# Effect of selective removal of organic matter and iron oxides on the specific surface areas of some tropical soil clays

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## ABSTRACT

The effect of selective removal of organic matter and amorphous and crystalline iron oxides on $N_2$-BET specific surface areas of some soil clays was evaluated. Clay fractions from 10 kaolinitic tropical soils were successively treated to remove organic matter by oxidation with Na hypochlorite, amorphous Fe oxide with acid ammonium oxalate, and crystalline iron oxides by reductive dissolution with dithionite-citrate-bicarbonate solution. The removal of organic matter resulted in an increase of 7-70 per cent in specific surface areas of most of the samples. By contrast, the removal of amorphous and crystalline iron oxides reduced the specific surface areas of the soil clays by 5-26 per cent and 18-66 per cent, respectively. The estimated specific surface area of the crystalline iron oxides of the soil clays varied from 117 to 365 $m^2 g^{-1}$. The changes in specific surface area after the removal of organic matter and iron oxides could affect the physico-chemical properties of the soils.

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## RÉSUMÉ

OSEI, B. A. & SINGH, B.: *Effet d'enlèvement sélectif de matière organique et des oxydes de fer sur les superficies de surface spécifique de quelques argiles de sol tropical.* L'effet d'enlèvement sélectif de matière organique et des oxydes de fer amorphe et cristallin sur $N_2$-BET superficies de surface spécifique de quelques argiles de sol était évalué. Les fractions argile de 10 sols kaolinitiques tropicaux étaient traitées successivement pour enlever la matière organique par oxydation avec Na hypochlorite, oxyde de fer amorphe avec oxalate d'acide d'ammonium et les oxydes de fer cristallin par dissolution réductrice avec la solution de dithionite-citrate-bicarbonate. L'enlèvement de la matière organique aboutissait à une augmentation de 7-70 pour cent dans les superficies de surface spécifique de la plupart d'échantillons. Par contraste, l'enlèvement des oxydes de fer amorphe et cristallin réduisait les superficies de surface spécifique des argiles de sol respectivement par 5-26 pour cent et 18-66 pour cent. La superficie de surface spécifique estimée des oxydes de fer cristallin des argiles de sol variait de 117 à 365 $m^2 g^{-1}$. Les changements dans les superficies de surface spécifique suite à l'enlèvement de matière organique et les oxydes de fer pourraient avoir un effet sur les propriétés physio-chimiques des sols.

## Introduction

The specific surface area (SSA) of soils is closely related to, and has a determining influence on, many soil properties (Theng *et al.*, 1999). It has been related to the type and quantity of clay (Tiller & Smith, 1990), water content (Newman, 1983), and cation-exchange capacity of soils (De Kimpe, Laverdiere & Martel, 1979). Soil physical properties such as stability, dispersibility, and erodibility are also influenced by the SSA of soils (Churchman & Burke, 1991; Barberis *et al.*, 1991). Since the SSA determined by adsorption methods is a function of reactions between surface functional groups and the probe molecules (Sposito, 1984), these methods could be used to evaluate adsorption of chemicals, metals and phosphates on oxides and minerals in soils (Peter & Weber, 1985).

The significance of SSA on the management of soils has been emphasized by Wann & Juang (1985) and Buol (1985).

Iron oxides in tropical soils have substitution of Fe (III) by Al (IV) in their lattice structures (Anand & Gilkes, 1987). Such substitution reduces both crystallinity and size of crystals of iron oxides (Van Ranst *et al.*, 1998). Iron oxides, therefore, have large surface area which results in large amount of valuable charge (Van Ranst *et al.*, 1998). In strongly weathered tropical soils, the dominant minerals in the clay-sized fraction is usually kaolinite, with varying amounts of Fe oxides (Van Ranst *et al.*, 1998). Organic matter may also be present in the clay fraction. The organic matter content, the content of kaolinite, and the degree of inter-particle association would influence the SSA values of these soils.

The objective of the study was to evaluate the effect of selective removal of organic matter and iron oxides on the SSAs of some tropical soil clays.

## Materials and methods

### *Soils*

Ten soil samples from six tropical countries were used for the study. Table 1 shows the description of the soils. The clay fractions (<2 μm) of the soils were dominated by kaolinite and goethite together with varying amounts of quartz (Osei & Singh, 1999) (Table 2). The soils were saturated with NaCl and dispersed by sonification. The < 2 μm fraction was separated by repeated dispersion and centrifugation.

### *Pre-treatments*

The soil clay extracted after ultrasonic dispersion was designated as untreated clay. Some of the untreated clays were successively treated with the following: sodium hypochlorite (NaOCl) solution adjusted to *p*H 9.5 with concentrated HCl (Cavallaro & McBride, 1984) to remove organic matter; ammonium oxalate (Mckeague & Day, 1966) to remove amorphous iron oxide (FeO); and sodium dithionite in sodium citrate solution together with sodium bicarbonate (CBD) to remove the remaining well-crystalline iron oxides (Fed) (Mehra & Jackson, 1960).

The NaOCl treatment involved treating 5 g of untreated clay sample with 50 ml of 5.25 per cent NaOCl solution for 15 min in a boiling water bath. At the end of the digestion period, the suspension was cooled and then centrifuged at 1600 rpm for 30 min. The extraction process was repeated four more times. The clear supernatant was stored and

TABLE 1

*Description of the Soils*

| *Sample no.* | *Soil series* | *Country of origin* | *Soil taxonomy*[a] | *Depth (cm)* |
|---|---|---|---|---|
| 1 | Barombi Kang | Cameroon | Typic Paleudult | 20 - 40 |
| 2 | Bassachia | Ghana | Oxisol[b] | 0 -20 |
| 3 | Bediesi | Ghana | Ultisol[b] | 0 - 20 |
| 4 | Kumasi | Ghana | Plinthic Paleudult | 0 - 20 |
| 5 | Menzenzo | Ghana | Ultisol[b] | 0 - 20 |
| 6 | Munchong | Malaysia | Tropeptic Haplorthox | 20 - 35 |
| 7 | Onne | Nigeria | Typic Paleudult | 20 - 30 |
| 8 | Red Yellow Latosol | Brazil | Typic Acrustox | 20 - 40 |
| 9 | Richelieu | Mauritius | Ultisol[b] | 0 - 10 |
| 10 | Segamat | Malaysia | Typic Acrorthox | 0 - 20 |

[a] Soil Survey Staff (1975)
[b] Detailed classification not available

TABLE 2

*Organic Carbon and Mineralogical Contents of the Clay Fractions of the Soils*

| *Sample no.* | *Organic carbon*[a] *(g kg$^{-1}$)* | *Kaolinite*[b] | *Geothite*[b] | *Hematite*[b] | *Gibbsite*[c] | *Quartz*[c] | *Smectite*[c] | *Illite*[c] |
|---|---|---|---|---|---|---|---|---|
| 1 | 5 | +++[d] | ++ | - | - | + | - | - |
| 2 | 42 | +++ | ++ | - | - | + | + | - |
| 3 | 7 | +++ | ++ | - | - | + | - | - |
| 4 | 27 | ++ | ++ | - | - | + | - | + |
| 5 | 69 | +++ | ++ | - | - | + | - | + |
| 6 | 5 | +++ | ++ | - | - | + | - | - |
| 7 | 17 | ++- | ++ | + | - | + | - | - |
| 8 | 22 | +++ | ++ | + | + | - | - | - |
| 9 | 22 | ++ | ++ | - | - | + | - | - |
| 10 | 11 | +++ | -+ | - | - | - | - | - |

"-" not detected by XRD and DTA/TG techniques

a. Organic carbon (Nelson & Sommers, 1975)

b. Determination of kaolinite, goethite and hematite by thermogravimetric analysis

c. Determination of gibbsite, quartz, smectite and illite by X-ray diffraction analysis

d. +++ = abundant; ++ = present; + = traces

later analyzed for Fe, Si and A1. The residue was dried in an oven at 50 °C and then stored.

The ammonium oxalate extraction involved reacting 3 g of NaOC1-treated clay with 150 ml of 0.3*M* ammonium oxalate (adjusted to *p*H 3 with 0.2 *M* oxalic acid) for 4 h in the dark. At the end of the extraction period, the suspension was centrifuged at 1600 rpm for 30 min. The clear supernatant was analyzed for Fe, Si and A1. The residue was stored in a plastic bottle after drying in an oven at 50 °C.

In the CBD extraction, 2 g of the oxalate-treated clay sample were reacted with 40 ml of 0.3 *M* sodium citrate, 5 ml 1.0 *M* sodium bicarbonate, and 0.5 g of sodium dithionite in a water bath. The extraction process was repeated until all the iron was removed as evidenced by the sample being light grey. After centrifugation at 1600 rpm for 30 min, the clear supernatant was poured off into a volumetric flask for Fe, A1 and Si determination. The residue was dried at 50 °C in an oven and then stored in a plastic bottle.

*Determination of Fe, A1 and Si in NaOC1, oxalate, and CBD extracts*

The Fe, A1 and Si in the NaOC1, oxalate, and CBD extracts were measured by Inductively Coupled Plasma atomic emission spectroscopy (Perkin Elmer Optima 3000).

*Surface area*

The specific surface areas of the untreated and treated clay were determined by the N$_2$-BET method (Feller *et al.*, 1992) with the computer-controlled Micromeritics Gemini 2375.

## Results and discussion

*Constituent dissolution*

Table 3 presents the amounts of Fe, A1 and Si extracted by the NaOC1, oxalate, and CBD treatments.

The NaOC1 treatment extracted the lowest amounts of Fe (< 0.1 g kg$^{-1}$ clay), implying there were no significant amounts of organically bound Fe in the samples. The CBD treatment also extracted quite large amounts of A1. This could be due to A1 substituting for Fe in the structure of goethite, the mineral dissolved on CBD treatment, and therefore more A1 was extracted (Osei & Singh, 1999). The CBD treatment extracted more A1 than the oxalate treatment, while the NaOC1 treatment dissolved the lowest amounts

TABLE 3

*Iron, Aluminium and Silicon Contents (g kg$^{-1}$) Following Sodium Hypochlorite (NaOCl), Ammonium Oxalate (0), and Dithionite - Citrate Bicarbonate (d) Treatments of the Clay Fractions of the Soils*

| *Sample no.* | *NaOCl* | | | *Oxalate* | | | *CBD* | | |
|---|---|---|---|---|---|---|---|---|---|
| | *Fe* | *Al* | *Si* | *Feo* | *Alo* | *Sio* | *Fed* | *Ald* | *Sid* |
| | *g kg$^{-1}$ untreated clay* | | | | | | | | |
| 1 | - | - | 0.02 | 0.8 | 0.8 | 0.4 | 93.5 | 26.2 | 5.7 |
| 2 | 0.03 | 0.1 | - | 0.3 | 0.7 | 0.4 | 4.8 | 5.0 | 5.3 |
| 3 | - | 0.03 | 0.04 | 1.2 | 1.3 | 0.6 | 37.3 | 7.6 | 5.5 |
| 4 | - | - | - | 0.6 | 0.7 | 0.3 | 40.3 | 31.1 | 4.5 |
| 5 | 0.01 | 0.08 | 0.01 | 1.0 | 1.8 | 0.5 | 27.9 | 27.9 | 2.4 |
| 6 | - | - | 0.02 | 0.7 | 0.9 | 0.5 | 86.3 | 27.1 | 6.4 |
| 7 | - | 0.01 | 0.01 | 0.3 | 1.7 | 0.4 | 28.4 | 10.6 | 9.8 |
| 8 | - | 0.01 | 0.02 | 0.4 | 1.2 | 0.1 | 45.0 | 23.9 | 3.3 |
| 9 | - | - | 0.01 | 2.5 | 1.8 | 1.3 | 69.7 | 17.7 | 6.2 |
| 10 | - | 0.01 | - | 3.1 | 0.8 | 0.2 | 77.8 | 26.8 | 7.5 |

of Al (< 0. 1 g kg$^{-1}$ clay ). The amounts of Si extracted by the CBD, oxalate and NaOCl treatments were small, the Si contents following the decreasing order: CBD > oxalate > NaOCl.

*Specific surface area of untreated soil clays*

Table 4 shows the results of $N_2$-BET specific surface area (SSA) measurements for the untreated clay fractions.

The SSA values for the untreated soil clays ranged from 13.6 to 90.8 m$^2$ g$^{-1}$ (mean = 48.2 -23.6 m$^2$ g$^{-1}$). The Ghanaian soil clays had smaller SSA values than the other tropical soil clays. This could be explained with the difference in the degree of inter-particle association and the average size of the particles. The Ghanaian

TABLE 4

*Specific Surface Area (m$^2$ g$^{-1}$) of Untreated and Treated Soil Clays*

| *Sample no.* | *Untreated* | *Hypochlorite* | *Oxalate* | *CBD* | *Change in surface area associated with removal of 1 g of* $Fe_d$[1,2] |
|---|---|---|---|---|---|
| 1 | 73.8 | 84.1 | 66.1 | 49.0 | -186 |
| 2 | 15.4 | 11.9 | 14.7 | 10.1 | -315 |
| 3 | 41.5 | 44.9 | 40.8 | 23.6 | -365 |
| 4 | 41.2 | 46.0 | 40.2 | 32.5 | -166 |
| 5 | 13.6 | 23.1 | 19.4 | 10.0 | -172 |
| 6 | 59.3 | 65.1 | 51.9 | 17.8 | -302 |
| 7 | 53.9 | 59.3 | 53.6 | 40.9 | -307 |
| 8 | 45.5 | 48.7 | 45.3 | 36.8 | -155 |
| 9 | 90.8 | 106.9 | 79.8 | 57.0 | -300 |
| 10 | 47.2 | 45.0 | 42.7 | 33.3 | -117 |

[1] Calculated as {CBD surface area (1 - Wc)} - Oxalate surface area

where Wc = weight loss resulting from CBD extraction expressed as a fraction of the clay weight

[2] Negative sign means a decrease in surface area

samples might have large particles and relatively tight-particle association. The SSA values were strongly related to the organic carbon and iron extracted by the dithionite-citrate solution (Fed). For instance, a positive relationship was observed between SSA and Fed ($r = 0.747$, $P < 0.05$). The correlation between SSA and FeO, though positive, was not significant. The correlation between SSA and organic carbon content was negative ($r = -0.676$, $P < 0.05$). Organic matter appeared to either block the pores (Weiler & Mills, 1965; Williams, Greenland & Quirk, 1967) or coat clay aggregates (Burford *et al.*, 1964), thereby restricting $N_2$ molecules from entering the micropores of the clay aggregates (Theng *et al.*, 1999). It was, therefore, possible that as the organic matter content of the clays increased, $N_2$ molecules were more precluded or restricted from the micro-pores within the clay domains, thereby reducing the SSA value.

### *Specific surface area of hypochlorite-treated soil clays*

The SSAs of the clays measured by adsorption of $N_2$ after treatment with NaOC1 (Table 4) showed that the removal of organic matter usually resulted in a substantial increase (7 - 70 %) in the $N_2$-BET surface areas. Many workers have reported that removing or oxidizing the organic matter resulted in a marked increase in the $N_2$-BET SSA of both soils (Feller *et al.*, 1992; Pennel, Boyd & Abriolda, 1995) and sediments (Weiler & Mills, 1965; Titley *et al.*, 1987). This observation has been explained with the blocking of pores (Weiler & Mills, 1965; Williams *et al.*, 1967) or the coating of clay aggregates (Burford *et al.*, 1964) by the organic matter, which restricted $N_2$ molecules from entering the micro-pores of clay domains (Theng *et al.*, 1999).

The removal of organic matter enhanced the accessibility of micro-pore surfaces to nitrogen (Theng *et al.*, 1999). The enlargement of SSA was especially marked for soils 3, 4, 5, 6, 7, 8, and 9. This seemed to be linked to the organic carbon contents of the soil clays. A strong positive correlation ($r = 0.912$, $P < 0.01$) was observed between organic carbon content and the percent increase in SSA. The samples (Soils 1 and 10) which recorded a reduction in SSA after organic matter removal might be because the organic fractions seemed to have contributed to the total surface area, and that organic matter did not have coating or blocking effect on the clay aggregates.

### *Specific surface area of oxalate and CBD-treated soil clays*

After the oxalate treatment, there was a relatively small decrease in the SSA values (Table 4, 5.1 - 25.4 %) of the soil clays, except in one example. The small decrease in SSA is in line with the relatively small amounts of oxalate extractable Fe, A1 and Si (Table 3). The SSA values reduced after the CBD treatment (18.8- 65.7 %, Table 4). The reduction for Sample 2 (Bassachia series) was higher than that for Sample 14 (Kumasi series), even though Sample 4 contained more CBD-extractable Fe (Table 3). This could imply that the particles of crystalline Fe oxides of Sample 2 might be finer than those of Sample 4. The SSA values for the relatively pure soil kaolinite (CBD- treated samples) agreed well with values reported for kaolinite extracted from some tropical soils (Singh & Gilkes, 1992).

It appeared the reduction in SSA was not solely due to the removal of Fe oxides, and also the contribution of these Fe oxides to SSA might not be additive. Notwithstanding this observation, an attempt was made to estimate the SSA for crystalline Fe oxides of the soil clays. The weights of iron oxide removed by CBD extraction were corrected for in the calculation, as suggested by Bigham *et al.* (1978). The calculated SSA values for crystalline Fe oxides varied from 117 to 365 $m^2 g^{-1}$ (Table 4). These values were consistent with those reported by Gallez, Juo & Herbillon (1976), and Deshpande, Greenland & Quirk (1968). However, the values were much less than those reported by Curi & Franzmeier (1984, 600-1200 $m^2 g^{-1}$) for goethitic-hematitic Oxisols from Brazil. The relatively large values reported by Curi

& Franzmeier (1984) might not reflect the true value for soil Fe oxides, and the method used might be responsible for such large values (Börggaard, 1982). Statistical analysis of the surface area data showed that the treatment effects were different ($P < 0.01$) from those of the untreated soil clays. There were also significant differences in the SSA between hypochlorite, oxalate, and CBD treatments.

## Conclusion

Iron oxides extracted from the soil clays had large SSA. The large, specific surface Fe oxides may have a significant effect on the physical and chemical properties of the soil clays, such as bulk density, porosity, structure, and surface charge. The humic substances influenced SSA values of the soil clays. They appeared to either aggregate clay particles together or block pores of the clay aggregates; hence, their removal resulted in an increase in SSA of most of the soil clays. Changes in specific surface areas associated with the removal of Fe oxides and organic matter could affect the physico-chemical properties of the soils.

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