

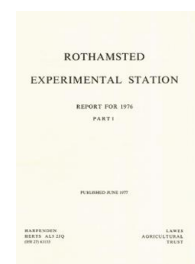
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Introduction

Improvements giving a large increase in the diffracted intensity from clays have been made in the collimation of the X-ray powder diffractometer. Our initial survey of the mineralogy of Nigerian soils has been completed, and we have studied the Angular Chert Drift soils near the Medway valley. In collaboration with the Chemistry Department we have examined the mineralogical composition of size fractions of soils from the Saxmundham experiment in relation to their abilities to release K. We have studied the composition of insoluble Cu compounds formed in Cu-enriched superphosphate fertilisers, and the mineralogical composition of ochre deposits formed in field drains in pyritic soil at the Arthur Rickwood Experimental Husbandry Farm.

We have continued our work on soil structure by investigating the applicability of Hg-intrusion porosimetry to the measurement of the pore size distribution of soil crumbs dried by various methods.

The relationships between the minor element contents of soils of N.W. Pembrokeshire and their associated herbage have been studied, as well as the geochemistry of reclaimed sediments from The Wash. We have collaborated in the Canada Certified Reference Materials Project by determining major and minor elements, by physical and chemical methods, in four standard soil samples.

The unique collection of information and soil samples from the Rothamsted Classical field experiments have been used to develop and fit a model for the changes in the organic carbon contents of these soils. This model, which is based on decay and transfer between five types of organic matter, should also have applications to other soils and environments.

Our work on organic matter in soils of the humid tropics, which is now completed, has shown that although plant remains decompose about four times as quickly under tropical as under temperate conditions, in other respects the decomposition processes are remarkably similar. We are attempting to measure the extents to which various kinds of mechanical disturbance accelerate the decomposition of soil organic matter.

In field studies in Malaysia we have measured the pH changes that occur in flooded

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acid sulphate rice soils, in an attempt to establish the cause of their poor yields; this work has been supplemented by a laboratory study of the influence of the kind and amount of plant material on the pH changes undergone by flooded soils.

Our study of the complexing of minor elements by plant decomposition products continues, as does our work on toxic metals in sewage sludge, on the acidification of pyritic mine waste, and on the application of infra-red spectroscopy to problems of clay mineralogy.

As in previous years the X-ray fluorescence spectrometer has been used extensively on behalf of other departments and outside bodies.

Mineralogy

X-ray diffractometry of clays. Most commercial X-ray powder diffractometers are designed for the examination of well-crystallised materials, for which line widths are largely determined by instrumental functions such as source width, slit width and axial divergence. To limit aberrations that broaden reflections the collimation systems supplied are unnecessarily restrictive when a high degree of resolution is not essential.

Because of their small crystal size and structural faults, the intrinsic line widths of many natural materials such as clays are many times greater than those obtained from well-crystallised materials such as quartz. By relaxing the collimation conditions it is often possible to increase the diffracted intensities from soil clays and similar materials by an order of magnitude or more. Simple, cheap and readily reversible modifications that provide large increases in intensity, with little or no loss of information in the patterns, have been made to the collimation system of a Philips diffractometer.

The advantages gained are (i) X-ray patterns of better quality can be obtained in the same time as before, or patterns of the same quality can be obtained much more quickly, (ii) the extra intensity allows useful diffraction patterns to be obtained from materials that are so poorly crystalline that with standard collimation conditions the signal could not be reliably distinguished from background variations, (iii) the intensities obtained from the clay component of unfractionated soils seem to be sufficient to allow identification of the main fine-grained components in soils containing more than about 30% clay. This promises to make the currently practised tedious separation and preparation of clay-sized fractions unnecessary for X-ray diffraction examination, and obviates the possibility of alteration of chemically sensitive clay-sized material by the separation procedures.

Application of this modification is not restricted to soils and soil clays; it should prove useful in studies of many other poorly crystalline materials such as catalysts, plastics and other organic products. (Brown)

Mineralogy of Saxmundham soil in relation to the release of potassium. The differences between the K-releasing properties of surface soils from the Nil and K plots of the Saxmundham Rotation 1 experiment, and of the Ca, Ca + K, and K forms of size fractions of the Nil plot were compared with differences in mineralogical composition. (See also the Chemistry Department section of this Report, p. 96.)

The granulometric and mineralogical compositions of the Nil plot surface soil are given in Table 1.

The interstratified expanding minerals of the fine and coarse clay fractions superficially resemble the random mica-smectite interstratification described from a soil of the Denchworth series in weathered Oxford Clay (*Rothamsted Experimental Station, Report for 1972, Part 1, 67-68*). However, the apparent exchange capacities of the fine and coarse clay fractions decrease by 18 and 20% respectively when changing from Mg-Ca to K-NH₄ exchange, i.e. these proportions of the exchange complex behave like vermiculite

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TABLE 1

Granulometric and mineralogical compositions of size fractions of surface soils from the Saxmundham experiment, Rotation 1, Nil plot

Fractions	Coarse sand	Fine sand	Silt	Coarse clay	Fine clay
Size range (μm e.s.d.)	2000–210	210–20	20–2	2–0.2	<0.2
Wt % in soil	23.7	30.3	11.1	12.8	22.1
Wt % of fraction:					
Quartz and flint	98	86	64	12	0
Alkali feldspar	1	11	13	3	0
Iron oxides	1	1	2	7	5
NaOH-soluble $\text{SiO}_2 + \text{Al}_2\text{O}_3$	0	0	1	3	6
Kaolinite	0	0	3	16	13
Mica	0	1	10	24	10
Interstratified expanding minerals	0	1	7	32	66

and the remainder like smectite. When exchange capacity is measured as the difference in the total K of K- and Ca-forms, the capacities of the same fractions increase by 18 and 30% in comparison with those measured by Mg–Ca exchange. This suggests that blocking materials, such as hydroxy Al-polymers, possibly associated with other cations such as Mg, are present in the clay, and that these are either partially removed or penetrated during K-saturation. In the coarse and fine fractions, components containing these materials form part of the interstratification. They may occur similarly in part in the silt fraction, but they also form a separate 14 Å phase that is present in the Ca and Ca + K forms, but absent from the K form. The interstratified minerals are thus complex, and although mica and smectite are major components, vermiculite- and chlorite-like components are also present. (Weir, with Talibudeen, Chemistry Department)

Angular Chert Drift soils. The Hythe Beds dipslope on either side of the Medway valley in west Kent and east Surrey is covered by a thick superficial deposit of stony clay, which has been mapped as Angular Chert Drift by the Institute of Geological Sciences. The soils of this area have many features in common with those in Clay-with-flints on the Chalk dipslope in southern England in that they have thin silty surface horizons, and deep sub-soil horizons composed of reddish mottled clay with stones derived from siliceous nodules in the subjacent limestone, and they occur mainly on plateau remnants between valleys dissecting the dipslope, though there is some evidence for local mass movement of the reddish stony clay down valley sides.

Detailed mapping at a scale of 1:2500 of a small area of the Hythe Beds escarpment north of Sutton Valence (Sheets TQ 8050 and 8051) showed that the reddish mottled clay with chert stones occurs on an even, gently-sloping surface, which is also occupied in places by small outliers of the glauconite-rich basal Sandgate Beds. This suggests that the Angular Chert Drift was formed by weathering of a thin cover of Sandgate Beds in the same way that the Clay-with-flints over Chalk is derived from a thin remnant of basal Reading Beds (Hodgson, Catt & Weir, *Journal of Soil Science* (1967), **18**, 85–102). We attempted to verify this by analysing mineralogically the fine sand (62–250 μm) fractions from various horizons in a deep profile in Kings Wood (TQ 831509), and comparing these with the same size fractions from samples of Hythe and Sandgate Beds. Unfortunately all three deposits have the same assemblage of resistant sand minerals, and on this evidence alone the reddish mottled clay could be derived either from the basal Sandgate Beds or from the natural insoluble residue of the Hythe Beds limestones. The chert nodules and fragments in the Angular Chert Drift are most likely to be derived from the Hythe Beds, as these contain cherty layers (Worssam, *Geology of the country around Maidstone, Memoirs of the Geological Survey of Great Britain* (1963), 30), but the acid-insoluble

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residue of the Hythe Beds contains too little clay for the Angular Chert Drift to have originated simply by natural dissolution of the limestone. Thin sections from various horizons in the Kings Wood profile showed that much of the clay, especially below 130 cm depth, is well-oriented and therefore derived by eluviation from overlying deposits, some of which may subsequently have been removed by erosion. The red mottles are usually closely associated with the oriented clay bodies, and are caused by hydrated iron oxides also translocated from weathered overlying horizons.

Mineralogical analyses of the upper silty horizons of the same profile showed that these are composed largely of loess resembling that described elsewhere in Kent (Weir, Catt & Madgett, *Geoderma* (1971), **5**, 131–149), which is probably Late Devensian in age. The translocation of clay and red hydrated iron oxides therefore seems to be associated with a period of weathering in fairly warm, humid conditions before the Late Devensian. They are paleosol features, and the rubified, clay-enriched horizons are paleo-argillic horizons (Avery, *Journal of Soil Science* (1973), **24**, 333). The chert nodules in the deepest subsoil layers above the Hythe Beds often closely interdigitate with reddish brown, unoriented clay, as though the clay had formed by weathering of the chert. The problem of this unlikely weathering process was resolved when we found that the chert in parts of the Hythe Beds is closely intergrown in this way with a green, glauconite-like clay, the weathering of which must have produced the reddish brown clay. Red clay was also observed as subsoil mottles in profiles on the very glauconitic basal Sandgate Beds, which form outliers surrounded by Angular Chert Drift. These mottles seem to have formed *in situ* also by weathering of glauconite, and the hydrated iron oxides responsible for red colours throughout the Angular Chert Drift probably originated in the same way.

We conclude that the reddish stony clay subsoil horizons of this area originated by pedological processes similar to those that gave rise to the Clay-with-flints. Dissolution of the Hythe Beds limestone beneath a thin (2–3 m) cover of basal Sandgate Beds provided spaces in which translocated clay and hydrated iron oxides, derived mainly from the weathering of glauconite, could be redeposited. Apart from the chert nodules, the limestone residue probably contributes very little to the Angular Chert Drift. Most of this weathering and reorganisation of the deposits occurred in the Ipswichian or earlier warm periods of the Quaternary, well before the deposition of loess in the Late Devensian. (Catt, with M. A. Carpenter and R. D. Green, Soil Survey)

Mineralogy of Nigerian soils. The initial survey of the mineralogy of Nigerian soils (*Rothamsted Report for 1975*, Part 1, 217) has been completed. As in many tropical soils, the dominant clay mineral in most of the soils belongs to the kaolinite group. Previously little has been done to differentiate the kaolin-rich soil clays of tropical regions; in the course of the preliminary survey we observed distinct differences between the kaolinite minerals from different soils. The intensity and width of the basal reflections of the X-ray diffraction patterns of oriented films varied considerably, and electron micrographs showed a wide range of particle size and shape. Because differences in crystal structure and particle morphology are probably associated with other differences, we are studying the variations in structure in relation to pedogenetic factors and physico-chemical properties.

From the original 206 samples, 26 clays from dominantly kaolinitic B or deeper horizons were selected to represent the range of chemical composition, and the range of climate and parent material that formed the basis of the original sampling design (*Rothamsted Report for 1974*, Part 1, 195), and X-ray diffraction patterns of randomly oriented powders were made to assess the range of structural perfection of the kaolinites. Many of the soil clays gave patterns that were intermediate between those of the well-known *b*-axis disordered type, and the highly disordered halloysite type, but some seemed to be less

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disordered. Several 'indices of crystallinity' have been published for kaolinites, (for example Hinckley, *Clays & Clay Minerals* (1963), 13, 229) but these apply only to materials between fully ordered triclinic kaolinite and the *b*-axis disordered variety. To find a readily measurable index of degree of disorder the X-ray diffraction patterns of 7 kaolinites with varying amounts of structural disorder, ranging from fully ordered triclinic kaolinite to halloysite, were studied. The ratio of the intensity of the 020 (or 02) reflection at 4.48 Å to twice the intensity of the minimum at about 2.44 Å gave an index that could be applied throughout the entire range and that gave results concordant with the Hinckley index where this could be used. The ratio ranges from about 2.5 for halloysite to 5 for *b*-axis disordered kaolinites, and to 43 for an exceptionally well-ordered triclinic kaolinite from Mexico. The index has values ranging from 2.2 to 7.1 for the Nigerian soil clays and affords a readily measurable empirical index of differentiation that is related to the degree of structural disorder. We are now attempting to relate the degree of structural disorder of the kaolinite to other properties of the clays. (Brown and Hughes)

Reaction of added copper salts with superphosphate fertilisers. To facilitate their uniform application it is a common manufacturing practice in Australia and USA to add micronutrients to a superphosphate carrier. In many instances chemical reactions between the micronutrient salt and the fertiliser compounds occur; sometimes the solubility of the micronutrient is increased, as with Zn, and sometimes decreased, as with Cu. Little is known of the reactions between copper salts and superphosphates, although several possible water-insoluble reaction products have been proposed.

Some Australian copper-bearing superphosphate fertilisers contain a slightly-soluble blue-green reaction product that persists for long periods in the soil. Electron probe microanalyses of fertiliser grains recovered from soils showed that much copper is present as inclusions in which it is associated with phosphorus, sodium and chlorine. Blue-green grains carefully selected from fertiliser were chemically analysed and examined by X-ray powder diffraction and infra-red spectroscopy. Their approximate structural formula was $\text{NaCu}_6\text{H}_3(\text{PO}_4)_5\text{Cl} \cdot 6\text{H}_2\text{O}$. Their X-ray powder pattern was similar to that of the mineral, sampleite, $\text{NaCaCu}_5(\text{PO}_4)_4\text{Cl} \cdot 4\text{H}_2\text{O}$ and to those reported for the synthetic compounds $\text{CuHPO}_4 \cdot \text{H}_2\text{O}$ and $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. A specimen of composition $\text{Cu}_{5.74}\text{H}_{3.54}(\text{PO}_4)_5 \cdot 4\text{H}_2\text{O}$ was synthesised and found to have a similar X-ray powder pattern. Infra-red absorption spectra of the blue-green fertiliser compound and the synthesised $\text{Cu}_{5.74}\text{H}_{3.54}(\text{PO}_4)_5 \cdot 4\text{H}_2\text{O}$ resemble that reported for $\text{Cu}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$. These similarities between chemically distinct compounds suggest that they belong to the same basic structural type, which is probably that of the mineral lavendulan $\text{Na}(\text{CaCu})_6(\text{AsO}_4)_4\text{Cl} \cdot 4\text{H}_2\text{O}$.

There is no similarity between the X-ray diffraction patterns of the fertiliser compound and published patterns of the several copper phosphates that have been postulated as likely reaction products. (Dr. R. J. Gilkes)

The formation of ochre in field drains. In the autumn of 1972 a combined subsoil-mixing and drainage experiment was set up at the Arthur Rickwood Experimental Husbandry Farm, in the Cambridgeshire fens, by the ADAS Field Drainage Experimental Unit. By January 1975 the drainage system had almost ceased to be effective and the site was waterlogged.

Although considerable deposits of ochre were found inside the drains, the waterlogging resulted from blockage of the entry slots in the pipes by material consisting mainly of gypsum, hydrous ferric oxides and some clay particles. Inside some drains the deposit had stratified into an upper iron-rich ochre layer, and a pale buff aluminium-rich lower layer. Inside other drains the deposit was entirely of iron-rich ochre. We are attempting to learn more about the nature of these deposits. (Brown and Ormerod)

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Differential thermal analysis. Differential thermal analysis (DTA) has been used to estimate the amounts of kaolin and goethite in clays from some Nigerian soils, by comparing the areas under their endothermic peaks with those of standard samples. Previous work has shown that the kaolin in these clays is of the general category of b-axis disordered kaolins, and so the Pugu D standard kaolin was used for calibration.

An atmosphere of nitrogen was used to prevent the oxidation of organic matter from obscuring the goethite endotherm, but despite this many of the samples gave an exothermic reaction at 840–880°C as well as the expected exothermic peak at about 950°C. One of the clays showed the double exotherm particularly well, and this was chosen for detailed study. After heating the gently-packed clay to 1000°C in the DTA apparatus the top of the sample was red, and the bottom black. The two colour zones obtained by heating the clay to different temperatures were examined by X-ray diffraction. The lower temperature exotherm was found to be associated with the formation of hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) and of mullite, the latter forming at a lower temperature than usual because of the presence of ferrous iron. The higher temperature exotherm was caused by the formation of $\gamma\text{-Al}_2\text{O}_3$, with only a trace of mullite, together with complete oxidation of iron to hematite. Covering the sample with calcined inert material and heating to 1000°C under nitrogen gave a completely black product that contained only hercynite and mullite, and only the lower of the two exotherms. In contrast, heating the uncovered sample in air gave only the higher exotherm, and a red product that contained hematite and $\gamma\text{-Al}_2\text{O}_3$.

Under standard DTA conditions it seems that in certain samples iron is reduced by organic matter and then reacts to form hercynite, which interferes with the normal kaolin exothermic reaction. (Hughes, with Dr. R. J. Gilkes)

Clay physics

Soil Structure. Work has continued on soils chosen for the Rothamsted Soil Structure Working Group. Initially the Group has been using various methods of measuring the physical state of soils that were chosen because of their contrasting behaviour in field management, with the aim of evaluating these methods. Our main contribution has been to assess mercury intrusion porosimetry for measuring the distribution of total porosity in the range of pores sized between 180 μm and 3 nm, both in directly dried soil and in soil dried by solvent replacement and super-critical evaporation. The total porosity of the supercritically dried samples was 1.5 to 3 times the porosity of the soils after direct drying, the ratio depending on the initial moisture content and hence the porosity of the field-moist soil. Also, the distribution of porosity may depend on the drying method, pores in the range 300–30 nm being particularly susceptible to partial collapse, with lesser changes in pores smaller than 3 nm; this cannot be unequivocally assessed by mercury intrusion porosimetry as this tends to cause some distortion of the soil fabric, particularly after supercritical drying.

Despite these problems of detailed interpretation, mercury intrusion curves on air-dried soil seem to provide a useful empirical way of comparing soils. With the soils so far sampled, mercury intrusion did not distinguish between the Flint and Salop series soils in the horizons studied (the upper 40 cm of the soils), but these two soils have relatively little clay to this depth, and hence much smaller porosities in the size range studied, so that large differences would not be expected. However, for the Evesham–Denchworth and the Hanslope–Ragdale series soils, both the Denchworth and the Ragdale subsoils have much of their total porosity in pores smaller than 0.1 μm (100 nm), whereas the Evesham and Hanslope series subsoils have a wider size distribution of pores extending up to 10 μm or larger. This could mean that much of the water in the Denchworth and

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Ragdale series soils is held in pores that are not emptied at conventional wilting point (15 bar tension) and is therefore unavailable to plants. Because these cohesive soils shrink as they dry, the moisture release calculated from soil moisture characteristics (moisture content as a function of water tension) is much greater than predicted from the pore size distribution, and it is therefore important to measure the extent to which these soils shrink as they dry. We have done this and determined the moisture content at which air begins to enter the pore system for each horizon of these soils. We find that the clay content is the main factor that delays air entry, i.e. increases shrinkage on drying, though the clay type may also be important. Organic matter appears to have the opposite effect of stiffening the soil fabric and allowing air to enter at higher moisture content. (Newman and Perrins)

Soil geochemistry

Soil contents and herbage uptake of Zn, Cu, Fe and Mn in N.W. Pembrokeshire. Mn, Cu, Zn and Fe have been determined in top soils and pasture plants collected in North West Pembrokeshire by Bradley and Rudeforth (*Rothamsted Report for 1970*, Part 1, p. 287) and Devonshire and Williams (*Rothamsted Report for 1972*, Part 1, p. 73). Although there was no straightforward relationship between the concentrations of these elements in the soils and the associated herbage, their contents in both soil and herbage differed between gleyed and ungleyed soils (Table 2). To a certain extent the soil contents and plant uptake of Mn etc. depend on the pH of the soil (Table 3). In more than half the herbage samples

TABLE 2
Differences between mean Cu, Zn, Fe and Mn contents of gleyed and ungleyed soils

	Soil			Herbage	
	Ungleyed	Gleyed		Ungleyed	Gleyed
Mn ppm	1460	534***		139	213***
Cu ppm	37	31*		7	6*
Zn ppm	72	55***		23	25 ns
Fe ₂ O ₃ %	5.9	4.4***	Fe ppm ^a	67	85 ns
No. of samples	145	26		137 (60)	29 (12)

^a Uncontaminated samples only, numbers in parentheses

ns Not significant

*** Significant at 0.1% level

** Significant at 1% level

* Significant at 5% level

TABLE 3
Differences between mean Cu, Zn, Fe and Mn contents of ungleyed soils of various pH values

	Soil					Herbage			
	4-5	5-6	6-7	>7		4-5	5-6	6-7	>7
pH									
Mn ppm	1392	1304	1661	1618		157	174	104	77
Cu ppm	37	41	38	38		9	6	6	7
Zn ppm	69	77	69	68		29	24	21	22
Fe ₂ O ₃ %	5.8	6.0	5.9	6.5	Fe ppm	71	68	66	77
No. of samples	8	62	63	8		6 (2)	61 (24)	59 (29)	8 (3)

Numbers of herbage samples in which Fe was determined in parentheses

Herbage samples from soils of pH 5-6 have significantly different Mn contents ($P = 0.001$) and Zn contents ($P = 0.05$) to those from soils of pH 6-7. Other values are not significant

the Fe and Ti contents were correlated, which indicates contamination with soil. (Wilkins)

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Relationships between the major and minor element contents of topsoils from North Pembrokeshire. Samples of topsoil from sites on the 2½ in. O.S. sheet SM 93 were investigated to find the relationship between the contents of major and minor elements in 46 samples, of which 32 were brown earths (Rudeforth & Bradley, *Soil Survey Special Survey No. 6* 1972).

Using a Genstat program for generating correlation matrices, it was found that the following relationships existed: K with Al, K with Fe and Mn, Al with Mn, Cu with Ni, and Ca with pH. In well drained soils the following additional relationships were found: Fe with Ti, Si with Zr, Pb with Zn and Sr with Cu. In poorly drained soils there was a relationship between Br and loss on ignition, and Zr was correlated with Y rather than with Si; P was related to Rb, Al, Mn and Cu. (Devonshire, Perrins and Wilkins)

The geochemistry of reclaimed sediments from The Wash. We are continuing to investigate the geochemistry of soils developed by reclamation of saltings. Studies of the major and minor element distribution in profiles taken from reclamation projects of different ages have shown that the profile distribution patterns of most elements (Ti, K, Al, Zn, Cu, Ni, Fe, Rb and As) are similar, as are the distributions of Ca, Sr and Mg. However Si and Zr do not seem to behave in a related manner, and because of the small organic contents of these profiles Pb and Br do not show their usual correlation.

No great changes can be seen between profiles of different ages, but more profiles must be investigated for a fuller picture to emerge, as there is a strong particle size differentiation within each reclamation. (Devonshire and Wilkins, with Robson, Soil Survey)

Determination of major and minor elements in soils intended for use as standards. A project to provide four standard analysed soils was instigated by the Canada Certified Reference Materials Project. We have collaborated in this project and supplied results for major elements, determined by wet chemistry, atomic absorption and X-ray fluorescence spectrometry (XRFS), and for minor elements determined by XRFS. As yet ours is the only laboratory to have supplied information on Y, As and Br, which is unfortunate because very few standards for these elements are available. (Devonshire, Pruden and Wilkins)

Soil chemistry

Mathematical models for the turnover of organic matter in cultivated soils. A model to fit changes in the organic matter content of soils in the Rothamsted classical field experiments has been devised. Data was assembled on the effects of long term continued cropping and manuring on the amount and age of organic matter, on the amount of microbial biomass in the soil, and on the rate at which plant residues decompose in these soils. The model is an elaboration of the much simpler one needed to fit the changes that occur during 10 years following the addition of ¹⁴C labelled plant material to the soil. This early part of the decay is well represented by two exponential decay rates, one of half-life 0.25 years and one of 8 years, but the 1450 year radiocarbon age of topsoil that has been cropped steadily for many years shows that there is at least one much more resistant fraction.

To fit all the data and to use fractions that are as far as possible identifiable parts of the soil organic matter, a model with five compartments is used. Plant carbon entering the soil is taken to be of two types that decay by first order processes, i.e. decomposable plant material (DPM) that after fitting the model to the data is 83.7% of input and has a half life of 0.165 years, and resistant plant material (RPM, half life 2.31 years). After decomposition (and later decompositions of other fractions are assumed to yield the same products), 80% of reacting carbon is lost as CO₂, 8% remains in living microbial tissue

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(BIO, half-life 1.69 years) and 12% and 0.3% go into two resistant forms, physically protected organic matter (POM, half-life 49.5 years) and chemically resistant organic matter (COM, half-life 1980 years). The model predicts that if 1 t of plant carbon is added to the soil every year, after several thousand years a steady state will be reached with 0.01 t DPM, 0.47 t RPM, 0.28 t BIO, 11.3 t POM and 12.1 t COM. The predicted radiocarbon age for soil in this steady state is 1240 years.

There are no serious differences between the proposed model and the experimental data. Five factors are unlikely to be enough to model the decomposition of plant residues in all circumstances—but these and other simplifying assumptions, such as that all the plant material is added at one time in the year, or that all fractions decompose alike, can be relaxed when more data become available. (Rayner and Jenkinson)

The decomposition of plant material in the humid tropics. Uniformly ^{14}C labelled ryegrass and maize were used to follow the decomposition of plant material in soils from the forest zone of Nigeria, at the International Institute of Tropical Agriculture in Nigeria. One-fifth of the ryegrass carbon originally added to the soil remained after one year, and one-seventh after two years. After a year the soil retained slightly less maize- than ryegrass carbon, but the difference was slight and the overall patterns were similar. There was little difference between the rate of decomposition in the open or under forest shade, even though the temperatures were considerably greater in the open. In general, different soils retained similar amounts of plant carbon, with a tendency for very sandy soils to retain a little less.

The decomposition pattern was very similar under Nigerian conditions to that previously observed for the same plant material in England (*Rothamsted Report for 1972*, Part 1, 74) except that the whole decomposition process was four times faster in Nigeria. (Jenkinson, with Dr. A. Ayanaba, International Institute of Tropical Agriculture)

The effects of mechanical disturbance on the decomposition of soil organic matter. Continuing earlier work in which we studied the effect of ultrasonic dispersion on the decomposition of soil organic matter (*Rothamsted Report for 1974*, Part 1, 197) we have started to examine less drastic treatments, e.g. grinding. An arable soil (Broadbalk, plot 08, fallowed section) and a grassland soil (Broadbalk Wilderness, grazed section) were incubated for 20 weeks so that the effects of disturbance during sampling had completely subsided. Grinding the moist soil to pass a 1 mm sieve almost trebled oxygen consumption by these soils during a subsequent 10 day incubation. The increases in respiration caused by grinding portions of the same soils that had been fumigated with chloroform at the beginning of the 20 week incubation were about half those in the unfumigated portions. At the time of grinding the fumigated soils contained only one tenth of the biomass in the corresponding unfumigated soils. These results suggest that the grinding treatment released approximately equal amounts of substrate by the killing of organisms and by the exposure of non-living parts of the soil organic matter to microbial attack. (Powlson and Jenkinson)

The growth of rice in acid sulphate soils. The coastal lowlands of Malaysia include at least 140 000 ha of pyritic soils. Drainage promotes oxidation of the pyrite and the formation of acid sulphate soil, the pH of which is commonly around 3. Pyrite oxidation is inhibited when such soils are flooded for single-crop rice cultivation, and reactions that occur in flooded soils tend to increase the pH; however pyrite oxidation recommences during the subsequent dry season. Since 1970 when double cropping was started in the Muda Irrigation Scheme, Kedah, rice yields have increased in most of the 20 000 ha of acid sulphate soil in the Scheme. This is probably because the soils are now flooded for

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most of the year and there is no longer an annual regeneration of sulphuric acid during the dry season. However, very low yields are still obtained in a few of these areas and attempts are being made to determine whether this is due to soil acidity (possibly combined with iron toxicity) or to one of several other adverse conditions that have been identified in flooded soils elsewhere, such as toxicity from hydrogen sulphide or organic acids.

Soil pH measurements were made weekly during the rice growing season at two sites on the acid sulphate Guar Series, where yields are less than half the average for the Scheme, in comparison with measurements on another acid sulphate soil (Telok Series), where yields are 65–80% of the average, and on the non-acid sulphate Sedaka Series. The 0–7.5 cm soil at the two Guar sites remained between pH 4.5 and 5.5 for most of the period, similar to the top-soil at the Telok site (around pH 4.5) and only slightly less than at the Sedaka site (pH 5.0–5.5). However, the pH decreased more sharply with depth in the Guar soil than in the others, to around pH 4 or less at 7.5–15 cm, and to pH 3.5 at 15–30 cm. The pH of the Telok soil was mostly about 0.5 units greater throughout the period, and the Sedaka soil remained at about pH 5 at both the lower depths. It therefore seems likely that the more acid conditions below 7.5 cm account for the lower yields of rice at the Guar sites. (Powlson, with Mr. S. J. Samy, Malaysian Agricultural Research and Development Institute)

Factors affecting the pH of flooded soils. The less acid reaction of the surface horizon of flooded acid sulphate rice soils described in the previous section presumably results from the influence of plant residues that accumulate at the surface when the soil is puddled prior to planting. To complement the Malayan field studies described above we have studied the influence of the amount and kind of plant matter on the various factors that influence the pH of a flooded soil. The effects of lucerne and oat straw, representing extremes of nitrogen content, on soil from the 18–27 in. horizon of the Geescroft Wilderness (no P plot) and a Malayan acid sulphate soil (Selangor Series) were compared.

After 100 days' anaerobic incubation, up to 10% of its dry weight of lucerne had no significant effect on the final pH of the Geescroft soil, the net effect being to increase the pH of the soil from 6.5 to 7.0–7.2. However, the sequence of pH changes during the first 50–70 days' incubation was very dependent on the amount of lucerne. With up to 5% dried lucerne the pH increased sharply during the first 5–7 days, decreased during the next 1–4 weeks, and then increased to more or less the final value by the 10th week. With 10% lucerne the pH decreased steadily to 5.6 during the first two weeks and increased to 7.0 by the 10th week. These changes were roughly correlated with the formation of NH_4^+ , which rose to a maximum in the first two weeks and thereafter remained more or less constant, and of organic acids, which rose to a maximum during the first 4 weeks and disappeared almost completely by the 10th week. However, the sequence of pH changes was affected by the formation of soluble Fe^{2+} and by exchange reactions of K, Na, Ca and Mg with the clay, which were complicated by the significant amounts of these elements contributed by the lucerne.

The overall effect of oat straw was different in that with 2.5–10% straw the initial increase in pH obtained with 0–5% lucerne was absent, and after 15 weeks the pH ranged from 7.1 for the control to 6.3 with 10% straw.

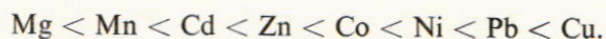
With the acid sulphate soil the sequence was further complicated by the superposition of sulphate reduction once the pH rose to around 5, i.e. the minimum tolerated by sulphate-reducing bacteria. With no organic addition the pH remained close to 3 throughout, although the concentration of dissolved sulphate increased from 0.025 to 0.05 m equiv g^{-1} soil. With 5% lucerne the pH rose to 4.9 in 10 weeks, and did not change significantly thereafter. With 10% lucerne, pH 5 was achieved after 4 weeks and sulphate reduction

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was apparent at this point; thenceforward the pH increased steadily to 6.5 by the 15th week, while the concentration of dissolved sulphate decreased almost to zero. The incidence of sulphate reduction coincided with a release of soluble K^+ , which presumably resulted from the decomposition of jarosite-type minerals in the presence of S^{2-} .

There was less difference between the effects of lucerne and oat straw on the acid sulphate soil than with the Geescroft sample. As with lucerne, 5% oat straw did not increase the pH to the critical value for sulphate reduction. With 10% straw this value was achieved some two weeks later than with the same amount of lucerne. This work is continuing. (Bloomfield and Pruden)

Reactions between minor elements and organic matter. We have continued our study of the interactions between the constituents of humified organic matter and ions of trace metals in solution. Experiments with a Cu^{2+} -sensitive electrode have confirmed our conclusions that weight for weight the dialysable material of the smallest molecular size present in water extracts of aerobically composted lucerne or peat, and chelating resin extracts of Rothamsted topsoil, is the most active material at complexing copper, and therefore probably has an important role in the migration of copper and other trace metal ions in the soil. We have determined the relative extent of complexing of various divalent ions by these extracts using visible and near-ultraviolet spectroscopy; for all the materials we have studied the order of complexing is



In an extension of this work we found that the organic matter present in rainwater that, had percolated through the top 22 cm of a Rothamsted soil, on which grass was growing, resembles that of the aerobically composted lucerne extract in both its ability to complex copper and the molecular size distribution of the dialysable organic material it contains.

We have also studied the influence of the organic matter in these extracts on the initial rates of oxidation of iron (II) and reduction of iron (III) compounds in solution. The rate of oxidation of iron (II) increases with increasing pH and increasing concentration of organic matter for all the extracts. In the presence of concentrations of organic materials of equal complexing abilities, at pH 5.0 the oxidation rate is almost equal in the presence of water extracts of aerobically composted lucerne, of drainage from Rothamsted soil or of chelating resin extracts of this soil; this rate is greater than that obtained in the presence of freshly prepared water extracts of peat, and especially of extracts of anaerobically composted lucerne. In contrast, the anaerobically composted lucerne extracts are the most effective at promoting the reduction of iron (III) at pH 3.5. (Bloomfield and Sanders)

Staff and visiting workers

H. H. Le Riche retired in June, after nearly 30 years in the department.

A. C. D. Newman returned from two years' leave of absence spent as Visiting Reader at Reading University, and D. S. Powlson returned from two years with the Malaysian Agricultural Research and Development Institute. D. S. Jenkinson visited research centres in The Netherlands, and in August left to spend a year at The Waite Agricultural Research Institute. Dr. R. J. Gilkes returned to The University of Western Australia after spending a year studying Cu compounds formed in Cu-treated superphosphate fertilisers.

J. A. Catt attended the Quarternary Research Association's field study course in southern Norway, and led field meetings for the Quaternary Research Association on The Chilterns, for the Yorkshire Geological Society in Holderness, for the geology section of the Hertfordshire Natural History Society in Kent, and for the Hertfordshire Association of Geology Teachers in Buckinghamshire. He also gave lectures on Chalkland soils at

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Bristol University, on Hertfordshire Quaternary deposits at Kings Langley and on the early history of man at St. Albans. C. Bloomfield attended the Malaysian International Oil Palm Conference in Kuala Lumpur, and visited the laboratories of United Plantations BHD to advise on research programmes. He also gave a talk on acid sulphate soils to the Perak Planters Association.

Publications

GENERAL PAPERS

- 1 CATT, J. A. & WEIR, A. H. (1976) The study of archaeologically important sediments by petrographic techniques. In: *Geoarchaeology*. Ed. D. A. Davidson and M. L. Shackley. London: Duckworth, pp. 65-91.
- 2 JENKINSON, D. S. (1976) The turnover of organic matter in agricultural soils. *Welsh Soils Discussion Group Report* No. 16, 91-105.
- 3 JENKINSON, D. S. & (AYANABA, A.) (1976) The humid tropics: can better farming systems feed more people? *Span* 19, 70-72.

PAPERS IN ROTHAMSTED REPORT, PART 2

- 4 CATT, J. A., WEIR, A. H., KING, D. W., LE RICHE, H. H., PRUDEN, G. & NORRISH, R. E. (1977) The soils of Woburn Experimental Farm. II. Lansome, White Horse and School Fields. *Rothamsted Experimental Station. Report for 1976*, Part 2, 5-32.
- 5 JENKINSON, D. S. (1977) The nitrogen economy of the Broadbalk experiments. I. Nitrogen balance in the experiments. *Rothamsted Experimental Station. Report for 1976*, Part 2, 103-109.
- 6 JENKINSON, D. S. & JOHNSTON, A. E. (1977) Soil organic matter in the Hoosfield Continuous Barley experiment. *Rothamsted Experimental Station. Report for 1976*, Part 2, 87-101.

RESEARCH PAPERS

- 7 (AYANABA, A.), TUCKWELL, S. B. & JENKINSON, D. S. (1977) The effects of clearing and cropping on the organic reserves and biomass of tropical forest soils. *Soil Biology and Biochemistry* 8, 519-529.
- 8 CATT, J. A. (& HODGSON, J. M.) (1976) Soils and geomorphology of the Chalk in south-east England. *Earth Surface Processes* 1, 181-193.
- 9 (KUDEYAROV, V. N.) & JENKINSON, D. S. (1976) The effects of biocidal treatments on metabolism in soil. VI. Fumigation with carbon disulphide. *Soil Biology and Biochemistry* 8, 375-378.
- 10 WILLIAMS, C. (1976) The rapid determination of trace elements in soils and plants by X-ray fluorescence analysis. *Journal of the Science of Food and Agriculture* 27, 561-570.
- 11 WILLIAMS, C. & RAYNER, J. H. (1977) Variability in the Denchworth soil map unit. III. Soil grouping based on chemical composition. *Journal of Soil Science* 28, 181-195.