Report for 1972 - Part 1

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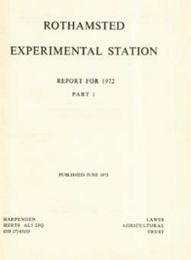

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PEDOLOGY DEPARTMENT

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Soil clays seldom have the structures and properties of type clay minerals, so that in this context the use of conventional names, e.g. vermiculite, smectite, etc., is often inexact. With the aim of improving our understanding of soil clays we have studied the nature of the imperfections in soil clays, and we report preliminary results of the application of crystallographic computations to the prediction of the diffraction profiles of mixed layer minerals that contain potassium, and of the effect of aluminium interlayering on the cation exchange properties of montmorillonite. By calculating the electrostatic energy of the structural components of clay minerals, we have continued our study of the factors that are responsible for the stability.

We studied the mineralogy of some saline/alkaline volcanic soils from Abadir, Ethiopia, from an area that is being developed for irrigation agriculture, under the auspices of FAO. The clay contents of these soils are not particularly large, but they have unusually large cation exchange capacities; this results partly from the presence of aggregates of expanding clay minerals formed by the weathering of strongly silicic and alkaline volcanic glass.

Our study of loess was extended to silty soils over various substrata in south Devon. Small changes in the mineralogy and particle size distribution of the windblown silt across southern England indicate winnowing by easterly winds during deposition.

Among the many requests we received for data on clay minerals in soils and sediments, two we studied this year were of particular interest. One concerned a soil from an apple orchard at East Malling, and we attempted to relate its clay mineralogy to the mobility of magnesium in the soil. The other dealt with the transportation and burial of soil materials formed by the weathering of basalt in a diatomite deposit at Loch Cuithir, Skye.

Using new methods of dehydrating clay that limit the extent of shrinkage, we have studied the changes undergone by a clay soil during the kinds of manipulation involved in farming operations. Preliminary results suggest that pores of 0·5–0·03 μm diameter are those mainly affected by manipulation, and that pores of this size are important in determining the behaviour of the soil.

The distribution of minor elements in relation to the major soil constituents is presumably involved in determining their availabilities to plants. We are studying this by determining total major and minor elements in soils and herbage over a wide area in Pembrokeshire, and by detailed examination of the distribution of major and minor elements in a soil developed in uniform parent material at Pegwell Bay, Kent, in which it is possible to attribute profile variations to pedogenic processes. On a more academic level, we have continued our study of the mobilisation of minor elements by decomposing plant matter, and of the reactions between the metals and humified organic matter.

Our study of the turnover of organic matter in agricultural soils is proceeding along three lines: we are determining the rate at which uniformly labelled plant matter decomposes in the field, and radiocarbon measurements on soils from the Rothamsted Classical experiments, taken before and after thermonuclear testing, are being used to determine the amount of the yearly entry of plant matter into the soil. Measuring the radiocarbon age of soil samples collected before thermonuclear testing also gives information on the mean age and stability of the organic matter.

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Mineralogy

Interlayering in soils and clays. During work on soils from Barnfield it was found that clay pretreated with citrate to complex iron and aluminium released more potassium to $BaCl_2$ than untreated clay (*Rothamsted Report for 1971*, Part 2, 32). In a further investigation of this observation, the effect of two reagents, one complexing and one non-complexing, on the release of K was compared; three surface soils were used, one with a neutral pH from Barnfield and two acid soils from Sawyers and Woburn. The amounts of K, Al, Fe, Ca and Mg extracted by $0{\cdot}06M$ solutions of strontium chloride and strontium citrate were measured for all three soils; separated clay fractions were similarly extracted so that changes in mineralogy could be followed by X-ray diffraction. Three extractions with citrate solutions removed 3% of the total Al and 4% of the total Fe from the Barnfield and Sawyers soils, and rather more Fe relative to Al from the Woburn soil, whereas the chloride solutions removed neither Al nor Fe. By contrast with this large difference in the amounts of Al and Fe that were extracted, the effect of citrate on K-release was much smaller, and K-concentrations in citrate were only 10–20% greater than those in the chloride extracts. If citrate extracts Al and Fe from positive charged interlayers in the layer silicates, some increase in the cation exchange capacity would be expected as a result of the extraction, but the measured increases were in fact rather small, 4–7 meq/100 g for the acid soils, and no increase was detected in the Barnfield clay. The diffraction profiles of citrate and chloride-treated clays differed little, and citrate treatment changed the structure of the clays very little. It was concluded that citrate dissolves sesquioxide surface coatings much more readily than interlayer aluminium or iron, and that a more effective treatment for removing interlayers is needed.

These results emphasise the difficulty in detecting non-crystalline sesquioxides in soils, whether as surface coatings or as interlayers. Surprisingly little is known about the structure and properties of Al clays, particularly those in which a chlorite-like structure cannot be recognised, and this has probably hindered their positive identification in soils. To provide the basic information needed, the interaction of aluminium solutions and montmorillonite was investigated with the aims of finding the most useful way to describe clay–Al interaction and also of preparing material that would assist in the identification and description of interlayer–Al in soil clays. Preliminary work showed that Al–montmorillonite behaves as if it contains a mixture of Al^{3+} and a basic aluminium cation of mean composition $Al_2(OH_5)^+$, and the first stage hydrolysis product $AlOH^{2+}$ makes little contribution to the equilibrium. The basic aluminium cation is not exchanged by unbuffered Ca^{2+} or Ba^{2+} solutions but is hydrolysed further if the pH of the ambient solution is increased by buffering at pH 7. Further work will be required to find out whether the exchange capacity can be restored to the original value by further increasing the pH, or by extracting aluminium with complexing reagents. The structure of aluminium montmorillonite varies with the basicity of the sorbed aluminium, and has not yet been interpreted in detail. (Newman)

X-ray diffraction patterns of interstratified fine clays. The properties of the clay fractions of many soils do not closely match the properties that would be expected from their mineralogical composition, as this is usually determined by X-ray diffraction. For example, in S.E. England the clay fraction of many soils contains what seems to be a poorly crystallised smectite, and as the cation exchange capacity of this would presumably be quite large, the exchange capacities of the soils would be expected to be considerably larger than they are.

In an attempt to improve the characterisation of soil clay constituents we have made a more thorough examination of the effects of disordered stacking of the various layers on the properties of montmorillonoids. Two samples, one of clay (< 2 μm) and one of fine clay ($< 0{\cdot}1$ μm), from a soil of the Denchworth Series in weathered Oxford clay, are being examined in detail. From its diffraction patterns the clay fraction appears to contain smectite, mica and kaolinite, but reflections from the mica and kaolinite obscure all but the first peak of the smectite, and prevent any detailed description that would define its expected ion exchange properties. The fine clay fraction is almost entirely a smectite-like mineral, with only a little mica and kaolinite impurity. The peaks in the diffraction pattern are not rational sub-multiples of a single layer spacing, but are characteristic of particles in which layers of two different thicknesses are stacked together. To find the nature and thickness of the constituent layers the diffraction pattern was compared with patterns calculated for different likely stacks of layers.

Comparison of the diffraction pattern of an ethylene glycol-saturated specimen of fine clay with those calculated for interstratified mica and glycol-expanded smectite, by the method of Reynolds and Hower, suggests the presence of appreciable amounts of 10 Å mica interstratified with the expanding layers. Use of Reynolds' criteria, based on the peak positions of calculated patterns for particles containing 7–13 silicate layers, gave an estimate of 40–50% expanding layers, but the calculated patterns all had a sharper peak than the observed patterns, which suggests that the real particles contained fewer layers. A new series of patterns, calculated for smaller particles with ranges of 3–7 and 3–9 silicate layers, had broader peaks but the new patterns showed changes of position for the other less sharp peaks. It is clear that the numbers of layers per particle, as well as the proportion of types of layer and their spacing, must be taken into account in interpreting fine clay peak positions. (Rayner)

The electrostatic energy of clay mineral structures. Understanding of the behaviour of clay mineral materials is based on knowledge of their structures, and for many minerals the structure adopted is close to the arrangement of ions for which the electrostatic energy is a minimum. A programme to calculate electrostatic energies for ionic crystals (written by Dr. W. H. Baur of Chicago University) has been adapted to the 4–70 computer and is being used to calculate the relative electrostatic stability of different clay mineral models.

The central layer of clay minerals contains octahedrally coordinated magnesium or aluminium atoms, but the octahedra are not regular; the O–O edges (S) shared between two octahedra are shorter than the unshared edges (U). The distortion can be described by the ratio S/U, and is about 0·92 in a clay mineral such as talc. Similar octahedral layers occur in the simpler structures $Mg(OH)_2$ and $Ca(OH)_2$, and electrostatic energy calculations for these show that the electrostatically most stable structures have distortions similar to those found by X-ray crystal structure analysis ($S/U = 0{\cdot}89$ for $Mg(OH)_2$ and 0·86 for $Ca(OH)_2$).

Model structures for talc can be constructed from such an octahedral layer and two tetrahedral layers contracted by rotation of the tetrahedra, in one of two directions, until the layers are the same size. In the structure found by X-ray analysis the tetrahedra are rotated in the direction that brings the basal tetrahedral oxygen ions a little closer to the magnesium ions in the octahedral layer. The attraction between these ions might be thought to make this structure more stable, but an electrostatic energy calculation in which all ion interactions are included shows that this structure is electrostatically no more stable than the structure with the opposite rotation, so the stability must depend on some other feature of the structure—perhaps a small difference in the van der Waals contacts between the layers. (Rayner)

Loess in Devonshire soils. In Devon, soils derived partly from thin silty drift deposits occur on the East Devon Plateau (Hook, Batcombe, Dunkeswell and Blackdown series), the Devonian Limestone Plateau (Ipplepen, Ogwell and Nordrach series), the Haldon

Hills (variant of the Southampton series), and parts of Dartmoor and the Budleigh Salterton Pebble Beds outcrop. We studied the particle size distribution and fine sand (60–250 μm) and coarse silt (20–60 μm) mineralogy of eight samples representing the silty drifts of these areas. Their particle size distribution is similar to that of partly weathered loess in eastern England, except that samples from Little Haldon (SX 919767) and Lympstone Common (SY 040854) contain more sand. At these two localities the drift overlies sandy substrata (the Haldon Gravels and Budleigh Salterton Pebble Beds respectively), so that incorporation of material from beneath may explain the increased sand content.

The mineralogical composition of coarse silt fractions from all the samples resembles that of the loess in eastern England (*Rothamsted Report for 1969*, Part 1, 76–78; *for 1971*, Part 1, 79–80), but muscovite, biotite, chlorite and tourmaline are slightly more abundant. In the silty drift from east of the R. Exe the fine sand is mineralogically similar to the coarse silt, although in the sample from Lympstone Common part of the sand resembles that of the underlying Budleigh Salterton Pebble Beds, and evidently is derived from them. However, in samples from further west the fine sands differ from the coarse silts, and are largely derived from the rocks beneath. The peak of the particle size distribution curve for samples taken east of the Exe is near 36 μm, but for samples from further west it is near 26 μm. This suggests that the windblown silt (loess), of which the deposits are largely composed, was blown from the east; the relatively coarse particles were deposited nearer the source, but the finer ones, especially of platy minerals (muscovite, biotite and chlorite), were carried further. In the east of the county, the windblown component contains a little fine sand, but further west it has little or no sand. (Catt and Weir)

Genesis of volcanic soils in the Ethiopian rift valley. We studied a sequence of soils developed mainly from volcanic pumice in the Abadir cotton plantation, near Metehara, in the Middle Awash Valley, Ethiopia. The plantation is about 200 km east of Addis Ababa, and lies on the Metehara Plain, which is part of the floor of the East African Rift Valley adjacent to L. Besaka. Most of the late Tertiary and Quaternary lavas of the area (the Aden Volcanic Series) are basaltic, but some of the recent flows are more silicic and alkaline. At Abadir the basalts are covered by an extremely silicic white pumice (pantellerite), composed mainly of glass with phenocrysts of quartz, anorthoclase, aenigmatite and sodic ferrosalite.

The soils we studied form a topographic sequence northwards across the Metehara Plain, from pumice flows in the south, across a gently sloping surface of colluvial and alluvial deposits derived from the lavas, towards the southern margin of L. Besaka. The main soil types are:

1. Shallow greyish-brown calcareous loams, with pumice at 50–200 cm depth, occurring on 1–2° slopes on the pumice flows. At the surface the soil is hard and brittle when dry, but does not crack; platy or blocky structures are common.
2. Deep, dark greyish-brown calcareous loams, with fine gravel at 100–150 cm depth, occurring on 0·5° slopes. The gravelly colluvium is 3–5 m deep over pumice rock. The surface soil is platy structured, and does not crack when dry, so that surface sheet flow and shallow erosion occur during rainstorms.
3. Dark greyish-brown clays of variable depth, over calcareous silty colluvium or alluvium, occurring on almost level ground. Non-saline non-alkaline (3), saline non-alkaline (3s) and saline alkaline (3sa) phases can be distinguished. The surface soil has strongly developed fine to medium blocky structure; 2–3 cm deep cracks are common, and a few narrow fissures extend to about 30 cm.
4. Brown saline alkaline clays and clay loams, about 50 cm deep, on variably textured

alluvium, occurring on almost level ground. Fine blocky structure occurs above 5–10 cm depth, but prismatic and coarse blocky structures occur below. Rusty mottles, black manganiferous deposits, and hard irregular carbonate concretions occur at depth, and salt accumulates on exposed surfaces as they dry.

Our laboratory studies included particle size analyses by the pipette sampling technique, mineralogical analyses of the fine sand (50–250 μm) fractions using a petrological microscope, and of the clay (< 2 μm) fractions by X-ray diffractometry, and determinations of pH and cation exchange capacities. The composition of the fine sands showed that all the soils are derived mainly from the pantellerite; small amounts of basaltic material (recognised by the presence of labradorite and augite) occur in soil types 2, 3 and 4, but no other source material is evident. The glass fragments, which are the main constituent of the fine sand fractions, are partly altered to birefringent clay aggregates, which increase in abundance progressively from soil type 1 to type 4. All the soils are neutral or alkaline, the pH increasing to approximately 10 in subsurface horizons of 3sa and 4. The alkalinity and salinity probably result from sodium released by weathering of the alkali-rich glass in the semi-arid climate.

All the soils have very large cation exchange capacities, which are mainly attributable to inorganic constituents, as even in surface horizons the amounts of organic matter are small. The exchange capacities increase with increasing clay content of the soils, and extrapolation suggests that the exchange capacity of the clay is approximately 140 meq/100 g, which could only be provided by a large proportion of 2 : 1 expanding layer silicates. Clays of this type usually show strong swelling and shrinking properties, especially in a semi-arid climate with well-marked seasons, but the soils show little evidence of deep fissuring or coarse structures. Further, X-ray diffractometry of the clays showed that, in addition to expanding minerals, they contain 10–25% of material (mica, kaolinite, quartz and felspar) with little or no exchange capacity, and that the expanding mineral itself is an interstratified clay containing a large proportion of smectite layers, which would have an exchange capacity no larger than 110 meq/100 g. The amounts of amorphous clay constituents, determined by alkali extraction, are also too small to account for much of the exchange capacity.

The only remaining soil constituent able to increase the total cation exchange capacity is the clay aggregates formed in and from glass fragments. The weathering residue from leaching of alkalis from the glass is at first mainly an interstratified clay containing a large proportion of smectite layers, the particles of which are held together by glass and other amorphous materials. Further weathering diminishes the size of these aggregates, and seems to increase the proportion of smectite layers in the interstratified mineral. The amounts of clay are thereby increased in soil materials, such as those of types 3 and 4, which have been weathered for comparatively long periods. However, some glassy and/or amorphous material probably remains in the finer fractions of even these soils, and may help limit their swelling and shrinking properties. (Catt, Weir and Ormerod, with Findlay, Soil Survey)

Clay mineralogy of a soil from the Malling series. At the request of Dr. M. Allen, East Malling Research Station, we studied the clay mineralogy of a Malling series soil from the East Malling Experimental Farm in connection with the appearance of Mg-deficiency symptoms in M7 apple root stocks. Samples were taken at four different depths from a pit adjacent to the experimental plots containing the apple trees. The finest clay fractions ($< 0{\cdot}1$ μm) consist of interstratified mica–smectite, mica, kaolinite, goethite and a trace of quartz. They have a mean exchange capacity of 48 meq/100 g, individual values varying little with depth, and non-exchangeable K contents varying from 46 meq/100 g in the surface to 39 meq/100 g in the deepest horizon. The coarse clay fractions (0·1–2 μm) differ from the fine clays in that they contain more mica and quartz, some felspar and a trace of chlorite, and the minerals are better crystallised. The average exchange capacity is 26 meq/100 g and non-exchangeable K, part of which is in felspar, decreases with depth from 62 to 45 meq/100 g. On the basis of their chemical compositions the interstratified minerals were very approximately estimated to be 1 : 4 mica : smectite mixtures in the coarse clays. The amounts of exchangeable magnesium in the whole soil vary between 0·4 and 0·5 meq/100 g throughout the profile. This represents 4% of the ammonium acetate exchangeable cations, the predominant ion being calcium, and 3–6% of the total non-exchangeable magnesium, which is situated mainly in the clay fraction.

The clay minerals in the Malling series soil appear to be similar to those found in many other soils. We therefore conclude that the inability of the tree roots to obtain magnesium, either native or added as fertiliser, is more likely to be caused by special physical conditions of the soils than by unusual chemical properties of the clay minerals. (Weir and Ormerod)

Clay from a diatomite deposit, Loch Cuithir, Skye. Calcined diatomite from Loch Cuithir, Skye, readily reacts with lime and is therefore potentially valuable for making refractory bricks. In response to a request for information on the non-diatom fraction of the deposit we studied its clay mineralogy. The clay minerals have the same settling velocity in water as fine fractions of the diatom valves and therefore cannot be separated by decantation in the normal way. Fairly complete separation was achieved by repeatedly dispersing a sample of a separated fine clay fraction (0·1–0·4 μm) in dilute sodium hydroxide solution, pH 9, and flocculating the clay with minimum additions of a divalent salt solution. The diatom fragments were not salted out and were removed by decantation. Further concentration of the clay minerals was made by dissolving the remaining amorphous silica of the diatom fragments in boiling dilute caustic soda solution. The residue from this treatment, which did not differ in its X-ray diffraction pattern from the untreated but Na-saturated diatom-containing clay, was an interstratified chloritised smectite—it showed incomplete expansion when solvated with ethylene glycol and incomplete collapse when heated at various temperatures up to 265°C. Heating to 550°C and extraction in boiling caustic solution caused a net loss of alumina, and the residue from the treatment had the expansion and collapse characteristics of a smectite. The interlayer material that impedes expansion and collapse thus appears to be some form of hydrated alumina.

Chemical analysis of ignited Na-saturated clay after removal of interlayer hydrated alumina gave the following composition:

$$Na_{0\cdot74}\,K_{0\cdot02}\,Ca_{0\cdot02}\,(Al_{1\cdot28}\,Fe_{1\cdot42}\,Mg_{2\cdot07})\,(Si_{6\cdot96}\,Al_{1\cdot04})\,O_{22}$$

This composition is unusual in that the total of octahedral cations is almost 5, whereas for most minerals of this type the value is either 4 or 6. It does not result, however, from the chemical pretreatment, because the untreated clay has a very similar total of octahedral cations—the interlayer Al-ions being distributed by this method of calculation between octahedral and tetrahedral positions. The clay gave only one d_{06} reflection, corresponding to a spacing of 1·529 Å. This is similar to those given by both trioctahedral and iron-rich dioctahedral minerals, and is thus consistent with the chemical composition of the mineral. The clay appears to have originated as a weathering product of basaltic rocks that surround the lake where the diatoms accumulated. It may thus represent a primary weathering product of the basalt or a later modification following accumulation in the lake of expanding 2 : 1 layer silicate minerals formed by weathering of different minerals in the basalt. (Weir and Ormerod)

Clay physics

Structural studies on clay soils. Minimisation of shrinkage during the dehydration of clay soils is a key problem in the laboratory study of soil structure. In an improved method we exchange soil water with methanol vapour, and follow this by liquid carbon dioxide infiltration in a pressure vessel. The sample is heated when infiltration is complete, and the carbon dioxide converted to gas which is slowly vented. The advantages of the new technique are that vapour exchange is less likely to disintegrate samples than is immersion in liquid, and that the removal of liquid from the soil is unaccompanied by shrinkage due to surface tension. Drying clay soils in this way permits their microstructures to be investigated by many methods. The methods at present available are kerosene and mercury porosimetry, pore-size distribution methods using sorption of carbon tetrachloride and of nitrogen, and microscopy. Not only do these methods span various pore and particle sizes, but they give different kinds of information. These methods are being evaluated for clay soils, particular attention being paid to features that change greatly with the kind of manipulation that might be used in soil management, e.g. disturbance and consolidation.

A study of undisturbed samples from the B2tg horizon of a Ragdale soil, for example, showed that this blocky-structured material has nearly 90% of its pore volume in pores of less than 0·5 μm diameter, and 25% in pores of less than 0·03 μm diameter. Remoulding and consolidation, either by compaction or by drying, had little effect on the volume of pores of less than 0·03 μm diameter, which clearly constituted a relatively permanent feature of the soil. The volume of coarse pores (greater than 0·5 μm diameter) decreased as a result of both remoulding and compaction. However, the main effect of compaction was to decrease the volume of pores of 0·5 to 0·03 μm diameter and this was also observed on drying. Mercury intrusion curves were always monotonic, which indicates the absence of distinct agglomerates of particles. Microscopy of the undisturbed material showed that the fabric was markedly anisotropic, i.e. sepic, and it was virtually unaffected by compaction to a pressure of 8600 kN/m^2 or by drying to pF 6. The strongly anisotropic, and presumably strongly orientated material had no clearly defined boundaries and was embedded in a less well-orientated matrix. This suggests that it did not constitute an agglomerate in any identifiable sense, e.g. a domain, and would explain why none were observed during mercury porosimetry.

This and similar studies show that manipulation of clay soils not only changes the volume of large pores, e.g. those that are important in relation to the movement of water in the field, but also affects a wide range of much finer pores, particularly in the 0·5–0·03 μm diameter range. The significance of these changes in the microstructure of clay soils with respect to their bulk properties is not clear, and further work is in hand.

The bulk shrinkage of clay soils containing montmorillonite minerals is likely to be accompanied by the contraction of clay crystals. We investigated the range of suction (pF) in which this is likely to occur, and its influence on bulk shrinkage. The volumes, weights and X-ray basal reflections of two soil discs were measured from pF 2 to 6. The soils were both montmorillonitic but one had a pH of 4·8 and the other a pH of 9·2 and contained 3·7% $CaCO_3$. Both showed a steadily diminishing basal spacing at pFs between 4·6 and 6·0, and an inflection in the pF-volume curve at pF 4·6. The inflection can be accounted for if it is assumed that most of the interlamellar contraction is shown as a bulk volume change, but the magnitude of the change is small in relation to the bulk shrinkage between pF 4 and 6, and cannot explain the enhanced shrinkage of these samples when compared with ones of smaller expansible mineral content. The strong statistical relation previously found between bulk shrinkage (pF 4–6) and expansible mineral content is therefore not simply due to crystal contraction on drying but to another property of expansible minerals, for example their possibly smaller rigidity allowing the matrix to contract more under compressive stresses. (Gallavan and Greene-Kelly)

Soil geochemistry

Distribution of minor elements in soil. The investigation of the distribution of minor elements among soil components by removing organic matter and sesquioxides and separation of the mineral residue into particle-size fractions was continued; the study by this method of the loess soil at Pegwell Bay, Kent (*Rothamsted Report for 1971*, Part 1, 82) was concluded.

The uniformity of the parent material of this soil permitted the extent to which major soil constituents have been translocated down the profile to be established, and thus allowed the association of minor elements with these constituents to be detected. Some elements (Co, Cu, Mn, Mo) were associated mainly with the sesquioxides or organic matter, whereas others (Ba, Cr, Ga, Ni, Pb, Sn, Sr, Ti, V, Zr) were associated mainly with the silicate minerals, with only minor proportions in the sesquioxides. Downward movement of clay ($< 0{\cdot}5\ \mu m$) was accompanied by movement of extractable Al_2O_3 and Fe_2O_3, thus identifying these with the mobile fraction; the extractable Al_2O_3 in the eluvial horizon was depleted to a greater extent than the Fe_2O_3, so that a significant proportion of the Fe_2O_3 was not mobile with the clay, and therefore not directly associated with it. This could result from part of the Fe_2O_3 being present as separate aggregates rather than as coatings on clay particles. Because of this different behaviour the extractable material remaining in the eluvial horizon was depleted of Al_2O_3 and correspondingly enriched in Fe_2O_3, relative to the amounts in the other horizons. It was also enriched in Cr, Ga, Pb, Sn, Sr, Ti, V, Zn and Zr, indicating that the extractable fractions of these elements, like Fe, are less mobile than Al.

Boron occurred predominantly in the silicate minerals of the silt and clay fractions, in which it ranged from 30 to 120 ppm; it was most strongly concentrated in glauconite (580 ppm), of which the sand fraction of the lower horizons contained up to 2%. In the upper horizons glauconite had weathered to iron oxide and clay (Weir, Catt & Madgett (1971) *Geoderma*, **5**, 131–149), with most of the boron being retained in the clay and little being lost in solution.

The range of concentrations of water-soluble boron in soils that plants can tolerate is quite small (0·4–4 ppm approx.), and to keep the concentration within such narrow limits there must be a controlling mechanism dependent on the state of combination of boron in the soil. Minor soil constituents can occur in much wider concentration ranges than can major ones, which suggests that the small range of water-soluble boron concentration results from its slow release during the weathering of major soil constituents. Such a slow release would be expected to bring a more constant amount into solution than would a rapid release from scarce boron-rich minerals, the abundance of which is more erratic. (Le Riche)

Geochemistry of Pembroke soils. The distribution of trace elements in the soils of Pembroke is being mapped, and sampling is now complete. Soil sampling at 10 and 50 cm depth on alternate points of a 1 km grid has been complemented by collecting herbage throughout the growing season. Grab pasture samples were collected at each grid intersect in the northern half of Pembroke, and as the concentration of trace elements in plants varies greatly throughout the season, two areas were selected for monthly sampling to investigate the seasonal variations in the uptake of trace elements.

The contents of Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr and Pb in the herbage are being determined by a rapid semiquantitative method of X-ray fluorescence spectroscopy, matching the heights of characteristic peaks against those of standards prepared by adding known amounts of the elements to cellulose. Computer programs have been written to process XRFS data on soils and herbage; the distribution of the elements in the soils was plotted by computer, using a synagraphic mapping program (SYMAP). (Brown and Carolyn Williams)

Geochemistry of soils mapped as Denchworth series. The Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe, Mn, Cu, Zn, As, Br and Pb contents of 30 cores of soil mapped as Denchworth series and sampled in a 0·4 km grid pattern on Gault, Kimmeridge and Oxford clays in Bucks, Berks and Oxon were determined as part of a project to estimate the degree of uniformity within a mapping unit (see *Report of Soil Survey of England and Wales* in *Rothamsted Report for 1969*, Part 1). There is little difference between the minor element concentrations in the soils from different areas, or on different parent materials. There are strong correlations between Pb, Br, S and organic matter concentrations, but the affinities of other elements are more complex.

At the request of the Metropolitan Police Forensic Science Laboratory, major element and particle size analyses were done on 30 Denchworth topsoils. This was a preliminary investigation into the variability of similar soils in different areas, made to assess the usefulness of these methods of analysis for forensic work. (Brown and Carolyn Williams)

Soil chemistry

Decomposition of plant material in soil. An experiment on the decomposition of ryegrass, uniformly labelled with carbon-14, in a range of contrasting soils was terminated. The experiment was started in 1962, and earlier results were given in the *Rothamsted Reports for 1963*, 67 and *for 1967*, 76. Table 1 gives the amounts of plant carbon retained by the soils after exposure in the field for ten years. All the soils listed in Table 1 were kept bare during the whole of the experiment.

Although the labelled ryegrass was cut at flowering, and was therefore green and succulent, after ten years 10–14% of the ryegrass carbon remained in the soil. The great stability of a small part of the ryegrass-derived carbon is in accord with the results of recent work on the age of soil organic matter, which are discussed below. Organic carbon already present in the soil had no effect on the decomposition of labelled ryegrass (soils 1 and 2). For a given clay content, decomposition is less complete in strongly acid soils (5 and 7) than in those that are more nearly neutral, but the difference is small and less marked than in the early years. Clay gave some protection to the ryegrass carbon; thus

TABLE 1

Decomposition of labelled ryegrass in bare soil

Soil No.	pH	Clay (%)	Organic C in soil (%)	Plant addition*	Ryegrass C retained in soil after 10 years† (%)
1	8·1	18	0·97	Tops	12·0
2	7·8	18	2·43	Tops	12·1
3	6·9	20	4·57	Tops	12·1
4	4·8	21	3·87	Tops	13·3
5	3·7	21	3·96	Tops	13·6
6	6·2	8	1·60	Tops	9·8
7	3·7	5	2·86	Tops	12·7
8	7·1	19	4·18	Roots	12·2

* 0·125% labelled ryegrass C added to each soil
† Standard error of difference ± 0·22

soil 6 (8% clay), lost slightly more labelled carbon than soils 1, 2 and 3, all of which contained about 20% clay. (Jenkinson)

Radiocarbon dating of soil organic matter. Table 2, taken in conjunction with earlier work (*Rothamsted Report for 1971*, Part 1, 84), gives measurements of the radiocarbon content of soils from Bridgets, Rosemaund and Gleadthorpe Experimental Husbandry Farms. The soils came from the all-arable rotation of the ley fertility experiments. In all three sites enough bomb-derived radiocarbon had entered the soil by 1971 to invalidate the radiocarbon dating of contemporary soils; pre-1955 samples were used.

Table 2 also shows the radiocarbon ages of different fractions of the organic matter in soil from the unmanured plot on Broadbalk. The method of fractionation was the traditional one in which soil is extracted with alkali and the extract divided into humic and fulvic acids by acidification. The oldest part of the soil organic matter is the fraction insoluble in alkali; the youngest is the fulvic acid fraction. As conventionally prepared humic acid clearly carries younger sorbed material, boiling with 6*N* HCl increases the measured age of the humic acid. (Jenkinson)

TABLE 2

Radiocarbon dating of organic matter in arable soils

Site	Sampling depth (cm)	Sampling date	Fraction	Organic C (%)	Nitrogen (%)	δC^{14}	Equivalent age, years
Gleadthorpe	0–30	1971	Whole soil	1·13	0·077	−166	1460±95
Rosemaund	0–15	1971	Whole soil	1·75	0·185	+46	—
Bridgets	0–15	1955	Whole soil	2·37	0·281	−138	1190±90
Bridgets	0–15	1971	Whole soil	2·39	0·266	+47	—
Broadbalk	0–23	1881	Whole soil	0·94	0·105	−165	1450±95
			Humic acid	0·14*	—	−89	750±90
			Hydrolysed humic acid	0·09*	—	−125	1070±105
			Fulvic acid	0·22*	—	−51	420±85
			Soil residue (humin)	0·43*	—	−258	2395±90

* Organic C in fraction, g per 100 g oven-dry original soil

The measurement of soil biomass. The method previously described for the measurement of soil biovolume, by direct microscopic observation of stained agar films (*Rothamsted Report for 1971*, Part 1, 83), was applied to six of the soils used in our work on the effects of fumigants on soil respiration (*Rothamsted Report for 1970*, Part 1, 75). With the exception of an acid woodland soil, there was a linear relationship between total soil biovolume (or biomass calculated from biovolume) and the flush of decomposition caused by fumigation with chloroform. From the gradient of this line about 40% of the biomass carbon is mineralised when fumigated soil is incubated for 10 days at 25°C. This confirms the suggestion (Jenkinson (1966) *Journal of Soil Science*, *17*, 280–302) that the size of the soil biomass can be estimated from the size of the flush of decomposition.

The soils used came from contrasting sites, three of which were arable, two woodland and one under grass. The total numbers of organisms and total biovolumes of the soils differed over a 20-fold range, but despite this diversity the distribution of numbers and biovolume between spherical and cylindrical organisms (hyphae), and between the different size classes, was remarkably similar in all the soils. Spherical organisms smaller than 1·36 μm in diameter accounted for at least 95% of the numbers of organisms, but for only 7–14% of the biovolume. Very small organisms, presumably bacteria, were commonest; roughly two-thirds of all the organisms counted in all the soils were less than 0·5 μm in diameter. Cylindrical organisms accounted for less than 1% of the numbers, but for 50–70% of the biovolume.

Although it contained an appreciable biovolume (3100 × 10^6 μm^3/g oven-dry soil), the acid woodland soil (pH 3·9) gave no flush of decomposition when fumigated with either chloroform or methyl bromide. This could not have been caused by slower decomposition of the organic matter released by fumigation under acid conditions; when incubated for ten days a cell-free extract of yeast decomposed to almost the same extent in the acid- and non-acid soils.

Soil that has previously been fumigated in the field gives a smaller flush of decomposition when fumigated for a second time than soil that has never been fumigated before (*Rothamsted Report for 1968*, Part 1, 72; *for 1969*, Part 1, 82–83). This effect, which persists for several years, was attributed to the elimination and incomplete recovery of a section of the biomass in the field fumigated soil. The biovolumes of a fumigated and an unfumigated soil from a field experiment have now been measured. The biovolume of the field fumigated soil (2700 × 10^6 μm^3/g oven-dry soil) was only slightly less than that of the previously untreated soil (3000 × 10^6/μm^3/g oven-dry soil), yet the flush of decomposition in the field fumigated soil was less than half that in the previously unfumigated soil. A possible explanation of this discrepancy between the two methods of measuring biomass is that cell walls of killed organisms persisted in the fumigated soil and were then stained and counted as intact organisms. This possibility is being investigated further. (Powlson and Jenkinson)

Reactions between minor elements and organic matter. Continuing this work (*Rothamsted Report for 1971*, Part 1, 86), we have studied the dialysable fractions of the metals mobilised by aerobic incubation of Cu, Ni, Co and Mn oxides with lucerne. The metals remain in solution when the pH of dialysates from lucerne incubations, or from soil organic matter extracts, is increased to 10–11. The behaviour of lucerne-oxide dialysates towards anion and cation exchange resins suggests that the metals are combined in complex anions, but as they are retained against dialysis when treated with metal-free colloidal lucerne decomposition products, it seems that the complexes dissociate sufficiently readily for cation exchange on the colloidal organic matter to be appreciable. It seems that the overall process of mobilisation by aerobically decomposing plant matter consists firstly of dissolution of the metal into true solution as a complex metal–organic anion. Later, when colloidal humified matter has formed, dissociation of the complex yields metal cations that exchange with the colloidal organic matter.

The extent of sorption of Mo(VI) and V(VI) on a soil clay, between pH2–9, and of Cu, Ni, Co, Zn and U between pH 2–4 or 5, was scarcely affected by the presence of non-dialysable lucerne decomposition products, and the presence of organic matter had similarly little effect on desorption of the metals between pH 2–7. With respect to both sorption and desorption, Mo and V behaved as would be expected of anionic species, but up to around pH 4–5, U and the other elements behaved as cations. Below this value more metal and less organic matter was sorbed with increasing pH, so that there seems to be no strong association of the metals with humose matter within this pH range. Above pH 4–5, increasing alkalinity increased metal sorption in the absence of organic matter, but in the presence of humose matter less metal was sorbed as the pH increased; this could mean that the metals are strongly bonded to organic matter in the pH range of normal soils.

The amino acids present in acid hydrolysates of humic acids prepared from a soil organic matter extract, and from lucerne that had been incubated aerobically for 12 months, were determined by T. Z. Nowakowski (Chemistry Department). The two were surprisingly similar, the same 23 amino acids being present in each, in roughly the same relative proportions. (Bloomfield, Kelso and Pruden)

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Apparatus and techniques

X-ray fluorescence analysis. Rubidium taken up from the leaves of host plants by insects has been proposed as a marker. At the request of R. Bardner, Entomology Department, the possible use of X-ray fluorescence analysis to detect marked wheat bulb flies has been tested. Using specimens in the form of thin films the detection limits for Rb and Cs were considerably less than 0·1 μg, when precautions are taken to minimise background count rates; for wheat bulb flies this corresponds to concentrations of less than 10 ppm. If wheat bulb flies can take up as little as 10 ppm of Rb and/or Cs from plants treated with these elements, and if natural flies contain much less than this amount, dispersal patterns could be traced by the analysis of trapped flies. Sample preparation is simple; air-dried flies are squashed between thin films of melinex or polycarbonate and the double film is mounted directly into the X-ray spectrometer; the analysis time is less than 5 minutes per sample, so many analyses can be made.

Although the Br content is a useful guide to the genesis of halites, analysis is difficult because the Br concentrations are small and differ rapidly within small areas, necessitating small samples. By dissolving the halite in a small quantity of liquid (2 ml) and containing the solution in a cell of less than half the area of the normal solution sample holder, a lower limit of detection of 1·3 μg/ml was attained, equivalent to 5 ppm in the halite. Care must be taken to irradiate equal depths of solution in samples and standards as these small amounts of liquid are not infinitely thick for Br Kα-raditiation. (Brown and Carolyn Williams)

Two methods of pore-size distribution analysis. In connection with our structural studies on soils we have developed a suction method applicable to clay soils. The method involves placing samples saturated in kerosene in contact with a membrane held at a pre-determined kerosene suction. The volume of kerosene held by the sample at a particular suction can be related to the volume of pores of less than a critical size. The method is applicable to pores 1000–1 μm diameter, the lower limit being determined by a considerable increase in the time taken to achieve equilibrium. The procedure is simple and the apparatus easily constructed, but in common with other suction methods, the determinations are lengthy. The results show reasonable agreement with mercury intrusion, although the intrusion method is more sensitive to packing discontinuities, e.g. agglomerate formation.

For smaller pore sizes we use carbon tetrachloride vapour sorption from hexadecane solutions in the range of relative pressures 0·75 to 0·995, corresponding to pore diameters of 0·016 to 0·8 μm. The sorption is conveniently done in a desiccator with a 'viton' sealing ring and a 'viton'-sealed tap. No special precautions are necessary, except that temperature gradients should be avoided at the larger relative pressures, and enough time should be allowed for equilibration (e.g. seven days at 0·995 p/po). (Gallavan and Greene-Kelly)

Staff and visiting workers

Dr. S. J. Kalembasa, of the University of Agriculture, Szczecin, Poland, worked with us for two months on methods of determining organic carbon in soil. Dr. Blair F. Jones, of the U.S. Geological Survey, spent five months studying the clay mineralogy of sediments from salt lakes in Western U.S., and Dr. J. Hutton, CSIRO, worked for six months on XRF analysis, and the uptake of silica by wheat. Mr. El Mansey, of Cairo University arrived in December to spend a year with us, under the auspices of UNESCO, studying the clay mineralogy of sediments from the Nile delta.

D. S. Jenkinson attended a seminar on Research on Tropical Soils at the International Institute of Tropical Agriculture, Nigeria. A. C. D. Newman was invited to attend the 9th Colloquium of the International Potash Institute, in Landshut, W. Germany. G. Brown and A. H. Weir attended the International Clay Conference in Madrid, at which the former chaired a session and gave a critical appraisal of some of the contributions.

C. Bloomfield and J. K. Coulter gave papers, and assisted with the organisation of the Conference on Acid Sulphate Soils at Wageningen.

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