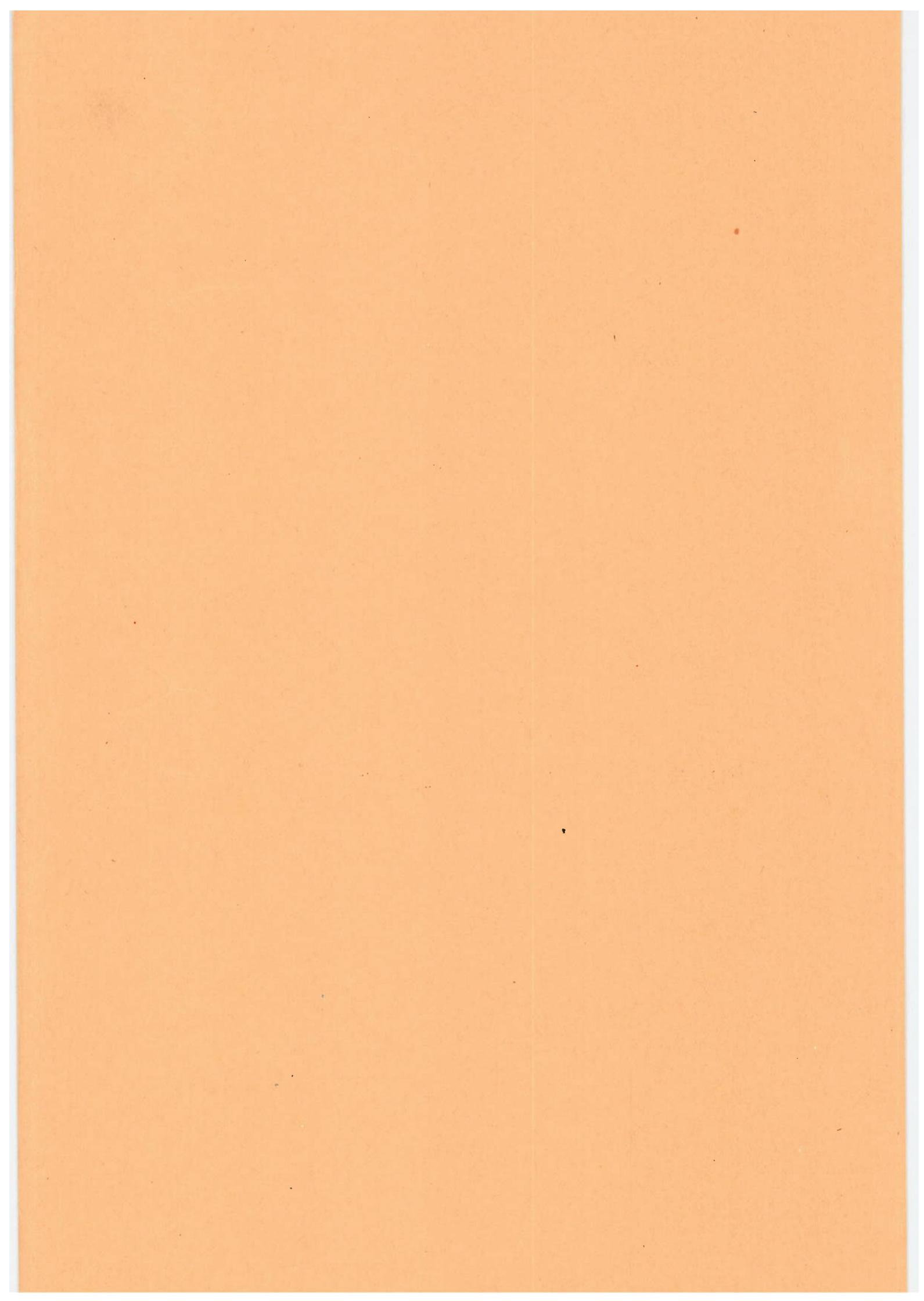


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SOIL ORGANIC MATTER

Welsh Soils Discussion Group
Cylch Cymreig Trafod Priddoedd

REPORT No. 16
1975



WELSH SOILS DISCUSSION GROUP

CYLCH CYMREIG TRAFOD PRIDDOEDD

REPORT No. 16

SOIL ORGANIC MATTER

Collated and Produced

by

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Field aspects of soil organic matter are discussed in this paper. The author is indebted to the following for their assistance in the field work: Dr. J. H. ...

PART I

FIELD ASPECTS OF SOIL ORGANIC MATTER

Year	Location	Soil Type	Organic Matter (%)	Notes
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960

(Continued on page 2) The present paper is based on the data collected during the field work...

THE DISTRIBUTION OF PEAT DEPOSITS IN THE BRITISH ISLES

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BASIC STATISTICS

Peat deposits have traditionally been regarded as a 'minor' organic resource except in countries or areas where coal has not been available. However, peats have undoubtedly considerable agricultural and industrial potential. Peatland agriculture, peat products and peat industries have acquired considerable status in such large countries as the U.S.S.R., the U.S.A. and Canada and such small countries as Finland, Denmark and, nearer home, the Republic of Ireland. Table (1) lists known and available peat reserves on a national basis

Table 1

The World's Peat Resources

Country	% of World Resources	Country	% of World Resources
(1) U.S.S.R.	60.8	(9) Indonesia	0.9
(2) Finland	9.5	(10) Norway	0.7
(3) Canada	9.1	(11) Cuba	0.3
(4) U.S.A.	5.0	(12) Japan	0.2
(5) Germany (East and West)	3.5	(13) Denmark	0.08
(5) Gt. Britain and the Republic of Ireland	3.5	(13) Italy	0.08
(7) Sweden	3.4	(13) France	0.08
(8) Poland	2.3	(16) Others	0.56

(Olenin, 1963). The British Isles are ranked fifth at 3.5% alongside East and West Germany, with only the U.S.S.R. (60.8%

Finland (9.5%), Canada (9.1%) and the U.S.A. (5.0%) recording higher percentages. The first three include vast areas of 'organic terrain' (Radforth, 1968) in the tundra belt. The inclusion of extensive and analogous upland peats in the British Isles statistics lead to a substantial increase in the British figures and it is clear that the peat cover of these islands is one of the most intensive per unit area in the world.

Table (2) provides details of peat areas for the political subdivisions of the British Isles. Northern Ireland (17.8%) and the Republic of Ireland (14.1%) have the greatest

Table 2

The British Isles : National Peatland Areas

Country	Total land area (sq. mls)	Peatland area hect-ares	sq. mls	Percentage of land surface peat-covered
England	50,056	361,690	1,397	2.8
Scotland	29,795	821,381	3,171	10.7
Wales	7,967	158,770	613	7.5
N. Ireland	5,206	240,000	927	17.5
U.K. Totals	93,024	1,581,841	6,108	6.6
Rep. of Ireland	26,600	970,800	3,748	14.1
Brit. Isles Totals	119,624	2,552,641	9,856	8.3

(Sources: Robertson, 1968; Taylor and Tucker, 1968).

proportional land area in peat with Scotland (10.7%), Wales (7.5%) well behind and England (2.8%) trailing. Territorially, however, the rank order is (1) the Republic of Ireland (970,800 ha = 3748 sq. miles), (2) Scotland (821,381 ha = 3171 sq. miles), (3) England (361,690 ha = 1397 sq. miles), (4)

Northern Ireland (240,000 ha = 927 sq. miles), and (5) Wales (158,770 ha = 613 sq. miles). These peat areas, if nationally consolidated, would be comparable in area in the Republic of Ireland, with the largest county, Cork, plus the adjacent County of Waterford; in Scotland, to most of the area of the Central Valley; in England, to the County of Cornwall; in Northern Ireland, to County Down; in Wales, to the old Pembrokeshire. For the U.K. taken as a whole, the total consolidated peat area would obliterate Yorkshire with some to spare.

LOCATION AND DISTRIBUTION

Peatlands are both extensive and widespread in the British Isles (Fig. 1). The primary sources for this map are (i), the Peat Survey of Scotland, based since 1962 at the Macaulay Institute for Soil Research at Aberdeen; (ii), the Peat Survey of Wales directed by the author in 1965-67 from Aberystwyth on behalf of the Natural Environment Research Council; (iii), the Geological Survey in England and Northern Ireland; (iv), the Fuel Research Board, London (Purcell, 1920) and (v), Bord na Mona in the Republic of Ireland.

Secondary sources, consulted for cartographic purposes, include the Atlas of Britain and Northern Ireland (1963) and Dwyer (1962).

Upland peat (shown in black in Fig. 1) is inevitably concentrated in the northern and western moorlands and mountains i.e. the Highland Zone of Britain, and almost absent from the Lowland Zone of Britain. Lowland peats (shown in stipple in Fig. 1) are locally grouped in central and western Ireland, the Lancashire and Solway 'mosses', the East Anglian Fenlands and the Somerset Levels. These constitute areas of high water-table and bad drainage associated with a flat relief, hydrological convergence and an impervious geological substrate. Lowland or 'basin' peats are more terrestrial in

FIGURE 1

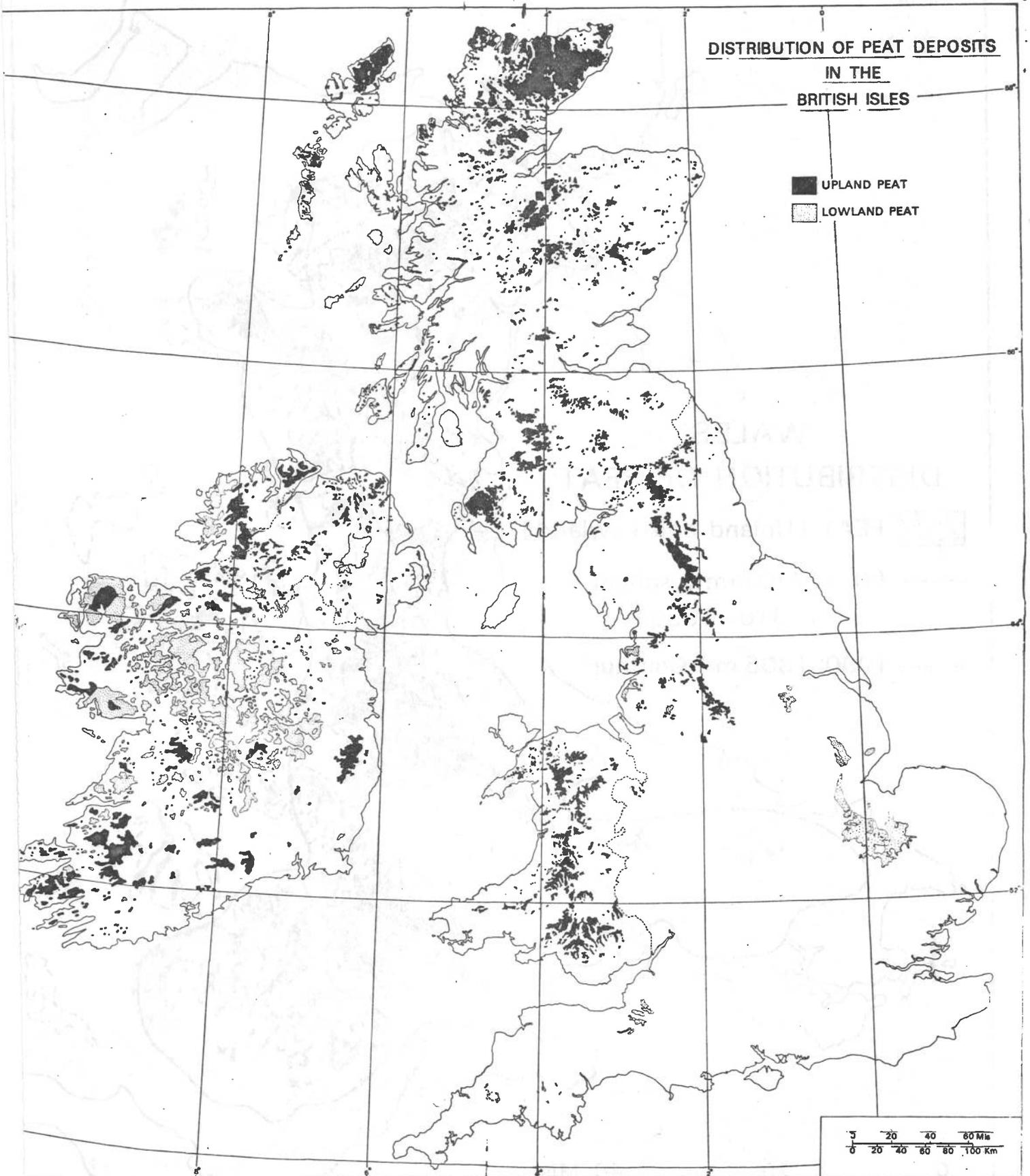
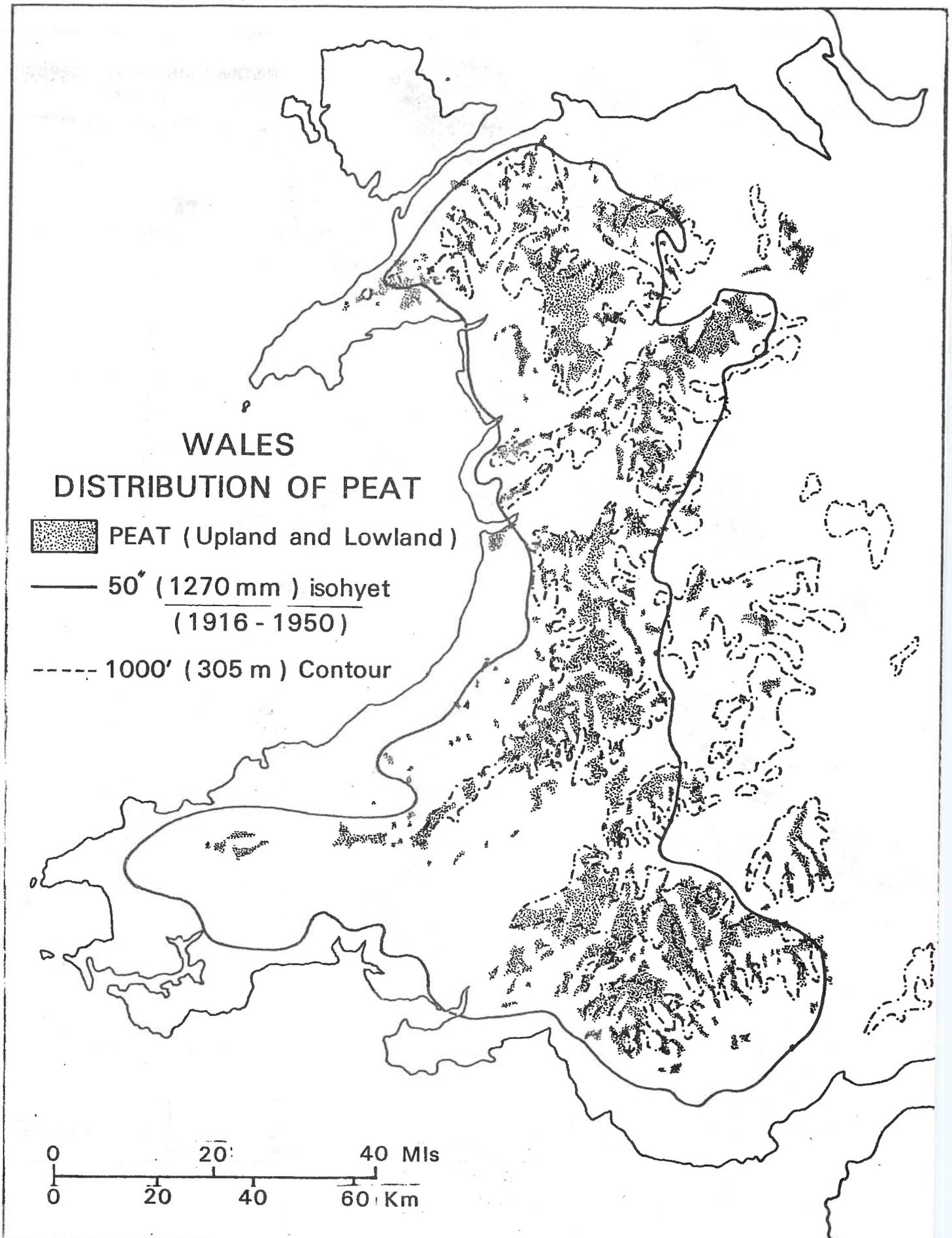


FIGURE 2 Wales: Distribution of peat deposits in relation to altitude and rainfall.



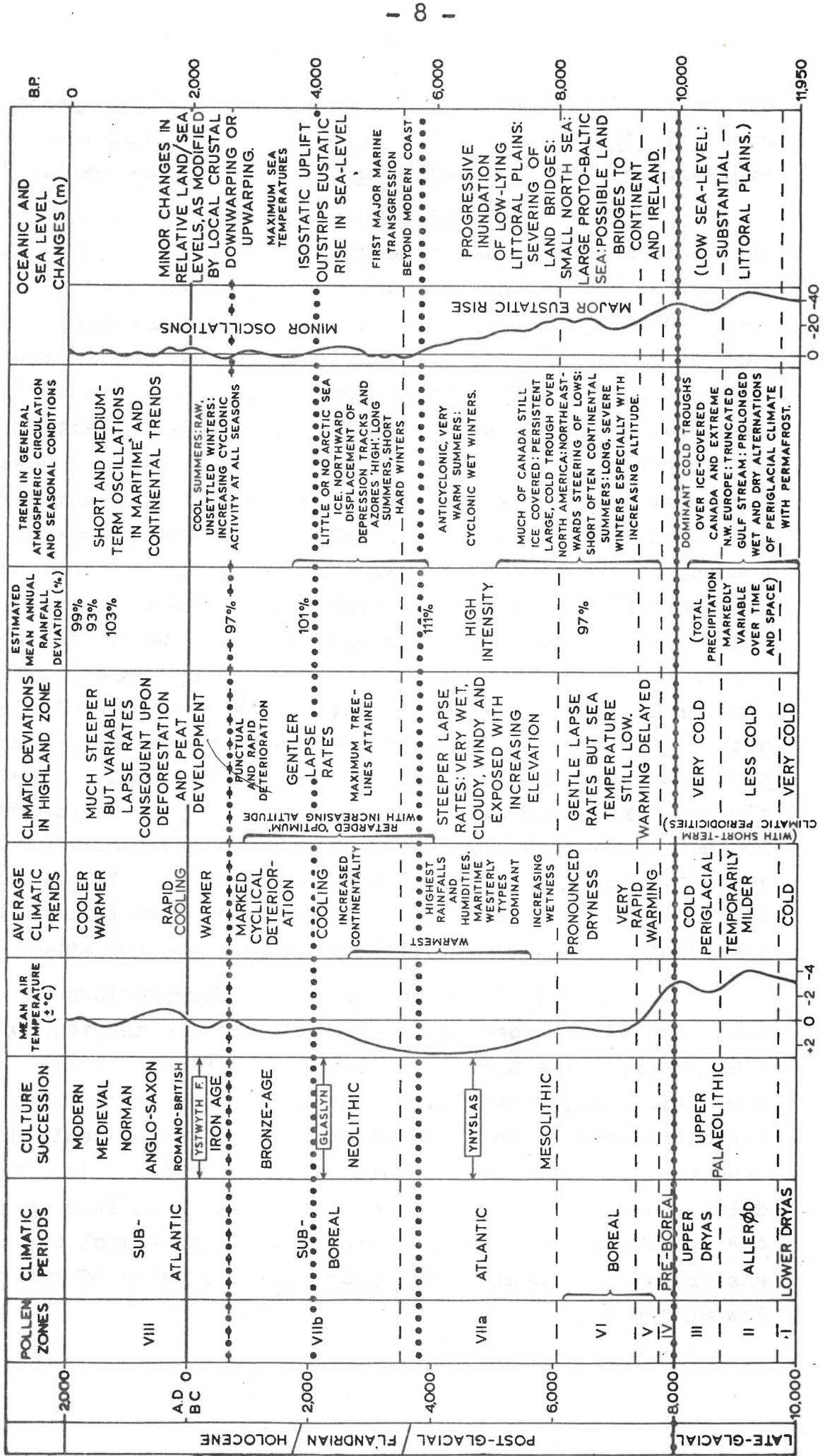
origin and development, while upland or 'blanket' peats are more climatic in origin and development and their initial evolution has been termed pedogenic (Taylor and Smith, 1972).

In Wales, the distribution of peat (upland and lowland) may be related to areas receiving more than 50" (1270 mm) rainfall p.a., on average, and areas lying above 1000' (305 m) above sea-level (Figure 2). Pearsall (1950) first proposed that the 50" isohyet in Britain was a broad indicator of the location at which the excess of precipitation over evaporation began to favour peat accumulation on the soil surface. The isohyetal pattern and the peat distribution display a better general match in east Wales than west Wales. However, the major anomaly, in south-west Wales and up the Towy Valley, is simply due to the absence of high ground. In any event, the rainfall gradients on western slopes are sharper than on eastern slopes where rainfalls are relatively low compared with similar altitudes on the west and summer evaporation is substantially higher (Taylor, 1976). On a less crude scale, the local peat limits show a broad accordance with the 1000' contour. Again, there is a greater frequency of peat near and below that contour on western than on eastern slopes where substantial areas, especially in the central and southern Border country are peatless and also outside the 50" isohyet. Clearly, the local modifications in altitude and rainfall must be considered in explaining local variations in the peat distribution as affected by evaporation and aspect.

In Scotland, following the interpretations of Robertson (1971), peatlands are broadly circumscribed by the 1000 mm (40") average annual isohyet, more especially in eastern Scotland. A major exception, however, is the continuation northeastwards towards the tip of the Caithness peninsula of a concentrated peat cover outside this limit (Fig. 1). In the driest parts of Ireland the distribution is defined by the 40" isohyet which crudely encloses an east-central and north-eastern core without upland peats but inclusive of substantial lowland peats.

CHRONOLOGY OF ENVIRONMENTAL AND CULTURAL CHANGES IN BRITAIN SINCE CIRCA 12,000 B.P.

Table 3



CLASSIFICATION AND INTERPRETATION

The classification of peat deposits has acquired a complex, and sometimes confusing, international literature (Taylor and Smith, 1972; Taylor, 1974), but following Abolin (1914 and 1928), Sukachev (1915 and 1926), Tansley (1939) and Pyavchenko (1963) a complete and valid interpretation of peat deposits must integrate origins and evolution over time with a contemporary eco-systematic and environmental appraisal of habitat in space.

Table 3 presents the standard Late-glacial and Post-glacial chronologies for the British Isles over the past 12,000 years or so (Godwin, 1956; West, 1968; Taylor, 1975). During the Late-glacial period (Zones I to III inclusive) peat formation must have been as ephemeral and localised as in the modern tundra with much subsequent deformation in Zone III (Taylor, 1973). Fossil survivals so far identified are modest in dimensions but in certain localities a continuous record of peat accumulation in individual basin bogs since the Late-glacial period has been proved (e.g. Moore, 1970). The major basin and 'raised' bogs of Britain are mostly post-6700 B.P. in age (corrected ^{14}C date, vide Olsson, 1970). In geochemically base-poor catchments such as the Lancashire and Solway plains, oligotrophic bogs derived from a restricted and relatively poor quality flora develop. In base-rich catchments like the English Fenlands or, to a lesser degree, the Somerset Levels and central Irish plain (which is floored with extensive Carboniferous Limestone), eutrophic fens, derived from a richer flora, accumulate. Once the water-table is reached, peat growth above that level becomes progressively more immune to ground-water chemistry and under the control of atmospheric moisture. Thus, peats accumulating above ground-water control are normally acidic.

Upland peats are generally younger than basin peats, being mostly dated post-5000 B.P. \pm 500 years, corrected ^{14}C time, i.e. deriving from the Sub-Boreal and especially the

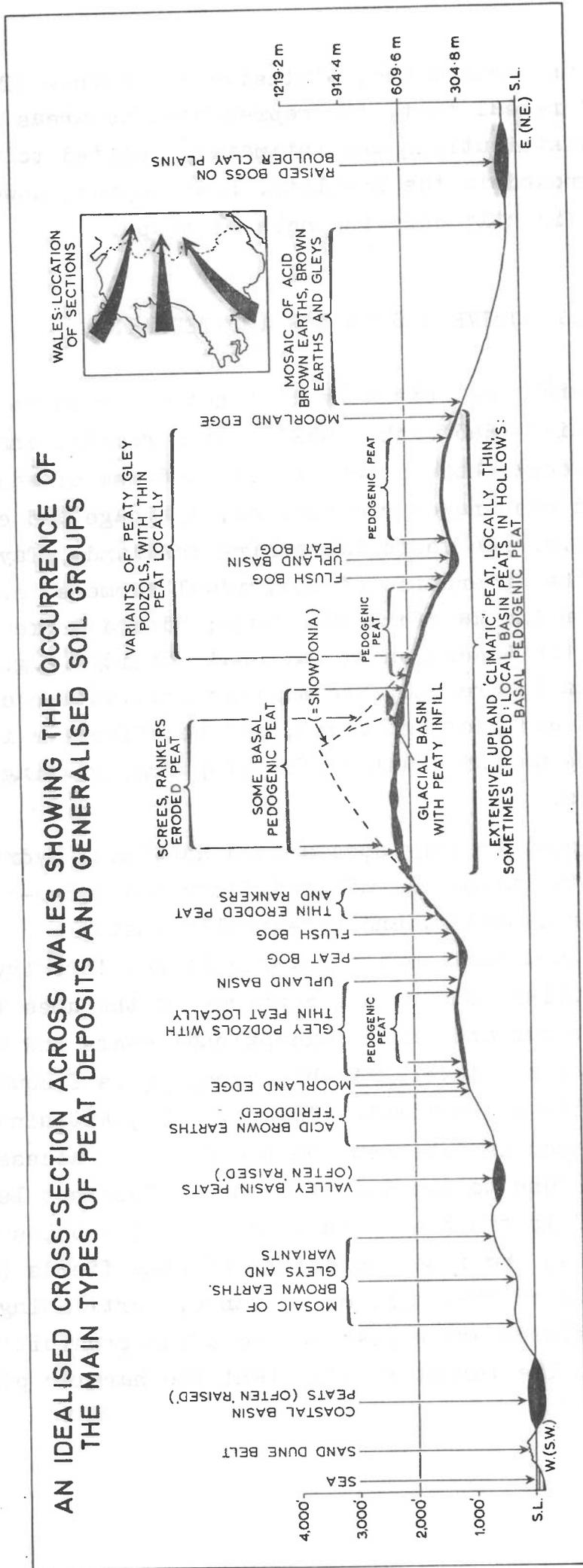
wetter, cooler Sub-Atlantic periods and often being initiated after deforestation of upland sites by Neolithic and, in particular, Bronze Age man (Smith, 1970; Taylor (ed) 1972, and Taylor, 1974); hence the variable date of origin. A standard indicator of the first major deforestation phase is a marked decline in the proportion of elm pollen in the fossil record. This 'elm decline' has been broadly regarded as synchronous in Britain (Godwin, 1970; Pennington, 1970) but some evidence for Scotland (Pears, 1972) and Wales (Smith and Taylor, 1969, and Taylor, 1973) suggests a greater variation in timing, at least of the order of \pm 500 years.

Taylor and Smith (1972) have proposed that the 'climatic' control of upland or blanket peat accumulation is preceded by a discrete pioneer stage when soil processes at ground control the formation of basal 'pedogenic' peat. A model section across Wales in Figure 3 indicates the locational sequences of basin, pedogenic and climatic peats (Taylor, 1974). This model may also be applicable to Southwest and Northwest England without major modifications. In western Scotland (Robertson, 1971) and even more so in Western Ireland, forms of blanket peat extend down eventually to sea-level on exposed maritime littorals where regularly high humidities, strong winds off the sea and persistent ground wetness create a climatic environment which bears some comparison with the British uplands, except that it is warmer, more equable and virtually winterless.

In summary, the distribution of peat deposits in the British Isles is specialised on both the general and local scales. The bulk of the deposits comprise upland peats which account for about 90% of Welsh peatlands (Taylor and Tucker, 1968), about 90% of Scottish peatlands (Robertson, 1968) and about 46% of Irish peatlands (Purcell, 1920). These peats are generally assumed to be thin e.g. less than 6' (1.83 m) but more than 2' (0.61 m) in depth and although locally up to 10' (3.05 m) or more. On extensive, gently sloping upland surfaces, it is highly probable that the depths of upland peats have been

FIGURE 3

AN IDEALISED CROSS-SECTION ACROSS WALES SHOWING THE OCCURRENCE OF THE MAIN TYPES OF PEAT DEPOSITS AND GENERALISED SOIL GROUPS



considerably underestimated. Statistical analyses (Taylor and Tucker, 1972) reveal that, for representative areas in mid-Wales, peat distributions are intimately related to the amount of flattish ground in the locality. Peat depths, however, were related significantly only to angle of slope.

DISTINCTIVE ECOSYSTEMS AND TERRAIN

Peatlands are initially distinctive as forms of 'organic terrain' (Radforth, 1952), often remote, inaccessible and avoided except where intensity of land-use of adjacent mineral ground encourages reclamation, drainage and economic development, e.g. the South Lancashire mosslands (Taylor, 1952). In addition, the enterprise of individual farmers, e.g. James Heyes (1974) on the Rainford mosslands; Edward Drake (1960) on Borth Bog, or the injection of national subsidy (e.g. the work of Bord na Mona in Ireland, the wartime cultivation of selected English, Welsh and Scottish bogs), may be effective in stimulating the use of peatland for cropping, grazing or industrial uses.

Peat bogs are very specialised habitats, hydrologically defined and with intimately adapted flora and micro-climate. They constitute mandatory and potentially unstable environments. When reclaimed for agriculture, forestry (or any other use) peculiar constraints continue in the uses to which the land may be put and in the exceptional costs and managerial care required at all levels. Arable cropping is frequently restricted by the microclimate (Taylor, 1952; Aitchison, 1968). The grazing season is dependent on the physical accessibility of the peaty ground to the animals; on the Somerset Levels, cows are milked in the fields in special mobile bales because of the remoteness and inaccessibility of many fields (Taylor, 1973). The costs of drainage, maintenance, fertilising and weeding of peatlands are excessive and often prohibitive (Taylor, 1949). The forester must plant the hardier pine on the

upland bog rather than the fir or the larch. Engineering risks and costs in the building of houses or roads over peatlands are normally prohibitive also. However, Smiles (1904) describes how George Stephenson successfully 'suspended' the Manchester-Liverpool railway across Chat Moss west of Manchester in 1830. However, it was not until 1974 that the M62 motorway was taken 'through' the southern lobe of the same moss. However, the unforeseen costs of controlling and banking the fluid peat meant a final costing of £1.1/3 million per mile as against the normal estimate of £1 million. This particular stretch of motorway, being in a hollow as well as being peat-bound, could also prove to be a bad accident blackspot because of its susceptibility to fog and frost. Thus, peatlands may create hazard not only in their natural state but also in the various forms of land-use to which they may become adapted.

DIVERSITY OF EVALUATIONS

Raw, unreclaimed Lancashire mossland has been valued at only a few pounds to the acre, but fully matured, reclaimed mossland may approach several hundred pounds per acre in value (James Heyes, 1974). This transformation, however, demands prodigious investment and immaculate management. Scandinavian peatland is usually grazed and rarely cropped, in contrast, Lancashire peatland is nearly always cropped and rarely grazed. Somerset peatlands carry permanent pasture for dairy cattle. The drier edges of Irish bogs are more usually grazed on the small holdings but their suitability for the growth of main crop potatoes is well known and recent research at Glenamoy (O'Hare, 1972) has taught the Irish farmer to "float" this cultivation and cropping on a shallow surface layer of the bog, avoiding deep ploughing and excessive drainage and costs.

Upland peats have traditionally been regarded as too thin, too poor and too variable for harvesting on a mechanical scale. Yet in 1974, with the world energy crisis looming large,

serious re-evaluations of Welsh upland peats are being attempted by a number of authorities and institutions. The upland peat-cover represents a vast, semi-natural regulating reservoir which, however, is liable to erosion. It also has a high absorptive capacity for industrial pollution and exerts a considerable control on water quality. The admirable softness of moorland water is countered by the possible presence of potentially toxic organic residues and cycled pollutants.

POTENTIALITIES

The peat deposits of the British Isles offer a wide range of potentialities. On one hand, the industrialised bogs of Central Ireland which yield milled and sod peats by highly mechanised and internationally approved techniques and the first class agriculture of the Lancashire mosses and the English Fenlands are highly productive, on the other hand the vast peat concentrations in Western Scotland, parts of Western Ireland and the British uplands, are utterly isolated and little used. The latter are colder, later and slower in terms of growing season because of their peat cover than even their altitudinal rankings would suggest: and the British altitudinal lapse-rates of temperature are among the greatest in the world (Manley, 1970; Taylor, 1976). However, the stripping of the peat from the uplands would be a difficult and expensive operation with serious hydrological and land-use risks. At the same time, a carefully selected site could be empirically studied with a view to (i) a detailed field inventory of the peat deposits, (ii) peat harvesting for industrial products, e.g. compost, (iii) preparation of a surviving basal peat and the mineral substrate to produce an adaptable soil for (iv) a planned and integrated programme of land-use catering for agriculture and forestry, water supply and amenity, scenery and tourism. Greater productivities per acre and per unit of investment may be obtained but the major constraint to the initiation and fulfilment of such a project would be the

pattern and style of present-day land-ownership, including state ownership of common land and Forestry Commission land, and the recurrent truth that the reclamation, maintenance, adaptation and management of peatlands or their derived cut-overs, is normally beyond the scope and skill of individual entrepreneurs. The future development of peat resources will, however, as in the past, be more or less conditioned by their peculiar locations and distributions.

REFERENCES

- Abolin, R.I. (1914) An attempt at an epigenological classification of bogs. Bolotovedenie, Nos. 3/4.
- Abolin, R.I. (1928) On the classification of bogs in the north-western region of the U.S.S.R. Moscow.
- Aitchison, J.W. (1968) The Land factor in agricultural production in West Central Lancashire in Agricultural Geography I.G.U. Symposium. Univ. of Liverpool Research Paper No.5, 3-13.
- Atlas of Britain and Northern Ireland (1963) Clarendon Press, London.
- Drake, E. (1960) Private Communication.
- Dwyer, D.J. (1962) The peat bogs of the Irish Republic : a problem in land use. Geog. J., CXXVIII, Pt.2, 184-93.
- Godwin, H. (1970) The contribution of radiocarbon dating to archaeology in Britain in Symposium on the impact of the natural sciences on archaeology. Proc. Roy. Soc. Series A, 269, 57-75.
- Godwin, H. (1956) History of British Flora, C.U.P.
- Heyes, J. (1974) Private Communication.
- Manley, G. (1970) The climate of the British Isles in Wallen, C.C. (ed.), Climate of Northern and Western Europe; World Survey of Climatology. Elsevier, 81-133.
- Moore, P.D. (1970) Studies in the vegetational history of mid-Wales, II : the Late-glacial period in Cardiganshire. New Phyt., 69, 363-75.
- O'Hare, P.J. (1972) A comparison of the effect of young forest and grassland on the water table in blanket peat in Taylor, J.A. (ed.) Research papers in Forest Meteorology; an Aberystwyth Symposium. Cambrian News, Aberystwyth, 126-33.
- Olenin, O.S. (1963) The peat stock of the U.S.S.R. Second Int. Peat Congress, Leningrad.
- Olsson, I.U. (ed.) (1970) Radiocarbon variations and absolute chronology in Proc. Twelfth Nobel Symp., Uppsala, Sweden.
- Pears, N.V. (1972) Interpretation problems in the study of tree-line fluctuations, in Taylor, J.A. (ed.) Research papers in forest meteorology : an Aberystwyth Symposium. Cambrian News, Aberystwyth.
- Pearsall, W.H. (1950) Mountains and moorlands. New Naturalist Series, London.

- Pennington, W. (1970) Vegetational history in the north-west of England : a regional synthesis in Walker, D. and West, R.G. (eds.), Studies in the vegetational history of the British Isles, C.U.P., 41-79.
- Purcell, P.F. (1920) The peat resources of Ireland. Fuel Research Board Special Report No.2, London.
- Pyavchenko, N.I. (1963) Basic terminology in bog science. Second Int. Peat Congress, Leningrad, 111-14.
- Radforth, N.W. (1952) A suggested classification of muskeg for the engineer. Tech. Memo. Assoc. Comm. Soil Snow Mech. Can. No.24.
- Radforth, N.W. (1968) New developments in peatland studies. Keynote address : Third Int. Peat Congress, Ottawa, 1-3.
- Robertson, R.A. and Jowsey, P.C. (1968) Great Britain : Peat resources and development in the U.K. Third Int. Peat Congress, Ottawa, 13-14.
- Robertson, R.A. (1971) Nature and extent of Scottish Peat Resources in Suomen Maataloustietellisen Seuran Julkaisula, 123, Acta Agralia Fennica, Finland.
- Smiles, S. (1904) 'Lives of the Engineers', Vol. V, 208-18.
- Smith, R.T. (1970) Studies in the Post-glacial soil and vegetation history of the Aberystwyth area (Unpubl. Ph.D. thesis, U.C.W. Aberystwyth).
- Smith, R.T. and Taylor, J.A. (1969) The Post-glacial development of soils and vegetation in northern Cardiganshire. Trans. Inst. Brit. Geogrs. 48, 75-96.
- Sukachev, V.N. (1915) The formation, evolution and properties of bogs. in Collection of lectures : third supplementary course for foresters, 1914, Petrograd.
- Sukachev, V.N. (1926) Bogs, their formation, development and properties. (Third edition) Moscow.
- Tansley, A.G. (1939) The British Isles and their vegetation. C.U.P.
- Taylor, J.A. (1949) Mossland farming in South-west Lancashire. Unpubl. M.A. thesis, University of Liverpool.
- Taylor, J.A. (1952) The relation of crop distributions to the drift pattern in South-west Lancashire. Trans. Inst. Brit. Geogrs. No.18, 77-91.
- Taylor, J.A. (1953) Peatland agriculture in South Lancashire and central Somerset. First Int. Peat Congress, Dublin, 11-19.

- Taylor, J.A. (ed.) (1972) Research papers in forest meteorology : an Aberystwyth Symposium. Cambrian News, Aberystwyth.
- Taylor, J.A. (1973) Chronometers and chronicles : a study of the palaeoenvironments of west central Wales in Progress in Geography No. 5, Arnold, 247-334.
- Taylor, J.A. (1974) Organic soils in Wales in Soils in Wales, Welsh Soils Discussion Group Report No.15, 30-
- Taylor, J.A. (1975) The role of climatic factors in environmental and cultural changes in prehistoric times in The Effect of Man on the Landscape. C.B.A. Symposium Volume (in press*)
- Taylor, J.A. (1976) Upland climates in Gregory, S. and Chandler, T.J. (eds.) Climate of the British Isles Longmans.
- Taylor, J.A. and Smith, R.T. (1972) Climatic peat - a misnomer? Fourth International Peat Congress, Helsinki, Vol.1, 471-84.
- Taylor, J.A. and Tucker, R.B. (1968) The peat deposits of Wales : an inventory and interpretation. Third Int. Peat Congress, Ottawa, 163-73.
- West, R.G. (1968) Pleistocene Geology and biology. Longmans.

CLASSIFICATION OF PEAT SOILS

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INTRODUCTION

The classification of peat soils has only recently received the same attention as that given to mineral soils, and the new Soil Survey classification (Avery, 1973) includes a major group of peat soils, in which the separations are derived from systems devised in North America and the Netherlands. As yet, this part of the classification is provisional, and further research within the Survey aims to investigate the range of peat soils known in England and Wales and to identify the best diagnostic properties. These results will be reported elsewhere and incorporated into a Technical Monograph on soil classification now in preparation. The purpose of this paper is to review some systems of classification of the organic soils found in other countries and to consider how they could help to classify these soils in Britain.

Peat soils can be defined as those derived mainly from organic deposits, which are saturated with water most of the time and/or have been artificially drained. This excludes the more or less freely drained organic soils which are derived from leaf litter, twigs and branches resting on rock or fragmental material, and occur principally in very humid climates; they are thought to be rare in this country.

The classification of peat soils requires suitable definitions of the depth and composition of the organic materials. In distinguishing organic and mineral soil materials, the Soil Survey has adopted the limits proposed

by the American Soil Conservation Service, which differ little from those used in the Netherlands. Organic materials or horizons (peaty, if usually wet or artificially drained) have more than 12-18% organic carbon depending on clay content. Other soils are considered mineral, but within these, a horizon with more than 4.5-7% organic carbon (approximately 8-12% organic matter) is described as humose. Peaty materials can be divided into:

peat - >40-60% loss on ignition (depending on clay content)

sandy peat - <40-60% loss on ignition and > 50% sand in mineral fraction

clayey peat - others.

These variable limits accord with field experience as a given proportion of organic matter modifies the physical properties of a sand more than those of a clay. Organic horizons are thus distinguished from humose mineral soil horizons.

The thickness limits adopted also follow American practice. Uncultivated peat soils must consist of at least 40 cm of organic material (or 30 cm, if over rock); in cultivated soils, the organic layers should extend at least 10 cm below the ploughed or Op horizon. Soils conforming to these limits include nearly all those previously described as organic or peat soils in Britain. Very shallow peaty soils over rock or little altered unconsolidated material are now classed as humic rankers. It is further stipulated that any mineral surface layer should not be thicker than 30 cm, nor should any mineral layers within the upper 80 cm of the profile, taken cummulatively, exceed 40 cm.

BASIC TYPES OF ORGANIC MATERIAL

The classification of peat soils can be approached in several ways. Traditional European methods have used their botanical composition, the physiography or mode of origin of the parent deposit, and their base status. The Canadian (Canada Department of Agriculture, 1970; Day, 1973) and the American systems (Soil Survey Staff, 1968; in press) are based, however, on identifiable profile characteristics, particularly the amount and durability of plant fibres and pyrophosphate solubility.

Fibres can be defined as fragments of plant tissue, excluding live roots, retained on a 100-mesh (0.15 mm diameter) B.S. sieve, except for wood fragments that cannot be crushed or shredded in the hand and are greater than 2 cm in their smallest dimension. Wood fragments are considered to be coarse fragments analogous to stones and boulders in mineral soils.

Three basic types of organic material can be distinguished in this way, fibrous, semi-fibrous and amorphous. They are very similar to the fibrous, pseudo-fibrous and amorphous categories introduced by Fraser (1933) for Scottish peats or the bog peat types of the Polish classification (Okruszko, 1974) or the three categories in the classification of Puustjarvi (1974) which was recommended for international use. However, they are defined more precisely with the assistance of two tests.

- (1) the estimation of fibres that do not break down on rubbing. Peat samples in the wet state are rubbed between thumb and forefinger ten times. They are moulded into a ball, which is broken in half and the broken face scanned with a lens. Comparable laboratory methods are being devised so that a range of standard samples will be available to help the surveyor calibrate his estimates.

(2) the solubility in pyrophosphate. A white filter paper is inserted into a paste of organic material in saturated sodium pyrophosphate solution and the Munsell colour of the moist paper recorded. High values with low chromas in the Munsell notation are evidence of insolubility and a Pyrophosphate Index can be obtained by subtracting the chroma from the value. This is claimed to be more precise than the estimation of rubbed fibre. A development of this method now under test is the measurement of the carbon content of a pyrophosphate extract (C.L. Bascomb, private communication).

Several important physical properties of organic materials are related to differences in the degree of decomposition. Boelter (1969) has shown that as peat decomposes the particle-size diminishes, the pores become smaller and the bulk density greater. Water retention increases since the most humified material has the highest content of capillary pores. However, the saturated water content decreases with decomposition since the total pore space decreases. The hydraulic conductivity decreases greatly as the many small pores of well-humified peat permit much less rapid water movement than the few large pores of the less decomposed material, although this is not necessarily true of drained peats which have developed structure or shrunk irreversibly.

The least decomposed material is termed fibrous (or fibric). More than two-thirds of the organic fraction consists of little decomposed, readily identifiable plant remains. It is commonly light yellowish-brown, dark brown or reddish-brown in colour. If squeezed when wet, a colourless or only slightly turbid liquid is exuded. Most fibres retain enough mechanical strength to resist disintegration when wet. Other physical properties are listed in Table 1. Fibrous materials are often rich in the remains of the moss Sphagnum.

Table 1

Physical properties of organic material types.

	Fibrous	Semi-fibrous	Amorphous (humic)
Rubbed fibre content %	> 40		< 10
Pyrophosphate Index	> 5	has	< 3
Typical bulk density (g/cc)	< 0.1	intermediate	> 0.2
Typical saturated water holding capacity %	850-3000	values	> 450
Typical hydraulic conductivity (cm/day)	> 150		2

The most humified material is termed amorphous, equivalent to humic (Canada) or sapric (U.S.A.) fractions, although also including some limnic (fresh-water lake) deposits, which have a pyrophosphate index comparable with fibric materials. The amorphous material is well decomposed and macroscopic plant remains, chiefly resistant woody or fibrous tissue, make up less than one-third of the organic fraction. It is often black or very dark grey and can contain significant amounts of mineral matter. If squeezed when wet, it exudes a muddy liquid and much peaty material escapes through the fingers. An intermediate stage is recognized and termed semi-fibrous (or pseudo-fibrous or mesic or hemic). This material, which is commonly dark greyish-brown to dark reddish-brown, is partly altered, both physically and bio-chemically (see Table 1).

CLASSIFICATION AT THE HIGHER TAXONOMIC LEVELS

The identification of the different kinds of peat soil in North America is based on the organic material type in an arbitrary "control section", divided into three "tiers":

- (i) a surface tier, 30 cm thick
- (ii) a subsurface tier, 60 cm thick or to any contact with bedrock
- (iii) a bottom tier, 40 cm thick

The most abundant (i.e. occupying the greatest volume) type of material in the subsurface tier normally determines the primary classification. Thus, in Canada, the Organic Order is divided into Fibrisol, Mesisol and Humisol Great Groups and in the U.S.A., the Histosol Order is divided into Fibrist, Hemist and Saprism Sub-orders.

Both the American and Canadian systems place emphasis on the nature of subsurface layers and the surface tier is not used to distinguish classes at the higher taxonomic levels. However, Farnham (1968), discussing peat soil classification in the U.S.A., states that the degree of decomposition of surface layers could be the basis for distinguishing peat soils at the lowest levels of classification. In some countries, peat soils have been farmed intensively for hundreds of years. The direct result of initial drainage is a partly irreversible loss of water from the peat, a process called "physical ripening" by Pons (1960). Aeration is improved, leading to the oxidative breakdown of the upper part of the peat by micro-organisms, and to the formation of a distinct surface horizon. In this the peat is moulded into a mull-like earthy material in which virtually no plant remains can be found. This is the "prominent organic A1" horizon of Jongerius and Pons (1962), or the "peaty earthy layer" of de Bakker and Schnelling (1966), or the "muck peat" layers of Okruszko (1974). These pedologists believe that soil forming processes in peat are akin to those in mineral soils and their importance should be reflected in classification. In Britain, Avery (1973) recognizes an "earthy topsoil" at least 20 cm thick, consisting of ripened humic material or a ripened mineral surface layer.

The present intention of the Soil Survey is to divide

the major group of peat soils into subgroups, allowing as much weight to the presence or absence of an earthy topsoil as to the type of organic material in a subsurface tier (Avery, private communication). Provisional subgroups are:

raw fibrous	raw semi-fibrous	raw amorphous
earthy fibrous	earthy semi-fibrous	earthy amorphous

Two other possible subgroups are:

- (i) earthy sulphuric. This is very acid peat, originally containing sulphides, which are oxidized on drainage. It normally shows straw-coloured mottles of jarosite, and may contain gypsum.
- (ii) earthy humilluvic. In drained and cultivated land, humus can be leached from the upper layers of peat and redeposited lower down the profile in a similar manner to the leaching of clay and humus in mineral soils; ¹⁴C-dating shows this illuvial humus to be younger than overlying organic material. It has a greasy, glossy appearance, a very large solubility in pyrophosphate, and should constitute at least half the volume of a horizon at least 2 cm thick. Humilluvic layers are not well known in Britain, but several types have been recognized in Holland (van Heuveln and de Bakker, 1972).

CLASSIFICATION AT LOWER TAXONOMIC LEVELS

Each subgroup can be further divided into several constituent series, the basic taxonomic unit. Possible differentiating criteria include:

- (i) Contrasting layers. Peat soils in which a subdominant layer occupies more than a critical thickness of the organic section beneath the surface tier are distinguished as subgroups in the Canadian and American systems, e.g. Fibric or Humic Mesisols as distinct from Typic Mesisols in which virtually all the subsurface tier is mesic.

- (ii) Reaction class. Avery (private communication) now intends to drop the subgroup separations based on soil reaction outlined in his (1973) classification scheme. Three classes had been suggested:

oligotrophic - pH (undried sample in 0.01M CaCl₂)
< 4.5 throughout a subsurface tier, and no sulphuric layer.

eutrophic - pH > 4.5 in some part of a subsurface tier.

calcareous - the greater part of a subsurface tier is appreciably calcareous or a strongly calcareous layer is present at less than 50 cm from the surface.

- (iii) Botanical composition of partly decomposed plant remains (in semi-fibrous and fibrous subgroups). Moore (1974) has attacked the simplified and subjective methods of peat classification, such as those based on the macrofossil assemblage, as inadequate for investigating the complex process of mire succession. He prefers a phytosociological analysis of the total macrofossil assemblage supplemented by statistical techniques. Although objective, such methods are time-consuming and unsuited to the mapping of large areas. For soil surveying it is probably adequate to adopt simple groupings such as those used by Hall and Folland (1970) in Lancashire:

reedswamp peat - layers of comparatively uniform botanical composition, consisting of reed (Phragmites communis) and sedge (Carex spp.)

fen and fen-carr peat - very mixed botanically, an assemblage of grass and sedge species.

carr peat - largely woody remains

raised moss peat - here the bog has accumulated above ground water level, leading to the formation of oligotrophic peat with much Sphagnum, Eriophorum or other sedges, and often Calluna.

hill peat or blanket bog..

- (iv) The particle size class of mineral layers within or at the surface of the peat (in amorphous subgroups).
- (v) The presence of limnic deposits such as marl or detrital organic muds (in amorphous subgroups).
- (vi) The presence of hard rock or unconsolidated mineral substrate within 80 cm.
- (vii) Soil temperature regime. The American system uses this criterion to separate Great Groups within Suborders. Ragg and Clayden (1973), in their assessment of the American system, recognize Boro- and Medi- Great Groups in Britain.

CLASSIFICATION OF SOME BRITISH PEAT SOILS

Raw fibrous subgroup

The definition of fibrous material largely restricts soils of this kind to those developed in Sphagnum-rich raised mosses in Lancashire (in the Turbary Moor complex) and some hill peats.

Representative profiles:

SD 42/3809 (Crompton, 1966, p.94), oligotrophic, raised moss peat.

NT 45/3080 (Ragg and Clayden, 1973, p.195), oligotrophic, hill peat.

Earthy fibrous subgroup

These soils occur over cultivated raised mosses in Lancashire.

Representative profile:

SJ 79/1757 (Hall and Folland, 1970, p.139), oligotrophic, raised moss peat.

Raw semi-fibrous subgroup

This includes many of the soils in hill peat or blanket bog mapped as the Winter Hill series in the Pennines, the Chains series in Exmoor and the Caron series in Wales. It also includes some soils, lacking a predominantly fibrous sub-surface layer, in raised mosses and upland acid basin peat.

Representative profiles:

SE 49/9330 (Bendelow and Carroll, n.d. 1), oligotrophic, hill peat.

SD 49/7687 (Hall, 1968, p.29), oligotrophic, raised moss peat.

SD 58/7589 (Furness and King, 1972, p.79), oligotrophic, reedswamp peat.

Earthy semi-fibrous subgroup

Many English cultivated peat soils can be placed in this category, which includes some of the soils mapped as Adventurers series in East Anglia, as the Altcar complex in Lancashire, and as Godney and Sedgemoor series in Somerset; the limits of these overlap and better correlation seems possible in future. Cultivated soils developed on raised moss have been mapped as the Westhay series.

Representative profiles:

SD 31/8360 (Hall and Folland, 1967, p.79), oligotrophic, raised moss peat.

SD 41/4485 (Crompton, 1966, p.94), oligotrophic, reedswamp peat.

SE 60/4472 (Jarvis, 1973, p.56), eutrophic, reedswamp peat.

TM 49/0909 (Corbett and Tatler, 1970, p.91), eutrophic, fen-carr peat with clay layers.

SD 33/6335 (Hall and Folland, 1970, p.137), eutrophic, carr-peat.

Raw amorphous subgroup

Soils in this subgroup have apparently amorphous subsurface layers, while the surface layer contains too much rubbed fibre to be considered as earthy top-soil. It also includes undrained "muck" or flush peats in which the surface layer (even though amorphous) is unripened and squeezes through the fingers.

Representative profiles:

NT 56/5406 (Ragg and Clayden, 1973, p.199), oligotrophic, hill peat.

SE 79/8137 (Bendelow and Carroll, n.d. 2), oligotrophic, basin peat.

Earthy amorphous subgroup

Some soils in the fen-carr peats of East Anglia and Lancashire belong to this category, as do the soils developed from the lacustrine organic deposits of Lancashire (Martin Mere complex). Some Prickwillow series profiles, where the peat contains some thin mineral layers, also belong here.

Representative profiles:

TL 56/5785 (Hodge and Seale, 1966, p.128), calcareous peat with marly layers over calcareous fine loamy drift.

SD 41/0371 (Hall, 1968, p.26), eutrophic mud.

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REFERENCES

- Avery, B.W. (1973) Soil classification in the Soil Survey of England and Wales. *J. Soil Sci.* 24, 324-38.
- Bakker, H. de, and Schelling, J. (1966) *Systeem van bodemclassificatie voor Nederland, de hogere niveaus.* Pudoc, Wageningen.
- Bendelow, V.C. and Carroll, D.M. (n.d.1) Soils in Yorkshire: sheet SE 58 (Riveaulx) with parts of SE 49 and 59 (Upper Ryedale). *Soil Survey Record.* (in preparation).
- Bendelow, V.C. and Carroll, D.M. (n.d.2) Soils in Yorkshire: sheets SE 79E/89K (Pickering Moor) and SE 88NE/89SE/98NW/99SW (Troutsdale) *Soil Survey Record.*
- Boelter, D.H. (1969) Physical properties of peats as related to degree of decomposition. *Soil Sci. Soc. Amer. Proc.*, 33, 606-9.
- Canada Department of Agriculture (1970) System of soil classification for Canada.
- Corbett, W.H. and Tatler, W. (1970) Soils in Norfolk I : sheet TM 49 (Beccles North). *Soil Survey Record No.1.*
- Crompton, E. (1966) The Soils of the Preston district of Lancashire. *Memoir of the Soil Survey of Great Britain.*
- Day, J.H. (1973) Report of the Subcommittee on Organic Soils. *Proc. 9th meeting of the Canada Soil Survey Committee.*
- Farnham, R.S. (1968) Classification of peat in the U.S.A. *Trans 2nd Int. Peat Cong., I*, 115-32.
- Fraser, G.K. (1933) Studies of Scottish Moorlands in relation to Tree Growth. *Forestry Comm. Bull. No.15*, HMSO, London.
- Furness, R.R. and King, S.J. (1972) Soils in Westmorland I : sheet SD 58 (Sedgwick). *Soil Survey Record No. 10.*
- Hall, B.R. (1968) Report on a Field Meeting in South-West Lancashire. *Proc. North of England Soils Discussion Group, 4*, 25-36.
- Hall, B.R. and Folland, C.J. (1967) Soils of the south-west Lancashire coastal plain. *Memoir of the Soil Survey of Great Britain.*
- Hall, B.R. and Folland, C.J. (1970) Soils of Lancashire. *Bulletin of the Soil Survey of Great Britain, No.5.*
- Heuveln, B. van and Bakker, H. de (1972) Soil forming processes in Dutch peat soils with special reference to humus-illuviation. *Proc. 4th Int. Peat Congr.*, 289-97.

- Hodge, C.A.M. and Seale, R.S. (1966) The soils of the district around Cambridge. Memoir of the Soil Survey of Great Britain.
- Jarvis, R.A. (1973) Soils in Yorkshire I : sheet SE 60 (Armthorpe) Soil Survey Record No.12.
- Jongerijs, A. and Pons, L.J. (1962) Soil genesis in organic soils. Boor en Spade, 12, 156-68.
- Moore, P.F. (1974) Objective classification of peats on the basis of their macro fossil content. Proc. Comm. I, Int. Peat Soc. Symp., Glasgow.
- Okruszko, H. (1974) Classification of peat soils for agriculture now in use in Poland. Proc. Comm. I, Int. Peat Soc. Symp., Glasgow.
- Pons, L.J. (1960) Soil genesis and classification of reclaimed peat soils in connection with initial soil formation. Trans. 7th Int. Congr. of Soil Sci. IV, 205-11.
- Puustjarvi, V. (1974) Classification of peat. Proc. Comm. I, Int. Peat Soc. Symp., Glasgow.
- Ragg, J.M. and Clayden, B. (1973) The classification of some British soils according to the comprehensive system of the United States. Technical Monograph of the Soil Survey of Great Britain. No.3.
- Soil Survey Staff, (1968) Supplement to soil classification system, 7th Approximation, Histols. Washington: U.S. Department of Agriculture.
- Soil Survey Staff, (In press) Soil taxonomy, a basic system of soil classification for making and interpreting soil surveys. Agric. Handbook U.S. Department of Agriculture. No.436.

AGRICULTURAL AND HORTICULTURAL PROBLEMS OF PEATS
AND HIGHLY ORGANIC SOILS

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INTRODUCTION

In Ireland as in most of Great Britain, peats can be broadly classified into raised and blanket bog; a notable exception being the East Anglian fen peats which were never covered by an ombrogenous layer. A shallow layer of forest peat is frequently sandwiched between the fen and raised bogs. Fen peat is derived from plants such as reeds, sedges, mosses and various tree species, all growing under the influence of base-rich groundwater. When the plant debris becomes elevated to a point beyond the influence of the groundwater, the peat becomes colonised by calcifuge plants such as Sphagnum mosses, heather and bog cotton. Thus the highly acid blanket peat is confined to high rainfall areas, as the plants depend on atmospheric precipitation for water, and covers the entire landscape irrespective of elevation.

The exploitation of both raised and blanket bog for fuel and horticultural peat moss may expose several peat types. The potential use of this land in agriculture and horticulture will depend on the depth and characteristics of the layers that are exposed. The water permeability characteristics range from 1 cm per day for blanket peat to 70 cm for woody fen (Dowling, 1969). The distribution of 12 physical and chemical properties in six cut-over raised peat profiles was investigated by Barry et al. (1973).

The reclamation of untouched bog for arable cropping is not economically feasible because of the high cost of drainage

and amelioration but such areas have been successfully reclaimed for grass production. However the considerable problems of grass utilisation due to high rainfall and poor drainage are unresolved. Under these conditions poaching losses are serious and the control of liver fluke difficult. The use of new drainage techniques combining the principles of grading to facilitate surface water removal to open drains, with closed drains filled with permeable backfill, have been found to be very successful. In such cases dried grass production and sheep farming may be considered as, on the wettest peat soils, grass yields equal those on wet mineral soils have been obtained.

Reclamation prospects for grassland are best in the least exposed, low rainfall situations where the peat has been cutover for fuel to shallow depth, although deep fen peat has also been found to be an excellent medium for grassland. The output of grassland from cutover raised bogs in Ireland is similar to that on the better mineral soils (Cole, 1968). Nutrient reserves in peat are low, but the efficiency of fertiliser utilisation is high. About 80 percent of applied fertiliser N, P and K is recovered from herbage treated at the optimum rate of application. Liming is necessary when the pH is below 5.0.

LIVESTOCK PRODUCTION

1) Cattle: Grazing trials on shallow cutover raised bog have shown that the optimum stocking rate is 4.3 store cattle per hectare where clover supplies most of the nitrogen requirements of the sward (Unpublished data). At this stocking rate, an overall seasonal liveweight gain of 0.8 kg/day was recorded over a 184 day grazing period. A lower stocking rate had no advantage as judged on a liveweight gain per bullock or per hectare basis but a significant reduction in the liveweight gain per bullock was shown at a higher stocking rate (5.6 store cattle per hectare) over the August/October period. In these trials

supplementary copper slightly increased liveweight gains (Table 1).

Table 1

The effect of copper on the liveweight gain of store cattle

Stocking Rate Bullocks/ha	Liveweight gain per bullock (kg)			
	1968		1969	
	No copper	Copper	No copper	Copper
3.0	173	177	158	164
4.3	162	167	147	158
5.6	123	142	112	117

The trend towards a greater response to copper therapy at high stocking rates especially in 1968, may be associated with higher levels of pasture nitrogen and molybdenum. Herbage molybdenum levels were far above desirable levels and in some samples, values of over 40 ppm were recorded. Some of the herbage molybdenum probably came from the poorly drained calcareous subsoils. Herbage molybdenum was over double the level previously recorded on grass-only swards on shallow peat (Cole, 1965). These trials also showed that nitrogen increased the copper content of grass and lowered the molybdenum content.

Higher stocking rates (4.3, 5.6 and 6.8 bullocks/ha) were used to determine animal output over the grazing season from grass grown on deep-cutover, raised bog and treated with 524, 474 and 336 units N per hectare per annum in 1971, 1972 and 1973 respectively. The results are presented in Table 2.

Table 2

The effect of stocking rate on the liveweight gain of bullocks
1971 - 1973

Stocking rate (bullocks/ha)	Liveweight gain (kg)					
	per bullock			per hectare		
	1971	1972	1973	1971	1972	1973
4.3	138	171	162	593	735	697
5.6	125	153	140	700	857	784
6.8	-	137	105	-	932	714

In the first year (1971) performance was lower than expected because poor ground conditions prevented early grazing of the sward. This resulted in seed heads appearing before the first rotation was completed. Management problems were further aggravated by the appearance of nitrogen deficiency in June which was thereafter corrected by nitrogen top dressings after each grazing. It is suggested that damage from poaching of first year pasture by cattle under farm conditions is best avoided by shortening the grazing season, making more silage from a greater area and consequently using a very high stocking rate during mid season. Where poaching is still a hazard, late varieties of ryegrass should be used and nitrogen applications delayed.

In the second year there was a positive correlation between liveweight gain per hectare and increasing stocking rate but the liveweight gain per bullock was better at the lower stocking rates. A noteworthy feature of the second year sward was a spectacular improvement in the bearing strength which enabled earlier and heavier stocking of paddocks despite an 80 percent increase in the April/May rainfall figures. Grass was more efficiently utilised in 1972 by improved timing of the basal fertiliser application, earlier application of nitrogen top dressing and earlier grazing.

The effect of stocking rate on the liveweight gain per hectare over the grazing season in 1973 was not very marked because of the very poor performance of animals at the higher stocking rates during the latter half of the year. In 1972 a second top dressing of nitrogen was applied but was omitted in 1973 because of the improvement in clover growth. It appears that the clover's contribution to the nitrogen requirements of the sward may not have been sufficient to sustain good pasture yields and consequently very low liveweight gains were recorded during the latter part of the season. The effect of insect damage and a reduction in the stand of the sown species on herbage yield was not assessed. Nitrogen shortage and faecal contamination of pasture may also have contributed to the poorer performance by reducing the voluntary intake of herbage at high stocking density. The absence of any serious poaching during a wetter than average July/September period reflected the continued improvement in the bearing pressure of the sward since its establishment.

The objective of present livestock investigations is to test the feasibility of breeding, rearing and finishing single sucklers on cutover peatland. The liveweight gain responses of animals so reared are presented in Table 3.

Table 3

Liveweight gain of Friesian cross calves born and fattened on peat grown herbage

Date	Liveweight (kg)	
	Bulls	Heifers
3rd November, 1972	73.5	77.0
26th April, 1973	208.0	176.0
11th October, 1973	397.5	341.0
27th March, 1974	430.6	-

The liveweight gains of the inwintered bulls were unsatisfactory. Type II Osteragiasis was diagnosed and the silage had a high molybdenum content (20 ppm). Scouring was corrected by anthelmintic dosing and feeding with a high copper mineral supplement. A single selenium injection, given to both bulls and heifers at pasture, had no effect on liveweight gain. However, the need for this and other essential elements will be continuously reviewed.

2) Sheep: Current work on sheep is aimed at examining the effect of mineral and anthelmintic treatment on lamb performance and the incidence of parasitism (Tables 4 and 5).

Table 4

The effect of anthelmintic and selenium/cobalt treatment on the average liveweight per lamb (kg) 1972

Treatment	Liveweight per lamb (kg)					Mean Increase	
	Date	22/8	4/9	28/9	20/10		10/11
Thibenzole only		20.4	22.7	24.9	27.2	28.6	8.2
Thibenzole + Se		20.4	24.5	26.8	29.9	31.3	10.9
Thibenzole + Co		20.4	22.2	24.9	27.9	28.6	8.2
Se + Co		22.7	23.1	24.9	27.2	29.5	6.8

Table 5

The effect of mineral feeding on the liveweight per lamb (kg) 1972

Date weighing	Liveweight (kg/Lamb)	
	+ mineral	- mineral
11th April	18.6	18.1
23rd May	29.0	28.1
29th June	32.2	31.7
9th August	28.1	25.9
*22nd August	30.8	26.8
6th September	32.7	29.5
27th September	34.9	31.7

*Routine thibenzole dosing introduced.

The results of these initial trials suggested that the effect of trace minerals especially copper and selenium and anthelmintic treatments on the liveweight gain and parasite control in sheep at high stocking density is worthy of further investigation.

ARABLE CROP PRODUCTION

Deep fen peats found in situ or exposed by the removal of acid Sphagnum peat have special advantages over most mineral soils and other peat types in horticultural crop production. Deep cut-over raised bogs with a surface Sphagnum layer are also suitable provided these have undergone physical, chemical and biological ripening processes, however the cost of drainage and amelioration of these deep unripened Sphagnum peats for arable cropping is prohibitive. Shallow peat areas are sometimes used for crop production but due to subsidence their productive life is limited depending on depth. All peat soils are subject to an annual subsidence which varies from a couple of inches after drainage to a fraction of an inch after initial settlement.

Deep fen peats on the other hand when properly drained, fertilised and managed are ideal for arable cropping because of their good physical properties.

1) Water Control: Good drainage installations are the most important feature of peatland development. The first essential in any drainage system is the provision of an adequate outfall. Generally internal drainage is through a system of open or closed ditches spaced at variable distances. Closed drains are favoured to facilitate machinery movement and prevent weed spread. In Florida open drains enclose 16-32 hectare blocks. The closing of all lateral drains and surface grading is now recommended practice in Ireland. The land is then carefully floated and levelled each year to ensure even drainage and a firm and level

seedbed. Sometimes on newly reclaimed areas crops are planted on ridges to avoid temporary water logging. Physical improvement of the peat is subsequently achieved through crop growth and some irreversible surface drying. In Ireland fen peats mostly occur in the 30-40" rainfall zone. They rarely suffer from moisture deficit unless rooting is restricted through disease, insect damage or acidity. Irrigation is sometimes required for crops that are seeded or transplanted in the June/August period. Irrigation also helps to achieve good weed control and to combat erosion and frost damage.

2) Nutrition: The pH of organic soils is crucial in planning treatments and cropping procedures that must be followed for maximum yield and quality of vegetable crops. The most favourable soil reaction for most vegetable crops seems to be on moderately acid soil about pH 5.8. If liming is necessary, great care must be exercised to ensure thorough incorporation.

All fen peats have a considerable store of soil nitrogen in organic form. However, in a newly drained, limed and fertilised peat, the amount of nitrogen released for plant growth depends largely on the available carbohydrate, nitrogen content and microbial activity of the peat. Generally on older peats which have undergone physical, chemical and biological ripening processes, nitrogen requirements are half the recommended dressing for new peat and are omitted entirely for low requirement crops like carrots and cereals. High nitrogen causes lodging in cereals and prolonged vegetative growth of sugar beet and potatoes at the expense of root and tuber development. A knowledge of previous cropping experience is a useful guide in predicting nitrogen requirements. As environmental factors, especially temperature and rainfall, play a very important part in mineralisation and nitrogen utilisation by crops, the appearance and growth rate of the crop should be used to determine top-dressing requirements.

Phosphorus is necessary for crop establishment on raw

peat soil. However, all applied phosphorus is readily available to plants because of the low levels of aluminium (0.09%) and iron (0.3%) and calcium (1.5%) present in Irish peats (Cole, 1965). Heavy applications of monocalcic phosphate, although readily lost by leaching, will adversely affect the availability of some trace elements e.g. zinc. Generally crop requirements for phosphorus on peat soil need not exceed 1.25-1.5 times the total phosphorus uptake by the crop.

Large increases in yield are obtained from potassium application as peat has no insoluble potassium reserves. The element is held as an easily exchangeable cation adsorbed to the organic colloid surface and will be leached if attempts are made to build excessively high levels. Potassium recommendations may also be based on the amount removed by crops. Generally recommended rates need not exceed 1.25 times plant removal. Luxury consumption of potassium by plants occurs at high soil levels of potassium thus, reducing the effectiveness of biennial treatment.

Peat soils are deficient in most essential trace elements. Deficiencies of copper, zinc, boron, molybdenum, magnesium, manganese, iron and more recently sulphur have been diagnosed in medium to highly sensitive crops grown on peat in Ireland. Elemental deficiencies may be prevented by soil and/or foliar treatment but great care must be taken to ensure uniformity of distribution.

3) Weed Control: A major management factor in successful vegetable growing is the ability to control weeds. All sources of weed spread should be eliminated. Under Irish conditions, rotation and a small amount of hand or mechanical weeding especially of the most chemically resistant weeds will be necessary to obtain the best results. However, in the absence of a reliable weed control programme based on herbicides, the cost of production of arable crops is prohibitive. On peat soils,

weed populations build up rapidly and weed growth is exceptionally vigorous. Successful weed control programmes based on herbicides have been drawn up for carrots, celery, onions, lettuce and potatoes (MacNaeidhe, 1966, 1970a, 1970b, 1972a, 1972b) but the satisfactory control of weeds in brassica crops still remains a problem (MacNaeidhe, 1972c). Preliminary trials have shown that pre-emergence application of paraquat combined with the standard herbicide to a stale seed bed prepared 3-4 weeks in advance of sowing can provide excellent weed control compared with standard herbicides applied to a fresh seed bed (MacNaeidhe, 1974). Generally the residual activity of herbicides on peat is low (MacNaeidhe, 1973).

4) Disease and Pest Control: Diseases of vegetables have not been a problem at Lullymore or in peat soils at other locations. 'Take-all' was a serious problem in cereals from 1963 to 1965, but has not re-occurred in recent years. Routine applications of fungicides are necessary in celery and onion production to control celery leaf spot and onion mildew. Cabbage root fly and carrot fly are more serious pests than on mineral soil. In the case of brassicae, the vigorous root regeneration obtained on the peat counteracts the root fly attack and the crops yield well, provided the recommended pesticides are applied. Severe damage occurs only when growth is retarded as a result of nutrient deficiency. Supplementary doses of pesticides are required late in the season for effective control of carrot root fly.

5) Cultivar Selection and Breeding: Due to the unique physical and chemical characteristics of peat, the behaviour of many of the vegetable cultivars is different from that found in mineral soil. Cultivar screening trials are necessary so that the ones most suited to this soil can be selected (O'Toole et al., 1968; Prendiville, 1972).

6) Mechanisation: Peat soils because they usually occur as large flat deposits are ideally suited to mechanisation. Most machines have been specially adapted for use on peat soil by reducing their ground pressure. There is very little wear on machinery on peat soils, because of their friability and freedom from stones. It is essential for small and large growers alike to take advantage of the full benefits which can be obtained from the mechanised sowing and harvesting of crops on peat.

7) Shelter: The risk of crop damage due to high winds and blowing peat is a definite hazard of peat farming. The problem is usually worse on the more highly decomposed peats. However, where good cultural and management practices are adopted crop damage can be greatly reduced.

CONCLUSIONS

Fen peat soils in many countries especially in the United States are much more highly valued than other soil types for the production of high value cash crops. These soils when properly drained, fertilised and managed are exceedingly productive of high quality crops. The limitations in the use of these soils are small compared with the advantages which fen peat has over many mineral soils as a growing medium. In Ireland large flat areas of cutover raised bog offer considerable scope for future low cost highly mechanised crop production.

ACKNOWLEDGEMENTS

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REFERENCES

- Barry, T.A., Carey, M.L. and Hammond, R.F. (1973) A Survey of Cutover Peats and Underlying Mineral Soils, Bord na Mona Cnoc Dioluin Group.
- Cole, A.J. (1968) Grass Production on Cutover Raised Bog - Nitrogen, Phosphorus and Potassium Requirements. Third International Peat Congress Quebec, Canada, 251-257.
- Cole, A.J. (1965) The Effects of Fertiliser applied to a Ryegrass Cocksfoot Sward on Cutover Raised Bog. Thesis, University College Dublin.
- Dowling, P.C. (1969) The Hydraulic Conductivity of Peat. Thesis, University College Dublin.
- MacNaeidhe, F.S. (1966) Preliminary Weed Control Investigations on some vegetable crops on cutover raised bog. Proceedings Crop Protection Conf. Dublin. 143-150.
- MacNaeidhe, F.S. (1970a) Evaluation of herbicides in drilled lettuce on peat soil. Proceedings 10th British Weed Control Conf. 227-231.
- MacNaeidhe, F.S. (1970b) Evaluation of herbicides in carrots and celery. Proceedings 10th British Weed Control Conf. 193-197.
- MacNaeidhe, F.S. (1972a) Pre- and Post- emergence weed control in drilled onions. Proceedings 11th British Weed Control Conf. 173-179.
- MacNaeidhe, F.S. (1972b) Evaluation of herbicides for post-emergence application in carrots. Proceedings 11th British Weed Control Conf. 202-207.
- MacNaeidhe, F.S. (1972c) Weed Control in Brassica Crops on organic soils. Proceedings 11th British Weed Control Conf. 143-149.
- MacNaeidhe, F.S. (1973) Weed control trials on peat. Research Report Horticultural Division, An Foras Taluntais, Dublin.
- MacNaeidhe, F.S. (1974) Weed control in lettuce on organic soil. Proceedings 12th British Weed Control Conf.
- O'Toole, L., Dallyn, S. and Cassidy, J.C. (1968) Vegetable production on cutover peat. Research Report Horticultural Division. An Foras Taluntais, Dublin. 39-43.
- Prendiville, M.D. (1972) Cultivar trials. Research Report Horticultural Division, An Foras Taluntais, Dublin, 24-25.

HUMUS AND STRUCTURE PROBLEMS IN LOWLAND BRITISH ARABLE SOILS.

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INTRODUCTION

Concern has been expressed in recent years over both the declining levels of organic matter in permanently cultivated fields in lowland Britain, and the continuing expansion of the acreage under such cropping. Where soils have been monitored for long enough periods the decline appears to follow an asymptotic form, with a levelling off at values between 1 and 3% after several decades of continuous cultivation. It has been questioned whether present farming methods can be maintained on soils of such low organic levels.

The concern over such reduction in organic content is not related to the influence of organic matter on soil fertility as many studies have demonstrated that balanced and well-timed applications of chemical fertilizers adequately control plant nutritional requirements. It is the influence of organic matter on soil physical conditions which has been stressed. This role has been acknowledged by the farming community for a long period, but because of the large number of components to soil structure and the complexity of organo-mineral associations, the mechanisms and magnitude of the effects of organic matter on soil physical behaviour are still disputed. It is also not easy to isolate structural effects on plant growth from the other effects of organic matter such as microbiological activity and water retention.

Definitions of what constitutes 'good' or 'bad' structure have proliferated in the literature, but in this country few structural situations could be considered totally limiting. The severity of the individual soil problem has to be

judged in the context of the crop requirements and the farming system under which it occurs. The present paper takes its data from the intensively cultivated silts and Boulder clay loams of East Anglia, where stress levels and crop requirements are both high. Nevertheless there are soil properties, plant responses and mechanisms of particle association which are common to most British arable structure problems, and may give more general relevance to the results.

The main types of structural problem encountered are

- i) mechanical instability as the result of externally applied forces, such as the passage of animals and machinery over or through the land, leading to surface and subsoil compaction, plough pans and puddling.
- ii) instability to sudden wetting, with resultant slaking, and dispersion, giving rise to crusted or capped surface soils.
- iii) adverse alterations to aggregation, generally as a result of untimely or inapplicable cultivations, resulting in surface tilths of poor crumbs size distribution and porosity features.

Major factors contributing to these features are

- a) marked profile stratification
- b) a textural class which predisposes the soil to instability to give naturally weak or massive structures.
- c) naturally poor drainage through topographic or parent rock situation.
- d) low levels of organic matter.
- e) clay containing swelling minerals or, infrequently, appreciable exchangeable sodium or potassium.

The soils selected for this study showed all the structural problems mentioned and came from the 'difficult' Beccles and Fen silt soils. Sites were chosen which had adjacent low and high organic matter levels as a result of management

differences. The site pairs had the same textures, mineralogy and topography.

EXPERIMENTAL STUDIES AND DISCUSSION

When the soils were tested in the laboratory, increased organic matter influenced every physical response in ways which were favourable for crop production. Summarising the results, higher organic matter contents gave greater available water contents, higher total and air filled porosities at each suction, increased the liquid limit and the plasticity index. There were concomitant decreases in bulk density, maximum compaction density and tensile strength. Particle density also correlated closely with total organic matter content. Values for the heaviest textured soils illustrate this point.

Table 1

Porosity features in the High and Low organic matter analogues of a silty clay loam (40% clay).

pF	Total porosity (cc/100cc)		Air-filled porosity.		Bulk Density (gm/cc)		Shrinkage (cc/100cc)	
	H	L	H	L	H	L	H	L
1.0	47.5	42.5	0	0	1.30	1.50	23.7	19.2
2.0	46.0	38.4	2.1	0.5	1.32	1.54	22.2	18.4
2.8	40.9	32.9	5.4	1.1	1.46	1.75	14.3	8.8
3.2	38.7	30.0	10.6	7.0	1.50	1.82	8.7	5.2
4.2	29.3	26.5	12.8	13.4	1.71	1.93	2.8	0.8

Structural stability is frequently measured by some sort of wetting treatment. With the rather narrow range of textural and pedogenic classes used here, it was found that some frequently used tests were insufficiently sensitive to discriminate effectively between sites, or were of low reproducibility. Childs' (1940) method of comparing the pore

size distribution curves of slow and fast wetted moisture characteristics, proved to be the most effective (Fig. 1). The ratio of the peak heights obtained from this test provide a measure of stability. The high organic matter analogues all had higher ratios than their counterparts and the values gave a positive correlation of three star significance with the organic matter content of the material in the soil of 20-50 μ size, separated by short ultrasonic treatment.

To establish what aspects of the organic matter were thus responsible for aggregate stability to wetting, a set of experiments were carried out to extract different constituents and measure the alteration in permeability of beds of soil crumbs. The extracting reagents included 5% Na_2CO_3 , a specific polysaccharide extractant, $-\text{NaIO}_4$ followed by $\text{Na}_2\text{B}_4\text{O}_7$, $\text{Na}_2\text{B}_4\text{O}_7$ as a control, $\text{Na}_2\text{P}_2\text{O}_7$ as a strong metal complexing reagent, and acetyl acetone specifically to remove co-ordinated Al and Fe. A further set of shaken extracts also included acidified CaCl_2 to remove hydroxy-Al, and dithionite-citrate to extract iron oxides.

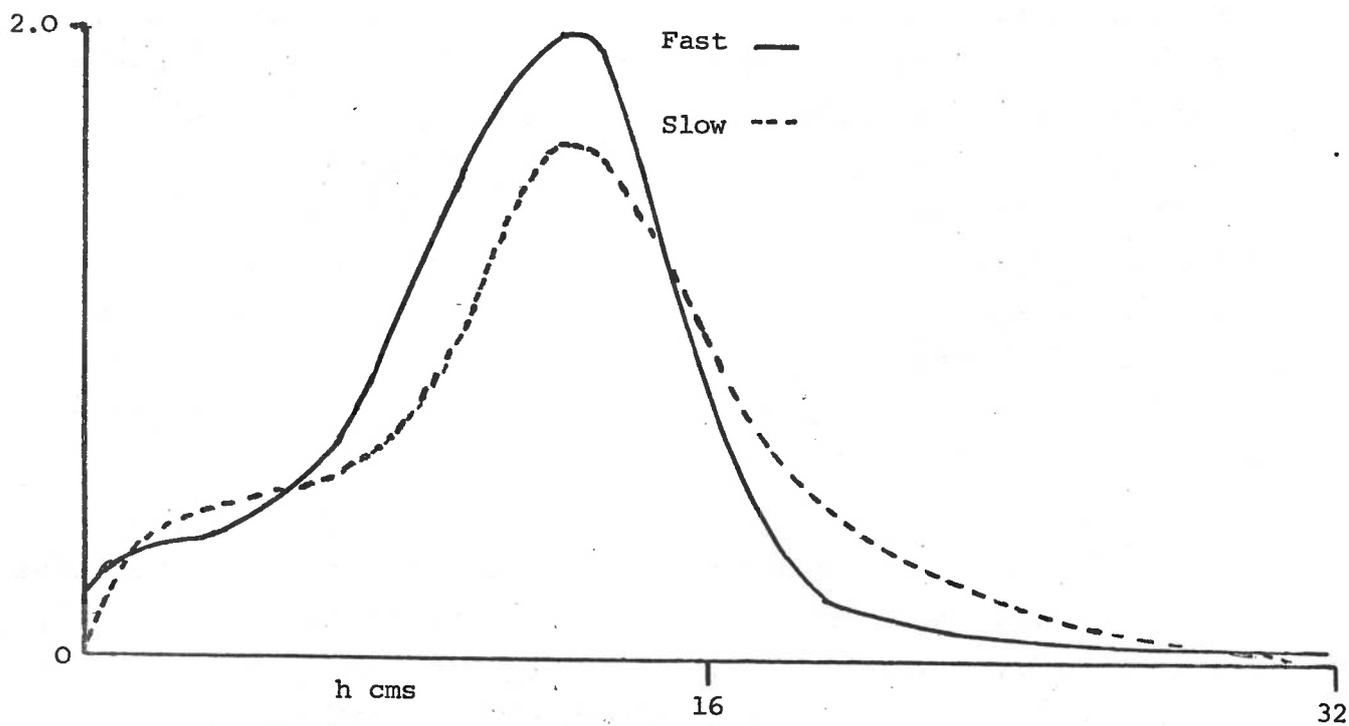
The results showed the high organic matter soils were more stable to each reagent. Pyrophosphate was the most effective overall in reducing permeability, but acetyl acetone was equally or more rapidly effective on the low organic analogues. Periodate plus borate was only moderately effective, and the major part of the reduction could be attributed to the borate ion. The effect of the dilute carbonate was similar to borate. The Beccles sandy clay loam also slaked in the wash liquid of 0.1M NaCl. The occurrence of montmorillonite in this soil explained the instability to this level of electrolyte concentration.

From an analysis of the extracted leachates it was concluded that Al was the most significant metal involved in the organo-mineral combinations. Two forms of Al were equally important; the co-ordinated ionic type in 'bridging' situations, and the hydroxy-polymers in clay or clay-organic interfaces. The role of uncharged polysaccharides appears to be small, but both

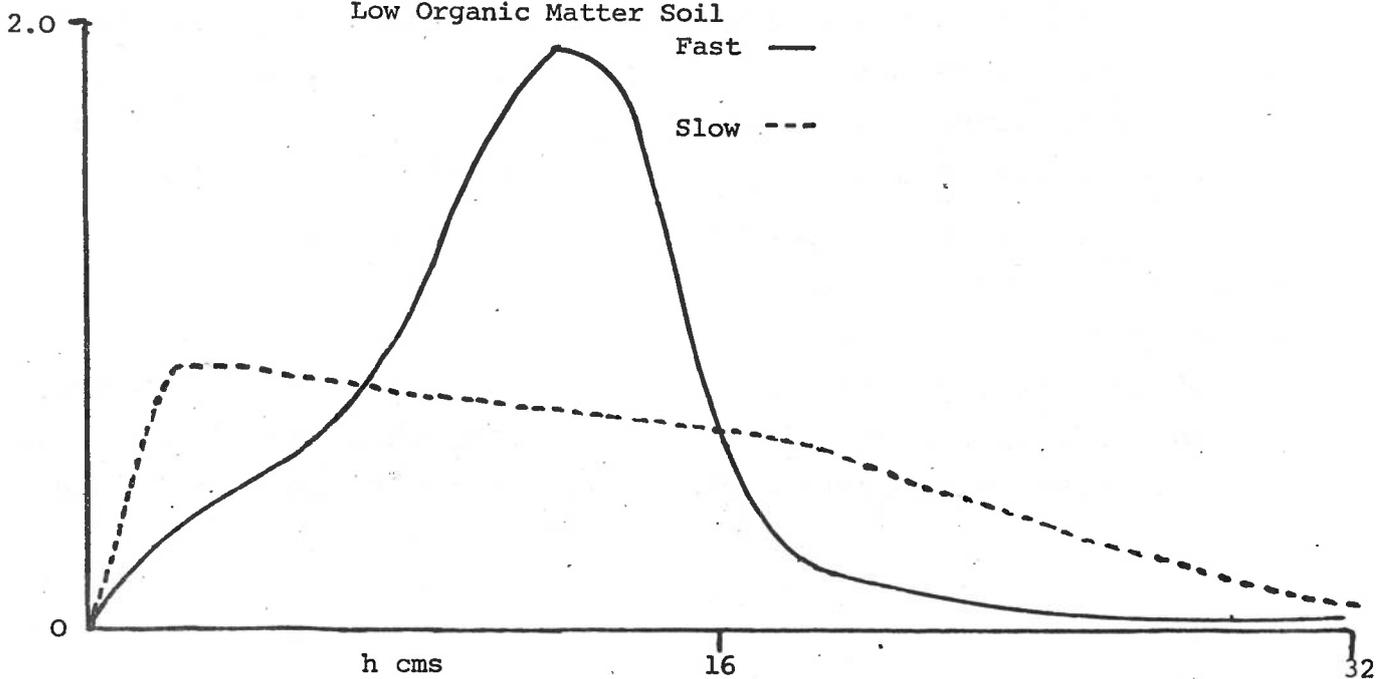
Figure 1

Slow and Fast Wetting Curves Extrapolated to display the Pore Size Distributions for Suctions up to 40 cms. for a Silty Clay Loam.

High Organic Matter Soil



Low Organic Matter Soil



fulvic and humic charged groups may be involved in the association with metals.

The ultrasonic treatment referred to previously, dispersed the low organic matter soils more than the others. The amount of carbon retained in each size fraction was also found to vary consistently between high and low sites, with more of the total organic matter present in the clay sized fraction of the low sites. The organisation of clay, silt and organic matter into stable aggregates of the silt sized dimensions (particularly 20-50 μ) would appear to be lower in soils with a net organic matter loss. Where organic matter is lost, some of the associated Al and Fe is also lost, and the remaining mineral complexes more readily decomposed.

The situation so far described refers to soils tested in the laboratory, in the field many studies have been undertaken to relate physical conditions to crop yield. The results have frequently been inconclusive but as yield, like structure itself, is a composite feature of which soil conditions are only some of a large number of environmental factors, this is not too surprising. It seemed more realistic initially to look only for differences in rooting behaviour. Two sites were studied; a silt loam where the high level site had been out of grass for 16 years and was sown to winter wheat, and a silty clay loam where the high level site had been out of grass for 6 years and was sown to sugar beet. The soils and roots were sampled by means of a hollow, hammer operated corer to a depth of 80 cms and the cores were cut into 5 cm sections to estimate root number, moisture, nitrate content, bulk density and total and air filled porosities.

Differences in rooting were observed in both sites between the two organic matter levels.

Taking the sugar beet first:- the crop was drilled during a very dry spring, and emergence was considerably affected by the cool, dry weather which continued till the end of May, 1974. Emergence was eventually about 55% on the high organic

matter side and only about 7% on the low side. The condition of the two seed beds were found to have been the decisive factor in this difference. Clod size was on average smaller with fewer big clods in the high level plot, and this in turn influenced the real drilling depth. Although set for 3.1 cms, the drill had actually penetrated to 3.8 cms in the high level plot, and only to 1.8 cms in the low level plot. The extra depth provided necessary moisture as the surface 2 cms on both sites were very dry. Once germinated the greater water content of the high level soil, 38% as against 27%, allowed better and more rapid root extension. By late May the average root weights were 257 and 95 gms respectively, and the plants on the low level side never caught up.

In the case of the winter wheat, Figures 2 and 3, the situation was more complex. By March the crop had already rooted to a depth of 65 cms on the low level soil and over 80 cms on the high level. There were noticeable differences in bulk density and moisture content in the top 35 cms of the soil, while the nitrate level was higher in the high plot subsoil. By May the degree of root proliferation was greater on the high level plot while the difference in bulk density in the top soil was even more marked, presumably as a result of greater shrinkage upon drying giving larger cracks through the soil. Both soils had good values for air filled porosity by this stage. Nitrate had almost completely disappeared from the low level plot by this stage.

It is suggested that initial establishment was more rapid and to a greater depth in the autumn on the high level side (although unfortunately this was not sampled) because of the more rapid return to field capacity of this soil after a dry autumn. Lower soil density would have aided root extension through this period. Higher organic matter levels would have stimulated the production of nitrate in the topsoil, providing additional encouragement to pre-winter growth. In February rain would have leached nitrate into the subsoil, but this was then to the benefit of the secondary growth of rooting in the spring, as dry

Figure 2

Numbers of Roots, Bulk density, Nitrate level, and Water content in the first 80 cms of a Silt Loam in March 1974.

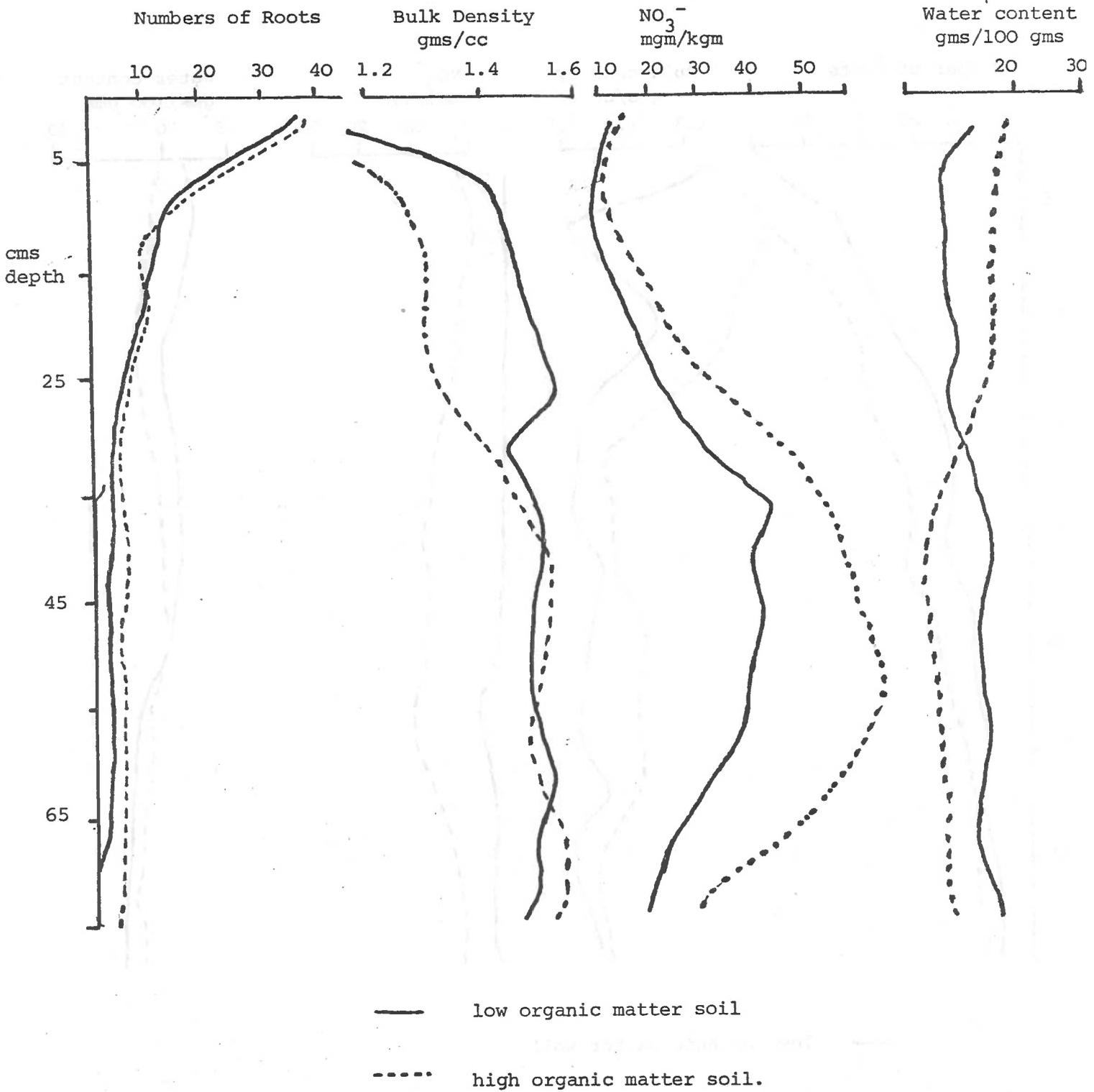
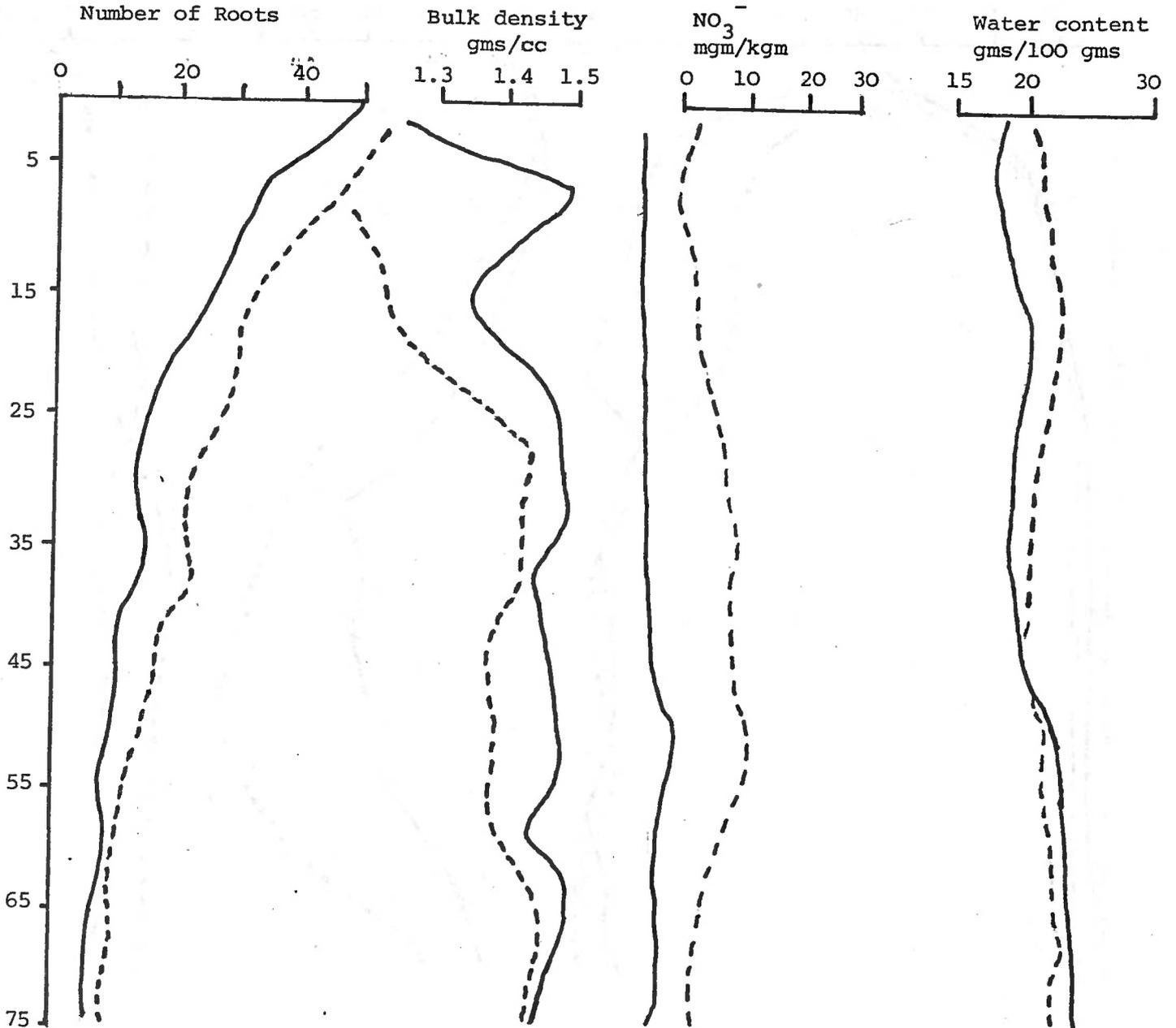


Figure 3

Number of Roots, Bulk density, Nitrate level and Water content in the first 80 cms of a Silt Loam in May 1974.



— low organic matter soil

- - - high organic matter soil.

weather from March onwards ensured that this subsoil nitrate was not removed completely from the profile.

There was therefore both a structural and a nutritional effect of organic matter on this site. Different factors were influential at different stages of growth. A small positive difference in yield was eventually recorded, although the high level crop was slower to mature, having made additional vegetative growth. This example comes from an unusually dry year. In wet years the soils would respond very differently, yet still to the advantage of the high organic level plot. This soil is known to recover more rapidly from the effects of late wet harvesting conditions, to drain more rapidly after heavy rain and to compact less when cultivated at high moisture contents.

The situation which has been described concerns soils with an unusually high proportion of very platy silt particles. Upon microaggregate disruption such particles, together with the platy clay packets, will align themselves in parallel orientation when subjected to external stresses, or possibly even with drying conditions. A pore geometry results which is very far from the idealised circular model, and large scale cracking is of low incidence in soils of rather low clay content. In soils of different textural assemblages the prevailing form of mineral association may differ, but the importance of the role of organic matter to small aggregate stability may well be very similar. In soils containing swelling clays the instability resultant upon organic matter decline seems to be greater, and to occur at higher organic matter values than in soils containing minerals of moderate charge and swelling behaviour, such as illites or chlorites.

The benefit of incorporated organic matter, in the form of leys, straw etc. is likely to be small in most structural situations. Most studies have concluded that the residual effects were generally nutritional although increased water holding capacity could be of benefit, and improved porosity and reduced shear strength might also result. Such amelioration would only be

possible where a pore size distribution already existed which would allow complete aerobic decomposition to occur; this is frequently not the case in practice. The stability of the soil to water or combined water and mechanical stress would seem to depend largely upon the processes of long term humification and microbiological action. Thus in intensive continuous arable systems farm management must ensure the least damage, through the use of careful cultivation techniques, suitable rotations and adequate drainage. Where low levels of organic matter already exist farming must frequently accommodate to this less than optimal condition, unless soil conditioners and direct drilling can be employed in the future.

REFERENCE

E.C. Childs, The Use of Soil Moisture Characteristics in Soil Studies. Soil Science 50 (1940), 239.

THE ASSESSMENT OF BIOLOGICAL ACTIVITY IN SOILS

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ENERGY-LINKED REACTIONS

During the late 1950's and early 1960's, soil microbiologists tended to move from the identification of isolates and the estimation of populations to the study of the role of micro-organisms in soil processes. This led to increased interest in methods for estimating the activity of soil micro-organisms. There is often a considerable discrepancy between bacterial counts obtained by dilution plate methods and by direct observation, possibly due to cells clumping or differences in the ability of cells to grow on culture media (Burgess, 1966). Fungi present even more difficult problems. Levels of activity may be different in different parts of the mycelium. A pressing problem for microbiologists at present is how to determine the level of metabolic activity of living hyphae.

One way of looking at this problem is to study the processes involved in free energy changes in the organisms. It is a basic property of living organisms that they need a continuous flux of energy to drive a whole range of metabolic activities. Fundamental to this energy flux is respiration, a spontaneous process in the sense that it proceeds with an overall loss of free energy to the organism and the foodstuff. This free energy is defined as the maximal amount of energy available to do work when the foodstuff is oxidised at constant temperature and pressure to carbon dioxide and water. The adoption of the carbon dioxide and water level as the reference level for energy changes is a biological convention, and differs from the physico-chemical one. The part that respiration plays is twofold,

first it promotes intermediate compounds from which further living matter may be built, second, it canalises the energy flux into paths promoting the same end (James, 1971).

The first tool available for the measurement of respiration in tissues and cell cultures was measurement of oxygen uptake and carbon dioxide evolution. In the simple, controlled, conditions of tissue and cell suspensions, the interpretation of such measurements may not be too difficult. However, although measurements of oxygen uptake and carbon dioxide evolution are frequently made on soils, their interpretation requires some caution. For example, there may be in soil some inorganic reactions involving carbon dioxide, or it may be that the presence of anaerobic zones in crumbs in even well-drained soil (Greenwood, 1961) may complicate the gas-exchange picture. Enzymatic oxygen uptake may also occur which is not related to the 'mainstream' respiration (see below).

As understanding of the enzyme systems involved in respiration increased, there seemed to be the possibility that the rate of oxidation of substrates might be measured by the activities of appropriate enzymes. The oxidation of organic compounds most commonly occurs by the removal of hydrogen, i.e. by dehydrogenation. This process is catalysed by a class of enzymes called dehydrogenases, which are often specific to one substrate (Baldwin, 1952). Oxidation chains are not identical in all cells, nor is it clear that any given cell has only one. Nevertheless, there is one chain now known to occur very widely and to be likely to account for at least a major part of the respiration when it is present. It may perhaps be regarded as the main aerobic pathway in the final stages of cell respiration but probably shows considerable variation (James, 1971). In this pathway, the hydrogen is transferred through a chain of intermediate carriers, nicotinamide adenine dinucleotide (NAD), flavoprotein, and cytochromes, which finally use oxygen as a hydrogen acceptor to form water (James, 1971;

Yudkin and Offord, 1971). Some of the energy released, is used to synthesise adenosine triphosphate (ATP) and other "high energy" compounds, which are used as energy sources for the energy-requiring processes of the organism. In anaerobic metabolism, the hydrogen is used in the synthesis of a variety of end products. The efficiency of anaerobic respiration in terms of energy transfer is lower than in aerobic respiration (James, 1971).

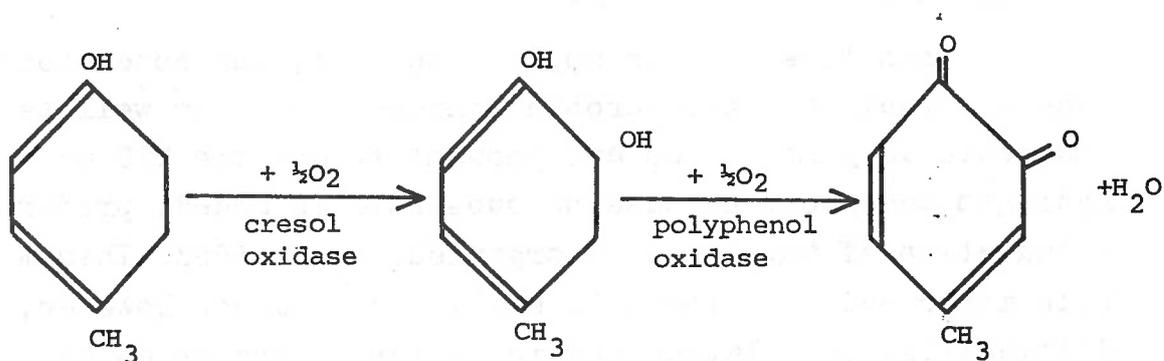
It is clear that if we could measure the rate of activity of one or more enzymes in the respiratory chain, we might get a measure of the rate of energy transfer. Efforts in this field have been aimed chiefly at the dehydrogenases. It has long been known that certain organic compounds can act as hydrogen acceptors for dehydrogenases in vitro (Baldwin, 1952). Lenhard (1956) appears to have been the first to use 2,3,5-triphenyltetrazolium chloride (TTC) to study microbial activity in soil. In theory, in the absence of oxygen, TTC acts as the terminal hydrogen acceptor for dehydrogenase systems, with the formation of coloured triphenylformazan (TPF) which can be determined colorimetrically.

When this test is applied to soil, the conditions are made anaerobic and the aerobic dehydrogenases as well as the anaerobic dehydrogenases are thought to use the TTC as a hydrogen acceptor. Because no substrate is added, preferential stimulation of any group of organisms is avoided. This method, with minor modifications, is still widely used. However, difficulties in relating TPF formation to oxygen uptake (Howard, 1972) or carbon dioxide evolution (Novak and Kubat, 1972) led us to doubt the efficiency of TTC as a hydrogen acceptor in the conditions used in this test. We have been experimenting with a different tetrazolium compound, 2-P-iodophenyl-3-P-nitrophenyl-5-phenyltetrazolium chloride (INT), which appears to be more efficient as a hydrogen acceptor (Benefield et al, in prep.). However, this method should be regarded with suspicion until more is known about the efficiency of the hydrogen acceptor. Benefield has also attempted to measure the rate of transfer of hydrogen by NAD, but without success. It seems likely that the main

respiratory enzymes and acceptors are so tightly linked in the cell that it is extremely difficult to break into the system.

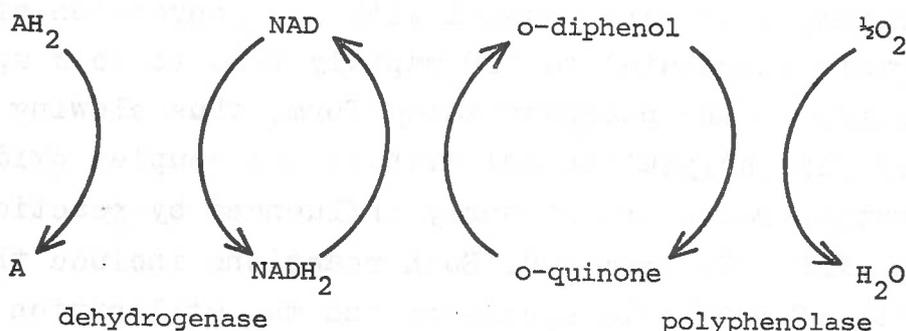
Some of the oxidative enzymes can exist and function outside living cells, although it is not known how long they can survive free in soil. James (1971) states that the dehydrogenases as a class are 'soluble', i.e. readily brought into an aqueous solution outside the living cell without losing their activity. Furthermore, the activities of any pair of dehydrogenases that use NAD to transfer hydrogen could, in theory, be linked. Such an effect has been demonstrated in certain cases. This is of great interest in connection with the polyphenolase reaction described below.

There are enzymic oxidations not directly linked with the main stream of respiration. Perhaps the most important of these in soils are the phenol oxidases, a rather complex group of enzymes coming from a multiplicity of sources. James (1971) suggests that they fall into two groups, the cresolases and the laccases. The cresolases have a two fold reaction, e.g.



The cresolase and polyphenolase activities may be due to two separate enzymes, but so far they have defied separation and are usually regarded as depending on two sites on the same enzyme. Laccases have no monophenolase activity. The quinones formed as the primary products of such activities are highly susceptible to further oxidation and condensation with, for example, amines and amino acids. The most striking feature of phenolase activity is the extent to which it runs wild after

mechanical or other damage to living cells, or at senescence, when the cell structure is beginning to break down (James, 1971). It is possible to obtain smooth-running systems in vitro in which the o-quinones from polyphenolase reaction readily oxidise natural reductants such as NADH_2 , e.g.



Work in our laboratory has shown that observed soil dehydrogenase activity (using INT acceptor as well as TTC) fails to account for a substantial proportion of the observed oxygen uptake (Benefield et al., in prep.). No doubt this is partly due to the inefficiency of the tetrazolium compounds as hydrogen acceptors, but it may also be due to open phenol oxidase systems, i.e. those not linked with other hydrogen acceptors such as NAD. Phenolic materials occur in soils, and may come from a variety of sources such as polyphenols from plant litter (Coulson et al., 1960), products of lignin break down in soil (Hurst and Burges, 1967) or synthesis by micro-organisms. Baldwin (1952) pointed out that once a quinone has been formed from the corresponding phenol, a series of reactions can take place spontaneously yielding a hydroxyquinone which then undergoes polymerization to yield complex, dark-coloured, products. It has been suggested that humic acids are formed by similar processes and also involving nitrogenous compounds (Kononova, 1966; Flaig, 1966; Swaby and Ladd, 1966). Such reactions could account for some of the oxygen uptake, and it is possible that some such reactions could occur outside living cells. Some enzymes can exist and function in soils outside living cells (Skujins, 1967; McLaren, 1974) so it is not too difficult to understand why observed enzyme activity rates may not correlate well with numbers of organisms. This

aspect especially needs further study.

As mentioned earlier, ATP is used in cells to couple the basic energy sources to the energy-requiring processes of the organism. The total concentration in cells of ATP plus the diphosphate ADP is always small, and mature cells have little ability to synthesize either compound de novo. It follows that oxidations, which are coupled with the conversion of ADP + Pi (inorganic phosphate) to ATP rapidly tend to lock up the nucleotide in the phosphorylated form, thus slowing down the rate of phosphorylation and with it the coupled oxidation. Hence respiration rates are strongly influenced by reactions which release ADP + Pi from ATP. Such reactions include the great majority of metabolic syntheses and the utilisation of energy in flagellar activity (James, 1971). It would clearly be very useful to be able to measure the rate of turnover of ATP by soil organisms, but so far this has not proved possible.

DEGRADATIVE REACTIONS

Another approach is to study the conversion of specific substrates in soil. For example, cellulose is a major constituent of plants and its decomposition is of some importance. Cellulose may be defined as long-chain molecules of D-glucopyranose linked 1-4 β with a molecular weight of at least 1.5×10^6 , which represents a degree of polymerisation of 9200 (Rogers, 1961). The breakdown of cellulose by soil organisms may be studied in a variety of ways. Some workers (e.g. Grossbard, 1973; Heal et al., 1974) have placed cotton strips in soils and measured the change in tensile strength after a period of time. Although this method gives a quantitative measurement, it is by no means clear what it means, since the mechanisms by which the tensile strength is changed are largely unknown. The structure of cotton fibres is complex. It seems to be generally agreed that the glucose units are linked together to give a somewhat kinked but rather rigid chain about 20,000 Å long and 7.5 Å wide. This

structure alone, however, is not sufficient to account for the physical properties of cellulose fibres (Rogers, 1961). The strength of cotton fibres depends on many structural features, such as the average chain lengths of the molecules, their homogeneity, and orientation. A close correlation has been found between the strength of a fibre and the degree of polymerisation of the component cellulose molecules (Siu, 1951). Bundles of chains are thought to be held together by hydrogen bonds and van der Waals' forces to form microfibrils about 50 Å in diameter. Few, if any, cellulose chains cross from one microfibril to another, and the microfibrils are built up into layers (Selby, 1968).

The mode of breakdown of cotton fibres by soil organisms is not fully understood. The most obvious enzymatic attack on cellulose would be non-specific hydrolysis of the glycosidic linkages leading eventually to glucose. The available evidence suggests that this is the case. A consequence of random severing of the glycoside linkages in cellulose of cotton fibres would be to bring about a reduction in both the chain length of the molecules and their homogeneity. In this way, the tensile strength would be expected to fall without much loss of cellulose units. The relationship between tensile strength and weight loss suggests such an effect (Siu, 1951; Selby, 1968). Furthermore, Halliwell (1965), found that enzymatic degradation of purified cotton fibres suggested a random breakdown in the substrate with the release of 1) insoluble, non-filter-passing, very short fibres, 2) insoluble, filter-passing products, 3) soluble products, mainly glucose. Nilsson (1974) found that 15 out of 20 fungal species tested could produce cavities in cotton fibres and 18 species could produce surface erosion. Localized effects of this type could produce a loss of tensile strength with small weight loss. At present it is difficult to see what meaningful conclusions can be drawn from tensile strength measurements of cotton strips.

By contrast, if we regard the decomposition of cellulose

by micro-organisms as serving to release glucose units which can be used in respiration, then it is reasonably easy to measure the rate of release of such units (Benefield, 1971). Similarly, there are a whole range of specific biochemical activities occurring in soils which can be readily determined, many of them involving enzymes (e.g. Skujins, 1967). The study of soil enzymes is relatively new but although much work remains to be done in developing and improving techniques, many interesting results have been obtained. For example, Ross and Roberts (1970) obtained correlations of some carbohydrase activities with environmental and soil factors in New Zealand pastures, and effect of herbicides on soils enzymes have been demonstrated (Namdeo and Dube, 1973; Voets et al., 1974).

VARIATION OF ACTIVITY WITH TIME

One problem in comparing biochemical or physiological properties of different soils has been that such properties usually show marked variations with time, often over short periods. It is therefore necessary to sample the soils at intervals, and the problem then is to find some way of comparing the overall performance of different soils, and of allowing for the occurrence of occasional or unique measurements which are unusually high or low. This problem may be illustrated using data for dehydrogenase (using TTC), cellulase, and phosphatase activities as well as oxygen uptake (laboratory), moisture content, pH and loss-on-ignition of soils from 48 woods in Cumbria (Howard and Benefield, 1970). This work was largely a feasibility study of the collection and handling of such data for comparative purposes. The data have not yet been fully analysed, and full results will be published elsewhere.

One quadrat of 1.6 x 1.6 m, subdivided into 20 x 20 cm sampling squares, was laid out in each wood. Each wood was visited once every four weeks for a total of 56 weeks and on

each occasion a sample was collected at 0 to 5 cm from a randomly chosen square. Measurements were made on soils passed through a 4 mm sieve in the fresh condition. The data were examined by principal component analysis, the 14 different sampling times for each property measured being considered as variables. Briefly, principal component analysis is a method of displaying relationships among multivariate data (see Seal, 1968). The original observations are referred to a set of axes which are the original variables measured (or in our case the 14 different samplings). By a mathematical transformation, each original observation is referred to a new set of axes, or components, which are orthogonal (i.e. uncorrelated). The meaning of these components has to be interpreted, and to assist in the interpretation we have, for each component, an eigenvalue and an eigenvector. The eigenvalue gives the proportion of the variability accounted for by that component. The eigenvector is a vector of values, one for each original variable, or in our case sampling time, and gives an indication of the contribution of each original variable to that component.

With our data the first component represents the relative positions of the sampling plots with respect to each property. The other components were found to represent some aspect of variation between samples, in time (or in space within the sampling quadrat). That is, if all the soils showed a change in a property with time, and all changed at a similar rate, then there would be no variation between soils with time, and the first component would account for most of the total variability. The same would apply if the property showed no variation at all with time. On the other hand, if a soil behaved differently from the others, this would appear in a separate component and would reduce the proportion of the variability accounted for by the first component. Thus, with pH, which we would not expect to show measurable variation within a year, the first component accounted for 92% of the variability and the second component only 2%. Similarly, the first component of loss-on-ignition

accounted for 77% of the variability and the second component 5%. It is interesting that for moisture content (oven dry basis), which might be expected to show fairly pronounced between-site differences over a year, the first component accounted for 75% of the variability and the second 7%. When orthogonal polynomial regressions of moisture content on time were fitted for each soil it was found that of the 48 soils, 11 showed significant linear trends and only three had a significant quadratic term, which one would expect if there was a regular seasonal variation. The remaining properties (oven dry basis) are shown in Table 1.

Table 1

Statistical analysis of activity data.

Enzyme activity (O D basis)	% of variability accounted for	
	by first component	by first n components
phosphatase	59	83 n = 4
cellulase	38	83 n = 5
dehydrogenase	48	84 n = 4
oxygen uptake	56	72 n = 3

It is interesting to examine the coefficients of correlation between the first component values of the various properties. On an oven-dry basis (Table 2) certain of the properties are significantly correlated, but the fact that most are significantly correlated with loss-on-ignition, may explain some of the other correlations. If the effects of the different organic matter contents of the soils are removed by expressing the results on a per gram loss-on-ignition basis (Table 3) it is seen that the only highly significant correlations are between respiration and phosphatase ($R = 0.616$, $R^2 = 0.379$) and between

cellulase and dehydrogenase ($R = -0.637$, $R^2 = 0.406$). The R^2 values give the proportion of the variability accounted for by the regression, and in these cases it is clearly less than half. This suggests that a soil which is high in one activity is not necessarily high in other activities. It is also worth noting that there are no significant correlations between the first component of monthly mean temperatures and any of the other properties, that is, there is probably no simple relationship between yearly temperatures and any of the activities. This is scarcely surprising when one considers the wide range of factors which can influence respiration and enzyme activities in soils.

The conclusion to be drawn from this review seems to be that there is no single method suitable for determining the level of 'biological activity' in soils because the term 'biological activity' covers such a broad spectrum of individual activities and processes. The level of activity of a specific process (e.g. cellulose decomposition) does not tell us anything about other processes which may be taking place. At the moment, it seems that it will be most rewarding if several activities are studied simultaneously.

ACKNOWLEDGEMENTS

In the work on the Cumbrian woods, cellulase and dehydrogenase activities were measured by Mr. C.B. Benefield, phosphatase activity by Dr. A.F. Harrison and Mrs. H.T. Pearce, respiration by Mrs. D.M. Howard, and temperature by Mr. K.L. Boccock, Mr. A.D. Bailey and Mr. J.K. Adamson.

Table 2

Correlation coefficients of first component values
Oven-Dry basis.

Parameters	Correlation Coefficients						
	B	C	D	E	F	pH	Temp
A	0.431**	0.899***	-0.008	0.733***	0.866***	-0.497***	-0.029
B	1	0.435**	0.538***	0.449**	0.462**	-0.067	0.095
C		1	-0.005	0.729***	0.794***	-0.421**	-0.058
D			1	0.047	0.063	0.281	0.102
E				1	0.878***	-0.464**	-0.028

Parameters A. respiration rate D. Dehydrogenase
 B. Cellulase E. Moisture Content
 C. Phosphatase F. Loss-on-ignition

** significant at 1% level

*** significant at 0.1% level

Table 3

Correlation coefficients of first component values
Loss-on-Ignition basis

Parameters	Correlation Coefficients					
	B	C	D	E	pH	Temp
A	-0.201	0.616***	0.061	-0.182	0.231	0.019
B	1	-0.249	-0.637***	0.298*	-0.439***	-0.076
C		1	0.100	-0.219	0.259	-0.003
D			1	-0.298*	0.575***	0.136
E				1	-0.464**	-0.028

Parameters A. respiration rate D. Dehydrogenase
 B. Cellulase E. Moisture Content
 C. Phosphatase

* significant at 5% level

** significant at 1% level

*** significant at 0.1% level

REFERENCES

- Baldwin, E. (1952) *Dynamic Aspects of Biochemistry*. Cambridge: University Press, 544 pp.
- Benfield, C.B. (1971) A rapid method for measuring cellulase activity in soils. *Soil Biol. Biochem.* 3, 325-329.
- Burges, A. (1966) The estimation of the activity of micro-organisms in the soil. *Rev. Roum. Biol. Ser. Bot.* 11, 57-60.
- Coulson, C.B., Davies, R.I. and Lewis, D.A. (1960) Polyphenols in plant, humus, and soil. 1. Polyphenols of leaves, litter, and superficial humus from mull and mor sites. *J. Soil Sci.* 11, 20-29.
- Flaig, W. (1966) The Chemistry of Humic Substances. In "The Use of Isotopes in Soil Organic Matter Studies", 103-127, New York: Pergamon Press.
- Greenwood, D.J. (1961) The effect of oxygen concentration on the decomposition of organic materials in soil. *Plant and Soil* 14, 360-376.
- Grossbard, E. (1973) Rapid techniques for the assessment of the effect of herbicides on soil micro-organisms and cellulolytic activity. *Bull. Ecol. Res. Comm. (Stockholm)*. 17, 473-474.
- Halliwell, G. (1965) Hydrolysis of fibrous cotton and reprecipitated cellulose by cellulolytic enzymes from soil micro-organisms. *Biochem. J.* 95, 270-281.
- Heal, O.W., Howson, G., French, D.D. and Jeffers, J.N.R. (1974) Decomposition of cotton strips in Tundra. In "Soil Organisms and Decomposition in Tundra", 341-360. Eds. A.J. Holding, O.W. Heal, S.F. Maclean, and P.W. Flanagan. Stockholm: Tundra Biome Steering Committee.
- Howard, P.J.A. and Benfield, C.B. (1970) Selection of characters for the classification of soil humus types. Merlewood Research and Development Paper No. 21, 9 pp.
- Howard, P.J.A. (1972) Problems in the estimation of biological activity in soil. *Oikos*, 23, 235-240.
- Hurst, H.M. and Burges, N.A. (1967) Lignin and Humic Acids. In "Soil Biochemistry" Vol. 1, Eds. A.D. McLaren and G.H. Peterson, 260-286. London: Edward Arnold.
- James, W.O. (1971) *Cell Respiration*. English Universities Press. 138 pp.

- Jones, P.C.T. and Mollison, J.E. (1948) A technique for the quantitative estimation of soil micro-organisms. *J. gen. Microbiol.* 2, 54-69.
- Kononova, M.M. (1966) *Soil Organic Matter*. 2nd English Edition. London: Pergamon Press, 544 pp.
- Lenhard, G. (1956) Die dehydrogenaseaktivitat des Bodens als Mass fur die Mikroorganismenaktivitat im Boden. *Z. PflErnahr. Dung.* 73, 1-11.
- McLaren, A.D. (1974). *Soil as a system of bound enzymes*. *Chemistry and Industry*, p.316.
- Namdeo, K.N. and Dube, J.N. (1973) Residual effect of urea and herbicides on hexosamine content and urease and proteinase activities in a grassland soil. *Soil Biol. Biochem.* 5, 855-859.
- Nilsson, T. (1974) Microscopic studies on the degradation of cellophane and various cellulosic fibres by wood-attacking microfungi. *Studia forestalia Suecica* Nr. 117, 32 pp.
- Novak, B. and Kubat, J. (1972) On the relation between dehydrogenase activity and CO₂ evolution in soil. *Zbl. Bakt. ParasitKde* 127, 246-252.
- Rogers, H.J. (1961) The dissimilation of high molecular weight substances. In "The Bacteria, Vol. 2 Metabolism", Eds. I.C. Gunsalius and R.Y. Stanier. 257-318. New York and London: Academic Press.
- Ross, D.J. and Roberts, H.S. (1970) Enzyme activities and oxygen uptakes of soils under pasture in temperature and rainfall sequences. *J. Soil Sci.* 21, 368-381.
- Seal, H. (1968) *Multivariate Statistical Analysis for Biologists*. London: Methuen, 209 pp.
- Selby, K. (1968) Mechanism of biodegradation of cellulose. In "Biodeterioration of Materials" Eds. A.H. Walters and J.J. Elphick. 62-78. London and New York: Elsevier.
- Skujins, J.J. (1967) Enzymes in soil. In "Soil Biochemistry Vol. 1" Eds. A.D. McLaren and G.H. Peterson. 371-414. London: Edward Arnold.
- Siu, R.G.H. (1951) *Microbial decomposition of cellulose*. New York: Reinhold. 531 pp.
- Swaby, R.J. and Ladd, J.N. (1966) Stability and origin of soil humus. In "The Use of Isotopes in Soil Organic Matter Studies", 153-159. New York: Pergamon Press.

Voets, J.P., Meerschman, P. and Verstraete, W. (1974) Soil Microbiological and biochemical effects of long-term atrazine applications. *Soil Biol. Biochem.* 6, 149-152.

Yudkin, M. and Offord, R. (1971) *A Guidebook to Biochemistry*. Cambridge: University Press. 195 pp.

QUESTION

Dr. Adams: Do you consider moisture content as percent oven dry weight or as coefficient of humidity to be a satisfactory assessment of moisture state against which to compare, for example, cellulase activity? You mention that correlations between variables was relatively low. Have you any facility to take into account the possibility that one variable depends on the interplay of two other variables, e.g. enzyme activity depends upon moisture state and soil temperature?

REPLY

Mr. Howard: Soil water presents special problems, because it is part of a complex associated with texture, structure, and gas exchange. As far as water itself is concerned, the volume of water needed for the formation of a few centimetres of hyphae or a few million bacteria is so small that it will be contained within one gram of many apparently dry soils. The microbiological importance of soil water lies in the other properties with which it is correlated (Griffin, 1972).

Soil moisture can be measured as matric, osmotic, gravitational, and pneumatic potentials, or the total of these. In soil microbiology, the gravitational and pneumatic potentials relevant to the system are normally zero, so that the total potential and the water potential (osmotic plus matric) become the same (Griffin, 1972).

Most fungi are restricted, as far as reasonably rapid growth is concerned, to potentials exceeding -60 or -80 bar, while bacteria are, in general, limited to potentials greater than -100 bar. For a loam soil, the lower limit would be about 5% moisture (Oven Dry basis) and for a clay soil about 15% (Griffin, 1972). In our work we have not so far observed values as low as this, and so we conclude that in the soils with which

we are working, moisture as such is not limiting microbial activity. Associated factors, such as aeration and solute mobility, are more likely to be important.

In reply to the first part of the question, a great deal depends on the objectives of the research. If the aim is to study the effect of water specifically as water, then clearly the gravimetric method is not adequate. However, this method is of use in ecological studies such as ours, where one is interested in the complex of properties associated with water content.

In reply to the second part of the question, the answer is that this could be done, but not in this project, which was designed to investigate the feasibility of making between-soil comparisons in levels of activity. The design of the experiment would be different if the aim were to study the effects of temperature, moisture, and interactions, on the levels of the processes in different soils. I mentioned the results of the correlations between first component values to illustrate the fact that a site which ranked high in one activity did not necessarily rank high in other activities, and that there were no simple rankings related to temperature or moisture (gravimetric).

Griffin, D.M. (1972) Ecology of Soil Fungi. London: Chapman and Hall. 193 pp.

PART II

LABORATORY STUDIES ON SOIL HUMUS

THE COMPOSITION OF SOIL HUMUS

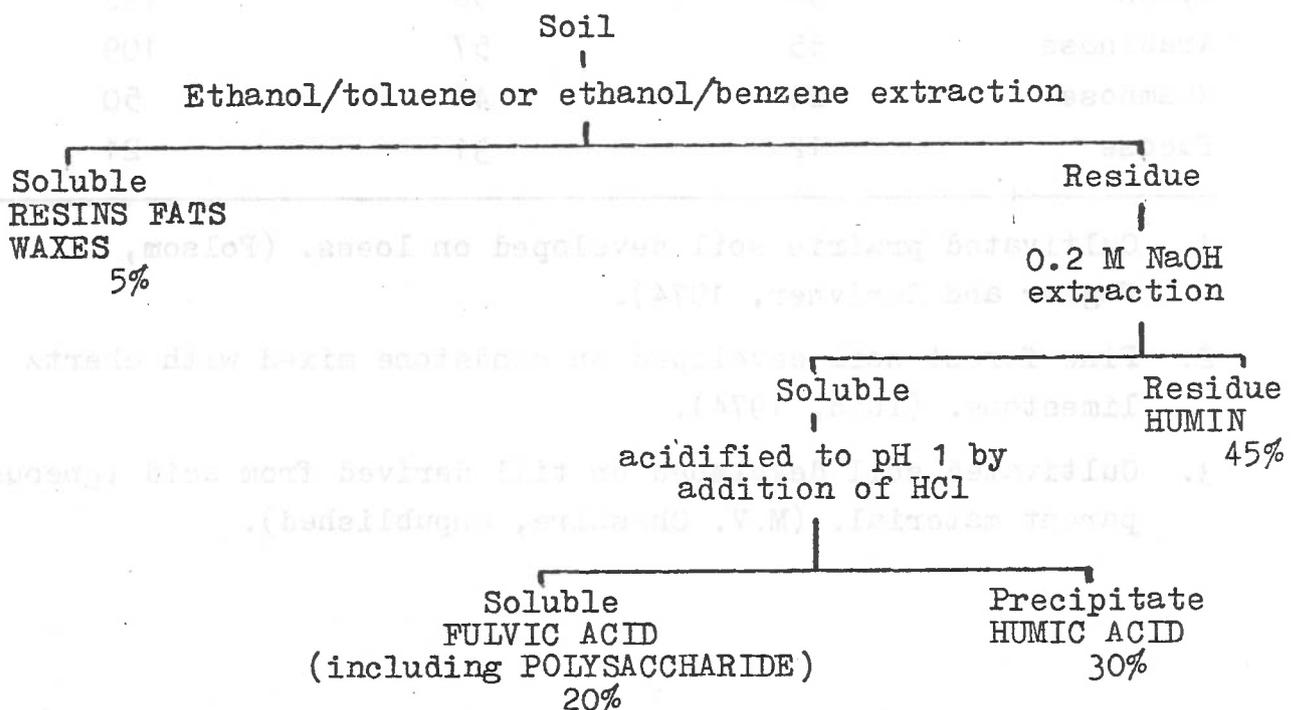
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INTRODUCTION

Humus, which will be defined here as the non-living organic matter fraction of soil, is composed not only of organic substances found in animals, insects, plants and micro-organisms but also of substances peculiar to soil. Since many of the former have not themselves been characterized, although they can be isolated from the organisms with comparative ease, the difficulties of characterizing the organic matter when mixed in soil and undergoing biochemical modification will be appreciated.

The diagram shows a chemical fractionation scheme for the organic matter in a Scottish soil, which cuts across biological divisions; the percentages indicated being those in the total organic matter in the soil.



Because both polysaccharide and humic acid usually form a large and widely studied proportion of the soil organic matter (Martin and Haider, 1971), these components will be discussed in some detail.

THE POLYSACCHARIDE FRACTION

Carbohydrates constitute the largest organic fraction of defined composition in soil, usually accounting for about 10 per cent of the soil organic matter. Most of the carbohydrate is present as polysaccharide and hydrolysis of soils shows that the sugars are present in relatively consistent proportions. Values for three soils are shown in Table 1.

Table 1

Sugars in soil hydrolysates

Sugars mg. 100g ⁻¹ soil	Soil		
	1	2	3
Glucose	133	276	420
Galactose	90	94	113
Mannose	82	139	124
Xylose	56	58	118
Arabinose	65	57	109
Rhamnose	24	46	50
Fucose	12	31	21

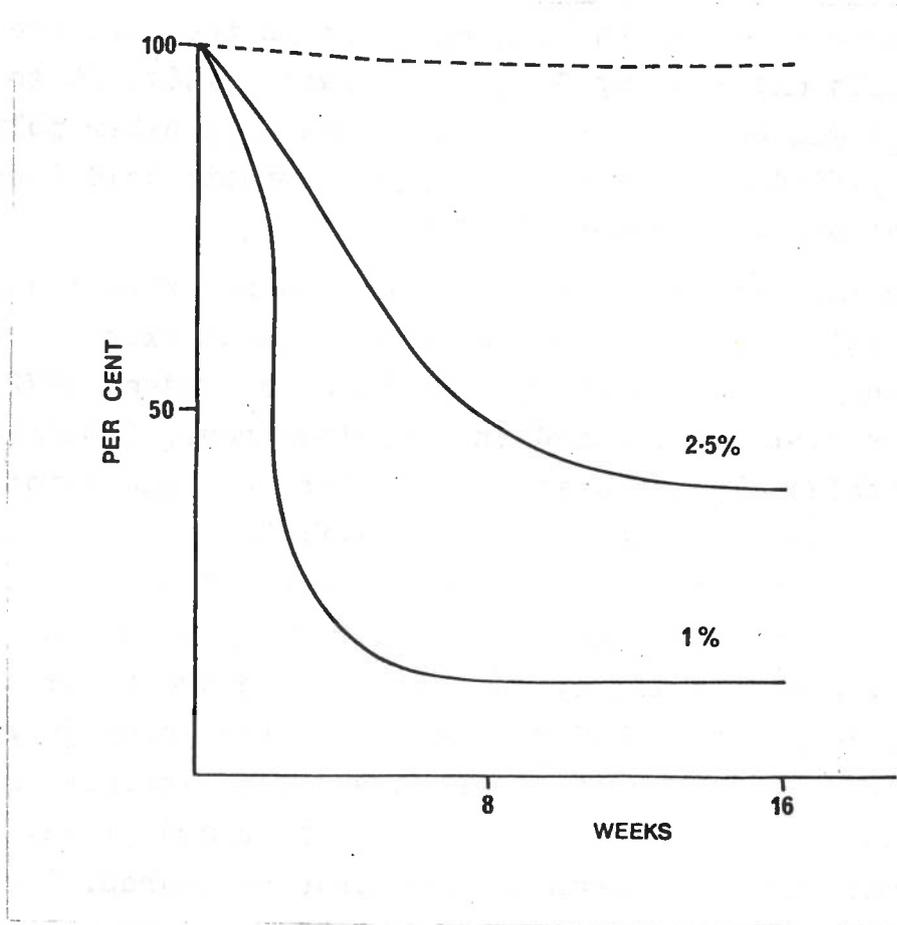
1. Cultivated prairie soil developed on loess. (Folsom, Wagner and Scrivner, 1974).
2. Pine forest soil developed on sandstone mixed with chertz limestone. (ibid, 1974).
3. Cultivated soil developed on till derived from acid igneous parent material. (M.V. Cheshire, unpublished).

In addition to these neutral sugars there are glucuronic and galacturonic acids, the amino sugars glucosamine and galactosamine, and small proportions of methyl sugars. Most of the structures in which the sugars occur in the soil are unknown. In soils examined by Gupta and Sowden (1964) 20 to 40 per cent of the glucose occurred as cellulose. No other polymers have been identified apart from a polygalacturonic acid (pectic acid) in podzol organic matter (Anderson, 1970).

About half of the polysaccharide can be extracted from soil with hot water or alkali and with subsequent extraction using acetic anhydride/sulphuric acid mixtures (Oades, 1972), a total of 80 per cent is released in many instances. Generally the alkali-soluble polysaccharide is similar in composition to that of the residue, but there are some differences; for instance, the extract obtained by acetylation has a higher proportion of glucose. The alkali-extracted polysaccharide fraction, after purification by adsorption on charcoal or alcohol precipitation, is found on hydrolysis to be only about 30 per cent sugar. Substances present other than sugars include amino acids, of which alanine, glycine, aspartic acid and glutamic acid are predominant, and organic phosphorus compounds. The composition and the resistance to hydrolysis by pronase strongly suggest that much of the material is of a microbial cell wall origin. Attempts to separate the various classes of compound present in the polysaccharide, without hydrolysis, have so far been unsuccessful, suggesting that they are chemically linked.

It would be surprising if plant products apart from cellulose made no contribution to the polysaccharide fraction. The amount of carbohydrate in the form of polysaccharide added annually to the soil by plants has been estimated to be equivalent to about 5 per cent of the soil organic matter or 25 per cent of the soil carbohydrate. Although many plant polysaccharides such as starch have been shown to break down rapidly when added to soil in an isolated form, the rate of decomposition may be considerably reduced when they are combined in mature or lignified plant structures. Thus with the

FIGURE 1



The effect of incubation on the reducing sugar present in hydrolysates of soil (---) and soil plus 1 per cent or 2.5 per cent soil polysaccharide (—). Reducing sugar expressed as a percentage of that present in the original soil or added to the soil.

hemicellulose fraction of ^{14}C -labelled cereal rye, 25 per cent of the xylose remained in the whole plant material after incubation for 14 months (Cheshire et al., 1974) compared with only 2 per cent in the isolated hemicellulose.

Incubation experiments with simple ^{14}C -labelled substrates have so far failed to reproduce polysaccharides with the neutral sugar composition of that of soil. At incubation temperatures of between 20 and 30°C the polysaccharide is deficient in xylose and arabinose, but at 5°C only in arabinose. The xylose is synthesized by yeasts which cannot compete with the bacteria at the higher temperature. The question arises whether such experiments sufficiently reproduce natural conditions. The only alternative to a microbial origin for arabinose is plant material. The stability of the polysaccharide appears to depend on the form in which it exists in the soil. When the isolated material is returned to soil it is readily decomposed, unlike the unextracted indigenous polysaccharide (Figure 1).

Humus is a comparatively inert material, and there are probably at least two reasons for this. On the one hand the relatively well defined constituents such as polysaccharide and protein are protected by the physical form in which they occur or by the materials, for example clay minerals, with which they are associated. They have, after isolation, little intrinsic stability. For example alkali extraction would remove acetyl groups which are known to be present in plant polysaccharides (Northcote, 1972) and are thought to hamper enzymic attack (Bacon and Gordon, in press). On the other hand it is suggested that the more humified substances present are stable because of their irregularity of structure which is a hindrance to enzymic attack (Kleinhempel, 1971).

THE HUMIC ACID FRACTION

Non-carbohydrate fractions in ^{14}C -labelled rye straw appear to persist for longer during soil incubations than the carbohydrate fraction, 72 per cent remaining after 14 months (Cheshire et al., 1973), suggesting that lignin is relatively stable in soil. Normally at any one time some plant material will be present and alkaline extracts of soil will contain lignin from this source in addition to humified materials. This leads to difficulties in the characterization of the structure of humic acid since it is clearly a mixture. Using Sephadex gels some separation of a fraction poor in lignin, polysaccharide and protein has recently been achieved (Macaulay Institute for Soil Research Annual Report, 1973-4).

Part of the non-humic components associated with humic acid can be released by boiling with water. Much of the nitrogen is released as amino acids during acid hydrolysis but some amino acids remain in the residue and it would be a mistake to oversimplify the concept of the structure by implying that some components were present in a mixture with humic acid only because of similar solubilities, adsorption etc. For example, although derivatives corresponding to fats and waxes have been obtained from soil by ethanol/benzene extraction (Morrison and Bick, 1967). Subsequent extraction of humic acid, isolated from the soil residue, released further fats and waxes. Derivatives in the form of straight chain aliphatic acids or alkanes also form a significant fraction of the humic acid degradation products by KMnO_4 oxidation (Schnitzer and Ortiz de Serra, 1973), by zinc dust distillation (Cheshire et al., 1967) and by high pressure hydrogenation (Felbeck, 1965). Nevertheless it is possible to remove many of these relatively simple components apparently without changing the chemical characteristics associated with humic acid.

Attempts to elucidate the structure of humic acid have been made by chemical degradation studies.

Oxidative methods

Oxidation by permanganate of methylated humic acid results in the release of phenolic and benzene carboxylic acids and small amounts of aliphatic carboxylic acids equivalent in all to about 25 per cent of the humic acid (Khan and Schnitzer, 1972). The benzene carboxylic acids are considered to arise from benzene rings not substituted by oxygen, and the relative distribution of the acids is as follows:

Number of carboxyl groups per ring	2	3	4	5	6
per cent	4	30	47	15	4

In a similar fashion nitric acid oxidation gives rise to a series of nitrophenols, nitrobenzene carboxylic acids and benzene carboxylic acids (Hayashi and Nagai, 1961). The nitrophenols are thought to relate to aromatic rings substituted by one or two carbon and one or two oxygen atoms. In organic matter from a podzol, the benzene carboxylic acids have from one to six acid groups with the tetra and penta acids predominating (Hansen and Schnitzer, 1967).

It has been argued that these highly substituted substances originate either from polycyclic aromatic structures, or are formed from simple substituted benzene compounds under the oxidizing conditions. Thus it is envisaged that lignin-type structures undergo ring formation (Read and Purves, 1952).

Methylation alone releases phenolic and benzene carboxylic acids from humic acid although in much smaller yield than with the oxidative techniques. However, in the case of fulvic acid at least, the penta and hexa carboxylic acids account for 45 per cent of the mixture of carboxylic acids (Khan and Schnitzer, 1971) and any oxidative step must relate to the soil.

Permanganate oxidation of humic acid has also produced other compounds which suggest a more condensed structure than the solitary benzene ring. These include anthraquinone, 2-methyl naphthalene, fluorenone and xanthone (Kumada et al., 1961; Cheshire et al., 1967).

Reductive methods

Reduction of humic acid by sodium amalgam gives rise to phenols and phenolic acids. Although the relative proportions of phenols differ considerably from soil to soil, the overall distribution of substituents shows a predominance of phenols with one carbon and two oxygen substituents, then 1 carbon and 1 oxygen, then 1 carbon and 3 oxygens (Piper and Posner, 1972). This may be partly a reflection of the difference in stability of these compounds during isolation since it is known that some naphthalenic compounds are easily destroyed (Martin *et al.*, 1974). This method has also given rise to phenylpropane derivatives in the form of ferulic acid and coumaric acid.

Zinc dust distillation at 440°C gives rise to aliphatic straight chain compounds and polycyclic aromatic compounds (Cheshire *et al.*, 1967) and it has been estimated that in one humic acid these latter products account for 7 per cent of the starting material (Felbeck, 1971a). Similarly, treatment with HI/red phosphorus at 250°C also results in polycyclic aromatic hydrocarbons such as pyrene and perylene (Cheshire *et al.*, 1968).

Craggs, Hayes and Stacey (1974) have recently confirmed the unpublished finding of the late Dr. R.I. Morrison at this Institute that treatment of humic acid with sodium sulphide, a delignification process, leads to the formation of phenylpropane derivatives.

Other methods

Biological degradation of humic substances using various organisms has resulted in the release of salicylaldehyde and salicyl alcohol from humic acid (Mathur and Paul, 1967), and *p*-benzoquinone and 2-methyl-1,4-naphthaquinone from fulvic acid (Mathur, 1971). The latter accounted for about one quarter of the fulvic acid. However as cell-free extracts were used which contained well-organized particulate structures, the possibility of the quinones being synthesized from simpler starting products cannot be excluded.

Evidence about the linkages between units in humic acid comes from a technique aimed at replacing other aryl units by phenol (Jackson et al., 1972). By identification of the substituted products the authors were able to suggest that about 20 per cent of the inter-aryl linkages were through carbon atoms. It is assumed that ether bonds and/or hydrogen bonding account for some linkages.

Analysis of the oxygen-containing functional groups of humic acid has shown the presence of -COOH , (2 - 5 meq/g), phenolic-OH (2 - 6 meq/g), alcoholic-OH (3 - 4 meq/g) and carbonyl. These groups account for 90 per cent of the oxygen in some cases, but the implication that the remainder is present in ether bridges is refuted by Dubach et al., (1964) who suggested that it may be in extremely stable quinones or lactones.

There is, however, still controversy over the quinone content. Recognition of specific quinone reactions usually depends on the observation of colour changes and it is not surprising that results from humic acid are inconclusive because it is such a strongly coloured material (Mathur, 1972). A method for the determination of quinone groups based on the oxidation of stannous chloride gives values of the order of 1 to 4 meq/g but one of the difficulties with this method is the strong complexing reaction of the humic acid with tin (Schnitzer and Riffaldi, 1972).

Some observations on the presence of quinones in humic acids have been based on infrared spectrometry. Quinones absorb at about $6.0 \mu\text{m}$ which is a region of variable intensity in humic acid spectra but hydrogen bonding can cause a shift in the absorption to $6.2 \mu\text{m}$ and absorption in this region is invariably observed. No unequivocal interpretation of this absorption, which is also a prominent feature of the infrared spectrum of coal, has yet been given.

The absorption has been variously attributed to:

- (a) aromatic $\text{C} = \text{C}$ vibrations
- (b) strongly hydrogen bonded $\text{C} = \text{O}$ of quinones

(c) hydrogen bonded and conjugated ketones

(d) C = O of carboxylate

If quinones hydrogen-bonded to phenolic-OH groups cause the absorption at 6.2 μm , methylation of the phenolic-OH would increase absorption of unbonded quinone at 6.0 μm while reducing that at 6.2 μm . In fact methylation of humic acid only partially reduces the absorption at 6.2 μm and does not increase 6.0 μm absorption (Stevenson and Butler, 1969). This is thought to be because hydrogen bonding prevents the methylation of the -OH (see Stevenson and Butler, 1969). Such an effect would be overcome by reductive acetylation of the humic acid but when this is done, although the 6.2 μm absorption is reduced, phenolic acetate absorbance (6.35 to 6.4 μm) is not measurably increased. Absorption indicative of alcoholic-OH acetate (8.25 μm) is, however, increased (Theng and Posner, 1967). Non-reductive acetylation increases the absorption at 6.0 μm , typical of unbonded carbonyl groups, suggesting that the carbonyl groups are hydrogen bonded by alcoholic hydroxyl groups. Such carbonyl groups would appear as acetylated alcohols by the reductive treatment (Theng and Posner, 1967). The characteristics described above could be related more easily to carbonyl structures such as enolic $\alpha\beta$ -diketones or $\alpha\beta$ -unsaturated- β -hydroxy ketones.

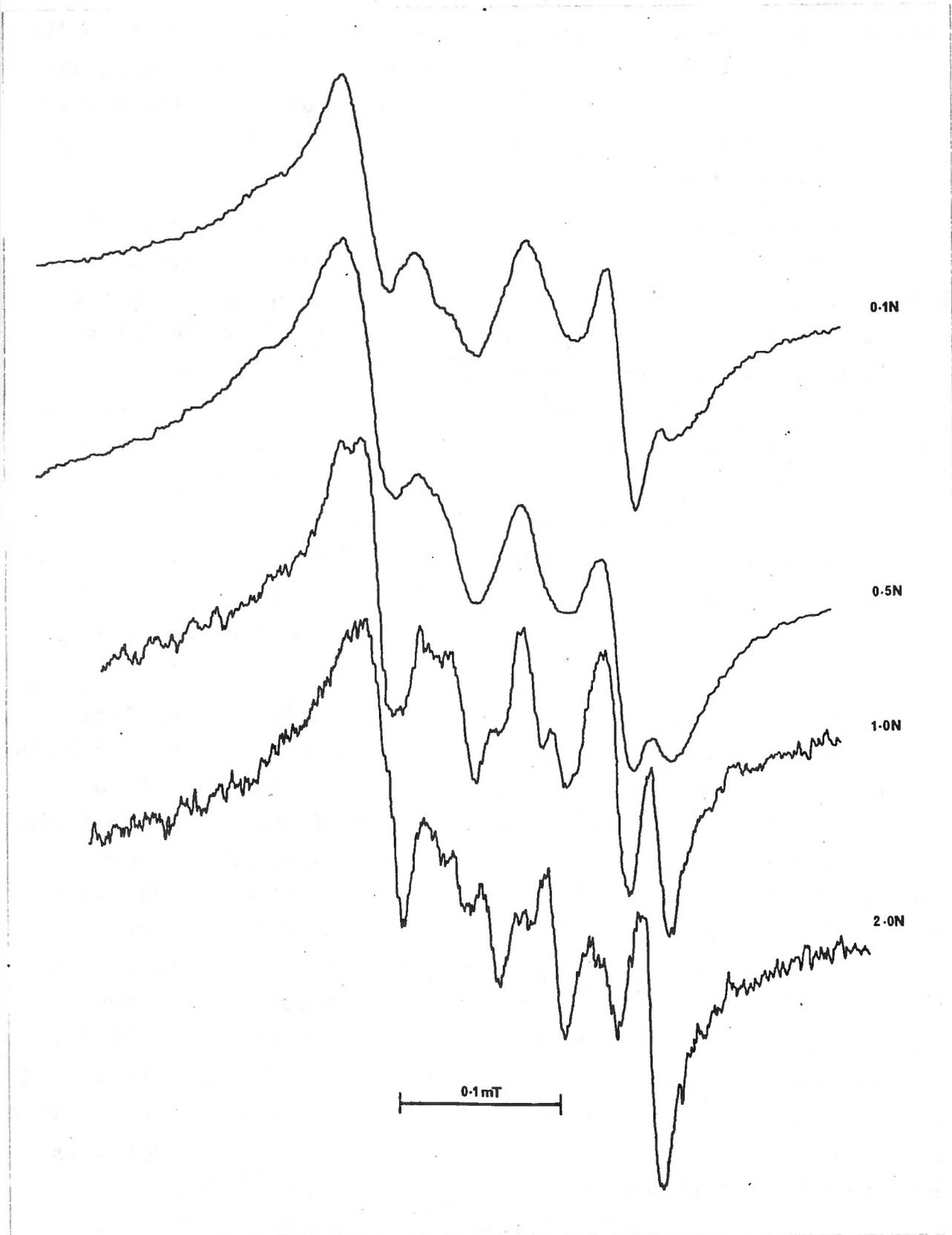
Absorption bands in the 6.3 μm region have been assigned to hydroxyquinone salts but Farmer and Morrison (1960) suggested that these substances cannot be present in large amounts because reductive methylation of humic acid does not significantly increase the methoxyl content. Unless the rings are highly substituted, absorption at 9.7 μm and 11 to 14 μm (aromatic structures), appears too weak in relation to the 6.3 μm region to be caused by phenoxy structures (Friedel and Retcofsky, 1970). Alternatively the persistent 6.2 μm absorption, which is not removed by reduction or esterification, may be attributable to the C = O of carboxylate (Schnitzer, 1965). The $-\text{COO}^-$ group may well resist being esterified because it is in the form of a stable salt. For example it is very difficult to remove metal ions such

as Al^{3+} from humic acid and some of the sodium added during the preparation can remain even after boiling with 6N HCl. Alternatively an organic cation or positively charged site in the molecule might be involved. For a number of humic substances it has been observed that the intensity of absorption in the 6.2 μm region is inversely proportional to that in the carboxyl (5.8 μm) region (Stevenson and Goh, 1971).

Electron paramagnetic resonance (epr) has been used to study humic acids and has shown the presence of a stable organic radical which is thought to be a semiquinone. In the solid state humic acids give a single peak spectrum of signal width 0.5 m Tesla with a weaker signal width 1.5 m Tesla seen as an inflection. Temperature and hydrolytic effects have led Steelink and Tollin (1962) to suggest that two separate radical species might be present, a semiquinone type radical and quinhydrone type. Later Steelink (1966) suggested that the paramagnetic species is a hydroxyquinone capable of forming both mono and biradicals. The signal increases with the degree of condensation of the humic acid as judged by colour but there are contradictory reports about the effect of methylation.

In solution in 0.1 M alkali, humic acid derived from peats or soils having pH values < 4.2 shows a hyperfine structure with a four peak spectrum (Haworth, 1965). In the case of one humic acid sample, Haworth (1971) described finding a small fifth peak. Recently re-examination in this laboratory of the epr signals from humic acid solutions has shown that with increasing concentration of alkali another four peak spectrum appears (Figure 2). Haworth's fifth peak probably corresponds to one of the second spectrum peaks. As this second spectrum increases in strength so the original one weakens, both may be expressions of the same chemical structure. It can be deduced from Figure 2 that only two nonequivalent protons interact with the unpaired electron in the humic acid radical. In dilute alkali one has a hyperfine coupling constant (0.11 mT) commensurate with the spin polarization of a C - H σ orbital by the unpaired electron in a

FIGURE 2



Electron spin resonance spectra of solutions of humic acid from the H horizon of a podzol in various concentrations of NaOH.

π type orbital of a benzene ring, whereas the other has a smaller hyperfine coupling constant (0.04 mT) and is probably not on the same ring. In increasingly basic conditions it would appear that the electron spin density on this latter proton increases (hyperfine coupling constant 0.06 mT).

The small number of protons interacting with the unpaired electron implies that the structure has a high degree of substitution. With the humic acid from less-acid soil no hyperfine splitting is observed. The spectra show a broader signal probably because more than one type of radical is present.

There are some similarities between the epr spectra of humic acid and lignin. These are: 1. Formation of the sodium salt considerably increases the strength of signal (Tollin and Steelink, 1966); 2. In solution there is an oxygen effect; 3. Different concentrations of alkali give different signals (Fitzpatrick and Steelink, 1969). Steelink (1964, 1966) has suggested that a similar class of compound, a quinhydrone, may be involved. In the case of hardwood lignin it is suggested that the signal is from 2,6-dimethoxy benzoquinonoid units (Fitzpatrick and Steelink, 1972) but this is not the origin of the signal in humic acid. The relationship between the signal from solid humic acid and from humic acid in solution has not yet been elucidated.

Electron paramagnetic resonance has also shown the presence of copper porphyrin structures in humic acids (Goodman and Cheshire, 1973). The porphyrin is probably derived from chlorophyll residues of plants, but it has yet to be shown whether the copper complex occurs naturally in soil or whether it is created by the chemical conditions required to extract and isolate the humic acid.

To summarize these findings humic acid appears to contain both aromatic and aliphatic components. Much of the aromatic material involves structural units with a single benzene ring, some of which resemble those of lignin although part of this is in more condensed structures.

The approximate percentages by weight of some of the known components of humic acid are as follows (based on Felbeck, 1971b):

	%
amino acids	10
hexosamines	3
polycyclic aromatics	10
single ring aromatics	15
functional groups	26
aliphatics	4

More specific structures which have recently been proposed for humic acid include a pyrone polymer linked through the 2,6-positions (Felbeck, 1965), a hydroxypolystyrene polymer (Finkle, 1965), an amino acid-sugar condensate (Meneghel *et al.*, 1972), p-linked phenyl ethers (Murphy and Moore, 1960) and m-linked phenyl ethers (Swain, 1963).

THE FULVIC ACID FRACTION

The brown polymeric material of the fulvic acid fraction has a higher -COOH content (6 to 9 meq/g) than humic acid. It has been suggested that in the lower molecular weight material phenolic acid units are bonded together by hydrogen bonding (Schnitzer and Khan, 1972). The higher molecular weight fractions give rise to fatty acids (nC_{14} to C_{18}) on oxidation and it is suggested that these may be combined with phenols through ester bonds (Neyroud and Schnitzer, 1974).

THE HUMIN FRACTION

The insolubility of a large fraction of humus in alkali is not explained by the quantities of the various functional groups present since these fall within the range of values for humic acid. It has been suggested that the composition of humin is not different from that of humic acid, only the firmness with which the material is combined with the mineral part of the soil (Kononova, 1961).

REFERENCES

- Anderson, H.A. (1970) Some aspects of the chemistry of the Glentanar podzol profile. Rep. Welsh Soils Discuss. Grp No. 11: 124-133.
- Bacon, J.S.D. and Gordon, A.H. Comparisons of walls derived from different cell types in grasses. J. Sci. Fd Agric. in press.
- Cheshire, M.V., Cranwell, P.A., Falshaw, C.P., Floyd, A.J. and Haworth, R.D. (1967) Humic acid - II Structure of humic acids. Tetrahedron 23: 1669-1682.
- Cheshire, M.V., Cranwell, P.A. and Haworth, R.D. (1968) Humic acid III. Tetrahedron 24: 5155-5167.
- Cheshire, M.V., Mundie, C.M. and Shepherd, H. (1973) The origin of soil polysaccharide: transformation of sugars during the decomposition in soil of plant material labelled with ^{14}C . J. Soil Sci. 24: 54-68.
- Cheshire, M.V., Mundie, C.M. and Shepherd, H. (1974) Transformation of sugars when rye hemicellulose labelled with ^{14}C decomposes in soil. J. Soil Sci. 25: 90-98.
- Craggs, J.D., Hayes, M.H.B. and Stacey, M. (1974) Sodium sulphide reactions with humic acid and model compounds. Trans. 10th int. Congr. Soil Sci., Moscow, U.S.S.R. 2: 318-324.
- Dubach, P., Mehta, N.C., Jakab, T., Martin, F. and Roulet, N. (1964) Chemical investigations on soil humic substances. Geochim. Cosmochim. Acta 28: 1567-1578.
- Farmer, V.C. and Morrison, R.I. (1960) Chemical and infrared studies on Phragmites peat and its humic acid. Scient. Proc. R. Dubl. Soc. A 1: 85-104.
- Felbeck, G.T. (1965) Studies on the high pressure hydrogenolysis of the organic matter from a muck soil. Proc. Soil Sci. Soc. Am. 29: 48-55.
- Felbeck, G.T., Jr. (1971a) Structural hypotheses of soil humic acids. Soil Sci. 111: 42-48.
- Felbeck, G.T. (1971b) Chemical and biological characterization of humic matter. pp 36-59 In "Soil Biochemistry", vol. 2. ed. A.D. McLaren and J. Skujins. N.Y.: Marcel Dekker Inc.
- Finkle, B.J. (1965) Soil humic acid as a hydroxypolystyrene: A biochemical hypothesis. Nature, Lond. 207: 604-605.

- Fitzpatrick, J.D. and Steelink, C. (1969) Benzosemiquinone radicals in alkaline solutions of hardwood lignins. *Tetrahedron Lett.* No. 57: 5041-5044.
- Fitzpatrick, J.D. and Steelink, C. (1972) The origin of the paramagnetic species in lignin solutions. Autoreduction of 2,6-dimethoxy-benzoquinone and related quinones to radical anions in alkaline solution. *J. org. Chem.* 37: 762-767.
- Folsom, B.L., Wagner, G.H. and Scrivner, C.L. (1974) Comparison of soil carbohydrate in several prairie and forest soils by gas-liquid chromatography. *Proc. Soil Sci. Soc. Am.* 38: 305-309.
- Friedel, R.A. and Retcofsky, H.L. (1970) Spectrometry of chars - structure studies. pp 46-69 In "Spectrometry of Fuels", ed. R.A. Friedel N.Y.: Plenum.
- Goodman, B.A. and Cheshire, M.V. (1973) Electron paramagnetic resonance evidence that copper is complexed in humic acid by the nitrogen of porphyrin groups. *Nature, New Biol.* 244: 158-159.
- Gupta, U.C. and Sowden, F.J. (1964) Isolation and characterization of cellulose from soil organic matter. *Soil Sci.* 97: 328-333.
- Hansen, E.H. and Schnitzer, M. (1967) Nitric acid oxidation of Danish illuvial organic matter. *Proc. Soil Sci. Soc. Am.* 31: 79-85.
- Haworth, R.D. and Atherton, N.M. (1965) Humic acid. *Bull. natn. Inst. Sci. India* No. 28: 57-60.
- Haworth, R.D. (1971) The chemical nature of humic acid. *Soil Sci.* 111: 71-79.
- Hayashi, T. and Nagai, T. (1961) On the components of soil humic acids. 8. The oxidative decomposition by alkaline potassium permanganate and nitric acid. *Soil Pl. Fd, Tokyo* 6: 170-175.
- Jackson, M.P., Swift, R.S., Posner, A.M. and Knox, J.R. (1972) Phenolic degradation of humic acid. *Soil Sci.* 114: 75-78.
- Khan, S.U. and Schnitzer, M. (1971) Further investigations on the chemistry of fulvic acid, a soil humic fraction. *Canad. J. Chem.* 49: 2302-2309.
- Khan, S.U. and Schnitzer, M. (1972) Permanganate oxidation of humic acids, fulvic acids, and humins extracted from Ah horizons of a black chernozem, a black solod, and a black solonetz soil. *Can. J. Soil Sci.* 52: 43-51.

- Kleinhempel, D. (1971) Theoretical aspects of the persistence of organic matter in soils. *Pedobiologia* 11: 425-429.
- Kononova, M.M. (1961) Soil organic matter: its nature, its role in soil formation and in soil fertility. London: Pergamon Press.
- Kumada, K., Suzuki, A. and Aizawa, K. (1961) Isolation of anthraquinones from humus. *Nature, Lond.* 191: 415-416.
- Macaulay Institute for Soil Research Annual Report (1973-4) Nature and transformation of soil organic matter. Ann. Rep. No. 44: 35.
- Martin, J.P. and Haider, K. (1971) Microbial activity in relation to soil humus formation. *Soil Sci.* 111: 54-63.
- Martin, J.P., Haider, K. and Saiz-Jimenez, C. (1974) Sodium amalgam reductive degradation of fungal and model phenolic polymers, soil humic acids, and simple phenolic compounds. *Proc. Soil Sci. Soc. Am.* 38: 760-765.
- Mathur, S.P. and Paul, E.A. (1967) Partial characterization of soil humic acids through biodegradation. *Can. J. Microbiol.* 13: 581-586.
- Mathur, S.P. (1971) Characterization of soil humus through enzymatic degradation. *Soil Sci.* 111:147-157.
- Mathur, S.P. (1972) Infrared evidence of quinones in soil humus. *Soil Sci.* 113: 136-139.
- Meneghel, R., Petit-Sarlotte, C. and Bloch, J-M. (1972) Sur la caracterisation et l'isolement des produits de degradation d'un acide humique apres oxydation peracetique. *Bull. Soc. chim. Fr.* 7: 2997-3001.
- Morrison, R.I. and Bick, W. (1967) The wax fraction of soils: Separation and determination of some components. *J. Sci. Fd Agric.* 18: 351-355.
- Murphy, D. and Moore, A.W. (1960) A possible structural basis of natural humic acid. *Scient. R. Dubl. Soc. A* 1: 191-195.
- Neyroud, J.A. and Schnitzer, M. (1974) The chemistry of high molecular weight fulvic acid fractions. *Can. J. Chem.* 52: 4123-4132.
- Northcote, D.H. (1972) Chemistry of the plant cell wall. *An. Rev. Pl. Physiol.* 23: 113-132.
- Oades, J.M. (1972) Studies on soil polysaccharides III. Composition of polysaccharides in some Australian soils. *Aust. J. Soil Res.* 10: 113-126.

- Piper, T.J. and Posner, A.M. (1972) Sodium amalgam reduction of humic acid II. Application of the method. *Soil Biol. Biochem.* 4: 525-531.
- Read, D.E. and Purves, C.B. (1952) Isolation of penta and 1,2,4,5-benzenetetracarboxylic acids from wood lignins oxidized with alkaline permanganate. *J. Am. chem. Soc.* 74: 120-123.
- Schnitzer, M. (1965) The application of infrared spectroscopy to investigations on soil humic compounds. *Can. Spectrosc.* 10: 121-127.
- Schnitzer, M. and Riffaldi, R. (1972) The determination of quinone groups in humic substances. *Proc. Soil Sci. Soc. Am.* 36: 772-777.
- Schnitzer, M. and Khan, S.U. (1972) Humic substances in the environment. N.Y.: Marcel Dekker Inc.
- Schnitzer, M. and Ortiz de Serra, M.I. (1973) The chemical degradation of a humic acid. *Can. J. Chem.* 51: 1554-1566.
- Steelink, C. and Tollin, G. (1962) Stable free radicals in soil humic acid. *Biochim. biophys. Acta* 59: 25-34.
- Steelink, C. (1964) Free radical studies of lignin, lignin degradation products and soil humic acids. *Geochim. Cosmochim. Acta* 28: 1615-1622.
- Steelink, C. (1966) Electron paramagnetic resonance studies of humic acid and related model compounds. *Adv. Chem. Ser.* 55: 80-90.
- Stevenson, F.J. and Butler, J.H.A. (1969) Chemistry of humic acids and related pigments. pp 534-557 (Chap. 22) In "Organic Geochemistry", ed. G. Eglinton and M.T.J. Murphy Berlin-Heidelberg-N.Y.: Longman.
- Stevenson, F.J. and Goh, K.M. (1971) Infrared spectra of humic acids and related substances. *Geochim. Cosmochim. Acta* 35: 471-483.
- Swain, F.M. (1963) Geochemistry of humus. pp 87-147 In "Organic Geochemistry", ed. I.A. Breger Berlin-Heidelberg-N.Y.: Longman.
- Theng, B.K.G. and Posner, A.M. (1967) Nature of the carbonyl groups in soil humic acid. *Soil Sci.* 104: 191-201.
- Tollin, G. and Steelink, C. (1966) Biological polymers related to catechol: electron paramagnetic resonance and infrared studies of melanin, tannin, lignin, humic acid and hydroxyquinones. *Biochim. biophys. Acta* 112: 377-379.

THE TURNOVER OF ORGANIC MATTER IN AGRICULTURAL SOILS

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INTRODUCTION

The annual input of organic carbon into soil carrying cereals is of the order of 1-2 tonnes per hectare, with grassland receiving perhaps twice as much. In the long run, all this organic matter is decomposed, no fraction being completely resistant to decay. This process, in which losses and gains proceed simultaneously, is described as turnover and may be defined as the flux of carbon through the organic carbon in a given volume of soil. Turnover time is then the amount of carbon in the soil system once equilibrium has been reached, divided by the annual input of carbon into that system.

This process is illustrated in Fig. 1, which shows the effects of long continued manuring on the organic nitrogen content of soil from the Broadbalk continuous wheat experiment at Rothamsted (Johnston, 1969). The C/N ratios of all these Broadbalk surface soils lie between 9.5 and 10.5, so that diagrams showing changes in organic carbon or organic matter would look very similar to Fig. 1. The organic content of the unmanured plot has remained steady over the whole period of the experiment, at a level a little less than that of the plot receiving inorganic nitrogen, phosphorus, potassium and magnesium. The plot receiving 35 tonnes of farmyard manure per hectare each year has gained organic matter steadily (apart from a setback during the period when the soil was fallowed every fifth year) and after more than 120 years has still not reached equilibrium.

Table 1 shows the turnover time for the organic matter in two of the Broadbalk plots. The annual input of organic matter

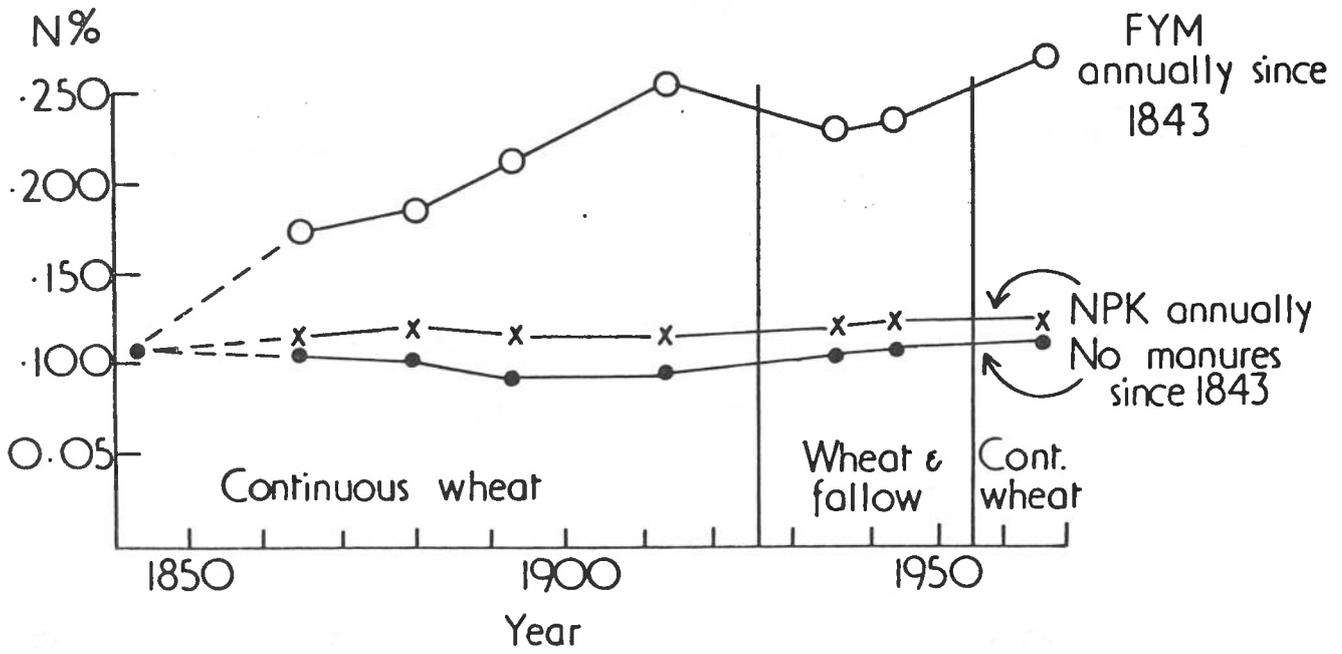


Fig.1 Nitrogen content of Broadbalk soil

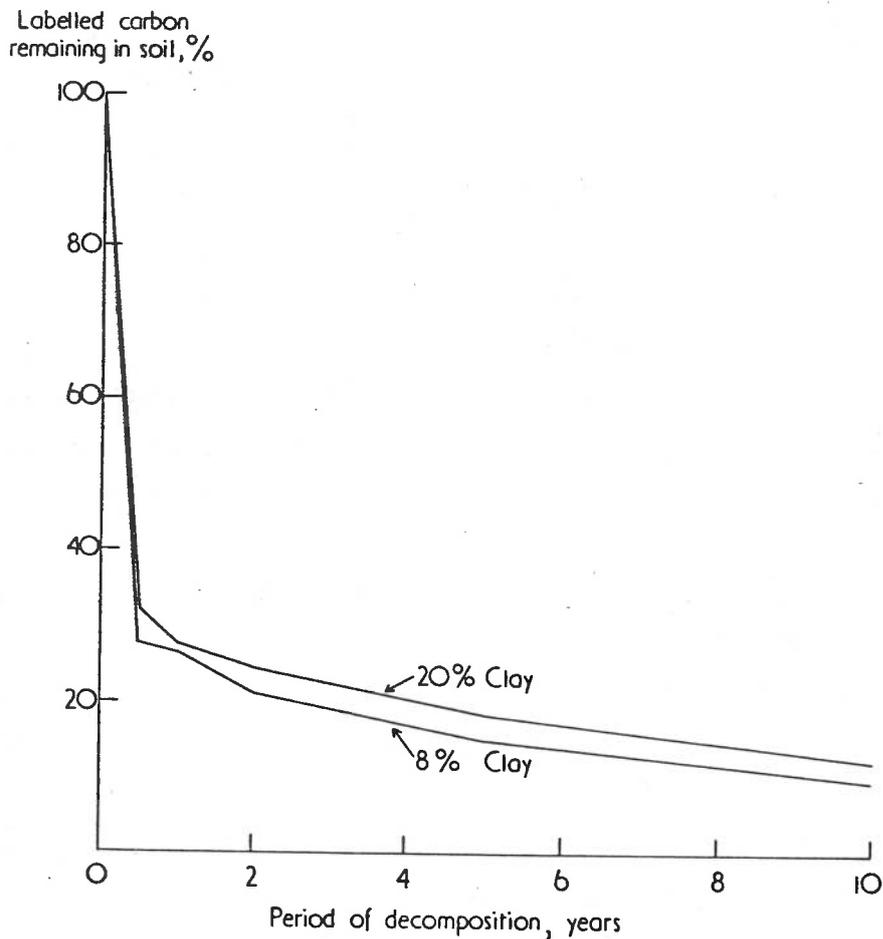


Fig. 2. The decomposition of ^{14}C labelled ryegrass in soil kept in the field

was calculated from the amount of thermonuclear radiocarbon that has entered the soils, assuming (from Fig. 1) that the organic carbon of both plots had reached equilibrium. The annual inputs thus calculated amount to 5-6% of the total organic carbon in the soil and the gross turnover times are correspondingly short, 16 years for the plot receiving inorganic fertilizers and 22 years for the unfertilized plot.

Table 1

Fresh carbon entering the soil each year in two plots (03 and 08) of the Broadbalk continuous wheat experiment.

Treatment	Organic carbon, tonnes per hectare			Gross turnover rate, years
	Total in soil to a depth of 23cm	Entering soil each year	Harvested in crop (grain + straw) each year	
Unmanured	26	1.2	1.4	22
Inorganic fertilizers	30	1.9	3.2	16

RADIOCARBON STUDIES

With these gross turnover rates as background, recent work on the stability of soil organic matter and its different fractions may be considered. The first approach has been to follow the decay of labelled plant material in soil. By using plant material uniformly labelled with the long-lived radioisotope of carbon, ^{14}C , it is possible to follow the loss of carbon from a given addition of plant material for many years under field conditions. Figure 2 shows the rate at which uniformly labelled ryegrass (cut just before flowering) decayed in two soils - a soil from Broadbalk containing 20% clay and a sandy soil from Woburn Experimental Farm with 8% clay. About

two-thirds of the plant carbon was lost in the first year, but thereafter the rate of loss became much less, so that after 10 years 10-12% still remained in the soil. A little less organic carbon was retained by the sandy soil throughout the 10-year period. This experiment shows that a very small fraction of the plant-derived carbon possesses great stability, even though the original plant material was green, succulent and readily decomposable.

Radiocarbon dating has also been used in the study of the stability of different fractions of soil organic matter.

Table 2

Radiocarbon age of organic matter in soil collected in the last century from the unmanured plot of Broadbalk.

Sampling depth, cm	Organic carbon, %	Equivalent age, years*
0 - 23	0.94	1400
23 - 46	0.61	2000
46 - 69	0.47	3700
114 -137	0.24	9900
206 -229	0.20	12100

* The equivalent age is defined as the age of a homogeneous sample with the same value of ^{14}C as that of the (heterogeneous) soil sample analysed.

Table 2 shows the equivalent age of the organic matter down a profile on the unmanured plot on Broadbalk. Although there is coal and charcoal in the surface horizon of this profile, there is not enough of either to contribute appreciably to the measured radiocarbon age. Despite adequate aeration, a near-neutral pH, a moisture regime favouring microbial activity over much of the year and a mean monthly soil temperature that varies from 3°C in January to 16°C in July, most of the organic matter in this profile is of great antiquity. Such ages are quite

widespread: Table 3 shows the radiocarbon ages of topsoils collected before 1955 from experimental farms in different parts of England. Four had ages of between 700 and 1200 years; the fifth (Gleadthorpe) had a much greater age, probably because it contained much coal-like carbonised material.

Table 3

Radiocarbon age of organic matter in arable soils from different experimental farms.

Farm	Sampling depth, cm	Year of sampling	Organic carbon, %	Equivalent age, years
Woburn	0 - 23	1888	1.34	685
Saxmundham	0 - 23	1944	1.37	1200
Gleadthorpe	0 - 30	1955	1.06	2395
Rosemaund	0 - 15	1955	2.16	685
Bridgets	0 - 15	1955	2.37	1190

The radiocarbon ages given in Tables 2 and 3 were measured on samples collected before 1956. This was done because the thermonuclear tests of the last two decades have caused the radiocarbon ages of biologically-active soils to decrease. The neutrons released during a thermonuclear explosion interact with nitrogen in the atmosphere to produce ^{14}C which is then oxidised to $^{14}\text{CO}_2$. From the atmospheric carbon dioxide pool, the radiocarbon enters green plants and thence soil organic matter. Figure 3 (redrawn from Nydal and Lovseth, 1970) shows how atmospheric radiocarbon has increased over the last 20 years from the pre-1950 (natural) level. A small maximum in 1959 was followed by a larger one in 1964. Since 1964 there has been a steady fall, caused mainly by exchange between atmospheric carbon dioxide and oceanic bicarbonate.

Soils from the unmanured plot on the Broadbalk continuous wheat experiment were used to study the effect of bomb-derived

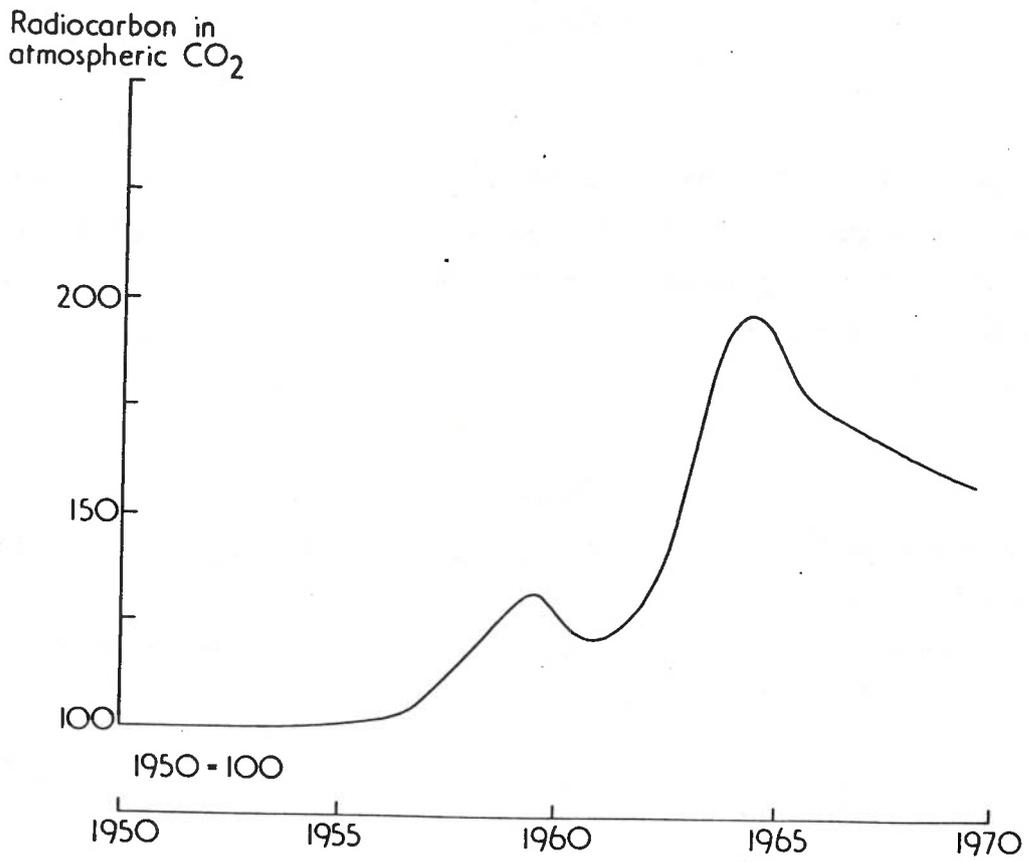


Fig.3. Thermonuclear radiocarbon in atmospheric CO₂

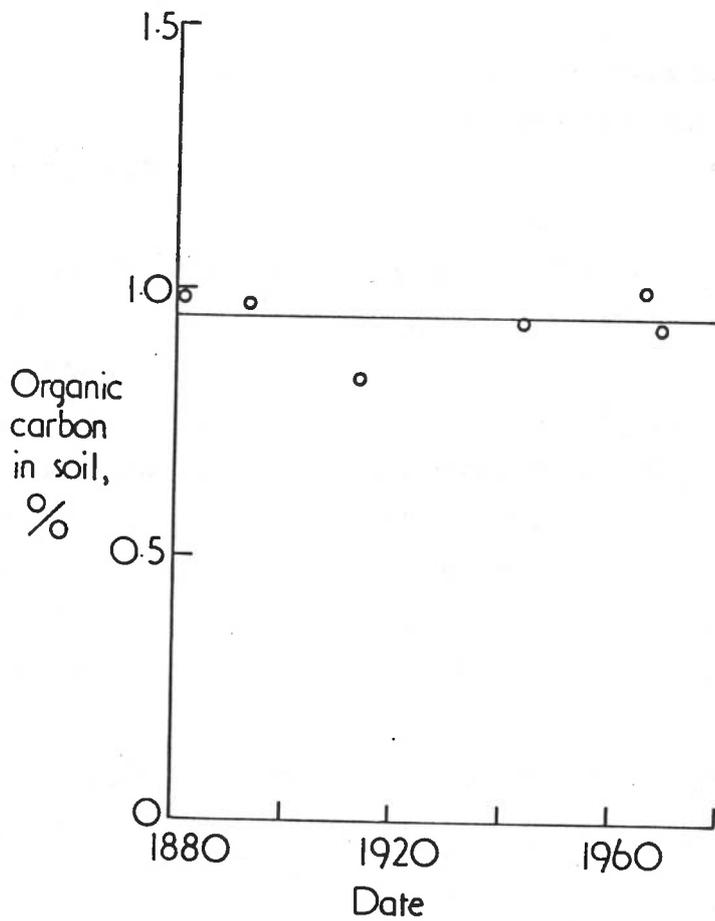


Fig.4. Organic carbon content of soils 1881-1969

radiocarbon on the measured radiocarbon age of soil. These soils were collected at intervals over the last 100 years and stored air-dry in sealed bottles. An advantage in using soil from this particular plot is that the carbon content has changed little since 1881 (Fig. 4), so that the organic matter it contains is at or near equilibrium, with the annual gain of organic matter exactly balanced by the annual loss.

Figure 5 shows that by 1969 the radiocarbon age of the post-bomb samples was less than half that of the pre-bomb samples. A similar effect has been noticed in New Zealand soils by Stout and O'Brien (1972) who also attribute it to bomb radiocarbon.

This effect presented one hopes, a never-to-be-repeated opportunity of measuring the amount of organic matter entering the soil each year. The study of the stability of soil organic matter and its turnover, requires an estimate of the quantity of organic matter entering the soil each year. This annual addition comprises organic matter from roots, root hairs, root exudates and organic carbon from autotrophic organisms living in the soil, as well as material from those above-ground plant parts, such as stubble, that enter the soil.

The calculation of the annual addition from pre- and post-bomb dating of soil organic matter requires three parameters:

Firstly, the radiocarbon age of the soil, pre- and post-bomb. The site being investigated must be under constant management over the period bracketed by the pre- and post-bomb samples.

Secondly, the specific activity of the carbon in each year's plant. This can be obtained from data such as that in Fig. 3.

Thirdly, how much carbon remains in the soil after 1, 2, 3 ... years in the field. This is known for Rothamsted conditions from the experiments on the decomposition of labelled plant material in soil (Fig. 2). Table 1 shows the results of such calculations for two of the plots on Broadbalk - the unmanured (03) plot and one of the plots (08) receiving inorganic nitrogen, phosphorus, potassium and magnesium.

There is a most interesting paradox in these results. The

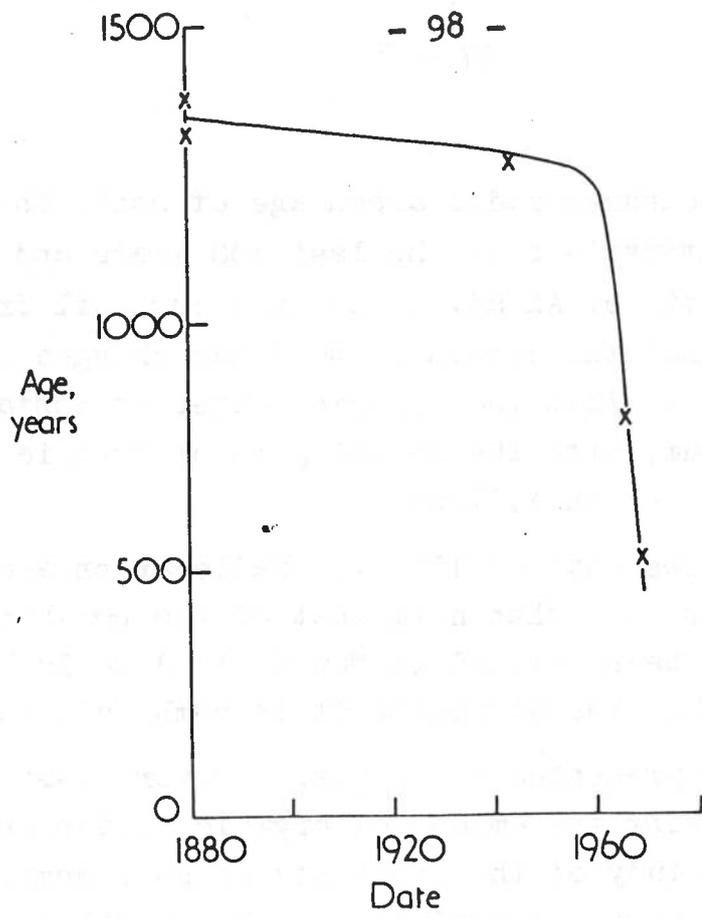


Fig.5. Age of soil organic carbon before and after 1950

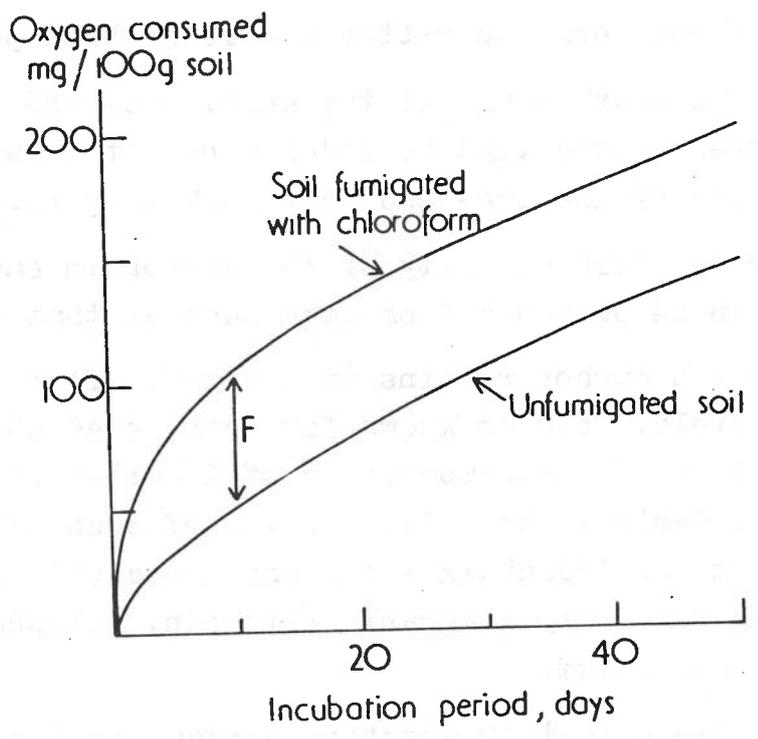


Fig.6 Effect of fumigation on oxygen consumption by soil

radiocarbon age of the soil is very great (Table 2), yet the annual input of organic matter is large (Table 1). There can be little doubt that soil organic matter contains fractions of great stability and that calculated turnover times of the order of 20 years are the resultant of a range of values. It may be that there is a very long 'tail' to the decomposition curve of organic matter, with a small fraction, perhaps 0.1%, of the incoming carbon converted to a form that persists for centuries. Alternatively, organic matter may be fixed irreversibly during the early development of a soil, so that subsequent events in its history take place against a background of this stabilised material.

Another aspect of our work on the radiocarbon dating of soil organic matter is illustrated in Tables 4 and 5, which show the ages of different fractions of the soil organic matter. Hydrolysis with 6N hydrochloric acid under reflux is very effective in revealing fractions of different age. Table 4 shows that the acid-soluble carbon from a soil sampled in 1881 from the unmanured plot on Broadbalk was younger than the acid-insoluble part. A similar effect has been observed in numerous short-term experiments in which labelled plant material was mixed with soil, allowed to decompose and then hydrolysed. The specific activity of the hydrolysate is always greater than that of the acid-insoluble residue (see, for example, Jenkinson, 1968; Persson, 1968).

When a soil collected in 1969 from the same plot was hydrolysed, so much bomb radiocarbon had entered the acid hydrolysate that it contained more than the contemporary standard (Table 4). No real age can therefore be calculated for this hydrolysate. Some bomb radiocarbon had also entered the acid-insoluble fraction of the soil organic matter.

Table 4

Radiocarbon age of fractions of soil organic matter separated by hydrolysis with 6N HCl under reflux.

	Fraction					
	Decalcified soil*		Hydrolysate		Residue from hydrolysis	
Sampling date	1881	1969	1881	1969	1881	1968
% total soil organic C in fraction	100	100	37	40	37	43
$\delta^{14}\text{C}$	-165	-63	-62	+8	-273	-220
Equivalent age, years	1450	520	515	-	2560	1995

* From the unmanured plot on Broadbalk, sampled on both occasions to a depth of 23cm

The traditional separation of soil organic matter into humic and fulvic acids also leads to fractions of different radiocarbon age. Table 5 shows that the complex mixture called 'humic acid' dates older than the mixture called 'fulvic acid'. The heterogeneity of the humic acid is clearly demonstrated by hydrolysis; hydrolysed humic acid dating older than unhydrolysed.

Table 5

Radiocarbon age of fractions of soil organic matter separated by the traditional alkaline extraction process.

	Fraction				
	Decalcified soil*	Humic acid	Hydrolysed humic acid	Fulvic acid	Humin
Origin of fraction	-	Extracted with NaOH, precipitated with acid	Humic acid hydrolysed with 6N HCl under reflux	Extracted with NaOH, not precipitated with acid	Not extracted with NaOH
% total soil organic C in fraction	100	15	10	23	46
$\delta^{14}\text{C}$	-165	-89	-125	-51	-258
Equivalent age, years	1450	750	1070	420	2395

* From the unmanured plot on Broadbalk, sampled in 1881 to a depth of 23cm.

STUDIES ON THE SOIL BIOMASS

The biomass occupies a central position in studies on soil organic matter, being involved in the transformations undergone by both fresh and humified organic matter. Our work on the soil biomass started because of an interest in the effects of fumigation on soil metabolism. Fumigation causes a transient increase in respiration which is known as the 'flush' as illustrated in Fig. 6. The consumption of oxygen in a soil is enhanced following the sequence of fumigation with chloroform, fumigant removal, inoculation, and re-incubation. This increase in oxygen consumption is accompanied by increased evolution of carbon dioxide and mineralisation of nitrogen (Table 6).

Fumigation with chloroform vapour more than doubled carbon dioxide

evolution; nitrogen mineralisation is particularly sensitive to fumigation and in this experiment increased more than 11 times.

Table 6

Effects of chloroform fumigation on metabolism in soil.

	Unfumigated soil	Fumigated soil
	mg/100g soil*	
O ₂ consumed in 10 days	36	99
CO ₂ -C evolved in 10 days	13	33
N mineralised in 10 days	0.6	6.7

* From the plough layer of the plot on Broadbalk (02) that receives farmyard manure annually.

From a detailed study of this flush (Jenkinson and Powlson, 1975) we have concluded that the flush that follows fumigation is largely, if not entirely, caused by the decomposition of organisms killed by the fumigant. The killed organisms are decomposed by the survivors or by organisms added in the inoculum. As a rough working rule, about half the carbon in a killed organism is mineralised to carbon dioxide in 10 days. Using this factor of 0.5, it is then possible to calculate the amount of biomass in a soil from the size of the flush. This has been done in Table 7, which shows the biomasses in a diverse group of 8 soils, as calculated in two different ways, from direct counts of the number and size of the soil population and from the size of the flush. With the exception of an acid woodland soil, the agreement between the two totally different methods of measuring biomass is close.

Table 7

Biomass carbon in soil as calculated (a) from direct counts of stained organisms and (b) from the size of the flush caused by chloroform fumigation (Jenkinson, Powlson and Wedderburn, 1975).

Location	Soil Management		Biomass from Biovolume	Biomass from Flush
			mg biomass C per 100g soil	
England	Continuous wheat (FYM annually)		55	50
England	Continuous wheat (unmanured)		19	20
England	Deciduous woodland (pH 7.8)		154	111
England	Mixed arable		39	32
England	Old grassland (organic soil)		320	334
England	Deciduous woodland (pH 3.9)		33	5
Nigeria	Secondary forest		43	49
Nigeria	Arable (cleared 2 years)		26	25

This new method of measuring soil biomass has been applied to soils from the Rothamsted classical experiments and Table 8 shows some of the results. In the arable soils about 2% of the soil organic carbon is in the biomass; under grassland or woodland slightly more, up to 3%.

Table 8

Biomass carbon in soil (0-23cm) from some of the Rothamsted classical experiments (Jenkinson and Powlson, 1975).

	Continuous Wheat			Woodland	Old Grassland
	Unmanured	NPK	FYM	Unmanured	Unmanured
Total organic carbon, tonnes per ha	26	29	61	65	70
Biomass carbon, tonnes per ha	0.5	0.6	1.2	2.0	2.0

The biomass is of course one of the most labile parts of the soil organic matter and is therefore a more sensitive indicator of changes brought about by management than relatively slow-moving parameters such as total carbon. Some work done on soils from Dr. A.S.R. Juo and Dr. R. Lal's field experiments on the effects of vegetation and soil management on soil chemical and physical properties at the International Institute of Tropical Agriculture in Nigeria illustrates this (Table 9). Clearing and cultivation cause the well-known decline in total organic carbon, a decline that is slower when the crop is mulched than when it is not. Biomass carbon declined more sharply than total carbon; two years' cropping without mulches causing it to fall to one-quarter of the original value.

Table 9

The decline in total and biomass carbon in soil when secondary tropical forest is cleared and cultivated (Ayanaba, Tuckwell and Jenkinson, 1976).

Management	Total carbon, %	Biomass carbon, mg/100g soil
Secondary forest	1.52	34
Secondary forest cropped 2 years to maize, crop residues returned to soil	1.43	20
Secondary forest cropped 2 years to maize, crop residues not returned to soil	1.11	9

CONCLUSIONS

There has been a fundamental change in our views on the stability of soil organic matter over the last ten years. Earlier calculations had suggested that, apart from the relatively small amount of fresh plant material in soil, turnover times were measured in decades. Now we know that certain fractions have turnover times measured in thousands of years, if indeed they are

not completely stable, whereas other fractions have turnover times that are measured in years or even months. We need to use the new data to produce more realistic models that can be used to predict the long-term effects of a given system of management on the amount of organic matter in a given soil. Better models should also be of help in predicting the effects of a change in management on the amount of inorganic nitrogen released for crop growth each year.

REFERENCES

- Ayanaba, A., Tuckwell, S.B. and Jenkinson, D.S. (1976) Changes in the carbon, nitrogen and sulphur reserves of soil caused by the clearing and cropping of tropical forest. *Soil Biol. Biochem.* 8, 000-000.
- Jenkinson, D.S. (1968) Studies on the decomposition of plant material in soil. III. *J. Soil Sci.* 19, 25-39.
- Jenkinson, D.S. and Powlson, D.S. (1975) The effects of Biocidal treatments on metabolism in soil. V. *Soil Biol. Biochem.* 7, 000-000.
- Jenkinson, D.S., Powlson, D.S. and Wedderburn, R.W.M. (1975) The effects of biocidal treatments on metabolism in soil. III. *Soil Biol. Biochem.* 7, 000-000.
- Johnston, A.E. (1969) Plant nutrients in Broadbalk soils. Rep. Rothamsted exp. Stn. for 1968, Pt. 2, 93-115.
- Nydal, R. and Lovseth, K. (1970) Prospective decrease in atmospheric radiocarbon. *J. geophys. Res.* 75, 2271-2278.
- Persson, J. (1968) Biological testing of chemical humus analysis. *Lantbrukshogsk. Ann.* 34, 81-217.
- Stout, J.D. and O'Brien, B.J. (1972) Factors affecting radiocarbon enrichment in soil and the turnover of soil organic matter. Proc. 8th int. Conf. on Radiocarbon Dating. Wellington, N.Z. E13-E26.

AVAILABILITY AND IMMOBILIZATION OF SOIL NITROGEN

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ABSTRACT

Plant protein returned to soil is rapidly attacked by soil micro-organisms and converted into microbial cell components. Part of this nitrogen is eventually mineralized but some of it is converted into stable nitrogen complexes and experiments using ¹⁵N suggest this latter process may begin in the early stages of decomposition.

Trace amounts of ammonium and nitrate nitrogen, free amino acids and amino sugars have been identified in soils, the remainder being in the form of organic polymers. Fractionation of soils on the basis of particle size shows that a small amount of nitrogen is associated with plant residues which can be separated by floatation but most of it is associated with the silt and clay fractions and the C:N ratio decreases with decreasing particle size.

Approximately 50% of soil organic nitrogen can be accounted for as amino acid and amino sugar nitrogen and identification of individual acids suggest they are of microbial origin. This is supported by the appearance of amino sugars during early stages of decomposition.

The composition of organic nitrogen components will be discussed and possible reasons for their relative stability to microbial decomposition will be considered.

THE ROLE OF ORGANIC MATTER IN PESTICIDE BEHAVIOUR

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INTRODUCTION

The factors governing the behaviour of pesticide chemicals in soils are rather complex but the main process which affects pesticide activity is the extent to which the pesticide is adsorbed into soil particles. The rate at which a pesticide is absorbed by plant roots and the rate at which it is lost from the soil by decomposition, evaporation or leaching is highly dependent, not only upon the degree of adsorption but also on the strength of this adsorption. The adsorption of herbicides by soils have been studied by Osgerby (1970), Hance (1965) and Knight *et al.*, (1970) and they concluded that the process is reversible to a greater or lesser extent and dependent upon the molecular structure of the chemical and soil type. The adsorption or partition constant (K) between the soil particles and soil moisture is a characteristic of the particular soil/pesticide combination. The value of K will vary from soil to soil and many attempts have been made to correlate the extent of adsorption with a number of individual soil properties such as clay content, organic carbon, cation exchange capacity and pH. This has given rise to some confusion and different conclusions since it was not always appreciated that these soil properties are frequently inter-related. Nevertheless there is a great deal of evidence to suggest that organic matter is the most influential soil property governing pesticide adsorption and therefore its activity and behaviour in soil. This is largely associated with the high adsorptive capacity of organic matter towards unchanged pesticide molecules. There are exceptions, however, such as in the case of the bipyridyls which exist in ionic form and consequently the clay

fraction plays a significant role.

The type of soil to which the pesticide is applied also influences the persistence of the chemical. Pesticides become adsorbed on the surface of the organic matter and, in this adsorbed state, they are not so readily degraded by soil micro-organisms and are not so easily leached. Although they may persist longer in organic or peaty soils, they are usually less active than very much smaller amounts in lower organic matter sandy soils. Soil moisture also plays a part in that it influences the activity of both herbicides and insecticides by acting as a competitor for adsorption sites. In dry soils, for example, there is less competition from water molecules and the pesticide becomes strongly adsorbed. The rate of biochemical degradation is also affected by moisture supply and persistence will be increased if moisture supply is limiting.

Soil temperature is probably less important than soil moisture in affecting the behaviour and persistency of a pesticide in soil but it does have some effect on rate of breakdown and/or loss from the soil. Higher temperatures accelerate the rate of volatilisation and the chemical or biochemical degradation. Provided that soil moisture supply is adequate, pesticides degrade more slowly over the winter compared with the summer period.

HERBICIDE ACTIVITY AND SOIL TYPE

Measurements of soil organic matter or laboratory estimates of adsorption have proved very useful in predicting herbicide activity but, in the field, climatic factors such as rainfall, temperature, light intensity and transpiration play a very important role particularly when considering phytotoxicity to the crop.

In attempting to classify soils according to their adsorption characteristics, use has been made of the textural scale in use by ADAS Soil Scientists. In effect it does give a fairly good indication of the exchange capacity of soils which is

governed by the clay/humus content. Decreasing size of sand particles and increase in the clay and/or silt content is usually associated with increasing organic matter. Thus it is possible to list the soil textures in order of increasing organic matter content and a classification for the arable soils of Eastern England is shown in Table 1.

Table 1

Soil texture classification and organic matter contents.

Textural Class	Symbol	Group	Organic Matter Range (%)
Coarse sand	CS		
Sand	S	Sands	
Fine Sand	FS		Less than 1.0
Very fine sand	VFS		
Loamy coarse sand	LCS		
Loamy sand	LS	Very light	1.0 - 1.6
Loamy fine sand	LFS	Soils	
Coarse sandy loam	CSL		
Loamy very fine sand	LVFS		
Sandy loam	SL	Light soils	1.5 - 2.5
Fine sandy loam	FSL		
Very fine sandy loam	VFSL		
Silty loam	ZyL	Medium	2.0 - 3.0
Loam	L	soils	
Sandy clay loam	SCL		
Clay loam	CL		
Silty loam	ZL	Heavy	2.5 - 3.5
Silty clay/loam	ZyCL	soils	

Although there may be occasions when over-riding climatic factors can affect predictions of herbicide dose, nevertheless an

assessment of soil texture in the field does provide a means of making a reasonable estimate of herbicide dose. The scale is widely used by agrochemical advisors who have in practice found it particularly useful as an "on the spot" assessment in the field.

ORGANIC MATTER AND HERBICIDE ADSORPTION

The phenomenon of adsorption results in a partitioning of the herbicide between the soil water and the surface of the soil particles. Most herbicides, like nutrients, can only enter plants via the aqueous phase and the quantity of herbicide which is available to the plant at any one time is much less than the quantity added to the soil. The degree of adsorption increases with increasing organic matter content. It is for this reason that high organic matter soils require higher doses of herbicide to achieve an acceptable level of weed control compared with mineral soils. It is often not possible to obtain an acceptable level of weed control with most surface applied soil acting herbicides on peaty soils simply because they are held so strongly on the surface of peat that active concentrations are never achieved in the rooting zone of the germinating weeds irrespective of the rainfall which follows immediately after application. There are instances however where shallow incorporation of the herbicide into the surface 2.5-5.0 cm of a peaty soil, e.g. lenacil, has given fairly good weed control in sugar beet. However the depth of incorporation is critical and, unless carefully controlled, crop injury can result.

Since there is an excellent correlation between adsorption and soil organic matter it would be reasonable to express the adsorption of a soil acting herbicide as the amount adsorbed by unit weight of organic matter when in equilibrium with unit concentration of herbicide in solution. This quantity (Q) has been calculated for a number of substituted urea herbicides on different soils by Hance (1965) and by Osgerby (1970) for the adsorption of the herbicide chlorthiamid on 6 soils with a range of

organic matter contents. The data and Q values are shown in Tables 2 and 3.

Table 2

Values of Q for some substituted urea herbicides.

Herbicide	Q values in different soils					*Average Q Value
	% SOM (by wt. of soils)					
	3.0	3.3	6.4	20.7	62.9	
Chloroxuron	2333	3636	2734	2294	-	2749
Diuron	357	412	250	361	426	361
Monolinuron	270	291	172	121	129	197
Phenylurea	43	48	34	42	68	47

* Calculated from values of K determined from the Freundlich adsorption isotherm $\frac{x}{m} = KC^n$ where $\frac{x}{m}$ is the amount of pesticide adsorbed per unit weight of soil, K and n are constants and C is the equilibrium concentration of the herbicide in solution.

$$Q = \frac{100 \times K}{\% \text{ Org. Matter (OM)}}$$

Table 3

Adsorption characteristics of chlorthiamid on six soils.

Soil No.	% Org. Matter	K*	Q*
1	33.2	7.95	24.0
2	9.6	3.00	31.3
3	8.1	2.29	28.3
4	7.9	2.14	27.1
5	6.8	2.18	32.1
6	5.9	2.04	34.6

* Definitions see Table 2.

In principle, the Q values are useful since they provide a means of predicting the adsorption of a herbicide on any soil provided the adsorption of that herbicide has been measured on one soil of known organic matter content. The constancy of Q however will depend on the correct determination of the organic matter content and on the nature and activity of that fraction. On soils with more than 10% organic matter the values of Q often decrease indicating that adsorption is proportionately less than in soils of lower organic matter contents. This could well be due to differences in the way in which the organic matter is combined with mineral particles in highly organic matter.

The exact significance of herbicide residue concentrations is difficult to interpret for all soils as the organic matter content plays an important role in modifying the availability of the residue to plant roots. Biological assay studies coupled with information from field cases have provided some guidance on this aspect and, threshold levels for simazine, for example, related to organic matter contents are shown in Table 4.

Table 4

Safe residue levels of simazine related to organic matter.

Organic Matter %	1.5	1.5-2.5	2.6-3.0	3.1-5.0	5.0
Safe Concentration (ppm in air-dry soil)	0.05	0.10	0.15	0.20	0.25

Temperatures and light intensity are factors which can influence the safe residue level. Conditions which favour greatly enhanced transpiration rates result in increased adsorption of the herbicide which cannot be metabolised rapidly enough by the plant and toxic levels build up within the tissue. The question often arises of how these residues may be deactivated and conditions rendered safe for subsequent crops. Dilution through cultivation followed by deep ploughing will reduce the risk of damage quite appreciably. Activated charcoal adsorbs and inactivates simazine

but very large amounts would need to be incorporated into soil to produce the desired effect. With transplants, however, root dipping in a charcoal slurry has proved quite successful.

The bipyridylium herbicides (paraquat and diquat) are salts of strong bases which readily undergo base exchange with cations on clay minerals. They are rapidly inactivated on coming into contact with most soils as a result of strong adsorption on the clay lattices. There are reports that damage can occur in seedlings sown in very light sandy soils, dead organic litter or light peat (Calderbank, 1962; Hammerton and Johnson, 1962; O'Toole, 1965; Watkin and Sagar, 1971). Damage to seedlings of grasses, whiteclover, rape have been reported by these workers when sown up to 14 days after the application of paraquat. The writer has observed phytotoxic symptoms in crops grown on light Fen peat soils in East Anglia; seedlings of red beet and carrots and also bulbs emerging through a paraquat treated surface soil have exhibited severe chlorotic symptoms of leaves which have come in contact with the treated soil. On such soils, although the herbicide is adsorbed on the surface of organic matter, it is obvious that it is only weakly adsorbed and concentrations in soil water are sufficient to damage the crop.

ORGANIC MATTER AND INSECTICIDE ADSORPTION

The organophosphorus insecticides in general are strongly adsorbed on soil colloid. The degree of adsorption is governed by the organic matter content; high organic matter reduced the active concentration in soil moisture, increases persistence, decreases insecticide movement and reduces uptake by the crop. Adsorption studies on soils can provide useful information on the likely behaviour of soil acting insecticides such as leaching and movement, persistency and dosage rates required to give adequate active concentrations for pest control. Adsorption and desorption studies using ^{14}C labelled chlorfenvinphos (CFVP), an organo-

phosphorus insecticide, have been carried out and the results are described using the Freundlich isotherm, $W/m = KC_E^n$.

Where W/m is the mass of insecticide adsorbed per gramme of soil, K and n are constants and C_E is the equilibrium concentration of insecticide in solution.

K was measured at a solution concentration of 1 μ M/ml.

The adsorption (K_A) and desorption (K_D) constant were determined and from these were calculated the Q values $\left(\frac{K \times 100}{\% \text{ Loss on Ignition}} \right)$ using the loss on ignition after 2 hours at 450°C. The results obtained are shown in Table 5 for soils of different texture ranging from 3.4 to 33.9% loss on ignition.

Table 5

Q values for CFVP calculated from adsorption (K_A) and desorption (K_D) for different soils.

Soil Type (Texture)	Loss on Ignition (%)	Mean K_A	Q_A Value	Mean K_D	Q_D Value
Loamy sand	3.4	5.4	159	0.62	18.2
Very fine sandy loam	5.2	7.0	135	0.80	15.4
Clay loam	6.7	9.7	145	0.88	13.1
Organic sand	14.7	19.6	133	1.50	10.2
Loamy peat	33.9	48.5	143	2.79	8.2

The values of the adsorption and desorption constants increase regularly with organic matter content whilst the Q_A values are fairly constant ranging from 133 to 159 with an average of 143 showing that adsorption is strongly correlated with organic matter. Values of Q calculated from the desorption isotherms (Q_D) show a greater variation than Q_A values which may be due partly to the fact that the insecticide had degraded to some

extent towards the end of the experimental period of 7 to 10 days, probably more so in some soils than others.

ORGANIC MATTER AND INSECTICIDE PERSISTENCE

The organophosphorus insecticides are generally considered to be metabolised fairly rapidly in the soil environment and rarely persist into the second year. Some degree of persistence is desirable if insect pests are to be controlled and, on mineral soils, short persistence is probably one of the main reasons for the lack of success of some organophosphorus compounds against certain soil insects. On organic soils, however, degradation is very much slower and, although appreciable residues may be present, insecticidal activity is low because of the strong adsorption on to the organic matter resulting in low concentrations of the insecticide in soil moisture. The degradation of chlorfenvinphos was studied in mineral and peat soils in Eastern England. Comparative data for the different soils are shown in Table 6 (Williams, 1975).

Table 6

Chlorfenvinphos residues in soil.

Soil Type	Org. Matter (%)	Interval between Application and Sampling	% of Applied dose remaining
Loamy sand (pH 7.1)	1.6	28	25
		56	9
		125	2
Sandy loam (pH 6.8)	2.2	30	46
		60	17
		142	15
Loamy peat (pH 6.0)	48	30	87
		90	82
		120	75
		300	34

Thus on the very low organic matter loamy sand, only 25% of the applied dose remained after 28 days, whilst on the sandy loam 46% remained after 30 days. On the high organic matter soil, however, 87% of the applied dose remained after 30 days. Subsequent degradation was slower but after 4-5 months only 2 and 15% of the applied dose remained in the loamy sand and sandy loam soils respectively, whilst on the peaty loam soil 75% remained. Thus, chlorfenvinphos is very inaccessible to microbiological degradation in the adsorbed state on high organic matter soils.

Studies carried out by Suett (1971) at the National Vegetable Research Station, comparing the persistency of 4 organophosphorus insecticides indicated that persistence decreased in the order fonofos > chlorfenvinphos >> chlormephos > diazinon in both mineral and peat soils. The times taken for 50% of the applied dose to disappear when incorporated into the soil are shown in Table 7.

Table 7

Degradation of soil applied organophosphorus insecticides.

Insecticide	Time taken for 50% Loss of Insecticide (weeks)	
	Sandy loam	Light peat
Fonofos	11	22
Chlorfenvinphos	10	18
Chlormephos	5	11
Diazinon	<3	5

Thus the time taken for 50% of the applied insecticide to disappear on the peat soil is approximately twice the time taken on the mineral soil.

Organic matter similarly affects the persistence of the organochlorine insecticides. Recent data by Edwards (1969) and

obtained by the author for residues of dieldrin in randomly selected soils of the UK are shown in Table 8.

Table 8

Dieldrin (HEOD) residues in soils of the United Kingdom.

Location	Date	Soil Texture	Dieldrin (ppm DW soil)	
			Range	Mean
Norfolk and Beds.	1968	Sandy loam	<0.01-0.07	<0.03
Warwicks	1966/7	Clay loam	<0.01	<0.01
Glam. and (a) Rads.	1971	Silty loam	0.14-0.18	0.15
Glam. and (b) Rads.	1971	Silty loam	0.06-0.09	0.07
Norfolk	1968	Light Fen peat	0.51-1.47	1.13
Cambs.	1968	Light Fen peat	0.66-0.84	0.76
Lancs.	1968	Light peat	0.81-0.83	0.82

(a) 2-5 years after application

(b) 6-10 years after application.

The largest residues (up to 1.50 ppm) were found in the Lancashire and Fenland peats containing more than 45% organic matter on which dieldrin becomes strongly adsorbed and inaccessible to microbial attack. On the sandy and clay loam arable soils with their low organic matter contents (1.5-2.5%), the dieldrin residues found were of a very low order (0.03 ppm) following regular treatment of crops like carrots and potatoes with dieldrin and aldrin respectively. In the grassland areas of Glamorgan and Radnorshire where the soils contain 4-5% organic matter, dieldrin residues were higher than on the sandy soils, being of the order of 0.14-0.18 ppm, 2 to 5 years after application and 0.06-0.09 ppm 6-10 years after application. These residues resulted from an application of 3.0 kg. a.i./ha of aldrin to seed potatoes every 5 or 6 years.

Although carrots grown in treated soil may contain high residues of dieldrin (up to 1.40 ppm), these occur almost entirely in the skin with the flesh containing less than 0.05 ppm. The residue levels in carrots grown in soil treated in previous years were much smaller (Lee, 1968).

Radish crops grown in a light Fen peat soil treated with up to 3.0 kg active ingredient of chlorfenvinphos per hectare on four occasions in one season were found to contain less than 0.004 ppm of the insecticide even though the surface 10 cm of soil contained up to 6.5 ppm of active chlorfenvinphos. Unlike carrots, radish grow virtually on the soil surface and insecticide uptake is primarily via the roots. The strongly adsorbed insecticide is obviously not readily adsorbed by the plant roots. In the case of carrots which grow completely below the soil surface, the process whereby the insecticide is taken up is probably one of surface adsorption.

Interacting factors such as pH and moisture can modify the behaviour of the organic matter towards soil acting pesticides. The nature and state of decomposition of the organic matter must play an important part and there are indications that humus developed under the more acid, high rainfall conditions in the north and west of the British Isles, behaves differently to that in the drier, eastern parts of the country. The former would appear to possess a lower adsorptive capacity than the latter since soil acting herbicides are more active in the more acid type of humus developed under higher rainfall conditions.

REFERENCES

- Calderbank, A. (1962) Plant Protection Ltd. Rep. of Symposium at Elvetham Hall. 2.
- Edwards, C.A. (1969) Problems of insecticidal residues in agricultural soils. NAAS Quarterly Review No. 86, 47-83.
- Hance, R.J. (1965) Adsorption of urea and some of its derivatives by a variety of soils. Weed Res. 5, 98-107.
- Hammerton, J.A. and Johnson, R.J. (1962) Establishment of rape in grass swards by use of sod seeder and herbicides. J. Brit. Grassld. Soc. 17, 229-30.
- Knight, B.A.G., Coutts, J. and Tomlinson, T.E. (1970) Sorption and transport processes in soil. SCI Monograph No. 37, p.54.
- Lees, D.F. (1968) Pesticide residues in foodstuffs in Great Britain. IX. Aldrin, dieldrin and other organochlorine pesticide residues in potatoes and carrots. J. Sci. Fd. Agric. 19, 701-5.
- Osgerby, J.M. (1970) Sorption and transport processes in soil. SCI Monograph No. 37, p.63.
- O'Toole, M.A. (1965) Residual effects of paraquat on a peat soil. Irish J. Agric. Res. 4, 231-3.
- Suett, D.L. (1971) Relevant aspects of persistence of insecticides in soil (Private Communication).
- Watkin, E.M. and Sagar, G.R. (1971) Residual activity of paraquat in soils. I. Factors affecting persistence. Weed Res. 11, 1-10.
- Williams, J.H. (1975) The persistency of chlorfenvinphos on different soil types (In press).

THE ROLE OF ORGANIC MATERIALS IN HEAVY METAL
PROBLEMS OF SOIL AND WATER

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INTRODUCTION

Soil chemistry is concerned with 'secondary' geochemical dispersion, i.e. the transport and cycling of elements at the earth's surface, in contrast with geochemistry which is also concerned with 'primary' processes, e.g., magmatic crystallisation or metamorphism. Three dispersal processes are generally recognised at the earth's surface, namely,

- 1) Hydromorphic dispersion; the transport of elements in the soil water or by surface waters.
- 2) Clastic dispersion; the physical movement of solid particles by windblow or stream sediment transport.
- 3) Biogenic dispersion; dispersal by organisms.

It is conventional, and often convenient, to represent the first two of these as though they are solely inorganic in character. But the ample supply of organic materials which is available in the biosphere strongly influences all aspects of secondary dispersion.

The heavy metals (conventionally those with a density greater than 4 g/cc) in soil present problems of deficiency in some areas and, through pollution, problems of excess or toxicity in others. In all cases the abundance of organic materials, which adsorb and complex metals, in the soil modifies their mobilisation, transport and fate to give results which might not be expected if the relevant chemical reactions were only inorganic. This paper reviews some aspects of the influence of

organic materials on heavy metal problems with illustrations from the literature and from current work at Aberystwyth.

There are four broad categories of organic matter:

- 1) Living tissue; the composition of organisms often differs markedly from their environment. They secrete organic materials and, after death, may become incorporated in humus and peat.
- 2) Mobile forms; soluble and colloidal forms are free to migrate in soil and surface water and they interact with metals as they move.
- 3) Immobile and semi-stable; peat and soil humus persist for periods ranging from hundreds to thousands of years and act as geochemical sinks in which trace metals are temporarily immobilised.
- 4) Immobile and fossil; coal and oil are ancient fossil organic deposits which are enriched in many trace elements. Their use by man allows the metals to be mobilised and enter the biosphere afresh for further cycling.

Each of these is now reviewed to illustrate some topical heavy metal problems.

LIVING TISSUE

The mass of the biosphere is tiny compared with other geochemical zones. Kovda (1974) has estimated that the weight of living matter on land is about 10^{12} - 10^{13} tonnes most of which is accounted for by plants, whereas the mass of the whole earth is of the order of 10^{21} tonnes. But the biosphere is characterised by very great chemical activity and Mason (1958) has suggested that during the last 500 million years (0.1% of the age of the earth) the total amount of matter that has passed through the biosphere is comparable with the total mass of the earth.

The composition of organisms is not a passive reflection of that of the environment since sometimes they may exclude from their tissues the metals available to them and in other cases they concentrate metals. Marine organisms are well known for their ability to concentrate ions from sea water as was dramatically shown by the events in Minamata Bay, Japan, in 1950. A local factory caused a small, but apparently not serious amount of mercury pollution in its discharge water (0.0016 - 0.0036 ppm), yet 111 people in the local fishing were made seriously ill (46 fatally) by eating shellfish which contained between 30 and 102 ppm Hg (fresh weight basis) (Lagerwerff, 1972). Even more important was the fact that the mercury was present as the highly toxic methyl mercury (CH_3Hg^+) or dimethyl mercury ($(\text{CH}_3)_2\text{Hg}^+$) which were first synthesised by bacteria in bottom sediments and concentrated in the food-chain.

In recent years improved, easier methods of analysis for mercury have become available and the recognition of bacterial methylation of mercury in an aerobic environments have, together, promoted more research on soil mercury. A report by Warren (1969) suggested that very high levels might occur in some British soils. A new survey (Davies, unpublished) has revealed levels of up to 1780 ppb (background threshold = 90 ppb) in soils contaminated by lead from old mine workings. The chemical form of mercury in these soils is uncertain but in a recent paper Berkert *et al.*, (1974) have found evidence that methylation of mercury can occur in wet soils. In British mining areas the worst affected soils are often those in valleys close to a river and it is accepted that even in freely drained soils the interiors of peds can be anaerobic. Accordingly, it would be of great interest to know more of the chemical forms in which mercury occurs in soils.

Land plants also concentrate trace elements and this may be specially relevant in crops and vegetables growing on contaminated ground. Some data from a paper by Davies and Roberts (1975) referring to Halkyn Mountain, Clwyd, illustrate this differential

uptake of heavy metals. Radish (Raphanus sativus) was grown as a test crop in the area. Harvested plants were analysed for Pb, Zn, Cu and Cd and the soils were assessed for the plant-availability of these metals by extracting them with neutral diammonium EDTA (0.05M) solution. The results are given in Table 1 where the Concentration Factor is the plant ash metal content divided by the soil available content. It is seen that cadmium is readily absorbed by plants. Ordinarily, soil contains less than 1 ppm Cd and it represents no apparent hazard despite its extreme toxicity to mammals. But cadmium is a natural impurity of zinc compounds and in many places is becoming enriched in soil as a result of urban and industrial activity.

Table 1

Concentration of heavy metals by radish.

		Heavy metal content			
		Pb	Zn (ppm metal)	Cu	Cd
Soil (EDTA Extract)	Mean	2036	513	18	6.1
	Minimum	825	34	9	1.1
	Maximum	5325	3039	46	29.3
Radish (Ash Content)	Mean	182	1465	20	5.9
	Minimum	25	127	4	1.5
	Maximum	777	2857	44	15.0

		Concentration Factor*			
Mean	0.10	4.08	1.32	1.50	
Minimum	0.03	0.57	0.37	0.74	
Maximum	0.67	12.80	2.56	5.00	

* Content of metal in ash divided by that in soil extract.

In contrast, lead is not easily absorbed by plants and Jones and Clement (1972) have suggested four barriers which restrict the movements of lead from soil to man. These are the small proportion of lead in soil which is plant-available, storage in the roots with little translocation to the shoots, low absorption in the gut and immobilisation in the bones. The data in Table 1 illustrates the low availability to the plant of soil lead. But reduced translocation to the shoots does not mean no translocation as shewn by an experiment by Alloway (1969) who grew radish on several levels of lead and analysed both roots and leaves (Table 2).

Table 2

Lead uptake by radish.

	Pb (ppm)		
	Soil Total	<u>Radish DM.</u>	
		Roots	Leaves
CONTROL	44	10	10
HIGH	11200	499	136

It must also be noted that there is a marked seasonality in the uptake of lead by grasses. Mitchell and Reith (1966) found the normal lead content of mixed pasture herbage during the period of active growth was between 0.3 and 1.5 ppm (DM) but by late winter lead contents may reach 30-40 ppm. They pointed out that these high lead contents justify consideration of possible effects on the health of animals grazing pastures in late winter or early spring and they suggested that the commonly observed enrichment of topsoil by lead might be accounted for by the incorporation of lead-rich plant material. The soil in question (Tarves association near Aberdeen) contained around 10 ppm. In Cardiganshire we find that soils typically contain around 40 ppm Pb

Finally, animal residues must also be considered. The beneficial role of manures in soil fertility is well known but

these manures are often not available now. Many farmers have therefore turned to using sewage derived materials which are readily available near many towns. Unfortunately, in many towns metal-rich industrial effluents are passed into the foul sewer along with human sewage and the organic sludge which results from the bacterial digestion of sewage is a very effective scavenger of metals, especially zinc, copper and nickel. Continuous, agricultural use of these materials may lead to metal toxicity problems (e.g., v. Le Riche, 1968). Berrow and Webber (1972) concluded that 'the use of such materials as fertilizers is not without serious hazards particularly when used at heavy rates of application over a number of years'.

MOBILE ORGANIC MATTER

The role of soluble organic materials in mobilising heavy metals is exemplified by the movement of iron in podzols. In freely drained soils redox potential (Eh) commonly varies between +300 and +800 mV and reaction (pH) between 4.0 and 8.0 (Baas Becking et al., 1960). Under these conditions ferric iron is the stable species (e.g., vide Hem, 1972) and, even accepting that soil reactions may not be in equilibrium and that ped interiors may be anaerobic even in freely drained soils, one would expect ferric iron to accumulate in top soils as, of course, it does in the tropics. But work in recent years at Bangor and Rothamsted has revealed how organic chelating agents originating from tree leaves can mobilise iron and account for the podzol process and the same organic materials can mobilise other heavy metals.

Ong et al. (1970) used an alkali-soluble fraction of peat to represent organic acids found in nature. When present in concentrations commonly found in natural water (4-40 ppm carbon) copper, aluminium, iron, lead and zinc were readily brought into solution and stabilised for transport even at pH values where, without organic acids, the metals would precipitate. They quoted some Russian work where it was found that more than half the total

quantity of iron, manganese, nickel and copper in the river Dnieper is transported in the form of organic acids. Gardiner (1974) studied the adsorption of cadmium on river muds and concluded that humic material appears to be the main component responsible for adsorption. De Groot (1966) found that sediments in transit from a river to the sea can undergo changes in trace element composition because of mobilisation as soluble metallo-organic complexes. A loss of copper in this way might lead to deficiencies in plants grown on reclaimed sediments. There is some talk of a Severn Barrage involving reclamation of estuarine muds where some of these problems could occur since the estuary is polluted.

A paper by Hodgson et al. (1966) has shed some light on chemical conditions within the soil solution. They noted that zinc deficiencies are prevalent on many soils in Colorado but that copper deficiencies were rare on calcareous soils. The soil solution was obtained by displacement from a number of calcareous soils and they concluded that 99% of the soluble copper was organically complexed. This level of complexing effectively increased the total concentration of copper in the soil solution 100 fold. In contrast, only about 60% of the zinc was complexed and the content in the soil solution thereby only doubled. This strong complexing was believed to explain the lower prevalence of copper deficiencies even though both cations shew similar decreases in solubility with increase in pH.

Further studies on the relevance of complexing of heavy metals in both plant and animal nutrition would seem worthwhile. The availability to trees of chelated iron added to calcareous soils suggests that roots can adsorb the whole chelate. Perhaps this happens for other metals. Similarly, it may be that some heavy metals in some public water supplies are also chelated which might affect their absorption in the human gastro-intestinal tract.

IMMOBILE AND SEMI-STABLE FORMS

Soil Humus

The influence of soil humus on the availability of heavy metals is well known, e.g., the amount of organic matter in soil exerts a very strong influence on the availability of copper. The work of Hodgson on copper deficiencies in Colorado soils contrasts with the well established problem of copper-induced melanism of wheat in the south east of England. The plant changes from dark green to black, yields are severely reduced and nitrogen applications increase the severity of the attack. The disease is associated with the Icknield series, which is a highly organic and highly calcareous rendzina, and is caused by the very low copper content of these soils (EDTA-extractable levels are generally below 1 ppm). Recently, McLaren and Crawford (1973) have published a fractionation scheme for soil copper which distinguished between soil solution and exchangeable copper, extracted by 0.05M CaCl₂; inorganically bound copper, extracted by 2.5% acetic acid; and organically bound copper, extracted by 1.0M potassium pyrophosphate. This scheme has been applied to some soils from the south-east of England. The contrast between the Icknield series and the Hamble series, a calcimorphic brown earth, is shown in Table 3. In the Icknield series EDTA extractable copper averaged 0.8 ppm, and in the Hamble series, 7.7 ppm. Thus, in the rendzina most of the small amount of available copper was bound in the organic matter.

Table 3

Fractionation of copper in two soils.

Soil Series	pH	%OM	% Extracted Copper		
			Exch. and Soil Soln.	Inorg. bound	Organic bound
Icknield	7.8	21.0	0	12	88
Hamble	7.3	5.6	59	0	41

At Aberystwyth the standard method of approximating the total heavy metal content of contaminated soils is an extraction with hot, concentrated nitric acid. Compared with physical methods this extracts about 75% of the total metal. It has also been found that neutral diammonium EDTA is a useful extractant for predicting plant uptake of lead. Accordingly, many soils have now been analysed by both nitric acid and EDTA methods and an interesting pattern has emerged (Table 4). EDTA is assumed to extract the exchangeable metals, readily soluble metals, organically complexed metals and part of those sorbed by sesquioxides. Its utility as an extractant for copper is a reflection of the fact that much plant-available copper is organically bound. Accordingly the proportion of the total copper extracted by EDTA is explicable. Similarly, in view of Hodgson's work on the complexing of zinc quoted above the low amount of zinc extracted are also reasonable. But, in view of the chemical similarity between zinc and cadmium the high proportion of cadmium extracted is remarkable as is the high proportion of lead. Each area suffers from industrial contamination and most of the lead may be assumed to have first occurred as inorganic lead (particles of galena, PbS, or as lead halides from vehicle exhausts). The partitioning of this added lead so that a high proportion becomes organically bound poses some interesting questions. In particular, as humus levels commonly decline when pastures are ploughed for arable cropping, it may be important to know if the lead released by organic mineralisation be taken up by crops.

Table 4

Proportions of organically bound metals in contaminated soils.

Study Area	% Soil total metal extracted by EDTA			
	Pb	Zn	Cu	Cd
Halkyn Mountain	77	29	57	72
Tamar Valley	59	24	56	-
Manchester	71	31	61	71

Peat

Surface accumulations of organic matter readily retain metals. Peats, especially climatic peats, have a low ash content and, therefore, initially low metal contents. But their metal contents may be supplemented from water flowing through the bog, from atmospheric fallout and from agricultural chemicals.

Occasionally, the accumulation of heavy metals in peat can render it economically valuable. One of the best examples was the Turf Copper Mine at Dol Frwynog near Dolgellau. According to North (1962) a certain Mr. Parry learned that the peat ashes there could not be used to manure the fields since they would make the ground more sterile. An assay of the ashes revealed a large amount of copper and in some parts of the bog metallic copper was found. Mining consisted simply of cutting the turf and ashing it: in one year 2000 tons of ashes valued at £20,000 were sent to Swansea for smelting. There is no peat there now but the mineral substratum is still heavily impregnated with copper and pine trees growing on the site are stunted and chlorotic.

Cannon (1969) has reported that several peat bogs in Orleans County, New York were mineralised by ground water and shortly after their being drained some areas would not support any vegetation because of high zinc (up to 16%) whereas the non-mineralised peat contained less than 1 ppm.

However, peats are better known for causing metal deficiencies in crops, particularly the Fenlands of East Anglia. Caldwell (1971) records that 9,700 ha of organic soils are copper deficient and the first case of copper deficiency arose on a reclaimed deep peat in Methwold Fen, Norfolk. Copper deficiencies arise throughout the pH range (4-7.2) but are not found where crops have received copper based fungicides or where the peat has wasted to an organic loam or silty loam. For soils with > 45% OM, deficiencies are found where EDTA extractable copper is less than 4 ppm.

The Fenlands are not the only intensively used lowland peats: there are also the Lancashire Mosses and the Somerset Levels where copper deficiency problems do not seem to occur. Hall and Folland (1967) reported the copper contents of some Lancashire peat samples which ranged from 8.7 - 47.9 ppm (EDTA-extractable) in the Ap horizon. These values are above the limit for deficiencies and no instances of 'reclamation disease' have been reported for the area. They suggested that industrial pollution might be responsible for these high levels. Some support for this idea come from a recent study of trace elements in these peats (Davies, unpublished). Heavy metal data are given for these organic soils in Table 5. The lead and copper levels are generally high and suggest metal contamination which is reinforced by data for samples from a profile where there is marked accumulation in the surface of the soil, especially for lead. There are two possible explanations. Until the mid-nineteenth century night soiling was extensively practised in south-west Lancashire and some sewage sludge is used today. But the industrial towns upwind of the peat contain many metal using industries and refineries so that fallout of heavy metals could also explain the high soil levels. Further evidence for enrichment of topsoils by atmospheric deposition is found in the work of Jenkins and Bower (1974) who concluded that atmospheric pollution by copper, lead, tin and zinc was widespread rather than localised and current rates of atmospheric deposition could account for a lead content of 75 ppm in the A1 horizon of a podzol in North Wales. Sapek (1974) has also found marked accumulation of lead in the upper layers of profiles from a bog at Kuwasy, Poland with levels up to 85 ppm. The area is situated far from industrial centres, busy roads and large settlements and he concludes that this contamination is a consequence of world wide fallout.

In Somerset copper problems occur only in relation to the teart pastures and we have no data for trace elements in the peats of that area. It may be relevant that the low lying areas receive drainage water from the mineralised Mendip Hills.

Table 5

Metal contents of Lancashire peats.

	Total metal : ppm soil			
	% OM	Pb	Zn	Cu
<u>Organic Topsoils (Mean)</u>	33.9	324	240	80
<u>Profile</u>				
0-12 cm	49.8	167	142	66
12-55 cm	63.8	70	75	44
55+ cm	86.8	17	41	32

IMMOBILE AND FOSSIL FORMS

Large quantities of the fossil organic materials, coal and oil, are being mined or pumped and ultimately burned as fuel. Coal is the metamorphosed remains of forest humus from earlier geological times and many studies have shown that such humus is enriched in trace elements. It is not surprising, therefore that coal is enriched in heavy metals and augmented in others by deposition in the coal beds from external sources. Gibson and Selvig (1944) have reviewed the literature concerning the rare and uncommon chemical elements in coal. Besides the lead and zinc present in the organic material both galena and sphalerite are often found associated with coal beds. They quote work by Dunn and Bloxham in 1932 in which sufficient lead was found deposited on grass and soil of pastures near a coking works in Leeds to cause the death of a sheep by lead poisoning. A large proportion of the ash from domestic chimneys falls to the ground close to the source and this, together with direct additions of ash and soot to soil, can explain the high lead levels observed in private gardens. A soil near Swansea may be quoted as an example; the garden soil contained 560 ppm EDTA-extractable lead, high values

of the other metals, and a loss on ignition of 32.2%. As the garden was some distance from urban Swansea and the old smelters, these high values cannot be attributed to those causes. But a visit shewed that the householder had dug in coal ash for many years and this could be detected by a finger assessment of texture.

CONCLUSIONS

In conclusion the modifying role of organic materials must always be taken into consideration in any heavy metal problem. Immobile organic forms are reservoirs which trap metals while mobile forms can profoundly alter the solubility of inorganic ions.

REFERENCES

- Alloway, B.J. (1969) Unpublished Ph.D. thesis: Wales.
- Baas Beeking, L.G.M., I.R. Kaplan, and D. Moore (1960) *J. Geol.* 68, 243-284.
- Beckert, W.F., A.A. Moghissi, F.H.F. Au, E.W. Bretthauer and J.C. McFarlane (1974) *Nature (Lond.)* 249, 674-675.
- Berrow, M.L. and J. Webber (1972) *J. Sci. Fd. Agric.* 23, 93-100.
- Caldwell, T.H. (1971) in 'Trace Elements in Soils and Crops'. *Tech. Bull. 21. MAFF (HMSO) London.* 217 pp.
- Cannon, H.L. (1969) *Trace substances in environmental health.* 3, 21-43.
- Davies, B.E. and L.J. Roberts (1975) *Sci. Total Env.* 4 (in press).
- De Groot, A.J. (1966) *Trans. Comm. II and IV Int. Soil Sci. Soc. (Aberdeen)* 267-279.
- Gardiner, J. (1974) *Water Research* 8, 157-164.
- Gibson, F.H. and W.A. Selvig (1944) *U.S. Bureau of Mines. Tech. paper* 669.

- Hall, B.R. and C.J. Folland (1967) Soils of the S.W. Lancashire Coastal Plain. Memoir Soil Survey England and Wales.
- Hem, J.D. (1972) Geol. Soc. Amer. Bull. 83, 443-450.
- Hodgson, J.F., W.L. Lindsay and J.F. Trierweiler (1966) Soil Sci. Soc. Amer. proc. 30, 723-726.
- Jenkins, D.A. and R.P. Bower (1974) Trans. 10th Int. Congr. Soil Sci. VI (2), 466-473.
- Jones, L.H.P. and C.R. Clement (1972) in 'Lead and the Environment'. Inst. Petroleum. London. 82 pp.
- Kovda, V.A. (1974) Trans. 10th Int. Congr. Soil Sci.: special report: Biosphere, soils and their utilization.
- Lagerwerff, J.V. (1972) in 'Micronutrients in Agriculture'. Soil Sci. Soc. Amer. Madison.
- Le Riche, H. (1968) J. Agric. Sci. Camb. 71, 205-207.
- Mason, B. (1958) Principles of Geochemistry. Wiley N.Y. 310 pp.
- McLaren, R.G. and D.V. Crawford (1973) J. Soil Sci. 24, 172-181.
- Mitchell, R.L. and J.W.S. Reith (1966) J. Sci. Fd. Agric. 17, 437-440.
- North, F.J. (1962) Mining for Metals in Wales. National Museum, Cardiff. 112 pp.
- Ong, H.L., V.E. Sanson and R.E. Bisque (1970). U.S. Geol. Survey, Professional Paper 700-C, 130-137.
- Sapek, A. (1974) Proc. Int. Peat Symposium. 174-185.
- Warren, H.V. and R.E. Delavault (1969) Oikos 20, 537-539.

Major, B.S. and D.S. Johnson (1948) - 1948
 General, Walter B. Johnson (1948) - 1948
 Major, J.D. Johnson (1948) - 1948
 Major, J.F. Johnson (1948) - 1948
 Major, D.A. Johnson (1948) - 1948
 Major, J.H. Johnson (1948) - 1948
 Major, V.A. Johnson (1948) - 1948
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PART III

FIELD MEETING

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SOILS OF THE LIMESTONE REGION OF EAST CLWYD
AND THEIR LAND USE CAPABILITY

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Mold: Y Wyddgrug, Clwyd, Wales

INTRODUCTION

Carboniferous Limestone forms small outcrops along the north coast of Wales, flanks the western edge of the Flint and Denbigh coalfield and occurs again along the west of the Vale of Clwyd. The block west of Holywell on which the excursion was based covers some 150 sq. km and is one of the largest in North Wales.

The rocks of north-east Wales dip generally to the east so that a section east from the Silurian greywackes of the Clwydian Range passes through progressively younger beds and reaches Triassic Sandstones at the Dee. Much of the succession is obscured by glacial drift, and only the Silurian rocks and the succeeding unconformable Carboniferous Limestone are widely exposed. Shaly and shelly beds occur only rarely in the Carboniferous Limestone sequence, and the rocks are usually pure light grey limestone which are thickly bedded, widely jointed and deeply fissured and, where exposed, carry characteristic limestone pavements. Only in the east close to the Chert Beds of the Millstone Grit does the limestone become sandy.

The lead and zinc lodes which supported the widespread mining of the last century occur along the eastern and northern margins. The extensive mine waste, much of it from small surface workings, and natural drainage through ore-rich rock have left a legacy of soils contaminated with lead, zinc, copper and cadmium

(Davies and Roberts, 1975).

The district is flat to rolling at about 150-180 m (500-600 ft) with more hilly country to the east reaching almost to 300 m (1000 ft), and is characterised by the almost complete absence of surface streams. Only the Afon Pant Gwyn occupying a subglacial drainage channel carries surface water.

SOIL-FORMING MATERIALS

Tertiary deposits in solution hollows are described by Walsh and Brown (1971) but most of the material covering the limestone is glacial drift. The whole of Clwyd is believed to have been glaciated during the Devensian and fresh glacial landforms occur. The Cae Gwyn and Ffynnon Bueno caves at 105 m (350 ft) and 140 m (450 ft) west of the district which contained Aurignacian remains dated to 28,000 BP were sealed with glacial deposits and there seems every reason to believe that the Holywell area was overrun by ice during the last advance. Till of Welsh origin, in places containing Triassic material from the Vale of Clwyd, is extensive in the west of Sheet SJ17 and glaciofluvial sands with some gravels are widespread in the valleys of the Wheeler and its tributaries. Both pass laterally to thinner, less distinctive deposits up to 4m thick of unbedded drifts which occupy much of the limestone plateau and contain a varied assemblage of erratic stones with Lower Palaeozoic siltstone and sandstone most common.

The contribution to the soil parent material of limestone residue is thought to be very small; even drift only 10 cm thick contains largely detrital quartz grains with few bipyramidal crystals. Loess which occurs widely over limestone in several other parts of Britain has not been recognised here.

SOILS

In the first surveys (Robinson et al., 1928) on Carboniferous Limestone in north and south Wales the soils were divided into a lowland facies of reddish brown stony loams with rock at 60 cm or less, and an upland facies of very shallow soils. With the introduction of the American usage of soil series the Gower and Pentraeth series were named and described (Robinson et al., 1930), and grouped for convenience as the Gower Suite in materials from Carboniferous Limestone and derived drifts. The Gower series included naturally well drained and sedentary soils, and upland and lowland phases were described. The Pentraeth series was described as comprising "Drift soils corresponding with the Gower series. Reddish brown loams of considerable depth and fertility."

In work in east Flintshire (Hughes and Walters, 1932) the series were described as follows.

"Gower Series. The major portion of the area which may be classified in the Gower Suite consists of rough mountain common, strewn with coarse limestone debris and carrying inferior herbage. The cultivated limestone soils occupy a minor area.

The soils of the Gower Series, formed in situ on limestone, occupy isolated patches on the crests of the higher limestone features. They represent the thin upland facies of this series. The profile, which varies considerably in depth, consists of brown light loam over reddish-brown subsoil and is stony throughout, rock generally occurring within fifteen inches of the surface. The drainage is free and lack of moisture is a common limiting factor of growth.

Pentraeth Series. The Pentraeth Series, derived from limestone drift, occurs mainly on the western slopes of the Halkyn upland, a typical area lying in the neighbourhood of Lixwm. The drift varies considerably in depth owing to the hummocky nature of the underlying rock. Drainage is invariably free and there is often

liability to drought on the upper features, where the profile is shallow. The soils are reddish-brown light or medium loams eight inches to a foot in depth overlying yellowish-brown medium loam. There is also a gravelly stony type formed on gravel features.

The lime status of the Carboniferous Limestone soils generally appears to be satisfactory. Whilst in many cases there is a high content of carbonate, complete removal of carbonate is exceptional."

The Gower series was again described in the Vale of Clwyd (Hughes and Walters, 1932) the thin upland facies predominating. In north west Denbighshire and north east Caernarvonshire (Hughes and Walters, 1935) Gower soils were reported to show considerable variation particularly in depth. Deeper soils of the Pentraeth series occur mainly in locally derived glacial drift and sometimes in footslope colluvium. Gower and Pentraeth soils are described in Anglesey (Hughes and Walters, 1935) where in the Llangoed district Pentraeth soils are occasionally sandy suggesting that Triassic sand has contributed to the present material. In Glamorgan (Robinson and Hughes, 1936) it was noted that, as on the limestone of north Wales, there is commonly a rapid change from very shallow soils to deeper pockets of drift. Gower soils are described as non-calcareous light loams with often a very sharp transition from soil to rock. Pentraeth soils are in reddish brown drift or hill wash and are generally deep and fertile.

In a paper summarising some of the early soil survey work in Wales Robinson (1934) describes Red and Brown Limestone Soils as commonly associated with Carboniferous Limestone. "They are usually base-unsaturated and such carbonate as they contain is generally in the form of hard fragments. The colours are warm brown, brownish-red, and even bright terra-cotta red ... The colour ... is sometimes very vivid, as in parts of South Wales, and it seems reasonable to conclude that they have affinities with the terra rossa of Mediterranean regions.

A characteristic feature of soils derived in situ from

Carboniferous Limestone is the sharp transition from soil to rock. In some cases it is impossible to distinguish more than a single soil horizon, particularly when the mineral colour is sufficiently bright to mask the colour of the humus."

Later work by the Soil Survey of England and Wales, following Smithson's (1953) investigation of the mineralogy of some soils in north Wales, recognised that the thick drift deposits forming the parent materials of the Pentraeth soils were unlikely to be derived solely from Carboniferous Limestone.

In Anglesey Roberts (1958) describes the Pentraeth soils as deep reddish brown sandy loams with good drainage becoming slightly more clayey with depth. They are classified as Brown Earths of High Base Status while the Gower series is included under Red and Brown Calcareous Soils.

Ball (1960) notes that much of the parent material of the Gower soils in the Rhyl and Denbigh district is also derived from rocks other than limestone, since the sand fraction contains much well-rounded quartz which is not present in the insoluble residue of the local Carboniferous Limestone (Smithson, 1953). He suggests that the sand is derived from the coast by wind, from fluvio-glacial sands, or from a former cover of Northern Drift largely from Triassic rocks. Associated Pentraeth soils occur in deeper pockets of drift. Pentraeth soils are described as Brown Earths of High Base Status occurring along the outcrop of Carboniferous Limestone in drift containing little material from Silurian rocks or Carboniferous Basement Beds. A comparison of the mineral assemblages suggests that the parent material may be largely derived from a former extension of Northern Drift. The soils are loamy becoming somewhat coarser with depth and are described as friable and porous throughout. Depth is variable but rock is usually at 60 to 75 cm.

In the Rhyl and Denbigh district Pentraeth soils pass to soils of the Dinorben series on Carboniferous Limestone where the

amount of material from Silurian rocks increases. A shallow phase is recognised with rock usually at about 45 cm, and a deeper phase on slopes flanking the limestone developed partly in colluvium. The profile contains small stones of shale together with limestone, and the particle-size is described as a U.S.D.A. loam.

Gower, Pentraeth and Dinorben soils are also described around Bangor and Beaumaris (Ball, 1963) where the parent material of the Dinorben series is described as a mixture of local drift from Lower Palaeozoic shales with colluvium from Carboniferous Limestone and some Carboniferous sandstone. Hard drift was noted locally at 45 cm and Northern Drift was sometimes found in the subsoils in the Creuddyn Peninsula where the drift deposits are particularly complex.

Difficulty has been experienced in the current survey around Holywell in applying Ball's lithological criteria for distinguishing the Dinorben and Pentraeth series. However as stones of Silurian rocks are almost invariably present in drift over the limestone, even though they may occupy less than 5 per cent by volume, only the Dinorben series has been recognised. The soils are normally sandy silt loams (Hodgson, 1974) and the sand fraction is mainly composed of detrital rounded quartz. Bipyramidal quartz is scarce and that present may be attributed to the weathering of limestone fragments in the drift.

All the soils recognised are naturally well drained, even those having a fragipan, and are believed to come in Class I of the new Wetness Classes (Soil Moisture Regime Classes, Hodgson, 1974) in which "the soil profile is not wet within 70 cm depth for more than 30 days in most years." The soil series recognised are related to soil subgroups and major groups (Avery, 1973) in Table 1.

Table 1

Classification of soil series on the limestone platform near Holywell.

Major Group	Soil Group	Soil Sub-group	Lithology	Soil Series
Lithomorphic Soils	Rankers	Brown rankers	Loamy; drift over limestone (Carboniferous)	Lixwm series
			Coarse loamy; glaciofluvial drift containing sandstone	Radyr series
	Brown earths	Typical brown earths	Coarse loamy; drift (till) containing mudstone and sandstone (Lower Palaeozoic)	Dinorben series
Brown soils			Fine loamy or fine silty; drift (till) containing mudstone and sandstone (Lower Palaeozoic)	Sannan series (fragile phase)
	Brown sands	Typical brown sands	Sandy; glaciofluvial drift	Newport
	Argillic brown earths	Typical argillic brown earths	Loamy; drift (till) containing mudstone and sandstone (Lower Palaeozoic)	Ysceifiog

LIXWM SERIES

This is a new series although the soils can be correlated with those of the Gower series as mapped by Hughes and Walters (1932). On small convexities and dip/scarp features where the drift mantle is thin and irregular, shallow bedrock hinders cultivation and the ground is occupied by open scrub with herb-rich limestone grassland. The humic variant of this series is also common and contains more than 5.5 per cent organic carbon in the topsoil.

Representative profile description*

Profile No.: SJ17/6904; Lixwm series.

Location: Coed-y-Brain, Lixwm (169704).

Elevation: 180 m (600 ft). Slope and aspect: 3°S.

Land use: permanent grass.

Horizons:

cm	
0-14(18) Ah	Dark brown (7.5YR 3/2) clay loam; common fine distinct yellowish red (5YR 4/6) root mottles; rare gravel-size to small subangular and rounded sandstone with siltstone; moderate medium prismatic breaking to moderate medium subangular blocky and crumb; friable; abundant fine fibrous roots; slightly moist; sharp irregular boundary.
14(18) + Bw and R	Broken limestone <u>in situ</u> with interstices of dark yellowish brown (10YR 3/4) sandy silt loam; very stony with large subangular and angular limestone with yellowish red (5YR 5/6) coats; common fine fibrous roots; moist.

* The soils are described using the terms of the old Field Handbook (Soil Survey Staff 1960) though the new particle-size classes (Hodgson, 1974) are used.

Analytical data

Horixon	Ah
Depth	0-14
<hr/>	
Sand	{ 600 μ m - 2mm% 4
	{ 200-600 μ m % 17
	{ 60-200 μ m % 20
Silt	2-60 μ m % 36
Clay	2 μ m % 23
<hr/>	
Organic carbon %	3.7
pH in water (1:2.5)	6.3
pH in 0.01 M CaCl ₂ (1:2.5)	6.0
<hr/>	

NEWPORT SERIES

Typical brown sands of the Newport Series have been widely identified in England and Wales. In the Holywell district they are in red sand in the Wheeler Valley and in brown sand on the limestone platform where the material is largely derived from Carboniferous rocks. Profile SJ17/0917 is from red sands in the Wheeler valley whilst the excursion pit at 156715 was in brown sand with fragic lower horizons.

Representative profile description.

Profile No.: SJ17/0917; Newport series.

Location: Ty Draw, Bodfari (109717).

Elevation: 65 m (220 ft). Slope and aspect: 8°N.

Land use: permanent grass.

Horizons:

cm

- 0 - 30
Ap Dark brown (7.5YR 3/2); sandy loam with many bleached quartz grains; slightly stony with gravel-size to medium rounded and subangular sandstone, quartzite and siltstone, moderate very coarse subangular blocky; friable; slightly moist; abundant fine fibrous roots; narrow irregular boundary.
- 30 - 48
Ap and Bw Dark brown (7.5YR 3/2) and brown to dark brown (7.5YR 4/4) loamy sand with common bleached quartz grains; rare small rounded sandstone, quartzite and siltstone; weak to moderate very coarse subangular blocky; friable; slightly moist; common fine fibrous roots; narrow irregular boundary.
- 48 - 80
Bw Brown to dark brown (7.5YR 4/4) and strong brown (7.5YR 4/8) loamy sand; rare small rounded sandstone, quartzite and siltstone; very weak to medium and coarse prismatic; very friable; slightly moist; few fine fibrous roots; sharp irregular boundary.

80 - 100+
2Cu
Reddish yellow (5 and 7.5YR 3/6) and yellowish red (5YR 5/8) sand; slightly stony with small rounded sandstone, quartzite and siltstone; structureless single grain; loose; moist; very slightly compacted in parts.

Analytical data

Horizon	Ap	Ap & Bw	Bw	2Cu	
Depth	0-30	30-48	48-80	80-90	
Sand	(600 μ m - 2mm %	12	5	2	2
	(200 - 600 μ m %	31	28	27	42
	(60 - 200 μ m %	34	47	53	49
Silt	2 - 60 μ m %	15	13	12	5
Clay	2 μ m %	8	7	6	2
CaCO ₃ equivalent %			NIL	NIL	NIL
Organic carbon %		1.9			
pH in water (1:2.5)		5.9	6.5	6.6	6.9
pH in 0.01M CaCl ₂ (1:2.5)		5.2	6.0	6.1	6.6
Pyrophosphate ext.					
Fe %		0.15	0.10	0.09	0.03
Al %		0.07	0.04	0.03	0.02
Fe + Al %		0.22	0.14	0.12	0.05
Fe + Al/clay		0.03	0.02	0.02	0.03
Residual dithionite ext.					
Fe %		0.40	0.45	1.90	1.60

RADYR SERIES

Whilst no profile of this series was included in the excursion, it is one of the most extensive in the area. The series characteristically has sandy loam Ap and Bw horizons over bedded Cu horizons of loamy sand or sand in slightly stony brown glaciofluvial deposits.

DINORBEN SERIES

The Dinorben series with the Radyr and Ysceifiog occupies much of the limestone platform. Nearly all the soils correlate with Ball's deeper colluvial phase having limestone normally below profile depth at 2-4 m.

Representative profile descriptions

Profile No.: SJ17/7907; Dinorben series.

Location: Graig Farm, Lixwm (179707).

Elevation: 180 m (600 ft). Slope and aspect: 8°W.

Land use: permanent grass.

Horizons

cm

0 - 28

Ap

Dark greyish brown (10YR 4/2) sandy silt loam with few fine rusty root mottles in top 10 cm; slightly stony with small to medium rounded and subangular sandstone, limestone and siltstone; moderate very coarse subangular blocky breaking to moderate medium and fine crumb; friable; slightly moist; abundant fine fibrous roots; worm casts; merging even boundary.

28 - 61

Bw1

Dark yellowish brown (10YR 4/4) sandy silt loam with some ped faces of dark yellowish brown (10YR 3/4); slightly stony with small rounded and subangular sandstone, limestone and siltstone; moderate very coarse subangular blocky; friable; moist; common fine fibrous roots; worm channels and casts; merging even boundary.

61 - 75
Bw2
Dark yellowish brown (10YR 4/5) sandy silt loam with some ped faces of dark yellowish brown (10YR 4/4); rare small tabular siltstone; moderate coarse and very coarse subangular blocky; friable; moist; common fine fibrous roots; worm channels and casts; merging even boundary.

75 - 100+
BCw
Yellowish brown (10YR 4/6) sandy silt loam with some ped faces of dark yellowish brown (10YR 4/4); rare small tabular siltstones; very weak very coarse subangular blocky; very friable; moist; few fine fibrous roots; worm channels and casts of material from horizons above.

Analytical data

Horizon	Ap	Bw1	Bw2	BCw	
Depth (cm)	0-28	28-61	61-75	75-100	
Sand	(600 μ m - 2mm %	4	4	3	5
	(200 - 600 μ m %	17	17	15	20
	(60 - 200 μ m %	22	22	24	23
Silt	2 - 60 μ m %	41	42	43	38
Clay	2 μ m %	16	16	15	14
CaCO ₃ equivalent %		NIL	NIL	NIL	
Organic carbon %	2.3				
pH in water (1:2:5)	6.0	6.7	7.0	7.3	
pH in 0.01M CaCl ₂ (1:2.5)	5.7	6.4	6.5	6.9	
Pyrophosphate ext.					
Fe %	0.15	0.17	0.21	0.29	
Al %	0.08	0.08	0.09	0.13	
Fe + Al %	0.23	0.25	0.30	0.42	
Fe + Al/clay	0.01	0.02	0.02	0.03	
Residual Dithionite ext.					
Fe %	0.07	0.25	0.95	1.25	

Micromorphological data

BCw (75-83 cm). Argillic material less than 1 per cent as few fine void cutans.

SANNAN SERIES, FRAGIC PHASE

These stagnogleyic brown earths in compact Welsh till occupy land between Caerwys and Llyn Helyg. The fragipan is normally at 40 cm depth and whilst being pervious to water appears to inhibit profile development. Very rarely do profiles have B horizons but A, AB, BC, C horizon sequence.

Representative profile description.

Profile No.: SJ17/1949; Sannan series, fragic phase.

Location: Wern Fawr, Caerwys (119749).

Elevation: 180 m (580 ft). Slope and aspect: 3°E.

Land use: permanent grassland.

Horizons:

cm

- 0 - 23
Ap
Dark greyish brown (10YR 3/2) clay loam; slightly stony with small to large angular tabular siltstone with rounded and subangular limestone and chert; moderate very coarse subangular blocky breaking to fine subangular blocky; friable; moist; abundant fine fibrous roots; narrow even boundary.
- 23 - 33
Ap/Bw
Dark brown (10YR 3/3) clay loam; stony with small to large tabular siltstone; weak coarse subangular blocky and medium prismatic; friable; moist; common fine fibrous roots; sharp very irregular boundary tonguing to 37 cm.
- 33 - 44
BCgx1
Brown (7.5YR 5/4), yellowish brown (10YR 5/4 and 5/6), light yellowish brown (10YR 6/4) and light brownish grey (2.5YR 6/2) clay loam with patches of very compact reddish brown (5YR 4/4); slightly stony to stony with small to large tabular siltstone; much fine siltstone gravel; weak coarse prismatic with horizontal fissures imparting platiness; firm; slightly moist; roots present only in worm channels.

44 - 65
BCgx2 Yellowish brown (10YR 5/4), reddish brown (5YR 4/4) and light yellowish brown (2.5YR 6/3) clay loam; stony with fine gravel-sized to small rounded and tabular siltstone; massive; very firm; moist; 3 cm layer of loamy sand at 59 cm.

65 - 80+
BCgx3 Yellowish brown (10YR 5/4), reddish brown (5YR 4/4) and light yellowish brown (2.5YR 6/3) clay loam; stony with fine gravel-size to small rounded and tabular siltstone; massive; firm; moist; vertical worm channels at 70 cm.

Analytical data

Horizon	Ap	Ap/Bw	BCgx1	BCgx2	
Depth (cm)	0-23	23-33	33-44	44-65	
Sand	(600 μ m - 2mm %	4	7	13	10
	{ 200 - 600 μ m %	8	9	13	12
	{ 60 - 200 μ m %	15	15	13	13
Silt	2 - 60 μ m %	50	49	43	43
Clay	2 μ m %	23	20	18	22
CaCO ₃ equivalent %			1	1	
Organic carbon %	5.3				
pH in water (1:2.5)	5.8	6.3	6.5	6.5	
pH in 0.01M CaCl ₂ (1:2.5)	5.3	5.8	6.1	6.1	
Pyrophosphate ext.					
Fe %	0.32	0.28	0.03	0.02	
Al %	0.16	0.17	0.09	0.06	
C %	0.90	0.55	0.13	0.10	
Fe + Al %	0.48	0.45	0.12	0.08	
Fe + Al/clay	0.02	0.02	0.01	0.01	
Residual dithionite ext.					
Fe %	1.00	1.24	1.48	2.04	

YSCEIFIOG SERIES

Argillic brown earths had not been identified on limestone in North Wales before the present survey. In this district, profiles may have limestone directly underneath the Bt horizon or below profile depth with interposed BCw and Cu horizons. While the general colour of the parent material is brown, Bt horizons may be reddish brown in which case they are narrow, sharply defined and with more clay than the brown Bt horizons which are less well defined and have a less pronounced increase in clay. In the profiles below, SJ17/7223 has a reddish brown Bt and in SJ17/7721 the horizon is brown; both horizons are in contact with the limestone. Reddish horizons are common in soils over limestone, and are widely reported (Findlay, 1965; Crampton, 1972; Hollis, 1975). They can be explained in a number of ways.

1. In the Holywell area, the limestone has veins of haematite of extractable size. The incorporation of this into the drift may cause the reddening of Bt horizons.
2. Triassic or Tertiary outliers may have survived the intervening glaciations.
3. Irish Sea drift contains much red clay. The drift on the limestone platform undoubtedly contains material of Irish Sea origin and clay illuviation may concentrate this and result in the colour change.
4. The redness is pedogenic and the soils are relicts from a former interglacial period when a warmer climate resulted in the development of 'terra rossa' soils (Kubiena, 1953).

The situation is not simple and there is probably more than one explanation. In this soil series, redness is always associated with a specific type of illuvial horizon - narrow, sharply defined and of strongly contrasting clay content - and seems likely to be pedogenic. Soils with red Bt horizons, paleo-argillic brown earths (Avery, 1973), are associated with the Ipswichian interglacial period and do not occur in areas, such as Holywell, overridden by the Devensian ice sheets. In thin sections

paleo-argillic horizons contain papules of illuvial material divorced from current voids. The Holywell soils appear in section no different from those with brown Bt horizons and illuviation is due, apparently, to current pedogenesis. No reason can yet be given for the duality of argillic soils in this area.

Profile No.: SJ17/7223; Ysceifiog series.
Location: Plas Captain, Lixwm (SJ172723).
Elevation: 210 m (690 ft). Slope and aspect: 3°SE.
Land use: permanent grass.
Horizons:

cm	
0 - 10	Brown to dark brown (10YR 4/3) sandy silt loam with few fine faint yellowish red (5YR 4/6) mottles; rare small to medium rounded sandstone and tabular siltstone; moderate medium to fine crumb; moist; extremely abundant fine fibrous roots; friable; few bleached quartz grains; narrow even boundary.
Ah	
10 - 22	Brown to dark brown (10YR 4/3) and dark yellowish brown (10YR 4/4) sandy silt loam; slightly stony with small and medium rounded sandstone and tabular siltstone; moderate very coarse subangular blocky; moist; common fine fibrous roots; worm channels; friable; narrow even boundary.
ABh	
22 - 46	Dark yellowish brown (10YR 4/4) sandy silt loam; slightly stony with small and medium rounded sandstone and tabular siltstone; weak to moderate very coarse to coarse prismatic; friable; moist; common fine fibrous live roots; worm channels; narrow even boundary.
Eb/Bt	
46 - 60	Dark yellowish brown (10YR 4/4); sandy silt loam; rare small and medium rounded sandstone and tabular siltstone; very weak very coarse subangular blocky; friable; moist; few fine fibrous roots; narrow irregular boundary.
Bt1	

60 - 80+
 Bt2
 on auger

Reddish brown (5YR 4/4); clay loam; very large weathered rounded limestone with black staining on faces; massive; firm; moist; slightly calcareous.

Merging to brown to dark brown (7.5YR 4/4); clay loam; moist; calcareous.

Analytical data

Horizon	Ah	ABh	Eb/Bt	Bt1	Bt2	
Depth (cm)	0-10	10-22	24-46	46-60	60-80	
Sand	(600 μ m - 2 mm %	4	3	3	2	9
	{ 200 - 600 μ m %	122	17	15	10	16
	(60 - 200 μ m %	21	22	23	28	21
Silt	2 - 60 μ m %	46	42	45	49	24
Clay	2 μ m %	17	16	14	11	30
Organic carbon %	3.5					0.6
pH in water (1:2.5)	5.3	5.5	5.8	5.6		6.6
pH in 0.01M CaCl ₂ (1:2.5)	4.8	5.1	5.3	4.8		5.8

Micromorphological data

Bt1 (54-62 cm). Apparently structureless with estimated porosity 8 per cent; noticeably sub-fragic appearance with very close packing of grains and few voids; estimated argillic material 4-6 per cent as fine and medium, orange and red well-oriented, highly birefringent void cutans and skeleton grain coatings.

Bt2 (71-79 cm). Argillic material 20 per cent as orange and red void cutans.

Profile No.: SJ17/7721; Ysceifiog series.
 Location: Pen Ucha Plwyf, Lixwm (177721).
 Elevation: 250 m (825 ft). Slope and aspect: 4°W.
 Land use: ley grass.

Horizons:

cm	
0 - 24 Ap	Dark brown (10YR 3/3); sandy silt loam; slightly stony with gravel-size to medium tabular siltstone and rounded sandstone, limestone and felsite; weak medium and coarse subangular blocky; friable; moist; common to abundant fine fibrous roots; narrow undulating boundary.
24 - 36(43) AEb	Brown to dark brown (10YR 4/3) sandy silt loam; slightly stony, stony at depth with gravel-size to medium tabular mudstone and rounded sandstone and limestone; weak to moderate coarse subangular friable; moist; common fine fibrous roots; worm casts of Ap material; broken irregular boundary.
36 - 47 Eb	Strong brown (7.5YR 5/8 and 7.5YR 5/6) clay loam; slightly stony with gravel-size and small tabular siltstone and rounded limestone; moderate fine subangular blocky; friable; moist; few fine fibrous roots; worm casts of very dark greyish brown (10YR 3/2) and brown to dark brown (10YR 4/3); merging undulating boundary.
47 - 74(48) Bt	Brown (7.5YR 5/4) and slightly redder at base clay loam; rare gravel-sized and small tabular siltstone and rounded limestone; moderate medium and coarse subangular blocky tending to prismatic with weak fine granular worm casts, moderate medium subangular blocky above limestone; friable; moist; few fine fibrous roots; worm channels up to 1 cm diam. to limestone; sharp irregular boundary.
74(48)+ R	Jointed weathered limestone with brown to dark brown manganiferous staining in hollows.

Analytical data

Horizons	Ap	AEb	Eb	Bt	
Depth (cm)	0-24	24-36	36-47	47-74	
Sand	(600 μ m - 2 mm %	4	4	3	1
	(200 - 600 μ m %	20	19	16	7
	(60 - 200 μ m %				
Silt	2 - 60 μ m %	35	36	41	56
Clay	2 μ m %	18	18	19	24
CaCO ₃ equivalent %		NIL	NIL	1	
Organic carbon %	5.5				
pH in water (1:2.5)	6.1	6.3	7.0	7.3	
pH in 0.01M CaCl ₂ (1:2.5)	5.4	6.2	6.4	6.7	
Pyrophosphate ext.					
Fe %	0.31	0.25	0.22	0.05	
Al %	0.20	2.17	0.20	0.10	
Fe + Al %	0.51	0.43	0.42	0.15	
Residual dithionite ext.					
Fe %	1.27	1.44	1.67	2.07	

Micromorphological data

Bt. (64-72 cm). Argillic material 2-3 per cent as orange and orange red void cutans.

LAND USE CAPABILITY

With rainfall of 760-890 mm (30-35 in.) at 150-180 m (500-600 ft), north-east Wales is the driest part of the Principality. Average annual rainfall less potential transpiration at Northop (SJ248673) at 138 m (420 ft) is -25mm (-1 in.) and the maximum cumulative potential moisture deficit (Hodgson, 1974) is only 104 mm (4 in.). Although exposure on parts of the limestone platform is moderately high, it is probable that socio-economic factors more than climate are responsible for the small acreage of arable farmland and the small size of most holdings. The area is largely level or gently sloping and gradient is seldom limiting.

Table 2

Land use capability of major soils of the limestone platform.

Class	Sub-Class	Unit ¹	Characteristics, limitations and special requirements	Soil Series
2	s	2s/1	Deep very permeable sandy soils, AWC 1-2*; stones further increasing water deficits in parts, weak structure allows capping in seed beds.	Newport
	c	2c/1	Deep or moderately deep loamy soils, AWC 2-3; at 150-230m (500-750 ft); parts may contain isolated limestone outcrops; moderately exposed to wind.	Dinorben, Radyr, Ysceifiog.
3	c	3c/1	Deep permeable loamy soils, AWC 2-3; above 230m (750 ft); isolated limestone outcrops; moderately severe exposure.	Dinorben, Radyr,
6	s	6s/1	Shallow soils over limestone, AWC 1; rock at 25 cm depth prevents cultivation and causes severe drought.	Lixwm

* Available water class (Hodgson, 1974).

¹ Soils placed in any one capability unit respond in a similar way to management and improvement practices.

The agricultural land capability map (M.A.F.F. 1966) shows the area as grade 3 land with Halkyn Mountain as the only notable exception in grade 4. Application of the Soil Survey land use capability system (Bibby and Mackney, 1969) places the soils mostly to class 2 with soils on Halkyn Mountain in class 3 because of climate. The land use capability of the major soils is shown in Table 2.

ACKNOWLEDGEMENTS

The author wishes to thank B. Clayden and J.W. Lea of the Soil Survey of England and Wales and G.R. Davies of the Agricultural Development and Advisory Service for considerable help with the preparation of both the excursion and this report. Analytical and micromorphological data were provided by staff of the Soil Survey of England and Wales under the supervision of C.L. Bascomb and Dr. P. Bullock respectively.

REFERENCES

- Avery, B.W. (1973) Soil classification in the Soil Survey of England and Wales. *J. Soil Sci.* 24, 324-38.
- Ball, D.F. (1960). The soils and land use of the district around Rhyl and Denbigh. *Mem. Soil Surv. Gt Br.*
- Ball, D.F. (1963) The soils and land use of the district around Bangor and Beaumaris. *Mem. Soil Surv. Gt Br.*
- Bibby, J.S. and Mackney, D. (1969) Land use capability classification. *Tech. Monogr. Soil Surv. Gt Br. No.1.*
- Crampton, C.B. (1972) Soils of the Vale of Glamorgan. *Mem. Soil Surv. Gt Br.*
- Davies, B.E. and Roberts, L.J. (1975) Heavy metals in soils and radish in a mineralised limestone area of Wales, Great Britain. *The Science of the Total Environment* 4, 249-261.
- Findlay, D.C. (1965). The Soils of the Mendip District of Somerset. *Mem. Soil Surv. Gt Br.*
- Hodgson, J.M. (1974) Soil survey field handbook. *Tech. Monogr. Soil surv. Gt Br. No.5.*
- Hollis, J.M. (1975) Soils in Staffordshire I: Sheet SK05 (Onecote). *Soil Surv. Rec. No.29.*
- Hughes, D.O. and Walters, W.G.D. (1932). Soil Survey of Wales. *Progress Report, 1929-31. Welsh J. Agric.* 8, 197-213.
- Hughes, D.O. and Walters, W.G.D. (1935) Soil Survey of Wales. *Progress Report, 1931-34. Welsh J. Agric.* 11, 188-208.
- Kubiena, W.L. (1953) *The Soils of Europe*, Murby, London.
- M.A.F.F. (1966) Agricultural land classification. Sheet 108 (Denbigh). *Ordnance Survey.*
- Roberts, E. (1958) The County of Anglesey - soils and agriculture. *Mem. Soil Surv. Gt Br.*
- Robinson, G.W. (1934) The soils of Wales. *Emp. J. expt. Agric.* 2, 258-73.
- Robinson, G.W. and Hughes, D.O. (1936) The soils of Glamorgan. In: *Glamorgan County History, 1 Natural History.*
- Robinson, G.W., Hughes, D.O. and Jones, B. (1930) Soil Survey of Wales. *Progress Report 1927-29. Welsh J. Agric.* 6, 249-65.

Robinson, G.W., Jones, J.O. and Hughes, D.O. (1928) Soil Survey of Wales. Progress Report 1925-27. Welsh J. Agric. 4, 3-21.

Smithson, F. (1953) The micro-mineralogy of north Wales soils. J. Soil Sci., 4, 194-210.

Soil Survey Staff (1960) Field Handbook. Soil Surv. Gt Br.

Walsh, P.T. and Brown, E.H. (1971) Solution subsidence outliers containing probable Tertiary sediment in north-east Wales. Geol. J. 7, 299-320.

The survey of 1:25,000 sheet SJ17 (Holywell) will be published by the Soil Survey as an uncoloured map at that scale with an accompanying Record (Soils in Clwyd II).

ANNUAL REPORT

16th Session 1974-75

SECRETARIAL REPORT

Membership of the Group has remained constant at 76 members. The theme for the year was "Soil Organic Matter" and three meetings were held. At the first meeting, in Lampeter on October 16, 1974, six papers were presented dealing with 'Field Aspects of Soil Organic Matter' and five papers were read at Bangor on March 19, 1975 covering 'Laboratory Investigation of Soil Humus'. The field meeting was held on May 14, 1975 in the Mold area under the leadership of Mr. T.R.E. Thompson (Soil Survey).

Officers and committee for the year were:-

Chairman	Mr. Evan Roberts
Conference Secretary	Mr. A. Singer
Assistant Secretary	Mr. W. Lea
Editor	Dr. G. Wyn Jones
Assistant Editor	Dr. D. Davidson
General Secretary	Dr. B.E. Davies
Publications Committee	Dr. A. Troughton Mr. H.T. Davies and A. Thomas

The AGM was on March 19, 1975 when officers for the 17th Session were elected including Mr. Ben Clayden as Chairman.

FINANCIAL REPORT

The Group's audited financial statement is attached and shew a small surplus of income over expenditure. The Reports continue to sell well and receipts from these sales largely cover the operating costs of the Group.

B.E. Davies.

Income and Expenditure Account for the year ended 30th September 1975.

Secretarial Account

Income

Members Subscriptions		143.65
Sundry income		
- Deposit account interest	43	
- Day subscriptions and lunch charges	25.00	25.43
		<u>169.08</u>

Expenditure

Publication costs	208.73	
Contribution from Publications Account	208.73	
		<u>62.69</u>
Preparation of reports and typing	11.11	
Secretarial expenses	11.81	
Costs of meetings	25.81	
Biological Council	1.00	
Audit fee - 1974 account	12.96	
		<u>106.39</u>
Surplus of Income over Expenditure		106.39

Publications Account

Income

Sale of reports including handling charges	480.98	
Savings bank interest	5.89	
		<u>486.87</u>

Expenditure

Contribution to Publication costs	208.73	
Postage and Stationery	38.39	247.12
		<u>239.75</u>
Surplus of Income over Expenditure		239.75
Net surplus transferred to Balance Sheet		<u><u>£364.14</u></u>

Welsh Soils Discussion Group

Balance Sheet as at 30th September 1975

Cash at Bank

- Secretarial Account - Current	51.27	
Deposit	5.29	
	<u>56.56</u>	
- Publications Account	638.18	694.74
	<u>638.18</u>	
Cash on hand		25.00
Subscriptions in arrears		1.75
		<u>25.00</u>
		<u>1.75</u>
		<u>721.49</u>
		<u>721.49</u>

Accumulated Fund

- Balance at 30th September 1974	375.35	
- Add: Net Surplus from Income and Expenditure Account	346.14	
	<u>346.14</u>	
		721.49
		<u>721.49</u>
		<u>721.49</u>

Auditor's Report

The above balance sheet as at 30th September 1975 and annexed Income and Expenditure Account for the year ended on that date have been checked and prepared from records produced to us and are correct in accordance therewith.

£25.67 owing at 30th September 1975 for reports sold but not paid for is considered irrecoverable and has not been brought into these accounts.

Midland Bank Chambers
Aberaeron.

Hubert & Winston Jones
Chartered Accountants.

11th March 1976.

