Changes in microstructure of soils following extraction of organically bonded metals and organic matter

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SUMMARY

The influence of selective removal of organically bonded metals and organic matter on soil microstructure was investigated. Two samples of soils with different mineralogical, chemical and mechanical composition were treated with acetylacetone in both polar and non-polar solvents to dissolve amorphous organic iron and aluminium, and with hydrogen peroxide to destroy organic matter.

Transmission electron micrographs of ultrathin sections and scanning electron micrographs of <5-μm fractions of the extracted soils showed distinct changes of microstructure of clays after successive removal of cementing agents. Although untreated soils showed flocculent or honeycomb structure, soils with organic matter and organically bonded metals removed showed turbostratic domain structure with stepped clusters. The changes in microstructure of soils following extraction were confirmed by determination of pore-size distribution and total cumulative volume of pores using the mercury porosimetry method. In addition, the surface area of the extracted soils was determined by water adsorption. The results showed that organically bonded iron and aluminium and organic matter distinctly influence the fabric of microstructure as flocculating agents.

INTRODUCTION

There is sufficient information available to indicate that a prerequisite for aggregate structure is flocculation of clay particles as the first stage in the construction of stable macroaggregates. Several models have been proposed to describe the way in which individual mineral particles are held together to form aggregates of soil. Edwards & Bremner (1967) suggest that macroaggregates consist of complexes of clay polyvalent metal organic matter, where clay and humified organic matter polyanions can be bridged by polyvalent cations. The cations normally considered are Fe, Al, Ca or Mg. Although the divalent ions may exist as single ions with double charge, which align water dipoles. Fe and Al are more likely to exist as hydrolysed species of indefinite composition and organization, but with a net positive charge (e.g. polycations; Oades, 1984*b*). Complexes of clay polyvalent metal organic matter are probably both included in the skeleton grains described by Bal (1973). Bonds of clay polyvalent metal–clay and organic matter polyvalent metal- organic matter, and even of aluminium or iron oxide. or H-bonds may also occur (Tisdall & Oades, 1982). Edwards & Bremner (1967) also suggest that fragments of humified organic matter may be bonded to one or more clay particles. The interactions between organic polymers and mineral surfaces are complex, but mechanisms are known and have been reviewed by Greenland (1965, 1971), Mortland (1970), Tate & Theng (1980) and Fortun & Fortun (1989). The most important mechanism of interaction probably involves bridges of polyvalent cations between the surface of the clay particles and the ligand groups of organic polymers. e.g. carboxyl groups.

There have been many studies on the role of organically bonded metals and organic matter. acting both separately and in combination, as cementing agents in soil aggregates (Stefansou, 1971;

Giovannini & Sequi, 1976a,b; Hamblin & Greenland, 1977). The importance of organo-mineral interactions has prompted an interest in the micro- and macrostructure of soils. There is a need for studies on the processes of aggregation in soil, including the possible role of organically bonded metals and organic matter.

We here report a study of the influence of selective removal of iron and aluminium polycations and organic matter, both separately and in combination, on soil microstructure and structural properties such as surface area, pore-size distribution and cumulative volume of pores of treated soils.

The main evidence for the role of organically bonded metals and organic matter has been based on investigation of changes of microstructure and structural properties after treatment of soil with complexing agents. The choice of extracting agents is of primary importance in the study of possible effects of organo-mineral complexes on soil aggregation. The ideal extractant must be mild and selective so that the soil aggregates remain in a condition where the variations in their type of microstructure can be observed. The extracting agents should not cause considerable changes of pH and ionic strength of the soil system, because it is known that changes in pH or ionic strength cause distinct changes in the type of microstructure of clays (van Olphen, 1963; Swartzen-Allen & Matijevic, 1976; Rand & Melton, 1977; Wierzchos, 1989; Stawinski et al., 1990). For these reasons, acetylacetone in non-polar and aqueous solvents appears to be suitable as an extractant. Giovannini & Sequi (1976a) have proposed the use of acetylacetone in benzene for the selective removal of trivalent iron and aluminium from soils. They hypothesized that polyvalent metal ions, which bond organic matter to clay minerals, would be chelated and extracted in the benzene. Acetylacetone in aqueous solution has also been used by the same authors as an extractant for polyvalent cations and organic matter. Martin & Reeve (1957a,b) suggested that this extraction proceeds in two stages, in which the acetylacetone first complexes with the metals linked to the organic matter, and then the organic matter is extracted by water. Hamblin & Posner (1979) concluded that, if extraction is carried out under conditions where some rehydration is possible, swelling and opening up of the structure will allow more complete penetration of the chelating agent into the polymer structure.

In the present study, transmission electron microscopy (TEM), scanning electron microscopy (SEM), mercury porosimetry and determination of surface area techniques were used to study the changes in microstructure of soils following extraction of organically bonded metals and organic matter.

MATERIALS AND METHODS

Soil samples
Soil samples were obtained from a gleic luvisol (Robledo de Corpes, Spain; RC) and an orthic luvisol (Sobieszyn, Poland; SB). Natural samples from Ah horizons (0–8 cm, Robledo de Corpes III) and (0–20 cm, Sobieszyn) were air dried, crushed to pass a 2-mm mesh, and stored until analysed. Some significant properties of these soils are listed in Table 1.

Table 1. Some properties of soils

Soil	pH (H$_2$O)	Organic matter (g kg^{-1})	Total		Sand 2–0.02 mm (g kg^{-1})	Silt 0.02–0.002 mm (g kg^{-1})	Clay <0.002 mm (g kg^{-1})
			Fe (g kg^{-1})	Al (g kg^{-1})			
RC	4.2	63.2	19.6	75.7	624	210	166
SB	6.6	25.4	25.9	67.1	682	148	170

Soil pH was determined by a combined electrode (soil:water 1:2.5). The content of organic carbon in soil residues was measured by the Walkley & Black (1934) method, and converted to organic matter content using a conversion factor of 1.72 (Giovannini & Sequi, 1976a). Total content of iron and aluminium in soils was determined by X-ray fluorescence (XRF) spectroscopy (Norrish & Hutton, 1969), using a Siemens SRS 300 XRF spectrometer. Particle size analyses were performed by the pipette method (Day, 1965).

The mineralogical identification of the <5-μm fraction was performed using X-ray diffraction (XRD) (Garcia-Gonzalez & Aragoneses, 1990). Patterns were obtained with a Philips PW 1130 diffractometer (graphite monochromated Cu Kα radiation). Semi-quantitative mineralogical composition (relative mass) was as follows: 38% quartz, 35% illite, 16% kaolinite, 5% feldspars, 4% goethite and 2% paragonite for RC and 43% illite, 35% quartz, 11% smectite, 6% kaolinite, 3% feldspars and 2% interstratified illite–smectite minerals for SB.

Treatment of soils

For the extraction of organically bonded Fe(III) and Al(III) with acetylacetone, 25 g air dried soil was mixed with 250 cm^3 of acetylacetone in benzene solution (5:95) at 20 °C, and gently shaken end over end for 10 d. Samples were then withdrawn, filtered, and washed with portions of anhydrous diethyl-ether. The filtrates and washings from each sample were collected and evaporated to dryness. The residue was dissolved with hydrochloric acid and diluted with deionized water. In these aqueous solutions, concentrations of Fe(III) and Al(III) were determined by inductively coupled plasma (ICP) spectroscopy on a ICP-5500 Perkin Elmer apparatus. Samples of soils treated with acetylacetone-benzene solutions are designated AAB.

For the extraction of organically bonded Fe(III), Al(III) and part of the organic matter, acetylacetone in water solution was used following the same procedure described above, except that after the extraction process, the soils were centrifuged and washed with deionized water until Fe cations were no longer detectable in the washing water. Extractable Fe(III) and Al(III) in the washings were detected by ICP spectroscopy. Soil samples treated by acetylacetone in water solution are designated AAW.

For the removal of organic matter, 50 g of each soil was treated with 10% hydrogen peroxide buffered at pH 5 (Jackson, 1975, pp. 215–223). After destroying the organic matter, soil samples were periodically shaken over a 10-d period, and then centrifuged and washed several times until the electrical conductivity of the supernatant was similar to that of the washing water. Soil samples treated with hydrogen peroxide are designated HP.

Afterwards, one-half (c. 25 g) of each HP soil sample was treated with acetylacetone in water solution to remove polycations of iron and aluminium and eventually the residual component of organic matter following the procedure described above. Extractable Fe(III) and Al(III) were identified by ICP spectroscopy. These soil samples are designated HPAAW.

Control samples of non-extracted soils were also prepared. Twenty-five grams of the original soil was mixed with 250 cm^3 of deionized water and gently shaken periodically for 10 d. These samples of non-extracted soils are designated CN.

Additional preparation of material

For the further study of microstructure and organo-mineral associations, subsamples of treated soils (AAB, AAW, HP and HPAAW) and one control sample (CN) were used. The water was replaced by methanol, and the samples were then air dried. These soil samples were used for surface-area studies. Residual components of five samples of each soil were suspended in deionized water. The <5-μm fractions of soils were obtained by syphoning. After freeze drying, part of this fraction was used for electron microscopy studies. After replacement of water by methanol and air drying, residual parts of the <5-μm fractions of each soil were used for mercury intrusion porosimetry analyses.

Ultramicrotomy and electron microscopy examinations

The small, dry (1 mm in diameter) specimens of <5-μm fractions of each soil were prepared for ultramicrotomy by vacuum impregnation with the vapour-phase transfer method, described by

Tchoubar *et al.* (1973) and Smart & Tovey (1982, pp. 63–65) using Spurr's hard epoxy resin (Spurr, 1969). The ultrathin sections (90 nm thick) were examined with a Philips 300 transmission electron microscope, operated at 100 kV.

For SEM studies, dry samples of < 5-µm fractions were mounted ou aluminium stubs and sputter-coated with gold and examined using a Zeiss DSM 962 instrument.

Porosimetry

The mercury iutrusion porosimetry method described by Diamond (1970) was used for examination of changes in total cumulative volume of pores (TCV) and pore-size distribution (PSD) of the treated < 5-µm soil fractions. The pressure range possible was 0.1 200 MPa, which corresponded to equilibrium penetration into pores of Kelvin radius 7.5–0.0037 µm. A Carlo Erba Porosimeter model 2000 instrument was used.

Surface area

External + internal surface area was determined from water vapour adsorption isotherms at 293 K, measured by the vacuum microbalance technique (Paterson & Stawinski, 1979). The surface area of the soil samples was calculated from the Brunauer–Emmett–Teller (BET) equation, and the area of a H_2O molecule was assumed to be 0.108 nm^2.

In addition, we calculated the surface areas of extracted organically bonded metals and organic matter using the equation:

$$S_s = (S_{CN} - S_T)/M$$

where S_s = surface area of extracted species, S_{CN} = surface area of non-extracted soils, S_T = surface areas for the AAB, AAW, HP and HPAAW treatments, and M = mass of extractable medium.

RESULTS AND DISCUSSION

Chemical analysis and specific surface area

The control (CN) samples were analysed for their content of iron, aluminium and organic matter. The concentrations of Fe and Al in extractable solutions and the content of organic matter in treated soils were also determined. The results of chemical analysis listed in Table 2 demonstrate that

Table 2. Chemical analyses and surface areas

Soil symbols	Extraction of Fe, Al (mol kg^{-1})		Extraction of Fe, Al and OM as g kg^{-1} of total Fe, Al and OM			H_2O area of treated soils (m^2 g^{-1})[a]	H_2O area of extracted Fe, Al. OM (m^2 g^{-1})
	Fe	Al	Fe	Al	OM		
Soil RC							
AAB	0.0189	0.0154	8.3	5.5	4.2	26.5	1085
AAW	0.0568	0.0297	161.8	10.6	143.0	22.4	438
HP	ND[b]	ND	ND	ND	ND	13.7	228
HPAAW	0.0814	0.0341	277.2	19.7	ND	10.6	934
Soil SB							
AAB	0.0084	0.0197	18.0	8.0	3.1	45.4	1300
AAW	0.0597	0.0278	128.4	11.2	228.3	39.8	699
HP	ND	ND	ND	ND	ND	39.2	295
HPAAW	0.0613	0.0473	164.9	23.8	ND	33.3	1256

[a]The surface areas are expressed as m^2 g^{-1} treated soils. Surface area of untreated soils: RC = 28.1; SB 46.7 m^2 g^{-1}; [b]ND = not determined.

acetylacetone in benzene extracts much less iron and aluminium from our soils than does acetylacetone in aqueous solution. These results are in contrast to those obtained by Giovannini & Sequi (1976a), who reported that acetylacetone extracted approximately the same amount of iron and aluminium from soils whether dissolved in benzene or in water. These differences are probably due to the fact that in our soil samples the rehydration process causes swelling and opening up of the structure, which allows more complete penetration of the chelating agent into the polymer structure (Hamblin & Posner, 1979). The largest amounts of polycations were extracted from samples without organic matter (HPAAW). This means that polycations were more easily removed from clay–polyvalent metal–clay than from clay–polyvalent metal–organic matter complexes.

The internal + external surface areas (H_2O area) of the soils are shown in Table 2. For all the soils which showed an increase in extractable amounts of Fe and Al polycations or organic matter, there was a decrease in the specific surface areas. The decrease in surface area following extraction of crystalline and amorphous iron oxides has been investigated by several researchers (Deshpande *et al.*, 1968; Gallez *et al.*, 1976; Bigham *et al.*, 1978), but the changes in surface area have been attributed to removal of iron oxides alone. Aluminium oxides and organic matter also influence the surface area of soil (Greenland & Mott, 1978) and may be extracted at least partially, together with iron oxides. In our study, amorphous 'organic' aluminium was extracted by acetylacetone in both non-polar and aqueous solvents. Furthermore, peroxidation of soils led to the decrease in H_2O surface area, in accordance with the results of Burford *et al.* (1964).

The calculated specific surface areas of extracted amorphous 'organic' species of Fe and Al (in AAB and HPAAW treatments), organic matter (in AAW treatment) and organic matter after peroxidation (in HP treatment) shown in Table 2 are expressed as $m^2 g^{-1}$ extracted species. Although these groups of species are different, the surface areas of amorphous 'organic' Fe and Al are remarkably similar. This appears to indicate that acetylacetone in benzene (AAB) and in aqueous solvents (but after the HPAAW treatment) removed a rather uniform fraction of organically bonded metals. The surface area of amorphous 'organic' Fe and Al species ranges from 934–1300 $m^2 g^{-1}$. This is slightly higher than the range of 300–900 $m^2 g^{-1}$ for Fe polycations, reported by Oades (1984a), and of 430–1000 $m^2 g^{-1}$ for amorphous iron oxides, reported by Greenland & Oades (1968). The decrease in surface area caused by removal of organic matter in two HP soil samples indicates that the surface area of the organic matter was 228 and 295 $m^2 g^{-1}$, respectively.

Electron-microscopy studies

The changes in microstructure type following extraction of organically bonded metals and organic matter were examined in TEM ultrathin sections of < 5-μm fractions of soils. Figure 1a shows the microstructure of an untreated sample of RC soil. Note that the clay particles are grouped in dense microaggregates of varying size (1–5 μm), which are themselves grouped loosely with relatively large voids between them (1–3 μm). The boundaries between microaggregates (rather circular shape) are distinct. Some of the microaggregates (to the right) are surrounded by cementing agents, probably organic matter; others (to the left and below) consist of closely packed clay particles with edge-to-face and face-to-face contacts between them. This type of structure is classified as Pusch's or flocculent structure.

The removal of organically bonded metals led to a visible decrease in pore sizes between the microaggregates (Fig. 1b). The microaggregates, cemented by organic matter, began to form a network with distinct edge-to-face contacts between them. This type of structure is related to open structure or honeycomb structure, and it is found in flocculated clay systems.

After extraction of organically bonded metals and part of the organic matter (Fig. 1c), a decrease in inter-domain void size was observed. The clay particles are grouped closely with oblique edge-to-face contacts at small angles between them, forming stepped clusters, sheets or chains. Note also that small clay particles are in face-to-face groups of domains (e.g. a stack in the centre of the micro-photograph). The contacts between curved domains are usually of an edge-to-face type, which tends towards discrete domain structure with elements that are characteristic of deflocculated structure.

The destruction of organic matter by peroxidation caused the particles to be grouped in domains, in which all or most of the particles lie in approximately the same direction—local preferred orientation, with an increasing amount of face-to-face contacts between clay particles (Fig. 1d). The
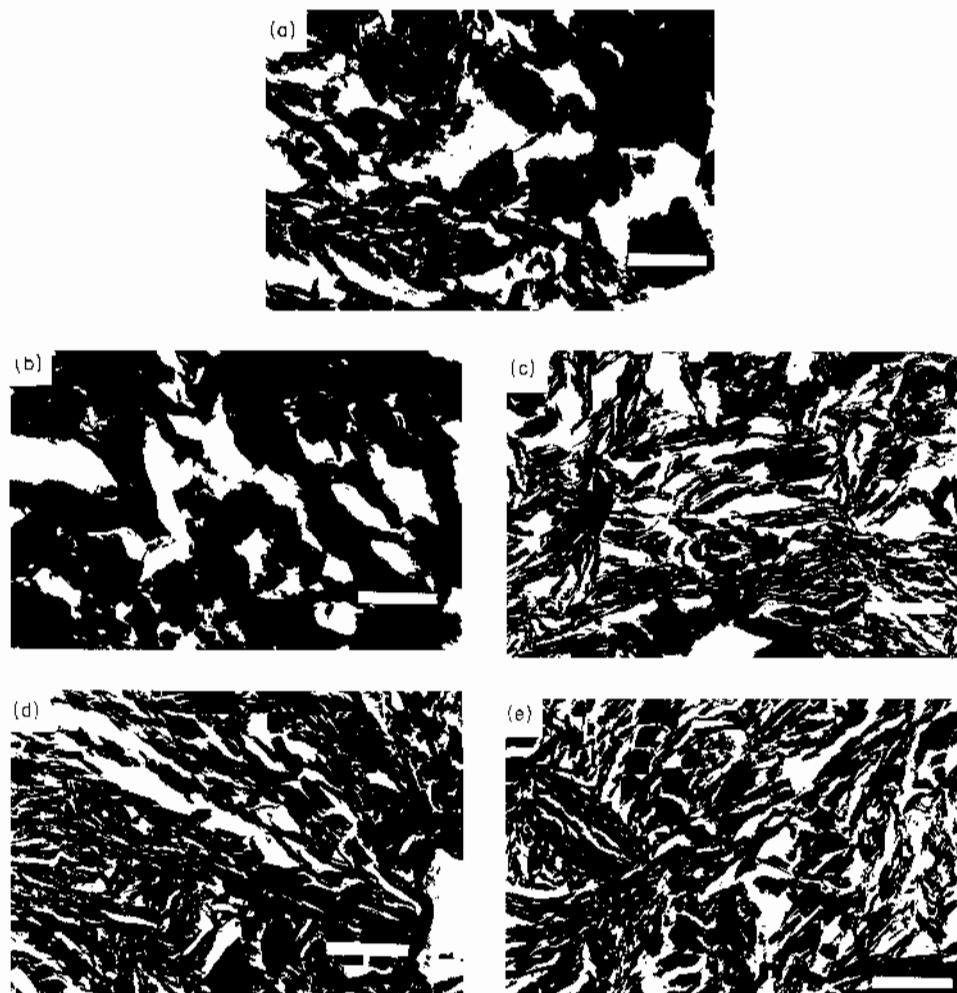
Fig. 1. Transmission electron micrographs of ultrathin sections of RC soil: (a) untreated: (b) treated with AAB;
(c) treated with AAW. (d) treated with HP, and (e) treated with HPAAW. Scale bar – 2 μm.

domains tend to be curved, and to be moulded together without very distinct inter-domain voids; we
classify this as a turbostratic domain structure. This type of structure is typical of dispersed clays
(Smart & Tovey, 1981. pp. 44–45).

The removal of organically bonded metals from samples without organic matter (Fig. 1c) did not
lead to a pronounced change in the type of structure. As in the previous example, almost all the clay
particles are parallel to each other in domains, and the inter-domain voids are very small and
difficult to designate. This means that extraction of polycations from clay–polyvalent metal–clay
type linkages did not substantially influence the degree of deflocculation of clays. A clear influence of
organically bonded metals on aggregation can be detected after removal of these polycations from
clay–polyvalent metal–organic matter type complexes (Fig. 1b), but organic matter plays a more
important role in the formation of open aggregated structure in this type of soil.

The TEM micrographs in Fig. 2 illustrate the changes in microstructure of SB soil following
treatments by different reagents. Figure 2a shows the organization of clay particles in an untreated
sample of SB soil. Note that clay particles are grouped closely in elongated microaggregates of
varying length (0.5–3 μm). with dominant face-to-face contacts between them. The domains are
surrounded by gel material, probably sesquioxides of iron and aluminium. The microaggregates, in

the form of stepped clusters or chains, create a loose interconnecting framework with oblique edge-to-face contacts and with relatively large voids between the sheets. This type of structure is related to honeycomb or cluster structure, and is typical of flocculated clays.
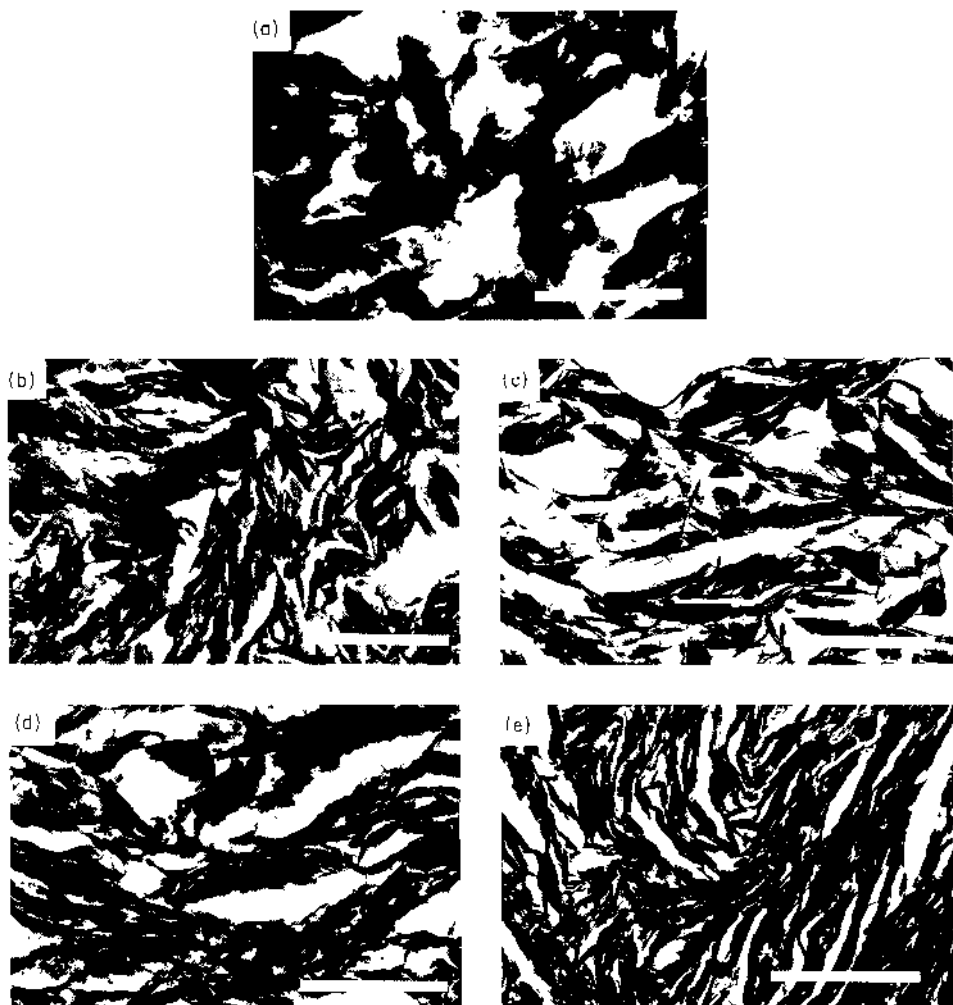

Fig. 2. Transmission electron micrographs of ultrathin sections of SB soil: (a) untreated; (b) treated with AAB, (c) treated with AAW; (d) treated with HP; and (e) treated with HPAAW. Scale bar – 2 μm.

The removal of organically bonded metals (Fig. 2b) led to a distinct decrease in pore size between the microaggregates. The stepped clusters of domains are composed of larger amounts of packets of clay particles. This micrograph shows an almost book-house or domain structure.

The extraction of polyvalent metals and part of the organic matter (Fig. 2c) did not cause marked changes in the type of clay structure compared to the previous situation, indicating that additional removal of organic matter did not provoke further deflocculation.

The destruction of organic matter (Fig. 2d) caused the clay particles to be grouped into larger flocs in which almost all the particles lie in approximately the same direction, with small angle edge-to-face or face-to-face contacts between them. Turbostratic domain structure was observed locally, but there were small intra-floc voids and some larger inter-floc voids. Thus in general we would classify this as flocculent structure.

The removal of polycations from samples in which organic matter was destroyed (Fig. 2c) caused clay particles to become oriented parallel to each other in large domains, which tend to be curved and moulded together without any distinct inter-domain voids. This type of dispersed clay structure is classified as turbostratic structure. Thus, polycations of iron and aluminium appear to play an important role in formation of the open aggregate structure in this type of soil. This was particularly evident with regard to changes in structure from flocculent to turbostratic after removal of these polycations from clay polyvalent metal–clay linkages (see Fig. 2e).

For additional examples of changes in microstructure, we compared SEM micrographs of SB soil in an untreated (CN) sample (Fig. 3a) and after removal of polycations with organic matter that had previously been destroyed (Fig. 3b). Figure 3a shows a honeycomb structure which is formed by sheet-like and elongated plate-like microaggregates with edge-to-face coagulation contacts. Isometric cell-like pores predominate here. Figure 3b shows a turbulent type of structure
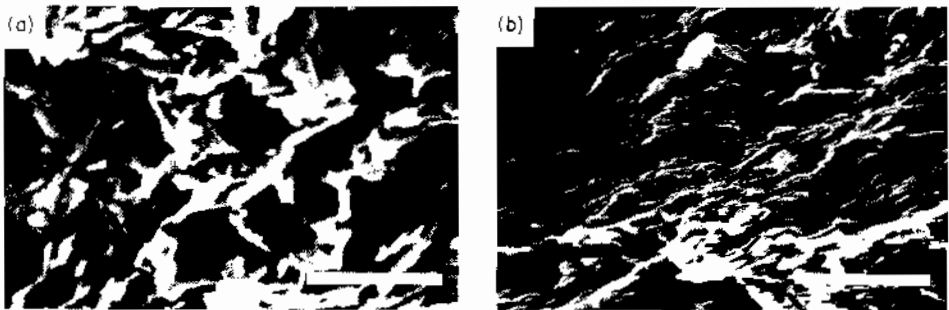

Fig. 3. Scanning electron micrographs of SB soil sample: (a) untreated; and (b) treated with HPAAW. Scale bar = 10 μm.

which is formed by elongated microaggregates oriented concordantly with the bedding. Contacts between microaggregates are face-to-face, and fissure-like pores predominate here.

The mercury intrusion porosimetry examinations

The control and treated samples of the < 5-μm fraction of soils were analysed by mercury intrusion porosimetry. A decrease in the total cumulative volume (TCV) of pores resulted from the successive removal of soil components as described above. Maximum porosity was obtained for untreated soil (CN). The presence of dispersible clay or an increase in the dispersibility of the clay decreases the porosity of the soils (Oades, 1984b). This indicates that removal of bridging agents such as Fe and Al polycations and organic matter caused deflocculation in the soil sample.

In this paper, the pore-size distributions (PSD) are presented in the form of cumulative pore radius distribution curves. The changes in PSD following successive removal of organically bonded metals and organic matter are presented in Fig. 4 for RC soil and in Fig. 5 for SB soil. The changes in PSD for both soils are similar, except that for RC soil samples the porosities were almost twice as large as those for the corresponding SB soil treatments. The extraction of Fe and Al polycations (AAB curves) and Fe and Al polycations plus part of the organic matter (AAW curves) caused a decrease in the volume of pores intruded by mercury, and a shift in the average pore radius from 0.16 to 0.12 μm for RC (AAB and AAW) soil, from 0.25 to 0.10 μm for SB (AAB), and from 0.25 to 0.06 μm for SB (AAW) soil. The removal of organic matter (HP curves) led to a distinct decrease in the volume of pores and a successive decrease in the average pore radius. The extraction of Fe and Al polycations from samples without organic matter (HPAAW curves) led to extremely 'tight' dispersible microstructure. Total penetration of mercury into these samples was 50% of that for the untreated soil samples. The average pore radius obtained for RC (HPAAW) soil was 0.025 μm, and that for SB (HPAAW) soil was 0.007 μm. The pore spaces that were intruded were only distributed over a small range below 0.1 μm for both soil samples.
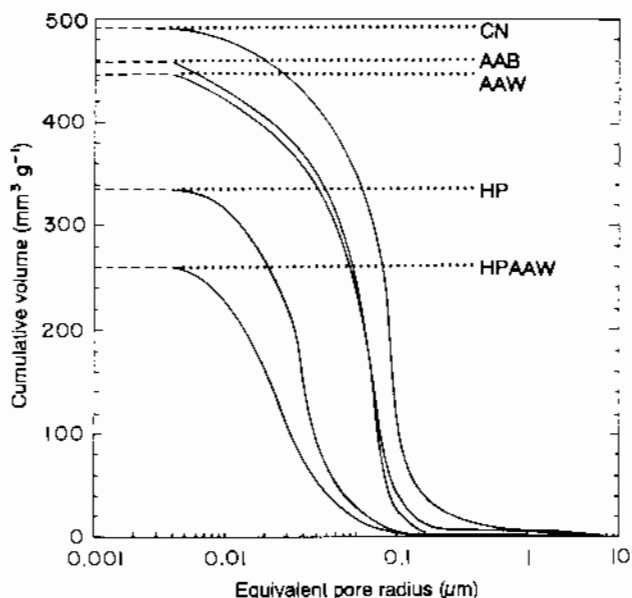
Fig. 4. Changes in pore-size distribution following removal of organically bonded metals and organic matter for < 5-μm fraction of RC soil.
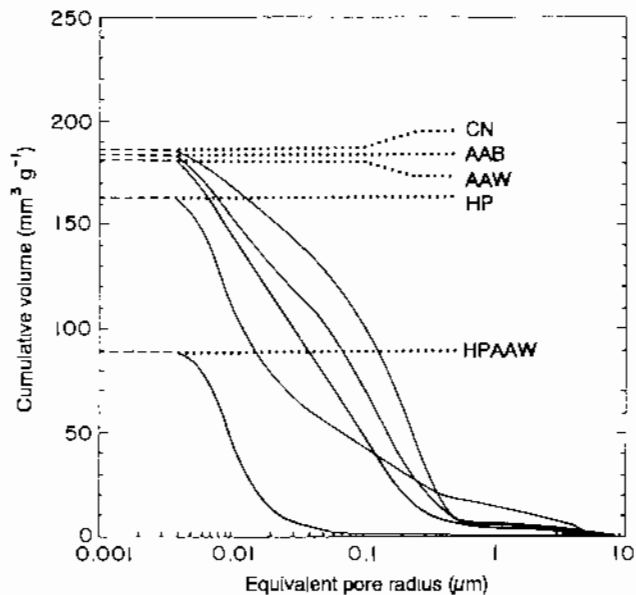

Fig. 5. Changes in pore-size distribution following removal of organically bonded metals and organic matter for < 5-μm fraction of SB soil.

Thus the decrease in pore volume and average pore radius results from the deflocculation process and dispersibility of clay particles following extraction of polycations of iron and aluminium and organic matter.

CONCLUSIONS

Our results confirm the importance of organically bonded iron and aluminium and organic matter as strong flocculating agents. In the course of extracting polycations of iron and aluminium. acetyl-acetone breaks down the junctions in clay–polyvalent metal organic matter linkages. and leads to some changes in the type of microstructure. but because organic matter is not removed, the network remains flocculated. Removal of the polycations of iron and aluminium from soils in which organic matter has been destroyed leads to distinct deflocculation of microaggregates.

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