Fe_t and Fe_p) % | Organic matter (L.O.I.) %

c. Profile D37: Powys series, brown ranker.



d. Profile D8: Manod series, typical brown podzolic soil.



e. Profile D16: Hiraethog map unit, ferric stagnopodzol (Hafren series).

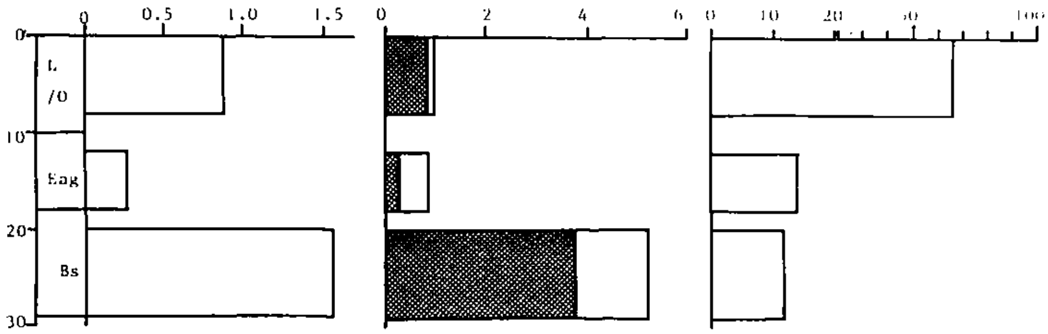
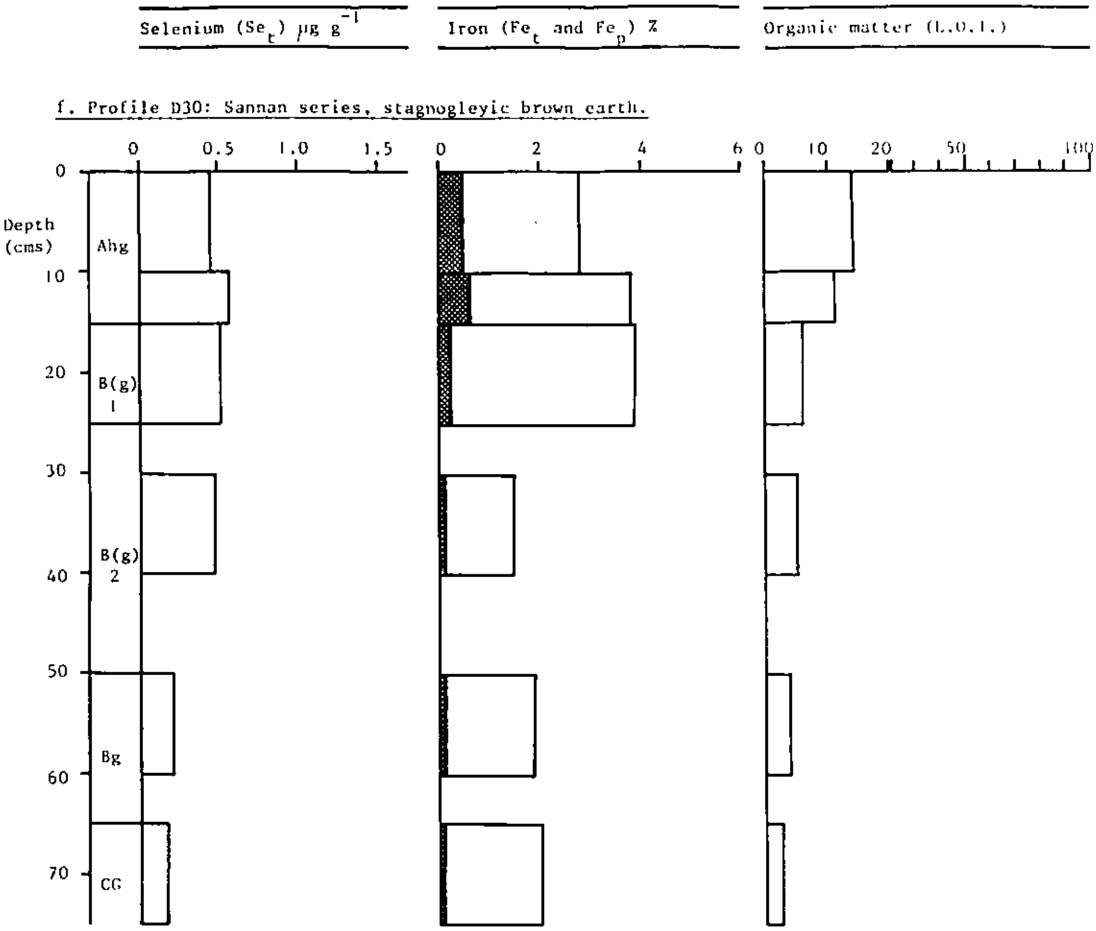


Figure 6.6. (Continued).

f. Profile D30: Sannan series, stagnogleyic brown earth.



g. Profile D17: Hiraethog series, ironpan stagnopodzol.

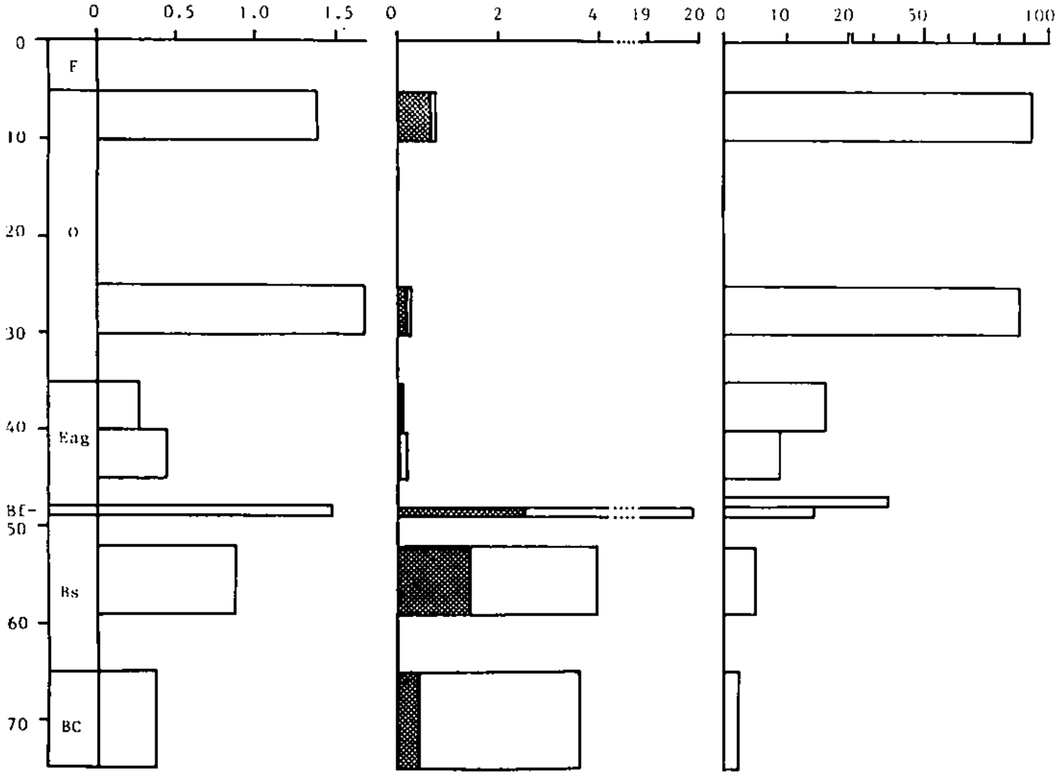
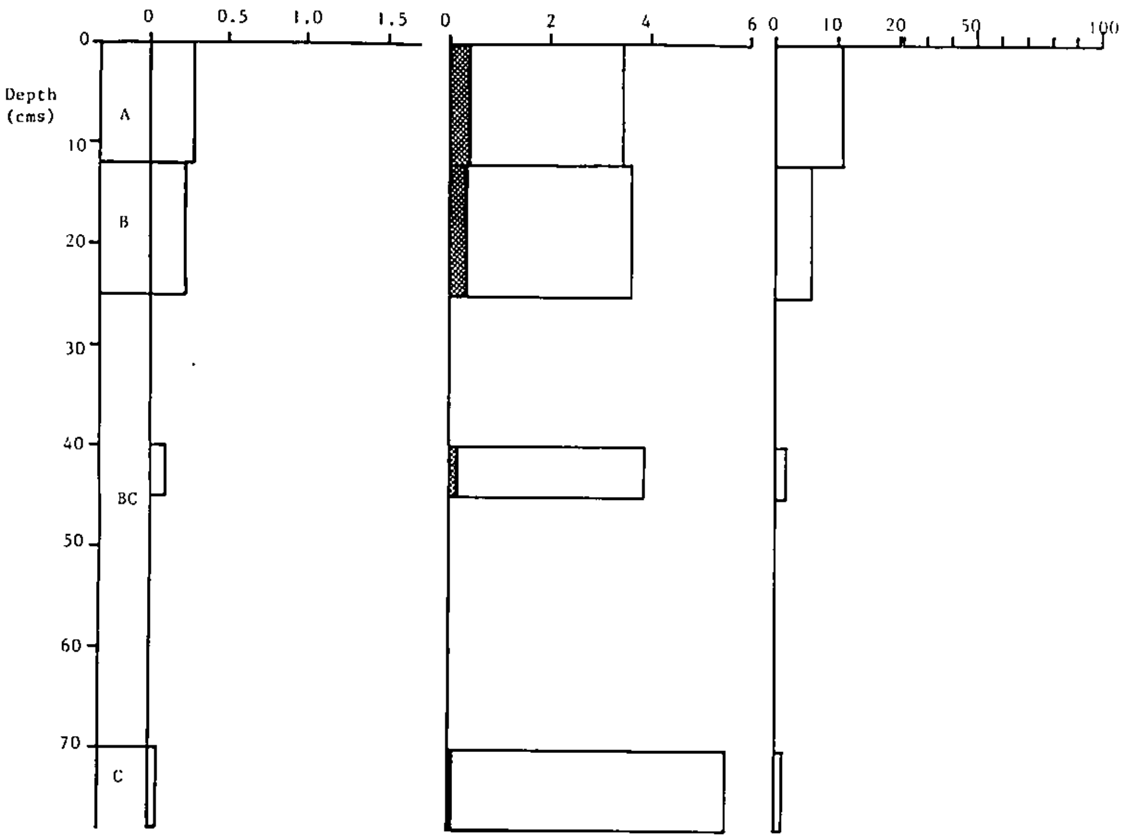


Figure 6.6. (Continued).

h. Profile D4: Aled series.



i. Profile D9: Ynys series, cambic stagnohumic gley soil.

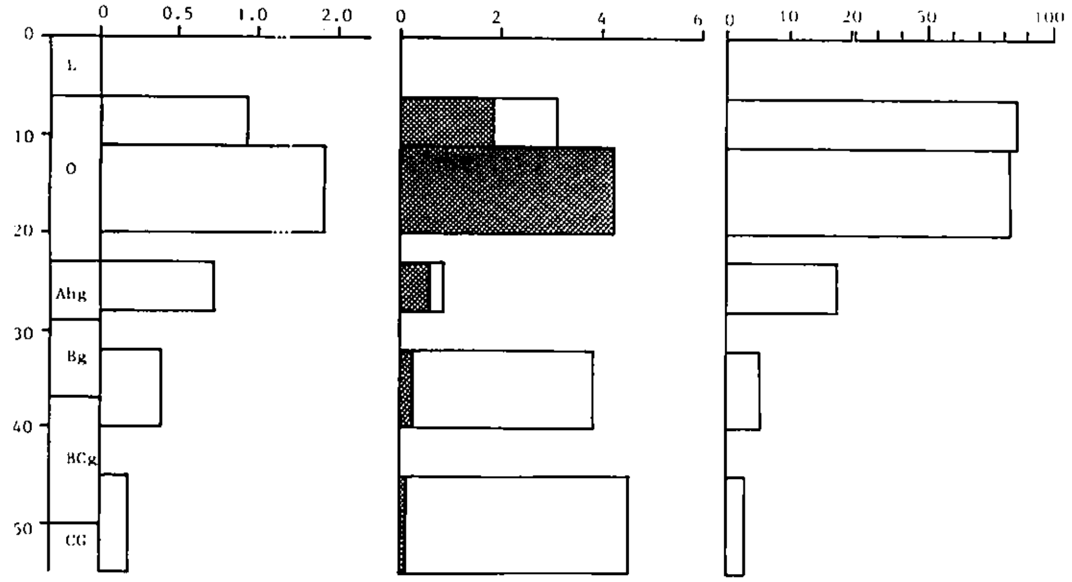
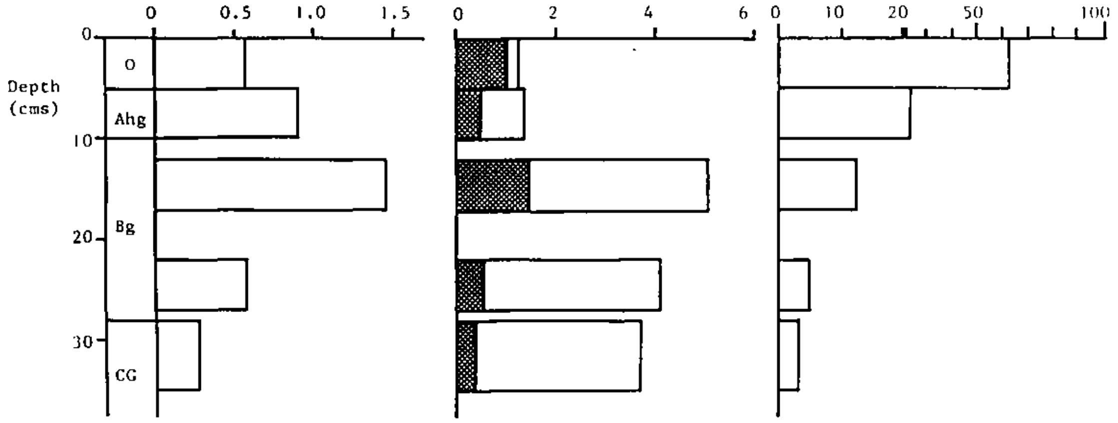


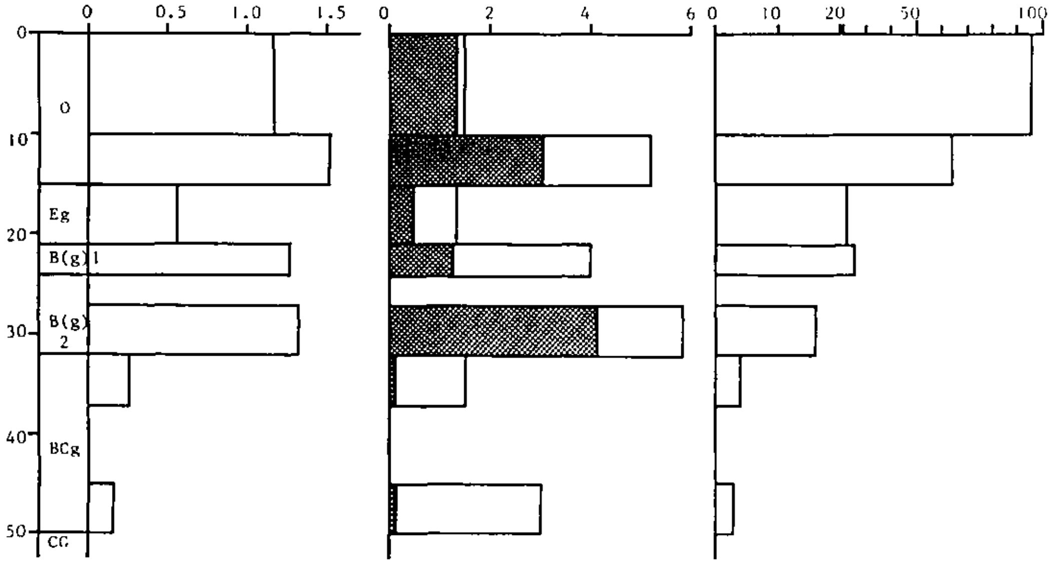
Figure 6.6. (Continued).

Selenium (Se_t) µg g^{-1}	Iron (Fe_t and Fe_D) %	Organic matter (L.O.I.) %

j. Profile D13: Ynys series, cambic stagnohumic gley soil.



k. Profile D14: Ynys series, cambic stagnohumic gley soil.



l. Profile D7: Ithel series, humic brown podzolic soil.

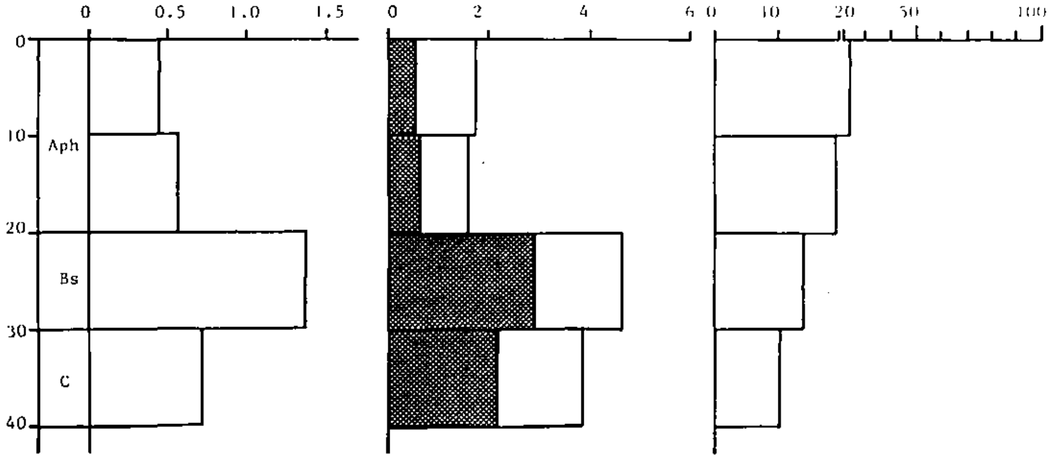


Figure 6.6. (Continued).

rest of the profile.

Bascombe (1968) suggested that iron oxides in brown earths are mostly in well crystalline forms, since their high base status and good aeration result in good microbial breakdown of organic matter, so that the reactive organic compounds which are able to dissolve and complex Fe do not persist in the soil. Consequently there is little mobilisation and transport of Fe, and typically in these soils the Fe_p content will decrease with depth and constitute only a small proportion of the total iron oxide content of the soil. Soils of the Denbigh series, however, are of low base status (Ball, 1960) and receive quite high rainfall (see section 6.1.2.), the soils are therefore naturally acid and this will result in the persistance of some organic complexing agents and some redistribution of Fe. This is much in evidence in profiles D3, D5, D29 and D31 which have peaks in Fe_p concentration in the B horizon coincident with those of Se_t. Fe_t concentrations are fairly uniform to depth in these soils, suggesting a uniformity in the parent material from which the soils are derived, but the fact that Fe_p and Fe_t are well correlated ($r = 0.780^{***}$) suggests that variations in Fe_t are due to redistribution of Fe.

Development of the B horizon in this way is most demonstrative in that of profile D3 which contains four times more Fe_p than the A horizon (2.8% compared to 0.7%), relative accumulation of Se_t in this horizon is also much greater in this soil (Figure 6.5.a.). This profile therefore has many of the characteristics of a Manod series soil (see section 6.4.1.c.), and although from an altitude of only 160 m is similar to the soils of the upland phase of the Denbigh series, being developed from only thin drift or rock material itself.

Those profiles showing the least differentiation of Se_t content with depth also exhibit very little variation in both the total and extractable Fe and Al contents. This suggests that there has been little vertical redistribution of Fe and Al, however, these three soils have in common that they occupy sites on relatively steep slopes (greater than c. 10^{o}) compared to the other four profiles examined. This suggests that movement of sesquioxides in these soils has primarily been laterally downslope, thus resulting in little accumulation of sesquioxides in the B horizon. Evans and Adams (1975b) studying a sequence of similar soils on a similar parent material in mid-Wales found that lateral movement of Fe downslope was a significant factor in its redistribution.

Profiles D5, D6, D9 and D29 are representative of the normal phase of the series. Profile D12, although found under rough pasture and evidently having been limed at some time as evidenced by its relatively high pH (mean = 5.8), has been classed as a steep phase soil, and as noted above it is thought that lateral movement of Fe and possibly Al from the profile has resulted in little variation in sesquioxide content with depth, and subsequently of Se. Profile D31 although quite deep (45 cms to the top of the BC horizon) is representative of an upland phase soil, and has a well developed accumulation of both sesquioxides and Se in the B horizon. This should be typical of the phase, which occurs at higher altitudes where there is greater rainfall, and is generally developed on the rock itself or thin drift, leading to better profile drainage than in the predominantly drift derived normal phase soils.

b. Powys series.

Soils of the Powys map unit are represented by profiles D11, D28, D32, D35 and D37. As with the Denbigh series soils the distribution of Se_t between the characteristic horizons of these soils conforms to a basic pattern, which is demonstrated in figure 6.5.b., showing the Se_t concentration of each horizon as a function of the Se_t content of its respective A horizon. In common with the Denbigh series soils the Se_t concentration increases into the B horizon, however, in these shallow soils there is no differentiation of an AB horizon and therefore no perceptable decrease in the Se_t content beneath the A horizon as a result of a decrease in the organic matter content (see Figure 6.6.c.). The contrast between the Se_t concentrations of the A and B horizons is on average greater than in the Denbigh series, and again this can be compared to the accumulation of Fe_p and Al_p in the B horizon which is also distinctly greater. The exception to this pattern is profile D35 where the Fe_p concentration is no greater in the B than the A.

Topsoil Se_t concentrations for the Powys series soils (mean = 0.56 $\mu g\ g^{-1}$) are significantly greater (at p = 0.05) than those of the Denbigh series (mean = 0.36 $\mu g\ g^{-1}$), as are those of Fe_p and loss on ignition (1.27% and 16.25% compared to 0.56% and 11.76% respectively). However, although only two Powys C horizons were sampled their mean Se concentration (0.31 $\mu g\ g^{-1}$) is very similar to that of the BC horizons of the Denbigh series (0.30 $\mu g\ g^{-1}$, n = 6). Also consistent with the uniformity of the parent material between the two series, both Fe_t and Al_t concentrations are comparable (Denbigh series mean = 3.55% and 1.98%, Powys series means = 3.31% and 1.85% respectively).

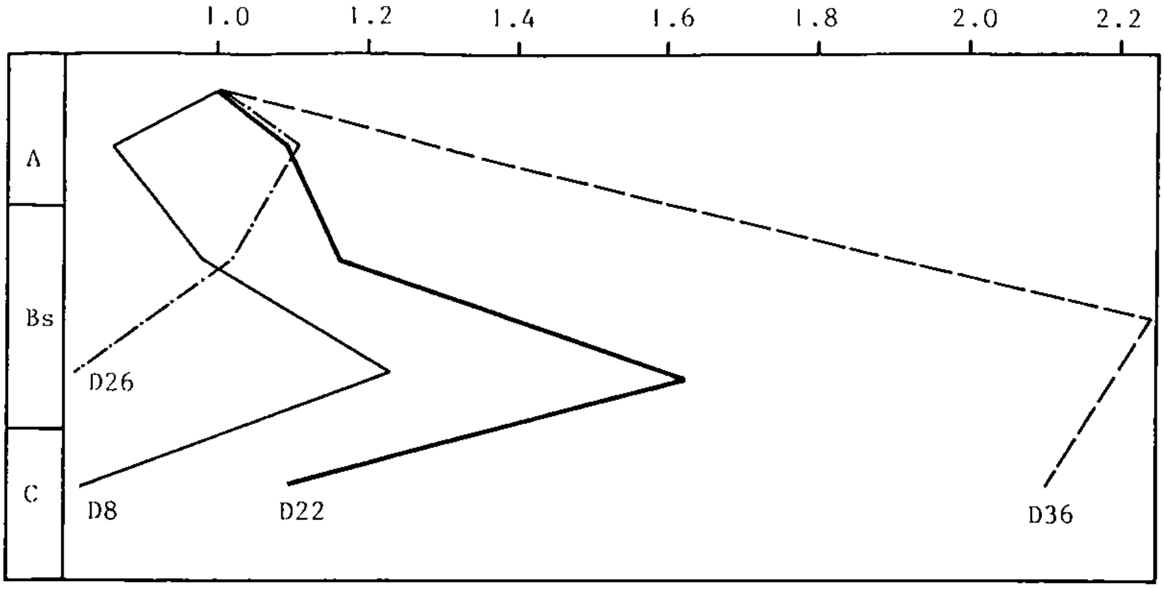
The greater enhancement of Fe_p concentrations in the B horizon of the Powys series, combined with the fact that the pyrophosphate extractable fraction of the Fe and Al constitutes a larger percentage of the total (mean values 43% and 40% respectively) than in the Denbigh series (mean values 19% and 18% respectively) is symptomatic of enhanced leaching in these very freely drained soils. More humose topsoils and naturally more acid soils will lead to the persistance of organic complexing colloids and therefore greater redistribution of Fe and Al.

All five of these profiles are, however, from altitudes above 230 m and so probably represent the high altitude phase of the series (Ball, 1960). Low altitude phase soils, despite having a less marked B horizon would still be expected to show and increase of Fe_p, Al_p and Se_t into the B horizon, because of the stony an more free draining nature of the soils.

c. Manod series.

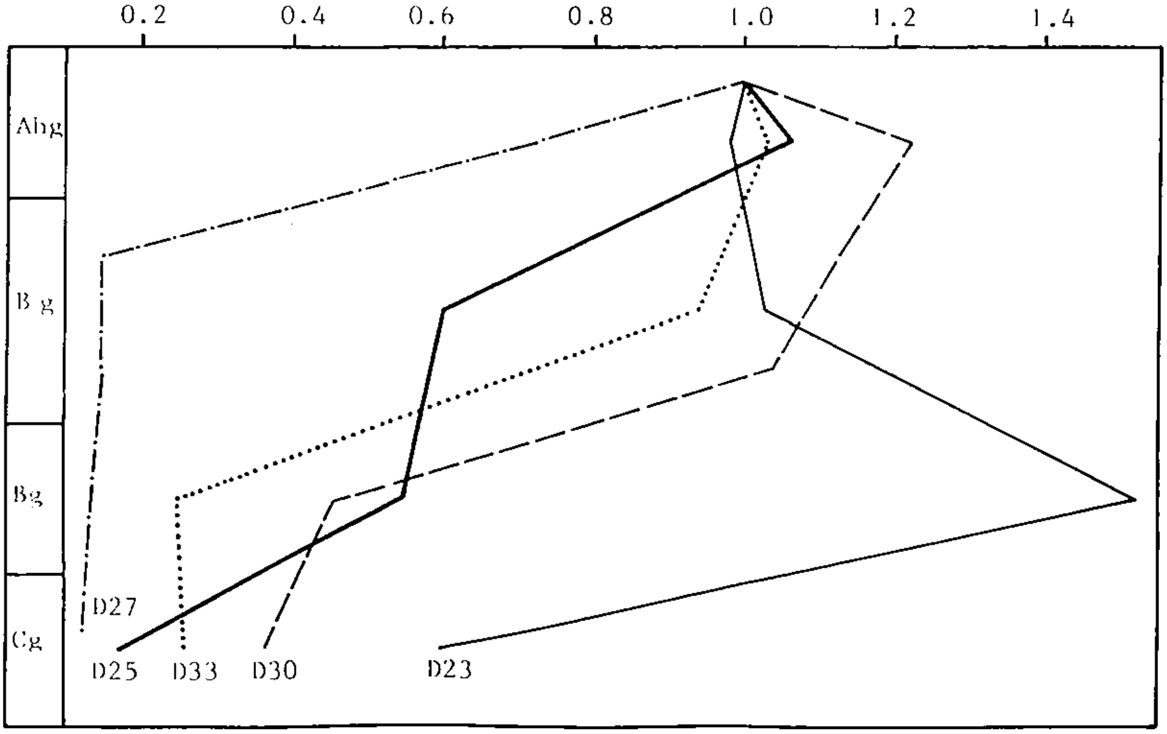
In general the soils of this map unit (profiles D8, D22, D26 and D36, Appendix 2.2.) demonstrate an extension of the trends which were described for the Denbigh and Powys series soils, in that the enrichment of the B horizon, in this case the Bs horizon, in both sesquioxides and Se is more pronounced. This is evidenced by the representative profile D8 in Figure 6.6.d. and by the plot of relative horizon Se_t concentrations given in Figure 6.7.a. The latter figure however, shows that there is considerable variation in the relative

a. Manod series.



Horizontal scale = horizon Se_t conc./A horizon Se_t conc.

b. Sannan series.



Horizontal scale = Horizon Se_t conc./Ahg horizon conc.

Figure 6.7. Relative Se_t concentrations in typical horizons of soil series in the Llansannan area.

enrichment of the Bs horizons, to the extent that, although from the Manod map unit, profile D26 exhibits very little B horizon enrichment of either sesquioxides or Se_t, and infact is better considered as an example of the Denbigh series with which it is more comparable (see section 6.4.1.a.).

Manod series soils are characteristically developed at high altitudes adjacent to the moorland, where the rainfall is higher than on the upland itself and also where drift cover is thin or absent. These criteria combine to produce freely drained soils with an acid reaction where the mobilisation of sesquioxides is therefore appreciable. The soils sampled are in general quite acid (mean value $pH_w = 5.85$), although liming will have taken place to ameliorate soil acidity under cultivation. Thus the Bs horizon of these soils, being more enriched in sesquioxides than the Denbigh series soils, is also more Se rich. Correlation of Se_t concentration is only significant however, with Fe_p ($r = 0.563^*$). The mean topsoil Se_t concentration (0.52 $\mu g\ g^{-1}$) is significantly greater ($p = 0.05$) than that of the Denbigh series (0.36 $\mu g\ g^{-1}$) but not the Powys series (0.56 $\mu g\ g^{-1}$). Mean topsoil Fe_p and L.O.I. values (0.90% and 12.11%) are not significantly different to those of the Denbigh series (0.56% and 11.72%) or the Powys series (1.27% and 16.52%).

Profile D22 exhibits an interesting variation in that the most Se rich horizon is above that of the greatest sesquioxide enrichment, and in fact corresponds to elevated L.O.I. values compared to the horizons above and below. It seems probable therefore that some accumulation of organics has taken place in this horizon, with which the Se is associated, as the concentration of Se_t is greater than would be expected from the sesquioxide content alone.

d. Sannan series.

The five representative profiles of the Sannan map unit (D23, D25, D27, D30 and D33), in contrast to the three series already studied, show a very marked relative depletion of Se_t content with depth, and with the exception of profile D3 no marked accumulation in the B horizon (Figure 6.7.b.). In general the sesquioxide concentrations decrease down the profile, this being most clear in the case of Fe_p. The decrease of Fe_p concentration with depth in these soils is characteristic of the gleying process, as in a permanently waterlogged horizon the majority of free Fe will be in a reduced form (Fe^{2+}) which is not peptised by potassium pyrophosphate (Bascombe, 1968). In horizons where oxygenated waters periodically penetrate the soil producing aerobic conditions, some iron oxides will be precipitated; this process will usually increase towards the surface as the soil is less permantently waterlogged. Such a relationship was clearly seen in the majority of the poorly drained soils in the Derbyshire and Staffordshire study areas (section 5.3. and 5.4.).

Correlation of Se_t is good with Fe_p ($r = 0.764^{***}$) and also with Al_p ($r = 0.603^{***}$). Unlike iron, however, aluminium is unaffected by changes in the redox conditions of the soil, and visual evidence, in for example profile D30 (Figure 6.6.f.), suggests that the relationship between Se_t and Al_p is not as clear as that between Se_t and Fe_p. It is noticeable that the correlation between Fe_p and Al_p is poor for these soils ($r = 0.557^{**}$) compared to that of the Denbigh, Powys and Manod series ($r = 0.925^{***}$). This suggests that good correlations between Se_t and Al_p in the previous three series could be and artifact of the relationship between Fe_p and Al_p.

In contrast to extractable values, total Fe has a tendancy to increase down the profile, which reflects the leaching of Fe as ferrous iron down the profile from the upper horizons. This difference in Fe_p and Fe_t distribution clearly implicates Fe_p iron rather than other forms in affecting the distribution of Se_t in these soils. In well drained Denbigh series soils, for example, a close relationship between Fe_p and Fe_t ($r = 0.780^{***}$) produced an artificial relationship between Se_t and Fe_t ($r = 0.602^{***}$). Interestingly, the peak in Se_t concentration in the Bg horizon of profile D23 (appendix 1.3.; Figure 6.7.b.) does coincide with a peak in Fe_t and Al_t concentration, although this particular phenomenon is difficult to explain.

In contrast to Denbigh, Powys and Manod series soils, correlation is also good with L.O.I. ($r = 0.662^{***}$), both parameters decreasing with depth. The mean topsoil Se_t concentration of 0.52 $\mu g\ g^{-1}$ is not significantly greater than that of the Denbigh series (0.36 $\mu g\ g^{-1}$) because of the wide range of values encountered in the Sannan series soils (0.14 - 0.68 $\mu g\ g^{-1}$), and is similar to the means for the Manod and Powys series soils. Topsoil L.O.I. values tend to be higher than for the Denbigh series, reflecting organic matter accumulation under more acid and water saturated conditions.

The depth at which Se_t concentrations, and those of Fe_p, decrease appreciably varies from soil to soil (Figure 6.7.b.) and will be a function of the drainage status of the soil. In soils that are permanently waterlogged to very near the surface there will be little Se_t in the soil immediately beneath the surface horizon; such a condition could be expected in the more poorly drained Cegin series soils, to which some of the soils in the Sannan map unit may be intergrades.

e. Aled series.

Soils of this series do not occur extensively within the study area (Table 6.1.), and only two profiles have been studied (profiles D4 (Figure 6.6.h.) and D10; Appendix 2.2.). Concentrations of Se_t are low in both of the soils (mean = 0.13 $\mu g\ g^{-1}$). Both profiles show signs of gleying (Appendix 1.3.), due primarily to high groundwater rather than impeded drainage, as both soils were quite stony to depth. Increased Fe_t concentrations at the base of the profile were common to both soils, and are probably due to secondary precipitation of iron oxides which was observed on the stones. Otherwise Fe_t concentrations varied little down the profiles. Evidence of oxidation of Fe and the preciptiation of iron oxides at depth suggests that the decrease in Fe_p concentrations down the profile is due to a decrease in the fine material content of the soil (Ball, 1960), rather than the effects of gleying as observed in the soils of the Sannan series. Concentrations of Se_t were again well correlated with those of Fe_p ($r = 0.880^{***}$) and also Al_p ($r = 0.995^{***}$) and L.O.I. ($r = 0.662^{***}$). As such the patterns of distribution of Se in these soils is similar to that in the alluvial gley soil at Onecote which was reported in section 5.3.2.

f. Hiraethog series.

Five examples of podzolic soils from within the Hiraethog map unit, which represents a variety of soil types (Ball, 1960), are presented (profiles D1, D2, D16, D17 and D21). Despite differences in the morphology of the soils, the distribution of Se$_t$ between the characteristic horizons complies to a basic pattern. This is evidenced in Figure 6.9.a. which shows the Se$_t$ concentration of each horizon as a function of the Se$_t$ concentration of its respective E horizon; the E horizon was chosen as a reference since there was considerable variation in the Se$_t$ content of the organic topsoil horizons (0.41 - 1.68 µg g^{-1}) and in most instances the E horizon contained the lowest concentrations of Se$_t$ (0.29 - 0.46 µg g^{-1}). This basic pattern is one of elevated Se$_t$ concentrations in the peaty O horizon, where there is a linear relationship between the Se$_t$ and organic matter (L.O.I.) contents providing good evidence for organic combination of Se (Figure 6.8.).

This relationship, however, raises an important point regarding concentrations in organic horizons. If these are expressed on a weight to weight basis, as in this study, concentrations are higher than they would be expressed on a weight to volume basis, and this is pertinent when comparing organic and mineral horizons of much higher bulk density. No bulk density measurements were made in this study and so such comparisons can not be made, Wells(1967) however, also made note of this and showed that an organic horizon with a Se concentration of 0.15 µg g^{-1}, would on a volume basis have a concentration of 0.006 µg cm^{-3} (bulk density 0.04 g cm^{-3}). Higher concentrations in organic horizons must therefore be viewed in the light of such information. However, close relationships between Se$_t$ and L.O.I. do suggest that Se is accumulating to a greater or lesser extent in combination with organic matter.

Below the organic topsoil Se$_t$ concentrations are lower in the eluvial horizon, however, here concentrations are similar to those in the majority of the upland soils (mean = 0.37 µg g^{-1}), as was that of the only BC horizon sampled, from profile D17 (0.33 µg g^{-1}). In the underlying illuvial B horizon there is a distinct accumulation

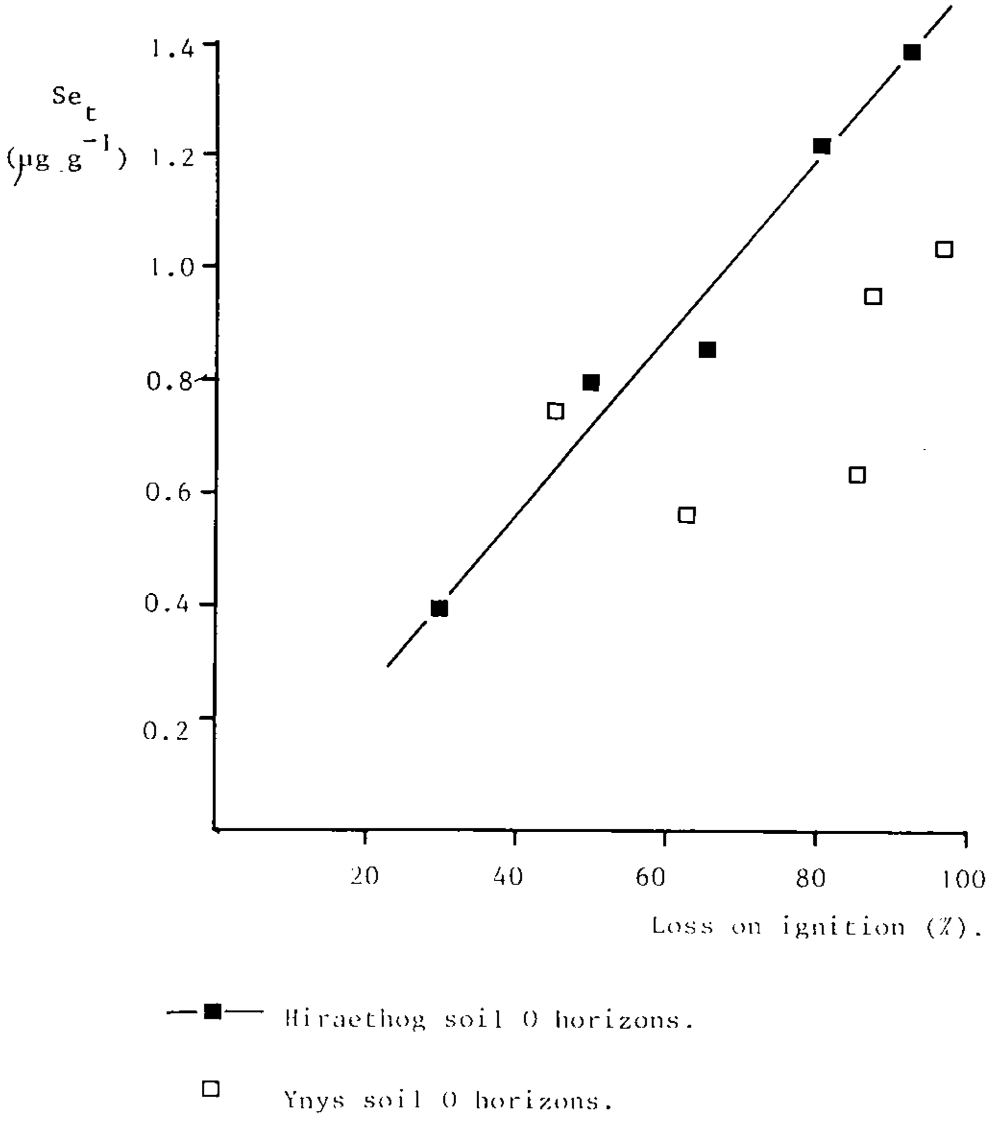
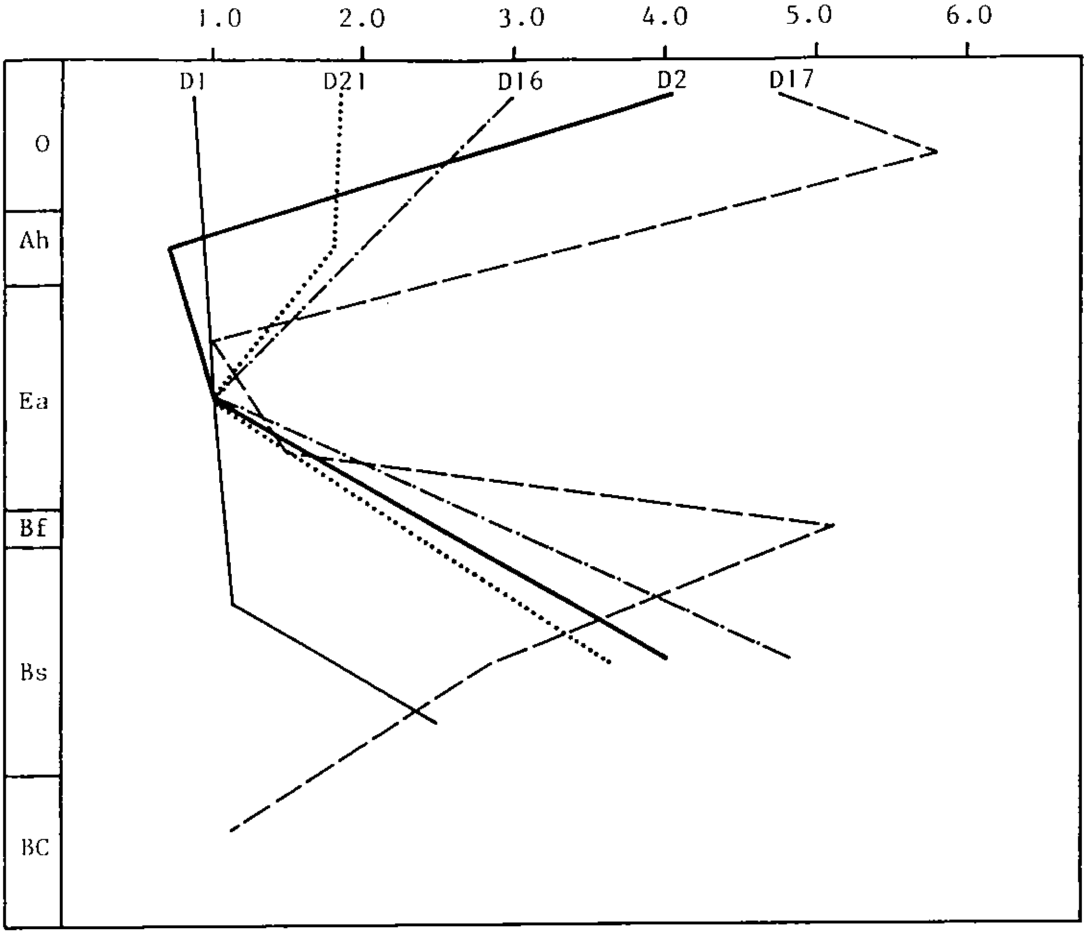


Figure 6.8. Relationship between Se$_t$ concentration and organic matter content (L.O.I.) in Hiraethog and Ynys soil O horizons.

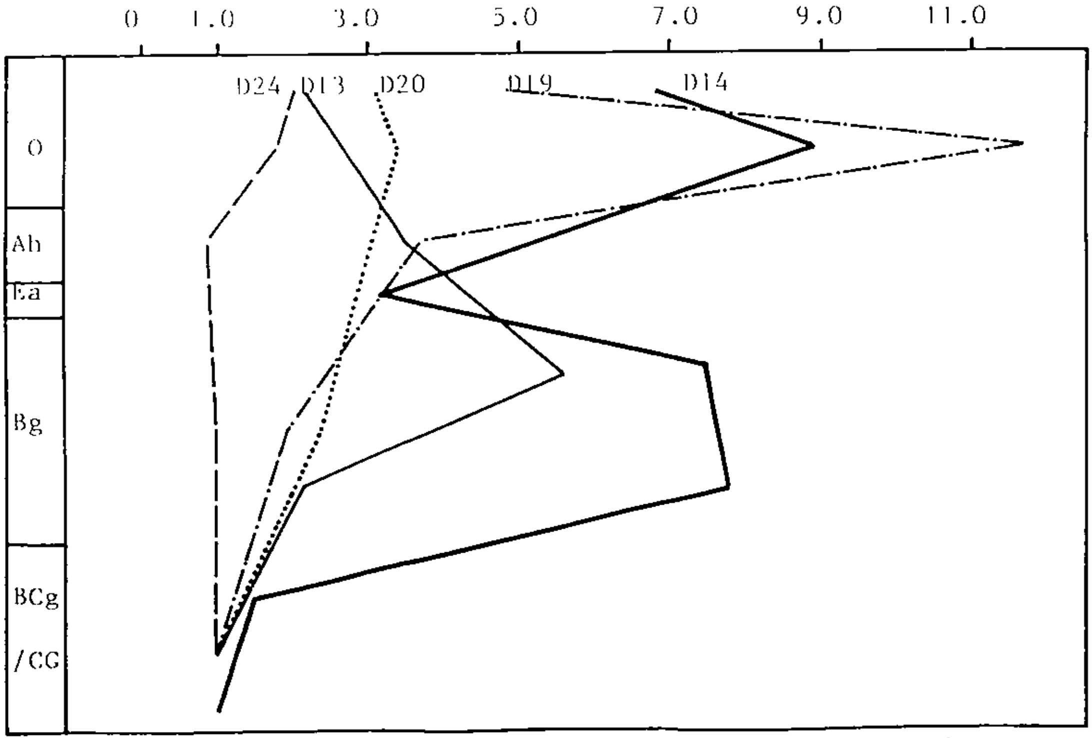
Figure 6.9. Relative Se_t concentrations in typical horizons of soil series from the Llansannan area.

a. Hiraethog map unit.



Horizontal scale = horizon Se_t concentration/Ea horizon concentration.

b. Ynys series.



Horizontal scale = horizon Se_t concentration/BCg or CG horizon conc.

of Se_t, which coincides with the accumulation of Fe, Al and also organic matter (L.O.I.). The pattern of Se_t distribution in these podzols is essentially similar to that of the coarse grained podzols which are developed on the Lower Greensand in south east England (section 4.3.2.), although Se_t concentrations are much higher in these soils.

Profile D17 most closely resembles the example given by Ball (1960) as being typical of the Hiraethog series. It is an ironpan stagnopodzol with a well developed ironpan (Bf) and gleyed eluvial horizon (Eag) as can be seen in Figure 6.6.g. The BC horizon at the base of the profile, which represents slightly weathered parent material, is comparable in composition to the basal horizons of the Denbigh series soils of the upland (Table 6.3.). In relation to the BC horizon Se_t has accumulated in the very acid (pH_w = 3.40) organic O horizon; below this the Se_t concentration of the Eag horizon is comparable to that of the BC (0.35 and 0.33 $\mu g\ g^{-1}$ respectively), and although impoverished in Fe_p in relation to the O and Bs horizons it contains appreciable amounts of Al_p and organic matter (Figure 6.6.g. and Appendix 2.2.). Both the clayey nature of this horizon, and the continuous ironpan below, serve to impede drainage and therefore the horizon is heavily gleyed and predominantly anaerobic conditions will prevail; the presence of ferric mottles is evidence of some degree of aeration, but very little of the Fe was freshly precipitated (Fe_p = 0.02%). Thus evidence suggests that Se present in this horizon may be associated with the appreciable organic component (L.O.I. = 16.8% in the top 5cms). In comparison, the well drained Bs horizon has a much higher concentration of Fe_p (0.84%; Fe_p:Fe_t = 0.36) and Se, which has also accumulated here, would predominantly occur as selenite adsorbed on ferric oxides (Geering et al., 1968). Strengthening the evidence for an association between Fe and Se it can be seen that the Bf horizon (Fe_t = 19.9%) is also enriched in Se_t (1.48 $\mu g\ g^{-1}$).

It is of interest that the ratio of extractable to total Fe (Fe_p:Fe_t) in the Bs of profile D17 is much lower (0.36) than that of the other four profiles of the Hiraethog map unit where there was no ironpan formation (mean ratio = 0.80), this being indicative of mobilisation and transport of Fe. It may be considered that enrichment of the Bs

Parameter.	Hiraethog series profile D17.	Denbigh series (mean, n = 6).
Se_t	0.33	0.30
Fe_p	0.41	0.49
Al_p	0.19	0.33
Mn_t	560	567
Fe_t	3.71	3.65
Al_t	2.00	2.18
Ca_t	0.003	0.073
Mg_t	0.736	0.760

Table 6.3. Comparison of BC horizon analytical results for Denbigh and Hiraethog series soils.

horizon is therefore less marked after formation of the ironpan, and this consequently can be linked to the lower Se_t content of the Bs horizon (0.84 $\mu g\ g^{-1}$) compared to the other four profiles (mean = 1.40 $\mu g\ g^{-1}$).

Profile D2 is a less well developed ironpan stagnopodzol. There is a smaller accumulation of surface organic matter (L.O.I. = 80.38%) and the Bf horizon is only weakly developed and discontinuous. However, the accumulation of Fe_p in the Bs accounts for 89% of the total Fe, and the accumulation of Se_t in this horizon is correspondingly higher than in profile D17 (Figure 6.9.a.).

In contrast, profile D1, which was situated only about 20 m from profile D2, shows no signs of ironpan formation, although there was gleying in the eluvial horizon, and hence has been classified as a ferric stagnopodzol. The organic topsoil was not well developed, being less than 10 cms thick and having a L.O.I. value of only 30%. There was also a noticeable difference between the top and bottom of the Bs horizon, the top Bs1 containing less Fe, Al and organic matter (L.O.I.) than the Bs2 (Appendix 2.2.). These factors provide evidence that podzolisation is less advanced in this soil than in the previous two examples from this map unit. The position of profile D1, on a steeper portion of the slope than profile D2, enabling better run off of rainwater, and thus less saturation at the surface and build up of organic matter, is probably the reason for the difference between the two soils. Adams et al. (1971) have commented that the degree of weathering in Hiraethog series soils is related to the surface accumulation of organic matter, and that the process of weathering in similar parent materials which are rich in chlorite, results in the textural degradation and gleying because of the resultant impermeability imparted. The three profiles already discussed do conform to this pattern, in a sequence of D17, D2 and D1, with D17 having the most marked development of organic matter and Eag horizon than in profile D2 and so on. The evidence suggests that the distribution of Se_t in these soils also varies according to the extent of the profile development, such that the more organic topsoils have greater concentrations of Se_t (Figure 6.8.), whilst the Se enrichment of the Bs horizon, relative to that of the Eag, increases in tandem with the development of the E horizon due to increased weathering;

that is until the development of an ironpan, which serves to inhibit further accumulation of Fe, Al and susequently Se_t in the Bs horizon.

In terms of the above defined sequence therefore, profile D16 (Figure 6.6.e.) lies somewhere between profiles D1 and D2, having a moderately organic topsoil (L.O.I. = 66.7%). Profile D21 has a very well drained, shallow profile, with little or no signs of gleying, despite some accumulation of organic matter (L.O.I. = 51.42%). In contrast to the similar profile at D1 this soil is probably developed upon a more permeable, or coarser, parent material; but may also represent an intergrade to the soils of the Powys series. Within the Hiraethog map unit therefore the following sequence of soils has been identified: Hiraethog series (D17), weakly developed Hiraethog series (D2), Hafren series (D16 and D1) and a Hafren - Powys intergrade (D21).

Ball (1960) demonstrated that translocation of clay into the Bs horizon of Hiraethog series soils took place; however, considering the stronger affinity of iron oxides for the adsorption of Se than clays (Hamdy and Gissel-Nielsen, 1977), it can be expected that the main role for clays is as a site for the precipitation of ferric and aluminium oxides which are transported to the horizon as complexes with organic matter (Jenne, 1977). In this respect it would seem reasonable to assume that the accumulation of such oxides would be enhanced in a more clay rich horizon.

g. Ithel series.

The distribution of Se_t in the two profiles from the Ithel map unit which were sampled (profiles D7 and D34, Appendix 2.2.) conforms to that which might be expected from the reclamation of a Hiraethog soil (Figure 6.6.1). Thus the mixing of an organic O and relatively impoverished E horizon from the Hiraethog soil produces a Aph horizon with a moderate organic matter content (mean = 17.9%) and quite high Se_t concentration for the soils of the area (mean = 0.57 $\mu g\ g^{-1}$). Beneath this horizon is a Bs horizon which is very similar to the Bs of the Hiraethog soils, having a high proportion of extractable Fe and Al (means 2.18% and 0.88% respectively) as well as a high Se_t concentration (mean = 1.0 $\mu g\ g^{-1}$). In both morphology, and the nature of the distribution of Se_t in the profile, these soils are very similar to those of the Manod series; and as with the Manod series the distribution of Se_t lower in the profile closely follows that of the Fe_p, whereas in the topsoil Se_t concentrations are higher than might be expected from consideration of the Al_p and Fe_p concentrations alone, which suggests an association with organic matter.

h. Ynys series.

Patterns of Se_t distribution in the five sampled profiles of the Ynys map unit (D13, D14, D19, D20 and D24, Appendix 2.2.) are quite varied, as demonstrated by Figure 6.9.b. In this figure the Se_t concentration of each horizon has been presented as a function of the Se_t concentration of the lowest part of its respective Bg or CG horizon; the mean Se_t concentration of these samples is 0.24 $\mu g\ g^{-1}$ (range 0.17 - 0.32 $\mu g\ g^{-1}$) whereas there is considerable variation in topsoil Se_t concentrations (0.58 - 1.15 $\mu g\ g^{-1}$).

Two factors common to these profiles are firstly high Se_t concentrations in the O horizons, which is characteristic of the peaty topsoils throughout the moorland, and secondly a marked decrease in Se_t concentrations at depth, especially in the Bg and CG horizons. The latter trend is generally paralleled by a decrease in Fe_p concentration with depth (example D13 in Figure 6.6.j; and appendix 2.2.); thus the relationship is similar to that in the gleyed horizons of the poorly drained Sannan series soils (section 6.4.1.d.). Two of the profiles (D13 and D14) have accumulations of Se_t in the Bg horizon, which is associated with an accumulation of Fe_p, and to a lesser extent Al_p. These two profiles also have distinct eluvial horizons, in the case of profile D14 this is clear between 15 and 21 cms (sample number 2224) where lower Fe_p, Al_p and Fe_t concentrations accompany a lower Se_t concentration than in the horizons above and below. The eluvial horizon in profile D13 is somewhat masked by the presence of organic material from above (L.O.I. = 21.55%), but Fe and Al concentrations are much lower in this horizon. Relatively high Se_t concentrations in this horizon are quite probably associated with the organic content.

Analytical values for the three remaining profiles (D19, D20 and D24;

Appendix 2.2.) provide evidence of an eluvial horizon in terms of Fe_t, Al_t and Mg_t, but there is no subsequent deposition of Fe_p, Al_p or Se_t lower in the profile. This distribution of sesquioxides and Se_t being consistent with the gleying process, in that below the O horizon the concentration of both parameters decreases with depth.

All the soils show signs of vertical redistribution of Fe. In profiles D13 and D14 this takes the form of an accumulation into the Bg horizon (see Figures 6.6.j and k.), whereas in the other three profiles Fe_t concentrations increase with depth (see the example of profile D19 in Figure 6.6.i.). The evidence presented suggests that profiles D13 and D14 are transitional to soils of the Hiraethog series, having horizons of depletion and enrichment of sesquioxides and subsequently Se_t. Consequently this suggests that oxidising conditions, probably due to oxygenated groundwaters, are prevelant for long periods of the year as deep as the Bg horizon. The distribution of Se_t, Fe_p and Al_p in profile D14 especially, shows a marked similarity to that of the Hiraethog series (example D17 in Figure 6.6.g.); however the profile displayed none of the visual characteristics of such soils, being more uniform in colour with depth (see Appendix 1.4.). The band of Mn concreations at 29 cms (20% Mn_t and 11.2% Fe_t) is indicative that oxidising conditions commonly penetrate to this depth, however, it is not clear how such concretions form (Rowel, 1981). In contrast, therefore, the latter three profiles (D19, D20 and D24) are more poorly drained and so oxidising conditions favourable to the precipitation of Fe occur less frequently at depth.

Compared to topsoils of the Hiraethog soils those of the Ynys series, especially in profiles D13, D14 and D19 (Figure 6.6. and Appendix 2.2.), contain much higher concentrations of Fe_t (mean values of 1.89% and 0.59%), which is probably due to secondary precipitation of Fe from drainage waters which have moved laterally after Fe has been mobilised from soils of the Ynys and Hiraethog series upslope. This phenomenon would not be expected in the Hiraethog soils which predominantly occupy shedding rather than receiving sites. This extraneous contamination with Fe, and possibly therefore Se also, could well be the reason for the lack of good correlation between Se_t and L.O.I. in Ynys series topsoils compared to that which has been demonstrated for the O horizons of the Hiraethog soils (Figure 6.8.). It is also possible that a similar process has contributed to the enrichment in sesquioxides of the illuvial Bg horizon of profiles D13 and D14.

Differences in the Se distribution in these soils, in relation to that of Fe_p, can generally therefore be related to differences in the drainage status of the soil and the depth to which waterlogged conditions are prevalent.

i. Caron series.

Deep raw peat soils of the Caron series (profiles D15 and D18; Appendix 2.2.) can be essentially considered as deeper variants of the Ynys series, where conditions of high rainfall, acidity and the accumulation of moisture in basin sites has resulted in the deep build up of organic matter. Thus the two profiles which were examined from the Caron map unit have a pattern of Se_t distribution which is similar to that of profile D24 from the Ynys map unit, which has a deep O horizon. Concentrations of Se_t are high in the peat, but also show variations as for example in profile D18 (Appendix 2.2.), and subsequently Se_t concentrations are lower in the gleyed mineral horizons below the peat and have only small concentrations of Fe_p. Reasons for the variations in Se_t concentration with depth in the peat are difficult to assess; Wells (1967) considered that similar patterns of Se distribution could be observed in organic soils as in mineral soils, such that quassi-eluvial and illuvial zones, in relation to Se concentrations, were apparent. No such trends were apparent in these soils. Variations in Se content could also reflect differences in the ability of various plant species to accumulate Se before their deposition as peat; or could be due to accumulation from drainage waters as above, which could obviously vary with both depth and time. However, comparison of Se_t concentrations in the Caron peat (mean = 0.88 $\mu g\ g^{-1}$, n = 5) to those of the other peaty topsoils of the moorland (mean = 1.03 $\mu g\ g^{-1}$, n = 15) suggests that accumulation of Se in basin sites is not a feature of these soils.

6.4.2. Statistical examination of the data from the soil profiles.

Basic statistical examination and observations of the data which are presented in section 6.4.1., for the thirty seven soil profiles included in this study, have indicated several interesting relationships between the Se_t content of the soil and the content or measure of other parameters. Most clear amongst these is the relationship between the Se_t concentration and that of the sesquioxides, represented by Fe_p and Al_p, in the soil, but it has also been demonstrated that organic matter has a role to play. In this section a more comprehensive statistical examination of the data is presented in order to attempt to both clarify, and better categorise, these relationships.

The data set used in these investigations is that given in appendix 2.2., however, before analysis the data for the following samples was removed:

i. Sample number 2187, a sample of drift material from 130 cms below the surface of profile D8 (Manod series), and as such was not considered as "soil" for this work.

ii. Sample number 2441, which is a sample of the ironpan (Bf) from profile D17 of the Hiraethog series. It was considered that its very high Fe content (Fe_t = 19.9%) would produce a disproportionate influence in correlation and regression analysis.

iii. Sample number 2222, was a sample of a zone of Mn concretions from Ynys series soil profile 14 and was removed because of its very high content of Mn and Fe (Mn_t = 20% and Fe_t = 11.2%) for the same reasons as sample number 2441 above.

a. Correlation analysis.

i. Results.

When the data from all thirty seven soil profiles were grouped (n = 167) highly significant correlation coefficients were found between Se_t and Fe_p ($r = 0.680^{***}$), Al_p ($r = 0.524^{***}$) and L.O.I. ($r = 0.524^{***}$).

Also there were highly significant negative correlations with Mg_t ($r = -0.526^{***}$) and pH_w ($r =-0.370^{***}$). The first three relationships were as expected, however, such a strong correlation with Mg_t is a little surprising, and will be discussed later. The negative correlation with pH_w, although highly significant, is not large and is probably a reflection of the fact that organic topsoils and podzolic B horizons which accumulate Se are more acid than most other samples. In all but two of the groupings of subsets of samples which follow their is no significant correlation between Se_t and pH_w. The exceptions are all B horizons ($r = -0.302^{*}$), where again the accumulation of Se_t by acid podzolic B horizons will influence the data; and for all samples of the Aled series ($r = -0.838^{***}$) which occurs because of the diversity between the only two profiles which were examined, profile D4 having on average acid samples ($pH_w = 5.10$) containing much Se_t (0.26 $\mu g\ g^{-1}$) and profile D10 being more alkaline ($pH_w = 6.4$) but containing little Se_t (mean = 0.11 $\mu g\ g^{-1}$).

Table 6.4. gives the correlation coefficients between Se_t and other parameters for the nine soil series which were examined. In all cases Se_t is significantly positively correlated with Fe_p, and in all but two cases with Al_p (Manod and Caron series). This reinforces the observed relationships between these parameters which was discussed in section 6.4.1. Correlation between Se_t and Fe_t is only highly significant for Denbigh series soils. Although evidence in the last section (6.4.1.) suggested a relationship between Se_t and L.O.I. in some instances, there is only a significant correlation between these parameters for four soil series; in the case of Aled and Ynys series this is a reflection of the coincident trend for both L.O.I. and Se_t content to decrease with depth down the profile. In the case of the Hiraethog series the coefficient is not highly significant ($r = 0.486^{*}$) but is a reflection of the accumulation of Se in the organic topsoil and also the Bs horizon where there were elevated L.O.I. values. When, however, certain series are grouped together, correlations with L.O.I. become more apparent, as for the grouping of the three well drained series of Denbigh, Powys and Manod ($r = 0.350^{**}$). This occurs because the grouping now includes a wider range of L.O.I. and Se_t concentrations compared to the more restricted range encountered within the soils of a single series. Correlation for

Soil series.	Number of pairs.	Fe$_p$	Al$_p$	Mn$_t$	Fe$_t$	Al$_t$	Ca$_t$	Mg$_t$	L.O.I.	pH$_w$
1. Denbigh.	31	.703***	.698***	.439*	.602***	.183	.111	-.460*	.191	-.160
2. Powys.	17	.538*	.524*	.471	.494*	.428	.146	-.111	.109	.003
3. Manod.	18	.563*	.430	.551*	-.025	.116	-.203	-.257	.168	-.098
4. Aled.	10	.880***	.955***	.045	-.563	-.198	.199	-.228	.882***	-.838***
5. Sannan.	26	.764***	.603***	-.396	-.128	-.355	.582**	-.607***	.662***	.302
6. Hiraethog.	21	.599**	.539*	.279	.437	.390	.273	.184	.486*	.294
7. Ithel.	9	.874***	.813***	-.554	.338	.373	-.153	-.321	.310	.284
8. Ynys.	26	.860***	.511**	.065	.415*	-.376	.171	-.536**	.564**	-.170
9. Caron.	9	.758*	-.059	-.267	-.096	-.483	.392	-.354	.435	-.468
All 1,2 and 3.	66	.693***	.670***	.301*	.392***	.070	.072	-.457***	.350**	-.146
1,2,3,4 and 5.	102	.686***	.688***	-.033	.113	-.060	.215*	-.575***	.549***	-.132
6,7,8 and 9.	65	.697***	.473***	.065	.348	-.035	-.011	-.320**	.428***	-.063
All 1 - 9.	167	.680***	.524***	-.226**	.068	-.219**	-.097	-.526***	.524***	-.370***

Superscripts: * - p=0.05
** - p=0.01
*** - p=0.001

Table 6.4. Correlation coefficients of the relationship between Se$_t$ and nine other variables for various soil series and groupings of soil series.

these two parameters is also significant for a grouping of all upland soils (Denbigh, Powys, Manod, Aled and Sannan series, r = 0.549^{***}), and of all moorland soils (Ithel, Hiraethog, Ynys and Caron series, r = 0.428^{***}).

A negative significant correlation between Se_t and Mg_t exists for the Denbigh series (r = -0.460^{*}), Sannan series (r = -0.607^{***}) and the Ynys series (r = -0.536^{**}), but as for the correlation with L.O.I. it is also significant in the case of all the groupings examined (Table 6.5.). As with L.O.I. this probably occurs because the restricted range of values within one soil series often masks any correlations which may be present.

Various groupings of soil horizon type were also made and the correlation coefficients calculated; those between Se_t and other parameters are given in Table 6.5. Again Se_t and Fe_p are positively significantly correlated for all groupings, as are Se_t and Al_p in all cases but for O and Bs horizons. For all groupings of horizons, with the exception of O horizons, Se_t concentration is significantly positively correlated with organic matter content (L.O.I.). There is also a negative significant correlation with Mg_t for all but O and Bs horizons. Significant positive correlations between Se_t and Fe_t for all O horizons (r = 0.573^{**}) and all types of B horizons (r = 0.571^{***}), probably reflect an actual correlation with Fe_p in instances where accumulation of Fe as Fe_p has lead to an increase in the total Fe content of the horizon. Except for a significant negative correlation with Mn_t for all mineral A horizons (r = -0.369^{**}) there are no significant correlations between Se_t and any of Mn_t, Al_t or Ca_t. No correlations with pH_w are significant but for a poor correaltion for all B horizons (r = -0.302^{*}).

ii. Discussion.

Broadly speaking and with certain specific exceptions Se_t is significantly correlated with Fe_p, Al_p and L.O.I. The inverse relationship between Se_t and Mg_t was unexpected. Whilst working on soils developed from similar lower Palaeozoic mudstones, containing chlorite, in mid Wales, Adams et al. (1971) concluded that the main

Horizon group.	Number of pairs.	Fe$_p$	Al$_p$	Mn$_t$	Fe$_t$	Al$_t$	Ca$_t$	Mg$_t$	L.O.I.	pH$_w$
All data	167	.680***	.524***	-.226**	.068	-.219**	-.097	-.526***	.524***	-.370***
All upland A	42	.579***	.640***	-.369*	-.183	.278	.058	-.610***	.445**	-.187
All O	21	.667***	.272	.111	.573**	.054	-.078	-.250	.340	.134
All B types	53	.779***	.690***	-.013	.571***	.302	-.156	-.576***	.770***	-.302*
All Bg	23	.779***	.851***	-.158	.453*	.207	-.203	-.589**	.748***	-.361
All Bs	11	.897***	.582	-.082	.797**	.452	-.551	-.529	.814**	-.562
All B	19	.667**	.685**	.361	.572*	.266	.139	-.524*	.603**	-.158
All gleyed horizons	54	.795***	.768***	-.154	.277	.091	.033	-.415**	.308*	-.182
All BC and C horizons	28	.786***	.849***	-.093	-.010	.283	.137	-.482**	.851***	-.172

Superscripts: * - p=0.05
** - p=0.01
*** - p=0.001

Table 6.5. Correlation coefficients of the relationship between Se$_t$ and nine other variables for various groups of soil horizons.

change in the sediments due to weathering was loss of chlorite, resulting in the release of Fe, Al, Mg and Si. Subsequent work demonstrated that Al, Mg and Si, but not Fe, showed net losses from soil profiles developed on such a parent material. In this work Mg_t is invariably negatively correlated with L.O.I. ($r = -0.634^{***}$ for all data) which, especially in the case of all the upland soils ($r = -0.717^{***}$) where L.O.I. decreases with depth, can be taken as an indication of the Mg_t content increasing with depth in the profile. This suggests that weathering in these soils results in the degradation of chlorite and the mobilisation of Mg as above; weathering will of course be more advanced in the top of the soil and it will be expected that more Mg will be lost. Mean Mg_t concentrations for A (0.44 $\mu g\ g^{-1}$), B (0.54 $\mu g\ g^{-1}$) and the BC and C horizons (0.72 $\mu g\ g^{-1}$) exemplify this relationship.

Similarly, negative correlation coefficients are found between L.O.I. and Fe_t or Al_t ($r = -0.520^{***}$ and -0.756^{***} respectively, for all the data, and -0.261^{*} and -0.453^{**} for all upland soils where n =102) however, in contrast to Mg_t these two elements tend to demonstrate relative accumulation lower in the B horizon of the profile, as demonstrated by the comparison of B and Bs horizons in Table 6.6. Lower mean Mg_t values in Bs compared to B horizons is probably an indication of a greater degree of weathering in these horizons. Thus the overall relationship is one where increased weathering results in the release of Mg, Fe and Al, and subsequent loss of Mg, whilst Fe and Al tend to remain and be reprecipitated as sesquioxides with which Se is associated. Negative corr alations between the Mg_t and L.O.I. content of specific horizon groupings (Table 6.5.) may also suggest that weathering is more advanced in the more organic and hence more acid soils. This is consistent with the findings of Adams et al. (1971), who suggested that the extent of chlorite weathering could be associated with the surface accumulation of organic material.

As Se_t is positively correlated with both Fe_p and Al_p in most groupings it is difficult to deduce whether there is a real relationship between Se_t and either or both of these two parameters. In most cases Fe_p is highly significantly correlated with Al_p ($r = 0.789^{***}$ for all 167 samples) suggesting that the same conditions favour the accumulation

Parameter.	Mean Bs horizon concentration (n = 11).	Mean B horizon concentration (n = 19).
Fe_t	4.65	3.94
Al_t	2.32	2.04
Mg_t	0.48	0.55

Table 6.6. Comparison of mean Fe_t, Al_t and Mg_t concentrations in B and Bs horizons.

of Fe_p and Al_p. However, for the following groupings the correlations attain less significance; Caron series (r = 0.011), Ynys series (r = 0.452^*), all O horizons (r = 0.154) and Sannan series (r = 0.557^{**}), these all being instances where gleying and anaerobic conditions are prevalent. However, the grouping of all gleyed horizons produces a highly significant correlation between Fe_p and Al_p (r = 0.723^{***}). The tendancy for all O horizons, especially of the Ynys and Caron soils to accumulate Fe, possibly as secondary precipitation products (see section 6.4.1.h.) may be the reason for this. In such instances where oxidation is causing the reprecipitation of Fe in an acid melieu, Al would not be precipitated, and the major portion of Al_p in such situations would be derived in-situ, hence the poor correlation between Fe_p and Al_p. The fact that in these O horizons the correlation between Se_t and Al_p is not significant suggests that Se is associated primarily with the Fe_p (r = 0.667^{***}). This phenomenon may therefore be the reason for the poor Fe_p to Al_p, and Se_t to Al_p correlations for Ynys and Caron soils. Hiraethog soils do not exhibit this relationship because as demonstrated in Figure 6.9. they tend to have a closer relationship between organic matter (L.O.I.) and Se_t content, probably because of a lack of secondary precipitation of Fe; these soils occupying predominantly shedding sites in the landscape (section 6.1.2.). This relationship between Se_t and Fe_p where there is differential accumulation of Fe_p over Al_p, suggests that an Fe_p - Se_t association is more important than that with Al_p. It is possible therefore that this is also the case where Fe_p and Al_p are correlated.

b. Regression analysis.

Analysis has already shown that largely the same factors correlate with the distribution of Se in all the soil series studied. It was therefore decided that the whole data set from thirty seven profiles (n = 167) could be used for regression analysis. Correlation analysis of this data has shown that significant correlations exist between several variables and the soils Se_t content, the highest correlations being with Fe_p which accounts for some 46% of the variation in soil Se_t concentration (r = 0.680^{***}). Regression of the Se_t content of the soil against more than one variable may therefore allow the development of a model which accounts for a greater proportion of the variation in the concentration of Se_t than does Fe_p alone.

Ridge regression analysis was chosen for the development of this model as it has the advantage over the more commonly used least squares regression techniques of being capable of handling predictor variables which are not independant of each other. That is, correlations between predictor variables tends to produce multiple regression coefficients which are too high and often of the wrong sign when least squares estimates are used; this problem is overcome by using ridge regression (Turner, 1980). Examination of the correlation coefficients in a matrix for these data shows that many of the predictor variables which could be used in this model are correlated (Table 6.7.).

The proceedure for ridge regression involves the addition of a small constant "k" to the diagonal elements of the covariance matrix. The estimates of regression coefficients obtained in this way are biased, but have small sums of squares deviations between the coefficients and their estimates (Turner, 1980). The optimum value for "k" is determined by the data itself; a plot of standard estimators against "k", called the ridge trace (example in Figure 6.10), is used as a means of determining subjectively the value of 'k". Turner (1980) gives the following criteria to be used in the selection of "k":

i. At the chosen value all changes of sign of the estimators should have occurred, as should all major changes in relative importance of the estimators.

ii. Coefficients with apparently incorrect sign at k = 0 will have changed to the proper sign.

iii. Varience inflation factors should be approximately equal to unity.

iv. The sum of inverse eigenvalues will be approximately equal to the number of variables in the model.

v. The residual sum of squares will not have been inflated to an unreasonable value.

	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
Fe_p	0.680^{***}								
Al_p	0.524^{***}	0.789^{***}							
Mn_t	-0.226	0.162	0.102						
Fe_t	0.068	0.520^{***}	0.324^{***}	0.615^{***}					
Al_t	-0.219	0.218	0.308^{***}	0.509^{***}	0.765^{***}				
Ca_t	-0.097	-0.076	-0.134	0.294^{***}	0.110	-0.038			
Mg_t	-0.526^{***}	-0.182	-0.168	0.479^{***}	0.581^{***}	0.761^{***}	-0.058		
L.O.I.	0.524^{***}	0.100	-0.034	-0.454^{***}	-0.520^{***}	-0.756^{***}	-0.104	-0.634^{***}	
pH_w	-0.370^{***}	-0.075	-0.091	0.609^{***}	0.563^{***}	0.563^{***}	0.570^{***}	0.596^{***}	-0.617^{***}

Superscript: *** p = 0.01.

Table 6.7. Correlation matrix for ten parameters for the Llansannan area profile data (n = 167).

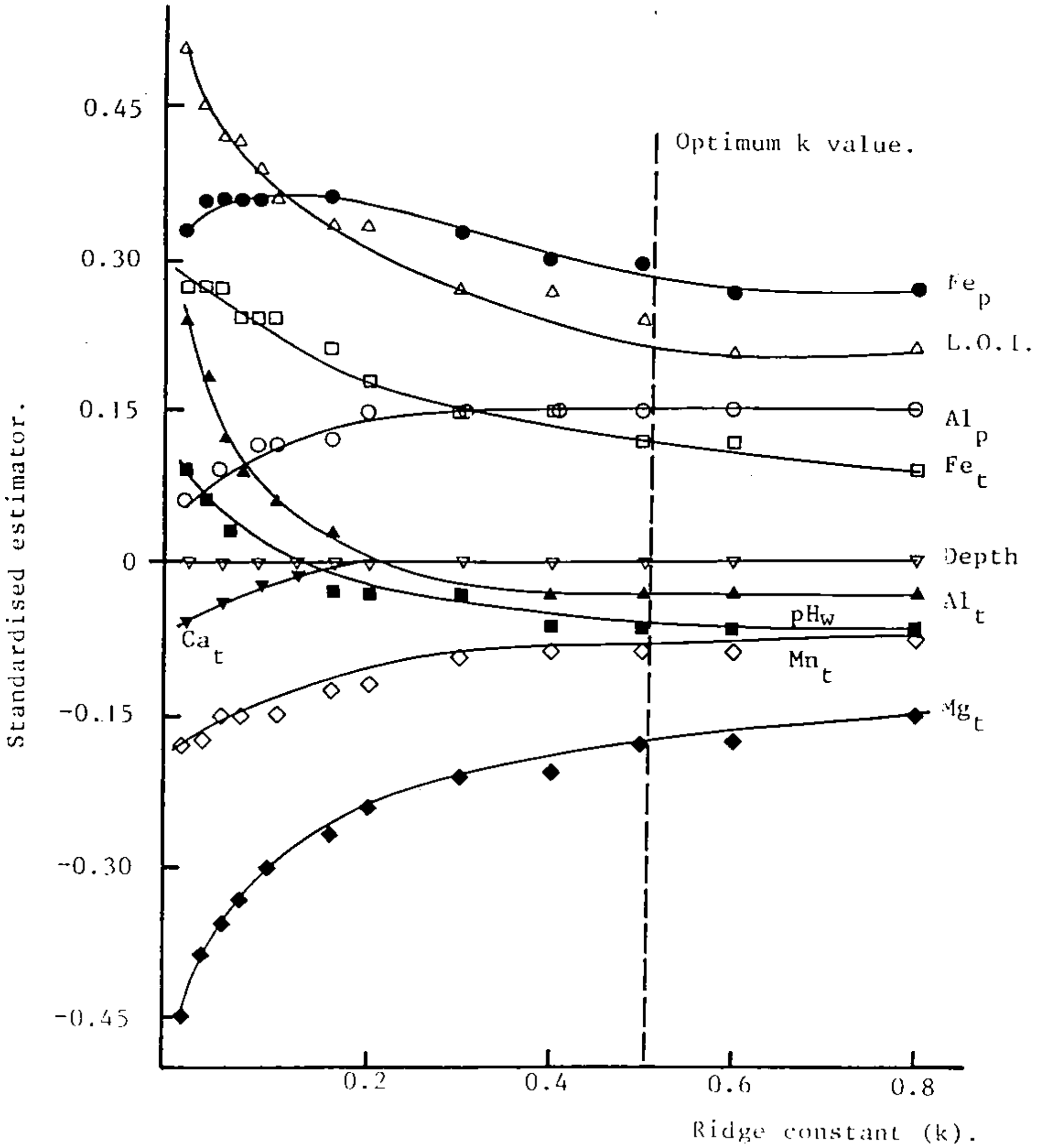


Figure 6.10. Ridge regression; ridge trace. Llansannan area profile data, ten predictor variables.

vi. The coefficients (estimators) will not have unreasonable values with respect to the factors for which they are representing rates of change.

The computer program used for ridge regression analysis in this work was developed by Dr. R. Howarth of the Applied Geochemistry Research Group.

Initially the ridge regression model was tried using ten predictor variables which were: Fe_p, Al_p, Mn_t, Fe_t, Al_t, Ca_t, Mg_t, L.O.I., pH_w and depth. Depth was taken to be the depth in cms. from the surface to the horizon midpoint, all other variables are as previously defined. In any ridge trace (example in Figure 6.10) the main trend is for the standardised estimators to tend towards zero as the value of k increases, all changes must therefore be assesed against this background condition. The ridge trace (Figure 6.10.) shows that the variables Ca_t and depth are of little value as predictors, having standardised estimators with values near to zero. The normal least squares estimate (i.e. when k = 0) would give Al_t to be as important a predictor as Fe_t, however as k increases the importance of Al_t declines until at k = 0.4 it becomes negative and of very small value. Conversely Al_p, which at k = 0 has a small standardised estimator, becomes increasingly important as the value of k increases, thus relationships between Se_t and Al_p which were masked probably because of correlation between Fe_p and Al_p become clearer. This demonstrates the value of ridge regression analysis in clarifying relationships which would otherwise be masked by correlations between predictor variables. although the value is small the ridge trace also shows the sign of the pH_w coefficient becoming negative, which is in line with the negative correlation between Se_t and pH_w (Table 6.7.). Clearly the most important predictors in the model are Fe_p, L.O.I. and Mg_t which have the largest standerdised estimators.

The optimum value of k was chosen as 0.5, since the stability of the ridge trace had been achieved at this value, and all the criteria given above for the choise of k are satisfied. Figure 6.11. shows the statistics comparing the least squares model with the ridge regression model when k = 0.5. It can be seen that the residual sum of squares for the ridge model has only been increased from 5.79 to 7.12, and that

Figure 6.11. Comparison of ridge regression and least squares multiple regression. Llansannan area profile data, ten predictor variables.

Ridge regression:

Variable.	Standardised estimator at k = 0.5	Normal estimator	Standard error of normal estimator.
Intercept	-------	0.476	-------
Fe_p	0.296	0.112	0.018
Al_p	0.157	0.192	0.0551
Mn_t	-0.083	-0.000073	0.000038
Fe_t	0.131	0.0341	0.0129
Al_t	-0.0230	-0.0139	0.0305
Ca_t	0.003	0.00669	0.110
Mg_t	-0.185	-0.233	0.0610
L.O.I.	0.240	0.00367	0.000705
pH_w	-0.057	-0.0228	0.0195
Depth	0.009	0.000169	0.000738

At k = 0.5, average variance inflation factor = 1.03.

Analysis of variance:

Source of variation	Degrees of freedom.	Ridge			Least squares		
		Sum of squares	Mean squares	F-ratio	Sum of squares	Mean squares	F-ratio
Regression	10	14.94	1.49	32.708	16.27	1.63	43.844
Residual	156	7.12	0.05		5.79	0.04	
Total variation	166	22.06			22.06		

	Ridge	Least squares
Multiple R^2 (%)	67.7	73.8
Standard error of estimator	0.214	0.193
Variance of error term	0.0457	0.0371
Sum of inverse eigenvalues	10.32	46.56

the sum of inverse eigenvalues (10.32) is approximately equal to the number of variables in the regression (10). Also at k = 0.5 the mean variance inflation factor is at an acceptable level of 1.03. The residual probability plot (Figure 6.12.) being nearly linear demonstrates that the data are relatively normally distributed and therefore suitable for application to this type of analysis. The multiple R^2 value has been reduced from 73.8 to 67.7% but the latter ridge model should be more reliable than the least squares estimate, which is partly evidenced by the reduction in the total variance of the estimators from 0.065 to 0.021.

This model can be reasonably simplified, and this was first attempted by removing variables from the model whose estimated coefficients, plus or minus its standard error, encompass zero (Figure 6.11.). Thus the analysis was repeated using only the following variables: Fe_p, Al_p, L.O.I., Fe_t, Mn_t, Mg_t and pH_w. The ridge trace for this model (Figure 6.13.) is stable at k = 0.35. Other statistics are given in Figure 6.14. and show that this new model accounts for some 66% of the variation in the Se_t concentration and that all coefficients are significantly greater or less than zero. Although this model contains all the useful predictors of Se_t, in terms of the amount of variation it explains it is no better than a simpler model containing only Fe_p and L.O.I. as predictors. The ridge trace for this model showed that there was no relative change in the position of the variables as the value of k increased and therefore it can be assumed that the least squares estimate is adequate. This model accounts for 67.3% of the variation in the Se_t concentration (Figure 6.15.) and is expressed as:

$$Se_t = 0.240\ Fe_p + 0.0071\ \text{L.O.I.} + 0.212$$

The residual probability plot given in Figure 6.16. shows that the data are reasonably normally distributed. However, five data points do deviate some way from the straight line, being those which fit the model least well. The three points with the largest residuals are sample numbers 2216, 2238 and 2223 and represent instances where the actual Se_t concentration is larger than that predicted by the model (see Appendix 2.2.). They represent either the bottom of O horizons (2238) or Ah horizons below an O horizon (2216 and 2223), where the organic matter may be particularly humic, and in which case L.O.I. as

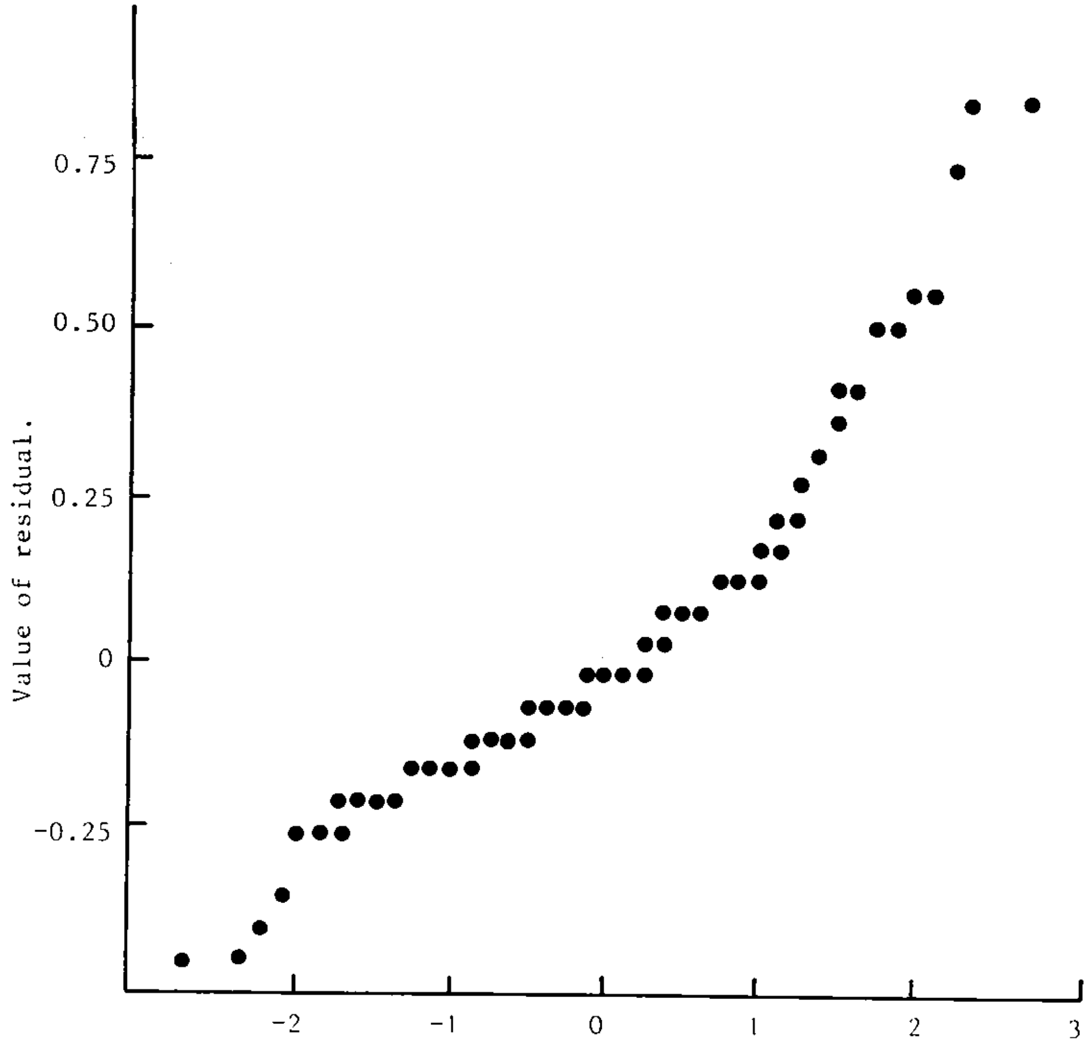


Figure 6.12. Residual probability plot for ridge regression. Llansannan area profile data, ten predictor variables.

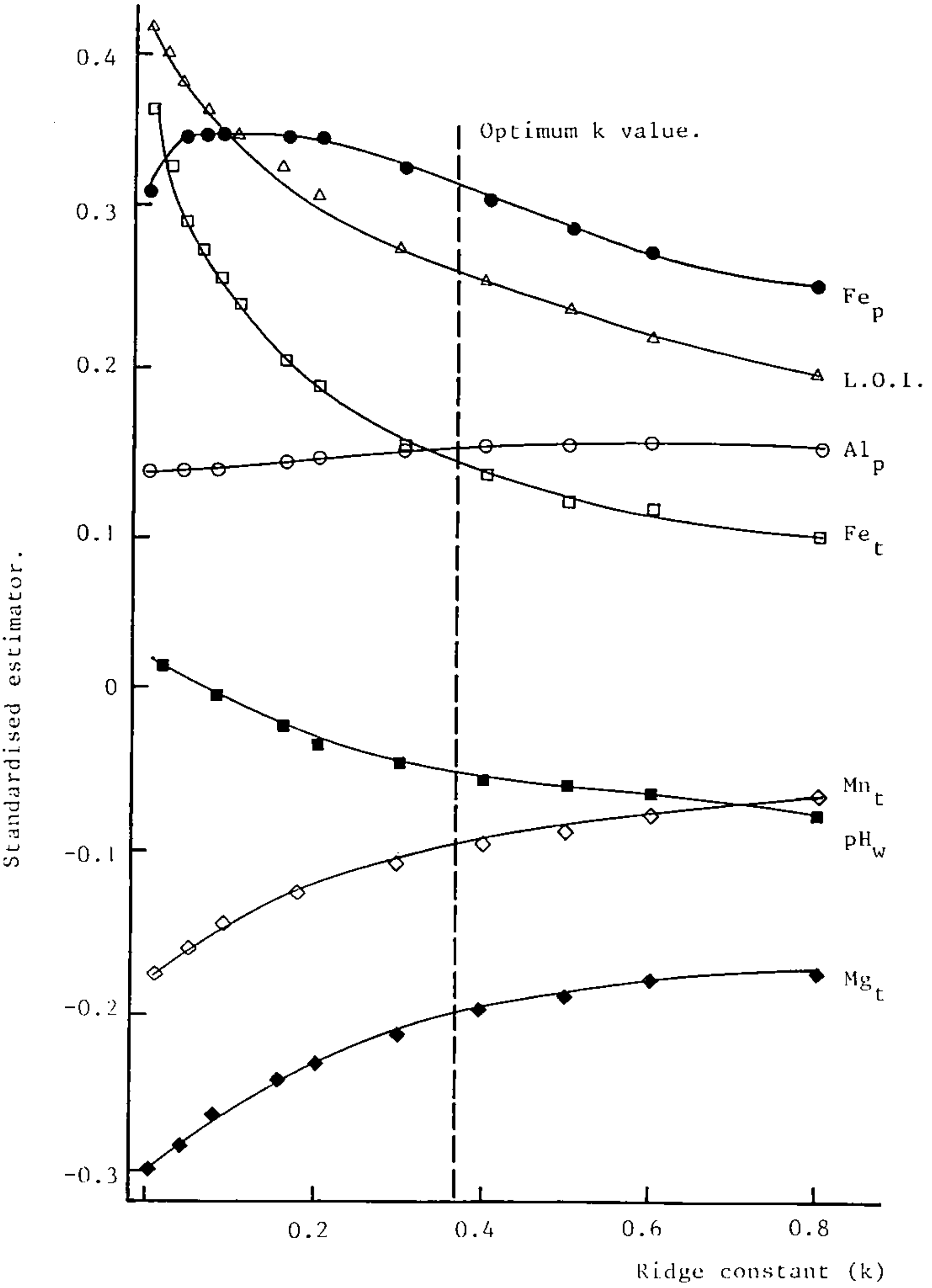


Figure 6.13. Ridge regression; ridge trace. Llansannan area profile data, seven predictor variables.

Figure 6.14. Ridge regression statistics. Llansannan area profile data, seven predictor variables.

Ridge regression:

Variable.	Standardised estimator at k = 0.35	Normal estimator	Standard error of normal estimator.
Intercept	-------	0.4281	-------
Fe_p	0.3174	0.1203	0.0196
Al_p	0.1509	0.1847	0.0574
Mn_t	-0.0982	-0.000085	0.000039
Fe_t	0.1527	0.0395	0.0137
Mg_t	-0.2090	-0.2620	0.0604
L.O.I.	0.2752	0.00421	0.00071
pH_w	-0.0472	-0.0191	0.0190

At k = 0.35, average variance inflation factor = 1.31

Analysis of variance:

Source of variation	Degrees of freedom.	Ridge at k = 0.35		
		Sum of squares	Mean squares	F-ratio
Regression	7	15.53	2.19	51.95
Residual	159	6.71	0.04	
Total variation	166	22.06		

	Ridge at k = 0.35
Multiple R^2 (%)	69.6
Standard error of estimator	0.205
Variance of error term	0.042
Sum of inverse eigenvalues	8.59

6.15. Multiple regression analysis of variance and estimators for Llansannan area profile data, two predictor variables (Fe_p and L.O.I.).

Variable.	Normal estimator.	Standard error of normal estimator.
Intercept	0.2120	-------
Fe_p	0.2402	0.017
L.O.I.	0.00707	0.000688

Analysis of variance:

Source of variation.	Degrees of freedom.	Sum of squares	Mean squares	F-ratio
Regression	2	14.84	7.42	168.56
Residual	164	7.22	0.04	
Total variation	166	22.06		
Multiple R^2 (%)		67.3		
Standard error of estimator		0.2098		
Variance of error term		0.044		

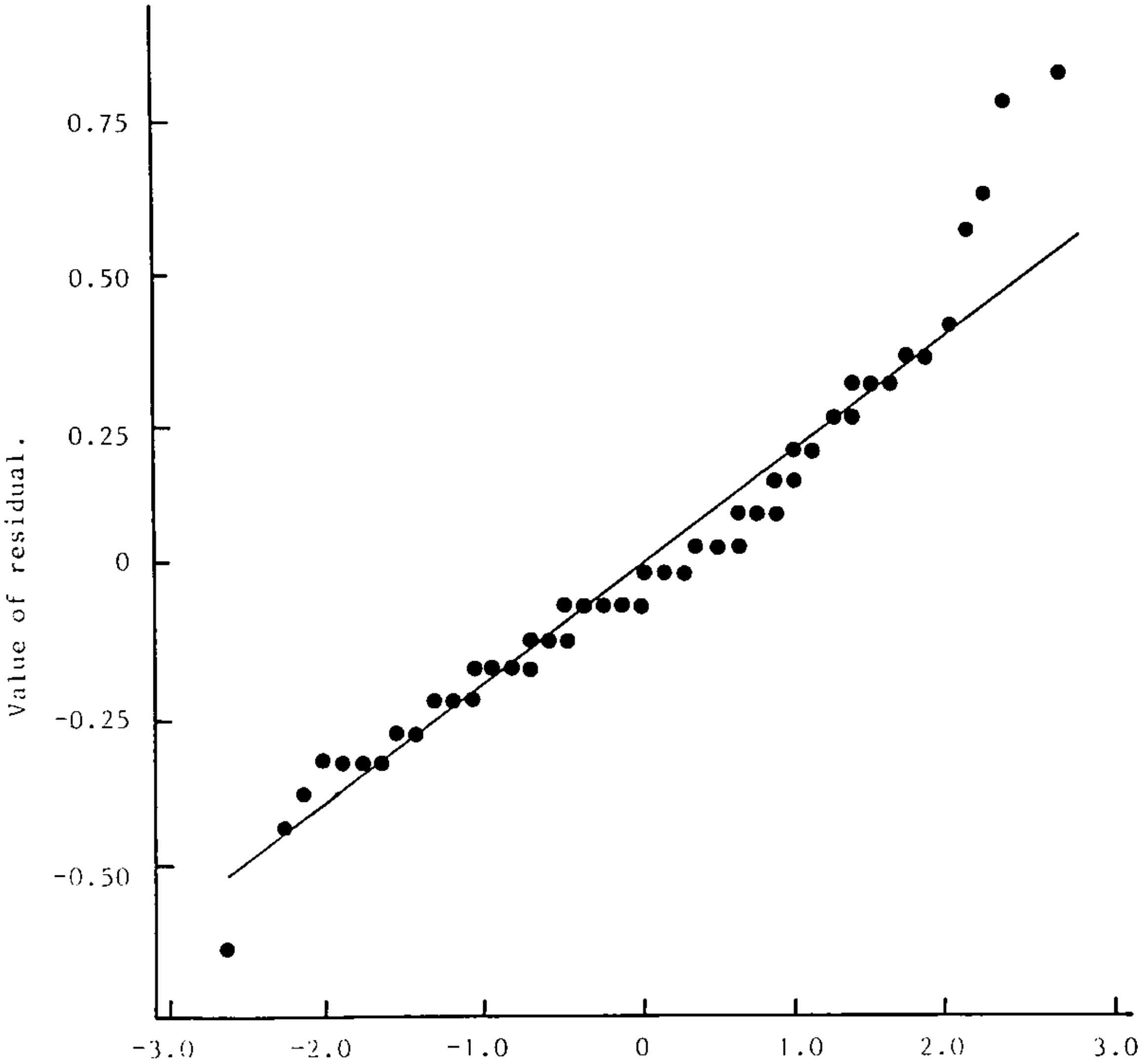


Figure 6.16. Residual probability plot for the regression of Se_t against Fe_p and L.O.I. Llansannan area profile data.

an assay of the organic matter content may underestimate the "active" component of the organic matter when compared to situations where more of the organic matter is in non humified forms (see conclusions).

The other two residuals are not as easy to explain but analytical error is a possible reason why the sets of data might not fit the regression equation very well.

6.5. Conclusions.

Differences in the pattern of Se distribution between soils of different soil series in the Llansannan area have been clearly demonstrated by this work. In the well drained Denbigh and Powys series soils, Se_t concentrations tend to be highest in the B horizon which contains the higher sesquioxide concentrations. In addition the A horizon of Denbigh series soils tends to contain more Se than the AB horizon, and this has been related to the higher organic matter content of the A horizon; such a relationship is absent in the Powys series soils where no AB horizon is differentiated. Greater leaching, resulting in a more acid soil, can take place either at high altitudes where the rainfall is higher, or when the soil is derived from rock which has no covering of drift, producing a more stony and freely drained solum. Such leaching leads to the greater differentiation of the B horizon, especially in terms of the sesquioxide content, but also notably in terms of higher Se concentrations; this is demonstrated by soils of the upland phase of the Denbigh series, and Manod and Powys series soils. Thus there is a sequence of B horizon development along the lines of: Denbigh (normal phase), Denbigh (upland phase) and Powys series, Manod series, through which the Se content of the B horizon tends to increase. Additionally, because surface acidity and wetness lead to the persitance of organic matter in the topsoil, with which some Se is evidently associated, the Se content of the topsoil in such soils is higher than that in the normal phase of the Denbigh series.

The sequence of profile development continues onto the moorland, where some examples of podzolic soils from within the Hiraethog map unit can be considered to be transitional to those of the Powys and Manod series. In these soils there is a surface accumulation of organic matter in the more acid and wet conditions, and the podzolisation has led to the greater redistribution of sesquioxides from the top of the soil into the B horizon, as well as a clearer distinction of surface organic matter. The effects of podzolisation may be responsible for some of the B horizon characteristics of upland phase Denbigh series soils and Manod series soils, that is in addition to the effects of leaching causing modification of the Fe_p and Al_p contents. Thus the highest concentrations of Se encountered occur in peaty topsoils (1.68 $\mu g\ g^{-1}$ in profile D17) and Bs horizons (1.56 $\mu g\ g^{-1}$ in profile D21) of the Hiraethog soils.

Within the Hiraethog map unit the podzolic soils demonstrate a basic pattern of Se distribution conforming to; enrichment of the O and Bs horizons, and also when present of the ironpan (Bf) which is consistent with the observations of Wells (1967) and Koljonen (1975), as well as with the reported trends in the podzolic soils developed on Lower Greensand sediments in south east England (section 4.3.2.). However, within this map unit there are variations in profile morphology with which there are concurrent variations in Se content and distribution. Generally, under greater accumulations of organic matter there is increased differentiation between the E and B horizons, the former horizon eventually becoming gleyed due to an increase in its clay content as a result of the weathering and physical degradation of chlorite (Adams et al., 1971), and subsequently formation of the ironpan results. At this stage enrichment of the B horizon in both sesquioxides and Se declines as these fractions become concentrated into the Bf.

Alongside this sequence in well drained soils, the effects of gleying in the more poorly drained soils of the Sannan and Ynys series also modifies the nature of the Se distribution. In the Sannan series Se concentrations decrease downwards from relatively high values in the humose topsoil; a similar pattern is observable in the gleyed subsurface horizons of the Ynys series soils. In the latter series, however, soils which appear to be intergrades to those of the Hiraethog and Hafren series occur, these soils demonstrate an enrichment of Se in the Bg horizon which is also enriched in sesquioxides, this probably being due to occasional periods when oxidising conditions prevail near to the surface of the soil.

The study of Se distribution in these soils lends support to the argument for them being members of a genetic sequence. Organic matter and sesquioxides, especially of Fe, with which Se appears to be associated are two of the more important factors in the visual and physical manifestation of soil profile development. Thus the differences in Se distribution between these soils are easy to deduce from the observable characteristics of the soil, such as gleying, organic matter accumulation and the redistribution of Fe species.

Despite differences in Se distribution between different soil types, it has been demonstrated that in all cases the distribution is determined largely by associations with organic matter and sesquioxides, such that 67% of the variation in soil Se content can be explained by that of pyrophosphate extractable Fe and organic matter, represented by L.O.I., using a multiple regression model. In many groupings of soil horizons or soil series, both Fe_p and Al_p were equally implicated in affecting Se distribution, however, it appears that often the same conditions favour the accumulation or production of both Fe_p and Al_p, such that the two parameters are strongly correlated. Exceptions to this relationship do exist, such that in situations favouring the accumulation of ferric oxides, for example O horizons of the Ynys series and Bs horizons, the content of Se is much better correlated with that of Fe_p than of Al_p. This suggests that correlation between Se_t and Al_p may be an artifact of the real relationship between Fe_p and Al_p, the evidence is not, however, conclusive. Hydrous oxides of Al have been shown to be capable of the adsorption of Se (Rajan, 1979), and to be important factors in controlling the amount of selenite adsorbed by soils (John et al., 1976). It is possible that in these soils both ferric and aluminium oxides are involved in Se adsorption. However, Evans and Adams (1975) have shown that in soils of the Denbigh, Hafren and Hiraethog series which were developed on a similar parent material to that of the soils in this study, the predominant trend is for a net loss of Al from the profile. This takes place despite the fact that some illuvation does occur; in the case of Fe however, there was no perceptable loss from the profile.

The high Se content of mineral topsoils compared to that of the local Silurian rocks from which they are derived (by a factor of as much as ten times), suggests that there has been no overall loss of Se from these soils on weathering of the parent material. Indeed it is possible that enrichment could have occurred. However, it is not possible to establish the exact balance without a careful quantitative assesment of horizon gains and losses, compared to the parent material, in relation to an inert internal reference component in the manner of those undertaken by Evans and Adams (1975). This was not possible during this study. However, the apparent persistance of Se against the processes of weathering in these soils is perhaps best explained by its intimate association with ferric species which suffer no overall loss from the soil also. The effect of plants in cycling Se to the surface horizons where it is intimately associated and apparently accumulates with the organic matter, will also be an important factor in this relationship.

Ball and Beaumont (1972) demonstrated that in a sequence of Denbigh, Manod and Hiraethog soils the release and illuvation of Al, which is extracted by pyrophosphate, tends to occur before that of Fe; such that the first signs of podzolisation in Manod series soils is the illuvation of Al. In Hiraethog series soils the Al has moved from the profile and the distribution of Fe is then indicative of the effects of illuvation. Thus it may be that in brown earths of the Denbigh series both Fe and Al hydrous oxides are responsible for the adsorption of Se. It has been shown that Se is most concentrated in the most weathered soils, being those of the Ynys and Hiraethog map units, and that the Mg content of the soils can give an indication of the extent of weathering, such that there is a linear relationship between the Se_t and Mg_t content of the soil. Since degradation of chlorite is believed to be the main weathering process in these soils, and that Al as well as Mg is lost from the profiles as a consequence (Adams et al., 1971), it might be expected that Al would also be negatively correlated with Se. However, there is only a poor negative correlation between Se_t and Al_t ($r = -0.219^{**}$, $n = 167$), the relationship being modified by the illuvation of Al which occurs. There is no evidence in these data for the redistribution of Mg, merely loss from the profile. Such a strong relationship between Mg_t and Se_t will therefore be particular to soils where chlorite, or a similar Mg containing mineral, is the principal weathered component; no such relationship was noted from either the Lower Greensand (section 4.4.) or the Carboniferous (section 5.6.).

The role of organic matter in influencing the distribution of Se is nowhere as clear as in the case of the peaty topsoils of the moorland. which contain high concentrations of Se. As mentioned in section 6.4.1., however, this must be viewed with caution in remembering that concentrations expressed on a weight to volume basis would be much lower in comparison with those of most of the mineral horizons; the real problem here lies in comparing two mediums which are essentially different in nature. The relationship between organic matter accumulation and increasing Se content was clear for the soils in the Hiraethog map unit (Figure 6.9.), but in the case of the Ynys and Caron soils the evidence presented suggests that secondary precipitation of ferric oxides from groundwaters and its association with Se masked any similar relationship. Elsewhere organic matter effects were evident where for example the more organic topsoils of the Powys series contained more Se than those of the Denbigh series.

The fact that organic matter and Fe_p (which accounts for Fe in organic combination, or which has been precipitated recently from such) together account for 67% of the variation in the horizon Se content suggests that much of the Se in the soil is involved in an organic cycle. This being the case it is also evident that if the primary source of the Se in these soils is from the parent material, then it must be present in forms which are readily oxidised and released on weathering. Selenium which has been assimilated by plants is clearly persistant in an organic form in the topsoil. Loveland et al (1981) demonstrated a strong correlation between the N and Se content of topsoils from some Welsh acid brown earths which they felt was indicative of the combination of Se in plant proteins. The fact that proteins and nitrogenous organic compounds tend to resist microbial breakdown more than other organics no doubt contributes to the accumulation of Se in organic topsoils. When and if Se is mobilised from the topsoil the association with Fe_p suggests that it may be either mobilised in combination with Fe and organic matter, or as a organic - Fe - Se complex as proposed by Levesque (1974b). Alternatively, if it is released as the soluble selenite ion it is readily adsorbed on the most retentive colloid surfaces, which would be expected to be hydrous oxides of Fe and Al (Hamdy and Gissel-

Nielsen, 1977), being represented in this work by Fe_p and Al_p.

Some 33% of the variation in soil horizon Se content is not accounted for by that of Fe_p and L.O.I., and none of the other parameters studied here greatly improves this value. Several factors may account for this. Obviously some Se may be associated with Fe and Al oxides which are not extracted by potassium pyrophosphate, Levesque (1974a) found that there was a significant relationship between the Se and oxalate soluble Fe content of some Canadian soil, oxalate extracting a broader spectrum of soil Fe species than pyrophosphate. Also loss of weight on ignition is a relatively indiscriminate assay of the organic matter content of the soil, in that it comprises all organics including simple humic and fulvic acids, amorphous carbon and "macro" organics in the form of plant roots and decomposing vegetation, all of which by unit weight may be expected to vary in their affinity for and content of Se. Thus dependant on the proportion each of these contributes to the whole, organic matter measured as L.O.I. will vary in its capacity to include Se. This work has also assumed uniformity in the composition of the soil parent material. However, Levesque (1974a) studying a wide variety of Canadian soils from different parent materials demonstrated that variation in the parent material Se content accounted for most of the variation in the Se content of soil horizons. The analysis of rocks from this study area demonstrated that although small, there was some variation in the Se content of the local rocks, and this could account for some of the variation in soil horizon Se content. This could be both in a single profile due to differences in vertically adjacent strata, and also between similar soils in different localities. The fact that the mean total Fe content of for example largely drift derived Denbigh series soils and of largely rock derived Powys series soils is similar (means 3.30 and 3.55 %respectively) goes some way to confirming that there is little difference in the composition of the drift and the solid rock from which it is derived. It can be considered that for the purposes of this study, however, assumptions on the uniformity of the parent material were mostly justified.

It is not possible to assess to what extent Se present in the soil in reduced forms such as elemental Se and selenides is unaccounted for by this model which demonstrates relationships between Se_t and sesquioxides of Fe and Al, and organic matter. Certainly some Se included in the assay of "total Se" (Se_t) could be present as an unweathered fraction of little weathered stones and rock fragments which are less than 2 mm in diameter, such Se would have little role in the organic cycle which was mentioned above.

CHAPTER 7. SELENIUM IN HERBAGE AND SOILS OF THE LLANSANNAN AREA OF CLWYD: EXPERIMENTS FOR THE SPECIATION OF SOIL SELENIUM.

7.1. Introduction.

The results of this work presented in the previous chapters have helped to define several factors which influence the content and distribution of Se in soils. In terms of geographical distribution the most important of these is probably the Se content and nature of the soil parent material. However, this basic relationship can be extensively modified by the process of soil formation, such that the soil concentrations may differ in soils developed from the same parent material. More specifically this is due to the effects of different soil forming environments on the distribution and content of soil organic matter, iron and aluminium with which the distribution of Se is related in the soil profile. This has been considered to be due to actual associations between Se species and these above named soil constituents.

So far in this work conclusions regarding the forms of Se in the soil, and their associations with organic matter, iron and aluminium have been based on the subjective appraisal of correlation and regression analysis data, and with comparison with other published findings on the subject (Geering et al., 1968; Howard, 1977). In this way the following forms and associations of Se have been postulated; organic - Se compounds, organic - Se and organic - Fe(or Al) - Se complexes, selenite mainly in equilibrium with a ferric oxide - selenite adsorption complex, and elemental Se and selenides in more poorly drained soils. It is thought that little selenate will exist in the majority of British soils.

It was felt therefore that the programme of research could best continue by attempting to investigate more fully the forms of Se in the soil and the nature of the above relationships, in such a way as to be able to quantify the various forms of Se existing in any particular soil type.

The original brief for this project also included proposals for the assesment of the uptake of Se by pasture herbage. Clearly this is most relevant in terms of actual animal health problems, as the Se content of the herbage should most closely control the actual intake of Se by the grazing animal. The assesment and prediction of soil Se status are only useful if ultimately they can be related to the dietary intake of the element by livestock from the herbage. Careful study of the effects of soil type, drainage, etc. on the uptake of Se by herbage would ideally necessitate the establishment of experimental plots or pot trials, as it is felt that the variations in sward species composition and also of management practice inherent in the sampling of established swards and vegetation would confer large influences on the levels of Se in the herbage. These difficulties could perhaps only be overcome by extensive soil and herbage survey work. Any such experimentation and surveys, however, could not practically be attempted in the time available for completion of the project which was insufficient for the establishment of swards, and harvesting of plots.

It was felt that this aspect of the work could be accomodated in the continuing research programme by relating quantified soil Se fractions to plant availability on the basis of established knowledge, and perhaps by developing a means of assessing this plant available fraction. The ability to identify soil conditions which favour or otherwise the existance of plant available fractions would be invaluable. Unfortunately analytical methods capable of determining plant available and other soil Se species were not readily available and would first have to be developed.

Because of the extensive background information which has been obtained on the soils of the area it was thought that the work outlined above should be carried out in the Llansannan area. It was considered that work of this nature would be more profitable in terms of establishing relationships between soil Se and animal health problems, than would be an extension of the work presented in Chapter 6 on the soils of the Llansannan area to other regions characterised by contrasting parent materials and supporting a broader range of soil types.

7.2. Sampling of soils and herbage.

It was decided that for the purpose of the fractionation work which was to be undertaken, it was necessary for fresh samples of soil to be taken. A limited number of soil profiles which represented the range of conditions found in the area were sampled, in order that the effects of all possible extremes of soil conditions could be studied. Thus soils which were typical of the following series were sought:

Denbigh series - typical acid brown earth.
Powys series - brown ranker.
Manod series - typical brown podzolic soil.
Sannan series - stagnogleyic brown earth.
Ynys series - cambic stagnohumic gley soil.
Hiraethog series - ironpan stagnopodzol.

It was planned that material from these soils was then to be used in the speciation studies which are detailed later (section 7.4.). In addition to the sampling of these profiles it was thought that as a preliminary investigation it would be beneficial to take some samples of herbage from each of the profile sampling sites. This would give an appreciation of the range of herbage concentrations which might be encountered in any subsequent survey of the area, and also of the extent of the variation in soil and herbage Se concentrations in a single locality on one soil series.

All the samples were taken in June, 1981. Soil samples were taken in the same way as in section 6.2., and subsequently the material was analysed for the following parameters: Se_t, Fe_p, Al_p, Mn_t, Fe_t, Al_t, Ca_t, Mg_t, L.O.I. and pH_w (section 3.2.). This allowed the characterisation of the soils in the same way as for the profiles described in Chapter 6, with which they could then be more easily compared.

Herbage and corresponding topsoils were sampled in the locality of each of the soil profiles. Four plots, 3m x 3m, at the corner of a square of side equal to approximately 25 m, of which one corner was the profile pit, were sampled. Representative herbage samples of the mixed sward were collected using a small pair of shears, and a bulked soil sample of 9, 0-15 cms auger samples was taken from the same plot.

Where the site of the profile was on a significant gradient the four plots were located at 25 m intervals along the strike of the slope where it was considered that there would be less variation in the nature of the soil. At some sites specific species were also sampled. It was hoped that a single, common species could be sampled from each site which might therefore aid in the comparison of sites; however, the composition of the swards was very variable and this was not possible.

All herbage samples were prepared and analysed for Se as given in sections 3.1.3. and 3.2.1.

7.3. Results and discussion.

7.3.1. Soils.

Due to the problems encountered in devising techniques for the speciation of selenium in the soil (section 7.4.) no such results were obtained for the soil profiles which were sampled. Basic characterisation of the soils in the manner of those reported in Chapter 6, showed that the distribution of total Se in these new soils conformed to the same patterns and it was therefore not considered necessary to present the data here.

7.3.2. Herbage and corresponding topsoils.

The results which are presented in Table 7.1. can conveniently be split into two groups; the first of herbage growing on the mineral topsoils of the upland (sited D40, D42, D43 and D44) which contain significantly less Se (mean 0.035 $\mu g\ g^{-1}$) than the herbage growing on the organic topsoils of the moorland (mean Se content 0.145 $\mu g\ g^{-1}$) at $p = 0.05$. This relationship is paralleled by the significantly higher mean Se content of the organic compared to the mineral topsoils (0.83 $\mu g\ g^{-1}$ compared to 0.47 $\mu g\ g^{-1}$, $p = 0.05$) as demonstrated by the plot of individual herbage and soil Se concentrations in Figure 7.1. Several factors could alone or together explain this relationship:

i. There may be a positive relationship between the soil and herbage Se concentration, this is however, difficult to substantiate from the

Table 7.1. The selenium content of herbage from the Llansannan area.

Site No. and grid reference	Soil series	Plot No.	Herbage Se (µg g^{-1})			Land type and dominant species.
			Mixed sward^{A}	Other species^{B}		
D40	Manod	1	0.016	0.020		Permanent pasture: Poa spp. Festuca pratensis, Holcus lanatus, Agrostis tenuis, broadleaves.
SH 890668		2	0.025	0.027		
		3	0.025	0.018		
		Mean	0.022^{a}	0.022^{1}		
D41	Hiraethog	1	0.200	0.075	0.166	Rough grazing: Nardus stricta, Festuca spp., Moss & locally Juncus spp.
SH 922575		2	0.104	0.074	0.137	
		3	0.225	0.143	0.193	
		4	0.114	0.185	0.200	
		Mean	0.160^{b}	0.094^{2}	0.174^{3}	
D42	Sannan	1	0.018			Permanent pasture: Lolium perenne, Trifolium spp., Poa pratensis. Dactylis glomerata.
SH 925649		2	0.028			
		3	0.067			
		4	0.036			
		Mean	0.037^{a}			
D43	Denbigh	1	0.036			Permanent pasture: Cynausaurus cristatus Festuca pratensis D. glomerata, L. perenne & broadleaves.
SH 954652		2	0.020			
		3	0.093			
		4	0.036			
		Mean	0.054^{a}			
D44	Powys	1	0.025			Permanent pasture: Agrostis tenuis. Festuca spp. H. lanatus, some Trifolium spp & broadleaves.
SH 918674		2	0.023			
		3	0.022			
		4	0.036			
		Mean	0.026^{a}			
D45	Ynys	1	0.120	0.137		Rough grazing: Nardus stricta. Festuca spp. Moss and locally Juncus spp & C. vulgaris.
SH 847597		2	0.140	0.196		
		3	0.126	0.154		
		Mean	0.129^{b}	0.162^{2}		

A - Means with different superscript letters are significantly different at $p = 0.05$ level.

B - Superscript numbers refer to species: 1: Holcus lanatus 2: Juncus spp. 3: Sphagnum moss.

limited results presented here which fall into two groups with no intermediate values (Figure 7.1.).

ii. Selenium in organic combination in organic topsoils could be in a form which provides more Se for plant uptake than in mineral soils.

iii. Herbage species on the moorland (predominantly N. stricta and Festuca spp.) could be capable of assimilating more Se than species found on the mineral topsoils of the upland.

There is little evidence in the literature that organic forms of Se in the soil, and particularly in organic soils, should be more available to the plant than those in mineral soils, which would be expected to be predominantly selenite in equilibrium with ferric oxide - selenite adsorption complexes. In fact in an acid and waterlogged soil it would be expected that Se would take the form of insoluble elemental Se or other reduced forms (Figure 2.2.). Watkinson (1962) noted that soils of high Se content on which livestock were responsive to Se administration were predominantly acid and organic.

When the mineral topsoils of the upland and their herbage are considered alone there is no real relationship between the concentration of Se in the herbage and that of the soil (Figure 7.1.); in fact for all but three of the samples the herbage Se concentration lies between 0.016 and 0.036 $\mu g\ g^{-1}$, there being no apparent reason for the higher Se concentrations in the three other samples (Table 7.2.). There is no significant difference between the mean herbage Se contents of any of the four upland soils (Table 7.1.). It is possible that variations in the sward species composition could mask differences in the ability of the soils to supply Se to the plant. There is little specific information regarding the difference between species in their ability to assimilate Se from soils low in Se in the literature; excepting that it is well established that clovers (Trifolium spp.) inevitably contain less Se than grass species on the same soil (Davies and Watkinson, 1966; Hupkens and Tetly, 1970). Ehlig et al. (1968) however, did note that species differences were much less marked on soils low in Se than on those containing much higher levels of soluble Se. On the Manod series soil at site D40 there was no

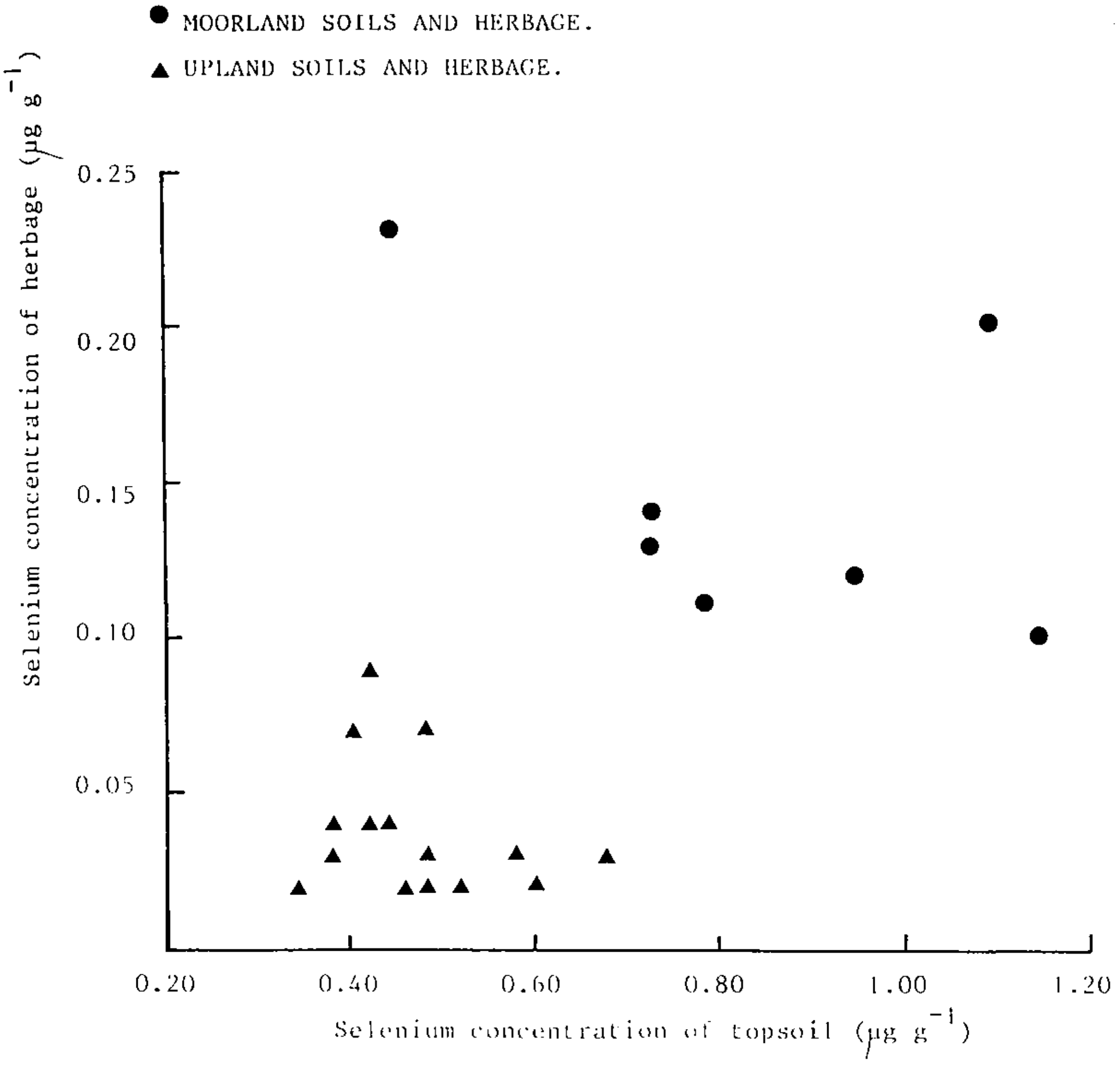


Figure 7.1. Relationship between herbage and soil Se_t concentrations from the Llansannan area.

			SOIL									
SITE	SAMPLE	Se Herbage	Se_t	pH_w	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
40	1	0.016	0.59	5.55	0.88	0.55	636	3.67	2.01	0.226	0.438	12.52
	3	0.025	0.48	5.70	0.80	0.53	632	3.38	1.86	0.264	0.360	12.96
	4	0.025	0.67	5.40	0.93	0.64	594	3.48	1.96	0.192	0.424	13.38
41	1	0.200	1.07	3.10	0.46	0.29	400	0.50	0.39	0.082	0.038	73.87
	2	0.104	1.14	3.40	0.59	0.30	400	0.62	0.34	0.120	0.040	86.78
	3	0.225	0.43	4.15	0.56	0.56	200	0.78	0.92	0.068	0.052	16.87
	4	0.114	0.78	3.40	0.90	0.32	400	1.22	0.56	0.096	0.032	61.56
42	1	0.018	0.33	6.30	0.35	0.19	476	2.92	2.08	0.330	0.532	8.71
	2	0.028	0.38	6.00	0.34	0.19	488	2.93	1.95	0.284	0.584	8.76
	3	0.067	0.40	6.10	0.37	0.22	596	3.08	1.97	0.320	0.552	8.23
	4	0.036	0.42	5.90	0.42	0.23	816	3.04	1.95	0.400	0.520	9.87
43	1	0.036	0.44	5.80	0.61	0.32	628	3.38	1.89	0.240	0.588	11.69
	2	0.020	0.45	5.60	0.58	0.32	712	3.10	2.06	0.256	0.572	12.05
	3	0.093	0.41	5.35	0.60	0.33	700	3.22	2.02	0.248	0.656	14.11
	4	0.069	0.48	5.65	0.68	0.36	628	3.31	1.89	0.240	0.588	13.27
44	1	0.025	0.57	5.95	0.64	0.45	1112	3.81	2.06	0.512	0.426	19.46
	2	0.023	0.47	6.10	0.57	0.39	400	3.39	2.05	0.336	0.440	13.26
	3	0.022	0.51	6.20	0.34	0.33	984	3.18	2.04	0.440	0.500	14.65
	4	0.036	0.38	5.60	0.48	0.33	528	3.21	2.14	0.320	0.460	13.52
45	1	0.120	0.94	3.80	0.61	0.40	320	0.76	0.67	0.062	0.061	62.49
	2	0.140	0.71	3.95	0.93	0.46	280	1.34	0.72	0.068	0.044	35.77
	3	0.126	0.71	3.90	1.06	0.53	200	1.40	0.68	0.056	0.028	42.60

Table 7.2. Mixed sward selenium content and soil analytical values for six sites in the Llansannan area.

difference between the Se content of Holcus lanatus and that of the mixed sward (Table 7.1.). Juncus spp. were also sampled on the moorland since Fletcher (1968) found that on a high Se soil from Derbyshire, Juncus spp. contained more Se than any of the other species which he sampled. The values here were contrasting, being higher than the mixed sward on the Ynys series soil (site D45) and lower on the Hiraethog series soil (site D41) as shown in Table 7.1.

The Se concentrations in the herbage from the upland sites (mean 0.035 $\mu g\ g^{-1}$) are low compared to those values generally quoted as providing sufficient Se for livestock nutrition at 0.10 $\mu g\ g^{-1}$ (Rickaby, 1980), although this level can vary, and be less than this figure, depending on the dietary levels of other factors, noteably of vitamin E (Diplock 1981). Thus plant concentrations as low as 0.02 $\mu g\ g^{-1}$ can in some cases provide adequate Se (Ehlig et al., 1968). In general these levels are not unexpected on such acid soils (mean pH 5.80, Table 7.2.) which contain only moderate concentrations of Se (mean 0.47 $\mu g\ g^{-1}$). These observations would have to be backed up by more extensive surveys of the herbage Se concentrations in the area, these results only being intended as a preliminary guide. It would appear that herbage growing on the organic soils of the moorland would provide adequate Se, based on the above criteria (mean Se concentration of 0.145 $\mu g\ g^{-1}$), although in terms of the selectivity of the grazing animal, the method of sampling used is rather indiscriminate in sampling the whole plant and not the more palatable portions of the sward in which the Se content of the plant may differ.

Any further extension of this type of work should also include some seasonal sampling to take account of the effects of stage of growth on herbage Se content. Little is at present known regarding this subject, although it has been shown that on low Se soils young growth contains more Se than that later in the season, being probably a dilution effect (Beeson, 1961; Ehlig et al., 1968).

An additional pathway of Se into the grazing animal could be by the ingestion of soil. This has been considered to be a potentially important source of several trace elements, including Se (Healy, 1969; Healy et al., 1970). Obviously the amount of soil ingested will depend on many factors including management practice, sward composition, rainfall and soil type. The availability of the element to the animal may, in addition, depend upon the forms of the element in the soil. Considering the relatively high Se concentrations in soil compared to herbage (means of 0.47 $\mu g\ g^{-1}$ soil and 0.035 $\mu g\ g^{-1}$ herbage for the soils in this study from the upland) it is clear that this factor requires further investigation, alongside that of the herbage Se contents.

7.4. Experimental work, fractionation of soil selenium.

7.4.1. Introduction.

Schemes for the fractionation of soil Se have been used by other workers, noteably Olson et al. (1942) and Cary et al. (1967), both of which were based upon selective chemical extraction from the soil of Se species, dependant upon their solubility in the various extracting solutions. For the present work it was proposed to adapt these techniques for the examination of the soils from the Llansannan area; however, certain problems could be envisaged.

The first problem was one of detection of trace amounts of Se; the mean total Se concentration of the soils studied in Chapter 6 was 0.55 $\mu g\ g^{-1}$, and the detection limit of the analytical system used was approximately 0.02 $\mu g\ g^{-1}$ of Se in the soil (section 3.2.1.). This meant that the detection of part fractions of the total soil Se might necessarily involve determinations near to the detection limit, unless methods such as preconcentration were adopted. In the case of the work of Olson et al (1942) the soils examined were seleniferous, producing toxic vegetation, and having total Se concentrations in the order of about 30 $\mu g\ g^{-1}$. In situations giving rise to toxic vegetation it is considered that large amounts of soil Se are in water soluble forms, and thus are available to the plant, and detection problems are therefore not serious. In the work of Cary et al. (1967), and also that of Hamdy and Gissel-Nielsen (1976b) which was based on the same proceedure, the intention was to study changes in the form of Se (as selenite) which had been previously added to the soil, and therefore the extraction proceedure was practised on soils to which had been added 2.5 $\mu g\ g^{-1}$ and 4.0 $\mu g\ g^{-1}$ respectively of largely water soluble Se. In comparison this study was to concentrate on acid soils to which no Se had been added; in such situations it has been considered that the majority of the soil Se is not readily soluble in water, or other similar extractants such as the K_2SO_4 which was employed by Cary et al. (1967).

Secondly it could be envisaged that some of the chemical extractents involved in the proceedure may interfere with the determination of Se using the available technique of hydride generation and determination by inductively coupled plasma source emission spectrometry. Such problems were not encoutered by either Cary et al. (1967) or Hamdy and Gissel-Nielsen (1976b), as they relied upon the assay of residual radioactivity present as a remnant of the ^{75}Se added as a component of the Se additions to the soils. Essentially therefore there was no interference between the extraction technique and that of the assay.

In addition to the above system of fractionation, and preliminary to it, water extraction of Se from soils was attempted. In this case a technique for the determination of Se in aqueous solution was available in the department, however, extraction techniques had to be developed.

7.4.2. Water extraction of selenium from soils.

Several workers have undertaken extraction of soil Se with water, or in some cases dilute solutions of $CaCl_2$, and the methods employed have been summarised in Table 7.3. This only includes work where the extraction was of the natural soil Se; similar techniques have been used to assay the solubility of residual Se remaining after plant uptake trials with Se additions (Cary and Gissel-Nielsen, 1973; Ganje and Whitehead, 1958) and also for assesing the availability of soil Se additions for microbial volatilisation (Zieve and Peterson, 1981). The majority of the soils studied (Table 7.3.) have been seleniferous soils containing up to several hundreds of $\mu g\ g^{-1}$ of Se, and water soluble Se accounted for up to 7% of the total, but more normally between 1 and 2%, which is also within the range reported by Levesque (1974b) for some "normal" soils from Canada. These techniques have been used as a guide to formulating an extraction technique for this work. Boiling water extraction was discounted as a suitable

Reference.	Extractant.	Soil: solution ratio.	Contact time.	Method of separation.	Method of Se determination.	Type of soil.	Total Se ($\mu g\ g^{-1}$)	Extracted Se (% of total)
Olson et al. (1942)	Boiling water.	1:5	30 min.	Filtration.	Acid digestion & distillation.	Seleniferous soils (U.S.A.)	2.7 - 38.4	1.08 - 50.1
Fleming and Walsh (1957)	Water.	1:2.5	Over-night.	Filtration.	as above.	Seleniferous soils (Eire)	20.4 - 850.	0.33 - 2.90
Williams and Thornton (1973)	Water.	1:10	Over-night.	Centifuge 3000 r.p.m.	Acid digestion & colourimetry.	Seleniferous soils (U.K.)	92 - 230	<1.0 - 2.2
Levesque (1974b)	Water.	1:10	Not known.	Not known.	Acid digestion & flourimetry.	"Normal" soils (Canada).	0.20 - 0.74.	1.9 - 6.9
Nye and Peterson (1975)	Water.	1:10	12 hrs.	Filtration.	Acid digestion & flourimetry.	Seleniferous soils (British Isles)	0.9 - 91.4	Mean of <1.0
"	0.1M $CaCl_2$	1:10	12 hrs.	Filtration.	"	"	"	Less than for water as above.

Table 7.3. Summary of published work involving the water extraction of native soil selenium.

method as it was considered that high temperatures might promote volatilisation and loss of Se unless measures were taken to ensure the oxidation of the Se in solution.

Determination of selenium in solution by hydride generation, as employed in this study, has one possible advantage over other methods, in that the formation of the hydride is only successful when the Se is in the 4+ oxidation state, Se^{6+} is normally pre-reduced to the 4+ form using KBr prior to determination (section 3.2.1.). Omission of the prereduction stage should therefore readily allow for the speciation of Se^{4+} and Se^{6+} forms.

Experiment 1.

Initially extraction of soils was undertaken using less than 2 mm air dried soil at a soil to solution ratio of 1:10 with either water or 0.01M $CaCl_2$, which was shaken overnight (18 hrs) in a polythene bottle. Calcium chloride solution was used as a comparison with water because it is considered to approximate to the ionic concentration of the soil solution (Hesse, 1971) and also because it would maintain the floculation of the soil colloids and thus aid the separation of soil and solution after the extraction. An aliquot of the supernatant produced by centrifuging the mixture at 3000 r.p.m. for 15 mins was used for the analysis. The supernatant of the water extract produced in this way was generally clouded by the presence of suspended colloids. This problem was reduced by filtration of the solution under suction through a 0.4 µm filter after centrifugation.

Analysis of the Se in the resulting solution was undertaken using the preconcentration method of Thompson et al. (1981). The hydride generation - I.C.P. system used provided a detection limit for Se in solution of 0.003 $\mu g\ ml^{-1}$. Assuming a water soluble Se percentage of around 2.0% (based upon the values in Table 7.3.), concentration factors were chosen which it was thought would provide final solution concentrations above the detection limit, these were 5 and 10 times pre-concentrations obtained as below.

The sample (50 or 100 ml) was placed in a large centrifuge tube and acidified with concentrated HNO_3 (1 or 2 ml). One ml of lanthanum nitrate (2.5% m/v) and 2 ml of diluted (1+1) ammonia solution were added successively and the sample mixed before centrifuging at 3000 r.p.m. for 2min. The supernatant was discarded and the precipitate dissolved in 10 ml of 5M HCl containing 5% KBr and the resulting solution was heated in a water bath for 50 min at 50°C. This solution was then used for analysis.

The above proceedure was carried out on soil numbers 2121, 2135, 2186 and 2459 (Table 7.4.) at both the 5 and 10 times pre-concentration. In no cases could Se be detected above the detection limit. This approximates to less than 0.006 and 0.003 $\mu g \ g^{-1}$ water soluble Se in the soils. In comparison with most of the methods described in Table 7.3. no acid digestion was involved in the proceedure, and it was thought that any Se present in organic forms might therefore remain undetected. In addition, and especially in the case of the water soluble extract, some soil colloids of less than 0.4 μm effective diameter would still remain in solution, onto which it is possible that oxidised species of Se may be adsorbed; it is possible that this takes place after separation of the solution therefore removing soluble Se from solution.

Experiment 2.

Water extracts were obtained in the same manner as in experiment 1. Then the following digestion was adopted:

A 100 ml aliquot of the solution was placed in a 250 ml beaker and 2 ml of concentrated HNO_3 added to maintain the Se in oxidised forms. The solution was then heated, on a temperature control hot plate, at 80°C until the volume was reduced to about 3 ml. This solution was transferred to a test tube with the addition of a further 1 ml of concentrated HNO_3. The volume was reduced to 3 ml at 100°C on a temperature control hot block. Then $HClO_4$ (0.05 ml) was added and the temperature was first raised to 150°C, until all the HNO_3 had fumed off, and then to 170°C until the volume of perchloric acid was also reduced. The resulting small amount of solution was then treated as for a soil digest as given in section 3.2.1.

Sample number.	Se_t	pH_w	L.O.I.	Origin and type of soil.
2121	4.09	5.00	14.4	Mixon area. Dale series Ahg horizon
2135	0.94	5.90	14.6	Mixon area. Wilcocks sereis Ah horizon.
2186	0.57	7.10	11.4	Llansannan area. Manod series A horizon.
2419	0.59	5.55	12.5	Llansannan area. Denbigh series A horizon.
2459	0.33	6.30	8.7	Llansannan area. Sannan series Ahg horizon.
D001	0.78	6.65	11.9	Tideswell Derbyshire. Soil developed from limestone.
D002	0.80	6.65	15.1	Tideswell,Derbyshire. Soil developed from limestone.

Table 7.4. Characteristics of the soils used in extraction and fractionation experimental work.

The digestion proceedure was designed to relaese into solution any Se which was in organic combination, or was sorbed onto, or in association with, suspended colloids. Soils 2419 and 2459 (Table 7.4.) were analysed in this way but again no values were obtained which were above the detection limit of the analytical sytem. The same proceedure enacted on spiked standard solutions of Se, taken from the post filtration stage, gave recoveries of above 95%. It was thought therefore that the content of "water soluble" Se in these soils was extremely low, for a soil which contained 0.50 $\mu g\ g^{-1}\ Se_t$ this would approximate to less than 0.6% water soluble Se (as a percentage of the total). This is a value which is much smaller than any of the values quoted by Levesque (1974b) for Canadian soils (least value 1.9% of total). Because of the relatively acid reaction of the soils used in this study (see Table 7.4.) conditions do not favour the formation of soluble selenate (Geering et al., 1968), and any selenite which may be present is likely to be almost fully adsorbed on soil colloids, as it appears that very little is in solution in equilibrium with this phase.

Some of the problems encountered here may be worthy of consideration when past results for water soluble Se are considered. The efficiency of soil - solution separation after the extraction is of great importance, in that few soils will remain totally flocculated after water saturation, and therefore the presence of suspended colloids in solution is likely, unless high efficiency of separation is achieved. Any Se which may be associated with such colloids will not be water soluble if plant availability estimation is the broad rationale for the extraction. To this extent also, the validity of assaying Se which is a component of water soluble or suspended organics is suspect (Levesque, 1974b). A more complete fractionation of the forms of Se which are present in these soils may shed some light it was thought on the reasons for their apparent lack of water soluble Se.

7.4.3. Fractionation of soil selenium.

The fractionation scheme to be developed was based on that originally devised by Cary et al. (1967) which is summarised in Figure 7.2.

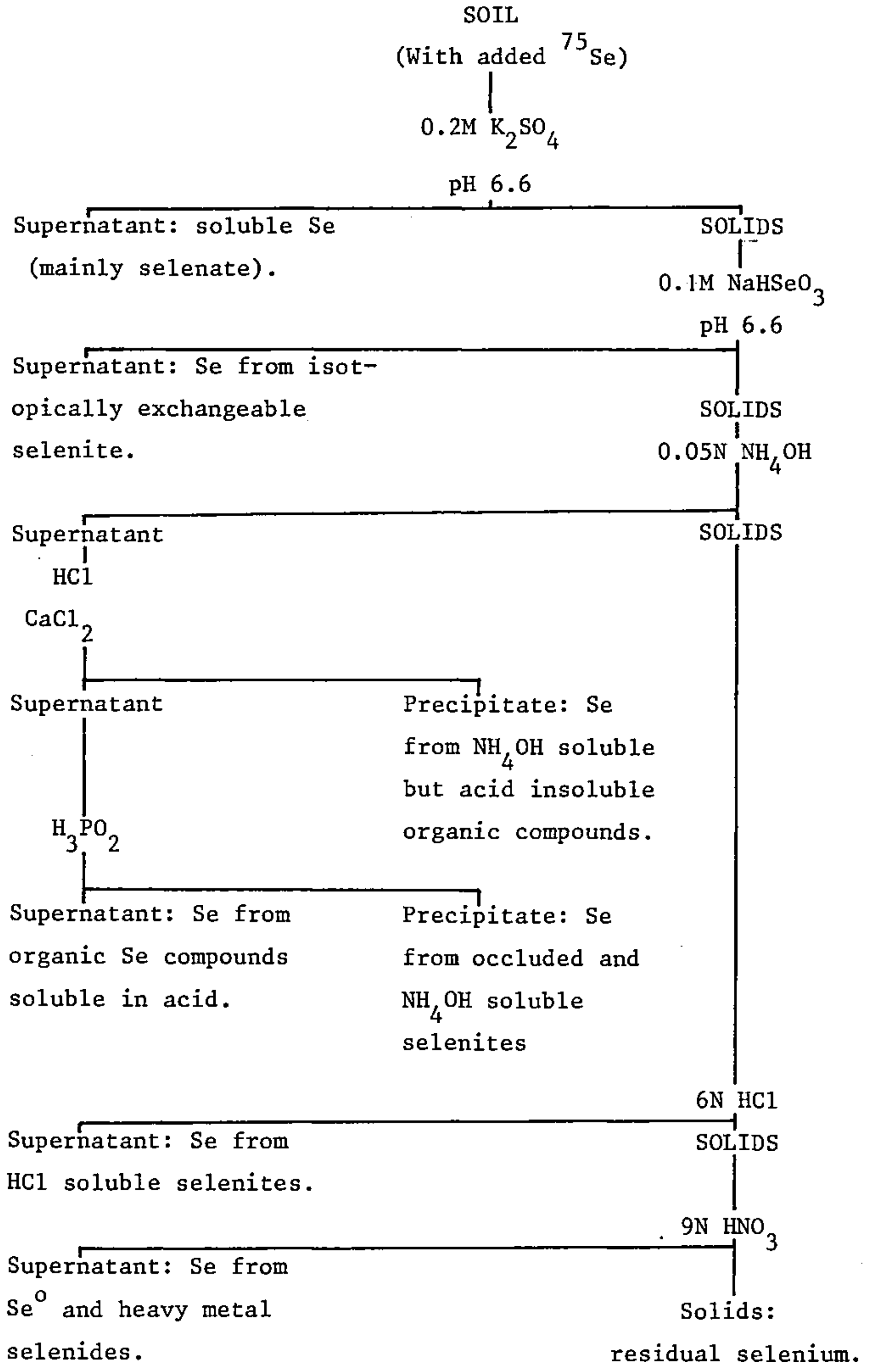


Figure 7.2. Flow diagram for fractionation of ^{75}Se from soil. (Cary et al., 1967).

Experiment 3.

In utilising this scheme it was proposed to assess the solubility of Se in each extractant by the measurement of the resulting solution concentration of Se at each successive stage. Both Cary et al. (1967) and Hamdy and Gissel-Nielsen (1976b) relied upon the assay of residual ^{75}Se remaining in the soil after each extraction. This means that the saturation of the soil with Na_2SeO_3 to remove isotopically exchangeable Se (Figure 7.2.) must necessarily be omitted from the proceedure, and therefore the K_2SO_4 extraction is followed immediately by extraction with NH_4OH. In this instance the final extraction was with 50% HCl, after which the remaining solids were to be digested as in the normal proceedure for measuring soil Se_t (section 3.2.1.).

The scheme is summarised in Figure 7.3., the extraction times which were adopted at this stage were those given by Hamdy and Gissel-Nielsen (1976b) as providing complete extraction at each stage for their soils. Initially centrifugation was chosen for soil-solution separation after the extraction. For the K_2SO_4 solution both acid digestion (as in experiment 2.) and lanthanum pre-concentration (as in experiment 1.) were investigated as means of measuring the Se solution concentration. As NH_4OH extractraction is designed to be specific for organics an acid digestion was considered to be necessary. Several problems were encountered with the proceedure which are reported below:

i. K_2SO_4 extraction: centrifugation produced an apparently clear solution, however, the precipitate produced during the lanthanum precipitation stage was darkly coloured, which was thought to be due to the presence of entrained organics or clays. Filtration (0.4 µm) of the supernatant removed this problem. Subsequently no Se was detected in solution.

Acid digestion of the extract was not possible using the normal oxidising acids as addition of HNO_3 to the solution produced crystalised KNO_3 which could not then be redisolved when the digestion was complete.

ii. NH_4OH extraction: once the conditions for the acid digestion had

Stage.	Proceedure.	Possible extracted forms.	
1.	12 g of less than 2 mm air dry soil.		
	120 ml 0.2M K_2SO_4 for 72 hrs.		
	Centrifuge 3000 r.p.m. for 15 mins. →	Supernatant:	Soluble Se Mainly selenate.
	SOLIDS		
2.	120 ml 0.05M NH_4OH for 96 hrs.		
	Centrifuge 3000 r.p.m. for 15 mins. →	Supernatant:	Organic Se forms and occluded and NH_4OH soluble selenites.
	SOLIDS		
3.	120 ml 6M HCl for 48 hrs.		
	Centrifuge 3000 r.p.m for 15 mins →	Supernatant:	Se from HCl soluble selenites.
	SOLIDS - - - - - - - - - - - - - - -	Residual Se and Se^o, and heavy metal selenides.	

Figure 7.3. Summary of initial fractionation proceedure.

been optimised the proceedure was enacted upon both soil which had been pre-extracted with K_2SO_4 and soil which had not had the pre-extraction; also the effects of filtration (0.4 μm) on the supernatant were investigated. The results (Table 7.5.) show that, for both K_2SO_4-extracted and non K_2SO_4-extracted soil, less Se (by approximately 10%) was present in solution after filtration, suggesting that centrifugation was not totally efficient. More surprisingly, and contrary to expectations, more Se was recovered in the extraction on the K_2SO_4-extracted soil (approximately 10%). The reason for this is not clear, however, the lanthanum precipitate produced in the preparation of these samples was considerably more ferric coloured; it is therefore possible that the K_2SO_4 extraction acted to solubilise ferric compounds, which on previous evidence might be expected to release Se, as selenite, into solution.

At a later stage in the investigation, centrifugation at higher speeds (13000 r.p.m.) became available, and was found to be comparable in effect (when used for 60 min) to the combined process of centrifugation at 3000 r.p.m. followed by filtration, and was subsequently adopted for soil - solution separation. Also during filtration the possibility of scavenging of Se from solution by the filter itself, or by the material entrained thereupon, had been considered as a possible explanation for very low Se concentrations in the water extracts. However, as centrifugation at 13000 r.p.m. and filtration produced similar results with NH_4OH extracts it was considered that this problem may not be important. It may, however, in future require further investigation. Because of the problems which were encountered with the analysis of Se in the extracting solutions, and also because high speed centrifugation allowed the clear separation of soil in the extracting bottle, an alternative strategy was sought. This was to dispose of the supernatant after extraction and to analyse for the amount of Se remaining in the soil after each stage.

Experiment 4.

The following scheme was adopted:

i. To each of three 250 ml polythene centrifuge bottles was added 5g of less than 2 mm air dry soil and 50 ml of 0.2M K_2SO_4. Bottles

Soil treatment.	Centrifuge at 3000 r.p.m. for 15 min.	Centrifuge at 3000 r.p.m. for 15 min & filter (0.04 µm)
Without previous K_2SO_4 extraction	0.127	0.111
With previous K_2SO_4 extraction	0.137	0.126

All values are in µg g^{-1} of air dry soil.

Table 7.5. Effects of previous K_2SO_4 extraction and filtration on the determination of NH_4OH soluble selenium, soil D001.

were then shaken for 72 hrs.

ii. All bottles were centifuged for 60 min at 13000 r.p.m. and the supernatant discarded, the soil was carefully allowed to drain.

iii. Solids from one of the bottles were transferred quantitatively to an evaporating basin, using minimum amounts of water, and then dried at 20°C in a drying cupboard.

iv. 50 ml of 0.05M NH_4OH was added to each of the two remaining bottles which were then shaken for 96 hrs before centrifuging as above.

v. The supernatant was discarded as above and the soil from one bottle was dried as in iii. above.

vi. 50 ml of 6M HCl was added to the remaining bottle which was shaken for 48 hrs after which the soil was separated, collected and dried as above.

vii. All the dried soils were ground to less than 200 μm and mixed thoroughly, a 0.5 g sub-sample was taken for total Se determination as given in section 3.2.1. for soils and rocks. All extractions were duplicated as were all Se determinations.

The use of three separate bottles per sample was preferred to the alternative of taking sub-samples from a single bottle used for all three extractions as during centrifugation solids settle out in sequence relative to their effective diameter and therfore it is difficult to take a representative and homogenous sample from the bottle without first removing and mixing the soil. It was felt that this process would impart greater errors in the technique than those inherant in the sub-sampling of three separate samples of dry soil initially. The soil was not washed, to remove salts, after each extraction as it was considered that this might result in further loss of Se either into solution (although this might be very small) or as a component of suspended colloids in solution. The total Se in untreated soil was also determined.

Soils D001 and 2419 (Table 7.4.) were used, and the results are given in Table 7.6. Duplicate Se determinations were good with precision of less than 10%; the comparison of duplicate extractions was also less than 10% calculated as:

$$\frac{\text{Difference between duplicates}}{\text{Mean of duplicates}} \times 100.$$

The results suggest that 0.2M K_2SO_4 extracts 20.5% and 32.2% of total soil Se for soils D001 and 2419 respectively, values which are much higher than those previously recorded for this extractant (Cary et al., 1967; Hamdy and Gissel-Nielsen, 1976b). The results also conflict with earlier work (section 7.4. experiments 2 and 3) when no Se could be detected in both K_2SO_4 extracts and water extracts. The variation in results between duplicate analyses and extractions are large compared to the recorded differences between some of the treatments, and therefore their reliability is in doubt. An appraisal of the technique located the following sources of error which might affect the results:

i. Firstly differences in the soil to solution ratio of the extractions are possible, these could be due to both variations in the volume of solution and the weight of soil. These, however, would be quite small.

ii. Residual K_2SO_4 and possibly HCl could remain after drying of the samples, this would increase the effective weight of the soil, and hence decrease the real weight of soil taken in a 0.5 g subsample.

iii. All results have been based on air dry weights. Air drying is considered necessary in order to reduce possible losses of Se due to volatilisation, and air dryness can vary due to changes in the temperature and humidity in which the material was dried and then stored.

iv. Loss of Se from the soil is possible during drying despite attempts to minimise this by air drying.

v. Losses of solid material during both centrifugation and the recovery and grinding of the air dry samples is inevitable. Although

Extraction step.	Se content ($\mu g\ g^{-1}$ air dry soil)*	
	D001	2419
Total Se.	0.78	0.59
After K_2SO_4	0.62	0.40
After NH_4OH	0.62	0.36
After HCl	0.56	0.28

* All results are means of duplicate Se determinations on duplicate extractions.

Table 7.6. Results of sequential extraction of soil Se, based on the analysis of Se in residual soil.

the former of these would lead to the loss of only small amounts of material, this would be predominatly of small particle size and would therefore constitute a proportionately larger loss of Se from the soil. These losses would be most critical after the first extraction.

Errors due to ii, iv and v would tend to result in the underestimation of the amount of Se remaining in the soil, whilst the errors due to i and iii could be positive or negative. The errors in ii, iii, iv and v might be eliminated or reduced by conducting the whole proceedure in a single tube, i.e. the shaking, centrifugation and acid attack on the solid residue, which should contain sufficient soil for the digestion proceedure; in this case drying of the soil would not be necessary. However, still inherent in the technique would be the problems of the precision and accuracy of the available method for Se determination in soils, which are large compared to the small differences in concentration which are to be assessed.

At this point no further development of the technique was attempted. It was considered that further progress along these lines would first require improvements to the accuracy and precision of the ana lytical method for the determination of Se in soils, such that smaller differences in concentration of soil Se, after successive extractants, could be measured with some certainty. These aspects were beyond the scope of this project in the available time. It is, however, considered that, by using some of the above mentioned improvements to the technique, it could be successfully used for the fractionation of "native" soil Se in low Se soils.

CHAPTER 8. CONCLUSIONS.

8.1. Selenium distribution in soil profiles.

The principal purpose of the work described in this thesis has been to determine the patterns of distribution of Se in some soils from England and Wales, and to elucidate the factors which influence and determine such patterns. Initially this took the form of a study of the vertical distribution of Se in soil profiles. This was first investigated in the podzols of the Lower Greensand, in which there is extensive redistribution of both organic matter, and the sesquioxides of Fe and Al, which are the soil constituents with which the distribution of Se was subsequently shown to be closely related. In these humo-ferric podzols Se is concentrated in the illuvial Bs and Bh horizons, and thought to be associated with Fe and Al, and also possibly with the illuvated forms of organic matter. In common with most soil constituents Se is relatively depleted in the eluvial E horizon. There is also evidence of Se association with the organic matter in the organic topsoils.

Patterns of Se distribution are essentially the same in the podzolic soils of the Hiraethog map unit in the Llansannan area, which includes a range of soil types from ironpan stagnopodzols through to better drained ferric podzols. The contrast between the Se content of the illuvial and eluvial horizons of these soils increases as the profiles become more poorly drained and the stagnopodzol features begin to predominate, and is most marked in the ironpan stagnopodzols where Se is also concentrated in the Bf horizon, in association with Fe. This sequence of profile development can be linked to the greater surface accumulation of organic matter, with which there is also an increased accumulation of Se.

Accumulation of Se in organic topsoils of the Ynys series and in the peats of the Caron series from the Llansannan area is also evident, although it is felt that the association of some Se with secondary precipitation of Fe masks any clear relationships between organic matter and Se accumulation in these soils. Caution must, however, be exercised in the interpretation of these results for peaty soils. All concentrations of Se in this study are expressed on a weight to weight basis, which in the case of mineral horizons allows for relatively straightforward comparisons of results, as their bulk densities vary over only a narrow range. In contrast the bulk density of organic soils can be appreciably lower and therefore any given weight of soil will occupy a larger volume in the profile. Therefore, concentrations expressed on a weight to volume basis might not demonstrate the same relative enrichment of organic compared to mineral soils. Unfortunately no bulk density measurements were taken in this study and therefore actual comparisons of this nature are not possible. Higher Se:Fe ratios in organic soils, however, do provide evidence of associations between Se and organic matter, suggesting that alternatives to Fe - Se associations do exist.

It is believed that in well drained acid podzolic B horizons, Se occurs predominantly as selenite adsorbed on ferric and possibly aluminium oxides. The mechanism of Se mobilisation from the horizon above is not, however, clear. It has been suggested that as ferric iron is reduced to the ferrous form and mobilised by organic complexes, the selenite with which it was associated is released and leached downwards to be re-adsorbed on precipitated sesquioxides in the B horizon. The Eh/pH information of Geering et al. (1968) and Howard (1977) does suggest that at pH's of less than about 6, ferrous iron may be formed whilst Se remains in the selenite form. As selenite is soluble in aqueous solution it may then be leached. Alternatively, or even in addition to the above mechanism, Se may be mobilised in the form of an organic - Fe - Se complex as suggested by Levesque (1974a and b). The process of podzolisation can therefore act to remove Se from the rooting zone, by the depletion ofthe Se content of the eluvial horizon.

Although podzols are atypical of most soils in England and Wales, these same associations could be implicated in influencing the distribution of Se in other soil types in the Llansannan area, such that in a linear regression model some 67% of the variation in the Se content of horizons of these soils is explained by the content of organic matter (represented by percentage loss of weight on ignition) and pyrophosphate extractable Fe. In typical brown earths, where there is little redistribution of sesquioxides, Se concentrations are relatively uniform down the profile. In stagnogleyic brown earths, and presumably in stagnogleys also, the concentration of Se decreased with depth, following a decrease in both organic matter and pyrophosphate extractable Fe. The effect of gleying is to reduce the quantity of sesquioxides which are capable of retaining Se in the soil. These results also suggest that there is little or no Se present in reduced forms, since these would obviously not be associated with the ferric oxides.

The poorly drained soils of the Mixon and Butterton Moor transect and the Bent Farm transect in Staffordshire and Derbyshire, exhibit a different mode of Se distribution, in that the vertical distribution of Se is more closely related to the total Fe content of the soil, rather than that extracted by pyrophosphate. This difference is not easy to explain by the data presented in this work. The most probable explanation is perhaps due to the type of the parent material and the mode of its weathering. In the Llansannan area of Clwyd, soil Se concentrations have been shown to be significantly higher than those in the solid rocks from which they are originally derived. In the case of the soils in Staffordshire and Derbyshire it appears that the local shales might contain more Se than the soils (section 5.4.). It is possible that the mode of weathering in the Llansannan area results in Se being principally retained in the soil; whilst in the Derbyshire soils some Se is lost from the solum, this being most pronounced in the most weathered surface horizons. Similar relationships between soil Se content and degree of weathering were noted by Watkinson (1962) for some New Zealand soils . An alternative explanation is that conditions in the gleyed horizons of the Sannan series soils from the Llansannan area may not be sufficiently reducing to cause the reduction of Se to the elemental or selenide forms, so that all the Se present occurs as selenite which is necessarily associated with ferric species. In contrast the association between total iron and Se in the gleyed soils in Derbyshire suggests that much of the Se is present as selenide (which may take the form of ferrous selenide) or be in selenide phases in unweathered fractions. In the soils of the Llansannan area and noteably in the groundwater gley (profile S8) on the Mixon and Butterton transect where the Se distribution was also related to that of Fe_p, the Se will occur primarily in the selenite form.

Problems in the interpretation of these observations derive from a general lack of information on the chemistry of Se in reducing conditions in waterlogged soils where Se is thought to exist in elemental or selenide forms. The behaviour of oxyanionic species of Se, selenate and selenite, have been better characterised since they are both soluble in aqueous solution and therefore available to plants.

8.2. A view on the chemistry and distribution of selenium in soils.

Evidence, both in this work and elsewhere, shows that Se in the soil is associated with organic matter and iron species, and in addition that Se as selenite may be associated with aluminium oxides. The results of this work do not provide conclusive evidence for the latter relationship since the patterns of distribution of Fe and Al sesquioxides are often similar. However, it is postulated that adsorption of Se on ferric oxides in the soils of the Llansannan area is the more important relationship. It is considered that in neutral to acid well drained soils most Se exists as selenite in association with a selenite - ferric oxide adsorption complex. Conditions favouring the formation of the soluble selenate anion are unlikely to occur in the majority of soils in England and Wales and therefore the resultant high plant concentrations of Se, and hence livestock toxicity problems are unlikely to be encountered.

Conditions which favour the reduction of ferric to ferrous iron may therefore release selenite into solution, and as such Se may be leached either vertically or laterally in the soil. Lateral movement of soil water is thought to account for the accumulation of Se in the soils at the base of a catenary sequence at Bent Farm in Derbyshire. As reducing conditions in the soil become more intense, selenite may itself be reduced to elemental Se, and then further to selenide-Se, in which form the element may again be associated with Fe, as a ferrous selenide. Both elemental and selenide forms of Se are thought to be insoluble and therefore largely immobile in the soil. The lack of success of the fractionation procedure examined in Chapter 7 means that it is not possible in this work to quantify the amounts of each Se species in the soil. More information is needed on this subject, and also more specifically on rates of conversion between the different forms in the soil. The effects of variations in redox conditions, during seasonal fluctuations of soil water status, may be important in releasing Se and affecting plant availability. Berrow and Mitchell (1980) have shown that the availability of several other trace elements is greater in gleyed compared to well drained soils, and work of a similar nature would be valuable in the case of Se, but would first require the establishment of a criteria by which to assess plant availability of Se.

Associations between organic matter, Se and pyrophosphate extractable Fe (representing Fe in, or recently precipitated from, organic combination) provide evidence for the involvement of Se in the organic cycle in soils. It can be envisaged that Se as selenite is absorbed by plants in the rooting zone and assimilated in the herbage and roots. As the plant material decays and humus accumulates at the surface, so will some Se. Eventually as the organic matter becomes mineralised, Se will be released to be either retained on ferric oxides, or transported down the profile. As previously stated this could be either as selenite in aqueous solution, or in combination with organic matter via chelated Fe or Al. Incidentally, the latter form of association has been postulated for phosphate anions which behave similarly (Mott, 1981), but it is not clear as to how mobile such complexes are.

Further work on Se chemistry in the soil is necessary in order to elucidate the availability of Se to herbage under different conditions of drainage, pH and organic matter status in surface soils. Variations in soil type, under conditions of uniform parent material as in the Llansannan area, actually impart only small differences in the total concentration of Se in the topsoil; however, such contrasting effects on the actual availability of Se to plants are not clear. Variations in the ability of different sward compositions to assimilate Se may also be important; differences between sward Se content on the mineral and organic topsoils of the Llansannan area, provide some evidence of this possibility.

8.3. The effect of parent material on the selenium content of the soil.

Examination of the soils developed on the four similar, predominantly sandstone, beds of the Lower Greensand formation in Surrey and Sussex which contain low levels of Se (mean = 0.14 $\mu g\ g^{-1}$), has demonstrated that there are differences in the Se content of soils developed on the various beds. This difference is only significant in the case of the more ferruginous soils on the Sandgate beds, which contain the highest concentrations of Se. No conclusive evidence could be provided to suggest that the Se and Fe content of the soils is linked to a common source in the parent rocks, since soils on all four beds in the north of the area, irrespective of the bed on which they were located, contained higher concentrations of Fe than soils in the south and the west of the area. All the soils are predominantly brown earths, belonging to the Bearsted, Barming and Stone Street series, and are relatively uniform in nature. Therefore differences between the nature of the parent material were perhaps more clearly manifested in the topsoil than would be the case if the soils were more varied in morphology.

In the Staffordshire and Derbyshire area the influence of parent material type on the Se content of the soil is very clear, especially in the soils on the Mixon and Butterton Moor transect. Seleniferous shales of the Gun Hill Siltstone formation give rise to a soil (profile S10) containing 22 $\mu g\ g^{-1}$ Se in the lower horizons. This transect also demonstrates that the Se content of the soil can vary considerably over relatively small distances, dependant upon the nature of the parent material; but also that the presence of locally derived drift may act to "smooth" these effects, especially in the topsoil. This is exemplified by the topsoil of profile S10, thought to be formed from a thin drift derived from the adjacent less seleniferous Onecote Sandstone formation, which contains only 2.75 $\mu g\ g^{-1}$ Se. It is pertinent to note here possible deficiencies in the use of geological drift maps for reconnaissance survey of soil Se concentrations, in that such shallow drift inclusions are not recorded. In this respect the examination of soil survey information will be important, as this will normally differentiate soils where vertical variations in profile morphology are due to lithological rather than purely pedological differences. For example in the Mixon area soils based on the Gun Hill Siltstone formation, but including surface horizons derived from head from the Onecote Sandstone formation, are mapped separately as the Ipstones series (Hollis, 1975).

Although uniformity of the parent material was assumed, and to some extent demonstrated for soils of the Llansannan area, it has been considered that residual variation (amounting to 32%) in the Se content of soil horizons, which was not explained by variation in L.O.I. and Fe_p, could in part be explained by differences in the geochemistry of the parent rock.

It is possible that the nature of Se associations in the parent rock could influence the retention, or otherwise, of Se in the soils on weathering of the parent material. This may be the reason for the apparent overall enrichment of Se in Llansannan area soils compared to possible losses in those of the Bent Farm transect. Information on the actual forms of Se in these rocks is limited, however. Close relationships between parent material and soil Se contents are to be expected in the relatively young soils of the British Isles, which are in the most part formed since the last major glaciation. Such associations may be much less apparent in highly weathered and leached soils in the tropics. In England and Wales, and elsewhere, such as Canada (Levesque, 1974a) and New Zealand (Wells, 1967), there is an overall trend for higher Se concentrations in soils compared to their parent materials. This is very clear in the soils of the Llansannan area, where enrichment may be as much as 10 times. This enrichment has been related to the close association between Se and ferric species, which acts to retain Se against the processes of weathering.

8.4. The regional distribution of selenium in soils in England and Wales.

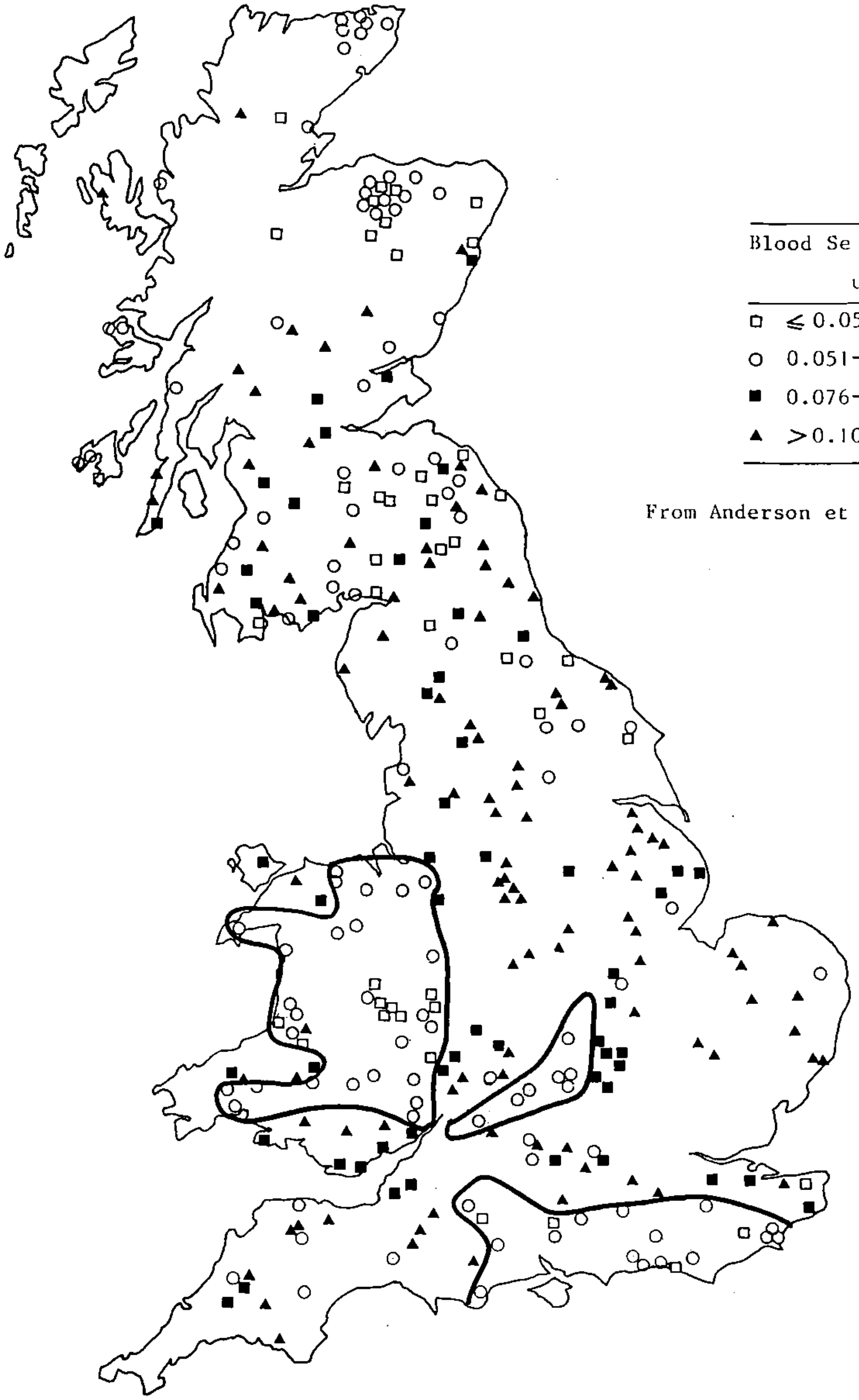
By using both the information presented in this work, and that of other workers, including Anderson et al. (1979) and Thornton et al. (in press) it is possible to develop a generalised picture of the overall distribution of Se in soils in England and Wales. The following discussion relies on the assumption that biological Se status of sheep, as reported by Anderson et al. (1979), is broadly related to the Se content of both the soil and herbage which they graze. Similar relationships have been demonstrated in New Zealand (Hartley, 1961) and Scotland (Sharman, 1960).

Anderson et al. (1979) noted distinct regional patterns in the distribution of the sheep flocks which fell into their two lowest categories of biological Se status; these and other regional groupings have been outlined in Figure 8.1.

The sampling in Scotland was not as extensive as that in England and Wales but two such low areas are clearly defined. One is in the northern Grampians and a second in the vicinity of Thurso on the northernmost part of the mainland. These low Se areas coincide with the outcrop of metamorphic complexes and Old Red Sandstone respectively. This is in accord with the findings of Sharman (1960) that the lowest soil Se concentrations in Scotland occur on the light textured soils derived from the arenaceous Old Red Sandstone and some granites.

The areas of low Se status flocks in England and Wales have also been outlined, for comparison, on a geological map (Figure 8.2.). As was the case in Scotland, these areas can be related to the incidence of specific geological formations. In Wales and the Welsh borders the low Se area coincides with the outcrop of Lower Palaeozoic, Silurian and Ordovician rocks, and also extends to the area of Devonian, Old Red Sandstone in S.E. Wales and the border counties. This latter association may be consistent with similar relationships on the Old Red Sandstone in Scotland.

The soils of the Llansannan area which are developed from Silurian rocks are typical of those of much of Wales where Silurian and Ordovician shales, slates and sandstones occur (Avery et al. 1974). Although the soils of the Llansannan area contain moderate concentrations of Se in the mineral topsoils (0.46 $\mu g\ g^{-1}$) and higher concentrations in organic soils (on a weight to weight basis) their general acidity is considered to render the Se largely unavailable for plant uptake. This information is consistent with the low levels of Se (mean = 0.035 $\mu g\ g^{-1}$) found in mixed swards developed on mineral topsoils of the area. This therefore provides some evidence that the characteristics of the Se distribution and status of the Llansannan area soils are typical also of the soils developed from most of the outcrop of Lower Palaeozoic rocks in Wales. In this respect it is probable that low availability of Se will be prevalent on the more acid and leached soils of the uplands which primarily coincide with the western and northern areas of England and Wales. A less well defined low Se area does also occur in the Scottish border counties and the Southern



Blood Se concentration ug/ml	Proposed significance
□ ⩽ 0.05	Deficient.
○ 0.051-0.075	Low marginal.
■ 0.076-0.10	Marginal.
▲ >0.10	Adequate

From Anderson et al. (1979)

Figure 8.1. Regions of lower biological selenium status in relation to the distribution of 329 sheep flocks according to their biological selenium status.

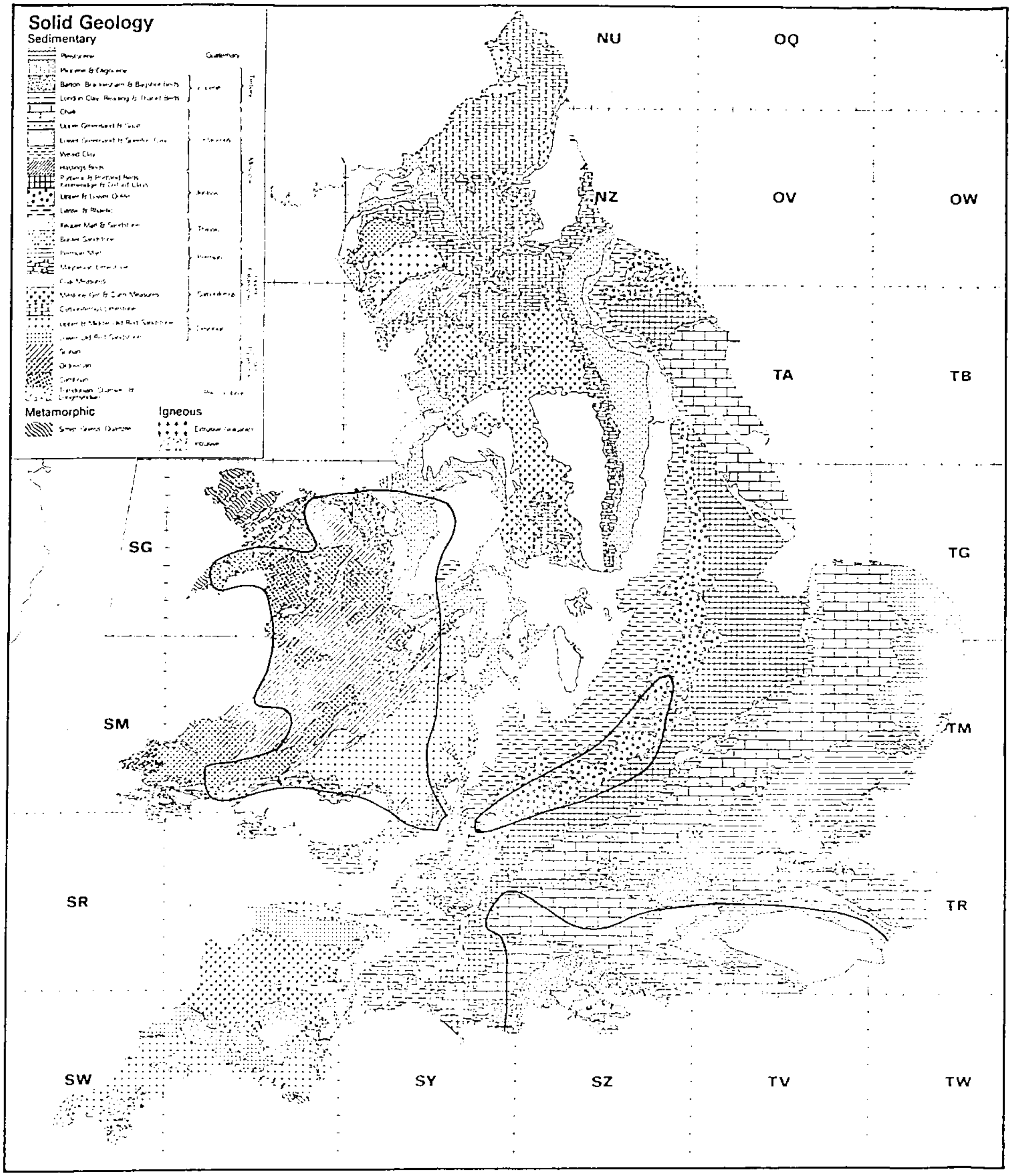


Figure 8.2. Regions of lower biological selenium status of sheep flocks in relation to the geology of England and Wales.

Uplands, which does partly coincide with a large outcrop of Lower Palaeozoic rocks.

A further area of low Se status is located in southern and south eastern England. This coincides less clearly with specific geological formations, but broadly corresponds to an area characterised by the Cretaceous chalk and associated Upper and Lower Greensands, and the Hastings beds. This conforms with the recorded low Se concentrations in soils developed from calcareous lithologies (Thornton et al, in press) of which the chalk represents a particularly pure member. A portion of the Lower Greensand has also been shown to give rise to soils low in total Se (Chapter 4), and low Se concentrations in soils developed from the coarse arenaceous Hastings beds are quite probable. The existence of similar relationships on the chalk in more northerly locations may be masked by the influence of extraneous drift deposits, which are not extensive in S.E. England.

The final low Se area in England centres on the Cotswolds and the north easterly extension of the middle Jurassic Oolites, which again are calcareous and could be expected to give rise to soils low in total Se (Thornton et al., in press).

Extensive areas of northern England, which relate to the outcrop of predominantly Carboniferous formations, and of the midland and eastern counties, underlain by Jurassic and Triassic rocks but largely covered by glacial drift, appear to be less prone to Se deficiency problems.

From the above information, therefore, three broad groupings of parent materials which may give rise to soils low in available Se in England and Wales have been recognised:

i. Coarse arenaceous formations on which light textured soils, characteristically brown earths, are developed. Most noteable are the Old Red Sandstone and the Cretaceous sands and sandstones of S.E. England.

ii. Ordovician and Silurian shales, slates and sandstones, occurring in upland regions and characterised by an association of brown earths, stagnogley soils and brown podzolic soils, and with predominantly stagnopodzols and stagnohumic soils on the higher ground.

iii. Chalk and Jurassic limestones giving rise to rendzinas and associated brown calcareous earths.

On top of this relationship there may be a trend that when such outcrops occur in upland western and northern regions, where higher rainfall produces more acid leached soils, Se availability to plants will be further impaired. These are also traditionally the areas of livestock rearing, especially of sheep.

It has to be noted that these are only tentative conclusions and more careful geographical characterisation of soils, their parent materials and the incidence of Se responsive diseases is necessary before such information could be of practical value. However, the concept of using soil parent material and soil survey information for the identification of problem areas is clearly viable.

8.5. Recommendations for further work.

Having established clear differences in the distribution of Se in soils of various groups, this work could be extended to cover all the principal soil groups in England and Wales. However, more important is the need to establish the effects of these differences on the availability of Se to the plant. Information of this nature is particularly lacking in the case of waterlogged soils where reducing conditions are prevalent for some or all of the year. Having more clearly characterised the soil - plant relationships, soil and soil parent material surveys could provide a useful basis for characterising potential areas of Se deficiency in England and Wales. Given that the above relationships are understood, soil, rather than herbage, measurements of Se status of pastures will provide a better long term assesment of the Se status of the land in that they are not affected by possible seasonal variations and species differences as in the case of herbage.

The possible contribution of Se contained in ingested soil, to the animals dietary Se intake should also be investigated, as it may provide an important portion of the total intake of Se, especially in marginal upland areas where sward production is low and hence the levels of ingested soil are higher, noteably in winter months. Characterisation of the forms of Se in the soil may also be important in this respect.

REFERENCES.

ABU-ERREISH, G.M., WHITEHEAD, E.I. & OLSON, O.E. 1968 Evolution of volatile selenium from soils. Soil Science 106, 415-420-

ADAMS, W.A., EVANS, L.J. & ABDULLA, H.H. 1971 Quantitative pedological studies on soils derived from Silurian mudstones III. In-situ weathering of chlorite. Journal of Soil Science 22, 158-165.

ALLAWAY, W.H., CARY, E.E. & EHLIG, C.F. 1967 The cycling of low levels of selenium in soils, plants and animals. In: Selenium in Biomedicine. 1st International Symposium, Oregon State University, 1966 (Ed. Muth, O.H.) pp 273-296. A.V.I. Publishing Co.

ALLAWAY, W.H. 1971 In: JOHNSON, C.M. 1975.

ANDERSON, P.H. 1979 Deficiency diseases. Selenium / vitamin E deficiency. Veterinary Record Supplement: In Practice 1, 25-28.

ANDERSON, P.H., BERRETT, S. & PATTERSON, D.S.P. 1976 Veterinary Record 99, 316.

ANDERSON, P.H., BERRETT, S. & PATTERSON, D.S.P. 1979 The biological selenium status of livestock in Britain as indicated by sheep erythrocyte glutathione peroxidase activity. Veterinary Record 104, 235-238.

ANDREWS, E.D., HARTLEY, W.J. & GRANT, A.B. 1968 Selenium-responsive diseases of animals in New Zealand. New Zealand Veterinary Journal 16, 3-17.

ARCHER, F.C. 1980 Trace elemants in soils in England and Wales. In: Inorganic Pollution and Agriculture, M.A.F.F. reference book 326. pp 184.

ATKINSON, W.J. 1967 Regional geochemical studies in county Limerick with particular reference to selenium and molybdenum. PhD Thesis. University of London.

AVERY, B.W. 1980 Soil classification for England and Wales. Soil Survey Technical Monograph No. 14. Harpenden.

AVERY, B.W. & BASCOMBE, C.L. (Eds.) 1974 Soil survey laboratory methods. Soil Survey Technical Monograph No. 6. Harpenden.

AVERY, B.W., FINDLAY, D.C. & MACKNEY, D. 1975 Soil map of England and Wales, 1:1 000 000. Ordnance Survey, Southampton.

BAAS BECKING, L.G.M., KAPLAN, I.R. & MOORE, D. 1960 Limits of the natural environment in terms of pH and oxidation - reduction potentials. Journal of Ecology 68, 243-284.

BALL, D.F. 1960 The soils and land use of the district around Rhyl and Denbigh. Memoirs of the Soil Survey of Great Britain, England and Wales. H.M.S.O.

BALL, D.F. 1964 Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. Journal of Soil Science 15, 84-92.

BALL, D.F. & BEAUMONT, P. 1972 Vertical distribution of extractable iron and aluminium in soil profiles from a brown earth - peaty podzol association. Journal of Soil Science 23. 298-308.

BARKES, L. & FLEMING, R.W. 1974 Production of dimethylselenide gas from inorganic selenium by eleven soil fungi. Bulletin , Environmental Contamination and Toxicology 12, 308-311.

BASCOMBE, C.L. 1968 Distribution of pyrophosphate-extractable iron and organic carbon in soils of various groups. Journal of Soil Science 19, 251-268.

BEATH, O.A., EPPSON, H.F. & GILBERT, C.S. 1935 Selenium and other toxic minerals in soils and vegetation. Wyoming Agricultural Experimental Station Bulletin 206, 1-55.

BEESON, K.C. 1961 Occurrence and significance of selenium in plants. In: Selenium in Agriculture. U.S.D.A. Handbook No. 200. pp 34-40

BERROW, M.L. & MITCHELL, R.L. 1980 Location of trace elements in soil profiles: total and extractable contents of individual horizons. Transactions of the Royal Society of Edinburgh: Earth Sciences 71, 103-121.

BIRD, M.L., CHALLENGER, F., CHARLTON, P.T. & SMITH, J.O. 1948 Studies on the biological methylation XI: The action of molds on inorganic and organic compounds of arsenic. Biochemistry Journal 43, 78-83.

BISBJERG, B. 1972 Studies on selenium in plants and soils. Risø Report No. 200, Danish Atomic Energy Commission, Risø.

BLAXTER, K.I. 1963 Effect of selenium administration on the growth and health of sheep on Scottish farms. British Journal of Nutrition 17, 105-115.

BOSWELL, P.G.H. 1949 The Middle Silurian Rocks of North Wales. Edward Arnold and Co., London.

BUTLER, J.R. 1954 Trace element distribution in some Lancashire soils. Journal of Soil Science 5, 156.

CARTER, D.L., ROBBINS, C.W. & BROWN, M.J. 1972 Effect of phosphorus fertilisation on the selenium concentration in alfalfa. Soil Science Society of America, Proceedings 36, 624-628.

CARY, E.E. & ALLAWAY, W.H. 1969 The stability of different forms of selenium applied to low selenium soils. Soil Science Society of America, Proceedings 33, 571-574-

CARY, E.E. & GISSEL-NIELSEN, G. 1973 Effect of fertilizer anions on the solubility of native and applied selenium in soils. Soil Science Society of America, Proceedings 37, 590.

CARY, E.E., WIECZOREK, A. & ALLAWAY, W.H. 1967 Reactions of selenite selenium added to soils that produce low selenium forages. Soil Science Society of America, Proceedings 31, 21-36.

CAWSE, P.A. 1980 Deposition of trace elelents from the atmosphere in the United Kingdom. In: Inorganic Pollution and Agriculture.

M.A.F.F. reference book 326. pp 22.

COX, D.P. & ALEXANDER, M. 1974 Factors affecting trimethylarsine and dimethylselenide formation by Candida humida. Microbial Ecology 1, 136-144.

DAVIES, E.B. & WATKINSON, J.H. 1966 Uptake of native and applied selenium by pasture species II. Effect of sulphate and soil type on uptake by clover. New Zealand Journal of Agricultural Research 9, 641-652.

DIPLOCK, A.T. 1981 Metabolic and functional defects in selenium deficiency. Philosophical Transactions of the Royal Society of London B294, 105-116.

DORAN, J.W. & ALEXANDER, M. 1976 Microbial formation of volatile selenium compounds in soil. Soil Science Society of America, Proceedings 40, 687-690.

DOYLE, P.J. & FLETCHER, W.K. 1977 Influence of soil parent material on the selenium content of wheat from west central Saskatchewan. Canadian Journal of Plant Science 57, 859-864.

EHLIG, C.F., ALLAWAY, W.H., CARY, E.E. & KUBOTA, J. 1968 Differences among plant species in selenium accumulation from soils low in available selenium. Agronomy Journal 60, 43-47.

EVANS, L.J. & ADAMS, W.A. 1975a Chlorite and illite in some lower Palaeozoic mudstones of mid-Wales. Clay Minerals 10, 387-397.

EVANS, L.J. & ADAMS, W.A. 1975b Quantitative pedological studies on soils derived from Silurian mudstones V. Redistribution and loss of mobilised constituents. Journal of Soil Science 26, 327-335.

FLEMING, G.A. 1962 Some factors affecting the uptake of selenium by plants. Irish Journal of Agricultural Research 1, 131-138.

FLEMING, G.A. 1890 Essential Micronutrients II: Iodine and Selenium. In: Applied Soil Trace Elements (Ed. Davies, B.E.) pp 215-234. John Wiley and Sons.

FLEMING, G.A. & WALSH, T. 1957 Selenium occurrence in certain Irish soils and its toxic effect on animals. Proceedings of the Royal Irish Acadamy 58, 151-167.

FLEMING, R.W. & ALEXANDER, M. 1972 Dimethylselenide and dimethyltelluride formation by a strain of Penicillium. Applied Microbiology 24, 424-429.

FLETCHER, W.K. 1968 Geochemical reconnsissance in relation to copper deficiency in livestock in the southern Pennines and Devon. PhD Thesis. University of London.

FORDHAM, S.J. & GREEN, R.D. 1973 Soils in Kent II: Sheet TR35 (Deal). Soil Survey Record. Harpenden.

FRANCIS, A.J., DUXBURY, J.M. & ALEXANDER, M. 1974 Evolution of dimethylselenide from soils. Applied Microbiology 28, 248-250.

FRANK, K.W. & PAINTER, E.D. 1937 Effect of sulphur additions on seleniferous soils. Binding of selenium by the soil. Industrial and Engineering Chemistry 29, 591-595.

GALLOIS, R.W. 1965 The Wealden District. British Regional Geology. H.M.S.O.

GANJE, T.J. & WHITEHEAD, E.I. 1958 Selenium uptake by plants as affected by the forms of selenium in the soil. Proceedings of the South Dakota Academy of Science 37, 85-88.

GARDENER, C.U.M. 1980 Distribution of ten trace elements in rocks, soils and sediments in seven areas of England and Wakes. PhD Thesis. University of London.

GARDINER, M.R. 1969 Selenium in animal nutrition. Outlook on Agriculture 6, 19-28.

GARDINER, M.R. & GORMAN, R.C. 1963 Further observations on plant selenium levels in western Australia. Australian Journal of Experimental Agriculture and Animal Husbandry 3, 284-289.

GEERING, H.R., CARY, E.E., JONES, L.P.H. & ALLAWAY, W.H. 1968 Solubility and redox criteria for the possible forms of selenium in soils. Soil Science Society of America, Proceedings 32, 35-40.

GISSEL-NIELSEN, G. 1971a Influence of pH and texture of the soil on plant uptake of added selenium. Journal of Agricultural and Food Chemistry 19, 1165-1167.

GISSEL-NIELSEN, G. 1971b Selenium content of some fertilizers and their influence upon uptake of selenium by plants. Journal of Agricultural and Food Chemistry 19, 564-566.

GISSEL-NIELSEN, G. 1974 Effects of fertilizers on the uptake of selenium into plants. In: Plant Analysis and Fertilizer Problems. Proceedings of the 7th International Colloquium. Hanover, September 1974.

GOLDSCHMIDT, V.M. 1954 Geochemistry. Clarenden Press, Oxford.

GREEN, R.D. & FORDHAM, S.J. 1973 Soils in Kent I: Sheet TR04 (Ashford). Soil Survey Record No. 14. Harpenden.

GUPTA, U.C. & WINTER, K.A. 1975 Selenium content of soils and crops and the effects of lime and sulphur on plant selenium. Canadian Journal of Soil Science 55, 161-166.

HAMDY, A.A. & GISSEL-NIELSEN, G. 1977 Fixation of selenium by clay minerals and iron oxides. Zeitschrift fur Pflanzenernahrung und Bodenkude 140, 63-70.

HAMDY, A.A. & GISSEL-NIELSEN, G. 1976a Volatilisation of selenium from soils. Ibid 6, 673-678.

HAMDY, A.A. & GISSEL-NIELSEN, G. 1976b Fractionation of soil selenium. Ibid 6, 697-703.

HARTLEY, W.J. 1961 Selenium treatment of animal diseases and unthriftiness. New Zealand Journal of Agriculture 103, 475-483.

HASHIMOTO, Y., HWANG, J.Y. & YANAGISAWA, S. 1970 Possible sources of atmospheric pollution of selenium. Environmental Science and Technology 4, 157-158.

HEALY, W.B. 1967 Ingestion of soil by sheep. Proceedings of the New Zealand Society of Animal Production 27, 109-120.

HEALY, W.B., McCABE, W.J. & WILSON, G.F. 1970 Ingested soil as a source of micro-elements for grazing animals. New Zealand Journal of Agricultural Research 13, 505-521.

HESSE, P.R. 1971 A textbook of soil chemical analysis. John Murray, London.

HINGSTON, F.J., POSNER, A.M. & QUIRK, J.P. 1968 Adsorption of selenite by goethite. Advances in Chemistry Series 79, 82-90.

HOLLIS, J.M. 1975a Soils in Staffordshire I: Sheet SK05 (Onecote). Soil Survey Record No. 29. Harpenden.

HOLLIS, J.M. 1975b Soil map, 1:25 000. SK05 (Onecote). Ordnance Survey, Southampton.

HOWARD, J.H. 1977 Geochemistry of selenium: formation of ferroselite and selenium behaviour in the vicinity of oxidising sulphide and uranium deposits. Geochemica et Cosmochemica Acta 41, 1665-1678.

HUPKENS, Van Der Elst, F. and Tetley, R. 1970 Selenium studies on peat. New Zealand Journal of Agricultural Research 13, 945-949.

HURD-KARRER, A.M. 1938 Relation of sulphate to selenium adsorption by plants. American Journal of Botony 25, 666-675.

INSTITUTE OF GEOLOGICAL SCIENCES. 1957 Sheet 317 (Chichester), solid and drift, scale 1:63 000.

INSTITUTE OF GEOLOGICAL SCIENCES. 1973 Sheet 107 (Denbigh), solid. Scale 1:50 000.

INSTITUTE OF GEOLOGICAL SCIENCES. 1976 Sheet 285 (Aldershot), solid and drift, scale 1:50 000.

INSTITUTE OF GEOLOGICAL SCIENCES. 1978 Sheet 111 (Buxton), solid and drift, scale 1:50 000.

INSTITUTE OF GEOLOGICAL SCIENCES. 1981 Sheet 301 (Haslemere), solid and drift, scale 1:50 000.

JENNE, E.A. 1977 Trace element sorption by sediments and soils - sites and processes. Chapter 5 in: Molybdenum in the Environment. Volume 2: The geochemistry, cycling and industrial uses of molybdenum (Eds. Chappell, W.R. & Peterson, K.K.). Marcel Dekker Inc., New York.

JOHN,M.K., SAUNDERS, W.M.H. & WATKINSON, J.H. 1976 Selenium adsorption by New Zealand soils I: Relative adsorption of selenite by representative soils and the relationship to soil properties. New Zealand Journal of Agricultural Research 19, 143-151.

JOHNSON, C.M. 1975 Selenium in soils and plants: contrasts in conditions giving safe but adequate amounts of selenium in the food chain. In: Trace Elements in Soil-Plant-Animal Systems (Eds. Nicholas, J.D.J. & Egan,A.D.) pp 165-180. Academic Press, London.

JOHNSON, C.M., ASHER, C.J. & BOYER, T.C. 1967 Distribution of selenium in plants. In: Selenium in Biomedicine. 1st International Symposium. Oregon State University, 1966 (Ed. Muth, O.H.). A.V.I. Publishing Co.

JORDON, W.J. 1975 The application of regional geochemical reconnaissance to arable cropping in England and Wales. PhD Thesis. University of London.

JUDSON, G.J. & OBST, J.M. 1975 Diagnosis and treatment of selenium inadequacies in the grazing ruminant. In: Trace Elements in Soil-Plant-Animal Systems (Eds. Nicholas, D.J.D. & Egan, A.E.) pp 385-405. Academic Press, London.

KEELEY, H.C.M. 1973 Cobalt, copper and manganese in relation to geochemical reconnaissance and agriculture. PhD Thesis. University of London.

KOLJONEN, T. 1973 Selenium in certain metamorphic rocks. Bulletin of the Geological Society of Finland 45, 107-117.

KOLJONEN, T. 1974 Selenium in certain Finnish sediments. Bulletin of the Geological Society of Finland 46, 15-21.

KOLJONEN, T. 1975 The behaviour of selenium in finnish soils. Annales Agriculturae Finniae 14, 240-247.

KUBOTA, J., ALLAWAY, W.H., CARTER, D.L., CARY, E.E. & LAZAR, V.A. 1967 Selenium in crops in the United States in relation to selenium responsive diseases of animals. Agricultural and Food Chemistry 15, 448-453.

KUBOTA, J., CARY, E.E. & GISSEL-NIELSEN, G. 1975 Selenium in rainwater of the U.S.A. and Denmark. Trace Substances in Environmental Health 9, 123-130.

LAG, J. & STEINNES, E. 1978 Regional distribution of selenium and arsenic in humus layers of Norwegian forest soils. Geoderma 20, 3-14.

LAKIN, H.W. 1961 Vertical and lateral distribution of selenium in sedimentary rocks of western United States; Selenium content of soils. In: Selenium in Agriculture. U.S.D.A. Handbook No. 200 pp 12-24; 24-33.

LAKIN, H.W. 1972 Selenium accumulation in soils and its adsorption by plants and animals. Bulletin of the Geological Society of America 83, 181-190.

LAKIN, H.W. & DAVIDSON, D.F. 1967 The relation of the geochemistry of selenium to its occurrence in soils. In: Selenium in Biomedicine. 1st International Symposium. Oregon State University, 1966 (Ed. Muth, O.H.) pp 27-56. A.V.I. Publishing Co.

LEA, J.W. 1975 Soils in Powys I: Sheet SO09 (Caersws). Soil Survey Record No. 28. Harpenden.

LESSARD, J.R., HIDIROGLOU, M., CARSON, R.B. & DERMINE, P. 1968 Intraseasonal variation in the selenium content of various forage crops at Kapuskasing, Ontario. Canadian Journal of Plant Science 48, 581-587.

LEVESQUE, M. 1974a Selenium distribution in Canadian soil profiles. Canadian Journal of Soil Science 54, 63-68.

LEVESQUE, M. 1974b Some aspects of selenium relationships in east Canadian soils and plants. Canadian Journal of Soil Science 54, 205-214.

LEWIS, B.G., JOHNSON, C.M. & DELWICHE, C.C. 1966 Release of volatile selenium compounds by plants. Collection proceedures and preliminary observations. Journal of Agricultural and Food Chemistry 14, 638-640.

LINDBERG, P. & BINGEFORS, S. 1970 Selenium levels in forages and soils in different regions of Sweden. Acta Agriculturae Scandinaviae 20, 133-136.

LIPMAN, J.G. & WAKSMAN, S.A. 1923 The oxidation of selenium by a new group of autotrophic micro-organisms. Science 62, 60.

LOVELAND, P.J., WRIGHT, P.S. & DIGHT, M.R. 1981 Basic research, Acid brown soils. In: Rothamsted Report, pat 1. pp 229-230. Harpenden.

LOVELL, J.S. 1979 Applications of vapour geochemistry to mineral exploration. PhD Thesis. Univeristy of London.

MACKENZIE, F.T., LANTZY, R.J. & PATTERSON, V. 1979 Global trace metal cycles and predictions. Journal of the International Association of Mathematical Geology 11, 99-142.

McKEAGUE, J.A., BRYDON, J.E. & MILES, N.M. 1971 Differentiation of forms of extractable iron and aluminium in soils. Soil Science Society of America, Proceedings 35, 33-38.

McRAE, S.G. & BURNHAM, C.P. 1975 The soils of the Weald. Proceedings of the Geological Association 86, 593-610.

MISRA, S.G. & TRIPATHI, N. 1972 Note on selenium status of surface soils. Indian Journal of Agricultural Science 42, 182-183.

MOTT, C.J.B. 1981 Anion and ligand exchange. In; The Chemistry of Soil Processes (Eds. Greenland, D.J. & Hayes, M.H.B.) pp 179-220. John Wiley and sons.

MUTH, O.H., OLDFIELD, J.E., REMMERT, L.F. & SCHUBERT, J.R. 1958 Effects of selenium and vitamin E on white muscle disease. Science 128, 1090.

NYE, S.M. & PETERSON, P.J. 1975 The content and distribution of selenium in soils and plants from seleniferous areas in Eire and England. Trace Substances in Environmental Health 9, 113-121.

OLSON, O.E., WHITEHEAD, E.I. & MOXON, A.L. 1942 Occurrence of soluble selenium in soils and its availability to plants. Soil Science 54, 47-53.

PAHLAVANPOUR, B., PULLEN, J.H. & THOMPSON, M. 1980 Determination of trace concentrations of selenium in soils and sediments by the introduction of hydrogen selenide into an inductively coupled plasma source for emission spectrometry. Analyst 105, 274-278.

PEARSALL, W.H. 1938 The soil complex in relation to plant communities. 1 Oxidation-reduction potentials in soils. Journal of Ecology 26, 180-193.

PETERSON, P.J. & BUTLER, G.W. 1966 Colloidal selenium availability to three pasture species in pot culture. Nature 212, 961-962.

PETERSON, P.J., BENSON, L.M. & ZIEVE, R. 1981 Metalloids. In: Effect of heavy metal pollution on plant functions (Ed. Lepp, n.w.) pp 279-342. Applied Science Publishers Ltd.

RAJAN, S.S.S. 1979 Adsorption of selenite, phosphate and sulphate on hydrous slumina. Journal of Soil Science 30, 709-718.

RAVIKOVITCH, S. & MARGOLIN, M. 1959 The effect of barium chloride and calcium sulphate in hindering selenium adsorption by lucerne. Empire Journal of Experimental Agriculture 27, 235-240.

REAMER, D.C. & ZOLLER, W.H. 1980 Selenium biomethylation products fom soil and sewage sludges. Science 208, 500-502.

RICKABY, C.D. 1980 A note on selenium for ruminants. A.D.A.S. Quarterly Review 38, 129-136.

ROBBINS, C.W. & CARTER, D.L. 1970 Selenium concentrations in phosohatic fertilizer materials and associated uptake by plants. Soil Science Society of America, Proceedings 34, 506-509.

ROBINSON, W.O. 1933 Determination of selenium in wheat and soils. Journal of the Association of Official Agricultural Chemists 16, 423-424.

RONNEAU, C. & HALIET, J.P. 1981 Sulphur and heavy metal deposition rates on agricultural soils of Belgium - extrapolation to Europe. In: Heavy Metals in the Environmnent. International Conference. Amsterdam, 1981. pp 314-317.

ROSENFELD, I. & BEATH, O.A. 1964 Selenium: Geobotany, Biochemistry, Toxicity, Nutrition. Academic Press, New York.

ROWELL, D.L. 1981 Oxidation and reduction. In: The Chemistry of Soil Processes (Eds. Greenland, D.J. & Hayes, M.B.H.) pp 401-462. John Wiley and sons.

RUSSEL, E.W. 1973 Soil conditions and Plant Growth. 10th Edition. Longman.

SAPOZHNIKOV, D.I. 1937 The exchange of sulphur by selenium during the photoreduction of H_2CO_3 by purple sulphur bacteria. Mickrobiologia 6, 643-644.

SARATHCHANDRA, S.U. & WATKINSON, J.H. 1981 Oxidation of elemental selenium to selenite by *Bacillus magaterium*. Science 211, 600-601.

SCHWARTZ, K & FOLTZ, C.M. 1957 Selenium as an integral part of Factor 3 against dietary necrotic liver degeneration. Journal of the American Chemical Society 79, 3292-3293.

SHARMAN, G.A.M. 1960 Selenium in animal health. Proceedings of the Nutrition Society 19, 169-176.

SHRIFT, A. 1964 A selenium cycle in nature? Nature 201, 1304-1305.

SMITH, B. & GEORGE, T.N. 1961 British Regional Geology, North Wales, 3rd Edition. H.M.S.O.

SMITHSON, F. 1953 The micro-mineralogy of north Wales soils. Journal of Soil Science 4, 194-210.

SWAINE, D.J. 1955 The trace element content of soils. Commonwealth Bureau of Soil Science, Rothamsted Experimental Station Technical Communication No. 48.

THOMPSON, M. & HOWARTH, R.J. 1973 The rapid estimation and control of precision by duplicate determinations. Analyst 98, 153-160.

THOMPSON, M., PAHLAVANPOUR, B. & THORNE, L.T. 1981 The simultaneous determination of arsenic, antimony, bismuth, selenium and telurium in waters by an unductively coupled plasma / volatile hydride method. Water Research 15, 407-411.

THOMSON, I. 1971 Regional geochemical studies of black shale facies with particular reference to trace element dissorders in animals. PhD Thesis. University of London.

THORN, J., ROBERTSON, J. BUSS, D.H. & BUNTON, N.G. 1978 Trace nutrients selenium in British food. British Journal of Nutrition 39, 391-396.

THORNTON, I. 1968 The application of regional geochemical reconnaissance to agricultural problems. PhD Thesis. University of London.

THORNTON, I., KINNIBURGH, D.G., ABRAHAMS, P., GAYE, C., RUNDLE, S., PULLEN, G. & SMITH, C.A. In press. The influence of parent material on the selenium content of British soils. Journal of the Science of

Food and Agriculture.

THURRELL, R.G., WORSSAM, B.C. & EDMONDS, E.A. 1968 Geology of the country around Haslemere. Memoir of the Geological Survey of Great Britain. H.M.S.O.

TUREKIAN, K.K. & WEDEPOHL, K.H. 1961 Distribution of the elements in some major units of the earths crust. Bulletin of the Geological Society of America 72, 175-338.

TURNER, M St. J. 1980 A comparative study of regression techniques in geochemsitry. MSc Thesis. Universtiy of London.

VAN RYSWYK, A.L., BROERSMA, K. & KALNIN, C.M. 1976 Selenium content of alfalfa grown on orthic grey luvisolic and carbonated orthic gleysolic soils. Canadian Journal of Plant Science 56, 753-756.

VINOGRADOV, A.P. 1959 The geochemistry of rare and dispersed chemical elements in soils. Consultants Bureau, New York.

WALKER, D.R. 1971 Selenium in forage species in central Alberta. Canadian Journal of Soil Science 51, 506-508.

WALSH, T., FLEMING, G.A., O'CONNOR, R. & SWEENEY, A. 1951 Selenium toxicity associated with and Irish soil series. Nature 168, 881.

WATKINSON, J.H. 1962 Soil selenium and animal health. Transactions, Joint meeting of Commisions IV and V, International Society of Soil Science. Palmerston North, New Zealand. pp 149-154.

WATKINSON, J.H. & DAVIES, E.B. 1977 Uptake of native and applied selenium by pasture species. IV Relative uptake through foliage and roots by White Clover and Browntop. Distribution of selenium in White Clover. New Zealand Journal of Agricultural Research 10, 122-133.

WEBB, J.S. & ATKINSON, W.J. 1965 Regional geochemical reconnaissance applied to some problems in Co. Limerick, Eire. Nature 208, 1056-1059.

WEBB, J.S., THORNTON, I. & FLETCHER, K. 1966 Seleniferous soils in parts of England and Wales. Nature 211, 327.

WEBB, J.S., THORNTON, I. & FLETCHER, K. 1968 Geochemical reconnaissance and hypocuprosis. Nature 217, 1010-1012.

WEBB, J.S., THORNTON, I., THOMPSON, M. HOWARTH, R.J. & LOWENSTEIN, P.L. 1978 The Wolfson Geochemical Atlas of England and Wales. Clarenden Press, Oxford.

WEISS, H.V., KOIDE, M. & GOLDBERG, E.D. 1971 Selenium and sulphur in a Greenland ice sheet in relation to fossil fuel combustion. Science 172, 261-263.

WELLS, N. 1967 Selenium in horizons of soil profiles. New Zealand Journal of Science 10, 142-179.

WESTERMAN, D.T. & ROBBINS, C.W. 1974 Effects of sulphate-S fertilizer on the selenium content of alfalfa. Agronomy Journal 66, 207-208.

WILLIAMS, C. & THORNTON, I. 1972 The effects of soil additives on uptake of Mo and selenium from soils from different environments. Plant and Soil 36, 395-406.

WILLIAMS, C. & THORNTON, I.. 1973 The use of soil extractants to estimate plant available molybdenum and selenium in potentially toxic soils. Plant and Soil 39, 149-159.

WHITBY, L.M., GAYNOR, J. & MACLEAN, A.J. 1978 Metals in some soils of some agricultural watersheds in Ontario. Canadian Journal of Soil Science 58, 325-330.

WOOD, P. 1975 Regional geochemical studies in relation to agriculture in areas underlain by sandstones. PhD Thesis. University of London.

ZIEVE, R. & PETERSON, P.J. 1981 Factors affecting the volatilisation of selenium from soil. The Science of the Total Environment 19, 277-284.

Appendix 1. Soil profile and site descriptions.

1.1. Soils developed on the Lower Greensand of the west Weald.

P1: Unnamed - humo-ferric podzol.

Location:	Frensham Common, Surrey.
Grid reference:	SU 843 404.
Slope and aspct:	2-3° SE.
Elevation:	c. 70 m.
Land use:	Lowland heath. Main vegetation Calluna, gorse and some deciduous trees.

Depth (cms)	Horizon and description.	
0-11	0	Black (7.5YR2/1) loamy sand, structureless single grain, contains some bleached sand grains, becomes darker towards the base, sharp wavy boundary.
11-40	Ah/Ea	Greyish brown (10YR5/2) coarse sandy bleached horizon, becoming paler to depth to pale brown (10YR6/3). Contains occasional darker humic patches. Abrupt wavy boundary.
40-50	Bh1	Black (10YR2/1) sandy with rusty tinges towards the top of the horizon, structureless becoming massive and compact towards the base. Abrupt broken boundary.
50-55	Bs1	Dark reddish brown (5YR2/3) sand, structureless becoming less massive and darker with depth. Clear broken boundary.
55-60	Bh2	Very dark brown (7.5YR2/1) structureless sand. Clear broken boundary.
60-64	Bs2	Discontinuous horizon similar to the Bs1. Clear broken boundary.
64-69	Bh3	Similar to Bh2. Clear broken boundary.
69-73	Bs3	Dark reddish brown (5YR2/2) sand.
73-76	Bh4	Similar to Bh2. Clear wavy boundary.
76-	Bs4/C?	Brownish yellow (10YR6/6) to dark brown (10YR3/3) locally structureless sand.

P2: Unnamed - Humo-ferric podzol.

Location: Bexleyhill Common, West Sussex.
Grid reference: SU 906 247.
Slope and aspect: 4-5° SSE.
Elevation: 153 m.
Land use: Coniferous plantation, *Pinus sylvestris* and locally *Pteridium aquilinum*.

Depth (cms)	Horizon and description.	
0-2.5	O	Black organic, abrupt smooth boundary.
2.5-10	Ea	Dark reddich brown (5YR3/2) loamy sand bleached horizon, few roots, clear wavy boundary.
10-15	Bh	Black (5YR2/1) loamy sand, few small soft stones, abundant roots. Occasionally discontinuous.
15-25	Bs	Dark reddish brown (5YR2/3) loamy sand, very few roots, few small soft stones, occasional darker humic patches.
25-	C	Red (2.5YR4/6) structureless, common small to medium soft stones.

P3: Unnamed - Humo-ferric podzol.

Location: Ludshott Common, Hampshire.
Grid reference: SU 846 358.
Slope and aspect: Level site.
Elevation: 145 m.
Land use: Lowland heath, mainly coniferous plantings with Beech locally.

Depth (cms)	Horizon and description.	
0-10	O/Ah	Black humified organic material containing bleached sand grains, becoming dark brown

		(7.5YR4/1) towards the base. Abrupt and wavy boundary.
10-(90)	Ea	Weak red (2.5YR5/2) structureless sand bleached horizon becoming darker to depth. Few small stones.

P4: Unnamed - humo-ferric podzol.

Location: Frensham Common, Surrey.
Grid reference: SU 843 404.
Slope and aspect: 1° SW.
Elevation: 70 m.
Land use: Lowland heath, vegetation mainly *Calluna*, gorse and some deciduous trees.

Depth (cms)	Horizon and description.	
0-5	01	Fibrous black organic material. Gradual boundary.
5-8	02	Black humified organic material containing bleached sand grains. Abrupt smooth boundary
8-30	Ah/Ea	Dark reddish brown (5YR4/2) sand, single grain bleached becoming paler with depth. Abrupt wavy boundary.
30-40	Bh	Black (10YR2/1) sand, single grain containing few small stones. Gradual boundary.
40-	Bs	Dark reddish brown (5YR2/2) sand, single grain with common small to medium stones, becoming redder to depth.

P5: Unnamed - Humus ironpan stagnopodzol.

Location: Tilford, Surrey.
Grid reference: SU 873 441.

Slope and aspect: 4-6° NE.

Elevation: 64 m.

Land use: Coniferous plantation.

Depth (cms)	Horizon and description.	
0-5	01	Fibrous organic material, mainly pine needles and moss.
5-7	02	Black humified organic material. Sharp smooth boundary.
7-16	Ea	Dark grey (2.5YR4/1 to 5YR4/1) loamy sand, bleached single grain. Abrupt wavy boundary.
16-20	Bh1	Black (5YR2/1) single grain loamy sand, few small soft stones. Gradual boundary.
20-33	Bh2	Reddish brown to dark brown (5YR4/4 to 5YR3/1) loamy sand becoming massive with depth. Sharp wavy boundary.
at 33	Bf	Thin iron pan continuous over the extent of the profile pit. Approximately 0.5 cms thick. Dark reddich brown (5YR2/2) on top and strong brown (7.5YR5/6) below.
33-45	Bs	Dark reddish brown (5YR2/2) single grain and massive, becoming less massive with depth. Gradual boundary.
45-	C	Strong brown (7.5YR5/6) to brown (5YR4/4) single grain, containing darker patches of dark reddish brown.

1.2. Soils developed from Carboniferous formations in N.E. Staffordshire and S.W. Derbyshire.

1.2.1. Mixon and Butterton Moor transect.

S6: Dale series - pelo-stagnogley soil.

Location:	Mixon Mines Farm, Onecote.
Grid reference:	SK 046 570.
Slope and aspect:	c. 5° E.
Elevation:	343 m.
Land use:	Permanent pasture, rough.

Depth (cms)	Horizon and description.	
0-15	Ahg	Dark grey brown with few rusty mottles along the root channels. Silty clay.
15-30	Bg	Grey with ochreous mottling.
30-75	Bg	Grey with less frequent ochreous mottling becoming heavier with depth.

S7: Dale series - pelo-stagnogley soil.

Location:	Mixon Mines Farm, Onecote.
Grid reference:	SK 048 570.
Slope and aspect:	c. 15° E.
Elevation:	323 m.
Land use:	Permanent pasture, rough.

Depth (cms)	Horizon and description.	
0-15	Ahg	Grey brown with few rusty mottles. Silty clay loam.
15-30	Bg	Grey with ochreous mottles common on ped faces.
30-45	Bg	Grey with many ochreous mottles. Silty clay.
45-60	BCg	Dark grey with only few ochreous mottles Silty clay.

S8: Unnamed - alluvial gley soil.

Location: Mixon Mines Farm, Onecote.
Grid reference: SK 049 570.
Slope and aspect: Level at stream side.
Elevation: 320 m.
Land use Permanent pasture.

Depth (cms)	Horizon and description.	
0-15	Ah	Humic dark red brown silty loam.
15-30	Bg	Grey brown silty loam with few rusty mottles along root channels.
30-45	Bg	Grey with common ochreous mottles.
45-60	Bg	Grey with many ochreous mottles.

S10: Onecote series - cambic stagnohumic gley soil.

Location: Fairview Farm, Butterton.
Grid reference: SK 055 564.
Slope and aspect: c. 1-2° NW.
Elevation: 350 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-15	Ahg	Dark brown humose sitly clay with mottling around root channels. Narrow boundary at 10.
	Bg	Grey with common ochreous mottles.
15-60	Bg	Dark grey with common ochreous mottling, becoming more abundant with depth.
60-75	BCg	Dark grey brown with few mottles, occasional fragments of dark shale.
75-85	BCg	Dark grey brown with frequent dark shale fragments.

S11: Wilcocks series - cambic stagnohumic gley soil.

Location:	Fairview Farm, Butterton.
Grid reference:	SK 058 564.
Slope and aspect:	c. 1-2° NW.
Elevation;	329 m.
Land use:	Permanent pasture.

Depth (cms)	Horizon and description.	
0-10	Ahg	Dark brown humose silty loam with few rusty mottles along root channels, narrow boundary
10-20	Eg?	Light grey brown silty loam with common ochreous mottles.
20-30	Bg	Light grey brown silty loam with common ochreous mottles, contains occasional stone fragments.
30-60	Bg	Light grey silty clay loam with many mottles and frequent stone fragments.

S12: Wilcocks series - cambic stagnohumic gley soil.

Location:	Butterton Moor House, Butterton.
Grid reference:	SK 058 562.
Slope and aspect:	c. 1-2° NW.
Elevation:	350 m.
Land use:	Permanent pasture.

Depth (cms)	Horizon and description.	
0-15	Ahg	Dark brown silty clay loam with few mottles along root channels.
15-30	Eg/Bg	Grey silty clay loam with many ochreous mottles.
30-45	Bg	Grey clay loam with common ochreous mottles.
45-60	BCg	Grey clay loam with some coarser patches and some stone fragments.
60-75	BCg	Grey clay loam with very little mottling and frequent stone fragments.

S13: Wilcocks series - cambic stagnohumic gley soil.

Location:	Butterton Moor Farm, Butterton.
Grid reference:	SK 059 562.
Slope and aspect:	c. 3° SW.
Elevation:	350 m.
Land use:	Permanent pasture.

Depth (cms)	Horizon and description.	
0-15	Ahg	Dark brown humose clay loam with few rusty mottles along root channels and frequent orange brown stone fragments.
15-30	Ahg/ Bg	Top 5 cms as above, narrow boundary to light grey clay loam with common ochreous mottles.
30-75	Bg	Grey clay loam with many ochreous mottles which become less frequent with depth.

S14: Wilcocks series - cambic stagnohumic gley soil.

Location:	Grindon Moor, Butterton.
Grid reference:	SK 059 559.
Slope and aspect:	Level site.
Elevation;	350 m.
Land use:	Poor permanent pasture adjacent to heather moor.

Depth (cms)	Horizon and description.	
0-15	Ah	Black humose sandy silt loam.
15-30	Eg/Bg1	Grey brown sandy loam with few rusty mottles along root channels, evidence of bleached sand grains.
30-45	Bg1	Grey brown sandy loam with common ochreous mottles.
45-75	Bg2	Grey sandy loam with many ochreous mottles.

1.2.2. Bent Farm transect.

All the soils were located at Bent Farm, Tissington, Derbyshire.

P1: Dale series - pelo-stagnogley soil.

Grid reference: SK 186 528.
Slope and aspect: c. 1-2° NW.
Elevation: 215 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-15	Ahg	Dark brown clay loam with common rusty mottles along root channels
15-30	Bg	Grey brown clay loam with common ochreous mottles and small black concretions
30-45	Bg	Grey clay loam with many ochreous mottles.
45-60	Bg	Grey clay loam with very many ochreous mottles.

P2: Dale/Alton series intergrade - pelo stagnogley soil.

Grid reference: SK 186 529.
Slope and aspect: c. 10°NW.
Elevation: 210 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-15	Ah	Grey brown silty loam.
15-30	Bwg	Grey brown silty loam with few ochreous mottles.
30-60	Bwg	Light brown silty clay loam with common ochreous mottles and few very small angular shale fragments.
60-75	Bg	Darker grey brown silty clay loam with many small to very small shale fragments and few ochreous mottles.

S3: Alton series (steep phase) - typical non calcareous pelosol.

Grid reference: SK 187 530.
Slope and aspect: c. 15° NW.
Elevation: 200 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-15	Ah	Dark brown silty loam with few fine mottles.
15-30	Bwg	Brown silty loam with darker patches, possibly of weatherd shale fragments, and with few fine mottles.
30-45	Bwg	Brown silty clay loam with many small to very small angular shale fragments.
45-60	Cr	Very dark brown silty clay loam with abundant small to very small angular shale fragments.

S4: Onecote series - cambic stagnohumic gley soil.

Grid reference: SK 185 530
Slope and aspect: c. 3° NW.
Elevation: 180 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-15	Ahg	Dark grey brown humic silty clay loam with common mottles mainly along the root channels.
15-30	Bg	Grey clay loam with many ochreous mottles.
30-45	Bg	Grey clay loam with many to very many ochreous mottles.

S5: Unnamed - typical humic-alluvial gley soil.

Grid reference: SK 189 531.

Slope and aspect: Level site adjacent to stream.

Elevation: 170 m.

Land use: Marshy land with water lying on the surface at the time of sampling. Predominantly poor grasses with rushes (*Juncus spp.*) locally.

Depth (cms)	Horizon and description.	
0-15	L?	Wet organic, mainly undecomposed root and plant material.
15-30	O	Black organic silty loam.
30-45	Bg1	Very dark grey silty loam containing very little recognisable plant material.
45-60	Bg1	Dark grey silty clay loam with many ochreous mottles.
60-75	Bg2	Olive grey silty clay loam.
75-	Bg2	Olive grey silty clay loam.

(There was a noticeable odour of sulphur from the lower horizons when they were being sampled.)

1.3. Soils from the Llansannan area of Clwyd.

D3: Denbigh series - typical brown earth.

Location: Pencraigfawr, Llansannan.
Grid reference: SH 937 654.
Slope and aspect: 3-5° N.W.
Elevation: 160 m.
Land use: Permanent pasture.

Depth (cms).	Horizon and description.	
0-20	A	Very dark brown (10YR3/2) silt loam with common small and medium angular shale stones. Many fine to medium roots, abundant in top 5 cms. Crumb structure, friable. Clear smooth boundary.
20-32	AB	Dark brown (7.5YR4/2) silt loam with common small and medium shale stones and many fine roots. Abrupt boundary.
32-43	B	Yellowish brown (10YR5/6) silt loam with many small to medium shale stones and common fine roots. Weak crumb structure. Clear wavy boundary.
43-	BC	As for B but paler with more stones

D5: Denbigh series - typical brown earth

Location: Plasnewydd Farm, Llansannan.
Grid reference: SH 947 660.
Slope and aspect: 3-5° N.W.
Elevation: 215 m.
Land use: Arable rotation of one year cereal followed by two years ley. Under grass when samples.

Depth (cms).	Horizon and description.	
0-8	A	Dark brown (10YR4/3) silt loam with common small to medium angular tabular shale stones and many fine fibrous roots. Clear wavy boundary.
8-35	AB	As above but with common fine roots and common medium stones. Abrupt smooth boundary.
35-60	B	Yellowish brown (10YR5/8) silt loam with many small to medium stones. Clear wavy boundary.
60-	BC	Pale olive (5YR6/3) silt loam with abundant shale stones, many small and very small but some medium. Few roots and few strong brown mottles.

D6: Denbigh series - typical brown earth.

Location: Plasnewydd Farm, Llansannan.
Grid reference: SH 947 664.
Slope and aspect: 1-2° N.W., near level site adjacent to river.
Elevation: 150 m.
Land use: Arable ley as for D5.

Depth (cms)	Horizon and description.	
0-10	A	Brown silt loam (10YR4/2) with few common ochreous mottles along root channels. Common angular shale stones and many fine roots. Clear smooth boundary.
10-30	AB	Greyish brown (2.5YR5/4) silt loam with many fine and medium roots and stones as in A. Clear wavy boundary.
30-50	B	Brown (10YR5/3) silty clay loam with many medium and large stones and few fine roots. Clear wavy boundary.
50-	BC	Olive grey (5Y5/2) gritty loam, structureless.

D9: Denbigh series - typical brown earth.

Location: Plasnewydd Farm, Llansannan.
Grid reference: SH 948 663.
Slope and aspect: 10° W.
Elevation: 160 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-15	A	Greyish brown (2.5YR5/2) silt loam with common angular shale stones and abundant fine roots. Crumb structure, friable. Clear boundary.
15-35	AB	Dark greyish brown (10YR4/2) silt loam becoming greyish brown (10YR5/2) with many fine roots, otherwise as in A. Abrupt smooth boundary
35-55	B	Dark brown (10YR4/3) loam with many small to medium stones and many fine roots. Gradual smooth boundary.
55-	BC	Dark yellowish brown (10YR4/4) loam with many medium and large stones and common rooots.

D12: Denbigh series - typical brown earth.

Location: Plasnewydd Farm, Llansannan.
Grid reference: SH 943 667.
Slope and aspect: c. 30° S.E.
Elevation: 205 m.
Land use: Rough grazing with braken, probably reclaimed from woodland.

Depth (cms)	Horizon and description.	
0-13	A	Greyish brown (10YR5/2) silt loam with common small and medium stones. Abundant roots to 5 cms then many fine grass roots and coarse fibrous braken roots. Clear boundary.

13- 28	AB	Dark brown (10YR4/2) silt loam similar to A but many fine roots and many small and medium stones. Abrupt wavy boundary.
28-40	B	Dark yellowish brown (10YR4/4) silt clay loam with many fine roots and few braken roots. Many medium and large angular stones. Clear wavy boundary.
40-	BC	Abundant angular large shale stones in a yellow brown matrix, few fine roots.

D29: Denbigh series - typical brown earth.

Location: Nant Melai.
Grid reference: SH 903 662.
Slope and aspect: 10° W.N.W.
Elevation: 210 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description	
0-25	A	Dark greyish brown (10YR4/2) silt loam with common small to medium stones, mainly angular shale but some rounded. Root mat to 5cms then many fine and medium roots. Well developed crumb structure. Gradual wavy boundary.
25-40	AB	Brown (10YR4/3) as above but with many small to medium stones. Abrupt wavy boundary.
40-53	B	Yellowish brown (10YR5/6) silty clay loam with many small to medium stones and common mainly fine roots. Weak crumb structure. Gradual wavy boundary.
53-	BC	Yellow (10YR7/6) silty clay loam with abundant medium and large angular shale stones. Few roots.

D31: Denbigh series - typical brown earth.

Location: Bryn-y-clochydd Farm, Gwytherin.
Grid reference: SH 974 610.
Slope and aspect: 5° N.W.
Elevation: 270 m.
Land use: Recently reseeded permanent pasture.

Depth (cms)	Horizon and description.	
0-15	A	Dark grey brown (10YR4/2) silt loam with few small and medium mainly angular shale stones. Many fine and medium roots, moderate crumb structure. Clear boundary.
15-30	AB	Greyish brown (10YR5/2) as A but common small and medium stones. Abrupt smooth boundary.
30-45	B	Yellowish brown (10YR5/4) silty clay loam with common medium stones and common fine roots. Clear wavy boundary.
45-	BC	Paler yellowish brown (10YR5/6) silty clay loam with many medium and large angular shale stones and common fine roots.

D11: Powys series - brown ranker.

Location: Plasnewydd Farm, Llansannan.
Grid reference: SH 941 671.
Slope and aspect: Level portion of complex slope.
Elevation: 250 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description	
0-16	A	Very dark greyish brown (10YR3/2) silt loam with common small to medium stones. Abundant fine roots in top 5 cms then many. Friable crumb structure, abrupt smooth boundary.

16-25	B	Brown (10YR4/3) silt loam with many small to medium angular tabular stones and common roots. Clear smooth boundary.
25-	C	Abundant small to large angular tabular stones with paler material in the fissures.

D28: Powys series - brown ranker.

Location: Nant Melai Farm, Llansannan.
Grid reference: SH 897 664.
Slope and aspect: Level site in hummocky terrain.
Elevation: 245 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-10	A	Brown (10YR4/3) silt loam with common small to medium stones. Abundant roots in the top 4 cms then many. Abrupt smooth boundary.
10-30	B	Brown (7.5YR5/4) silt loam becoming yellowish brown (10YR5/6) towards the base. Many small to medium stones and many fine roots. Clear wavy boundary.
30-	C	Abundant medium to large angular tabular stones with yellowish brown material in the fissures.

D32: Powys series - brown ranker.

Location: Ynys Rhys, Llangernyw.
Grid reference: SH 857 685.
Slope and aspect: Near level site on complex slope.
Elevation: 235 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-20	A	Dark brown (10YR3/3) silt loam with many small to medium stones and many roots. Crumb structure becoming greyish brown (10YR4/2) towards the base of the horizon. Abrupt wavy boundary.
20-30	B	Brownish yellow (10YR6/6) silt loam with many medium to large stones, many roots. Clear wavy boundary.
30-	C	Abundant andgular tabular stones with brownish yellow material in the fissures, few fine roots.

D35: Powys series - brown ranker

Location:	Foel Greon, Bylchau.
Grid reference:	SH 978 638.
Slope and aspect:	c. 8° N.N.E.
Elevation:	350 m.
Land use:	Permanent pasture.

Depth (cms)	Horizon and description.	
0-16	A	Dark brown (10YR4/3) silt loam with many small stones and many fine and medium roots. Crumb structure, friable. Abrupt wavy boundary.
16-23	B	Dark yellowish brown (10YR4/4) silt loam with many small to medium stones and many fine roots. Clear wavy boundary.
23-	C	Abundant medium to large stones with pale olive (5Y6/3) loam in the fissures, few fine roots.

D37: Powys series - brown ranker.

Location:	Melai Farm, Moel Unben.
Grid reference:	SH 910 677.

Slope and aspect: 12 - 15° S.S.W.
Elevation: 335 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-15	A	Dense root mat in the top 5 cms with little mineral material. Subsequent 10 cms comprise dark brown (10YR3/4) humose silt loam, becoming dark brown (10YR4/4) towards the base of the horizon. Common small angular stones with many fine roots. Crumb structure, moist and friable, abrupt smooth boundary.
15-25	B	Strong brown (7.5YR5/6) loam with many small to medium stones, common fine roots, abrupt smooth boundary.
25-	C	Abundant small to large angular tabular shale stones with interstitial yellowish brown (10YR5/6) loam.

D4: Aled series - typical brown alluvial soil.

Location: Llansannan, adjacent to Afon Aled.
Grid reference: SH 935 660.
Slope and aspect: Level.
Elevation: 157 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-12	A	Dark greyish brown (10YR4/2)silt loam with few very small stones and abundant fine to medium roots. Abrupt smooth boundary.
12-25	B	Brown (10YR4/3) silt loam with many small to medium stones and abundant fine roots. Clear smooth boundary, some mottling along root channels.
25-70	BC	Greyish brown (10YR5/3) silt loam with abundant very small to medium stones (rounded). Gradual boundary, some mottling along root channels.
70-	C	Very little fine material, consists mainly of very small to medium rounded shale pebbles, with Fe staining on surfaces.

D10: Aled series (?) - stagnogleyic brown alluvial soil.

Location: Plasnewydd, Llansannan.

Grid reference: SH 947 666.

Slope and aspect: Level site adjacent to river.

Elevation: 150 m.

Land use: Arable rotation of one year cereals followed by two years of grass. Under grass when sampled.

Depth (cms)	Horizon and description.	
0-8	A1	Greyish brown (2.5YR5/2) silt loam with few small to medium rounded shale pebbles. Abundant fine to medium roots with common strong brown mottles along root channels. Moderate crumb structure, moist. Clear smooth boundary.
8-18	A2	Greyish brown (2.5YR5/2) silt loam with few small to medium rounded shale pebbles. Many fine roots with few strong brown mottles along root channels. Abrupt smooth boundary.
18-38	Bg	Yellowish brown (10YR5/4) silt loam with few small to medium pebbles. Few fine roots, common distinct strong brown mottles. Becomes greyish brown (10YR5/2) lower in the horizon. Gradual wavy boundary.
38-60	BCg	Light grey (10YR6/1 to 5Y6/1) silt loam with many strong brown mottles and occasional Fe concretions. Very few roots. Few small to medium shale pebbles. Moderate prismatic structure. Clear wavy boundary.
60-	C	Abundant medium to large rounded stones, mainly of shale within a matrix of very small pebbles. Many of the larger pebbles are Fe stained.

D8: Manod series - typical brown podzolic soil.

Location: Nant-y-gareg Farm, Moel Grugoer.

Grid reference: SH 966 618.

Slope and aspect: 2-3° E.S.E.

Elevation: 360 m.

Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-20	A	Dark brown (10YR3/3) silt loam becoming dark greyish brown (10YR4/2) at depth. Few small subangular stones and abundant fine to medium roots. Clear smooth boundary.
20-27	AB	Brown (10YR4/2) silt loam as above except has common small to medium stones and few faint strong brown mottles along root channels. Abrupt wavy boundary.
27-42	Bs	Strong brown (7.5YR6/5) silt loam with common mainly medium stones and common fine roots. Clear wavy boundary.
42-	BC	Abundant small to medium/large angular tabular stones with yellowish brown material between.

D22: Manod series - typical brown podzolic soil

Location: Llyn Saint, near Gwytherin.
Grid reference: SH 871 604.
Slope and aspect: 5° E.
Elevation: 330 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-30	A	Dark brown (10YR4/3) silt loam with well developed root mat in the top 5 cms and many fine roots below. Common small to medium stones becoming more frequent with depth. Gradual smooth boundary.
30-50	Bs	Strong brown (7.5YR5/8) siltloam with few small grey mottles. Many fine roots to 35 cms becoming less common below. Many small to large stones, clear wavy boundary.
50-	BC	Yellowish brown (10YR5/6) silty clay loam with abundant mainly large stones and few roots.

D26: Manod series - typical brown podzolic soil

Location: Gorswen Fawr, near Llanrwst.
Grid reference: SH 839 622.

Slope and aspect: 5-7° N.W.
Elevation : 330 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-25	A	Dark greyish brown (10YR4/2) becoming greyish brown (10YR5/2) silt loam. Few faint strong brown mottles along root channels. Abundant fine roots, common small stones. Abrupt smooth boundary.
25-50	B	Yellow (2.5YR7/6) silt loam with common fine roots and common small stones to c. 40 cms then becomes brownish yellow (10YR6/6) with many medium and large stones. Clear smooth boundary.
50-	BC	Abundant medium and large stones (angular shale) with yellowish brown material between.

D36: Mnaod series - typical brown podzolic soil

Location: Pen-y-Mwdwl, near Llansannan.
Grid reference: SH 920 665.
Slope and aspect: c. 5° S.S.W.
Elevation: 335 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-18	A	Dark brown (10YR4/3) becoming dark greyish brown (10YR4/2) silt loam with common small to medium angular shale stones and many fine roots. Abrupt smooth boundary.
18-32	Bs	Yellowish brown (10YR5/6) loam with many small to medium angular tabular shale stones and many fine roots. Clear wavy boundary.
32-	BC	Abundant mainly large angular shale stones with silty yellowish brown (10YR5/6) material betweeen and few fine roots.

D23: Sannan series - stagnogleyic brown earth.

Location: Llwyn Saint Farm, near Gwytherin.
Grid reference: SH 867 602.
Slope and aspect: c. 2° S.W.
Elevation: 375 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.
0-20	Ah(g) Dark greyish brown (10YR4/2), becoming greyish brown (10YR5/2) silt loam with abundant mainly fine rusty mottles along root channels. Strong crumb structure, few small stones some soft. Clear smooth boundary.
20-30	B(g) Grey (10YR5/1) silt loam with common rusty mottles around root channels. Common fine roots and few small stones. Clear smooth boundary.
30-50	Bg Grey (10YR5/1) silty clay loam with very many yellowish brown (10YR5/6) mottles. Common small and medium angular stones to 40 cms then becoming many. Clear wavy boundary.
50-	Cg Abundant small to medium stones, many soft in a matrix of light olive grey (5Y6/2) silty clay loam.

D25: Sannan series - stagnogleyic brown earth.

Location: Gorswen Farm.
Grid reference: SH 837 622.
Slope and aspect: c. 1° N.N.W.
Elevation: 315 m.
Land use: Recently reseeded permanent pasture.

Depth (cms)	Horizon and description.
0-18	Ah(g) Dark greyish brown (10YR4/2) silty clay loam with few distinct rusty mottles along root channels. Many fine and medium roots. Clear wavy boundary.
18-35	B(g) Dark greyish brown (10YR4/2) silty clay loam

		with many distinct rusty mottles, mainly along root channels. Many fine and medium roots. Occasional strong brown Fe concretion. Clear wavy boundary.
35-55	BCg	Grey (10YR5/1) gritty clay loam with some darker patches (10YR3/3) becomes olive grey to depth (5Y5/2). Few roots and many small to medium stones.

D27: Sannan series - stagnogleyic brown earth.

Location: Pandy Tudur.
Grid reference: SH 852 642.
Slope and aspect: c. 3° N.N.W.
Elevation: 230 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.	
0-25	Ah(g)	Olive grey (5Y5/2) becoming grey (10YR5/1) silt loam, compact root mat in the top 7 cms, many fine and medium roots below. Common strong brown mottles along root channels, few small stones, abrupt smooth boundary.
25-45	B(g)	Light olive grey (5Y6/2) silt loam with common small to medium subangular stones, some soft. Common roots and clear smooth boundary.
45-60	Bg	Greyish brown (2.5YR5/2) silty clay loam with common strong brown mottles and many small to medium stones. Gradual wavy boundary.
60-	Cg	Abundant small to medium stones in a matrix of light grey (10YR6/1) gritty clay loam with common yellowish red mottles (5YR5/8).

D30: Sannan series - stagnogleyic brown earth

Location: Nant Melai.
Grid reference: SH 903 662.
Slope and aspect: Level adjacent to stream.
Elevation: 207 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.
0-15	Ah(g) Greyish brown (2.5YR5/2) silt loam with few fine strong brown (10YR5/8) mottles and abundant roots to 7 cms, then many fine roots. Few small stones. Abrupt smooth boundary.
15-25	B(g)1 Light brownish grey (2.5YR6/2) silty clay loam with many strong brown (7.5YR5/6) mottles and few small stones. Many fine roots, clear wavy boundary.
25-50	B(g)2 Light brownish grey (2.5YR6/2) silty clay loam with common strong brown (7.5YR5/6) mottles and common small to medium stones. Few fine roots, clear wavy boundary.
50-65	Bg Light brownish grey (2.5YR6/2) gritty silty clay loam with common small to medium stones. Few strong brown mottles (7.5YR5/6). Clear wavy boundary.
65-	Cg Light olive grey (5Y6/2) gritty silty clay loam with many small to medium angular shale stones and very few mottles as above.

D33: Sannan series - stagnogleyic brown earth.

Location: Nant Melai Fawr, near Llansannan.
Grid reference: SH 910 627.
Slope and aspect: Level.
Elevation: 300 m.
Land use: Permanent pasture.

Depth (cms)	Horizon and description.
0-20	Ah(g) Dark greyish brown (10YR4/2) silt loam with abundant mainly fine roots becoming grey (10YR5/1) with many fine and medium roots towards the base of the horizon. Very few rusty mottles along the root channels. Few small angular stones and abrupt smooth boundary.
20-35	B(g) Light olive grey (5Y6/2) with some brown (7.5YR5/2) material on the ped faces, silt loam. Many fine roots and common rusty mottles along root channels. Common small to medium angular

		stones. Abrupt smooth boundary.
35-50	Bg	Light grey (5Y6/1) silty clay loam with very few rusty mottles and few roots below 40 cms. Common small to medium stones. Gradual wavy boundary.
50-	Cg	Light grey (5Y6/1) gritty clay loam with common small to medium angular stones and common strong brown mottles.

D1: Hiraethog map unit - ferric stagnopodzol (Hafren s eries)

Location: Aled Isaf reservoir.
Grid reference: SH 912 604.
Slope and aspect: c. 10° S.E.
Elevation: 390 m.
Land use: Rough moorland grazing, mainly Nardus stricta.

Depth (cms)	Horizon and description.	
5-0	L	Remains of mainly N. stricta
0-9	O	Very dark grey (10YR3/1) mainly fibrous peat, clear wavy boundary.
9-15	Eag	Dark greyish brown (10YR4/2) bleached horizon with darker humic funnels and common bleached small to large tabular angular shale stones. Common fine to medium roots and abrupt smooth boundary.
15-22	Bs1	Yellowish brown (10YR5/6) silt loam with common unbleached stones as above. Dry with weak crumb structure and clear smooth boundary.
22-36	Bs2	Yellowish brown (10YR5/8) with few stones as above and common roots to 36 cms. Merges with paler yellowish brown C horizon containing many stones.

D2: Hiraethog map unit - ironpan stagnopodzol (Hiraethog series)

Location: Aled Isaf reservior.
Grid reference: SH 912 604.
Slope and aspect: 5° S.E.

Elevation: 390 m.

Land use: Rough moorland grazing of mainly *N. stricta* with some *Vaccinium myrtilis* and mosses.

Depth (cms)	Horizon and description	
0-14	O	Black mainly hunified organic horizon with clear boundary.
14-16	Ah	Black humose silt loam mainly amorphous carbon material from above. Abrupt smooth boundary.
16-25	Eag	Very dark greyish brown (10YR3/2) silt loam containing pale bleached stones mainly small. Few faint rusty mottles. At the base of the horizon is a thin discontinuous ironpan (Bf) of c. 0.5 cms thickness.
25-	Bs	Brown (7.5YR4/4) clay to clay loam, dry and porous with very few faint rusty mottles. Very few roots and common small to large stones.

D16: Hiraethog map unit - ferric stagnopodzol (Hafren series)

Location: Glan-y-gors, near Aled Isaf reservoir.

Grid reference: SH 912 606.

Slope and aspect: c. 3° W.N.W.

Elevation: 410 m.

Land use: Rough moorland grazing, mainly *N. stricta* with some *Calluna vulgaris* and mosses.

Depth (cms)	Horizon and description.	
2-0	L	Decomposing litter and root mat.
0-10	O	Mainly well humified black peat with few recognisable plant remains. Clear wavy boundary.
10-18	Eag	Dark brown humose silty clay loam in the top 3 cms, becoming grey brown (2.5YR5/2) silty clay loam with common small bleached stones and common fine roots. Abrupt wavy boundary.
18-29	Bs	strong brown (7.5YR5/6) clay loam with common diffuse grey mottles, very few roots below 20 cms. Common small to medium angular shale stones. Abrupt wavy boundary.
29-	C	Shattered shale with reddish yellow material in the fissures.

D17: Hiraethog map unit - ironpan stagnopodzol (Hiraethog series)

Location: Llyn Aled.
Grid reference: SH 921 576.
Slope and aspect: 3^{o} N.N.W.
Elevation: 385 m.
Land use: Rough moorland grazing predominantly of *N. stricta* with other subordinate grass species.

Depth (cms)	Horizon and description	
0-5	L	Decomposing plant remains and root mat.
5-35	O	Predominantly humified black peat with very few recognisable plant remains after 10 cms. Abrupt wavy boundary.
35-48	Eag	Brown (10YR4/3) silty clay loam with bleached material and few small bleached shale stones. Common strong brown mottles mainly along root channels, many fine to medium roots. Becoming light brownish grey (10YR6/2) below. At 47-48 cms there is a compact mat of root material.
48-48.5	Bf	Thin ironpan which is dark brown above and strong brown below, continuous and wavy. Sharp boundary.
48.5-65	Bs	Yellowish brown (10YR5/8) clay loam with few faint rusty mottles, no roots, porous. Gradual wavy boundary.
65-75	BC	Abundant medium and large shale stones with yellowish brown (10YR5/8) gritty clay loam between, gradual boundary.
75-	C	Very abundant shattered shale with very little interstitial material.

D21: Hiraethog map unit - ferric podzol (Hafren - Powys intergrade?)

Location: Near Llyn Bran.
Grid reference: SH 960 600
Slope and aspect: 3^{o} N.
Elevation: 442 m.
Land use: Rough moorland heath. Mainly *C. vulgaris* with some *V. myrtilis* and mosses

Depth (cms)	Horizon and description	
0-5		Compact root mat.
5-10	O	Black humified peat, few plant remains and many fine to medium roots. Abrupt smooth boundary.
10-15	Ah	Very dark brown (10YR2/2) humose silt loam with common small stones and many fine and medium roots. Clear wavy boundary.
15-20	Ea	Dark grey (5YR4/1) silt loam with many small bleached stones and many fine roots. Clear wavy boundary.
20-30	Bs	Brown (7.5YR4/4) silty clay loam with abundant small to medium angular shale stones. Porous and well drained with common mainly fine roots.

D7: Ithel series - humic brown podzolic soil.

Location: Moel Grugoer, near Bylchau.
Grid reference: SH 963 615.
Slope and aspect: 3-5° S.W.
Elevation: 360 m.
Land use: Rough grazing.

Depth (cms)	Horizon and description.	
0-20	Aph	Dark grey (10YR4/1) in top becoming very dark grey brown (10YR3/2) humose horizon containing few small stones (some are possibly portions of a former ironpan). Many fine and medium roots, abrupt wavy boundary.
20-30	Bs	Brown (7.5YR4/4) silt loam with common small to large stones which become more abundant to depth. Common roots, abrupt wavy boundary.
30-40	C	Abundant stones of grey shale with yellowish brown (10YR5/6) material between. Some stones had coatings of Fe on the surface.

D34: Ithel series - Humic brown podzolic soil

Location: Sportsmans Arms, neat Llyn Bran.
Grid reference: SH 952 591.
Slope and aspect: c. 2° S.E.

Elevation: 457 m.

Land use: Reclaimed permanent pasture.

Depth (cms)	Horizon and description.	
0-20	Aph	Dark greyish brown (10YR4/2) becoming dark grey (10YR4/1) humose silt loam with few fine mottles and few bleached stones. Many fine and medium roots. Gradual wavy boundary.
20-28	Ap/Bs	Mixed pockets of Ap type (brown 10YR4/3) and Bs type (yellowish brown 10YR5/6) material not all of which are connected to their respective horizons. Many fine and medium roots, gradual wavy boundary.
28-36	Bs	Yellowish brown (10YR5/6) silty clay loam with common fine roots and common small to medium stones. Clear wavy boundary.
36-40	BC	Yellowish brown (10YR5/4) paler than the Bs, silty clay loam with many small to large stones and few roots. Gradual wavy boundary.
40-	C	Shattered angular shale fragments with some yellowish brown material in the fissures.

D13: Ynys series - cambic stagnohumic gley soil

Location: Ochry Cefn, near Llansannan.

Grid reference: SH 918 623.

Slope and aspect: c. 2° N.W.

Elevation: 360 m.

Land use: Rough grazing, mainly *C. vulgaris* and *N. stricta*.

Depth (cms)	Horizon and description.	
0-5	O	Black (10YR2/1) predominantly fibrous peat.
5-10	Eg/ Ahg	Dark greyish brown (10YR4/2) silty clay loam with some darker funnels at the top of the horizon. Many fine and medium roots. Abrupt smooth boundary.
10-28	Bg	Greyish brown (2.5YR5/6) silt loam with strong brown mottles (7.5YR5/6) and darker organic material on the ped faces. Becomes light olive grey (5Y6/2) towards the base with fewer mottles.

		Few medium soft stones. Clear wavy boundary.
28-	CG	Light olive grey (5Y6/2) with few strong brown mottles. Gritty clay loam including many small to medium stones.

D14: Ynys series - cambic stagnohumic gley soil.

Location: Glan-y-gors, near Aled Isaf reservoir.
Grid reference: SH 910 608.
Slope and aspect: 2^{o} E.S.E.
Elevation: 400 m.
Land use: Rough moorland grazing mainly *N. stricta.*

Depth (cms)	Horizon and description.	
0-7	01	Very dark brown peat.
7-10	02	Black amorphous peat, abrupt boundary.
10-15	03	Dark brown amorphous peat with some mineral material. Abrupt wavy boundary.
15-21	Eg	Dark greyish brown (10YR4/2) silty clay loam & brownish yellow mottles (10YR6/8) along root channels. Many fine to medium toots and few small stones, abrupt smooth boundary.
21-24	Bg1	Very dark greyish brown (10YR3/1) silty clay loam with many fine to medium roots, then as above. Abrupt smooth boundary.
24-32	Bg2	Very dark greyish brown (2.5YR3/2) silty clay loam with many fine to medium roots. Towards the base of the horizon between 29 and 32 cms there was a band of dark brown (7.5YR3/2) concretions. Sharp wavy boundary.
32-50	BCg	Light grey (10YR6/1) clay loam with common dark brown mottles (7.5YR4/4). Abrupt smooth boundary.
50-	CG	Abundant medium to large stones many of which are Fe stained on the outside. The material in the fissures was similar to that of the BCg.

D19: Ynys series - cambic stagnohumic gley soil

Location: Llyn Aled.
Grid reference: SH 944 583.
Slope and aspect: 2° W.
Elevation: 455 m.
Land use: Rough moorland grazing, mainly *N.stricta* with *Juncus spp*.

Depth (cms)	Horizon and description.	
0-6	L	Litter layer of decomposing *N. stricta*.
6-15	01	Dark reddish brown (5Y3/2) fibrous peat.
15-23	02	Black humified peat with many fine roots. Abrupt smooth boundary.
23-29	Eg/ Ahg	Dark greyish brown (10YR4/2) silty clay loam with many mainly fine roots. Abrupt smooth boundary.
29-37	Bg	Light olive grey (5Y6/2) clay loam with common fine roots. Clear smooth boundary.
37-50	BCg	Light grey (5Y6/1) with common brownish yellow (10YR6/6) mottles and few small to medium soft stones.
50-	CG	Light grey as above gritty clay loam with many small to medium stones.

D20: Ynys series - cambic stagnohumic gley soil.

Location: Off the A543 near to the Sportsmans Arms.
Grid reference: SH 944 583.
Slope and aspect: 2° W.
Elevation: 455 m.
Land use: Rough moorland grazing, mainly *C. vulgaris* with some *N. stricta* and occasional *Juncus spp*.

Depth (cms)	Horizon and description.	
0-6	F	Thick root mat.
6-26	0	Peaty horizon consisting of four bands: 01 6-8 cms, Black fibrous peat. 02 8-13 cms, Reddish brown fibrous peat. 03 13-20 cms, Dark brown to black semi-fibrous peat.

		04 20-26 cms, Dark reddish brown humic peat Clear smooth boundary.
26-35	Bg	Light brownish grey (2.5YR6/2) silty clay loam with many fine roots and darker material on the ped faces. Few small stones and very few fine rusty mottles. Gradual wavy boundary.
35-	BCg	Olive grey (5Y5/2) gritty clay loam with many medium stones, including some rounded pebbles.

D24 Ynys series - cambic stagnohumic gley soil

Location: Llwyn Saint Farm, near Gwytherin.
Grid reference: SH 866 601-
Slope and aspect: Level.
Elevation: 381 m.
Land use: Rough moorland grazing, mainly of *N. stricta* but with *Juncus spp:* and C. vulgaris locally.

Depth (cms)	Horizon and description.	
0-5		Root mat.
5-50	O	Black semi-fibrous peat with few recognisable plant remains. Abrupt smooth boundary.
50-55	Ahg	Dark greyish brown (10YR4/2) apparently humose material from the above horizon. Abrupt smooth boundary.
55-70	Bg	Greyish brown (2.5YR5/2) silty clay loam with many mainly fine roots and few yellow brown mottles. Clear smooth boundary.
70-	BCg	Greyish brown (2.5YR5/2) gritty clay loam with common small to medium stones.

D15: Caron series - raw peat soil

Location: Glan-y-gors, near Aled Isaf reservoir.
Grid reference: SH 909 609.
Slope and aspect: Level basin site.
Elevation: 400 m.
Land use: Moorland, mainly *N. stricta*, *Juncus spp.*, sphagnum moss and *Carex spp.*

Depth (cms)		Horizon and description
0-5		Root mat and fresh litter.
5-75	O	Mainly semi-fibrous black peat with some banding of dark reddish brown.
75-90	Bg	Grey (10YR5/1) clay loam with few small stones.
90-	CG	Olive grey gritty clay loam with many small angular tabular stones.

D18: Caron series - raw peat soil

Location:	Llyn Aled.
Grid reference:	SH 921 576.
Slope and aspect:	Near level basin site.
Elevation:	380 m.
Land use:	Rough moorland, *Juncus spp.* some *N. stricta* and moss-

Depth (cms)		Horizon and description.
0-7		Root mat and fresh litter.
7-45	O	Mainly fibrous peat - dark brown to 30 cms then becoming black with few recognisable plant remains. Clear wavy boundary.
45-55	Ahg	Dark greyish brown (10YR4/2) humose silty loam with few small angular often soft stones. Many fine roots. Clear boundary
55-77	Bg	Greyish brown (2.5YR5/2) gritty clay loam with common soft stones and common roots. Clear boundary.
77-	CG	Greyish brown (2.5YR5/2) gritty clay loam with many medium and large stones and some rounded pebbles.

2.1. Soils developed on the Lower Greensand of the west Weald.

2.1.1. Topsoils, Area 1.

Sample No	Bed *	Grid reference	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
0001	4	48121390	6.50	6.10	0.10	0.09	0.01	124	0.80	0.19	0.19	0.028	2.72
0003	4	48181384	5.25	4.85	0.12	0.12	0.03	108	1.56	0.28	0.11	0.036	2.81
0004	3	48231378	6.75	6.35	0.22	0.06	0.02	480	2.32	0.32	0.15	0.032	3.25
0005	3	48141362	6.30	5.65	0.14	0.11	0.02	290	1.15	0.20	0.16	0.026	2.46
0006	2	48211367	6.25	5.70	0.09	0.06	0.01	276	0.80	0.18	0.14	0.020	3.47
0007	2	48201348	6.15	5.60	0.16	0.12	0.02	720	0.98	0.26	0.18	0.038	4.07
0008	1	48481362	5.95	5.35	0.08	0.06	0.01	32	0.43	0.06	0.14	0.004	3.21
0010	2	48341378	7.40	6.90	0.12	0.05	0.01	312	1.26	0.22	0.31	0.028	3.11
0011	3	48251385	6.70	5.80	0.15	0.10	0.02	364	1.15	0.30	0.20	0.032	3.53
0012	3	48301387	6.40	5.90	0.15	0.10	0.02	244	1.56	0.27	0.14	0.036	3.71
0013	3	48311388	5.60	4.90	0.24	0.12	0.02	404	2.23	0.43	0.13	0.044	4.18
0014	2	48841379	5.15	4.40	0.13	0.10	0.02	552	1.15	0.22	0.05	0.032	2.82
0015	2	48511375	6.10	5.55	0.10	0.04	0.01	475	0.70	0.16	0.09	0.020	2.76
0016	4	48411398	7.20	6.30	0.09	0.05	0.01	132	0.90	0.22	0.20	0.022	2.98
0017	4	48411403	5.10	4.40	0.12	0.07	0.01	40	0.59	0.05	0.09	0.008	5.36
0018	4	48431387	6.60	6.35	0.06	0.16	0.01	144	0.95	0.15	0.25	0.026	5.34
0019	1	48431326	6.10	6.00	0.09	0.05	0.01	244	0.43	0.14	0.13	0.016	2.58
0020	1	48501333	5.30	4.60	0.12	0.15	0.01	92	0.53	0.12	0.08	0.012	3.66
0021	1	48481325	5.90	5.30	0.16	0.08	0.02	400	0.70	0.28	0.14	0.032	3.49
0023	1	48571323	6.60	6.25	0.15	0.08	0.01	430	0.74	0.24	0.23	0.024	4.04

* Code to beds, 1. Hythe, 2. Bargate, 3. Sandgate, 4. Folkestone.

Sample No	Bed *	Grid reference	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
0024	1	49251232	5.75	5.60	0.12	0.08	0.02	492	0.71	0.23	0.08	0.032	3.25
0025	2	43951226	5.30	4.65	0.19	0.31	0.06	628	1.50	0.46	0.12	0.072	4.93
0026	3	48471225	[illegible]	[illegible]	0.24	0.12	0.07	596	2.45	0.36	0.17	0.036	3.81
0027	2	48971234	7.00	6.50	0.12	0.06	0.01	348	0.61	0.24	0.21	0.032	2.61
0028	2	48631234	6.90	6.50	0.09	0.07	0.01	264	0.72	0.18	0.15	0.032	2.16
0029	2	48691231	6.70	5.20	0.11	0.10	0.01	240	0.65	0.25	0.19	0.040	3.22
0030	1	48731233	6.70	5.20	0.12	0.07	0.01	304	0.52	0.22	0.13	0.032	2.07
0032	1	48751230	6.50	5.10	0.16	0.10	0.01	302	1.05	0.35	0.23	0.074	4.08
0033	2	49271227	5.90	5.30	0.17	0.11	0.01	600	0.79	0.26	0.16	0.036	3.67
0034	1	49371227	6.00	5.30	0.15	0.10	0.01	504	0.68	0.25	0.13	0.028	3.03
0035	1	49341226	6.90	6.30	0.12	0.08	0.01	360	0.52	0.25	0.24	0.028	3.84
0036	3	49281206	6.05	5.05	0.20	0.15	0.04	416	1.80	0.46	0.12	0.048	3.39
0037	3	49251205	6.60	6.30	0.17	0.13	0.02	308	2.26	0.32	0.18	0.032	4.26
0038	3	49101205	5.71	5.00	0.19	0.16	0.04	368	2.10	0.33	0.08	0.032	3.12
0039	4	48901203	6.10	5.50	0.17	0.19	0.05	52	0.45	0.15	0.24	0.018	7.35
0040	3	48611219	[illegible]	6.50	0.19	0.12	0.01	114	0.92	0.25	0.24	0.024	3.44
0041	4	48711204	5.45	4.85	0.13	0.15	0.03	44	0.33	0.10	0.15	0.016	5.91
0043	4	49091188	6.80	6.70	0.11	0.06	0.01	52	0.80	0.06	1.10	0.016	6.31
0044	4	49351182	7.20	6.80	0.20	0.11	0.02	100	0.49	0.14	0.64	0.012	6.64
0045	4	49441190	6.20	5.60	0.16	0.16	0.04	44	0.54	0.13	0.17	0.012	4.79

* Code to beds, 1. Hythe, 2. Bargate, 3. Sandgate, 4. Folkestone.

2.1.1. Topsoils, Area 2.

Sample No	* Bed	Grid reference	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I
2030	1	49771476	7.10	6.80	0.11	0.07	0.01	472	2.08	0.30	0.36	0.052	4.11
2031	1	49601457	6.50	6.40	0.11	0.13	0.02	312	1.30	0.22	0.36	0.032	4.25
2032	1	49571459	6.20	5.60	0.08	0.08	0.02	512	1.54	0.22	0.14	0.028	3.00
2033	1	50061464	6.00	5.20	0.09	0.11	0.02	184	1.10	0.15	0.11	0.020	2.40
2034	1	50061478	6.50	6.00	0.11	0.11	0.03	600	1.49	0.26	0.19	0.036	3.29
2035	2	49381459	7.30	6.55	0.13	0.04	0.01	516	1.86	0.29	0.48	0.048	2.87
2036	3	49241443	6.40	6.60	0.16	0.07	0.01	240	2.83	0.32	0.13	0.023	3.20
2037	3	49321447	6.50	5.90	0.25	0.14	0.03	220	2.56	0.34	0.20	0.048	3.53
2038	2	49531453	5.40	4.70	0.09	0.06	0.01	580	1.40	0.21	0.10	0.032	2.82
2039	2	49341465	7.10	6.70	0.13	0.09	0.01	692	1.62	0.26	1.02	0.048	4.22
2040	3	49311476	7.20	6.85	0.26	0.14	0.01	344	1.48	0.29	0.40	0.052	6.01
2040	3	49021445	7.60	6.30	0.14	0.06	0.01	590	2.55	0.24	0.09	0.020	2.90
2042	4	48671435	5.80	5.35	0.16	0.14	0.03	334	0.92	0.34	0.20	0.044	2.67
2043	4	48831464	4.90	4.10	0.11	0.12	0.03	172	1.76	0.20	0.04	0.024	4.60
2044	4	48861473	7.60	7.10	0.14	0.05	0.01	192	1.67	0.20	0.62	0.028	3.62
2045	4	49041476	5.60	4.70	0.06	0.12	0.01	60	1.47	0.09	0.11	0.012	4.60
2046	2	49541437	5.80	5.20	0.20	0.10	0.02	1012	1.90	0.34	0.13	0.040	3.08
2047	2	49411428	5.70	5.00	0.20	0.12	0.02	664	2.56	0.28	0.11	0.028	3.32
2048	3	49181459	6.90	6.70	0.17	0.05	0.02	428	4.20	0.42	0.16	0.036	3.59
2049	4	48921479	7.65	7.25	0.20	0.03	0.01	788	1.14	0.50	0.92	0.124	5.75

* Code to beds, 1. Hythe, 2. Bargate, 3. Sandgate, 4. Folkestone.

2.1.1. Topsoils, Area 3.

Profile No	Sample No.	Depth (cms)	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
P1	2014	0-6	3.60	2.60	0.07	0.04	0.02	BD	0.08	0.03	0.002	0.002	9.23
	2013	6-11	3.50	2.70	0.06	0.05	0.02	"	0.09	0.03	0.008	0.001	7.98
	2012	11-20	[illegible]	[illegible]	0.02	0.03	BD	"	0.09	0.01	BD	0.001	1.44
	2010	20-27	4.20	3.15	0.02	0.03	"	"	0.17	0.01	"	0.001	1.23
	2008	27-40	4.15	3.70	0.02	BD	"	"	0.14	0.02	0.004	0.003	4.40
	2007	40-47	ND	ND	0.19	0.52	0.19	"	0.52	0.20	0.004	0.003	4.40
	2003	47-51	3.65	3.00	0.17	0.29	0.17	"	0.31	0.18	BD	0.002	3.48
	2004	51-55	4.45	3.65	0.04	0.12	0.04	8	0.27	0.04	"	0.002	0.46
	2005	57-63	4.30	4.00	0.06	0.20	0.09	16	0.42	0.09	"	0.004	1.02
	2006	67-73	4.60	4.15	0.06	0.13	0.08	BD	0.34	0.13	"	0.004	0.68
	2001	76-80	4.75	4.30	0.04	0.05	0.03	"	0.20	0.06	"	0.002	0.33
P2	2050	0-2.5	3.45	2.70	0.37	0.10	0.03	116	0.44	0.22	0.143	0.043	34.44
	2051	2.5-10	3.50	[illegible]	0.11	0.12	0.03	BD	0.50	0.18	0.016	0.035	4.56
	2052	10-15	3.55	2.85	0.14	0.18	0.05	"	0.60	0.21	0.008	0.003	5.91
	2053	15-25	3.70	3.10	0.19	0.29	0.06	23	0.92	0.23	BD	0.039	3.15
	2054	25-30	4.20	3.50	0.11	0.10	0.06	BD	0.88	0.40	"	0.055	1.28
P3	2055	0-5	2.65	[illegible]	0.25	0.03	BD	BD	0.30	0.06	0.020	0.003	16.73
	2056	5-10	3.50	2.65	0.13	0.04	"	"	0.14	0.03	0.004	0.002	6.72
	2057	10-15	4.10	3.05	0.02	0.02	"	"	0.09	0.01	BD	0.001	0.95
	2058	15-25	[illegible]	3.40	0.01	0.04	"	"	0.07	0.01	0.004	0.001	0.34
P4	2059	0-5	3.40	2.55	0.35	0.07	0.03	16	0.28	0.06	0.064	0.010	23.40
	2060	5-8	3.45	2.55	0.09	0.07	0.02	BD	0.21	0.03	0.008	0.002	7.08
	2061	8-20	3.80	2.90	0.01	0.05	0.02	"	0.30	0.02	BD	0.001	1.30
	2062	20-30	4.10	3.25	0.01	0.03	BD	"	0.23	0.02	"	0.001	0.45
	2063	30-35	3.60	2.70	0.09	0.32	0.07	12	0.52	0.09	"	0.003	2.63
	2064	35-40	3.70	3.00	0.17	0.96	0.15	BD	1.06	0.18	"	0.005	3.14
	2065	40-50	4.00	3.30	0.16	0.80	0.15	"	1.02	0.16	"	0.004	2.23
P5	2067	5-7	3.25	2.50	0.27	0.09	0.03	20	0.39	0.06	0.004	0.008	21.27
	2068	7-12	3.50	2.60	0.04	0.11	BD	BD	0.64	0.02	BD	0.003	2.33
	2069	12-16	3.80	3.00	0.04	0.23	"	"	0.54	0.02	"	0.002	2.11
	2070	16-20	3.60	2.95	0.10	0.25	0.04	"	0.34	0.04	0.004	0.001	5.75
	2071	20-33	3.90	3.45	0.07	0.66	0.02	16	1.52	0.05	BD	0.003	1.93
	2072	33	4.00	3.60	0.11	0.94	0.11	BD	2.10	0.14	"	0.004	2.08
	2073	33-45	4.10	3.75	0.14	0.82	0.34	28	2.02	0.24	0.008	0.006	2.68
	2074	45-50	4.15	4.10	0.10	0.29	0.16	36	1.52	0.31	BD	0.024	0.83

2.1.2. Podzol profiles.

BD - Below detection limits.

ND - Not determined.

Profile No	Soil series	Samp No	Depth (cms)	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
D3	Denbigh.	2188	0-10	5.40	5.00	0.33	0.70	0.26	1160	3.55	1.75	0.380	0.448	14.83
		2189	10-20	5.40	4.70	0.30	0.77	0.35	1044	3.47	1.68	0.232	0.440	11.73
		2190	20-30	5.20	4.55	0.34	0.90	0.42	1064	3.90	1.84	0.120	0.454	9.70
		2191	30-40	5.15	4.60	0.50	2.80	1.07	1100	4.92	2.52	0.076	0.552	8.29
D5	Denbigh.	2172	0- 8	6.30	5.90	0.38	0.48	0.24	816	3.30	1.80	0.440	0.520	11.45
		2171	8-20	5.65	4.90	0.38	0.49	0.26	740	3.24	1.76	0.184	0.480	9.23
		2170	20-35	5.90	5.10	0.46	0.64	0.32	732	3.34	1.80	0.172	0.496	6.09
		2169	40-50	6.00	5.05	0.43	0.87	0.61	532	3.06	2.32	0.084	0.728	4.99
		2168	60-65	5.95	5.20	0.23	0.22	0.22	504	3.61	2.32	0.040	0.920	2.70
D6	Denbigh.	2176	0-10	5.50	5.00	0.29	0.36	0.17	760	3.01	1.84	0.232	0.600	10.91
		2175	10-30	5.40	4.60	0.25	0.32	0.16	812	3.06	1.84	0.164	0.570	7.72
		2174	40-50	5.85	4.95	0.28	0.32	0.16	748	3.37	2.04	0.140	0.670	4.61
		2173	50-55	6.00	5.05	0.16	0.21	0.06	276	3.11	2.08	0.064	0.960	2.19
D9	Denbigh.	2200	0- 8	6.35	6.00	0.33	0.34	0.19	680	2.94	2.00	0.086	0.700	9.33
		2197	17-23	5.80	5.05	0.30	0.35	0.20	664	3.28	2.00	0.144	0.672	5.85
		2199	30-35	5.95	5.30	0.29	0.34	0.20	760	3.44	2.04	0.121	0.665	5.45
		2198	45-50	6.10	5.30	0.23	0.43	0.22	716	3.49	2.00	0.100	0.720	5.15
		2196	57-63	6.10	5.30	0.31	0.70	0.30	548	3.34	1.84	0.092	0.520	4.32
D12	Denbigh.	2213	0- 8	5.30	4.60	0.38	0.56	0.30	1360	3.36	1.88	0.196	0.540	11.50
		2212	14-20	5.40	4.95	0.43	0.50	0.28	1360	3.62	1.92	0.231	0.535	8.36
		2211	28-33	6.10	5.35	0.46	0.52	0.28	1400	3.83	1.92	0.222	0.537	6.04
		2210	40-45	6.30	5.50	0.42	0.53	0.25	1000	3.88	2.12	0.177	0.632	3.93
D27	Denbigh.	2297	0-10	5.30	4.70	0.43	0.78	0.37	812	3.29	1.88	0.232	0.576	13.04
		2296	10-20	5.65	5.10	0.39	0.71	0.38	852	3.69	1.96	0.194	0.600	9.94
		2295	25-35	5.95	5.15	0.41	0.90	0.50	770	3.56	1.90	0.137	0.596	6.35
		2294	40-50	5.85	5.00	0.47	1.04	0.68	564	3.54	1.98	0.089	0.592	5.61
		2293	50-60	5.85	5.10	0.29	0.64	0.55	432	3.88	2.32	0.062	0.792	4.38
D31	Denbigh.	2308	0-10	5.60	5.00	0.37	0.73	0.36	1092	3.69	2.00	0.230	0.712	10.29
		2307	15-25	5.70	5.00	0.28	0.77	0.43	880	3.52	1.80	0.128	0.690	6.75
		2306	35-45	5.90	5.10	0.47	1.21	0.60	916	4.16	2.04	0.118	0.660	6.11
		2305	50-60	5.90	5.15	0.39	0.64	0.65	644	4.11	2.40	0.005	0.740	4.45

2.2. Soil profiles from the Llansannan area of Clwyd.

Profile No	Soil series	Samp No	Depth (cms)	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
D11	Powys.	2209	0-8	5.95	5.40	0.48	0.97	0.56	840	3.20	1.64	0.069	0.247	19.51
		2208	12-18	6.20	5.45	0.47	1.17	0.60	1040	3.58	1.64	0.403	0.323	13.49
		2207	20-28	5.65	5.15	0.54	2.40	0.99	640	3.61	1.88	0.090	0.686	11.34
D28	Powys.	2292	0-10	5.15	4.70	0.57	1.25	0.74	576	1.47	1.09	0.199	0.129	17.11
		2291	10-20	4.90	4.20	0.71	2.12	1.12	812	4.00	2.24	0.050	0.328	9.57
		2290	20-30	4.95	4.45	0.61	2.29	1.03	488	4.26	2.16	0.037	0.552	8.35
D32	Powys.	2311	0-10	6.40	5.70	0.65	1.13	0.60	1470	3.90	1.76	0.483	0.320	15.25
		2310	10-20	5.70	5.40	0.72	1.24	0.66	1192	3.54	1.76	0.290	0.220	13.55
		2309	25-33	5.50	4.95	1.07	2.84	1.05	1144	5.41	2.64	0.135	0.496	10.75
D35	Powys.	2325	0-8	5.25	4.70	0.56	0.95	0.45	712	3.35	1.58	0.140	0.536	12.29
		2324	8-15	5.30	4.60	0.58	0.95	0.47	832	3.53	1.84	0.164	0.580	10.93
		2323	15-23	5.40	4.75	0.81	0.90	0.54	740	3.66	1.92	0.104	0.660	7.39
		2322	23-25	5.30	4.85	0.26	0.26	0.21	310	3.10	1.68	0.027	0.780	2.44
D37	Powys.	2333	5-10	4.25	3.60	0.55	2.09	0.76	688	2.40	1.28	0.022	0.188	13.41
		2332	10-20	4.45	3.90	0.62	2.69	1.10	600	4.58	1.64	0.017	0.260	14.97
		2331	20-30	4.70	4.20	0.59	2.39	0.95	476	4.30	2.22	0.013	0.560	6.96
		2330	30-40	4.90	4.35	0.37	1.39	0.73	704	4.17	2.36	0.010	0.720	7.15
D8	Manod	2186	0-10	7.10	6.55	0.57	0.50	0.19	638	3.16	1.34	0.772	0.278	11.43
		2185	10-20	6.25	5.60	0.49	0.61	0.22	656	3.18	1.55	0.452	0.270	12.39
		2184	20-27	6.15	5.50	0.56	0.75	0.36	576	3.30	1.48	0.320	0.316	10.02
		2183	29-35	6.30	5.60	0.70	1.90	1.01	420	4.23	2.20	0.232	0.640	7.37
		2182	42-47	6.30	5.60	0.47	0.92	0.66	576	3.47	1.50	0.328	0.352	7.37
		2187	AT 130	6.25	5.50	0.21	0.13	0.17	1398	3.69	2.12	0.032	0.960	1.74
D22	Manod.	2264	0-10	6.00	5.30	0.55	0.83	0.30	720	3.45	1.60	0.322	0.340	10.35
		2263	17-22	5.85	5.10	0.60	0.90	0.37	680	3.82	1.76	0.180	0.466	7.91
		2262	30-35	5.55	4.80	0.54	0.95	0.34	480	3.63	1.60	0.067	0.424	5.54
		2261	40-45	4.95	4.15	0.89	1.32	0.60	960	3.57	1.52	0.028	0.146	6.21
		2260	50-60	4.75	4.15	0.60	1.87	0.80	620	4.71	2.16	0.015	0.631	5.51

Pro-file No	Soil series	Samp No	Depth (cms)	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
D26	Manod	2284	0-10	5.45	4.60	0.46	1.00	0.42	1028	4.10	2.16	0.231	0.640	10.03
		2283	10-20	5.75	4.95	0.53	0.79	0.48	944	4.12	2.00	0.175	0.508	7.27
		2282	28-34	5.56	4.75	0.49	1.54	0.88	916	4.48	2.96	0.072	0.712	7.02
		2281	38-45	5.60	4.70	0.39	1.49	1.02	892	4.40	2.52	0.052	0.600	5.17
D36	Manod	2329	0-10	6.35	5.45	0.49	1.29	0.58	840	4.84	1.88	0.763	0.280	16.14
		2328	10-20	6.05	5.30	0.54	1.29	0.61	629	3.34	1.32	0.371	0.240	13.35
		2327	20-30	6.00	5.60	1.12	2.19	1.12	1648	4.24	2.32	0.258	0.358	12.07
		2326	30-37	5.85	5.20	1.02	1.69	0.95	1044	3.65	2.40	0.165	0.520	12.27
D23	Sannan	2270	0-10	[illegible]	4.60	0.60	0.86	0.22	248	2.14	1.24	0.291	0.149	17.75
		2269	10-15	5.65	4.80	0.59	0.65	0.22	244	2.75	1.24	0.276	0.147	12.18
		2268	20-25	6.35	4.90	0.62	0.49	0.19	344	4.71	1.22	0.219	0.146	3.35
		2267	30-35	5.90	5.00	0.91	0.40	0.28	234	4.75	2.20	0.124	0.753	5.22
		2265	50-55	5.85	5.00	0.36	0.16	0.36	168	2.76	2.12	0.054	0.848	3.50
D25	Sannan	2280	0-10	5.35	4.70	0.53	0.66	0.32	240	1.42	1.29	0.323	0.180	18.15
		2279	10-20	5.29	4.45	0.56	0.76	0.37	212	1.57	1.36	0.258	0.172	15.59
		2278	20-25	5.15	4.20	0.32	0.20	0.30	96	1.01	1.24	0.106	0.173	4.74
		2277	35-40	5.35	4.40	0.29	0.13	0.31	268	2.57	2.04	0.093	0.624	5.99
		2276	50-55	5.50	4.50	0.06	0.07	0.18	344	3.34	2.12	0.071	0.797	4.25
D27	Sannan	2289	0-10	4.95	4.30	0.33	0.40	0.15	580	3.41	1.76	0.085	0.656	6.42
		2288	15-20	5.15	4.35	0.24	0.26	0.18	512	3.74	2.15	0.106	0.700	3.53
		2287	25-35	5.00	4.25	0.05	0.02	0.04	1080	4.60	2.28	0.039	0.850	2.43
		2286	40-50	4.90	4.00	0.05	0.02	0.04	1160	4.56	2.28	0.035	0.870	2.17
		2285	50-70	5.40	4.45	0.04	0.05	0.04	600	4.14	2.16	0.055	0.860	1.55
D30	Sannan	2304	0-10	[illegible]	5.65	0.45	0.46	0.17	178	2.82	1.76	0.379	0.418	13.94
		2302	10-15	6.05	5.35	0.56	0.57	0.20	112	3.81	2.24	0.319	0.432	11.25
		2301	15-25	5.55	4.70	0.52	0.20	0.10	96	3.83	1.80	0.173	0.424	6.84
		2300	30-40	5.10	4.25	0.47	0.04	0.09	64	1.49	1.70	0.142	0.248	5.42
		2299	50-60	5.30	4.35	0.21	0.05	0.20	108	1.84	1.72	0.091	0.524	4.17
		2298	65-75	5.35	4.45	0.17	0.05	0.18	132	2.03	1.84	0.088	0.624	3.77

Profile No	Soil series	Samp No	Depth (cms)	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
D10	Aled	2205	0-10	6.52	6.10	0.14	0.33	0.09	1240	3.22	1.72	0.328	0.731	7.51
		2204	10-20	6.11	5.78	0.13	0.24	0.07	1220	3.89	1.88	0.173	0.872	4.82
		2206	20-25	6.21	5.50	0.12	0.26	0.08	1520	3.15	1.95	0.051	0.758	3.13
		2203	30-35	6.00	5.70	0.11	0.17	0.04	1280	3.67	1.80	0.089	0.840	2.47
		2202	35-43	5.30	5.70	0.07	0.13	0.04	1600	3.70	1.60	0.093	0.840	2.03
		2201	50-60	4.40	5.62	0.10	0.12	0.05	880	4.11	2.16	0.226	0.397	1.37
D33	Aled	2316	0-12	5.10	4.50	0.88	0.64	0.53	536	2.60	1.91	0.153	0.416	14.54
		2315	12-18	5.18	4.50	0.75	0.64	0.56	536	2.74	2.12	0.140	0.436	13.12
		2314	25-30	5.50	4.50	0.64	0.34	0.39	308	2.59	2.28	0.085	0.560	11.12
		2313	40-50	5.50	4.60	0.17	0.04	0.14	296	3.32	2.64	0.052	0.960	3.58
		2312	50-60	5.55	4.75	0.1	0.03	0.19	292	3.28	2.40	0.058	0.920	3.53
D4	Aled	2192	0-12	5.10	4.50	0.26	0.38	0.14	1126	3.43	1.84	0.142	0.754	10.62
		2193	12-20	5.1	4.40	0.22	0.32	0.14	1144	3.62	1.96	0.104	0.840	5.32
		2194	40-45	5.71	4.75	0.10	0.14	0.06	906	3.91	1.56	0.046	0.978	1.72
		2195	70-75	5.70	5.20	0.04	0.10	0.02	824	5.52	2.04	0.052	1.100	1.05
D7	Ithel	2180	0-10	5.50	4.95	0.46	0.58	0.27	132	1.69	0.84	0.576	0.120	21.24
		2179	10-20	5.70	5.25	0.54	0.60	0.29	116	1.61	0.80	0.500	0.076	14.00
		2178	20-30	5.35	4.10	1.37	2.90	1.14	100	4.68	2.35	0.072	0.352	13.55
		2177	30-40	5.00	4.20	0.72	2.20	1.08	146	3.93	2.45	0.028	0.630	10.20
D34	Ithel	2321	0-10	4.75	4.20	0.67	1.00	0.48	568	3.12	1.60	0.065	0.500	14.64
		2320	10-20	4.86	4.10	0.73	1.09	0.59	540	3.36	1.52	0.070	0.496	12.72
		2319	20-30	5.20	4.30	0.64	1.49	0.63	620	3.84	1.96	0.058	0.524	5.53
		2318	30-38	5.10	4.40	0.33	1.01	0.46	504	4.17	1.96	0.026	0.780	5.19
		2317	38-45	5.30	4.40	0.17	0.32	0.20	1040	3.91	1.92	0.022	0.816	3.35
D1	Hiraethog	2160	0- 7	3.50	2.70	0.41	0.26	0.20	32	0.46	0.60	0.024	0.026	29.93
		2161	9-16	4.[illegible]	3.35	0.46	0.75	0.45	324	3.01	1.16	0.004	0.162	10.47
		2162	16-22	4.32	3.70	0.52	1.55	0.43	440	2.90	1.44	0.001	0.120	8.43
		2163	26-35	4.50	3.90	1.14	4.60	1.48	704	5.76	2.76	0.008	0.408	13.75

Pro-file No	Soil series	Samp No	Depth (cms)	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
D2	Hiraethog	2164	0-14	[illegible]	[illegible]	1.22	0.24	0.25	44	0.32	0.38	0.076	0.044	80.39
		2165	14-16	[illegible]	[illegible]	0.22	0.56	0.42	20	0.71	0.59	0.032	0.020	55.39
		2166	16-2[illegible]	[illegible]	3.20	0.30	0.14	0.53	84	0.96	1.04	0.008	0.055	12.25
		2167	25-[illegible]	[illegible]	[illegible]	1.[illegible]	5.70	1.5[illegible]	552	5.84	2.66	0.012	0.248	25.19
D16	Hiraethog	2233	0-[illegible]	[illegible]	[illegible]	0.87	0.04	0.35	12	0.98	0.60	0.038	0.027	65.70
		2232	12-1[illegible]	[illegible]	[illegible]	0.29	5.36	0.47	52	0.57	1.20	0.008	0.107	13.58
		2231	20-2[illegible]	[illegible]	4.10	1.55	3.60	1.10	[illegible]20	5.24	2.62	0.005	0.421	11.82
D17	Hiraethog	2239	5-10	[illegible]	[illegible].80	1.3[illegible]	0.74	0.17	28	0.51	0.24	0.046	0.032	93.37
		2238	25-30	3.35	2.70	1.66	0.21	0.65	14	0.26	0.89	0.027	0.011	89.09
		2237	35-4[illegible]	3.40	3.00	0.29	0.02	0.33	4	0.08	0.80	0.001	0.015	15.5[illegible]
		2236	40-4[illegible]	3.70	3.20	0.42	0.02	0.20	12	0.16	0.65	0.001	0.254	9.49
		2235	52-5[illegible]	4.05	3.75	0.84	1.45	0.46	1120	4.00	1.52	0.001	0.267	5.13
		2234	65-75	4.35	3.75	0.33	0.41	0.19	560	3.71	2.05	0.003	0.736	2.37
		2241	40-4[illegible]	4.10	3.75	1.46	2.50	0.20	222	19.92	1.32	0.002	0.033	14.20
D21	Hiraethog	2259	0-1[illegible]	3.75	2.80	0.80	0.64	0.47	18	0.72	0.73	0.057	0.038	51.42
		2258	10-15	3.70	3.10	0.78	0.55	0.47	16	1.56	0.96	0.012	0.108	19.65
		2257	15-2[illegible]	3.90	2.40	0.43	0.75	0.48	74	1.57	0.30	0.013	0.051	10.30
		2256	23-2[illegible]	4.50	3.70	1.55	4.90	0.90	400	6.17	2.40	0.004	0.331	15.59
D15	Caron	2230	5-15	3.45	2.50	1.14	0.38	0.09	48	0.72	0.15	0.136	0.056	95.87
		2229	30-45	3.15	2.60	0.69	0.36	0.10	18	0.46	0.14	0.091	0.053	97.15
		2228	50-75	3.90	3.30	0.60	0.23	0.56	12	0.34	0.80	0.010	0.027	31.99
		2227	80-[illegible]	4.35	3.75	0.50	0.06	0.27	136	1.74	1.85	0.001	0.556	5.47
D18	Caron	2246	6-12	3.70	2.15	0.79	0.65	0.50	68	1.13	0.60	0.178	0.049	95.00
		2245	20-25	3.50	3.00	0.34	0.00	0.07	48	0.73	0.11	0.043	0.046	96.03
		2244	35-40	3.02	2.95	1.39	1.14	0.32	32	1.32	0.44	0.019	0.044	84.55
		2243	45-50	3.35	3.40	0.31	0.20	0.41	12	0.46	1.12	0.003	0.048	64.51
		2242	50-65	4.00	3.95	0.41	0.17	0.23	176	2.96	1.84	0.006	0.533	5.07

Profile No	Soil series	Samp No	Depth (cms)	pH_w	pH_{Ca}	Se_t	Fe_p	Al_p	Mn_t	Fe_t	Al_t	Ca_t	Mg_t	L.O.I.
D13	Ynys	2214	0-5	4.1[illegible]	3.60	0.56	1.01	0.51	52	1.26	0.96	0.073	0.069	61.85
		2215	5-10	3.95	3.50	0.90	0.49	0.45	32	1.35	1.20	0.009	0.099	21.55
		2216	12-17	4.30	3.80	1.47	1.49	0.70	152	5.04	2.20	0.004	0.439	11.15
		2217	22-27	4.4[illegible]	4.00	0.57	0.55	0.34	224	4.08	2.32	0.001	0.820	4.52
		2218	28-35	4.4[illegible]	4.15	0.26	0.39	0.24	226	3.71	2.16	0.011	0.970	3.07
D14	Ynys	2226	0-10	3.6[illegible]	3.30	1.15	2.29	0.24	256	1.42	0.25	0.010	0.056	95.37
		2225	10-15	4.05	3.45	1.52	7.99	0.54	112	5.19	0.92	0.032	0.034	64.42
		2224	15-21	4.15	3.70	0.55	0.41	0.40	116	1.27	1.20	0.012	0.031	21.41
		2223	21-27	4.50	4.60	1.25	1.20	0.59	356	3.98	1.64	0.024	0.028	24.27
		2221	27-32	4.25	4.00	1.32	4.20	0.90	1160	5.86	2.04	0.021	0.049	15.49
		2220	32-37	4.30	3.90	0.26	0.01	0.15	400	1.45	1.68	0.007	0.300	4.77
		2219	45-50	4.50	4.00	0.17	0.07	0.17	348	2.92	2.28	0.013	0.797	2.59
		2222	AT 27	4.6[illegible]	4.30	0.1[illegible]	1.31	0.43	20	11.12	2.04	0.032	0.015	14.76
D19	Ynys	2251	6-12	3.70	3.30	0.93	1.84	0.17	36	3.10	0.35	0.202	0.046	87.5[illegible]
		2250	12-23	[illegible]	2.92	2.2[illegible]	4.29	0.50	12	4.29	0.64	0.022	0.013	34.32
		2249	23-28	3.95	3.30	0.72	0.59	0.90	12	0.82	1.36	0.008	0.033	18.73
		2248	32-40	4.40	3.70	0.38	0.30	0.18	170	3.91	2.29	0.013	0.737	5.17
		2247	45-50	4.40	[illegible]	0.29	0.13	0.10	210	4.55	2.52	0.004	0.816	3.37
D20	Ynys	2255	8-14	3.65	3.10	0.71	0.45	0.34	[illegible]	0.48	0.72	0.024	0.024	45.27
		2254	22-27	3.60	3.00	0.81	0.28	0.70	4	0.39	1.09	0.007	0.014	37.79
		2253	30-35	3.85	3.50	0.58	0.05	0.57	168	1.52	1.96	0.002	0.356	12.59
		2252	38-43	4.40	3.90	0.24	0.04	0.23	340	2.91	2.12	0.005	0.615	6.56
D24	Ynys	2275	5-15	3.60	3.35	0.65	0.70	0.24	52	0.72	0.40	0.029	0.036	85.40
		2274	30-40	3.85	3.30	0.50	0.19	0.34	1	0.22	0.64	0.004	0.019	42.71
		2273	50-55	3.95	3.10	0.29	0.08	0.44	4	0.13	0.92	0.003	0.027	11.34
		2272	60-65	4.10	3.45	0.32	0.09	0.54	80	1.22	1.76	0.003	0.393	10.53
		2271	70-80	4.45	3.70	0.32	0.15	0.55	156	2.25	2.12	0.009	0.723	8.31