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A. C. D. Newman

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The significance of clays in agriculture and soils

By A. C. D. Newman

Soils and Plant Nutrition Department, Rothamsted Experimental Station,
Harpenden, Hertfordshire AL5 2JQ, U.K.

In managing soils for agricultural production, soil texture or particle-size distribution, and the amount of clay present are very important. Soil structure depends very much on clay: soils with little clay have a simple structure, whereas soils with much clay have complex structures and multimodal pore size distributions. Their response to changes in water content is structurally quite different from that of sandy soils.

Clays have a large specific surface, often predominantly negatively charged, that retains nutrients against leaching and reacts with hydrogen and aluminium ions, while buffering the soil against extreme pH changes. The clay itself may be a source of plant nutrients when it degrades.

Despite these known effects it is still difficult to predict soil behaviour from clay mineralogy. This is partly because the complexities of real clays in soil have been ignored in correlative studies, and that their effects on soil bulk properties are not understood. Future research should stress both of these factors and with improvement of techniques for describing the many structural imperfections in clays, new possibilities exist for predicting those of their properties that are important in agriculture.

1. Introduction

As the increase in agricultural productivity since 1940 has shown, man's intervention can vastly improve soil fertility on all of the types of soil with which he has to work (Cooke 1967, 1977). The actual productivity does, however, vary widely which shows that there are aspects of productivity outside man's direct control. One intrinsic factor in yield variation is soil type, which is related to the soil's composition and its position in the landscape (Burnham 1974). The amount of clay present is a prime consideration in the composition of the soil and has a highly important effect on its properties.

A soil usually contains at least some clay, and its clay content strongly influences its management and productivity (Davies *et al.* 1972). Soils with very little clay can be just as difficult to manage, for different reasons, as soils that contain large amounts, and in broad terms loam soils containing 15–25 % clay with particle sizes of under 2 μm and a larger proportion of silt particles sized 2–60 μm are the most productive. Such soils seem to contain enough clay to provide an adequate surface for interaction with water and nutrients, and to have a friable structure beneficial for tillage and root growth. Soils with more than 30–35 % by mass weight of clay tend to take on the properties of the clay itself, with the implications that they waterlog more easily during periods of excess rainfall, stay wet longer, require greater draft in cultivation and form large aggregates (clods) that must be broken down to form a favourable seed bed. In short, they pose more management problems than loamy soils.

Despite these apparently unfavourable properties conferred on soils by an excess of clay, clay makes a vital contribution to soil fertility. In combination with organic matter and sesquioxides, clay contributes coherence and structural stability which enables the soil to resist the mechanically destructive effects of rain and wind. Because clays have a large specific surface that is predominantly negatively charged, they retain cationic nutrients like K^+ and NH_4^+, and also absorb toxic substances. Layer silicate clays may also have plant nutrients present in their structure, and K^+ and Mg^{2+} can be released to soil solution under appropriate conditions.

Thus there is ample evidence to show that the amount of clay in a soil has a very important influence on the properties of that soil. In the present discussion, it is more interesting to consider what significance clay mineral *type* has in soils and agriculture.

The first problem that this question poses is the adequate identification, let alone quantitative estimation, of the clays actually present in soils. Soil clays differ in many ways from typical or standard clay minerals, and the variants likely to be encountered are discussed first. In succeeding sections the chemical and physical effects that clays have on soil properties are considered and finally an attempt is made to evaluate how far clay mineralogy has a proven or likely influence on soil properties.

2. Clay minerals in soils

The clay mineralogy of a soil is the result of several factors interacting with the soil parent material: climate and consequent intensity of weathering; accumulation and losses of substance within the soil profile, often related to its position in the landscape; vegetation; and the duration of these influences. Only in certain combinations of circumstances do soil forming processes have a uniquely determining effect on the clay mineralogy. Examples where this does happen are the highly weathered soils of the tropics where sesquioxides and kaolinite are dominant clay minerals (Oxisols) and the black soils where shrink–swell processes are attributed to the dominance of smectite (Vertisols). Another unique group of soils are those formed on volcanic ash rocks where allophane (amorphous silico-aluminas) are dominant. In many other types mineralogy is not a dominant characteristic and the soils can contain illite, smectite, vermiculite, kaolinite, chlorite and mixed-layer minerals inherited from the parent material, but partly altered and supplemented by the soil-forming processes (Jackson 1964). In England and Wales, Avery & Bullock (1977) found that the mineralogy of clay soils depended quite markedly on inheritance from the parent material. Mineralogical variability within a single geological formation could be as great as interformational variability and tended to obscure the influence of soil-forming processes. Apart from the relation between vertic features (that is, features similar to but less intense than those in Vertisols) and smectite content, they concluded that in England and Wales mineralogy was not crucial in soil classification.

Therefore, except for the specific instances mentioned, a search for links between soil mineralogy and soil properties of agricultural importance is likely to be difficult. It will be unreasonable to expect strong relations if, for instance, the description of the minerals actually present in the soil is inadequate or incomplete. Further, as soil minerals often differ from those already known and described as ‘type’ minerals, it is necessary also to investigate the properties of these minerals relevant to bulk soil properties.

In general, soil clays are mixtures of several components, and each of these components may have a relatively low order of regularity in its structure. The task of uniquely identifying the components is therefore complex, and much effort may be required to give an adequate description of a soil clay. In favourable circumstances, it can be shown that soil kaolinites are *b*-axis disordered and that illites have stacking disorder and contain less K and more H_2O than true micas. Many smectite-like minerals contain mixtures of two or more types of layer, illite-smectite being the commonest, but kaolinite-smectite and chlorite-smectite also being found, and combinations of three layer types are sometimes suspected, but are difficult to identify. As clay minerals have a large specific surface accessible to soil solution, substances are sorbed on the surfaces and may fundamentally alter their properties. For instance the sorption of hydroxy-aluminium polymers on the negatively charged surface may decrease the effective charge density and make it pH-dependent (de Villiers & Jackson 1967). Soil organic matter is strongly associated with the clay fraction by coordinating to such surface-sorbed polyvalent metals (Edwards & Bremner 1967) and often can only be removed by total destruction. Polymers are sorbed by cooperative van der Waals forces and the sensitivity of infrared spectroscopy has shown likewise that complete dissociation from the clay surface is very difficult. Most soil clays contain a very significant proportion of fine clay under 0.2 μm, with a tendency for the clays to become more poorly crystalline as the particle size decreases. Such fine particle fractions have a large specific surface and may exert an influence on soil bulk properties, for example in the imbibition of water, out of proportion to their concentration in the soil.

3. Chemical properties of clays

3.1. *The buffering action of clays*

Free hydrogen ions with an activity greater than at about pH 5 react with clays, dissolving octahedral Al, Mg and Fe (Osthaus 1955). In time, H^+-saturated clays become partly Al-saturated (Eeckman & Laudelout 1961), because according to the mass action equations for cation exchange, the trivalent aluminium ions are preferentially sorbed on the clay surface, displacing H^+ ions (Chernov 1947; Coulter 1969*a*, *b*). In solution, Al^{3+} hydrolyses readily to the binuclear species $Al_2(OH)_2^{4+}$ and to polymeric cations like $[AlO_4Al_{12}(OH)_{24}12H_2O]_7^+$ (Aveston 1965) and possibly $Al_8(OH)_{20}^{4+}$ (Akitt & Farthing 1981). These are strongly sorbed on the interlamellar surfaces of smectites and vermiculites, forming hydroxyaluminium interlayers (Rich 1968). The stoichiometry of the reactions is quite well defined (Brown & Newman 1973) and similar equilibria have been shown to exist in soils (Richberg & Adams 1970).

Soil-forming processes usually cause an accumulation of hydrogen ions in the soil. Biological activity releases organic acids and HCO_3^- into the soil solution, and rainwater also contains acids and CO_2. When there is leaching through the soil, bases are carried down with the leachate and there is a net accumulation of hydrogen ions. Thus in soils not containing free calcium carbonate, colloids in the upper soil layers tend to retain aluminium compounds complexed with organic matter and sorbed on clay surfaces.

This process of acidification and the consequent formation of hydroxyaluminium coatings on the surface of soil colloids is fundamentally important in pedogenesis and in determining soil properties of agricultural significance (Jackson 1963). For instance, it means that if soil acidity is allowed to increase and fall below pH about 5, the point at which hydrogen ions begin to depolymerise the hydroxyaluminium complexes, free Al^{3+} is released into the soil solution. Even in small concentrations, Al^{3+} is toxic to many agricultural crops, and generally speaking, concentrations in the range 2–5 μg cm^{-3} inhibit the growth of sensitive crops like barley. As is well known from the early analyses by Voelcker of drainage water from the Broadbalk experiment at Rothamsted (Lawes *et al.* 1882), nitrogen fertilizers and ammonium salts in particular greatly accelerate the leaching of bases from soil, and the consequent accumulation of acidity must be neutralized by regular additions of calcium carbonate.

Clays that contain hydroxyaluminium (Al–OH) compounds have different properties from those of the parent clay, and (Al–OH) smectite neither swells nor dehydrates like the parent smectite (Kidder & Reed 1972). The Al–OH polymers form 'islands' between the individual aluminosilicate layers as well as on the surface, and these islands do not dehydroxylate below 600 K. This property, together with the acidity function of the residual water coordinated to the polynuclear cation, gives such clays industrially useful catalytic properties (Vaughan *et al.* 1979). It may be that the presence of such interlayers in soil clays plays an important part in the chemistry of soil organic matter. Because interlayer Al–OH polymers are relatively immobile and inhibit changes in the interlayer spacing they alter the field strength within the interlamellar space, with consequences for cation exchange equilibrium (Kozak & Huang 1971; Coulter 1969) and for the fixation of K^+ and NH_4^+ (Barshad & Kishk 1970; see §3.4).

In general the practical consequences of aluminium interlayering in soils have been little studied and one reason for this is that the extent and structural consequences of interlayering have proved very difficult to describe accurately. For example, aluminium interlayering in mixed-layer illite-smectite is likely in the clay fraction of many acid brown earth soils but has never been investigated in detail owing to the complexities that it introduces to the X-ray diffraction profiles.

3.2. *Cation exchange phenomena*

Clay minerals have net negative charge at soil pH-values and in natural conditions the cations countering this charge are Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+ and Al^{3+} with its hydrolysed derivatives. Soils with pH above 6 have Ca^{2+} as the predominant cation unless Na^+ has accumulated in the profile, but at more acid pH values, increasing amounts of Al balance the negative charge. Soils with kaolinite as the predominant clay mineral also contain iron oxides as important accessory minerals, and there has been much interest in whether the two minerals act independently. The pH-dependent charge characteristics of the combination is effectively the sum of the component parts, so that they appear to behave as a mixture. However, because soil kaolinites have a relatively large specific surface, the negative charge is considerably larger than usual with mineral kaolinites (Greenland 1975). Soils with 2:1 minerals as the dominant clays have large exchange capacities and pH-dependent charge contributes a much smaller fraction of the total than with kaolinitic soils.

In general, exchangeable cations can be regarded as accessible to plants and are considered to be the immediately available sources of nutrient cations, e.g. K^+ and Mg^{2+}. However, balance sheet calculations in plant growth experiments have often shown (Arnold & Close 1961; Feigenbaum & Hagin 1967; Talibudeen & Dey 1968) that more K can be extracted from soils by plants than is exchangeable, and this has led to the hypothesis that several categories of soil K exist, with transfer between them. Micas and illites are the commonest and most effective ultimate sources of K in soils and a large volume of research was done 10–20 years ago on the mechanisms of potassium release from these minerals (Norrish 1973). Even if definite categories of soil K exist, equilibrium between them may not be established, because solid-state diffusion plays an important part in limiting the rate at which K can be released from soil particles (Talibudeen *et al.* 1978). As these ultimate diffusion rates are so slow, it would not be surprising if particle size was an important factor in K-release, the smallest particles having the largest specific surface and releasing K faster than the larger, as was suggested by Arnold (1960). However, the smallest particle sizes in soil illites are very resistant to attack, the optimum size for exchange of K being 1–5 μm (Scott 1968). As noted earlier, many soil clays are mixed-layer minerals, illite-smectite combinations being especially common in the finer clay fractions, whereas the coarser fractions usually contain appreciable amounts of unstratified illite. Consequently it is predicted that K-release is more rapid from the coarser soil fractions than the fine. Thus, whole soil clays with particle sizes under 2 μm from an experimental field at Rothamsted were extracted with hot $BaCl_2$, which is a very effective reagent for removing potassium from micas (Avery *et al.* 1972). The products were then fractionated into the sizes less than 0.5 μm, 0.5–1.5 μm, and 1.5–2 μm, which were individually examined by X-ray diffraction and analysed chemically. Under laboratory conditions in which almost all the discrete illite in the coarse clay fraction was converted into vermiculite, the mixed-layer minerals in the finest fraction were scarcely altered at all (table 1) and the mixed-layer clay was more stable than the discrete illite. In the field situation, this may not necessarily be true, because the presence of organic acids and carbon dioxide may alter the course of the weathering reaction towards mineral dissolution, so that the fine particles may be more vulnerable to attack than the coarse.

Table 1. Release of K from clay fractions of Barnfield soil, Rothamsted (after Avery *et al.* 1972)

(Mineralogy: before extraction: illite, mixed-layer; after extraction: vermiculite, mixed layer. The fine clay contains less illite and more mixed-layer mineral than the coarse clay.)

size fraction	1.5–2 μm	under 0.5 μm
K contents (%)		
before extraction with $BaCl_2$	2.36	1.70
after extraction with $BaCl_2$	1.22	1.55

Besides K, clays are also a potential source of Mg, which is essential not only for plant growth but also for the health of grazing animals (Bolton & Penny 1978). Most non-organic soil Mg is present in 2:1 layer silicate minerals, partly in the octahedral sheet, but also in the brucite sheets in chlorites. Much less research has been done on soil Mg than on soil K, but laboratory experiments show that the clay fractions of soils are able to release Mg to acid attack. Pot experiments have shown, however, that little Mg other than that exchangeable by ammonium acetate is actually extracted by ryegrass (Bolton 1973), and the rate of release is inadequate to supply the recommended amounts for plant and animal health.

Cation exchange equilibria studies on clays have generally used well-characterized minerals, but when the surface is modified by the introduction of Al–OH polymers, the selectivity relations may be changed. Kozak & Huang (1971) found that interlayering vermiculite with the Al–OH polymers decreased its selectivity for K^+ in $K^+:Ca^{2+}$ exchange equilibria, although montmorillonite was little affected. This appears to be another instance in which the specific nature of soil clay surfaces must be taken into consideration.

3.3. *Soil clay–phosphate interactions*

The reaction that occurs between clays and phosphates depends both on the nature of the clay surface and the concentration of the phosphate. If the concentration of phosphate is high, new phases are formed: in molar solutions of sodium and potassium phosphates, variscite ($AlPO_4 2H_2O$) and strengite ($FePO_4 2H_2O$) are formed from kaolinite and greenalite (Kittrick & Jackson 1956), and taranakite group minerals are formed by the reaction of ammonium phosphate with halloysite and allophane (Wada 1959). Such reactions, however, have only transient significance in agriculture, and it is the reactions of soils with small concentrations of phosphate that are most important.

Most attention has been directed to the sorption of phosphate on surfaces of variable charge, in particular calcium carbonate and the hydrous oxides of iron and aluminium (for a review see White 1980). Iron hydrous oxides are the soil constituents most implicated in phosphate sorption. The reactions that occur when phosphate is sorbed on goethite (α-FeOOH) have been studied in detail by Parfitt *et al.* (1976) who proposed that phosphate formed a bridging ligand between two Fe atoms on the 100 face of the crystal. Phosphate sorption on goethite reaches a fairly well-defined maximum, and pH changes during the reaction suggest that release of OH^- ions from the surface partly compensate for the increase in negative charge carried by the phosphate ions. Whether a similar reaction occurs in the surface of other hydrous oxides of iron depends on the detailed structure and the distribution of OH ions on the surface. The sorption of phosphate on gibbsite (γ-$Al(OH)_3$) is less well defined and does not reach a maximum; this may indicate that recrystallization is occurring at the surface as the phosphate builds up (van Riemsdijk & Lyklema 1980), as has been shown to occur on the surface of $CaCO_3$ (Griffin & Jurinak 1974).

Relative to alumina, kaolinite sorbs much less phosphate per unit of surface, one phosphate anion occupying 240×10^{-20} m^2 at pH 4.4 and 740×10^{-20} m^2 at pH 7.6 for the sorption maximum indicated by application of the Langmuir equation to the sorption isotherm (Chen *et al.* 1973). It is believed that phosphate is sorbed only on the non-basal crystal faces and the decrease in sorption maximum with pH is in line with the decrease in positive edge charge (Schofield & Samson 1954). Few studies have been made of the sorption of phosphate by 2:1 clay minerals, but Hall & Baker (1971) investigated the effect of laboratory-synthesized Al–OH interlayers in montmorillonite and vermiculite on phosphate sorption. They found that increasing amounts of phosphate were fixed by montmorillonite (as measured by ^{32}P exchange) as the pH was raised, but that the opposite occurred with vermiculite. They suggested that this was because the Al–OH interlayers are more stable in vermiculite than in montmorillonite (Rich 1968), so that with the latter mineral, there was a greater possibility of forming insoluble aluminium phosphate phases. This study emphasizes the general principle that phosphate reactions in soil are strongly dependent on the presence of surface alumina (Veith & Sposito 1977) and that an adequate description of such surface-sorbed species in soil is needed before the full nature of phosphate interaction with soil clays can be understood.

3.4. *Nitrogen compounds and clays*

As mentioned in §3.2, ammonium cations are retained as counter ions at negatively charged clay surfaces but interaction between the interlayer cation and the higher charge density minerals like vermiculite and weathered mica residues promotes dehydration of the interlamellar region. When the cation has a low hydration energy like NH_4^+ or K^+, the dehydration develops to the point where the cation is enclosed within the twelve-fold coordination cavity of the basal oxygen surfaces and exchanges only with difficulty. This is the origin of 'ammonium fixation' in vermiculite (Allison *et al.* 1953) and only a small proportion of ammonium fixed in this way is isotopically exchangeable (Newman & Oliver 1966), although it can be exchanged by successive extraction in the same way as potassium from micas (Newman 1969). Small quantities of ammonium occur naturally in clays and shales (Yaalon & Feigin 1970) but frequently sedimentary clays contain organic nitrogen compounds, often amines, amino acids and bases (Dungworth *et al.* 1977).

The polarizing action of surface cations on water molecules in the inner hydration shell imparts proton-donating properties (Bronsted acidity) to the clay which is capable of reacting with nitrogen compounds and other bases. This is evident not only with ammonia sorbed on montmorillonite and vermiculite, which has been shown by infrared examination to be converted into NH_4^+ (Mortland *et al.* 1963), but also with other bases (Mortland 1970). Two factors influence the protonation: the degree of the polarizing action of the cation on coordinated water, and the strength of the base. Thus H^+-, Fe^{3+}- and Al^{3+}-clays will protonate urea and amides, but the Na^+ and Ca^{2+} forms do not. Water content of the clay appears to be important in the reactions: as the water content of the clay is decreased, the polarizing action of the cations is concentrated on a smaller number of water molecules, and this increases their proton-donating ability (Mortland & Raman 1968).

Nitrate is the principal plant nutrient form of nitrogen. Unlike phosphate, no specific chemisorption reactions with oxide surfaces are known, so the main effect of clay on nitrate in the soil is to exclude it from a volume of the soil solution adjacent to the clay surface (van Olphen 1977). The extent of this exclusion is still unknown (Wild & Cameron 1980) but in clay soils with very small pore sizes (see §4) it could have the effect of concentrating nitrate on the surfaces of soil aggregates where it would be more prone to leaching but also more accessible to plant roots.

3.5. *Pesticide–clay interactions*

A wide range of interactions occurs between organic pesticides and clay minerals, depending on the nature of the compounds. The extremes are exemplified by paraquat, which is cationic and strongly sorbed, and picloram, which is acidic and repelled from the clay surface. In an excellent review, Green (1974) emphasizes the wide range of behaviour by juxtaposing the sorption isotherms of Na- and Ca-montmorillonite for paraquat, monuron, prometone, lindane, picloram and an organophosphate insecticide. The shape of the isotherm gives some indication of the nature of the adsorption reaction. Paraquat, 1,1′-dimethyl 4,4′-bipyridinium dichloride, is strongly sorbed by coulombic forces enhanced by van der Waals interaction, so the isotherm is very steep initially but has a definite sorption limit. Prometone is also strongly adsorbed, presumably because its basic nature allows a proton donation reaction at the clay surface. Monuron is less strongly sorbed but, as noted in section 3.4, in a system of high acid activity there may be protonation of the urea base. Little interaction can be expected between chlorinated hydrocarbons such as lindane and clays, and the isotherm suggests that there is a constant partition between the solution and sorbent.

Thus in deciding what may be the principal interaction mechanism between clay and a pesticide, the main points to consider are the acidity of the clay and the chemical nature of the pesticide.

4. PHYSICAL PROPERTIES OF CLAY SOILS

In each of the aspects of soil physical behaviour considered in this section the influence of clay content and mineralogy is closely related to the ability of the clay component to take up and release water. After the work of Schofield (1935), the relation between soil water content and soil water suction (negative pressure in pore water) is often used to characterize soil–water interaction. The maximum quantity of water that can be stored in a soil is considered to be that retained when the soil profile in the field is fully wet and excess has drained away, often defined as the water content at −5 kPa. Plant-available water is usually defined as the difference between this water content and the water content at −1.5 MPa, most plants being unable to extract water held at greater suctions. At this suction most clay soils still contain a substantial amount of residual water, but as the main drying action on subsoils comes from the extraction of water by plant roots, it is rare for subsoils to dry to greater suctions.

TABLE 2. VOLUMETRIC WATER CONTENTS (PERCENTAGE) IN SOILS OF CONTRASTING MINERALOGY

	soil mineralogy	water suction/MPa 0.01	1.0	difference
remoulded	a*	57.1	32.0	25.1
	b	49.9	31.2	18.7
	c	48.2	33.7	14.5
remoulded, dried and rewetted	a	46.4	32.1	14.3
	b	38.7	27.3	11.4
	c	46.2	32.8	13.4

* a: smectite; b; mixed-layer illite–smectite; c: illite.

The volumetric water contents at both of these limiting points increases linearly with clay content up to about 40%, but there is a wide scatter about the regression line. For instance, at 50% clay content, the water content at −1.5 MPa can vary between 22 and 37% (Hall *et al.* 1977) and although some of this scatter may be attributed to clay mineralogy, the structural arrangement of the particles may also contribute. If a London Clay soil is slurried with excess water and dried under gradually increasing suction, the water content decreases as shown by the solid line crossing figure 1 from right to left. If, after drying to 100 MPa suction, an attempt is made to rewet the soil by decreasing the suction, the drying curve is not retraced, and at each change in suction, the water content lags further behind that on the drying curve, giving the s-shaped full curve shown in figure 1. On further drying and rewetting cycles, the closed hysteresis loop shown is followed reproducibly. The natural soil, when dried, follows the intermediate (dashed) line. These results, which were obtained by Croney & Coleman (1954), appear to show that disruption of particle–particle associations in the clay (by remoulding or making the soil into a slurry) causes thicker water films to be interposed between the clay particles than would develop if the clay was allowed to swell freely but without the application of mechanical work.

The other soil physical property affected by loss of water is the soil volume, which contracts in response to the compression forces of capillary origin acting on the boundaries of the coherent soil aggregate. The general form of the relation between soil volume and water content is shown in figure 2. For remoulded clay soils, there is a region where the volume contraction

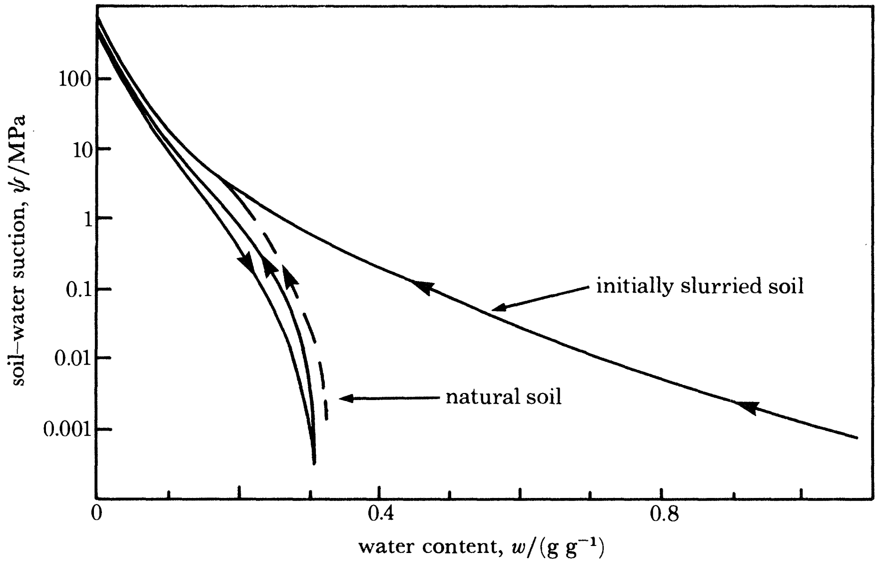

FIGURE 1. Matric suction–water content relation for London Clay soil. (After Croney & Coleman 1954.)

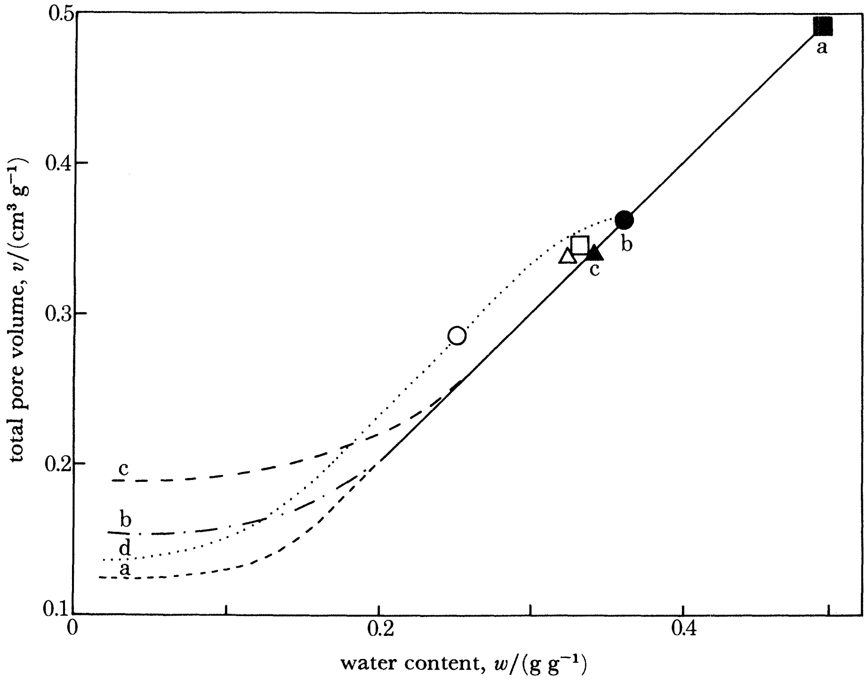

FIGURE 2. Shrinkage curves for remoulded soils containing (a) smectite, (b) illite–smectite (60:40), (c) illite. Curve (d) is the shrinkage curve for a natural unremoulded soil. The filled symbols (■, ●, ▲) represent soils freshly remoulded at -10 kPa, the open symbols (□, ○, △) soils dried to -100 MPa before wetting at -10 kPa.

(shrinkage) equals the volume of water removed by drying, this linear relation being known as 'normal shrinkage'. At some point on this line, which depends on soil composition, shrinkage starts to lag behind the change in water content, until no further shrinkage is possible and the 'shrinkage limit' is reached. At the point where shrinkage starts to lag, either fractures develop or air starts to enter the pore system of the soil, as the pore water pressure becomes sufficiently negative to draw liquid menisci through the soil capillaries. This condition is dependent on the size of the capillaries according to the Young–Laplace equation

$$-\Delta p = 2\sigma \cos \theta / r,$$

where Δp is the reduction in pressure across the menisci, σ is the surface tension of water, θ is the contact angle and r is the radius of the capillary. Fractures initiate and develop where the stress of shrinkage is concentrated at points of weakness on the boundaries.

An example of the shrinkage behaviour for a natural, unremoulded soil aggregate is given in figure 2. Natural aggregates show nearly normal shrinkage, the gradient of the linear section being very slightly less than unity for clay soils (Lawrence *et al.* 1979). As the amount of clay in a soil decreases, the length of the normal or nearly normal shrinkage line decreases until for soils with 25% or less clay, shrinkage lags behind water content change over most of the range.

The effect of mineralogy on shrinkage behaviour is also shown in figure 2. All three soils contained 45–55% clay, soil (*a*) having smectite as the dominant mineral, soil (*b*) containing mainly a smectite–illite mixed-layer mineral, and soil (*c*) containing predominantly illite. The soils were remoulded at −10 kPa until no further water was taken up, or were remoulded at −10 kPa, dried to −100 MPa and then rewetted without remoulding at −10 kPa. These two treatments of the soils are approximately equivalent to the initial state and the rewetted state in the experiment of Croney & Coleman (figure 1). The effect of remoulding and drying is mineral-dependent, with the smectite soil taking up a large quantity of additional water on remoulding at −10 kPa, but the illite soil taking up very little extra, the mixed layer mineral being intermediate. Furthermore, the shrinkage limit is also dependent on mineralogy, with the illitic soil shrinking least and the smectitic soil most. However, contrary to expectation, the plant-available water differs little between the three soils (see §4.1).

The origin of these differences can be shown to lie in the pore structure of the soils. Mercury porosimetry is a useful technique for studying pore structure when used in combination with critical point drying to preserve the wet volume of soil (Greene-Kelly 1973; Lawrence 1977) and mercury penetration data for the three soils is shown in figures 3 and 4. The smectitic soil (figure 3*a*) on remoulding develops a large volume of pores in the size range 30–100 nm but remoulding the illitic soil develops a much smaller volume of pores with a wider pore size distribution; again the soil with mixed-layer mineralogy is intermediate. When dried to the shrinkage limit, however, the situations are reversed, the illitic soil containing a larger volume of coarser-sized pores whereas the smectitic soil contains a small volume of very fine pores (figure 4). These pore size distributions show that air-entry should occur at a higher water content in the illitic soil than in the smectitic, as was found in the shrinkage behaviour.

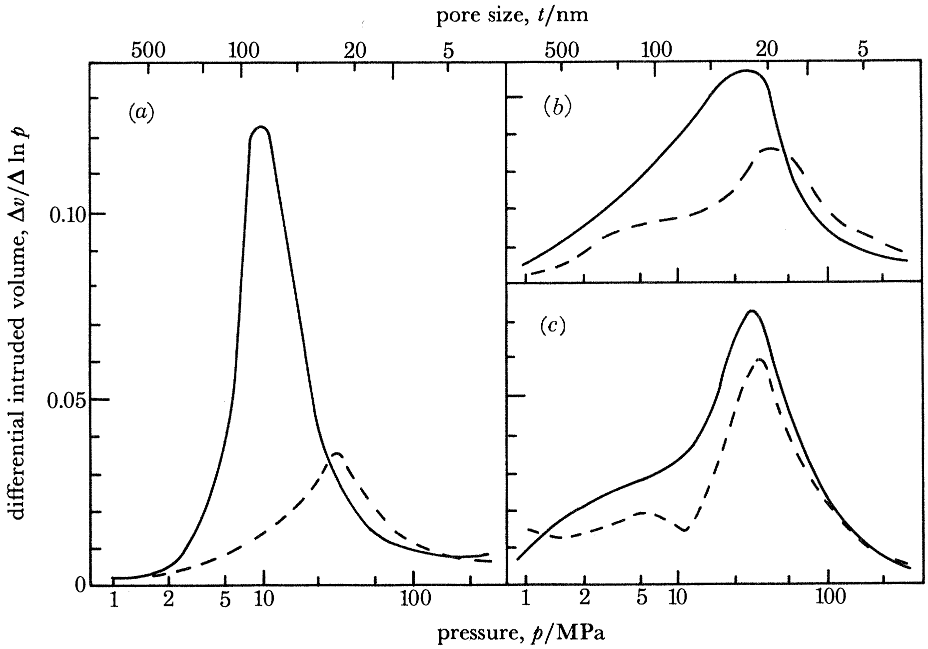

FIGURE 3. Mercury penetration of critical point-dried clay soils containing (*a*) smectite, (*b*) illite–smectite (60:40), (*c*) illite. Soil preparation: ——, remoulded at −10 kPa; ----, remoulded at −10 kPa, dried at −100 MPa, then rewetted at −10 kPa.

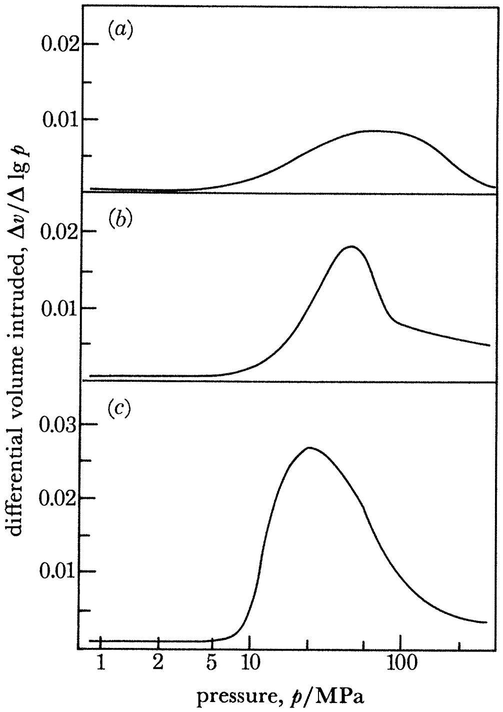

FIGURE 4. Mercury penetration of air-dried soils contains (*a*) smectite, (*b*) illite–smectite (60:40), (*c*) illite.

4.1. *Plant-available water*

There have been several investigations of correlations between conventionally defined plant available water and soil composition. Salter *et al.* (1966) used a limited range of coarse textured soils and derived a regression equation based on sand, silt and organic carbon contents. Using sieved and compacted topsoils, Archer & Smith (1972) found, with a smaller number of soils but of wider textural range, that available water was inversely related to dry bulk density (the weight of solid soil material in unit volume of whole soil in any specified condition). Reeve *et al.* (1973) confirmed this relation for some undisturbed soils and Hall *et al.* (1977) extended the correlation with samples from 261 soil profiles. The question that this work poses is whether dry bulk density at a defined pore water pressure is related to soil mineralogy when due allowance is made for the air-filled pore space within the soil sample. Clays that swell most should be capable of imbibing most water and contributing most to plant-available water. However, for a range of 63 non-remoulded clay soils Greene-Kelly (1974) found that both total and available water contents were poorly related to mineralogy. Equally, soils with widely different mineralogies may show little difference in water held between specific suctions (figure 2). The soil containing the mixed-layer smectite has relatively little plant available water presumably because microstructural arrangement of the clay particles affects the release of available water more than loss of interlamellar water from smectite layers (see §4.2).

4.2. *Shrinkage and swelling phenomena*

In clay soils the ability to swell and shrink in response to fluctuation in water addition and removal is vital to the active generation of the visible macrostructure, in which soil aggregates are bounded by fissures and channels that conduct excess water and allow air and roots to penetrate into the subsoil. Excess shrinkage and swelling, however, causes problems of structural stability in civil engineering and there has been much study of the relation of shrinkage and swelling to mineralogy. Smectite minerals in subsoils have been associated with such structural instability but Martin & Lambe (1957) suggested that mixed-layer smectite–illite was much less active in these processes than pure smectites. In the study of the relation of shrinkage and swelling to clay mineralogy referred to earlier (Greene-Kelly 1974) no distinction was made between smectite in the strict sense and smectite in mixed layer materials. It may be that a better correlation with mineralogy would have been found if this distinction had been made. Even so, the structural arrangement of the clay particles and the presence of sesquioxides and organic matter will also influence swelling.

The contribution of changes in interlamellar water content to shrinkage and swelling remains a debatable issue. Unless they are Na^+-saturated, smectites contain 3 interlamellar sheets of water when fully hydrated (1.9×10^{-9} m basal spacing), and it has proved difficult to define exactly at what water activity this dehydrates to the 2-sheet complex (1.5×10^{-9} m basal spacing). Present evidence suggests it is in the relative humidity range of 95–99 % (2–7 MPa negative pressure), which is outside the available water range and hence unlikely to be reached in subsoils (Ormerod & Newman 1983). This is supported by the data in table 2, in that the illitic soil contained as much water between 0.01 and 1 MPa as the smectitic soil.

4.3. *Soil and aggregate structure*

Soil structure may be briefly defined by the way a potentially continuous matrix of mineral particles is broken into a mosaic of subunits each with a quasi-independent existence. If the soil is coarse grained, the subunit is the individual mineral grain, but in coherent soil the subunits are compound and can themselves break up into smaller subunits at the submicroscopic level. Until recently, little has been known about these submicroscopic units except by inference from measurements like water retention and mercury porosimetry. However, the advent of the scanning electron microscope, and the preparation by ion-thinning of ultra-thin sections that can be examined in the transmission electron microscope (Bresson 1981) has been the stimulus for new ideas about soil microstructure. The present picture seems to be that soil structure is hierarchical, with a scale that ranges from the visible field structure with fissures 10–100 mm in size, down to pores of 1–10 nm diameter which represent the distances between clusters of units that diffract X-rays coherently, i.e. silicate layers which are oriented in a parallel way.

Within this hierarchy, the influence of clay mineralogy is likely to be considerable, but ancillary factors also contribute. Iron oxides affect the way that clay crystals aggregate (Blackmore 1973) and Al–OH polymers also induce strong aggregates to form (Kubota 1975; El-Swaify & Emerson 1975). The macroscopic strength of clays can be greatly modified by interaction with Al–OH polymers (Foster & Gazzard 1975) and organic compounds and soil organic matter influence macroscopic soil structure through their interaction at the submicroscopic level (Greenland 1965). The macrostructure of soils that develops on drying can be modified by amendments like calcium sulphate, calcium carbonate (O'Callaghan & Loveday 1973) and dextran (Pagliai *et al.* 1980). In all of these studies, the clay and the amendment combine to produce new structural units.

These microstructural influences on the macrostructure of soils have great practical importance because macropores 'short-circuit' water flow in clay soils (Hoogmoed & Bouma 1980). The drawing of mole channels through clay subsoils is an important management technique in draining excess water, and Spoor *et al.* (1982) consider that swelling processes related to clay mineralogy are important in destabilizing mole drains.

4.4. *Soil tillage*

The mechanical effort needed to draw a plough through soil depends on several factors, one of which is the amount of clay in the soil (Haines & Keen 1925). Soil consistency and the change in liquidity or solidity of soils with water content are related to the amount and type of clay in the soil (Spoor & Muckle 1974): the preparation of a satisfactory seedbed depends on cultivating at a soil water content at which the soil is friable, but not sticky (too wet) or cloddy (too dry). The range of water content over which the soil remains in a friable state is related to its mechanical composition, and also to the mineralogical and structural composition of the colloid fraction. Friability depends on the number of air–water interfaces within the soil aggregates, and this is likely to depend on the pore size distribution in the micropore regions.

5. THE ROLE OF SOIL CLAYS IN AGRICULTURE

Martin & Lambe (1957) in an investigation of soil composition and the engineering behaviour of soils, noted that although mineralogy was one essential factor, others, such as cementation and flocculation, and whether clays of different mineralogy were mixed together, were also vital.

A similar conclusion may also be reached from the present survey of soil properties with agricultural importance. Although clay mineralogy is clearly a primary factor, soil properties are likely to be influenced by the way that the surface of the clays is modified by relatively immobile contaminants and coatings. In particular, the modification of clay surfaces by cations and the acidic polynuclear products from the hydrolysis of Al and Fe affects cation exchange and enables anions to interact with clays negatively charged at the surface by isomorphous substitution. There is evidence also that the effect of mixed-layer minerals on soil properties is not quite what might have been anticipated, particularly in relation to their swelling properties.

It is clear that our present knowledge is still imperfect. The main need is to investigate the properties of the minerals, their mixtures and the surface modifications in the form that they occur in the soil. Normally we separate a clay fraction from the soil in order to identify it, but these procedures are destructive, particularly of the particle arrangement (fabric) in the soil, and also of the surface covering. Therefore, concurrent with the traditional procedures of clay mineralogy, we should be studying the properties of the clays *in situ* in the whole soil.

It must also be said that sometimes the identification and description of soil clays is oversimplified. A simple level of clay mineralogy does have its place in a preliminary study, and indeed should always precede a more detailed study. It is, however, unreasonable to expect detailed relations between soil mineralogy and soil properties unless the mineralogical description is accurate enough for the purpose intended. A scientifically exact description of soil clay mineralogy will always be complex: the aim is to simplify the aspects that are less important for the purpose in hand.

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