Report for 1971

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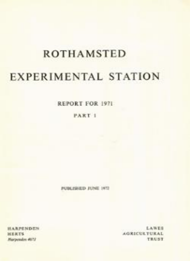

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PEDOLOGY DEPARTMENT

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Fine soil clays are commonly accepted to be the most important source of potassium available to plants, but clays finer than 0·5 μm, from Barnfield and elsewhere in the United Kingdom, are comparatively unreactive, and most of the potassium exchanged by barium comes from coarse clay micas.

We have extended our study of the distribution, composition and origin of loess (i.e. wind blown silt) to include some Norfolk soils, which are developed wholly or partly in loess, and provide better arable land than adjacent soils developed in glacial sand or till without loess cover.

Methods of studying pore-size distribution in soil require the sample to be dry, and for the results to have any relevance, water must be removed without changing the structure; this is especially difficult with clay soils, which commonly shrink a lot when dried directly. There is little shrinking when water is removed by solvent exchange, provided a small concentration gradient is maintained. We find that despite the substantial shrinkage that occurs when the solvent is removed, evaporating polyethylene glycol 200 causes no detectable structural change.

Work continues on the distribution of trace elements in soils, and using rapid XRF analytical methods we are cooperating with the Soil Survey in plotting the distribution of trace elements in soils of Pembrokeshire. The form in which minor elements are combined in soils is important nutritionally, and as evidence of pedogenic processes; in this context we are studying the association of minor elements with the major constituents of soils. The results obtained in our work on the reactions between trace elements and humified organic matter suggest that ion-exchange is the dominant factor. Steric factors may be responsible for the 'fixation' of, e.g., copper by soil organic matter.

The organic content of a soil depends on the amount of plant debris added, and the rate it decomposes. Radiocarbon measurements on soils taken from the Rothamsted Classical experiments before and after thermonuclear testing give information on the addition and decomposition of organic matter in arable fields, and on how changes in management influence the organic content of the soil. The turnover time of much of the organic matter in agricultural top soils seems to be of the order of thousands of years.

Fumigation briefly enhances both respiration and mineralisation of nitrogen in soil. This flush, which we associate with the decomposition of killed organisms, provides a sensitive test for following the recovery of the soil biomass after fumigation. Our work on this is designed to provide information on the long-term effects of repeated fumigation—information that will be needed should fumigation become more widely practised than now.

Our collaboration continues with The Field Drainage Experimental Unit of the Ministry of Agriculture, Fisheries and Food, in studying the oxidation of pyrite in soil as a cause of ochre blocking field drains. Laboratory experiments with undisturbed soil cores showed that, contrary to previous reports, the rate at which pyrite oxidises is decreased by liming, and that the total production of ochre is considerably diminished. Because of this, regular liming might well prolong the effective life of drains in pyritic soils, and we hope to test this in a field trial, with the cooperation of the Agricultural Development and Advisory Service.

We are collaborating with the National Vegetable Research Station in studying the harmful effects of pulverised fuel ash on plants.

Mineralogy

Interstratified clay minerals. Unless the layers are packed in a regular sequence, the X-ray diffraction patterns from clay mineral particles containing more than one type of layer have irregularly spaced peaks. McEwan interpreted these patterns by two Fourier transform methods; at first, from the observed pattern, he calculated a probability function W(R) representing the probability that the silicate layers common to both types of layer will occur at a distance R apart, and we described developments of this method last year. Later McEwan calculated X-ray diffraction patterns from the expected structure of the layers separated by distances determined by probabilities of succession of one type of layer by another. These methods do not include the difference in scattering of the interlayer material (K in illite, Mg and glycol in a glycol treated montmorillonite). Reynolds (*American Mineralogist* (1967) **52**, 661–672, synthesised patterns that include this interlayer material; his program was written in Basic for the General Electric 235 computer, and we have rewritten this in Fortran for use on the ICL 4-70 computer at Rothamsted. Patterns were calculated for illite–montmorillonite mixtures, and plotted automatically on the same scale as the X-ray diffractometer traces. The patterns we obtained are similar to those given by the clay fractions of many British sediments and sub-surface soil horizons.

The structural distribution of silicon and aluminium in clay minerals. In layer silicates the tetrahedral layer contains some silicon and some aluminium atoms at the centre of tetrahedra of oxygen atoms. The Si–O and Al–O bond lengths are 1·62 and 1·77 Å so the two types of tetrahedra are easily distinguished in crystal structures when they occur in distinct positions in the unit cell. In phlogopite and muscovite the ratio of silicon to aluminium is close to 3 : 1, but in the phlogopite cell there is only one type of tetrahedral site and the tetrahedra seem to be the size expected for an average of three Si tetrahedra and one Al tetrahedron. In muscovite there are two sites, but both are the size expected for a 3 : 1 mixture.

In an actual crystal each site is occupied either by Si or Al; a computer program was written to find what arrangement of tetrahedra is formed when Si and Al are allocated to the sites in different ways. The average arrangement must agree with that found by crystal structure determination; the spread of positions will be compared with the spread measured by X-ray diffraction, allowing for the spread caused by the thermal motion of the atoms. (Rayner)

Release of potassium from soils and minerals. The study of potassium release from British soils was extended to soils from a profile taken from the Barnfield Classical experiment. As with all other soils studied, potassium is extracted mainly from coarse clay-sized mica and clay smaller than 0·5 μm, although containing 1% or more K, releases very little. This work is described in more detail in the article 'The soil of Barnfield', *Rothamsted Report for 1971*, Part 2.

Alteration of muscovite. Although Ba is one of the most effective cations for extracting K from micas, even at 100°C the rate at which it exchanges K from muscovite, as measured by the movement of the optical discontinuity in a single flake, is very small. The rate constants for different muscovites are in the range $2{\cdot}4$–$4{\cdot}6 \times 10^{-10}$ mm^2 sec^{-1}, compared with 3×10^{-9} for synthetic fluorphlogopite, 3×10^{-8} for a natural phlogopite and 1×10^{-6} for a reactive biotite. Consequently, preparing a K-depleted mica from muscovite takes very much longer than with the other micas, and because the exchange of potassium is inhibited by traces of potassium in solution, until now the quantities prepared were too small for the composition of the alteration products to be established by chemical analysis. After several years' experiments, larger samples of two muscovites (M7 and M8, differing mainly in Fe content) were depleted of K until 75% was removed from M7 and 95% from M8. Untreated micas and alteration products were analysed chemically and formulae calculated on the basis of an anion structure unit of $O_{20}(OH)_4$. The K-depleted samples seemed to contain more Fe than the original micas, but as it is unlikely that the additional Fe could have been incorporated into the structure, the alteration products may contain free iron oxides. A structural formula calculated from the chemical analysis, corrected for free iron oxide, was very similar to that of the original mica, which supports this suggestion. As well as K, the alteration solutions dissolved appreciable amounts of Si and Al from the micas, so that Fe, which is relatively insoluble at the pH of the experiment, was concentrated in the remaining solid.

The net negative charge on the aluminosilicate layers was calculated from the Ba content of the alteration products, and measured directly by cation exchange of Mg. Both measurements agreed in showing that the alteration products had a smaller net charge than the original micas. The layer charge was similar to that of a high charge vermiculite, and evidence from X-ray diffraction confirms that the alteration product from muscovite is a high-charge dioctahedral vermiculite. A clay mineral giving a 14 Å reflection is common in soils and was identified with vermiculite formed by weathering of mica. Comparison of such soil minerals with the artificial product should enable us to decide on the correctness of this identification. (Newman)

Loess in Norfolk soils. Soil mapping in Norfolk showed that thin layers of silty material overlying the glacial deposits are widespread in the area bounded by Sheringham, Norwich Lowestoft, and the Norfolk coast. This material forms a blanket-like cover up to 2 m thick, except locally on steeper slopes, such as valley sides. Because its local distribution resembles that of the coarser coversands in parts of the Netherlands, it is called coverloam. The coverloam, which is silty or fine sandy loam with few stones, is much more even textured than the underlying strata, which range from stony sands, to sandy or stony clays. The soils with coverloam horizons are more valuable agriculturally than those without, and many (e.g. Hall, Wickmere, Aylsham and Sheringham series) have relatively large available water capacities, do not need draining, are easily worked, and have moderate or large reserves of plant nutrients.

In laboratory work designed to investigate the nature and origin of the coverloam, we studied the particle size distribution and mineralogical composition of samples taken from five widely separated localities. All the samples have much coarse silt, with a peak at approximately 40 μm, and most have subsidiary peaks in the fine sand fraction. The clay contents range from 7 to 18%, and the samples with most clay occur where the substrate is clay-rich. The coarse silt fractions of all the samples are mineralogically alike, with 76–78% quartz, 18–20% felspar, and much epidote, zircon, garnet, hornblende and chlorite in the heavy mineral fractions. The composition and abundance of the coarse silt suggest that the coverloam is composed mainly of loess, because the undoubted loess at Pegwell Bay (Kent) has a similar particle size distribution and mineralogy (*Rothamsted Report for 1969*, Part 1, 76–78). The sand and clay fractions of the coverloam samples are mineralogically more variable than the coarse silts and seem to be derived from the underlying deposits, possibly by cryoturbation.

To find the source of the loess we also analysed till samples from the Norfolk coast. The ones most closely resembling the loess are from the Hunstanton Till, which was probably deposited about 15 000 years ago. Workers in other countries have suggested that loess is derived from glacial debris, mainly by deflation of silt from the surface of proglacial outwash plains, but evidence of this relationship has not previously been shown for loess in England. (Weir, Catt and Madgett)

Clay mineralogy of soils from Nepal. Six soils from the Nawal Parasi District of Nepal were examined at the request of the Land Resources Division of the Directorate of Overseas Surveys, in the context of a development project for the Government of Nepal. Samples from three horizons of two separate profiles were examined. The soils each contain approximately 20% sand, 50% silt and 30% clay, and there is no evidence of clay enrichment within the profiles. All six samples contain a similar suite of clay minerals, in which mica is most abundant, amounting to 40% of the clay fraction in one profile and 30% in the other. Other layer silicate clay minerals include a non-expanding mixed layer mineral, chlorite, kaolinite, a little pyrophyllite and a little smectite-like expanding mineral. All the samples gave a strong colour reaction with Fieldes and Perrott's field test for allophane, which indicates that allophane or active free alumina forms more than 5% of the clay fractions. Small amounts of quartz, goethite and felspar also occur in the clay fractions. (Ormerod and Weir with Coulter, Tropical Soils Adviser).

Clay mineralogy of soils from the British Solomon Islands Protectorate. Thirty-three soil samples were examined for the Land Resources Division of the Directorate of Overseas Surveys as part of a programme of 'land capability appraisal' in the Solomon Islands. The samples were from four soil profiles in Guadalcanal, two in New Georgia and three in Malaita.

The Guadalcanal soils came from the Plain of Guadalcanal, where the profiles are developed in a very mixed material derived from volcanic deposits of differing ages, from Upper Tertiary to sub-recent, limestone of Middle Miocene age, recent calcareous sediments, and probably some material from the pre-Miocene Basement Igneous Complex. The mechanical compositions of the eight soils ranged from 12% sand, 56% silt and 30% clay to 4% sand, 44% silt and 42% clay, but their clay mineral suites were all very similar. The clay fractions contained dominant smectite, some kaolinite and halloysite, usually a small amount of chlorite and a little non-expanding mixed layer mineral, together with quartz, felspar and iron oxides. A positive reaction was obtained for allophane. K-bearing mica minerals were not detected by X-ray diffraction.

The New Georgia group of islands is considered to be geologically the most primitive of the Solomon Islands in that it is a group of volcanic cones, still emerging from the ocean bed, that will one day coalesce to form a single large island. The soils we studied were developed on raised coral terraces that are probably contaminated with weathered volcanic deposits of Late Tertiary to Recent age. The lowest horizons of the two profiles contain lumps of coral, but the clay contents, ($> 60\%$ by weight of the soil) and the clay mineralogy of the other horizons are fairly uniform. Hydrated oxide minerals of aluminium and iron are very prominent in the clay fractions of both profiles. In one, in which sesquioxides form more than half the clay fraction, the dominant mineral is nordstrandite. This rare crystalline form of $Al(OH)_3$ has only twice before been found in mineral deposits, in Sarawak and Guam, although in both of these it apparently resulted from crystallisation, in an alkaline environment, of solutions of aluminium ions produced by sub-aerial weathering. Similar weathering and crystallisation conditions may have formed the nordstrandite in the New Georgia soils. The nordstrandite occurs with other hydrated aluminium oxide minerals, gibbsite, halloysite and aluminous chlorite. The second New Georgia profile contains more layer silicate minerals than hydrated oxide minerals, and more gibbsite than nordstrandite.

The Malaita soils are formed in volcanic deposits overlying limestones of Upper

Tertiary age. Their clay minerals resemble those of the New Georgia soils, and differ mainly in the relative amounts present. Mixed layer minerals occur in increasing amounts with depth, and nordstrandite is much less abundant. As in the other Solomon Islands soils we examined, K-bearing mica minerals are very scarce, which explains the reported very large response of crops to K. (Ormerod, Pruden, Weir, with Coulter, Tropical Soils Adviser).

Clay physics

Pore size distribution in soils. We studied the undesirable structural changes that might occur when clay soils are prepared by solvent exchange for pore size distribution measurements. In this method water is removed by exchange with a water-miscible solvent (e.g. diethylene glycol, ethanol, dioxan) and the process usually involves little or no bulk volume changes. Incident light microscopy showed that these solvents differ considerably in their effect on the soil; diethylene glycol exchanged without any visible fabric changes, whereas ethanol, and to a greater extent dioxan, caused rapid dehydration with consequent micro-cracking and local shrinkage of clay aggregates. These undesirable effects can be minimised by maintaining a small concentration gradient in the sample. Comparison of thin sections from identical remoulded soil samples, prepared by slow exchange with different solvents, showed that the soil fabric is apparently unaffected by the kind of solvents used. Moreover there was a similar clay orientation pattern in fragments of the original wet soil that had been removed by peeling off adhesive films from the soil surface. It was therefore concluded that the soil fabric is unaffected, provided the exchange is done slowly.

Most methods of studying pore size distribution require the solid to be free from liquid. Evaporating water-miscible solvents from soils causes substantial shrinkage, which suggests the possibility of fabric changes involving the reorganisation of the clay into closer packed, and possibly better oriented, packets. The evaporation of polyethylene glycol 200 from soil-fracture surfaces was studied with the scanning electron microscope, in conjunction with incident light microscopy. No instance was detected of either flexing of pore walls during the recession of the liquid films, or of clay reorganisation during shrinkage. The latter observation was confirmed by comparison of thin sections of samples that had passed through the evaporation stage with those that had not been freed from liquid.

Theoretically, because of the diminished dielectric constant of the medium, the exchange of soil water with a less polar solvent (e.g. dioxan) must result in the collapse of the diffuse double layers, and the soil would be expected to shrink a lot during exchange. In fact the shrinkage is usually very small, and samples can even increase slightly in volume. This cannot be explained if it is assumed that the diffuse double layers control swelling and shrinking. More probably changes in soil volume are governed by such factors as elastic relaxation of distortion, inter-particle friction, and liquid-vapour interfacial tension. Substituting water by dioxan, for example, would increase inter-particle friction, and lessen surface tensional forces, so diminishing shrinkage when the liquid evaporates. Confirmation that the compressive stresses that occur when a clay soil is dried are generated principally from the liquid–vapour interfacial tension was obtained by drying a sample under n-octoic acid. The interfacial tension between water and octoic acid is only 8 dynes/cm compared with 73 dynes/cm for water in contact with its vapour, and for a given curvature of the water interface the pressure difference is therefore decreased by approximately one pF unit when octoic acid is substituted for air at the interface, so that normal shrinkage would cease at greater water contents if surface tensional forces predominated. In octoic acid, normal shrinkage ceased at 0·232 g/g compared with 0·122 g/g in air. (Gallavan and Greene-Kelly)

Soil geochemistry

Geochemical studies on the soils of Pembrokeshire. Few systematic studies have been made of the distribution of trace elements in soils in England and Wales. In a special soil survey of West and Central Pembrokeshire (Rudeforth and Bradley, *Rothamsted Report for 1970*, Part 1, 287) selected soil-profile and site characteristics were recorded at 670 1-km grid intersects, and samples taken from each profile at 10 and 50 cm depths. These samples afforded an opportunity to assess relationships between trace-element contents and readily identifiable soil attributes in an area of varied geology and relief.

Maps were prepared showing the distribution of 15 elements in the top soils in the northern half of the country, using 3700 XRFs determinations. The analyses are made by rapid method in which the < 2 mm fraction of the soil is ground and pelleted; chart recordings are made of the fluorescent X-ray spectra excited using Mo and Au X-ray tubes. The heights of characteristic peaks above background, corrected for matrix effects using background and scattered tube line intensities, are compared with those of standards prepared by adding known amounts of the elements to an artificial soil base. With United States Geological Survey standard rocks this method gave values within $\pm 10\%$ of the currently recommended values. Information was obtained for V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, W, Pb, and U. Examples of ranges of concentration are Cr 50–170, Mn 141–7843, Ni 16–56, Cu 17–67, Zn 33–174, Ga $<$ 5–32, As 3–35, Br 21–173, Rb 61–241, Sr 37–116, Y 16–68, Zr 119–472, Pb 13–130, ppm. (Carolyn Williams and Brown, with Bullock and Rudeforth, Soil Survey)

The distribution of minor elements between soil constituents. To determine with which of the major soil constituents (clay, sesquioxides, organic matter, unweathered minerals) trace elements are associated, we studied a soil developed on reasonably uniform loess (Weir, Catt & Madgett, *Geoderma* (1971) **5**, 131–149). Samples of each horizon were treated with H_2O_2, to destroy organic matter, and then with ammonium oxalate solution, in UV light, to dissolve sesquioxides. Less than 1% of the silica in the soil was dissolved, so the treatment caused little decomposition of silicates. The major and minor elements in the extracts were determined, and also the minor elements contained in the six fractions of different particle-sizes into which the treated soils were divided.

Throughout the profile the amounts of oxalate-treated clay and of extractable Fe_2O_3 are closely related. Both are enriched in the illuvial horizons, which suggests that the silicate minerals and Fe_2O_3 moved down the profile in close association, no doubt as surface coatings on the clay. The extractable fractions of minor elements associated with the sesquioxides are also enriched in the illuvial horizons, and for different elements represent very different proportions of the total contents, ranging from nearly 100% for Co, Cu and Mn to a few per cent, or less, for Zr and Sr. In this soil, the non-extractable fractions associated with minerals that are unaffected by oxalate treatment usually become more concentrated with decreasing particle size, partly because the coarser fractions are dominated by quartz, the lattice of which does not readily accommodate foreign elements. However, the concentrations of Co, Cr, Cu, Mn, Ni, Sr, Ti and V do not all increase to the same extent, indicating that they are not all combined in the same manner. Zirconium is an exception and reaches a maximum concentration in the silt fractions, in agreement with the mineralogical observation that zircon favours this particle size range, and indicating that Zr is almost entirely in this form.

The lower horizons of the soil contain glauconite, and there is nearly four times as much boron in the sand fraction of the lower than those of the upper horizons. The amounts of boron in the finer fractions, though greater, vary less with depth, but in all fractions the amount was unaltered by oxalate treatment. It can be concluded that the 'available boron', which is usually identified with water-soluble boron, was lost during separation of the fractions and that the remaining boron is not associated with the sesquioxides and resides entirely in silicate lattices. (Le Riche)

Soil chemistry

The effects of cropping history on the flush of decomposition following soil fumigation. The cropped and fallowed areas of Highfield and Fosters were used to study how cropping affects the flush of decomposition. The cropped soils, from continuous arable plots of the Ley–Arable Experiments, have received crop residues every year to act as substrate for the soil population. The fallowed soils have been kept bare for ten years and so have received little plant material; presumably the populations of these soils have decreased considerably—a point we hope to check by direct microscopic observation.

The cropped soil from Fosters, which contained only slightly more organic carbon than the fallowed soil (1·6 and 1·5% respectively) gave a much larger flush of decomposition when incubated after fumigation with chloroform. Respiration and mineralisation of nitrogen increased twice as much in the cropped soil as in the fallowed soil. After fumigation with chloroform, respiration and mineralisation of nitrogen were similar in the cropped soil from Highfield (2·3% organic C) and in the cropped soil from Fosters (1·6% organic C), despite the difference in content of soil organic matter. The fallowed soils from Highfield and Fosters (1·9 and 1·5% organic C respectively) gave flushes of similar size. The cropping history, and presumably the size of the biomass, thus had a greater influence than the organic contents of the soils on the magnitude of the flush of decomposition.

The 40-in. Barnfield drain gauge has been kept bare of all plants for 99 years and so would be expected to support only a small biomass. Fumigation with chloroform caused barely detectable increases in respiration, and mineralisation of nitrogen, even though the soil still contained 0·8% organic C. (Powlson and Jenkinson)

Direct estimation of soil biovolume. The Jones and Mollison method for the direct estimation of microbial numbers in soil was modified so that the soil biovolume could be measured. Stained organisms were counted and sized by comparison with circles of known diameter drawn on an eyepiece graticule. Spherical (or near spherical) organisms ranging in diameter from 0·3 to 20 μm were grouped into 13 diameter classes, and those in each class counted. Small organisms were examined under high magnification, and as larger organisms were counted the magnification was decreased, and the field scanned progressively increased. Fungal and actinomycete volumes were measured by grouping the hyphae into seven diameter classes and measuring the total length of hyphae in each diameter class, again using an eyepiece graticule.

Initially, the soil films were prepared for microscopic observation exactly as described by Jones and Mollison, but later we found that a more drastic procedure for dispersing the soil gave larger numbers, presumably because organisms dislodged from heavily-stained pieces of decaying plant material were revealed. With soil from the dunged plot on Broadbalk, the following values were obtained with the unmodified Jones and Mollison procedure, and after ultrasonic dispersion in the presence of detergent, respectively: spherical organisms, 3720×10^6 and 5500×10^6 per g oven-dry soil, with biovolumes 960×10^6 and 2240×10^6 μm^3; cylindrical organisms, $6{\cdot}5 \times 10^6$ and $17{\cdot}6 \times 10^6$ per g, with hyphal volumes 1030×10^6 and 2720×10^6 μm^3. Although ultrasonic dispersion did not greatly increase the number of small organisms counted, many more of the larger organisms could be seen and sized.

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TABLE 1

Radiocarbon dating of organic matter in arable soils

Site	Cropping	Sampling depth (cm)	Sampling date	Organic C, (%)	Nitrogen (%)	δC^{14}	Equivalent age, years
Woburn	Continuous barley, unmanured	0–23	1888	1·34	0·139	−82	685±90
Woburn	Continuous barley, unmanured	0–23	1927	0·94	0·082	−158	1380±90
Woburn	Cereals on site of continuous barley experiment	0–23	1971	0·77	0·070	−161	1410±90
Saxmundham	Rotation I, unmanured	0–23	1944	1·37	0·152	−139	1200±90
Saxmundham	Rotation I, unmanured	0–23	1969	1·07	0·119	−125	1070±90
Gleadthorpe	Ley fertility experiment, all arable rotation	0–30	1955	1·06	0·077	−258	2395±90
Rosemaund	Ley fertility experiment, all arable rotation	0–15	1955	2·16	0·216	−82	685±90

TABLE 2

Composition of soil solutions from successive horizons of a podzolised soil

		Organic C, γ/ml				Fe, ppm		Al, ppm		Mn, ppm	
	pH	17 000 rpm	<0·45 μm	<50 000 m wt	<10 000 m wt	17 000 rpm	<0·025 μm	17 000 rpm	<0·025 μm	17 000 rpm	<0·025 μm
Canopy wash	5·4	16	—	—	—	4	—	3	—	2	—
Effluent from A_{01}	5·0	190	170	120	40	5	2	3	3	5	4
Effluent from A_{02}	4·9	110	100	70	50	6	2	4	2	2·5	2
Effluent from A_2	5·0	180	170	75	20	11	3	7	3	2	2
Effluent from B_h	4·2	35	—	—	—	4	—	3	—	3	—
Effluent from B_{fe}	4·2	14	—	—	—	3	—	4	—	4	—

Soil from the unmanured plot on Broadbalk contained fewer organisms than the dunged plot, although the ratio of the spherical to cylindrical biovolume was similar in both soils. Ultrasonic dispersion of the unmanured soil gave counts of 1070 × 10^6 spherical organisms per g oven-dry soil, with a bivolume of 710 × 10^6 μm^3 and 7·0 × 10^6 cylindrical organisms per g soil, with a biovolume of 970 × 10^6 μm^3.

The amount of biomass carbon was calculated from the measured biovolumes by assuming that all the organisms had a density of 1 g per ml and contain 20% dry matter, of which 50% is carbon. Thus the dunged soil from Broadbalk, with a total biovolume of 4960 × 10^6 μm^3 per g oven-dry soil contains 49·6 mg biomass C per 100 g soil. The amount of biomass carbon calculated from the size of the flush after fumigation with chloroform was 54 mg C per 100 g soil, which is close agreement for two such different methods of measuring biomass (Jenkinson and Powlson)

Radiocarbon dating of soil organic matter. Table 1 gives measurements of the radiocarbon contents of seven arable soils from four different places. The three Woburn soils come from a site where the organic content is decreasing. As the amount of organic carbon decreases, the equivalent radiocarbon age increases, presumably because the old and biologically resistent fraction of the organic matter in the recent samples is a larger proportion of the total organic matter, and the amount of bomb-derived radiocarbon in the 1971 sample is not enough to mask this trend.

The 1969 Saxmundham sample contains less organic carbon than that of 1944, probably because the plough depth has increased, rather than because of an absolute decline in organic matter, as at Woburn. The equivalent age of the 1969 sample is less than that of the 1944 sample, presumably because bomb-derived radiocarbon has been incorporated.

With all the samples the results confirm the earlier finding (*Rothamsted Report for 1968*, Part 1, 73), established for Rothamsted soils, that in agricultural top soil in which decomposition is not restricted by deficient aeration or by acidity, much of the organic matter is extremely resistant to biological activity, with turnover times measured in millennia rather than in decades. (Jenkinson)

Sulphur deficiency in Malawi soils. Experiments in Malawi with tomatoes, millet and gram beans, grown in 60 representative soils (0–12 in.), showed widespread deficiencies of sulphur and boron. We determined the total sulphur contents of these soils by X-ray fluorescent spectrometry using calibration curves derived from values obtained chemically. The total sulphur contents were small, ranging from 26–207 ppm. The sulphate-adsorbing capacities of such soils are presumably important in determining the extent to which fertiliser-sulphate will be retained, and the best time of year, in relation to the onset of the rain, to apply fertiliser. Accordingly we determined sulphate-adsorption isotherms for 15 representative soils. Very little sulphate was adsorbed at the pH of the soils, and at the probable equilibrium concentrations in the field, so that sulphate would presumably readily be leached from the topsoil, requiring some to be added at the beginning of each season. Because the subsoils probably contain less organic matter, and are perhaps more acid, sorption of sulphate may be greater within the lower rooting zone; if this is so, only enough sulphur may be needed to provide the optimum conditions for growth during the early part of the growing season. (Bloomfield, Blaza and Carolyn Williams)

Acid sulphate soils and ochre deposits in field drains. It has been proposed that pyritic soils can be reclaimed economically by draining and irrigating, thereby promoting the oxidation of pyrite and removing the oxidation products. Bloomfield, Coulter and Kanaris-

Sotiriou (*Tropical Agriculture* (1968) **45**, 289–300) found large amounts of residual pyrite in a Malayan acid sulphate soil that for five years had been subjected to severe aeration and leaching, which indicates that the process is too slow to be useful in this context. Further, once the pyrite was destroyed, there would remain the problem of dealing with a considerable depth of very acid soil.

Liming has been claimed to increase the rate at which pyrite is oxidised in an aerobic soil, which is surprising, as the chemical process is catalysed by Fe^{3+} and catalysis by *Thiobacillus ferrooxidans* stops in conditions less acid than pH 3·5–4·0. In collaboration with the Field Drainage Experimental Unit, Ministry of Agriculture Fisheries and Food, we attempted to obtain quantitative information on the rate of oxidation/leaching of pyrite from undisturbed cores (1 × 0·5 m) of soil from Waxham, Norfolk. During 12 months we leached limed and unlimed soils with the equivalent of about twice the average annual rainfall, applied in weekly increments as distilled water. Analysis of the effluents showed that liming (20 tons $CaCO_3$/acre) greatly decreased the amounts of Fe and SO_4^{2-} (especially Fe) removed in the drainage water. Including the amounts originally present in the soil, the total production of SO_4^{2-} was equivalent to 429 and 763 gm S in the limed and unlimed soils respectively. Liming thus had the expected effect of slowing the oxidation of pyrite.

Sixteen per cent of the original total S was leached from the unlimed core, and on this basis, with the average annual rainfall of S.E. England, complete removal of inorganic S would take 12–13 years. This probably considerably underestimates the time that would be required in the field, as our experimental conditions tended to increase the rate of oxidation/leaching—oxidation was favoured by the average temperature being higher than in the field, and by the access of oxygen to the bottom of the soil column; the absence of a plant cover prevented transpiration, so that leaching was relatively more severe.

Thirteen and 67 g Fe were leached from the limed and unlimed soils, respectively, and as liming so greatly decreased the amount of iron removed from the column, it seems that liming would decrease the annual total ochre production and thus prolong the life of a drainage system. In collaboration with the Field Drainage Experimental Unit and A.D.A.S. a field trial to test this possibility is projected. (Bloomfield, Kelso and Pruden)

Sorption of organic matter-trace elements on soil clay. Continuing our study of the mobilisation of trace elements by aerobically decomposing plant matter, we studied the sorption/desorption of humified organic matter and its associated trace elements on soil clay.

It proved difficult to obtain soil clay completely free from organic matter. After three treatments with H_2O_2, a sample of Rothamsted subsoil (3–4 ft), selected to avoid obvious humose contamination, contained 0·5% organic carbon. The clay sorbed organic matter from extracts of rotted lucerne, but in desorption experiments the native organic matter gave very large blank values. It seems that we shall have to use organic-free clay minerals and artificial sesquioxides in the further study of desorption.

With K-saturated clay there is little sorption of organic matter above pH 6·5; the extent of sorption rapidly increases with increasing acidity, to a maximum at pH 3–4. As would be expected, the smaller molecular weight species in the fulvic acid fraction are sorbed much less extensively. The sorption characteristics of the K- and Ca-saturated clay differ considerably. With the Ca-form, the maximum sorption of organic matter was only 80% of that by the K-form; maximum sorption occurred between pH 3–5, and at pH 8–9 the extent of sorption was still 50% of the maximum value. Sorption thus seems to be much less pH dependent with Ca- than with K-clays.

Sorption of trace elements (Cu, Ni or Zn) seems to be independent of the sorption of organic matter from the same solution. Organic matter was sorbed to the same extent from H_2O-dialysed extracts of lucerne rotted in the presence or absence of the metal oxides (*Rothamsted Report for 1968*, Part 1, 74) and the metals were sorbed from extracts of rotted lucerne to the same extent as in the absence of organic matter from solutions of equivalent concentrations of the sulphates. Over the pH range 3–7 the specific sorption of organic matter from a dialysed Cu-lucerne decomposition extract decreased to near zero with increasing pH, but at the same time the sorption of Cu increased to a maximum. Aqueous $CuSO_4$ gave an almost identical sorption pH isotherm as the Cu-lucerne extract.

These observations suggest that cation exchange is predominantly responsible for the association of trace elements and humified organic matter. When the humose constituents of an extract of rotted lucerne are flocculated by adding a large excess of a Cu, Ni or Zn salt, the precipitated organic matter retains about twice as much metal when dialysed against water, or against 0·1 *N* HCl, as when the extract is dialysed after treatment with $CuSO_4$ etc. in such a way as to avoid flocculation. However, when the flocculated material is dispersed ultrasonically, the amounts of metal retained after dialysis are much the same as with the non-flocculated material. Apparently steric factors inhibit exchange of the metals in the flocculated organic matter.

Organic matter sorbed on the K-clay at pH 4–5 is almost completely extracted from the undried product by KOH at pH 10–12, but a considerable proportion seems to be retained when the clay is air-dried before treating with KOH. Because of the relatively large blanks caused by the organic matter contained in the original clay, these results await confirmation. (Bloomfield and Kelso)

Composition of soil solutions from a podzolised profile. We examined the canopy wash and soil solutions collected at the bases of successive horizons of a podzolised soil, under spruce. The solutions were provided by Dr. E. Klimo of The University of Agriculture and Forestry, Czechoslovakia.

Table 2 gives the organic carbon contents of filtrates from successively finer ultrafilters. It seems that although most of the organic matter is of large molecular weight, almost all is of considerably less than colloidal size. Much of the Fe and Al is removed by a 0·025 μm, filter, but most of the Mn is of smaller size.

The soil solutions were several weeks old when we examined them, so that they may have suffered a change similar to that undergone by the initially dialysable Fe dissolved by the action of leaf extracts on ferric oxide, which reverted to a non dialysable form when the solution was exposed to atmospheric oxidation. (*Rothamsted Report for 1968*, Part 1, 75). (Bloomfield, Kelso and Pruden)

Vivianite in gley soils. Gley soils can be divided into two broad groups—iron-depleted soils with neutral grey colours that are unchanged on exposure to atmospheric oxidation, and black, blue-green or bright blue soils that turn brown soon after exposure. The blue and blue-green colours are well outside the range of existing Munsell Soil Colour Charts.

An essential feature of the gleying process is the removal of ferric oxide coatings from soil particles; this reveals the grey colour of the substrate, which seems to be caused by small amounts of organic matter that is intimately associated with clay, and is probably of considerable age. The unstable black colour of some gley soils is that of ferrous sulphide, which results from the microbiological reduction of sulphates, whereas the bright blue-green colours are apparently caused by the presence of vivianite, i.e. ferrous phosphate.

We examined three intensely blue soils from Flitton, Beds., and Medmenham, Bucks.

When first exposed, the Flitton soil is a uniform bright blue; exposed surfaces show occasional white spots and filaments, which quickly change to a stable blue colour, whereas the originally blue soil mass becomes red-brown. The X-ray diffraction pattern of the blue oxidation product is that of pure vivianite, and the total P content of the air-dry soil is 0·4%. The Medmenham soils, which contain rather less P, are greenish-blue when first exposed, and quickly oxidise to brown. All three soils are calcareous, pH7+, and contain considerable amounts of mono-sulphide.

Sulphidic soils often have a bluish-black colour, rather than the pure black of ferrous sulphide. As ferrous phosphate and ferrous sulphide can occur together, so far as it is justified to generalise on the basis of these three soils, the black to blue colour range may reflect different proportions of the two ferrous compounds. Unfortunately, the precise chemical analysis of sulphidic soils presents formidable difficulties.

The blue colour of gley soils is often stated to be that of ferroso-ferric oxide, or $Fe_3(OH)_8$, the hydrated form of Fe_3O_4. This idea probably derives from the observation of transitory green-blue colours when ferrous hydroxide is precipitated in the presence of air, under moderately alkaline conditions. In these circumstances oxidation readily proceeds to completion, with the formation of hydrated ferric oxide. Pure ferrous hydroxide is white, so that if this process operates in the soil, the sequence white/grey–blue–brown would be expected as a gley soil oxidises, but no such colour change has been described. It is difficult to see how the intermediate blue-green colour of partially oxidised ferrous hydroxide could develop in the anaerobic state of the unexposed soil, thus explaining the existence of the unstable blue soils, as this would necessitate first the the reduction of all the iron involved in the formation of ferroso-ferric oxide, and its conversion to $Fe(OH)_2$, as such, and then its partial reoxidation. Gleying produces soluble ferrous iron, apparently complexed by organic matter, and there seems no reason to postulate the subsequent precipitation of ferrous hydroxide, which would presumably be an essential stage in forming ferroso-ferric oxide.

A black material of variable composition, corresponding very approximately to Fe_3O_4.aq, is formed when a ferrous salt is treated with a large excess of alkali in the presence of air. The ferrous iron contained in this product is stable to atmospheric oxidation, so that even if the method of formation and its colour did not make it irrelevant in this context, its presence would not explain the transitory blue colour of some gley soils. (Bloomfield, Kuhn and Pruden)

General

The separation and identification of oestrogenic isoflavones from red clover leaf protein. Paper- and gel-filtration chromatography were used to separate and identify the oestrogenic isoflavones biochanin A, formononetin, diadzein and genistein from red clover leaf protein. The crude isoflavone mixture was extracted from the protein with aqueous ethanol; chlorophyll and lipids were removed, and the partly purified isoflavone mixture passed down a column of 'Sephadex G-25', which was then eluted with dilute ammonium hydroxide. The concentration of the isoflavones in each of the four separated bands was measured spectrophotometrically, by comparison with a known concentration of the corresponding pure isoflavone.

The method promises to be of use in determining the oestrogenic contents of leaf proteins that could serve as food supplements. (King, with Festenstein and Glencross, Biochemistry Department)

Classification of soils from Stellenbosch. Field and laboratory properties of 65 soils from sites near Stellenbosch, South Africa, being considered for growth of deciduous fruit trees were recorded by Mr. W. A. G. Kotze of the Fruit and Food Technology Research Institute. We used these to calculate dendrogrammes and principal coordinates representing the horizon and the soil relationships. The first vector in the principal coordinate representation of the horizons is related to depth of the horizon; horizons at the same depth are more closely associated than in the Glamorganshire soils first studied by this method (J. G. Sheals (Ed.) *The soil ecosystem* 1969, London: The Systematics Association, p. 31). The critical soil property for the growth of the trees is thought to be aluminium toxicity. The soils with the most exchangeable aluminium in the top horizon tend to be close together in the dendrogramme, but they do not form a separate group. (Rayner).

Apparatus and techniques

Determination of total S in plant material. Because of the importance of sulphur in plant nutrition, a quick and accurate method of determining total sulphur in plant material is desirable. X-ray fluorescence spectrometry provides a rapid and accurate method for determining S in soils (Brown & Kanaris-Sotiriou, *Analyst* (1969) **94**, 782), and we have examined its use with plant materials.

X-ray fluorescence spectrometry is a comparative method and samples of known composition must be used for calibration. Because of matrix effects, the gross composition of the standard sample must be similar to that of the test material. Preliminary XRF examination of two sets of plant materials, each analysed by a different chemical method, gave different calibrations and a systematic error in one of the chemical methods was suspected.

A collaborative study, with the Chemistry Department, of different chemical methods for determining total S in plant material showed that the chemical procedures used in the two departments gave different results. The chemical methods involved two steps: oxidation of sulphur to sulphate, and determining the sulphate. Errors arose in both stages.

Following Swanson and Latshaw (*Soil Science* (1922) **14**, 421–430), Butters and Chenery (*Analyst* (1959) **84**, 239–245) oxidised sulphur compounds in soils and plants by digesting with HNO_3, followed by igniting with $Mg(NO_3)_2$, but give no reason for the necessity of the second operation. With a range of plant materials we obtained consistently greater total sulphur contents using $HNO_3/Mg(NO_3)_2$ than with HNO_3 alone. Similarly, with several pure organic compounds, $HNO_3/Mg(NO_3)_2$ gave slightly greater values, but except for 1-methionine HNO_3 alone gave almost theoretical recoveries. With 1-methionine HNO_3 and $HNO_3/Mg(NO_3)_2$ gave 0·79 and 21·32% S respectively, the theoretical value being 21·49. Three methods of determining sulphate were tested. Turbidimetric determination of $BaSO_4$ with the Technicon Auto-Analyser gave S values up to 40% larger than flame photometry of $BaSO_4$ dissolved in EDTA (Cunningham, *Chemistry & Industry* (1962) **51**, 2120–2121), or titration with mercuric acetate (Archer, *Analyst* (1956) **81**, 181) after reduction to S^{2-} (Luke, *Industrial & Engineering Chemistry, Analytical Edition* (1943) **15**, 602). Values obtained by the last method were used in the calibration.

The XRF intensities are proportional to the S contents, and a closely similar linear relationship was obtained using synthetic standards prepared by adding known amounts of l-methionine to cellulose. The method requires only grinding and pelleting of dry plant material and the only matrix interference was with mangolds, which contained more than $2\frac{1}{2}$% Si. Wheat flour, wheat straw, cabbage, kale, cauliflower, citrus, mangold and mixed pasture were tested. (Brown, Pruden and Carolyn Williams, with Bolton Chemistry Department)

Staff and visiting workers

G. Brown read a paper at the first joint conference of the Belgian, British, French and Spanish Clay Minerals Societies at Leuven, Belgium, which A. C. D. Newman and A. H. Weir also attended. C. Bloomfield read a paper at the International Society of Soil Science meeting on gley soils, in Stuttgart.

Professor Keino Nagasawa, Nagoya University, returned to Japan after spending a year studying the alteration of biotite. Dr. N. C. Kuhn, of the Swiss Forest Research Institute, returned after a year spent in studying sulphides in waterlogged soils, and Dr. R. M. Carr, University of Otago, New Zealand, left after working on organic complexes of halloysite for three months.

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