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Changes in soil mineralogy due to nitrogen fertilization in an agroecosystem

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ABSTRACT

Additions of nitrogen (N) fertilizer to surface soil can trigger a wide array of complex effects, including changes in soil chemical, physical, and microbial properties which impact both the nitrogen and carbon cycles. While abundant literature exists regarding the influence of N amendments on processes and properties influencing the soil carbon cycle, there is little recognition given to potential changes in soil mineralogy. We collected surface soil (Maury silt loam, Typic Paleudalf) from a long-term agroecosystem under no-tillage management which has received annual inorganic N additions (0, 168, 336 kg N ha^{-1}) for 34 years and characterized the soil mineralogy and other relevant properties. With recent liming, N fertilizer addition was associated with only slight changes in soil pH and the suite of exchangeable cations. Silt mineralogy was not influenced by N, but x-ray diffraction found changes in the clay fraction. The clay mineral assemblage in the control (0 kg N ha^{-1}) is complex, comprised of layers of pedogenic chlorite, vermiculite, hydroxy-interlayered vermiculite, mixed-layer chlorite–vermiculite, illite, kaolinite, and quartz. Fertilizer N additions resulted in a 3- and 3.3-fold decrease in the 1.4 nm/1.0 nm peak area ratios for Mg-clay slides in the 168 and 336 kg N ha^{-1} treatments. This decrease is likely due in part to fixation of NH_4^+ in vermiculite layers, corroborated by increases in the intensity of the infrared (IR) band at 1430 cm^{-1} (assigned to the N—H bending mode of NH_4^+) with added N. The role of biota emerged as shown by a negative relationship between water-soluble oxalate concentrations and the 1.4 nm/1.0 nm peak area ratios (r = —0.56, P = 0.06). Past acidification due to nitrification of added NH_4^+ which occurred prior to liming might have played a role in weathering of pH-sensitive minerals such as chlorite. Our findings raise questions about the capacity of reactive 2:1 mineral layers to fix NH_4^+ and how this is moderated by biota in no-till agroecosystems.

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1. Introduction

A widely-held view in soil science is that soil mineralogy is an inherent property, dictated by the integrated effects of the soil formingfactors and little affected by management (Palm et al., 2007; Brady and Weil, 2008). In agroecosystems, however, several lines of inquiry challenge this dogma. Addition of ammonium (NH_4^+)-based fertilizers to soils containing reactive 2:1 phyllosilicate minerals can lead to changes in mineralogy because the added NH_4^+ can become fixed in a similar manner as K^+ (Nieder et al., 2011; Skiba, 2013). Examples of such minerals which can fix NH_4^+ include layers of vermiculite and high charge smectite (Rich and Lutz, 1965; Ross et al., 1985; Chen et al., 1989; Rider et al., 2006). Soils with a history of N fertilizer applications contain greater levels of fixed NH_4^+ when compared with unfertilized plots (Baethgen and Alley, 1987).

Nitrogen fertilization can accelerate soil acidification due to the combined effects of ammonium nitrification, base cation removal with nitrate leaching, and the harvest of grain or other plant tissues (van Breemen et al., 1983; Barak et al., 1997). Soil acidification is accompanied by reductions in exchangeable cation (Ca^{2+} and Mg^{2+}) concentrations, effective cation exchange capacity (ECEC) and increased exchangeable Al^{3+} (Bouman et al., 1995; Barak et al., 1997), patterns which point to mineral weathering as an important buffering mechanism (Chadwick and Chorover, 2001). Mineral weathering can buffer against nitrification-induced acidification and has been reported to involve subtle changes in Al^{3+} (McGahan et al., 2003; Tye et al., 2009). Minerals susceptible to enhanced weathering under acid conditions include feldspars, micas, chlorites, and vermiculites (Wilson, 2004).

The N fertilization of no-till agroecosystems places biota in a unique position with respect to mineral weathering. Plants, and their associated microorganisms, impact soil minerals by releasing weathering agents, biocycling nutrients, secondary production of biogenic minerals, and altering water dynamics (Kelly et al., 1998; Lucas, 2001). The SOC, used as a proxy of plant production (Kelly et al., 1998), is stratified at the no-till soil surface when compared with plowed soil (Wells, 1984; Poirier et al., 2009) and increases with increased fertilizer N rate (Blevins et al., 1977; Kaufman et al., 2013). The SOC may supply organic acids to the water-soluble organic carbon (WSOC) pool, which can

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chelate and solubilize cations such as Al^{3+} from mineral structures (Drever and Stillings, 1997). Oxalate, a commonly identified aliphatic organic compound in the WSOC fraction (Fox and Comerford, 1990), is produced by plants and fungi (Paris et al., 1996; Gadd, 1999) and functions as a chelator. This latter attribute allows oxalate to promote smectite formation (Schumann et al., 2013), particularly as oxalate levels increase in response to greater net primary productivity (Barré et al., 2009). Other studies, however, report that oxalate can weather feldspar, chlorite, and vermiculite minerals (Hamer et al., 2003; Lawrence et al., 2014; Vicente et al., 1977). A comparison of no-till versus conventionally plowed soil has shown that SOC accumulation in no-till favors 2:1 clay minerals over 1:1 minerals such as kaolinite (Karathanasis and Wells, 1989), however, the impact of fertilizer N additions has not been explored.

If management practices such as N fertilization can impact soil mineralogy, then we must expand evaluation of this practice, as widespread N limitations to plant productivity drives extensive N use (Vitousek and Howarth, 1991; Robertson and Vitousek, 2009). Past studies at the long-term no-till agroecosystem in Kentucky have reported increased soil acidification, exchangeable Al^{3+}, and SOC with increasing N addition at the soil surface (Blevins et al., 1977; Blevins et al., 1983). Lime addition was required to counteract soil acidification and optimize crop production (Blevins et al., 1978; Grove and Blevins, 1988). It is possible that mineral weathering was engaged to buffer acidification (Chadwick and Chorover, 2001) prior to liming on this site, leaving behind a legacy effect (Foster et al., 2003; Monger et al., 2015). The purpose of this study was to determine if long-term N addition has altered soil mineralogy in the surface (0–5 cm) layer of a no-till soil. Given that vermiculite layers are an important component of the clay mineral fraction of this soil type (Six et al., 2000), we hypothesized that NH_4^+ would collapse these reactive 2:1 clay layers owing to increased ammonical N inputs. A second hypothesis is that previous acidification reported in this no-till surface soil prior to liming has left an imprint on the soil mineralogy. We further hypothesized that increases in SOC due to N fertilizer additions in no-till will result in greater appearance of 2:1 phyllosilicate minerals.

2. Materials and methods

2.1. Site description

The long-term experimental plots are located on the University of Kentucky's Agricultural Experiment Station research farm near Lexington, KY at about 38° 07′ N, 84° 29′ W. This site is within the larger Inner Bluegrass Region, where uplift along the Cincinnati Arch geological formation has exposed Ordovician-age limestone (Wharton and Barbour, 1991; McGrain, 1983). Mean annual precipitation averages 1100 mm and the mean annual temperature is 13.0 °C. The soil is a well-drained Maury silt loam (fine, mixed, semi-active, mesic Typic Paleudalf), formed in a thin loess mantle over Ordovician limestone residuum. The site was in bluegrass (*Poa pratensis*) sod for 50 years prior to cultivation (Ismail et al., 1994). Two long-term tillage treatments, no-tillage and moldboard plow, were established early in 1970 and are main plots laid out in four randomized blocks. In the no-till treatment, crop residues are left intact and the only soil disturbance is a narrow slit where seed is sown during planting. Corn (*Zea mays L.*) is grown on the site every year and a winter annual cereal cover crop is established following grain harvest. There are four fertilizer N (NH_4NO_3) rate (0, 84, 168, 336 kg N ha^{-1} yr^{-1}) subplots and the N is applied near corn establishment. Potassium (as KCl) is added at an average rate of 56 kg K ha^{-1} yr^{-1} to all plots. Phosphorus fertilization is not necessary because the residuum is high in apatite (Karathanasis, 1991). All plots began receiving dolomitic limestone beginning in 1975 at a flat rate for several application events and at recommended rates according to soil test since 2000 (Blevins et al., 1983; Grove and

Blevins, 1988). Thus, higher lime rates have been used on the plots receiving the highest rate of fertilizer N.

2.2. Soil sampling and characterization

Soil cores were taken in July 2004 over the 0–5 cm depth, between corn rows, from no-till subplots fertilized at 0, 168 and 336 kg N ha^{-1} yr^{-1} using a cylindrical probe 2.0 cm in diameter. Composites of ten to twelve cores per replicate subplot, for a total of twelve sampled plots, were kept field moist, sieved to pass a 2 mm screen, and stored at 4 °C in plastic bags. Subsamples were dried in the oven at 105 °C to determine gravimetric moisture content. Soil pH was determined in a 1:2 soil:solution ratio using deionized water and a pH meter (Metrohm 744, Herisau, Switzerland) with a combination glass electrode. Total carbon and nitrogen concentrations were determined using a CHN analyzer. Lack of effervescence with 2 M HCl ruled out the presence of calcium carbonate (residual liming material). Thus, total C by combustion represents total SOC. The WSOC was determined in extracts obtained by shaking 4.1 g of soil in 10 mL of deionized water, followed by centrifugation and filtration, and using a Shimadzu TOC-5050A analyzer. Oxalate and acetate were measured in the water extracts using a Metrohm ion chromatograph.

Potassium chloride-extractable inorganic N (NO_3^- and NH_4^+) was determined using a colorimetric plate reader method (Dorich and Nelson, 1984). Exchangeable cations (Ca, Mg, K, and Na) were determined in neutral ammonium acetate and exchangeable Al and Mn were measured in KCl extracts to compare with previous studies on this site (Blevins et al., 1977; Blevins et al., 1983). Summation of basic cations and Al and Mn was used to estimate ECEC.

2.3. Soil fractionation and characterization

Soil samples were fractionated into particles of sand (2000–50 μm), silt (50–2 μm), and clay (<2 μm) after organic matter removal using H_2O_2 as described elsewhere (Jackson, 1974; Karathanasis and Hajek, 1982). Texture was estimated by normalized recovery of each particle size separate after fractionation. Dilute Na_2CO_3 was employed as the dispersant and the free iron oxide removal step was omitted. The X-ray diffraction (XRD) analyses were conducted on a Bruker-AXS D8 Discover diffractometer equipped with Cu Kα radiation. Diagnostic treatments, consisting of Mg-, Mg-glycerol and K-saturated soil clay fractions mounted on glass slides (Drever, 1973) and heated at 25 and 550 °C, were imposed in order to discriminate clay minerals using (XRD) analysis (Harris and White, 2008). Clay fraction scans were run from 2 to 30° 2Θ with a step size of 0.02° 2Θ and a count time of 2 s/step for all four field replicates from each of the three N rate treatments. Diffractograms were baseline corrected in order to determine peak intensities. Integrated peak areas were calculated for the 1.4 and 1.0 nm peaks, corrected for quartz, and the 1.4/1.0 peak area ratio then determined in order to estimate relative 2:1 phyllosilicate mineral abundance at each N fertilizer rate. This approach has been used elsewhere (Tice et al., 1996; Calvaruso et al., 2009). The presence of halloysite was explored by reacting clay fractions with formamide followed by immediate XRD scans in the region from 6 to 14 ° 2Θ (Churchman, 1990). Silt fractions were also analyzed by XRD from 2 to 80° 2Θ.

In order to identify exchangeable cations in the interlayer, 1 M KCl was reacted with air-dried clay fractions using the protocol of Barré and Velde (2010) and Hong et al. (2014). Ammonium oxalate extractions were also performed on the clay-sized fractions by adding 10 mL of oxalate at pH 3 to 100 mg of clay followed by shaking for 18 h (McKeague and Day, 1966). Total Al, Si, Fe, Ca, Mg, and K were measured in the clay fractions after digestion using the Bernas method (Bernas, 1968).

Milligram quantities of clay samples were homogenized with 300 mg of spectroscopic grade KBr and analyzed using a Nicolet 6700