

Speciation of Phosphorus in Recently Acidified Soils



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Introduction

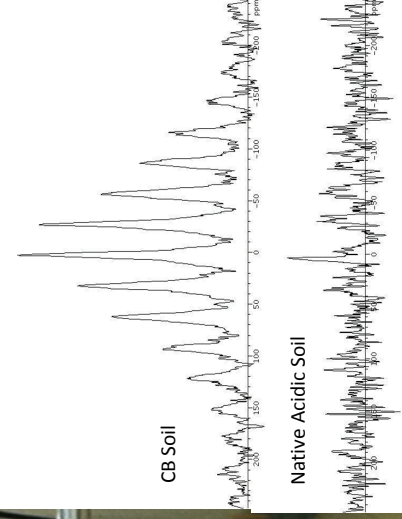
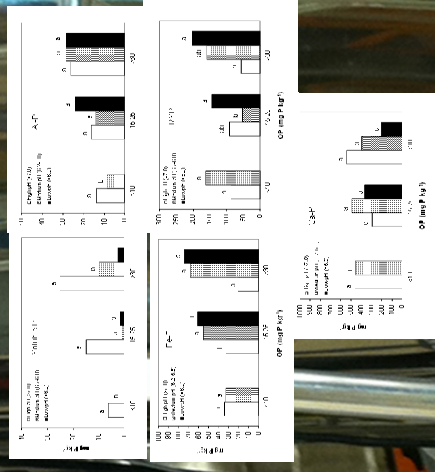
There is growing concern for excess phosphorus (P) in the environment. Agriculture is a large consumer of P fertilizer and efforts to maximize production should be tailored to soil conditions. The Columbia Basin of Washington State has seen gradual soil acidification from continual ammoniacal nitrogen application. The Olsen (OP) method is established as the method of choice for available phosphorus (P) measure in the region.¹ Because the chemistry of this method assumes a dominant calcium (Ca)—P chemistry the validity and interpretation of the method comes into question. The objective of our research was to determine dominant P species in recently acidified soils of the CB using traditional chemical fractionation and ³¹P NMR spectroscopy.

Materials & Methods

Soils were collected from 0-30 cm representing three pH levels (<6.0, 6.2-6.8, >7.0) and three OP levels (<10, 15-25, >30 mg P kg⁻¹) within each pH range. Additionally native CB, Palouse, and native acidic samples were analyzed. The inorganic P fractionation was performed by the method of Kuo² and determines the amounts of P in the soluble, Fe-(iron), Al-(aluminum), RSP (reductant soluble), and Ca-P fractions. Soil samples 1-15 were air-dried and ground to pass a 2-mm screen for analysis of solid-state ³¹P NMR. The spectra were collected with a spectrometer (Varian NMRs 500 MHz, Walnut Creek, CA) operating at 202.531 MHz. The P compounds were identified by their chemical shifts (ppm) and compared to published data for P speciation in soil samples.

¹ R. Miller, Personal Communication, 2011.
² Kuo, S. 1996. Phosphorus, p. 869-939. In: D. Sparks (Ed.) Methods of soil analysis, 2nd ed. SSSA, Madison, WI.
Soil Science Society of America, 666 R. Russell, 1705 North Central Expressway, WA. We also acknowledge the support of the Washington State University.

Results



This figure shows the inorganic P fractions of soluble, Al-P, Fe-, RSP and Ca-P for CB soils. The data represents mean values and are grouped by soil pH within an initial P (as OP) level. Means with different letters within an initial P group are significant ($\alpha = 0.05$). The significance of the Fe-P fraction in relation to CB soil pH demonstrates a possible state of transition for the soils examined, while the Fe-P constitutes only a small part of the inorganic soil P, there is evidence to suggest that this fraction is increasing as the soil pH decreases.

The chemical shift of the isotropic peak in these samples falls within the range of 1.69-2.89 ppm. However, assigning peak chemical shifts to chemical P species for different soil pH levels was not possible due to lack of resolution caused by the broadness of the peaks. These samples also have a significant spinning side band (SSB) pattern caused by the Chemical Shift Anisotropy (CSA). To reduce the SSB it is common practice to use smaller diameter rotors that are able to spin faster, but in this sample size the rotor rotation was low, in the range of 7.44 to 2281 mg P kg⁻¹.

Conclusions

Chemical P fractionation of CB soils demonstrated that Ca-P forms account for 60% or more of the total inorganic P. When comparing soil initial P levels, it was found that certain fractions of P are affected by soil pH. Specifically, the Fe-P fraction increased as pH decreased. While the Fe-P fraction makes up a relatively small portion of the total inorganic P compared to Ca-P, this may be a sign of potential transition from a predominant Ca-P chemistry. Soil chemical shift (MR shift) for the Fe-P fraction was similar to that of the Ca-P fraction. Low soil P together with the presence of native Ca-P may have inhibited our ability to observe a potential inorganic P fraction shift in the peak of the Ca-P fraction.