EFFECT OF ALUMINUM AND IRON OXIDES AND ORGANIC MATTER ON FLOCCULATION AND DISPERSION OF ARID ZONE SOILS

SABINE GOLDBERG,[1] B. S. KAPOOR,[2] AND J. D. RHOADES[1]

We investigated the structural stabilities of eight arid zone soils using percent optical transmittance as a measure of flocculation-dispersion behavior. The soils were sodium saturated and their stabilities determined in sodium chloride solutions of varying concentrations. We treated the soils with hypochlorite for organic matter removal, with oxalate for removal of amorphous aluminum and iron oxides, and with dithionite for removal of crystalline aluminum and iron oxides. The removal of amorphous and/or crystalline oxides increased the clay dispersivity. This indicated that amorphous and crystalline oxides play important, stabilizing roles in soil structure. The removal of organic matter decreased the clay dispersivity. This indicated that dissolved organic matter enhances clay dispersion. The well-known positive effect of organic matter on soil structure probably occurs through binding of soil particles by roots and hyphae at the aggregate level, but at the clay-particle level the negative charge of organic anions enhances clay dispersion.

Good tilth and stable soil structure are important requirements for productivity of cultivated soils. Structure of nonsaline, nonsodic soils is usually evaluated by determining the stability of soil aggregates. Aggregate stability is related to soil texture, organic matter content, iron oxide content (Kemper and Koch 1966), and aluminum oxide content (Bartoli et al. 1988a,b).

In arid zone soils, structure is often adversely affected by excess sodium in the soil solution and on the soil exchange complex. Sodic conditions can lead to aggregate slaking and disintegration, clay dispersion, particle migration, and plugging of water-conducting pores, thereby ultimately reducing soil-infiltration rates (Shainberg and Letey 1984). Two of the most signifi-

[1] USDA-ARS, U.S. Salinity Laboratory, 4500 Glenwood Drive, Riverside, CA 92501.
[2] Department of Chemistry, University of Delhi, Delhi—110007, India.

cant factors affecting clay dispersion are the electrolyte concentration and the sodicity of the irrigation water (Rengasamy et al. 1984).

Gupta et al. (1984) observed that additions of farmyard manure increased clay dispersion of a salt-affected soil at high sodium adsorption ratio (SAR). Shanmuganathan and Oades (1982a,b) decreased the amount of dispersible clay in an illitic soil by applying iron polycations. Because arid zone soils are usually low in organic matter and aluminum and iron oxide content, the effects of native amounts of these constituents on clay dispersion are difficult to investigate directly. Indirect evidence provided by factor analysis (Goldberg et al. 1988) suggests that aluminum and iron oxides play an important role as binding agents in the structure of arid zone soils. McNeal et al. (1968), measuring hydraulic conductivity of Hawaiian soils before and after iron oxide removal, showed that iron oxides stabilize the soils against dispersion under high-sodium and low-salt conditions. They postulated that iron oxides were also important in stabilizing an arid zone soil high in iron oxides studied by McNeal and Coleman (1966).

The objective of this study was to evaluate the role of native organic matter and aluminum and iron oxide contents on a commonly used index of aggregate stability of some arid zone soils. We investigated the flocculation-dispersion behavior of selected arid zone soils before and after various selective dissolution treatments.

MATERIALS AND METHODS

Soil classifications and chemical characteristics are given in Table 1. We determined cation exchange capacity (CEC) using the method for arid-land soils described by Rhoades (1982). Inorganic carbon (IOC) and organic carbon (OC) were analyzed as described by Nelson and Sommers (1982). We measured specific surface area using ethylene glycol monoethyl ether (EGME) adsorption as described by Cihacek and Bremner (1979). Clay mineralogy was determined on <2-μm, Mg-saturated fractions by x-ray diffraction analysis. We removed organic matter using sodium hypochlorite (Lavkulich and Wiens

TABLE 1

Classifications and chemical characterization of soil series

Soil	General character	Depth cm	CEC[a] mmol$_c$ kg^{-1}	IOC[b]	OC[c] %	SA[d] m^{2}g^{-1}	Dominant clay minerals[e]
Altamont	fine, montmorillonitic, thermic Typic Chromoxerert	0–25	152	0.001	0.85	102.5	smectite, illite, mixed-layer
Arlington	coarse-loamy, mixed, thermic Haplic Durixeralf	0–25	107	0.060	0.51	61.1	illite, smectite, mixed-layer, vermiculite
Bonsall	fine, montmorillonitic, thermic Natric Palexeralf	0–25	54	0.001	0.60	32.9	kaolinite, illite, smectite, mixed-layer, vermiculite
Fallbrook	fine-loamy, mixed, thermic Typic Haploxeralf	0–25	112	0.020	0.38	68.3	kaolinite, illite, mixed-layer, smectite, vermiculite
Imperial	fine, montmorillonitic (calcareous), hyperthermic Vertic Torrifluvent	Surface clods	222	1.88	0.89	196.0	smectite, illite, kaolinite, mixed-layer
Twisselman	fine, mixed (calcareous), thermic Typic Torriorthent	Surface	197	0.170	0.56	182.4	smectite, illite, chlorite, mixed-layer
Pachappa	coarse-loamy, mixed, thermic Mollic Haploxeralf	0–25	39	0.010	0.49	36.3	illite, smectite, mixed-layer
Ramona	fine-loamy, mixed, thermic Typic Haploxeralf	0–25	66	0.002	0.56	27.9	illite

[a] Cation exchange capacity.
[b] Inorganic carbon.
[c] Organic carbon.
[d] Specific surface area.
[e] Mixed-layer means 1.0–1.4 nm interstratification.

1970). Pyrophosphate-extractable, oxalate-extractable, and dithionite-extractable iron and aluminum oxides were determined as described by McKeague et al. (1971). These extractants are considered to have minimum effect on clay minerals. We analyzed all extracts for Fe, Al, and Si concentrations using inductively coupled plasma (ICP) emission spectrometry.

The <2-mm soil fraction of each soil was used throughout the study. Flocculation-dispersion behavior was investigated on untreated, hypochlorite-treated, hypochlorite/oxalate-treated, and hypochlorite/dithionite-treated soil samples. Before use, the samples were Na-saturated using 1 M NaCl, washed in sequence with water, 1:1 acetone: water, and acetone, centrifuged until free of Cl$^-$, and air dried. Subsamples of 0.5 g of soil were weighed into a series of 60 mL centrifuge tubes. Aliquots of 20 mL of NaCl solutions ranging in concentration from 0.01 to 0.25 M were added to the tubes; these were stoppered and shaken in a horizontal shaker for 30 min at 100 strokes per min. The tubes were left to stand for 20 h. Then, the upper 5 mL portion of each suspension was pipetted into a spectrophotometer cuvette. The optical transmittance (T) was measured in a Spectronic 20 which had been set to 100% T at a wavelength of 420 nm using distilled water. Felhendler et al. (1974) have indicated that at constant temperature and wavelength and for similar clays the optical density is proportional to the logarithm of the concentration of clay particles.

To further test the effect of organic matter on flocculation-dispersion behavior, the 5 mL aliquots of supernatant from the untreated soil samples were added back to the hypochlorite-treated samples which were still in the centrifuge tubes after decantation. These samples were again shaken, left to settle, and the per-

cent T of the upper 5 mL determined. In this fashion, the percent T of the identical soil sample could be compared both in the presence and absence of native, dissolved organic matter.

RESULTS AND DISCUSSION

An approximate differentiation can be made between organically-complexed Fe, amorphous Fe, and crystalline Fe oxides in soils by selective extraction with pyrophosphate, oxalate, and dithionite. These extractants are less specific and therefore less useful in differentiating Al forms than Fe forms (McKeague et al. 1971). Table 2 provides values for pyrophosphate-, oxalate-, and dithionite-extractable forms of Fe, Al, and Si. The difference between oxalate- and pyrophosphate-extractable is an estimate of amorphous forms, and the difference between dithionite- and oxalate-extractable is an estimate of crystalline forms. These values are also provided in Table 2.

The Altamont soil contains significantly more organically-bound Fe and Al than the other soils, whereas the Imperial and Twisselman soils contain the least amounts of these constituents. The Imperial soil contains the lowest amount of amorphous Fe, whereas the Twisselman soil has no measurable amount of crystalline Fe oxides. The amounts of extractable Fe consistently increase with extractant strength (pyrophosphate < oxalate < dithionite) as expected, whereas the amounts of extractable Al and Si are more variable. This result indicates that the extractants are less specific for Al and Si than for Fe.

Flocculation-dispersion behavior for four of the soils before and after selective dissolution treatments is presented in Fig. 1. The hypochlorite-treated samples were the least dispersed, requiring less salt to flocculate than even the controls. This result suggests indirectly that the presence of organic matter enhances clay dispersion, an observation previously found for farmyard manure by Gupta et al. (1984).

Hypochlorite/dithionite-treated samples were always more dispersive than the hypochlorite/oxalate-treated samples, which in turn were more dispersive than the hypochlorite-treated samples. These results indicate an important role for both amorphous and crystalline oxides in stabilizing soil clay against dispersion. Bartoli et al. (1988a) suggested that both crystalline and amorphous aluminum and iron oxides can act as aggregating agents in various soil types. The much greater dispersivity of hypochlorite/dithionite-treated Twisselman soil over the hypochlorite/oxalate treated sample is due to its much higher solution pH.

The untreated Altamont and Ramona soils were more dispersive than the untreated Imperial and Twisselman soils (Fig. 1). This result is surprising because these two soils are prone to structural problems under cultivation. Despite Na saturation, all of the soils released Ca during the flocculation-dispersion experiment, decreasing the SAR of the solutions below ∞. Release of Ca was much greater for the two calcareous soils Imperial and Twisselman, explaining their apparent reduced sensitivity to dispersion. Salt

TABLE 2

Analyses of extracts obtained from selective dissolutions[a]

Soil	Pyrophosphate[b]			Oxalate			Dithionite			Oxalate-Pyrophosphate[c]			Dithionite-Oxalate[d]		
	Fe	Al	Si	Fe	Al	Si	Fe	Al mg l^{-1}	Si	Fe	Al	Si	Fe	Al	Si
Altamont	59.3	71.1	158	171	45.7	43.4	688	64.5	136	112	—[e]	—	517	18.8	92.6
Arlington	7.96	10.3	25.9	242	43.0	58.7	759	48.1	103	234	32.7	32.8	517	5.1	44.3
Bonsall	18.2	21.0	33.6	129	22.6	22.3	962	51.4	77.2	111	1.6	—	833	28.8	54.9
Fallbrook	11.6	16.6	25.9	242	46.1	42.2	610	44.3	80.3	230	29.5	16.3	368	—	38.1
Imperial	5.53	4.71	27.4	92.7	37.9	76.2	503	39.2	171	87.2	33.2	48.8	410	1.3	94.8
Twisselman	3.71	3.12	47.0	162	114	197	161	38.6	208	158	108	150	—	—	11.0
Pachappa	19.4	11.0	15.5	294	42.1	39.2	670	45.1	62.0	275	31.1	23.7	376	3.0	22.8
Ramona	22.4	19.5	24.7	167	29.7	23.4	401	39.2	73.8	145	10.2	—	234	9.5	50.4

[a] Data for three combined extractions in duplicate.
[b] Represents organically-bound forms.
[c] Represents amorphous forms.
[d] Represents crystalline forms.
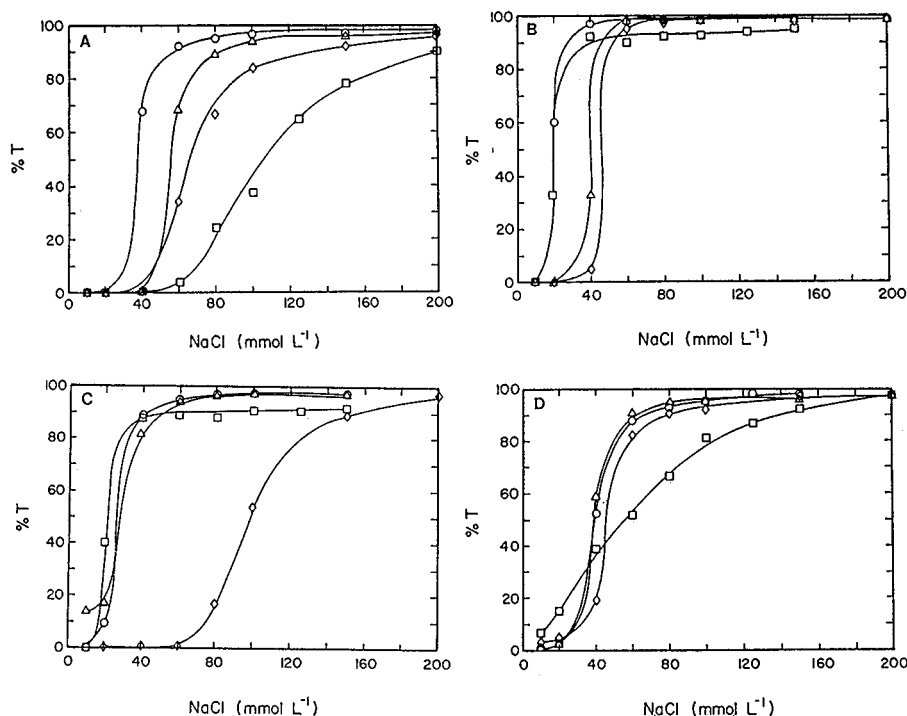[e] Dashes represent negative, therefore null, concentrations.

FIG. 1. Flocculation-dispersion behavior of arid zone soils: (a) Altamont; (b) Imperial; (c) Twisselman; (d) Ramona. Squares represent untreated soil. Circles represent hypochlorite-treated soils. Triangles represent hypochlorite/oxalate-treated soils. Diamonds represent hypochlorite/dithionite-treated soils.

TABLE 3

Salt concentration and sodium adsorption ratio at 50%T

Soil	Untreated		NaOCl		NaOCl/ Oxalate		NaOCl/ Dithionite	
	EC	SAR	EC	SAR	EC	SAR	EC	SAR
Altamont	107	558	35	281	54	316	70	611
Imperial	27	89	18	55	45	116	50	132
Twisselman	24	83	30	62	30	131	98	514
Ramona	57	504	39	604	37	305	50	442

[a] EC = electrolyte concentration ($mmol_c$ L^{-1}).
[b] SAR = sodium adsorption ratio ($mmol_c$ L^{-1})$^{1/2}$.

concentration measured as electrolyte concentration (EC) at 50% T was linearly related to its corresponding SAR:

$$EC = 22.6 + 0.0854\ SAR \qquad r^2 = 0.51** \qquad (1)$$

SAR ranged in value from 55 to 611; while EC at 50% T (used as a flocculation criterion) ranged in value from 18 to 107 $mmol_c$ L^{-1}. Significantly lower SAR values were obtained for the two calcareous soils (Table 3).

We investigated the dispersive effect of native soil organic matter further. The flocculation-dispersion behavior of hypochlorite-treated soils was evaluated with and without the addition of their corresponding untreated soil sample supernatants. In this way, the effect of dissolved organic matter could be tested on the same sample. Figure 2 shows the effect of adding back the untreated soil supernatant on the flocculation-dispersion behavior of a Ramona soil sample which had been treated with hypochlorite to remove organic matter. Adding dissolved or-
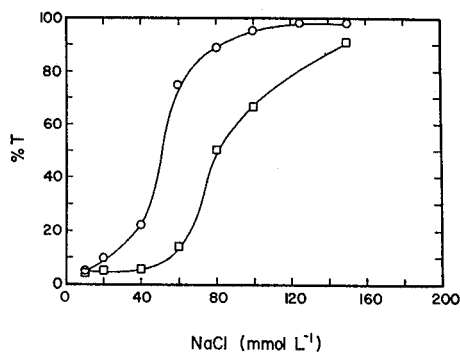
FIG. 2. Flocculation-dispersion behavior of Ramona soil. Circles represent hypochlorite-treated soil. Squares represent the same hypochlorite-treated soil with the addition of dissolved organic matter supernatant.

ganic matter increased the dispersibility of the clay in the treated sample.

Shanmuganathan and Oades (1983) observed that addition of organic anions (fulvate, citrate, oxalate, tartrate, salicylate, aspartate, lactate, and acetate) increased clay dispersion in an Australian soil, whereas water-stable aggregate content was unaffected. This apparent contradiction of the effect of organic matter was explained by Emerson (1983), as follows: organic bonds stabilize aggregates against slaking and disaggregation; however, once these bonds are broken and disaggregation has occurred, the organic matter acts as a deflocculant. An alternative explanation has been proposed by Durgin and Chaney (1984). These authors studied the effect of dissolved organic matter from Douglas fir roots on the dispersion of kaolinite and concluded that the size of the organic anion determines its influence. If the organic anion is no longer than the edge of the clay particle, its specific adsorption offsets the positive charge at the adsorption site, provides excess negative charge to the particle, and produces dispersion; if, on the other hand, the organic anion is longer than the clay edge, it will attach to the edges of several clay particles and bind them together (Durgin and Chaney 1984).

We suggest that the effect of organic matter on soil structure is also a function of the size scale of the soil particles investigated. Stability is usually measured on coarse sand-sized aggregates, which are stabilized mainly by roots and hyphae (Tisdall and Oades 1982). The effect of organic matter on clay-sized particles, however,

would occur mainly through its effect on particle charge.

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