Organic Matter Occlusion of Mineral Surfaces as a Function of Mineral Weathering in Volcanic Ash Soils

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Abstract

In upland soils in humid climates, mineral stabilization of organic matter (OM) on millennial scales is often driven by the abundance of poorly crystalline, metastable chemical weathering products. Studies of volcanic ash soils have demonstrated that these metastable materials transform into increasingly crystalline minerals at advanced stages of weathering, so that the overall affinity of mineral surfaces for OM declines with time. However, the abundance of clay-sized (<2 ?m diameter) particles tends to increase with weathering, enhancing soil specific surface area (SSA) and potentially compensating for the loss of mineral affinity for OM. As a first step towards understanding the net effects of these simultaneous transformations on OM stabilization, we compared the coverage of SSA by OM in A and B horizons of ash-derived soils sampled along an elevation gradient in Veracruz, Mexico. N2 adsorption isotherms and Brunauer–Emmett–Teller (BET) theory were used to estimate SSA of bulk soil versus samples from which OM had been removed via combustion (muffling) and chemical oxidation (bleaching). In addition to comparing the effectiveness of the OM removal treatments, we characterized the extent to which the treatments altered the mineral matrix and introduced errors into the estimates of mineral SSA. Pore size distribution was estimated via density functional theory as a complement to the BET analysis. N2-accessible SSA ranged from 9 to 105 m2 g-1 after removal of OM, with muffling yielding higher values than bleaching for most samples. The probable loss of SSA associated with mineral transformations (e.g., of Fe oxides) at high temperatures during muffling was evidently offset by the more thorough removal of OM by that treatment. Although SSA tended to increase with weathering status, relative coverage of SSA by OM was relatively consistent across profiles and tended to be greater on average in A horizons (bleaching: 45% SSA covered, muffling: 51%) than in B horizons (bleaching: 28%, muffling: 34%). The apparent lack of OM coverage of SSA in the B horizon of the most weathered soil (0% of 60 m2 g-1 covered) underscores the overall importance of mineral reactivity in determining OM stabilization. Future work will extend these analyses to examine land-use effects on SSA coverage by OM.

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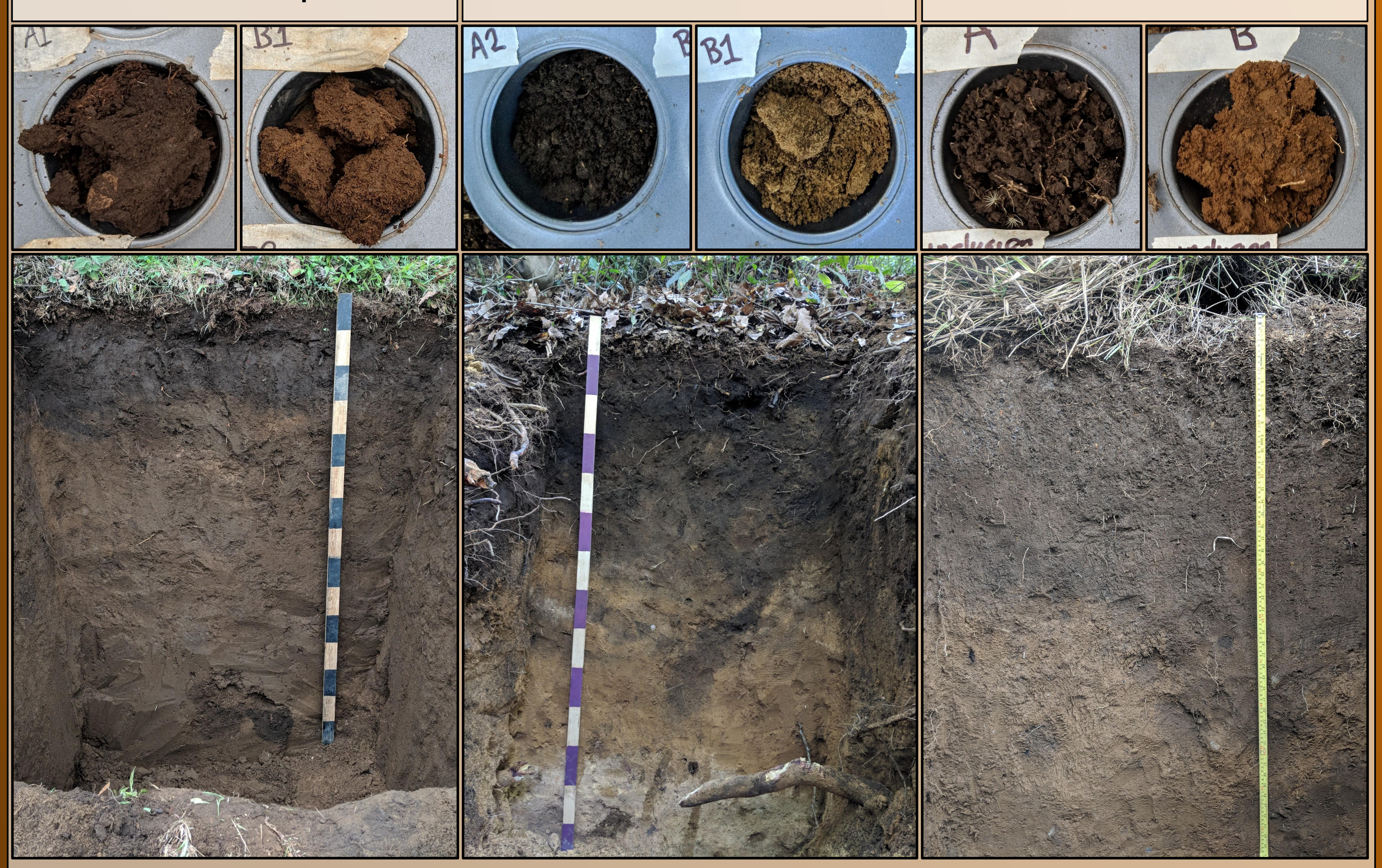
Rationale

In upland soils in humid climates, mineral stabilization of organic matter (OM) on millennial scales is often driven by the abundance of poorly crystalline, metastable chemical weathering products. Studies of volcanic ash soils have demonstrated that these metastable materials transform into increasingly crystalline minerals at advanced stages of weathering, so that the overall affinity of mineral surfaces for OM declines with time. However, the abundance of clay-sized (<2 μm diameter) particles tends to increase with weathering, enhancing soil specific surface area (SSA) and potentially compensating for the loss of mineral affinity for OM. As a first step towards understanding the net effects of these simultaneous transformations on OM stabilization, we compared the coverage of SSA by OM in A and B horizons of ash-derived soils sampled along an elevation gradient in Veracruz, Mexico. N_2 adsorption isotherms and Brunauer–Emmett–Teller theory were used to estimate SSA of bulk soil versus samples from which OM had been removed via combustion (muffling) and chemical oxidation (bleaching).

Site Description

We analyzed soils collected in a broader study of land-use effects on C stabilization along an elevation gradient in Veracruz, Mexico. Samples from A and B horizons were selected from two Andisols and one Inceptisol. The upper-elevation Andisol underlies a current pasture, whereas the lower-elevation Andisol supports a selectively logged cloud forest. The Inceptisol had undergone two years of fallow after abandonment of pasture at the time of sampling (2018). Sample depths were ~10-30 and 60-80 cm for A and B horizons, respectively.

1352 m Inceptisol	1412 m Andisol	2199 m Andisol

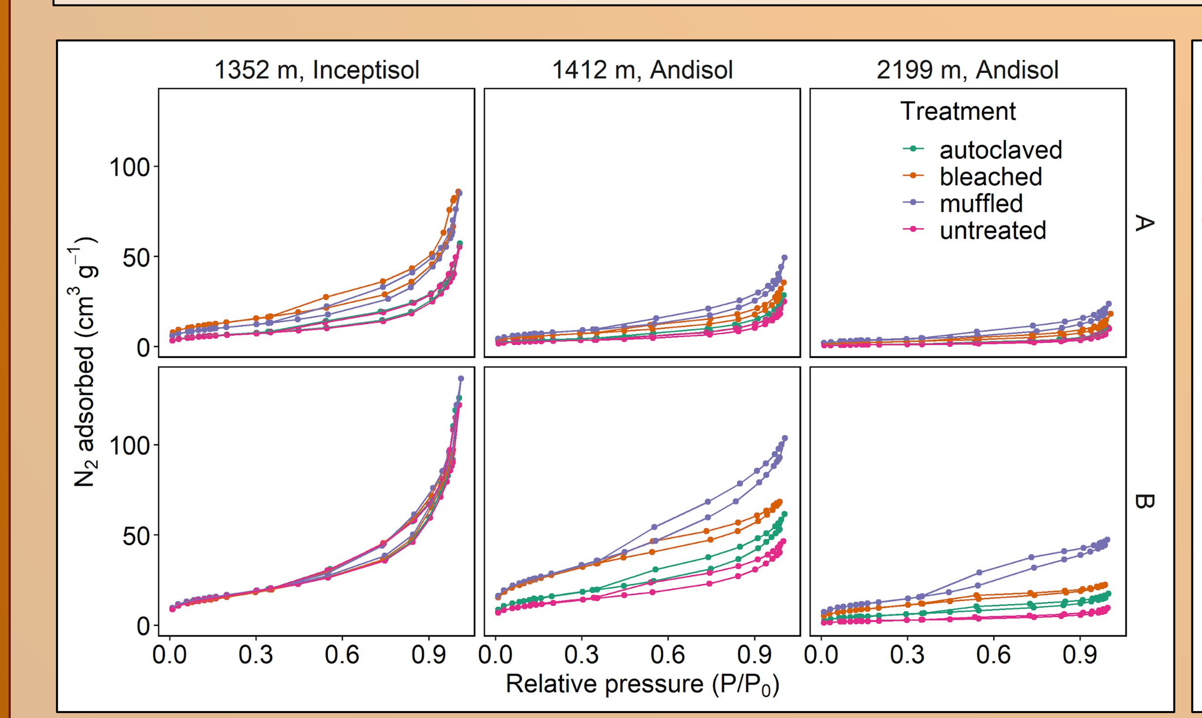


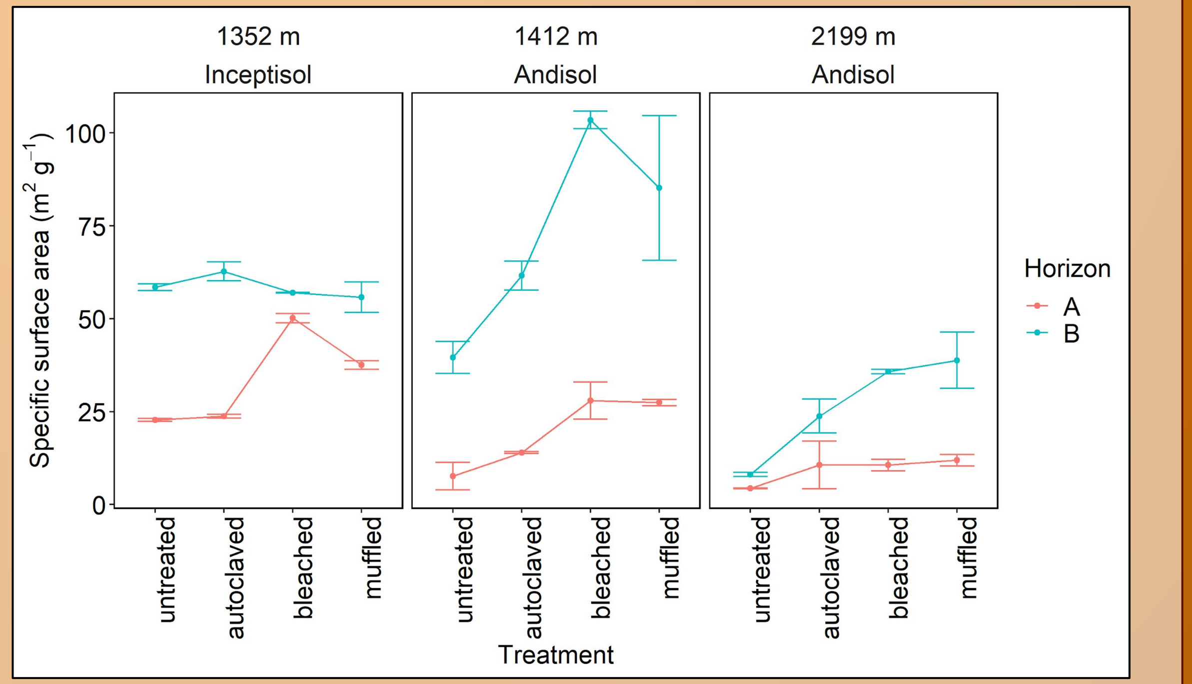
Methods

Specific surface area of samples was estimated via Brunauer–Emmett–Teller theory before and after autoclaving and organic matter removal via combustion and chemical oxidation. Autoclaving treatments were performed at 120° C for one hour. Combustion via muffling was undertaken at 350° C for 2 hours. Oxidation with bleach was repeated until discoloration of solution and effervescence ceased (bleaching and centrifugation repeated every two days for two weeks). Particle size distributions were estimated via laser diffraction analysis after dispersal in sodium hexametaphosphate and repeated sonication.

Key Findings

Specific Surface Area: Brunauer–Emmett–Teller (BET) theory analyzes specific surface area via adsorption of N_2 gas. This method can produce inaccurate results in soil samples due to the molecular sieving preventing N_2 from reaching the mineral matrix (de Jonge & Mittelmeijer-Hazeleger, 1996). This phenomena can be taken advantage of to study the percent occlusion of mineral surface area by OM (Wagai et al., 2009). As seen in the figure on the left there is an apparent increase in adsorption following treatment for OM removal. This is the result of greater exposed mineral SSA leading to an increase in accessibility for N_2 gas. Changes in SSA with OM removal treatments are correlated with stage of weathering. The 2199 m Andisol is the least weathered of the three sites and consistently exhibits the lowest SSA regardless of OM treatment method. The 1412 m Andisol and 1352 m Inceptisol have been subject to more extreme weathering leading to an increased abundance of clay-sized particles. These particles have greater SSA, apparently increasing potential for OM stabilization despite decreases in mineral affinity. This leads to a much more significant difference in SSA after OM removal treatment.

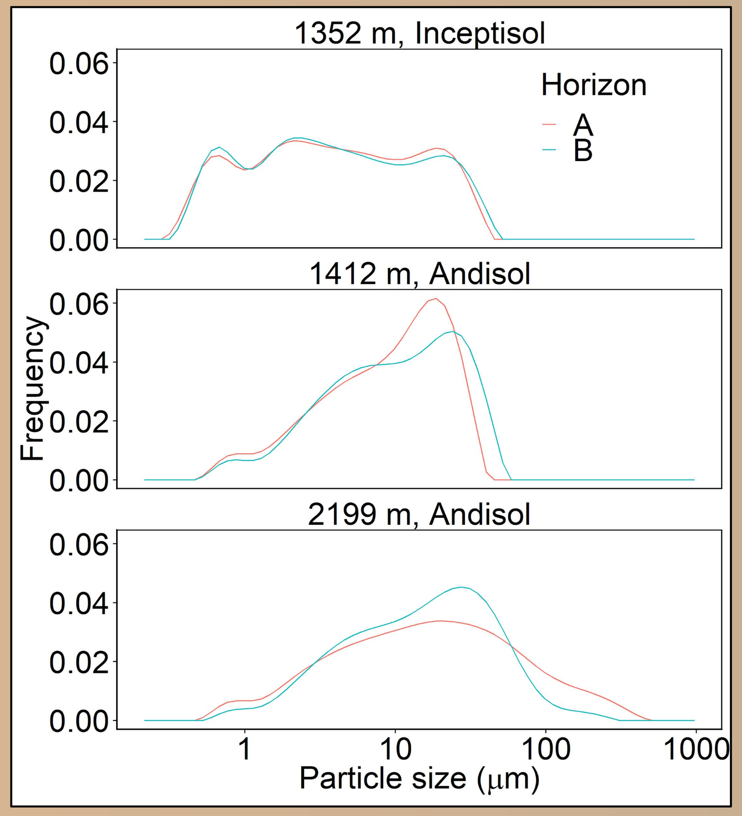




Treatment Efficiency: Autoclaving, a common pretreatment with USDA-regulated soils, increased SSA. This assuages concerns of mineral transformation but underscores how sample conditions prior to OM removal can affect estimates of SSA occlusion. Bleaching and muffling both removed similar amounts of organic matter, with bleaching being slightly more efficient in most cases. Heat degradation of iron oxides reducing SSA was an initial concern with muffling. Degradation of some iron oxides occurs at 300 °C while samples were muffled at 350 °C (Strezov et al., 2011). Differential scanning calorimetry/evolved gas analysis confirmed that the hydrous minerals in our samples dehydroxylate at higher temperatures (450-550 °C). More aggressive treatments (e.g., higher temperature muffling, hydrogen peroxide) may be required to remove a comparable proportion of OM from the higher-elevation Andisol due to greater abundance of highly reactive poorly crystalline minerals in those soils.

Percent SSA occluded by organic matter			$100 * (SSA_{TRT} - SSA_{REF}) / SSA_{TRT}$			
			Untreated reference		*Autoclaved reference*	
Elevation (m)	Soil order	Horizon	*Bleached*	*Muffled*	*Bleached*	*Muffled*
1352	Inceptisol	A	54.6	39.3	52.6	36.6
		B	-2.6	-4.8	-10.1	-12.4
1412	Andisol	A	72.7	72.2	49.9	48.9
		B	61.8	53.6	40.4	27.7
2199	Andisol	A	59.4	63.8	-0.2	10.7
		B	77.4	79.1	33.5	38.7

Particle Size Distributions: The soil weathering process generally leads to an increase in clay-sized particles, allowing us to estimate the relative weathering stage of each profile. As seen in the figure to the right there is a significantly increase in clay-sized particles in the Inceptisol indicating that it has undergone greater weathering than Andisol samples. This is associated with an increase in potential for OM stabilization.



Future Directions

Future work will extend these analyses to examine land-use effects on specific surface area coverage by organic matter. Deforestation and development of pasture is expected to influence alter C input pathways and lead to an increase in respiration rates by warming and aerating the soil. Under such circumstances a decrease in net organic matter stabilization may be observed, despite interaction with mineral surfaces.

Acknowledgements

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