NOTES

INCREASES IN EXTRACTABLE IONS IN INFERTILE AQUULTS CAUSED BY SAMPLE PREPARATION[1]

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Abstract

Effects of sample preparation on dilute acid-extractable ions were measured for paired unground field-fresh and ground air-dried soil samples taken from three depths at two sites in the coastal flatwoods of South Carolina. Concentrations of most extractable ions for the two preparation methods correlated closely. However, grinding and air-drying increased extractable NO_3^- concentrations by 6 to 10 times, NH_4^+ and PO_4^{3-} 2 to 3 times, and base cations up to 2.5 times. Ion releases from grinding and drying soils in the laboratory are related to soil organic matter and to field changes in soil moisture depletion.

Additional Index Words: soil preparation, soil P, soil organic matter, nutrient availability, drying effects.

S OIL CHEMICAL ANALYSES conventionally are performed on air-dried and ground samples because fresh samples are not handled easily. Such preparation alters many soil properties. Although effects have been studied extensively in agronomy, their implications are probably not well appreciated in forestry. Drying breaks H^+ bonds in humic and microbial constituents (Cohen, 1973), exposing new soil-organic surfaces. Clay minerals also become more acidic (Mortland and Raman, 1968). Many drying effects have been observed for N (Birch, 1960), P (Daughtrey et al., 1973), and K (Rich, 1968).

Air-drying and grinding create biases affecting interpretation. Luebs et al. (1956) found that plant-available K^+ was far better correlated with exchangeable K^+ of field-moist than air-dried soil. Daughtrey et al. (1973) found that acid-extractable P released during drying correlated closely with organic P mineralization. Soil grinding may create additional artifacts in soil chemical analyses from the physical breakdown of soil microaggregates. For example, Sollins et al. (1984) found different N mineralization rates to be associated with different soil particle size fractions. Information on nutrient supply is needed for forest soils (Stone, 1979), but samples routinely are dried and ground before chemical analysis. Thus, we examined effects of air-drying and grinding of soils on acid-extractable ions. We focused on P and N because these nutrients often account for soil infertility in the lower Coastal Plain. Changes in extractable Ca, Mg, K, and Na also were determined.

Methods

Study Site

Soils were sampled from the Santee Experimental Forest in South Carolina. Climate is humid mesothermal and annual precipitation averages about 135 cm. Soil samples were taken from two common series associated with topographic position: (i) Bethera series (clayey, mixed, thermic Typic Paleaquults) found in low-lying flats along drainages and (ii) Wahee series (clayey, mixed, thermic Aeric Ochraquults) found upslope on nearly level ridges (USDA, 1980). Bulk densities avg 1.1 Mg/m^3 for A horizons of both soils. Soil pH (1:1 water) ranges from 4.2 to 4.7.

Soil Sampling and Chemical Analysis

Five sampling areas, each having two 10- by 10-m plots, were established in both series. Organic horizons were discarded and mineral soil was collected at three depths (0–5,

Table 1. Acid-extractable ions of field-moist and air-dried Wahee and Bethera soils (mean ± standard error).

Treatment	PO₄-P	NH₄-N	NO₃-N	Ca	Mg	K	Na
				g/m³			
			Wahee soil				
			0-5 cm				
Field-moist	0.53 ± 0.10	2.67 ± 0.26	0.05 ± 0.01	107.7 ± 29.9	26.1 ± 5.1	27.3 ± 4.4	5.1 ± 0.5
Air-dried	1.36 ± 0.18	5.08 ± 0.16	0.50 ± 0.01	127.4 ± 30.1	30.8 ± 6.0	35.2 ± 3.9	10.6 ± 1.0
Release	0.83***	2.41***	0.45***	NS	NS	7.9*	5.5***
			5-10 cm				
Field-moist	0.60 ± 0.22	1.75 ± 0.12	0.06 ± 0.01	55.9 ± 18.2	14.5 ± 3.4	14.4 ± 2.3	3.0 ± 0.3
Air-dried	1.08 ± 0.27	3.65 ± 0.19	0.41 ± 0.02	70.7 ± 29.3	17.8 ± 3.7	22.0 ± 2.1	7.4 ± 0.6
Release	0.48***	1.90***	0.35***	NS	NS	7.6***	4.4***
			10-20 cm				
Field-moist	0.61 ± 0.30	1.51 ± 0.11	0.06 ± 0.01	59.2 ± 24.4	23.6 ± 5.5	12.2 ± 2.9	3.6 ± 0.3
Air-dried	0.90 ± 0.27	3.58 ± 0.27	0.40 ± 0.02	82.3 ± 38.3	30.6 ± 6.4	19.0 ± 2.4	8.0 ± 0.6
Release	0.29*	2.07***	0.34***	NS	NS	7.8***	4.4***
			Bethera soil				
			0-5 cm				
Field-moist	0.32 ± 0.02	2.35 ± 0.68	0.06 ± 0.01	214.8 ± 30.4	52.9 ± 5.9	19.9 ± 1.7	9.0 ± 1.1
Air-dried	0.93 ± 0.03	6.28 ± 0.48	0.50 ± 0.03	251.4 ± 40.4	63.9 ± 8.0	42.3 ± 2.9	17.8 ± 1.4
Release	0.61***	3.93***	0.44***	36.6*	11.0**	22.4***	8.8***
			5-10 cm				
Field-moist	0.32 ± 0.02	1.66 ± 0.15	0.06 ± 0.01	212.6 ± 34.8	61.4 ± 7.7	13.9 ± 1.3	8.3 ± 1.2
Air-dried	0.83 ± 0.09	4.38 ± 0.30	0.39 ± 0.03	267.1 ± 50.2	78.3 ± 13.4	31.4 ± 2.3	14.4 ± 1.7
Release	0.51***	2.72***	0.33***	54.5*	16.9*	17.5***	6.1***
			10-20 cm				
Field-moist	0.39 ± 0.05	1.40 ± 0.20	0.06 ± 0.02	243.6 ± 43.7	77.8 ± 10.1	11.5 ± 1.1	11.4 ± 2.3
Air-dried	0.68 ± 0.08	3.78 ± 0.22	0.34 ± 0.02	316.7 ± 58.4	107.2 ± 17.1	28.3 ± 1.6	18.6 ± 2.5
Release	0.29***	2.38***	0.28***	73.1**	29.4**	16.8***	7.2***

*,**,*** Air-drying effect (release) statistically significant at $p = 0.05, 0.01$, and 0.001, respectively.

5-10, and 10-20 cm) in November 1980, using a 2-cm diam sampling tube. Five pairs of samples were taken in each of the 20 plots and composited into two sets of paired samples. One set was air-dried in paper bags for about 20 d; the other was stored at 3°C in plastic bags.

Air-dried samples were ground in a hammer mill. Virtually all material passed a 2-mm screen. Field-moist soils were thoroughly mixed with a spatula but not sieved. Samples of about 10-g each were extracted with dilute double-acid solution (0.05 M HCl plus 0.0125 M H₂SO₄) at a 1:5 soil/solution volume ratio according to Mehlich (1953). These were agitated 5 min on a reciprocating shaker before filtering. Extractable NH₄⁺-N was determined by isocyanurate colorimetry (Reardon et al., 1966), NO₃⁻-N by Cd reduction and azo-dye colorimetry (American Public Health Association, 1976), extractable PO₄³⁻-P by molybdenum blue colorimetry (Mehlich, 1953), and extractable base cations by atomic absorption spectrophotometry (Isaac and Kerber, 1971). Air-dried samples also were analyzed for organic C (Graham, 1947), Kjeldahl-N (Crooke and Simpson, 1971), and total P (Technicon Industrial Systems, 1977).

Results

Air-drying and grinding of soils from both sites significantly increased most extractable ions compared with soils that remained field-moist (Table 1). Air-drying caused inconsistent changes in extractable Ca²⁺ and Mg²⁺, significantly increasing concentrations in Bethera soil, but not in Wahee soil.

Increases in extractable ions caused by grinding and air-drying often were substantial. Soil NO₃⁻-N, near detection limits in field-moist soil, was increased 5.7 to 10 times. Extractable NH₄⁺-N and PO₄³⁻-P were increased 1.9 to 2.7 times and 1.5 to 2.9 times, respec-

Table 2. Pearson product-moment correlation coefficients for extractable ions in air-dry and field-moist samples taken from both soils from each soil depth.

Depth	PO₄-P	NH₄-N	NO₃-N	Ca	Mg	K	Na
cm				r			
0-5	0.92***	0.36	0.30	0.95***	0.96***	0.41	0.89***
5-10	0.95***	0.15	0.23	0.97***	0.95***	0.58**	0.96***
10-20	0.98***	0.33	0.43	0.98***	0.98***	0.51*	0.97***

*,**,*** Significance at $p = 0.01, p = 0.001$, and $p = 0.0001$, respectively.

tively. Extractable bases increased up to 2.5 times, although monovalent cations, Na⁺ and K⁺, tended to increase more on a relative basis than the divalent Ca²⁺ and Mg²⁺ (Table 1).

In general, the Bethera soil had higher concentrations of extractable ions that Wahee soils, and increases were relatively greater following grinding and drying (Table 1). Although PO₄³⁻-P was lower in Bethera than in Wahee soil, relative increases were greater in Bethera. Extractable PO₄³⁻-P, Ca²⁺, Mg²⁺, and Na⁺ in field-moist soils were well correlated with extractable quantities in air-dried soils ($r \geq 0.89$, Table 2). Extractable K⁺ in field-moist and air-dry soils was significantly correlated in samples from 5- to 10- and 10- to 20-cm depths but not in samples from 0 to 5 cm. In contrast, mineral N was correlated poorly (Table 2).

Sample preparation generally increased extractable P and N by greatest amounts in samples from the surface 5 cm of soil, layers with the highest concentrations of organic matter (Table 3). In the Bethera soil, large releases of Ca²⁺ and Mg²⁺ occurred in sam-

Table 3. Mean organic C, total Kjeldahl N, and total P concentrations and ratios of C/N and C/P for each soil series and sample depth.

Soil depth	Total			Ratio	
	Organic C	Kjeldahl-N	P	C/N	C/P
cm	g/kg	g/m³			
Wahee soil					
0-5	36.9a†	1144a	180a	42.9a	209.1a
5-10	19.7b	497b	147b	40.7ab	137.1b
10-20	13.8c	329b	122b	34.3b	113.5c
Bethera soil					
0-5	48.9a	1702a	227a	29.9a	214.8a
5-10	21.3b	813b	149b	26.9ab	141.4b
10-20	13.5c	542b	121b	25.1b	114.4b

† Mean differences between sample depths within each soil by Duncan's Multiple Range Test, $p < 0.05$.

ples from 10 to 20 cm (Table 1), samples with the lowest organic contents (Table 3).

Discussion

The distribution of extractable PO_4^{3-}-P with soil depth suggests that organic matter was a major source for increased P after grinding and drying. Concentrations of extractable PO_4^{3-}-P in field-moist soils were relatively constant with soil depth, averaging only 0.47 g/m³ in both soils within the surface 20 cm. In contrast, extractable PO_4^{3-}-P in air-dry soils was inversely related to soil depth (Table 1) as was soil organic matter (Table 3). Drying and grinding increased extractable PO_4^{3-}-P by an average of 0.72, 0.50, and 0.29 g/m³ in the 0- to 5-, 5- to 10-, and 10- to 20-cm layers, respectively, soil layers that avg 42.9, 20.5, and 13.7 g/kg organic C, respectively. Further increases in extractable PO_4^{3-}-P caused by sample preparation may have come from mineral fractions, particularly at lower depths.

Factors influencing net mineralization of organic N and nitrification during drying are complex, as indicated by a lack of correlation between extractable NH_4^+-N or NO_3^--N in field-moist and air-dried soils (Table 2). Preparation differences for NH_4^+-N seemed unrelated to a C/N ratio. Changes are difficult to explain and emphasize the ephemeral nature of soil mineral N.

Findings from these and other studies raise questions concerning interpretations made form laboratory-prepared samples. Drying is known to alter concentrations of mineral N and P (Birch, 1960; Daughtrey et al., 1973), but even cation exchange data may be more empirical than frequently supposed. However, while sample preparation did create large biases, extractable ions generally were well correlated in field-moist and air-dry samples (Table 2). Therefore, soil analysis of air-dried samples may adequately represent relative abundance of nutrients under field conditions.

Changes in soil chemistry resulting from laboratory air-drying may be similar to changes noted for soils drying in the field. Luebs et al. (1956) found substantial increases in exchangeable K when soil moisture decreased to 50 to 100 g/kg. Similarly, Birch (1960)

found large increases in N mineralization in the field when soils were rewet after long periods of seasonal drying. Semb and Robinson (1969) demonstrated that drying stimulated nitrification under field conditions. Moisture fluctuations are seasonally extreme in Aquults examined in this study. Thus, natural wet-dry cycles may well influence seasonal availability of nutrients. Wells et al. (1973) set 0.003 g/kg of double-acid extractable PO_4^{3-}-P as a critical concentration for growth response of *Pinus taeda* L. to P fertilization in similar Coastal Plain soils. From a practical standpoint, sample preparation procedures can be particularly important if soil analysis is to be more effective in predicting tree-growth response to P fertilization.

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