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Role of Hydrophobic Components of Soil Organic Matter in Soil Aggregate Stability

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ABSTRACT

Little is known about the effects of the individual components of organic matter (OM) on aggregate stability (AS). We hypothesized that AS of a Typic Haplustalf from which native OM was either removed or retained would be affected by incubation periods and application rates of a hydrophilic polysaccharide gum (G) and a hydrophobic stearic acid (S) with or without pretreatment with a hydrophobic humic acid (HA). Removal of OM reduced AS of unmodified soil by ≈ 40 and 20% after soil incubation for 7 and 40 d, respectively. In both soil samples, AS was best at the highest rate of G (5.0 g kg^{-1}). Its effect was better on Soil A (where OM was removed) than Soil B (where OM was retained) but diminished rapidly during 40 d. At this rate, G increased AS by 750% in Soil A and by 335% in Soil B compared with no addition. With S, aggregate stability increased more with time in Soil B than in Soil A. Its maximum effect was also at the highest application rate (5.0 g kg^{-1}), where AS increased 100% on Soil A and 131% on Soil B. At the highest rate (0.2 g kg^{-1}), HA increased AS by 73% on Soil B and 27% on Soil A. The effect of HA alone did not vary with time. Soil pretreatment with HA before addition of G reduced significantly both the state of aggregation and AS of both soils. The reverse occurred when HA was applied before S. After 40 d, S+HA increased AS in Soil B by 34%, whereas G and G+HA decreased AS by 14 and 4%, respectively. We found that soil AS was improved and maintained with time more by hydrophobic than by hydrophilic components of organic matter. Long-lasting aggregate stability of soils can be thus achieved by addition of hydrophobic humic material with hydrophobic organic wastes.

A GOOD STRUCTURE is important for sustaining long-term crop production on agricultural soils because it influences water status, workability, resistance to erosion, nutrient availability and crop growth and development. One of the measures of good structure is the stability of soil aggregates in water, and this is influenced mostly by both the quality and quantity of OM in the soil (Piccolo, 1996). Several studies have focused on the use of organic materials to improve soil structural stability. Some of these studies reported positive effects of total OM (Tisdall and Oades, 1982), whereas others indicated that it is the composition of OM (especially

the humified fractions) rather than the total amount per se that is responsible for aggregate stabilization (Hamblin and Greenland, 1977; Dutarte et al., 1993).

Our information on the effects of OM on soil structure is rather empirical and still poor, as is knowledge of the actual mechanisms by which OM acts in the soil. Understanding the mechanisms involved is important in the choice of suitable soil organic matter (SOM) management practices. Conflicting reports on the role of OM in soil aggregation may be related to different mechanisms operating in the soil environment at different scales of measurement (Theng, 1982; Sullivan, 1990).

Following observations by Coughlan et al. (1973) that the advancing contact angles of water associated with the surfaces of some forms of SOM are greater than zero (which is the contact angle for most soil minerals), it was suggested that OM might increase aggregate stability by slowing water uptake by aggregates. By reinterpreting existing results in the literature, Sullivan (1990) showed that the nonuniform distribution of hydrophobic OM will retard water entry into aggregates, thereby increasing the resistance of such aggregates to slaking in water. The practical implication of this observation is that soil amendment with organic materials containing substantial amounts of hydrophobic compounds will stabilize soil aggregates more than those with predominantly hydrophilic compounds.

The major components of SOM implicated in stabilizing soil aggregates are humic substances (humic acids, fulvic acids, and humin) and nonhumic substances (carbohydrates, peptides, resins, and waxes). Several studies have shown that the humic substances (mostly humic acids) improve aggregate stability (Fortun et al., 1990; Piccolo and Mbagwu, 1990, 1994). Others indicated that the carbohydrate fraction is also involved in aggregation, especially in soils low in OM (Tisdall and Oades, 1982; Lynch and Bragg, 1985; Angers and Mehuys, 1989). In a series of studies with beeswax (a naturally occurring source of long-chain fatty acids), Diné et al. (1991a, 1991b; 1992) reported that aggregate stability

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Abbreviations: ANOVA, analysis of variance; AS, aggregate stability; G, polysaccharide gum (hydrophilic); G+HA, gum added to soil pretreated with HA; HA, humic acid (hydrophobic); OM, organic matter; S, stearic acid (hydrophobic); S+HA, stearic acid added to soil pretreated with HA; SOM, soil organic matter; WSA, water-stable aggregates.

was due to unbound OM (mainly the long-chain aliphatic and hydrophobic compounds).

Other studies have attributed increased aggregate stability obtained from OM to hydrophobic properties and stronger intermolecular associations of OM (Ae et al., 1987; Bartoli et al., 1988; Chen and Schnitzer, 1978; Haynes, 1993; Haynes and Swift, 1990). Adhikari and Chakrabarti (1976), using OM-free soils, showed that addition of both natural and microbially synthesized HA increased soil water repellency. They observed that this phenomenon was not due to any binding action of OM within the soil but probably due to the formation of a hydrophobic complex film on the soil.

In earlier studies (Mbagwu and Piccolo, 1989; Piccolo and Mbagwu, 1989, 1994), we explained experimental results with a mechanism by which humic substances (HS) improved aggregate stability through the formation of clay–metal–humic linkages with the O-containing, hydrophilic groups of HS. Such bonds will orient the hydrophobic moiety of HS outside the soil aggregates to form a water-repellent coating (with high surface tension) that is capable of reducing water entry into the aggregates, thereby enhancing their stability in water. Though the formation of clay–metal–humic complexes was confirmed by several studies (Singer and Huang, 1993; Theng, 1976; Varadachari et al., 1991), an increasing number of studies pointed out the importance of nonionic bondings or entropic factors in the interactions between clay and humic components of soils (Chassin et al., 1977; Dinel et al., 1991a, 1992; Theng et al., 1986; Nayak et al., 1990; Varadachari et al., 1994). Moreover, the influence of the molecular size of humic substances and of their stereochemical flexibility was shown in several instances (Jekel, 1986; Kretzchmar et al., 1993; Piccolo and Mbagwu, 1990; Theng et al., 1986).

Recent results (Piccolo et al., 1996a; Conte and Piccolo, 1999) have indicated that, rather than being polymeric, HS are composed of relatively small molecules which self-associate mainly by hydrophobic forces and their apparent high molecular size conformation in solution can be reversibly dispersed by the action of organic acids. These observations suggest that the increase of molecular association of humus by accumulation of hydrophobic compounds improves aggregation of particles and especially of microaggregates (Piccolo and Mbagwu, 1990). Stabilization by hydrophobic components of soil organic matter occurs since these preferentially escape from soil solution and are strongly adsorbed on soil inorganic phases. The effect of hydrophobic compounds on AS should be longer lasting than the more hydrophilic compounds such as carbohydrates, which by residing preferentially in the soil solution may be rapidly biodegraded.

Most studies conducted so far have not considered the aggregate-stabilizing effects of different SOM components simultaneously. Such studies are needed to obtain a clearer picture of the actual mechanism involved in soil aggregate stabilization. Our objective was to study the effects of a polysaccharide gum and stearic

acid (alone or in combination with exogenous humic acids) on aggregate stability of an arable soil before and after removal of its native OM.

MATERIALS AND METHODS

Soil

Soil was collected from the 0- to 20-cm layer of a Typic Haplustalf under a vineyard at Dugenta near Benevento (Campania Region) in southern Italy. It contained 425 g kg⁻¹ sand, 298 g kg⁻¹ silt, and 227 g kg⁻¹ clay. Its pH (H₂O) was 7.2, OM was 21.2 g kg⁻¹, total CaCO₃ was 111.5 g kg⁻¹, and cation-exchange capacity was 17.4 cmol_c kg⁻¹. The clay fraction was dominated by illite and kaolinite. Soil was air-dried at ambient temperature (~20°C) and sieved through a 2-mm mesh. Sieved soil was either (i) treated exhaustively (in batches) with 30% H₂O₂ to the extent that no oxidizable OM could be detected in the samples [Soil A (-OM)] or (ii) untreated [Soil B (+OM)].

Materials

Reagent-grade polysaccharide gum [a Galactomannan polysaccharide from seed of carob (*Ceratonia siliqua* L.) with a molecular weight of 310 000; Sigma-Aldrich Chemical, Milan, Italy] and stearic acid (formula weight of 284.48; Aldrich) were used without further purification. Humic acid (HA) was extracted under N₂ from a commercial North Dakota Leonardite (Mammoth Chemical Co., Houston, TX), purified and analyzed using procedures described previously (Piccolo and Mbagwu, 1989). The HA was 7.0% residual ash, 630 cmol kg⁻¹ total acidity, 250 cmol kg⁻¹ carboxyl functional groups, 370 cmol kg⁻¹ total hydroxyls, 240 cmol kg⁻¹ total ketones, and 3 g kg⁻¹ methoxyl groups. A solid-state ¹³C-nuclear magnetic resonance (NMR) spectrum of this HA was previously described (Conte et al., 1997) and revealed the following ¹³C-distribution: 0–40 ppm aliphatic C (44.1%), 40–110 ppm C–O and C–N (18.6%), 110–140 ppm aromatic C (13.6%), 140–160 ppm phenolic C (8.5%), and 160–190 ppm carboxyl C (15.2%). Aromaticity of this HA (110–160 ppm/0–190 ppm) was 22.1%, whereas the hydrophobicity ratio [(0–40 ppm) + (110–140 ppm)]/[(40–110 ppm) + (140–190 ppm)] was as high as 1.36.

Three stock solutions (a, b, and c) of G were prepared by dissolving 0.625, 1.250, and 6.250 g in 250 mL of distilled water, reaching the concentrations of 2.5 mg mL⁻¹ (Ga), 5.0 mg mL⁻¹ (Gb), and 25.0 mg mL⁻¹ (Gc), respectively. Stearic acid was first solubilized in diethylether (a volatile solvent) by also dissolving 0.625 (Sa), 1.250 (Sb), and 6.250 g (Sc) respectively, in 250 mL of the solvent and reaching the same concentrations as the G stock solutions. For the HA, three stock solutions were prepared by suspending 62.5, 125.0, and 250 mg in 200 mL of distilled water and dissolving by adding stepwise first 2 M and then 0.1 M NaOH until the pH stabilized at 7. The final HA volumes were adjusted to 250 mL to provide the respective concentrations of 0.25 mg mL⁻¹ (HAa), 0.50 mg mL⁻¹ (HAb), and 1.00 mg mL⁻¹ (HAc).

Amendments to Soils

Two sets of experiments were conducted to study the effects of these materials on soil aggregate stability. For both experiments, 100 g of soil was weighed into aluminum cans. The residual moisture content of the soils was <2%.

Experiment 1 studied the effects of five types of amendments (vs. a control) and three periods of incubation (7, 15, and 40 d) on AS on Soils A and B. The experimental design was a 6 by 2 by 3 factorial in a completely randomized design

with three replications. For the G and S treatments, the rate of 1.0 g kg⁻¹ was used, whereas for HA alone the rate was 0.1 g kg⁻¹. In the combined G+HA and S+HA additions, the 0.1 g kg⁻¹ HA rate was applied first, followed by 1.0 g kg⁻¹ of G or S after 1 h. To attain these rates, 20-mL aliquots were taken from stock solutions Gb, Sb, and HAb. In G+HA and S+HA, 10- and 20-mL aliquots were applied from stock solutions HAC and HAB, respectively, followed by addition of 20-mL aliquots from Gb or Sb to the appropriate treatments. Where necessary, appropriate volumes of distilled water were applied to each soil sample before the amendments to bring the total moisture content to 30 mL (i.e., 30% moisture content, which is the field capacity of the soil). The control received 30 mL of distilled water. Because diethylether is very volatile, the total volume in the soils treated with S was also brought to 30 mL after 1 h from the S addition. After 7-, 15-, or 40-d incubation at ≈25°C, aggregate stability in water was measured.

Experiment 2 studied the effects of rates of application of G and S (alone or in combination with HA) and HA alone on AS of Soils A and B. The experimental design was a 5 by 2 by 4 factorial in a completely randomized design with three replications. The five amendments (G, S, HA, G+HA, and S+HA) constituted the first factor, the two soils (A and B) were the second factor, and four rates of application (0, 0.5, 1.0, and 5.0 g kg⁻¹ for G and S and 0, 0.05, 0.1, and 0.2 g kg⁻¹ for HA), the third factor. Lower rates of HA than in the literature (Tschapek et al., 1973; Chaney and Swift, 1986; Piccolo and Mbagwu, 1989, 1994) were deliberately used in order to assess the interaction of HA rate with G and S and also to account for rates that could be used practically and economically in the field (Piccolo et al., 1996b, 1997). To attain these rates, 20-mL aliquots were taken from stock solutions Ga, Gb, and Gc for G and G+HA treatments; Sa, Sb, and Sc for S and S+HA treatments; and from HAa, HAB, and HAC for HA alone treatments. For G+HA the soil was pretreated with 10-mL aliquots from stock solution HAC 1 h before addition of the appropriate aliquots from the G stock solutions. Similarly, for S+HA the soil was pretreated with 20-mL aliquots from stock solution HAb 1 h before adding the required aliquots from S stock solutions. Again taking into account that the S solvent is volatile, appropriate volumes of distilled water were added (where necessary) to each soil sample to bring the total volume to 30 mL (as in Exp. 1). The control received 30 mL of water. After incubation for 15 d (at ≈25°C), samples were allowed to air dry before measuring AS.

In both experiments distilled water was used to replenish moisture lost by evaporation from the treatments every other day. Water and the stock solutions were either applied by capillarity suction or by slow addition at samples' edges so that no slaking of soil particles occurred and the samples were not disturbed throughout the duration of incubation.

Measurement of Aggregate Stability

The percentage of water-stable aggregates (WSA) > 0.5 mm index was used as a measure of AS in water because it is recognized as the agriculturally most important size fraction (Watts et al., 1996; Coughlan et al., 1973). Twenty grams of soil presoaked in distilled water for 30 min were placed on the topmost of a nest of four sieves with diameters of 2.00, 1.00, 0.50, and 0.25 mm. Using an apparatus similar to that described by Kemper and Rosenau (1986), sieves were vertically oscillated in water for 20 sec (4-cm stroke, 1 oscillation s⁻¹). Resistant soil materials on each sieve and the unstable (<0.25 mm) aggregates were quantitatively transferred into beakers, dried in the oven at 60°C for 48 h, and then weighed.

Correction for the sand fraction accumulated in the sieves was made to ensure that only the real aggregates were determined. After drying, the corrected total weights of all the resistant aggregates >0.50 mm were used to calculate the WSA > 0.50 mm index as the percentage ratio of this total weight to that of the initial weight sieved (20 g). Higher values indicated better stability.

To evaluate the state of aggregation of the samples following wet-sieving, the cumulative size distribution percentage of aggregate sizes was tabled against the aggregate diameters (Dinel et al., 1991b). The state of aggregation according to Allison (1973) is the set of naturally occurring discrete clusters or groups of soil particles (or peds) that can only exist if the forces holding the particles together are stronger than the forces between adjacent aggregates. A comparison of the cumulative size distribution of the control and treated samples gives an indication of the extent to which the treatments were effective in aggregating the smaller particles into larger clusters or aggregates. All data were analyzed by analysis of variance (ANOVA) for a factorial design.

RESULTS

Data Analysis and Role of Native Organic Matter Content

Our results indicated that amendment type, incubation period, and OM status all had significant effects on aggregation. Table 1 shows that the *F* values of the ANOVA for the effects of incubation periods on AS were significant for amendments, incubation period, OM status, amendments × OM, and OM × incubation period. Also, the *F* values for the effects of rates of amendment on AS (Table 1) were significant for amendments, application rates, OM status, amendments × OM, and OM × application rates.

Removal of OM decreased AS significantly (Table 2). The AS values in the control treatments at 7 d of incubation were 9.0% for Soil A (-OM) and 12.7% for Soil B (+OM). Relative to Soil B this represents a reduction of ≈40% (Table 2). Between the 15 and 40 d of incubation an average reduction in AS of 22% was observed. The AS values of Soil A (-OM) remained virtually constant throughout the incubation, whereas those of

Table 1. *F* values of the analysis of variance (ANOVA) of treatment effects on soils.

Source of variation	df	<i>F</i> values	Significance levels (<i>P</i>)
Incubation period			
Amendments (A)	5	15.08	**
Organic matter level (OM)	1	14.63	**
A × OM	5	9.79	*
Incubation period (T)	2	13.85	**
A × T	10	5.66	NS
OM × T	2	8.74	*
A × OM × T	10	10.22	NS
Application rates			
Amendments (A)	4	17.81	**
OM level (OM)	1	8.37	*
A × OM	4	10.59	*
Application rates (R)	3	23.01	*
A × R	12	3.89	NS
OM × R	3	8.78	*
A × OM × R	12	3.11	NS

*, ** Significant at 0.05 and 0.01 probability levels, respectively; NS is not significant.

Table 2. Variation in aggregate stability percentage (water-stable aggregates [WSA] >0.50 mm) of unamended soils at different incubation periods.

Soils†	Days after incubation			Relative change at 40 d‡
	7	15	40	
A (-OM)	9.0	9.1	9.2	2.2
B (+OM)	12.7	11.0	11.2	-11.8
% decrease§	41.1	22.2	21.7	-

† OM = organic matter.

‡ Relative change (RC) = $\{[(WSA_{40})/(WSA_7)] 100\}$, where 40 = 40 d and 7 = 7 d after incubation; a negative value indicates a reduction in WSA relative to Day 7.

§ % decrease = $\{[(WSA_B/WSA_A) - 1] 100\}$, where A = soil where OM was removed and B = soil where OM was retained.

Soil B (+OM) decreased by $\approx 12\%$ after 40 d of incubation. This suggests microbial degradation of the native OM in Soil B.

State of Aggregation

In both the incubation period and rate of amendment studies, the state of aggregation was generally better in Soil A (-OM) than Soil B (+OM) especially with G and G+HA (Tables 3-5). The state of aggregation decreased between 7 and 40 d of incubation in Soil A (-OM) (Tables 3 and 4). At 40 d the distribution of aggregates in this soil was similar for the control and amended samples (Table 4). The addition of the easily biodegradable G increased the percentage of the stable aggregates (>0.25 mm) at 7 d, thereby showing the best aggregation improvement among the treatments (Table 3). However, pretreatment with HA reduced slightly this G-induced high state of aggregation.

Conversely, soil B (where OM was retained) showed a significantly lower state of aggregation at 7 d but still with G and G+HA outperforming all other treatments (Table 3). However, at 40 d the aggregation effect due to G had waned to such an extent that soil samples pretreated with HA before application of S and those with S alone had a significantly higher aggregation than the rest of treatments (Table 4). Hence the high state of

aggregation induced by the hydrophilic polysaccharide gum was only transient, whereas that resulting from the hydrophobic stearic acid improved with time, especially on soil where the native OM was present.

Similarly, at the highest rates of the amendments, higher aggregation states were observed for G and G+HA in Soil A (-OM) than Soil B (+OM) (Table 4). However, in both soils, pretreatment with HA reduced significantly the aggregation effect of the polysaccharide gum. The best three treatments in Soil A (-OM) were: $G > G+HA > S+HA$, whereas in Soil B (+OM) the order was: $G > S+HA > S$. Hence, it appears that when the rather hydrophobic HA (highly rich in aliphatic and aromatic C) was added to soil prior to amendment with the hydrophilic polysaccharide gum the result was a reduction in aggregation state of the soil, thereby indicating antagonism between G and HA. Conversely, the synergistic effect of HA and S was shown by the enhancement of soil aggregation when the soil was pretreated with HA before adding the hydrophobic stearic acid.

Aggregate Stability of Incubated Samples

In Soil A (-OM) the highest AS values were obtained with addition of G followed by G+HA after 7 and 15 d (Fig. 1). However, at the 40 d of incubation, AS decreased by 74% for G and by 79% for G+HA relative to the 7 d values (Table 6). Therefore pretreatment with HA reduced the effectiveness of G by 21% in comparison with the treatment with G alone. The reverse occurred with S and S+HA since AS increased up to 15 d, followed by a slight decrease at 40 d. In fact, the HA pretreatment improved the effectiveness of S at 7 and 15 d, whereas at 40 d there was no significant difference between S and S+HA (Fig. 1). Also relative to the Day 7, AS increased by 30% for S alone and by 45% for S+HA at 15 d, but decreased slightly at 40 d (-4.7%) for the latter treatment (Table 6). Hence HA pretreatment enhanced the effectiveness of S by 15% after 15 d of incubation. The effectiveness of HA alone was optimum at 15 d, where a relative improvement of 20% was obtained.

Table 3. State of aggregation for two soils 7 d after application of amendments.

Soil†	Amendment‡	Cumulative water-stable aggregates			
		>1.00 mm	1.00-0.50 mm	0.50-0.25 mm	<0.25 mm
%					
Soil A (-OM)	C	2.07	8.98	13.28	100
	G	34.80	43.39	52.96	100
	S	2.62	9.26	20.56	100
	HA	2.34	9.22	20.60	100
	G+HA	32.10	41.54	52.03	100
	S+HA	3.06	10.63	22.05	100
Means (SE)		3.20	3.41	3.20	0.00
Soil B (+OM)	C	3.30	12.71	31.45	100
	G	6.20	22.30	57.01	100
	S	4.75	14.01	37.31	100
	HA	3.80	13.05	42.42	100
	G+HA	5.05	18.09	52.64	100
	S+HA	4.17	14.79	35.12	100
Means (SE)		0.21	0.74	2.01	0.00

† OM = organic matter.

‡ C = control, G = polysaccharide gum (hydrophilic), S = stearic acid (hydrophobic), HA = humic acid (hydrophobic), G+HA = gum added to soil pretreated with HA, S+HA = stearic acid added to soil pretreated with HA.

Table 4. State of aggregation for two soils 40 d after application of amendments.

Soil†	Amendment	Cumulative water-stable aggregates			
		>1.00 mm	1.00–0.50 mm	0.50–0.25 mm	<0.25 mm
		%			
Soil A (–OM)	C	2.13	9.20	23.50	100
	G	2.17	11.22	25.46	100
	S	2.31	10.67	25.05	100
	HA	2.27	9.06	19.93	100
	G+HA	2.05	9.34	22.86	100
	S+HA	2.24	10.10	22.65	100
	Means (SE)		0.02	0.18	0.40
Soil B (+OM)	C	3.00	11.15	26.35	100
	G	2.78	9.58	23.23	100
	S	5.34	13.88	35.44	100
	HA	2.86	10.81	25.39	100
	G+HA	3.46	10.90	24.85	100
	S+HA	5.98	15.03	28.50	100
	Means (SE)		0.28	0.42	0.87

† OM = organic matter.

‡ C = control, G = polysaccharide gum (hydrophilic), S = stearic acid (hydrophobic), HA = humic acid (hydrophobic), G+HA = gum added to soil pretreated with HA, S+HA = stearic acid added to soil pretreated with HA.

In Soil B (+OM) AS was best in G and G+HA-treated soils only at 7 d, beyond which a substantial reduction occurred (Fig. 2). At 40 d, AS values (especially in G alone) were lower than those obtained in the control (Fig. 2). Conversely, S and S+HA increased AS up to 15 d. The HA pretreatment improved the aggregate stabilization effect of S so that, at the 15 and 40 d, the highest AS values were obtained in the S+HA treatments. In contrast to this, at the 15 d of incubation, AS decreased by 13% in the control, by 47% in G, and by 42% in G+HA (Table 6). At 40 d the respective decreases were 12% for the control, 57% for G, and 40% for G+HA. This showed that in relative terms HA also preserved somewhat the effect of G on AS. The AS of HA alone decreased by 15 to 18%, with incubation time relative to values at 7 d. Pretreatment with HA before addition of S produced a significant synergistic effect in AS from Day 15 (Fig. 2). Relative to Day 7, improvement in AS was 27% for S and 39% for S+HA at 15 d (Table 6). Beyond this day AS was reduced but still slightly higher than the Day 7 values.

With reference to the unamended soils (Table 7), G

increased AS by 382, 264, and 22% at 7, 15, and 40 d of incubation in Soil A (–OM), whereas pretreatment with HA reduced the effectiveness of G by 20, 2, and 21%, respectively, for the same incubation period. The HA pretreatment before S enhanced AS at 7 d by 18% and at 15 d by 69%. When compared with S alone the S+HA treatment gave a relative increase in AS of 15% at 7 d and 36% at 15 d. It was only at 15 d that a significant increase in AS of 21% was obtained with HA alone.

Similar trends were obtained on Soil B (+OM) although the relative improvements in AS obtained from G and G+HA were lower than in Soil A (–OM) (Table 7). Conversely, higher relative improvements in AS compared with the controls were obtained from S and S+HA in this soil than in Soil A. Relative to S alone, S+HA improved AS by 7% at 7 d, 26% at 15 d, and 10% at 40 d (Table 7).

Aggregate Stability and Rates of Amendments

In Soil A (–OM), AS was a direct function of amount of amendment applied (Fig. 3). At the highest rate the

Table 5. State of aggregation for two soils at the highest rate of amendment 15 d after application of amendments.

Soil†	Amendment	Cumulative water-stable aggregates			
		>1.00 mm	1.00–0.50 mm	0.50–0.25 mm	<0.25 mm
		%			
Soil A (–OM)	C	1.91	9.12	20.54	100
	G	70.43	77.53	84.63	100
	S	13.10	20.25	30.83	100
	HA	3.32	11.50	24.03	100
	G+HA	27.04	37.37	47.70	100
	S+HA	16.59	24.84	36.99	100
	Means (SE)		5.08	5.08	4.71
Soil B (+OM)	C	2.78	11.13	16.92	100
	G	17.96	48.42	68.04	100
	S	12.84	23.34	39.69	100
	HA	3.36	17.26	20.52	100
	G+HA	5.01	13.27	22.53	100
	S+HA	13.49	30.83	50.08	100
	Means (SE)		1.27	2.79	4.03

† OM = organic matter.

‡ C = control, G = polysaccharide gum (hydrophilic), S = stearic acid (hydrophobic), HA = humic acid (hydrophobic), G+HA = gum added to soil pretreated with HA, S+HA = stearic acid added to soil pretreated with HA.

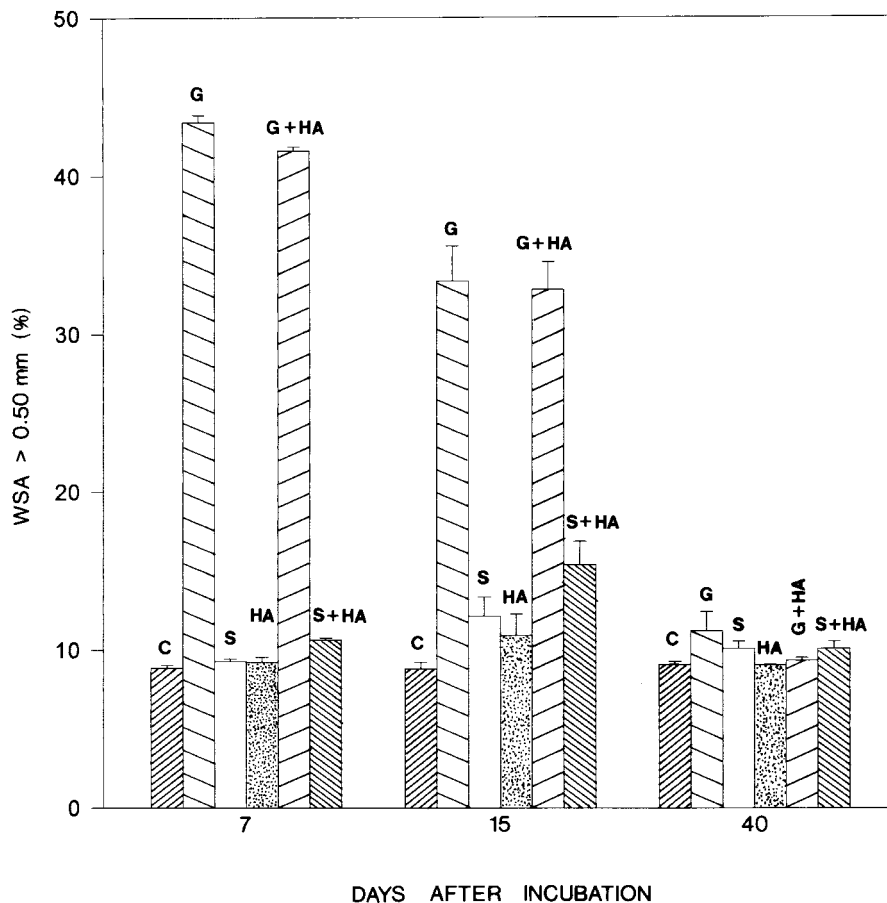


Fig. 1. Effects of incubation periods of different organic amendments on aggregate stability (percentage of water-stable aggregates [WSA] > 0.50 mm) of a soil from which organic matter was removed.

order of improvement was: G (76%) > G+HA (37%) > S+HA (25%) > S (20%) > HA (11%), where the figures in parentheses are the absolute AS values. In respect to the unamended soil, this represents relative improvements of 750, 308, 133, 100, and 27%, respectively (Table 8). Again the positive synergistic effect of S and HA was evident here, while the combination of HA with G produced an opposite effect.

In Soil B (+OM), a similar trend of AS increase with application rates was observed (Fig. 4). However, unlike the G and G+HA treatments, the combined action of S+HA progressively increased aggregate stability with increasing rates of added S. A significant effect of G was only observed at the highest rate of application.

At this highest rate the order of improvement was: G (48%) > S+HA (31%) > S (23%) > HA (17%) > G+HA (13%). Their respective relative improvements compared with the control were 335, 178, 131, 73, and 33% (Table 8). It is noteworthy that in the presence of native organic matter increasing amount of G added after a HA pretreatment did not have any effect on AS whereas this increased steadily with increasing S following the HA pretreatment. These results clearly show that both S and S+HA pretreatment performed better than G and G+HA in the presence of native OM. Conversely, both G and the mixture of G and HA were more effective when the native OM was removed from the soil. In Soil A (-OM) pretreatment with HA

Table 6. Percentage of change in aggregate stability (water-stable aggregates [WSA] > 0.50 mm) relative to the first 7 d of incubation as influenced by type of amendment.†

Soils‡	DAI	Treatments§					
		C	G	S	HA	G+HA	S+HA
%							
A (-OM)	15	1.0	-23.7	30.1	19.6	-20.9	45.3
	40	2.2	-74.2	13.0	-1.1	-79.1	-4.7
B (+OM)	15	-12.6	-47.0	27.1	-14.5	-42.0	39.2
	40	-11.8	-57.0	0.7	-17.6	-39.8	1.4

† Relative change (RC) = $\{[(WSA_{40})/(WSA_7) - 1] 100\}$, where 40 = 40 d and 7 = 7 d after incubation.

‡ OM = organic matter.

§ DAI = days after incubation, C = control, G = polysaccharide gum (hydrophilic), S = stearic acid (hydrophobic), HA = humic acid (hydrophobic), G+HA = gum added to soil pretreated with HA, S+HA = stearic acid added to soil pretreated with HA. Negative values indicate decrease in stability relative to 7 d after incubation.

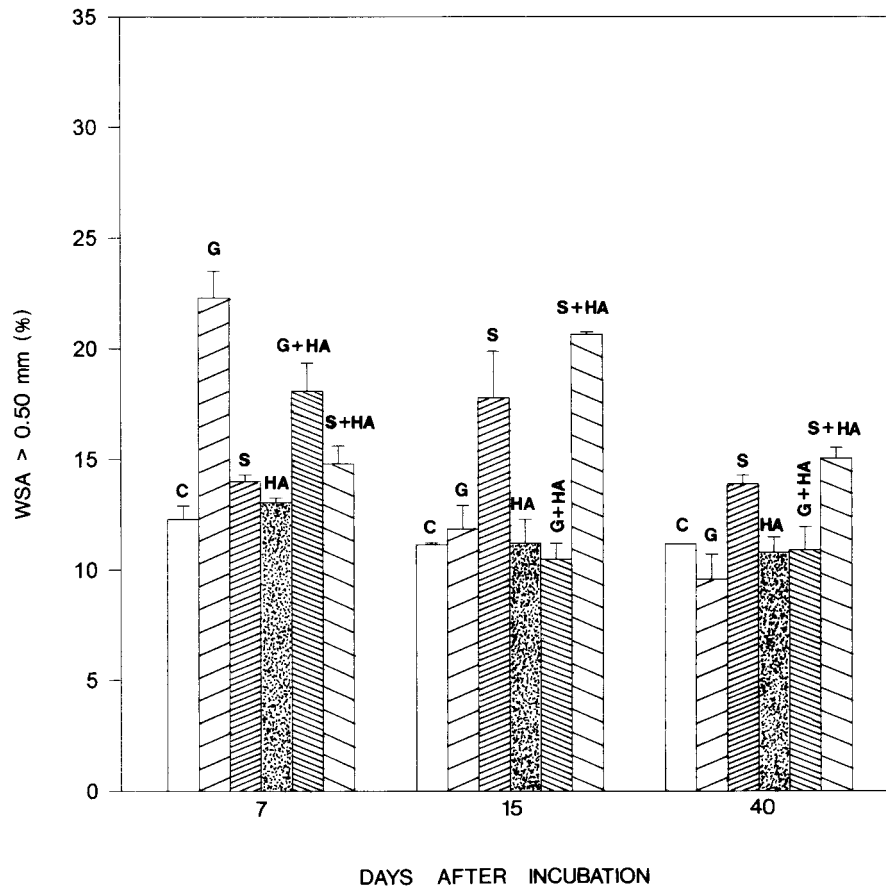


Fig. 2. Effects of incubation periods of different organic amendments on aggregate stability (percentage of water-stable aggregates [WSA] > 0.50 mm) of a soil in which organic matter was retained.

before adding G decreased AS by 442% whereas HA pretreatment before adding S increased AS by 33% relative to the control (Table 8). Similar observations made in Soil B (+OM) showed a decrease of 302% for G and an increase of 47% for S when in combination with the HA pretreatment (Table 8).

DISCUSSION

Results have shown that removal of native OM significantly reduced ($P = 0.05$) soil AS, confirming that OM is involved in stabilizing aggregates in this soil. Our experiments indicated that for both soils the effect of G, despite its extent, was only transient and diminished significantly ($P = 0.01$) during a short period of 40 d. Its effect was better on the soil where OM was removed than where it was retained. Moreover, pretreatment with HA before applying G very substantially reduced both the state of aggregation and AS. This showed that though G had a large but transient effect on AS the presence of either native OM or added HA considerably decreased its action, thereby indicating a limited aggregating capacity of polysaccharides in natural conditions. With stearic acid, AS increased slowly with incubation period (up to 15 d). Contrary to what is observed with G, the effect of S was better on soil with its native OM retained (Soil B) than where it was removed (Soil A) and HA pretreatment enhanced its effectiveness as an

aggregating agent. Apparently because of the very low rates used, the relative improvement in AS obtained by HA addition was low. However, at the highest rate used (0.2 g kg^{-1} , equivalent to 400 kg ha^{-1} assuming a bulk density of 1.3335 g cm^{-3} and a depth of incorporation of 0–15 cm), HA increased AS more in soil with native OM than where OM was removed. All these results suggest that AS in soil is better maintained by hydrophobic moieties interacting with each other (S with native

Table 7. Percentage of change in aggregate stability (water-stable aggregates [WSA] > 0.50 mm) relative to the unamended soils as influenced by type of amendment and incubation period.†

Soils‡	DAI§	Treatments				
		G	S	HA	G+HA	S+HA
%						
A (-OM)	7	382	3	2	362	18
	15	264	33	21	262	69
	40	22	16	1	1	10
B (+OM)	7	76	10	3	43	17
	15	6	60	1	-5	86
	40	-14	24	-4	-4	34

† Relative change (RC) = $\{[(\text{WSA}_t/\text{WSA}_c) - 1] 100\}$, where t = treated and c = control.

‡ OM = organic matter.

§ DAI = days after incubation.

|| C = control, G = polysaccharide gum (hydrophilic), S = stearic acid (hydrophobic), HA = humic acid (hydrophobic), G+HA = gum added to soil pretreated with HA, S+HA = stearic acid added to soil pretreated with HA. Negative values indicate decrease in stability relative to 7 d after incubation.

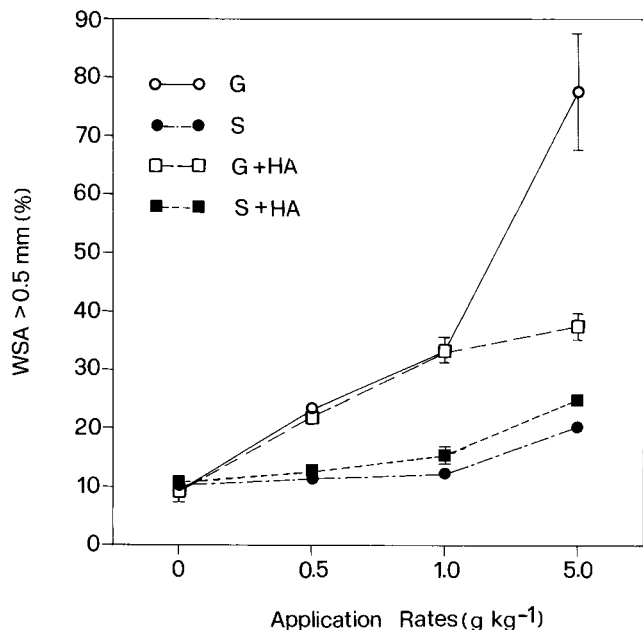


Fig. 3. Effects of application rates of different organic amendments on aggregate stability (percentage of water-stable aggregates [WSA] > 0.50 mm) of a soil from which organic matter was removed.

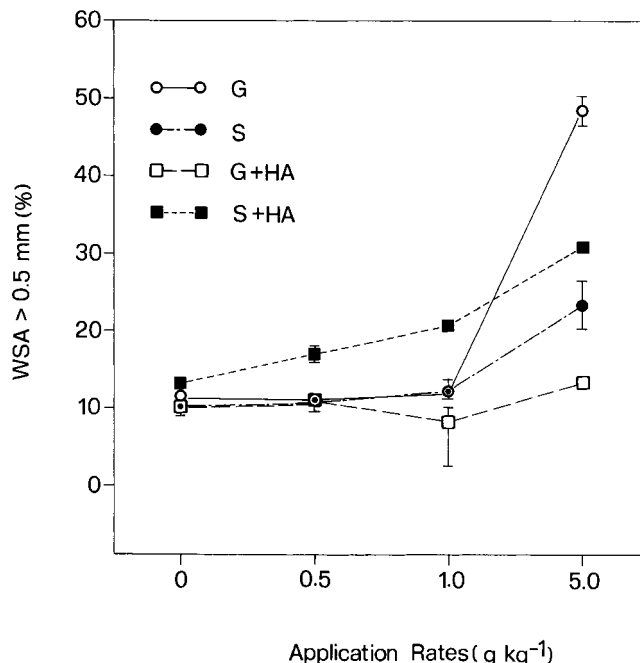


Fig. 4. Effects of application rates of different organic amendments on aggregate stability (percentage of water-stable aggregates [WSA] > 0.50 mm) of a soil in which organic matter was retained.

OM, S with HA, native OM with HA) than by hydrophilic binding agents.

The observation that OM removal reduced both the state of aggregation and AS of the soil is in conformity with the results of others (Chaney and Swift, 1984; Haynes et al., 1991). Organic matter removal by hydrogen peroxide, while by no means comparable to natural oxidation processes, was intended to approximate the degraded soil conditions occurring under intensive mechanized cultivation of arable lands without input of organic materials. Natural processes of OM accumulation such as root exudation or biological decomposition of fresh organic matter in soil are recognized to only slowly reestablish the stable humus pool in such degraded soils (Piccolo, 1996). Hence it is necessary to assess what chemical composition of soil amendments would rapidly improve the physical quality of degraded soils, if soil management practices had to be effective.

Previous results have shown that addition of humic substances to soils and especially the humic fraction of

high molecular size is effective in enhancing microaggregate stability (Piccolo and Mbagwu, 1990). An explanation for this effect is the formation of humic-clay complexes which may confer a hydrophobic character to the surfaces of soil aggregates due to the aliphatic and aromatic components of humic substances (Piccolo and Mbagwu, 1989).

On the other hand, a large literature has shown that the addition to a soil of a hydrophilic component of organic matter such as a polysaccharide can increase the amount and size of water-stable aggregates, especially in soils with low total OM (Hepper, 1975; Tisdall and Oades, 1982; Theng, 1982; Lynch and Bragg, 1985; Angers and Mehuys, 1989). However, it has been repeatedly pointed out that the effect of polysaccharides and of other carbohydrates on soil AS is only transient and never exceeds a few weeks (Chaney and Swift, 1986; Mbagwu, 1989).

Our results confirmed that the aggregation and the aggregate-stabilizing effect of a hydrophilic polysaccharide of high molecular weight was generally better in the soil where OM was removed than where it was retained but totally disappeared after 40 d in both cases. The enhancement of AS by high molecular-weight galactomannan polymer added to the soil without OM is explained by the high number of associations that may be established between the polysaccharides and the soil inorganic particles (Tisdall and Oades, 1982; Gu and Doner, 1992). The AS improvement in such a physically degraded soil had to be expected by any cementing agent. However, it was also expected that the carbohydrates effect would not have lasted long. During incubation soil microbial activity breaks down the polysaccharide chain and progressively annuls its interparticle aggregating effect (Insam, 1996).

Table 8. Improvement in aggregate stability (water-stable aggregates [WSA] > 0.50 mm) relative to the unamended soils at the highest rate of amendments.†

Soils‡	Treatments§				
	G	S	HA	G+HA	S+HA
	%				
A (-OM)	750	100	27	308	133
B (+OM)	355	131	73	33	178

† Relative improvement (RI) = $\{[(WSA_t/WSA_c) - 1] 100\}$, where t = treated at the highest rate of amendment; c = control.

‡ OM = organic matter.

§ C = control, G = polysaccharide gum (hydrophilic), S = stearic acid (hydrophobic), HA = humic acid (hydrophobic), G+HA = gum added to soil pretreated with HA, S+HA = stearic acid added to soil pretreated with HA. Negative values indicate decrease in stability relative to 7 d after incubation.

A novel finding of our experiments was the reduced effectiveness of the polysaccharide on the soil where the OM was retained and the further limitation of the gum action when both soil A (-OM) and soil B (+OM) were pretreated with HA. Haynes and Swift (1990) and Haynes (1993) studied aggregate stability of pasture soils vs. air drying. They speculated that in addition to the partial hydrophobic characteristics imparted by humic substances, another reason for the high AS of pasture soils is the formation of intermolecular associations between the organic materials (i.e., between humic substances and polysaccharides), which should enhance interparticle binding. In the case of polysaccharides, our study suggested an opposite effect by showing that the combination of HA and gum reduced AS relative to gum alone. This indicates that intermolecular association of the gum with either the native OM or the preadded HA was not effective in either enhancing soil aggregation or protecting the polysaccharide from microbial degradation.

Conversely, addition of stearic acid, a long-chain hydrophobic acid, had a slow but more lasting effect on state of aggregation and AS on the soil in which native OM was present than on that where it was removed. These results not only further clarify the actual aggregating mechanism of the process described by Haynes (1993) but agree with the works of Diné et al. (1991a, 1991b, 1992). The latter authors compared amendments with beeswax and peat fibric materials onto only one soil and reported higher soil aggregation with hydrophobic beeswax rich in aliphatic moieties than with fibric materials rich in polysaccharides. We further confirmed the beneficial effects of hydrophobic compared with hydrophilic amendments on two soils of different physical quality.

Of particular interest was the synergistic effect of S with HA on the state of aggregation and AS. At 40 d of incubation this effect was still persistent and was the most effective of all the amendments. The lignite HA used here contains higher amounts of hydrophobic than hydrophilic components and it is probably more similar to the hydrophobic S than to the hydrophilic polysaccharides. Stearic acid may thus favorably interact with either the native OM or the preadded HA through hydrophobic forces such as van der Waals bonds and can be considered to become part of the hydrophobic components of organic matter (Piccolo et al., 1996a). Such interactions are expected to increase the hydrophobic character of soil particles and promote interparticle hydrophobic associations which enhance the overall soil aggregation. Moreover, the hydrophobicity of aggregate surfaces may protect the binding agent from microbial attack, thereby enhancing its long-term effectiveness. The hydrophobic association of S with humic matter is also capable of reducing water entry into soil aggregates because of increased surface tension that makes them water repellent. The overall effect is enhanced soil structural stability, which is more lasting than that obtained from polysaccharide gum.

Addition of HA alone was more effective on the soil where native OM was retained and AS was significantly

increased (73%) over the control at the highest rate of HA (0.20 g kg⁻¹). This result supports earlier reports (Tschapek et al., 1973; Chaney and Swift, 1986; Piccolo and Mbagwu, 1994). Since this rate is equivalent to 400 kg ha⁻¹, this result reinforces our earlier conclusion that HA from highly humified material such as lignite or oxidized coal represent economically available sources of soil conditioner for the rehabilitation of physically degraded soils (Piccolo et al., 1997). While previous work (Ae et al., 1987; Piccolo and Mbagwu, 1989, 1994) attributed the aggregate stability improvement to the formation of clay-humic complexes via polyvalent cations, the results of this work and the indication that humic substances are stabilized by hydrophobic forces (Piccolo et al., 1996a), suggest that soil aggregation may also be favoured and maintained in large degree by interparticle hydrophobic associations.

In conclusion, these results have implications for SOM management practices to enhance stable OM pools, which would improve structural stability of fragile soils. Our study showed that organic materials composed predominantly of hydrophobic constituents are likely to be more effective and long-lasting aggregate-binding agents than those mainly made of hydrophilic compounds such as in root exudates or as polysaccharides of plant tissues. Soil amendments with exogenous "humified" or hydrophobic OM appear to be more suitable to rapidly improve soil physical quality than traditional practices based on soil incorporation of fresh organic matter.

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