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. 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 \(^{31}\)P 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 morgamic P fractionation was performed by the method of Kuo\(^2\) 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 \(^{31}\)P NMR. The spectra were collected with a spectrometer (Varian NMRS 500 MHz, Walnut Creek, CA) operating at 202.311 MHz. The P compounds were identified by their chemical shifts (ppm) and compared to published data for P speciation in soil samples.

Results
This figure shows the inorganic P fractions of soluble, Al-, Fe-, ASR and Ca-P from CB soils. The data represents mean values and are grouped by soil pH with an initial P (as OP) level. Means with different letters within an initial P group are significant (\(p = 0.05\)). 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 isotope 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 breadth 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 series the P concentration was low, in the range of 411 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 inorganic P. When comparing soil initial P levels it can be seen that certain fractions of P are affected by soil pH. Specifically, the Fe-P fraction increased as pH decreased below 6.8. While the Fe-P fraction makes up a relatively small portion of the total inorganic P compared to Ca-P, it is indicative of potential transition from a predominantly Ca-P chemistry. Low soil P together with the presence of paramagnetic ions inhibited any ability to assign the isotropic peak center chemical shift of each sample.

1 R. Miller, Personal Communication, 2011.