Soil surface properties affected by organic by-products

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A b s t r a c t. The beneficial effects of amending soils with organic by-products include improvement of both chemical and physical factors. Very few studies have investigated changes in the soil specific surface area (SSA) after amendments with manures or composts. Soil samples were taken from plots before and after four years' application of manures, composts or nitrogen fertilizer. A corn-wheat-soybean rotation was grown. Soil samples were tested for changes in water retention at -15 bar, bulk density, C content and SSA using nitrogen gas adsorption at 73 K. Both the increase in water retention and decrease in bulk density were related to total organic matter amendment. Increases in SSA were noted in all soils sampled. SSA changes were not related to either C increases or ash amendments. An amendment of crab waste compost increased SSA most, i.e., soil C increased by 4.45 m² g⁻¹. The fertilizer increased SSA to 0.5 m² g⁻¹ soil C increase. Although the calcium mineral content of crab waste compost may be the prime factor in the increasing of SSA, no single factor appeared to explain the increase of SSA in these field soils.

K e y w o r d s: soil specific surface area, compost, water content, N fertilizer, organic by-products

INTRODUCTION

Composting is an effective treatment process with organic by-products. The benefits of composting generally outweigh the drawbacks (Sikora, 1998). Composting results in a product that is drier, more biologically stable and easier to apply to land than the original uncomposted material. Effects of compost addition on soil properties have been widely studied (Guidi and Poggio, 1987; Chang *et al.*, 1983; Wang, 1977; Hernando *et al.*, 1989). Enhancement of soil nutrient pools is one of the benefits of compost application (Sikora and Enkiri, 1999; McCoy *et al.*, 1986; Tester, 1989). Composts were also found to improve soil hydraulic and

mechanical properties that are important for positive crop responses. Applications of municipal sewage waste composts increased soil permeability (Brudel and Vorwerk, 1977), porosity (Pagliai *et al.*, 1981; Guidi *et al.*, 1981), water holding capacity (Mays *et al.*, 1973; Epstein, 1975), and decreased penetration resistance (Tester, 1990).

Soil specific surface area (SSA) and water content measured at -15 bar capillary pressure are soil parameters that reflect soil ability to retain and transport nutrients and water. Both parameters characterize properties of the soil solid phase. Specific surface area of soils correlates with sorptive capacity and ion exchange capacity (Jurinak and Volman, 1957; Ben-Dor and Banin, 1995), retention and release of chemicals (Rhue et al., 1988; Valverde-Garcia et al., 1988; Ong and Lion, 1991), swelling (Sapozhnikov, 1985), water retention (Kapilevich et al., 1987), and dry-aggregate stability (Skidmore and Layton, 1992). Tester (1990) observed that SSA, as determined by the ethylene glycol method, increased with organic matter increases after compost application. Water content at -15 bar (WP) is a good predictor of soil water retention (Rawls et al., 1982). An increase in WP values due to compost and amendment of other organic application was observed by several authors (Epstein, 1975; Gupta et al., 1977; Sommerfeldt and Chang, 1987; Serra-Wittling et al., 1996).

Composition of organic by-products used to amend soils varies widely (Sommers *et al.*, 1976; Xin-Tao *et al.*, 1995). These differences in composition are expected to influence the efficiency of composts as nutrient sources and soil conditioners. However, limited information is available on how changes in specific surface area and in water content at -15 bar reflect and integrate differences in compost

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source and composition. The objective of this work was to compare changes in SSA and water retention of a highly eroded, rocky soil amended with several kinds of composts or manures.

MATERIALS AND METHODS

Field experimental setup

Plots were located on land that was formerly an orchard at the Beltsville Agricultural Research Center. For five years prior to the establishment of plots, the area was cropped to corn and soybeans using no-till methods. The soil was a Matapeake silt loam (Typic Hapludults) containing approximately 27% sand, 62% silt and 11% clay. Several areas throughout the plots had stones greater than 2 mm which were removed from the soil samples before analysis by screening.

Amendments were applied to single 6 x 24 m plots using a manure spreader; amount applied was based on the content of nitrogen available to plants of each amendment. A corn-wheat-soybean rotation was used. Approximately 70% of N required by corn or, 50% of N used by soybeans, was supplied by the amendment. The estimates for plantavailable N were made either from laboratory incubation studies (Sikora and Enkiri, 1999) or from mineralization estimates obtained from literature (Castellanos and Pratt, 1981; Tester, 1989). In the years when corn was planted, half of each plot received N fertilizer to increase the total plantavailable N to 100%. The fertilizer plot received N rates equal to those of the amendments. When corn was grown, half of the plot with fertilizer received 70% of the N rate and the other half received 100% of the N rate. The part of the plots which received fertilizer, was chosen randomly each year.

Ammonium nitrate or sulfate was the fertilizer added. This amendment strategy was used to minimize fertilizer addition so that the benefits of the organic amendment as well as synergy between organic amendments and fertilizer would be evident (Fauci and Dick, 1994). The chemical composition of the amendments is shown in Table 1 and the yearly amendment rates are presented in Table 2.

After amendment application, the plots were chisel plowed and then disked and planted. Crops were harvested using conventional harvesting equipment which left a 15 cm stem residue on the soil surface.

Soil sampling and analysis

Soil samples were taken from the entire plot disregarding fertilizer placement which was random and occurred only when corn was planted. Soil samples were taken in the spring prior to the annual application of amendments. Eight to twelve 10 cm cores taken to a depth of 15 cm were consolidated in a bucket, mixed thoroughly; a 1 to 2 kg composite sample was taken from this mixture for analysis. The

T a ble 1. Chemical constituents of manures and composts added to field plots from 1994 to 1997

Amendment —		Mean % (range)		Mean mg kg ⁻¹ (range) air-dried soil					
	С	Ν	Р	Ash	Mn	Cu	Zn	Cd	В	
Poultry	35.1	3.45	1.94	18.8	510	55	611	1(1)	23	
manure	(33.0-	(1.95-	(1.68-	(15-	(414-	(40-	(544-		(19-28)	
	36.9)	5.04)	2.28)	21.8)	662)	65)	688)			
Biosolids	22.1	2.02	1.09	56.9	1110	250	345	nd	7.8	
compost	(20.0-	(1.64-	(0.71-	(50-	(495-	(158-	(236-		(4-15)	
	26.45)	2.37)	1.34)	60.3)	1600)	343)	452)			
Municipal	25.4	1.25	0.20	47.7	647	614	859	3.5	22.5	
refuse	(18.0-	(1.01-	(0.13-	(32.6-	(372-	(439-	(667-	(3-4)	(18-28)	
compost	33.4)	1.71)	0.26)	70.5)	915)	718)	1110)			
Crab waste	14.2	1.02	1.11	79.7	242	33.8	112	nd	79.7	
compost	(8.82-	(0.81-	(0.6-	(74.3-	(132-	(27-	(61-		(74.3-84	
-	22.64)	1.21)	1.49)	84)	338)	41)	209)			
Cattle	37.7	2.24	0.61	13.2	146	21.8	130	nd	16.5	
manure	(28.3-	(1.87-	(0.44-	(5-	(102-	(13-	(85-		(12-24)	
	42.4)	2.96)	0.9)	30.7)	202)	33)	173)		. ,	
Farm	15.4	1.25	0.66	50.8	273	34.5	130	nd	8.8	
compost	(11.3-	(0.86-	(0.27-	(6.8-	(187-	(26-	(82-		(3-20)	
	16.4)	2.05)	1.1)	73.3)	357)	42)	215)			

	A	pplication ra	ate (dry t ha ⁻	¹)
Amendment -	1994	1995	1996	1997
Municipal refuse	42	33	37	21
Biosolids	30	37	5	5
Poultry manure	10	21	NA	2
Crab waste	40	35	37	28
Fertilized	NA	NA	NA	NA
Cattle manure	20	15	1	4
BARC farm	45	57	29	37

T a ble 2. Application rates during the period of the experiment

NA: not amended.

samples were air-dried and sieved through a 2 mm sieve. Soils were stored dry in glass jars at room temperature prior to analysis. Bulk density was determined using the volume extraction method (Blake and Hartge, 1986). Water retention data were taken with the pressure plate at -15 bar matric potential (Gardner, 1986).

Total C and N contents of the soil samples were determined by dry combustion using a Perkin Elmer 2400 CHN analyzer. Soil samples for CHN analyses were also sieved through a 60-mesh screen. Additional chemical analyses were performed by A and L Laboratories in Richmond, VA, using standard methods described in the Methods of Soil Analysis (Weaver, 1994). Composite samples of manures and composts were air-dried and ground to 2 mm using a mill. Chemical analyses were similar to those for soils, but methods for the analysis of solid waste were used instead.

Measurements of specific surface

Adsorption of nitrogen at low temperature (78 K) was used to estimate the specific surface values. The technique made use of pressure volume measurements to determine the amount of adsorbate gas before and after exposure to the adsorbent (Adamson, 1967). Successive portions of gas were admitted to the adsorbent from a volumetric measuring device. Duplicate soil samples (approximately 1.25 g) were analyzed for surface area.

The SSA of a sample was estimated with the following equation (Adamson, 1967):

$$A = 10^{-20} v_m \sigma \,\mathrm{N}/M \tag{1}$$

where A is the SSA (m^2g^{-1}) , σ is the average area occupied by a molecule of adsorbate in a completed monolayer (m^2) , N is the Avogadro constant, M is the molecular mass of the adsorbate, v_m is the monolayer capacity expressed as the volume of gas (reduced to standard temperature and pressure). In Eq. (1), the value of v_m has to be found from the measurements. To do that, amounts of the adsorbed gas v are measured for several nitrogen partial pressures p. The Brunauer, Emmett, and Teller (BET) equation is assumed as valid for the adsorption isotherm. This equation is used in its linearized form (Adamson, 1967):

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{(c - 1)p}{v_m c p_0}.$$
 (2)

Here, *v* is adsorbed amount (m³), *p* is partial pressure of the adsorbate, p_0 is partial pressure at saturation. The parameter *c* depends on the heat of adsorption. The expression on the left side of this equation $p/(v(p_0-p)) = y$ and the ratio $p/p_0 = x$ in the right side are known for each equilibrium measurement point. A linear regression of *y* on *x* gives values of slope $b=(c-1)/v_mc$ and the intercept $a=1/v_mc$. Then the value of the monolayer capacity to which shell be used in Eq. (1) is equal to $v_m = 1/(a+b)$.

RESULTS AND DISCUSSION

Figure 1 shows examples of nitrogen adsorption isotherms and their transformation for the application in the BET equation. The difference in adsorption is more apparent in BET-transformed data than in the original isotherms. Between relative pressures $0.05 < p/p_0 < 0.35$, the transformed adsorption data lay on a straight line as as suggested by Eq. (1). Therefore, BET equation is suitable for a description of adsorption in this range of relative pressures.

SSA values before and after four years of amendments are shown in Table 3. These are mean values of duplicate samples taken from a composite soil sample from each plot. The limited area available for plots and the number of treatments (14 total in 1998) precluded the use of an adequate number of replicates. It was also important to demonstrate an application of treatments using conventional farm equipment. Therefore, single, large (144 m²) plots were used and soil samples were taken randomly from the plots, combined, and sub-sampled for analysis. Four years of application resulted in an increase in the average SSA values in all treatments except the treatment with municipal refuse compost. Composts from municipal refuse are generally not as stable or mature as other composts and continue to decompose like manure when added to soils (Gallardo-Lara and Nogales, 1987). Higher decomposition of the organic matter added results in less organic C remaining in the soil. Decomposition rate of composts is usually half of the corresponding manure before composting (Castellanos and Pratt, 1981). Therefore, it may be assumed that more organic matter remains in the soils amended with composts than in the soils amended with an equal amount of organic matter as manure. Poultry and cattle manure would also continue to



Fig. 1. Examples of nitrogen adsorption data in the soil in this study: a) original adsorption isotherms; b) isotherms transformed for the application in BET equation; o - BARC compost, \Box - crab waste compost, Δ - original soil, ∇ - soil fertilized not amended. See Eq. (2) for description of terms.

Table	3.	Treatment	effects	on	physical	and	chemical	soil	properties

Treatment	Specific surface area $(m^2 g^{-1})$		Water content at -15 bar $(m^3 m^{-3})$		1998–1994 difference in	Bulk density in 1998 (Mg m ⁻³)	
	1994	1998	1994	1998	carbon content in soil (g kg ⁻¹)	with stones	without stones
Municipal refuse	2.07	2.02	4.3	7.2	16.3	1.15	1.00
Biosolids	2.20	2.75	5.9	7.2	6.1	1.30	1.15
Poultry manure	3.60	4.57	7.9	10.7	8.4	1.20	1.15
Crab waste	3.02	4.00	5.4	9.9	2.2	1.45	1.05
Fertilized (not amended)	3.55	4.02	6.1	6.4	10.0	1.65	1.25
Cattle manure	2.90	4.27	6.3	8.8	15.0	1.20	1.00
BARC farm	3.17	3.75	6.7	11.3	9.1	1.20	1.15

decompose rapidly in the soil because they are unstable. Even though they contained more organic matter per unit mass than the compost of municipal refuse (Table 1), the cumulative amendments of manures were about one-quarter of the municipal refuse compost.

The largest absolute increase in SSA was found in the soil receiving cattle manure and the lowest was observed in the soil receiving chemical fertilizer. Taking into account the total mass added, the percent of mass that is organic, and the relative rate of manure decomposition versus composts, all indications are that organic matter addition to soil was not related to SSA increases in this field study.

The compost of crab waste appliced caused a SSA increase of $4.45 \text{ m}^2 \text{ g}^{-1}$ soil C increase. Crab waste compost contained the highest ratio of ash to C (nearly 6) followed by farm compost. Amendments of crab waste compost added

111 Mg of ash, farm compost added 84, municipal refuse compost added 60 and biosolids compost added 45 Mg ha⁻¹.

Cattle manure added 8 and poultry manure added 6 Mg ha⁻¹. Composting concentrates inorganic material as organic matter decomposes. Accordingly, cattle and poultry manure had low ash content while farm compost, which is made primarily from manure, had a much higher ash percentage (Table 1). These data suggest that ash quantities added do not directly influence SSA, either.

All amendments resulted in an increase in water content at -15 bar (Table 3). The largest absolute increase occurred in the soils amended with crab waste compost and BARC farm compost. Gupta *et al.* (1977) observed a linear increase in water content at -15 bar with increasing amounts of sewage sludge applied. Both crab waste and farm composts had high cumulative amendment rates and high percent ash contents suggesting that inorganic constituents may affect water retention of soils in the low water content range.

An application of municipal refuse compost did not cause an increase in SSA, although an increase in the soil carbon content was recorded (Table 3). Application of composted biosolids, poultry manure, cattle manure and BARC farm compost provided an increase in SSA of $0.55-1.37 \text{ m}^2 \text{ g}^{-1}$ soil C increase. The fertilized soil showed an increased in SSA of about $0.50 \text{ m}^2 \text{ g}^{-1}$ soil carbon increase.

Differences in the amendment composition preclude a direct relation of SSA to carbon content in this study. Tester (1990) observed a linear increase in SSA with increasing amounts of soil organic matter when sewage sludge compost similar to the one used here was applied. We calculated an R^2 =0.97 for his data. However, other attempts to correlate the SSA to the organic matter content in different soils resulted in a relatively low R^2 coefficient of 0.5 (Ben-Dor and Banin, 1995).

An increase in SSA in this study should probably be attributed to types of organic matter and minerals in amendments as opposed to absolute changes in quantities. Chefetz et al. (1998) recorded significant changes in the humic acids of municipal solid waste after composting. They showed that after composting, polysaccharides, peptides and lipids were removed exposing the 'core' humic acid structure. SSA of the humic acids extracted from the soil is reported to be between 0.35 and 1.7 m² g⁻¹ (Ong and Lion, 1991; Chiou et al., 1990), the samples from organic soils preserved had SSA between 1 and 20 m² g⁻¹ (Pennell *et al.*, 1995). Values of SSA for clay minerals vary from 15 to 30 m² g⁻¹ when measured with N₂ adsorption (Ziper et al., 1988). Thus, clays affect the SSA far more than organic matter and, therefore, the mineral rather than organic constituents of the amendments may be responsible for the increase in SSA. This effect may explain why crab waste compost, which contains predominantly calcium carbonate and calcium phosphate (Laughlin et al., 1973), caused the highest increase in SSA parallel to very moderate changes in soil organic carbon content. This concurs with the fact that the crab waste compost caused the highest increase in water content at -15 bar which is usually well correlated with the amount of fine mineral particles (Rawls et al., 1982). The smallest increase in WP values was in the soil receiving fertilizer (Table 3) which resulted in small organic matter additions in the form of plant residues.

It is important to stress that SSA values measured with nitrogen adsorption differ from those measured with ethylene glycol (EG), and care needs to be taken in the comparisons of data obtained using these two methods. The SSA of organic matter measured with EG ranged from 100 to 800 m^2g^{-1} (Bower and Gschwend, 1952; Jurinak and Volman, 1957; Pennell *et al.*, 1995) and the values from nitrogen adsorption are much lower at 1 to 20 m^2g^{-1} (Chiou *et al*, 1990; Pennell *et al.*, 1995). The disparity may be due to

differences in the nature of adsorptive forces involved in sorption of polar EG vs non-polar N_2 molecules (Choudry, 1984). Nitrogen and the EG adsorption experiments produce similar SSA values only in the absence of expandable clay minerals and organic matter (Mudroch *et al.*, 1997). It is suggested that EG-SSA values should be regarded as the measure of soil uptake capacity for EG rather than the measure of surface area (Pennell *et al.*, 1995).

Amendments with organic by-products decreased bulk density measured with or without stones (Table 3). Without stones, the values ranged from 1 to 1.25 g cm^{-3} and were directly related to the amount of carbon present in the soil. Bulk density decrease after compost and manure applications was reported in other studies (Sommerfeldt and Chang, 1987; Tester, 1990).

CONCLUSIONS

No single factor appears to explain an increase in the specific surface area (SSA) in these field soils. Organic matter content and its opposite, ash content, do not fully explain the SSA values obtained. This may in part be due to the use of single large plots instead of numerous replicate smaller plots. However, several factors including organic matter content and moisture retention correlated to amendment type and rate of application in the samples taken in 1994 versus 1998. Therefore, the samples used for SSA seemed representative of the treatments and conclusions drawn from the study, valid. The highest increase in SSA g^{-1} C increase was registered with additions of crab waste compost. The mineral quality of crab waste compost, specifically the calcium compounds, may be responsible for the SSA increase. Water retention at -15 bar and bulk density were the physical factors affected by an addition of organic by-products. Surface area changes may be a result of several interacting factors that include organic matter and ash quality, plant residue amount and type, farming practice and soil type.

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