

Iron (Hydr)Oxide Crystallinity Effects on Soil Aggregation

Sjoerd W. Duiker, * Fred E. Rhoton, José Torrent, Neil E. Smeck, and Rattan Lal

ABSTRACT

Differences in crystallinity may explain why total Fe (hydr)oxide content has a variable effect on aggregate stability. Therefore, surface soil samples with a range of poorly crystalline Fe (hydr)oxide contents were characterized for water-stable aggregates >0.25 mm (WSA), mean-weighted diameter (MWD), soil organic C (OC), particle-size distribution, pH, exchangeable cations, citrate/bicarbonate/dithionite (subscript d), and acid ammonium oxalate (subscript o) extractable Fe, Al, and Si. The WSA and MWD range from 23 to 95%, and 0.3 to 5.1 mm, respectively. The effects of Fe_o (1.1–6.8 g kg⁻¹), Fe_d (3.2–19.6 g kg⁻¹), OC (2.4–24.0 g kg⁻¹) and clay (141–467 g kg⁻¹) contents on WSA and MWD of both A and B horizons of these soils was studied using linear regression. The poorly crystalline Fe (hydr)oxide (Fe_o) and OC contents are significantly correlated with WSA in the A horizons ($r^2 = 0.95$, $n = 6$, $p = 0.001$, and $r^2 = 0.93$, $n = 6$, $p = 0.002$, respectively) and in the B horizons ($r^2 = 0.73$, $n = 6$, $p = 0.029$, and $r^2 = 0.76$, $n = 6$, $p = 0.024$, respectively). When regressed against MWD, Fe_o has an r^2 of 0.89 ($n = 6$, $p = 0.004$) in the A, and 0.97 ($n = 6$, $p = 0.000$) in the B horizons. The coefficient of determination of MWD vs. OC contents is 0.98 ($n = 6$, $p = 0.000$) in the A and 0.79 ($n = 6$, $p = 0.018$) in the B horizons. Clay and Fe_d contents are not significantly correlated to WSA or MWD. Apparently, the Fe_o component (poorly crystalline) is more effective than Fe_d at stabilizing soil aggregates, even though it is present in lower concentrations. The Fe_o component appears more important than OC in terms of WSA and MWD for soils with relatively low soil organic matter contents.

SOIL AGGREGATES ARE FORMED as a result of flocculation, cementation, and arrangement of soil particles (Payne, 1988). Understanding soil aggregation is important because it affects infiltration capacity, hydraulic conductivity, water-retention capacity, tilth, gas exchange, organic matter decomposition, and erodibility (Shanmuganathan and Oades, 1982; Tisdall and Oades, 1982; Miller and Baharuddin, 1986; Farres, 1987; Dexter, 1988; Ley et al., 1995; Horn, 1998).

Iron (hydr)oxides have been observed to stimulate aggregation, but their role is still poorly understood. Some scientists report positive effects of Fe (hydr)oxides on aggregation (Shanmuganathan and Oades, 1982; Colombo and Torrent, 1991; Oades and Waters, 1991; Ferreira Fontes, 1992; Igwe et al., 1995), whereas others observe no effect (Desphande et al., 1968; Greenland et al., 1968; Borggaard, 1983). The reason for this variable effect of Fe (hydr)oxides on aggregation has to be because of either (i) differences between Fe (hydr)oxides not determined in their studies, or (ii) other soil characteristics that influence the aggregating capacity of Fe (hydr)oxides.

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One reason why the total Fe (hydr)oxide content of a soil does not always correlate with degree of aggregation may be the crystallinity of the Fe (hydr)oxides. Poorly crystalline Fe (hydr)oxides have a much larger and more reactive surface area than crystalline Fe (hydr)oxides, and may increase aggregation more than crystalline Fe (hydr)oxides. This suggestion was supported in a lab study with synthetic Fe (hydr)oxides (Schahabi and Schwertmann, 1970) and in a study of B horizons of Italian soils (Arduino et al., 1989; Barberis et al., 1991). According to Rhoton et al. (1998), Fe (hydr)oxide crystallinity explained differences in erodibility (a process highly correlated to WSA) of loess-derived soils in Mississippi.

Factors other than crystallinity that may influence the effect of Fe (hydr)oxides on aggregation are: pH, path of formation of the Fe (hydr)oxides, the size of Fe (hydr)oxide crystals, the ionic composition of the soil solution, and the presence of certain organic molecules. It has been suggested that the Fe (hydr)oxides form aggregates with clay particles only when the pH is below their zero point of charge (Goldberg, 1989). Although this may be true in many cases, some studies report opposite results (Desphande et al., 1968; Arduino et al., 1989; Colombo and Torrent, 1991; Ferreira Fontes, 1992). Both Blackmore (1973) and Muggler et al. (1999) indicate that translocation of Fe and its recrystallization in the presence of clay may be necessary for aggregation. Ferreira Fontes (1992) suggests that small crystal size may be an essential characteristic of crystalline Fe (hydr)oxides in aggregates. Inner-sphere complexes between Fe (hydr)oxides and phosphate or silicate increase the negative charge on Fe (hydr)oxide surfaces stimulating aggregation in some Oxisols (Cornell and Schwertmann, 1996). Some authors suggest that poorly crystalline Si oxides form bridges between Fe (hydr)oxides and quartz surfaces of silt- and sand-sized particles (Arduino et al., 1989; Colombo and Torrent, 1991). Finally, organic ions can form inner-sphere complexes on Fe (hydr)oxide surfaces, thus changing their charge, but little research has been done on the effects of this on aggregation (Greenland, 1971; Cornell and Schwertmann, 1996).

Most studies investigating the effect of Fe (hydr)oxides on aggregation compare particle-size distribution after vigorous shaking in a standard dispersion solution (usually sodium hexametaphosphate) with treatments that dissolve Fe (hydr)oxides (acid ammonium oxalate or citrate/bicarbonate/dithionite). Weak bonds between Fe (hydr)oxides and other soil particles are obviously not a subject of such studies, although weak bonds may facilitate soil structure development and are a major determinant of macroaggregation. The present experiment was conducted to determine if the crystallinity of

Abbreviations: subscript d, citrate/bicarbonate/dithionite extractable; MWD, mean-weighted diameter; subscript o, acid ammonium oxalate extractable; RR, redness ratio; WSA, water-stable aggregates.

Fe (hydr)oxides influences macroaggregation. Soils from Mississippi and Spain were selected because of differences in Fe (hydr)oxide crystallinity to test the hypothesis that poorly crystalline Fe (hydr)oxides facilitate formation of stable macroaggregates (>0.25 mm).

MATERIALS AND METHODS

Field

Samples of the A and B horizons of six Alfisols were collected that had a relatively wide range in color and Fe (hydr)oxide characteristics. Three soils were selected near Senatobia, MS (34° 31' Lat. N, 89° 57' Long. W). They were a Memphis silt loam (Typic Hapludalf), Grenada silt loam (Oxyaquic Fraglosudalf), and Routon silt loam (Typic Epiaqualf). These three soils are members of the Memphis catena, and range from well to poorly drained. Soil colors (especially in the B horizons) range from brown to gray as wetness increases. It was reasoned that, because of differences in oxidation state among the soils selected, Memphis should have the lowest proportion of poorly crystalline Fe (hydr)oxides and Routon should have the highest proportion of poorly crystalline Fe (hydr)oxides, with Grenada being intermediary between these two. It was known, however, that because of its young geological age, even the well-drained Memphis soil contains a substantial quantity of poorly crystalline Fe (hydr)oxides. Because we desired to compare the aggregate stability of these soils with others that contain very low quantities of poorly crystalline Fe (hydr)oxides, but equal amounts of total Fe (hydr)oxides, soils with these characteristics were collected in southern Spain, near La Fuencubierta, Province of Córdoba, Andalusia (37° 55' N Lat., 4° 43' E Long.). They will be referred to as soil S1 (Typic Haploxeralf), S3 (Calcic Palexeralf), and S8 (Calcic Rhodoxeralf). The most obvious difference between these soils was their color, ranging from yellow (S1) to red (S8), with one intermediary (S3). Previous research had shown that redness is a good indicator of the presence or absence of the crystalline Fe oxide hematite (Torrent and Barrón, 1993), thus we anticipated that these samples contained different amounts of hematite.

Laboratory

Soil samples used to evaluate aggregate stability were air-dried and sieved so that only air-dry aggregates >4 but <8 mm remained. The samples used for all other physical and chemical analyses were gently crushed and sieved to <2 mm. Water-stable aggregation was determined in duplicate by the procedures of Kemper and Chepil (1965), using a nest of sieves with openings of 4.00, 2.00, 1.00, 0.50, and 0.25 mm. Results of the duplicates were averaged before performing linear regression and aggregate-size distribution analyses. The sieve set was rapidly immersed in distilled water and oscillated at 37 rpm for 10 min (amplitude was 1.88 cm). In addition, the <0.25 -mm fraction was wet sieved by hand through a 0.125- and 0.053-mm sieve. All fractions were dried at 70°C and weighed. In the case of the soils from Spain, the WSA was dispersed in 50 g L⁻¹ sodium hexametaphosphate after drying and weighing, so that a coarse-fraction correction could be made for these soils. First, the dry weight of the aggregates plus coarse fragments remaining on each sieve was determined, after which the aggregates on the sieve were dispersed with sodium hexametaphosphate. Subsequently, the dry weight of the coarse fragments remaining on the same sieve was determined. No coarse fraction correction was necessary for the soils from Mississippi, which contained $<3.5\%$ sand

(>0.05 mm). Percentage of WSA was calculated as (oven-dry soil remaining on all sieves with openings >0.25 mm after sieving in water minus oven-dry soil remaining on the same sieves after dispersion in sodium hexametaphosphate)/(oven-dry weight of original sample minus oven-dry soil remaining on the same sieves as above after dispersion in sodium hexametaphosphate). Mean weighted diameter was calculated as $\sum w_i x_i$, where w_i is the mean diameter of each size fraction and x_i is the proportion of total sample weight in the corresponding size fraction, where the summation is performed over all size fractions, including the one that passes through the finest sieve (Kemper and Rosenau, 1986). For the calculation of MWD, the size of the smallest fraction was calculated as 0.053 mm/2.

Standard sieving and pipette procedures determined particle-size distributions after dispersion and overnight shaking in 50 g L⁻¹ sodium hexametaphosphate solution (Gee and Bauder, 1986). Soil color of wet samples was measured with a Minolta CR-200 chroma meter (Minolta Corp., Ramsey, NJ). The redness ratio (RR) was calculated as: $RR = (10 - H)/C/V$, where H is the numerical value of YR hue, C is chroma, and V is the value of the Munsell notation (Torrent and Barrón, 1993). Soil chemical analyses were conducted on the <2 -mm fraction, however, all samples extracted with acid ammonium oxalate (McKeague and Day, 1966) and citrate/bicarbonate/dithionite (Mehra and Jackson, 1960) were first pulverized in a mixer mill. The concentrations of Fe and Al in solution were determined by atomic absorption spectrophotometry (Baker and Suhr, 1982). Silica concentration was measured colorimetrically with the blue silicomolybdous acid procedure (Hallmark et al., 1982). Soil OC content was determined with a LECO-CN-2000 analyzer (Leco Corp., St. Joseph, MI) at 1000°C. The C measured in this way equaled the OC content, because the carbonate content was zero in all samples (measured with a pressure-calimeter apparatus; Nelson, 1982). Exchangeable cations were determined following extraction with 1 M ammonium acetate at pH 7.0 (Thomas, 1982) with atomic absorption spectrophotometry. The pH was measured in a 1:1 soil/water suspension (McLean, 1982). Results were analyzed statistically with the Statistical Analysis System (SAS, 1989).

RESULTS AND DISCUSSION

Physical and Chemical Characteristics

The colors of the soils used in this study (Table 1) range from 0.1Y 4/2 (dark grayish brown, Routon B) to 1.5YR 3/5 (dark red, S8 B). The content of hematite increases with the redness rating of the soils. Samples devoid of hematite have redness ratings <1 to 2 (Torrent and Barrón, 1993). Nevertheless, a soil with a high redness rating can also contain goethite, but because of the dominance of the red color of hematite, the redness rating does not allow estimation of the amount of goethite in a sample. Thus, based on redness ratings (Table 1), the B horizon of soil S8 has the highest hematite content, followed by S8 A, S3 B, S3 A, Memphis B and Grenada B. The other soils contain essentially no hematite, judged by their color. The redness rating increases as natural drainage improves in the soils from both Spain and Mississippi. Among the soils from Spain, natural drainage conditions improve in the order S1 $<$ S3 $<$ S8, whereas among the soils from Mississippi the order is Routon $<$ Grenada $<$ Memphis, corresponding to the order of redness rating in both cases.

The pH values of the soils from Mississippi range

Table 1. Some chemical and physical characteristics of soils used in this study

Soil	Horizon	Color	Redness ratio	pH	OC†	Particle-size distribution			Exchangeable cations			
						Sand	Silt	Clay	Ca	Mg	K	Na
		Munsell				g kg ⁻¹			cmol kg ⁻¹			
Memphis	A	8.1 YR 3/2	1.47	4.9	24.0	35	824	141	4.6	2.2	0.4	0.1
	B	7.7 YR 3/4	2.58	5.1	4.8	11	688	302	7.3	3.0	0.4	0.1
Grenada	A	9.5 YR 3/3	1.40	5.0	16.0	31	803	167	4.6	1.8	0.2	0.2
	B	8.1 YR 3/4	2.29	4.9	4.5	10	717	273	3.3	2.2	0.2	0.1
Routon	A	8.8 YR 4/3	0.86	4.9	18.4	21	875	104	2.7	1.3	0.3	0.1
	B	0.1 Y 4/2	0.00	5.1	2.7	6	644	350	1.9	1.9	0.2	0.9
S1	A	9.0 YR 3/3	0.94	5.7	4.8	675	170	155	6.4	0.9	0.2	0.1
	B	8.6 YR 4/5	1.58	6.4	2.4	567	149	283	9.2	1.0	0.2	0.1
S3	A	6.6 YR 3/3	3.40	6.3	6.5	603	198	199	7.4	1.1	0.3	0.0
	B	4.9 YR 3/4	6.03	6.6	3.7	360	173	467	16.8	1.8	0.4	0.1
S8	A	3.1 YR 3/4	9.43	6.4	5.6	647	172	180	7.0	1.1	0.7	0.1
	B	1.5 YR 3/5	13.03	6.8	2.8	425	123	452	14.3	1.7	0.5	0.3

† OC = soil organic C.

from 4.9 to 5.1, whereas the pH of the soils from Spain yields a range from 5.7 to 6.8 (Table 1). Organic C contents in the A horizons of the soils from Mississippi range from 16 to 24 g kg⁻¹, and the B horizons range from 3 to 5 g kg⁻¹ (Table 1). The predominant land use of the soils from Mississippi is pasture, resulting in relatively high OC contents in their A horizons compared with the OC content of the A horizons from Spain. The soils from Spain have a long history of intensive soil tillage and low crop residue inputs and therefore have low OC contents, ranging from 5 to 7 g kg⁻¹ in their A horizons and from 2 to 4 g kg⁻¹ in their B horizons.

Particle-size distributions (Table 1) of the two soil groups indicate that the soils from Mississippi have silt or silt loam A horizons with silty clay loam B horizons, and the soils from Spain have sandy loam A horizons and sandy clay loam or clay B horizons. The soils from Spain contain much more sand than the silty soils from Mississippi. The predominant exchangeable cation is Ca in all soils of this study (Table 1). The Ca content of the soils from Spain ranges from 6.4 to 16.8 cmol Ca kg⁻¹, and the soils from Mississippi from 1.9 to 7.3 cmol Ca kg⁻¹. Magnesium is the next most abundant cation after Ca. Potassium and Na are present in low concentrations in all soils.

The soils from Mississippi have citrate/bicarbonate/dithionite extractable Fe (Fe_d) contents that range from 3.2 g kg⁻¹ in the Routon B to 19.6 g kg⁻¹ in the Grenada B (Table 2). The A horizon of the Routon soil also has the lowest Fe_d concentration among the A horizons from

Mississippi. The low Fe_d content of the Routon soil is because of the poor natural drainage of this soil, which contributes to the reduction, mobilization and loss of Fe from the soil profile. The soils from Spain have Fe_d contents ranging from 8.3 (S8 A) to 17.9 g kg⁻¹ (S8 B).

The Fe_o contents of the soils from Mississippi range from 1.4 to 6.8 g kg⁻¹ and average 45% of the Fe_d contents (Table 2). In the A horizons from Mississippi there are negligible differences in Fe_o contents. In the B horizons, the Memphis has the highest Fe_o content, the Grenada has the second highest, and the Routon has the lowest concentration of Fe_o. This is contrary to the initial expectation (based on drainage characteristics) that the order of Fe_o contents would be Routon > Grenada > Memphis. Evidently, landscape position and natural drainage are not good predictors of Fe_o content. The soils from Spain have much lower Fe_o contents than those from Mississippi, ranging from 0.9 to 2.2 g kg⁻¹. These Fe_o contents are, on average, only 13% of the Fe_d content. The Fe_o contents of the soils from Mississippi are more than twice that in the soils from Spain, if the Routon is excluded. This indicates that the Fe (hydr)oxides in the soils from Spain are more crystalline than in the soils from Mississippi. Furthermore, the RR indicates that the crystalline Fe oxide hematite is present in substantial quantities in Soils S3 and S8 from Spain whereas goethite is the dominant crystalline Fe oxyhydroxide in Soil S1 and those from Mississippi.

The Al_d contents range from 1.0 to 3.2 g kg⁻¹ in the soils from Mississippi, and from 0.8 to 1.9 g kg⁻¹ in the soils from Spain. The Al_o concentrations are most often slightly lower than Al_d for both soil groups, whereas the soils from Mississippi tend to have slightly greater concentrations of Al_d than the soils from Spain. The two soil groups have low contents of Si_d and Si_o concentrations.

The clay mineralogy is predominantly illite and vermiculite in the soils from Mississippi (Hutcherson et al., 1959), whereas it is illite, smectite, and kaolinite (in decreasing order of importance) in the soils from Andalusia (Peña and Torrent, 1984).

Aggregation Versus Soil Properties

Differences in aggregation among the soils of this study will be discussed as a function of three factors: (i) clay contents, (ii) organic C contents, and (iii) Fe (hydr) oxide contents and types. Differences in sand and silt

Table 2. Distribution of citrate/bicarbonate/dithionite (CBD) and acid ammonium oxalate (AAO) extractable Fe, Al, and Si in the soil samples

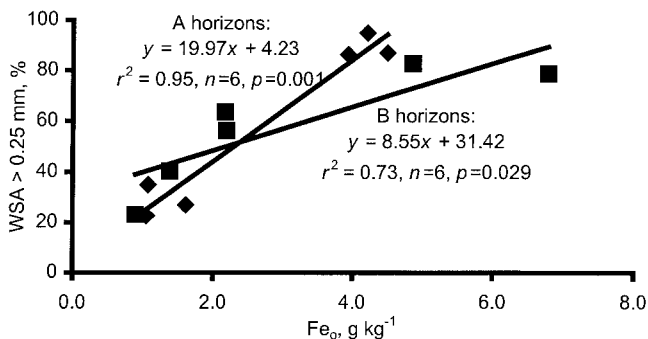
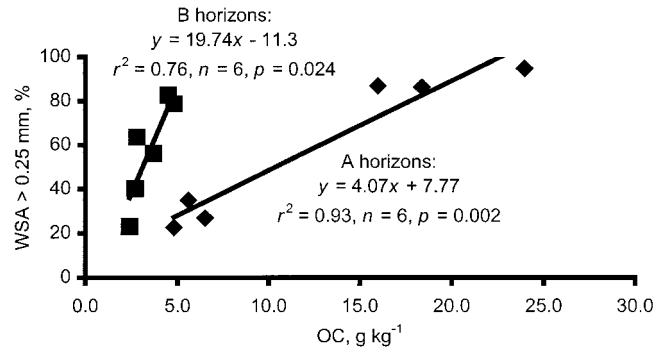
Soil	Horizon	CBD extractable			AAO extractable		
		Fe	Al	Si	Fe	Al	Si
		g kg ⁻¹					
Memphis	A	9.9	1.5	0.8	4.2	1.4	0.3
	B	16.9	2.4	1.0	6.8	2.5	0.5
Grenada	A	12.9	2.0	0.7	4.5	1.6	0.3
	B	19.6	3.2	1.2	4.9	2.3	0.5
Routon	A	5.2	1.0	0.8	3.9	1.1	0.2
	B	3.2	1.6	2.4	1.4	1.5	0.2
S1	A	8.9	1.2	0.9	1.1	0.7	0.4
	B	13.6	1.9	1.0	0.9	0.9	0.5
S3	A	8.5	1.2	1.1	1.6	1.0	0.4
	B	14.5	1.8	1.6	2.2	1.6	0.8
S8	A	8.3	0.8	0.8	1.1	0.8	0.4
	B	17.9	1.6	1.3	2.2	1.7	0.8

Table 3. Water-stable aggregates (WSA) and mean weight diameter (MWD).

Soil	Horizon	WSA	MWD
		%	mm
Memphis	A	94.9	5.1
	B	78.8	1.6
Grenada	A	87.0	3.6
	B	82.8	1.2
Routon	A	86.4	3.7
	B	40.3	0.5
S1	A	22.6	0.4
	B	23.1	0.3
S3	A	27.0	0.5
	B	56.2	0.5
S8	A	35.0	0.8
	B	63.6	0.8

content are not a probable cause of differences in aggregation, because these particles usually have low-activity surfaces and very low surface areas compared with clay particles. Calcium contents may also influence aggregation, but do not correlate well with any of the aggregation indices in this study and will not be discussed further. The RR does not correlate with aggregation indices, and will therefore not be discussed either. To determine if Fe (hydr)oxides play a role in aggregation, A horizons are considered separately from B horizons, because all A horizons contain low amounts of clay (from 104 to 199 g kg⁻¹), whereas the B horizons contain low amounts of OC (from 2.4 to 4.8 g kg⁻¹). The thought is that in the A horizons Fe (hydr)oxides and organic matter are the potential aggregating agents, whereas they are Fe (hydr)oxides and clay in the B horizons.

In the A horizons, the percentage of WSA >0.25 mm of the soils from Mississippi is much higher than that of the soils from Spain (Table 3). Within these two groups there are no great differences in WSA. The A horizons differ primarily in their OC contents and their Fe_o contents, not in their clay contents. The A horizons from Mississippi contain on average 19 g OC kg⁻¹ (range 16–24 g OC kg⁻¹), whereas the A horizons from Spain contain on average 6 g OC kg⁻¹ (range 5–7 g OC kg⁻¹). The Fe_o content of the A horizons from Mississippi is on average 4 g kg⁻¹ (range 3.9–4.5 g Fe_o kg⁻¹) whereas the A horizons from Spain contain only 1 g Fe_o kg⁻¹ (range 1.1–1.6 g Fe_o kg⁻¹). Regression analysis shows the absence of a relationship between Fe_d and clay contents vs. WSA in the A horizons ($r^2 = 0.03$ and 0.41, respectively, not significant with $p > 0.05$). Conversely, Fe_o and OC contents are both significantly correlated

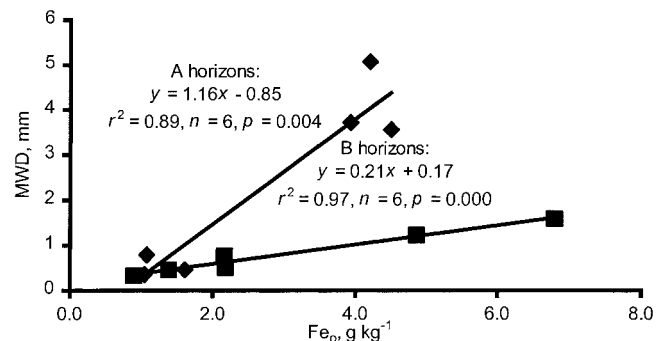
**Fig. 1. Relationships between water-stable aggregation and Fe_o for A and B horizons.****Fig. 2. Relationships between water-stable aggregation and soil organic C for A and B horizons.**

with WSA and MWD in the A horizons (Fig. 1, 2, 3, and 4). These results suggest that aggregation is positively affected by OC or Fe_o in the A horizons.

In the B horizons, there is no clear separation of WSA into two groups as in the A horizons. The WSA of the Memphis B and Grenada B soils are highest, followed by the WSA of S8 B, S3 B, Routon B, and S1 B (Table 3). Similar to the A horizons, there is no significant ($p > 0.05$) relationship between WSA and Fe_d or clay ($r = 0.41$ and 0.00, respectively). On the other hand there is a significantly positive correlation between WSA and MWD and Fe_o and OC in the B horizons (Fig. 1, 2, 3, and 4). It is likely that Fe_o is the major factor explaining differences in macroaggregation in the B horizons, because of the very low content of OC in the B horizons and because the correlation between MWD and Fe_o is better than between MWD and OC contents in the B horizons (Fig. 3 and 4). Samples with <5.0 g kg⁻¹ OC and low Fe_o contents in the A horizons have very low stability, whereas in the B horizons samples with <5.0 g kg⁻¹ OC but high Fe_o contents still have fairly high WSA and a large MWD. Apparently, Fe_o is more important for the stability of small macroaggregates (0.25–2 mm) in the B horizons of these soils relative to the A horizons. The greater effect of Fe_o on MWD in the B horizons suggests an interaction between Fe_o and the clay fraction which enhances the stabilization of larger aggregates. Organic C becomes less important in this zone because its concentration decreases relative to the A horizons.

Aggregate-Size Distribution

The cumulative aggregate-size distribution of the samples from the A and B horizons is given in Fig. 5a and

**Fig. 3. Relationships between MWD and Fe_o for A and B horizons.**

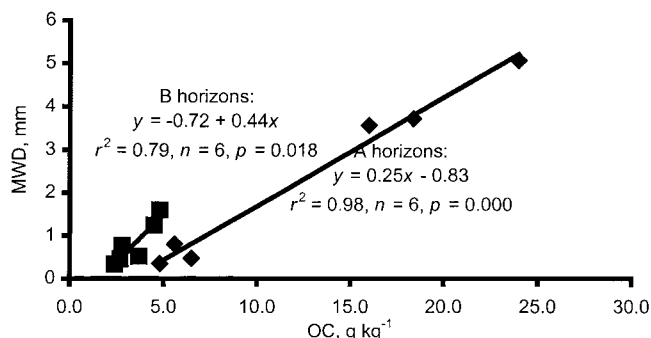


Fig. 4. Relationship between MWD and SOC for A and B horizons.

5b, respectively. These figures represent the cumulative percentage of eight aggregate fractions <8 mm (corrected for sand and gravel). The slope and inflection points of these curves provide a clue about the hierarchy of aggregation in these samples. Specific aggregating agents have been related to specific levels in a hierarchy of aggregation (Tisdall and Oades, 1982; Oades and Waters, 1991). In the hierarchy of these studies, plant roots and fungal hyphae were considered to be largely responsible for the stability of aggregates >0.250 mm, whereas decomposition products of plant debris stabilized aggregates 0.020 to 0.250 mm in diameter. Aggregates smaller than 0.02 mm were apparently held together by microbial products and their interaction with clays and sesquioxides. This order in hierarchy occurred in Alfisols, but not in an Oxisol, where long chains of clay-organic matter-(hydr)oxide bonds appeared to be responsible for very stable aggregates >0.250 mm (Oades and Waters, 1991).

The soils of this study in which fast wetting was em-

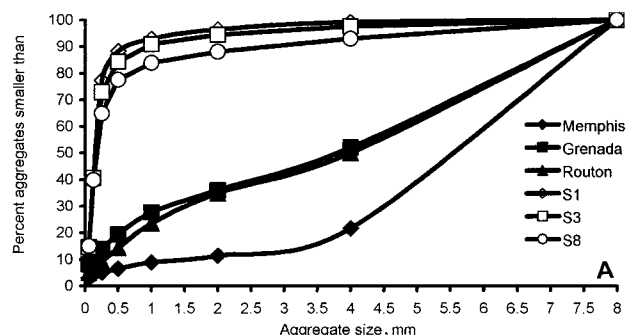


Fig. 5a

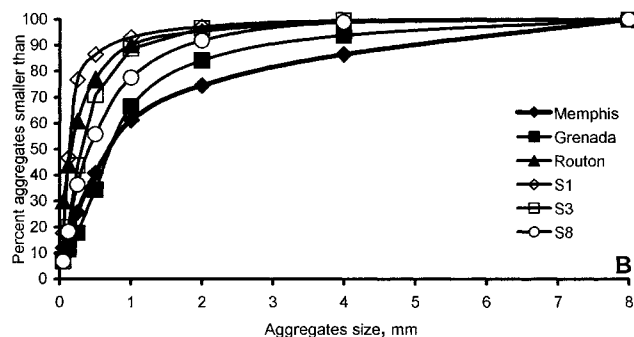


Fig. 5. Cumulative aggregate-size distributions of A and B horizons.

ployed show aggregate distribution similar to the Alfisols of Oades and Waters (1991), with the exception of the Memphis, Grenada, and Routon A horizons (Fig. 5a). Whereas the distribution of aggregates over the 0.05- to 8-mm size range is relatively uniform for the Grenada and Routon A horizons, most (>80%) of the aggregates in the Memphis A horizon are >4 mm. Both Oades and Waters (1991) and Tisdall and Oades (1982) distinguished only one level in the hierarchy of aggregation >0.250 mm, held together by roots and fungal hyphae. The data from this experiment suggest there may be an additional level in the hierarchy of aggregation (>4 mm) that would distinguish the Memphis A from the Grenada and Routon A horizons. The aggregating agent at this level in the hierarchy is probably biological, such as distinct types of roots or fungal hyphae. The Grenada and Routon soils are not as well drained as the Memphis, which may have influenced the type and amount of biological species present.

In all samples except the Memphis A, Grenada A, and Routon A, the inflection point in the distribution curves is located approximately between the first four data points (from 0.005 to 0.5 mm) and the last four data points (from 1 to 8 mm). Straight lines can be fitted through these two groups of data points for each soil. The two lines intersect at (0.48 mm, 94%) for S1 A, (0.44 mm, 83%) for S3 A, (0.56 mm, 92%) for S8 A, (0.88 mm, 66%) for Memphis B, (1.20 mm, 76%) for Grenada B, (0.61 mm, 92%) for Routon B, (0.50 mm, 95%) for S1 B, (0.63 mm, 92%) for S3 B, and (0.74 mm, 84%) for S8 B. These results show that most aggregates (always more than 83%) of both A and B horizons of the Spanish soils are smaller than 0.74 mm, with even distributions of these aggregates over the 0.05-inflexion point range. The Routon B horizon has the highest percentage (almost 30%) of aggregates and dispersed soil <0.05 mm, whereas most aggregates (92%) are <0.61 mm. This soil has the lowest amount of Fe (hydr) oxides, which likely explains its low stability. In contrast, the Memphis B and Grenada B have relatively high amounts of aggregates in the >0.5- and >1-mm fractions, likely because of the aggregating effect of poorly crystalline Fe(hydr)oxides.

CONCLUSIONS

In this study, no effects of RR, Ca, clay and Fe_d contents on soil aggregation indices (WSA and MWD) can be determined. Instead, Fe_o and OC content are well correlated with WSA and MWD in both A and B horizons. Although there is good correlation between Fe_o and OC and aggregation indices in both A and B horizons, Fe_o appears most important for macroaggregation in the B horizons because of the low concentration and small range of OC in the B horizons.

These results demonstrate the importance of poorly crystalline Fe (hydr)oxides in terms of stabilizing aggregates in the >0.25-mm fraction to the extent that its contribution equals or exceeds that of OC in soils with low organic matter contents. Similar results have been reported in other studies that attributed Fe_o enhancement

of aggregate stability to the gel-like, highly reactive surfaces of the poorly crystalline Fe (hydr)oxides (Schahabi and Schwertmann, 1970; Rhoton et al., 1998).

ACKNOWLEDGMENTS

We thank Vincent B. Campbell and Daniel S. McChesney, USDA-ARS, Oxford, MS for their assistance in field and lab. This research was done with partial support from the Universidad de Córdoba and the Junta de Andalucía, The Ohio State University Office of International Studies, and the Paul Clayton Fund.

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