

Changes in Phosphate Bonding as Affected by Level of Adsorption on Oxide Minerals

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Concern over declining surface water quality caused by transport of nutrients, particularly nitrogen and phosphorus, from agricultural fields into streams and rivers is a major issue in the U.S. and worldwide. Although inorganic phosphate typically binds strongly to soil particles, soils have a maximum capacity to retain (sorb) phosphate. Many soils have historically received inputs of phosphorus from sources such as fertilizers and animal wastes that were in excess of removal by crops, so levels of soil phosphorus have been continuously increasing. As the soil P concentration increases, the water solubility of phosphate increases, as would mobility. Over time, some portion of soil phosphate may transform into different chemical forms that are less susceptible to being dissolved; however, these transformations are poorly understood.

Observations on a number of different soils worldwide have shown that phosphate retention capacity and phosphate solubility are often related to some measure of chemically extracted Fe and Al (Beauchemin and Simard, 1999). Different extraction procedures have been used, but those targeting non-crystalline and poorly crystalline Fe- and Al-oxide minerals usually gave the best indicators of P sorption capacity. These minerals tend to have a high phosphate adsorption capacity. Extensive research on pure forms of crystalline and non-crystalline Fe- and Al-oxide minerals has provided ample evidence that phosphate is strongly bound by forming inner-sphere surface complexes. Two types of inner-sphere surface complexes, monodentate and bidentate, are illustrated in Figure 1 for phosphate on the Fe-oxide mineral goethite (α -FeOOH). Because these complexes bond with either one or two reactive surface sites, both the affinity of phosphate binding and the adsorption capacity of an oxide mineral would depend on the surface configuration.

Adsorption models have been developed to better understand and predict the effects of adsorbed phos-

phate level and other relevant soil properties such as pH on phosphate solubility. Surface complexation models assume a molecular configuration for adsorbed chemical species (surface species) and apply conditional equilibrium constants to quantify adsorption of these species. One such model, the constant capacitance model, has accurately described the concentration and pH effects on phosphate adsorption on pure Fe- and Al-oxide minerals by assuming that only monodentate inner-sphere surface complexes occur (Goldberg, 1992). Moreover, conditional equilibrium constants obtained from the pure oxide minerals successfully predicted phosphate adsorption on a number of non-calcareous soils (Goldberg and Sposito, 1984). However, the consistency of such models with macroscopic adsorption data does not confirm a given molecular configuration of phosphate on the oxide mineral surfaces. The accuracy of such models might be enhanced by molecular-scale data showing the distribution of surface species (e.g., monodentate versus bidentate complexes) at different pH and adsorbed phosphate concentrations.

Infrared spectroscopy has been used to study the molecular configuration of phosphate adsorbed on Fe- and Al-oxide minerals. These studies have also addressed the state of protonation of the adsorbed species, i.e., whether or not oxygens that are not bound to the surface (Fig. 1) carry a proton. Infrared studies of Parfitt et al. (1977) indicated that phosphate adsorbed on gibbsite [α -Al(OH)₃] was a bidentate complex bonded only to hydroxyls occurring on the edge surfaces of the gibbsite platelets. Their prediction of gibbsite adsorption capacity based on the estimated number of edge-surface hydroxyl groups and bidentate bonding configuration was consistent with macroscopic measurements of adsorption capacity. Tejedor-Tejedor and Anderson (1990) concluded that phosphate was adsorbed on goethite mainly as bidentate complexes,

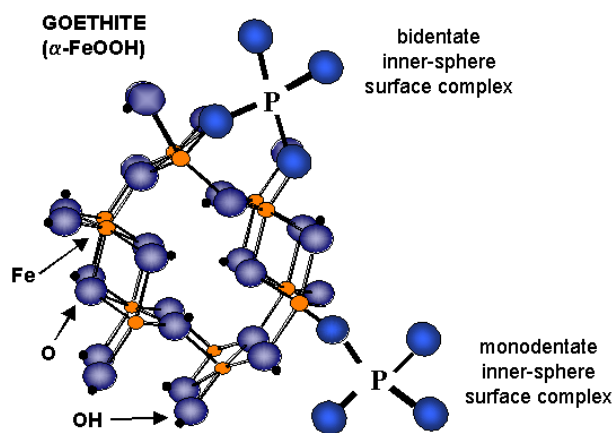


Figure 1. Schematic illustrating possible surface species of *o*-phosphate (PO_4) on an Fe-oxide mineral.

with monodentate complexes being detected by infrared spectroscopy under some pH conditions and adsorbed phosphate levels. In contrast, Persson et al. (1996) concluded that monodentate surface complexes were always dominant, regardless of the pH and adsorbed P concentrations studied, and that changes in infrared spectra were due to changes in the protonation state of the adsorbed phosphate species.

Our research objective is to determine whether phosphorus K-XANES analysis reveals differences in the surface speciation of phosphate on oxide minerals over a range of adsorbed P concentrations, and at constant pH. XANES analyses were done on aqueous samples over a range of phosphate concentrations, including concentrations that were lower than those reported in the infrared studies. Because essentially all phosphate in our samples was sorbed, spectra were not influenced by dissolved phosphate species. XANES spectra were collected at NSLS Beamline X-19A on samples containing phosphate adsorbed on goethite at levels between 10 and 480 mmol P/kg goethite (0.08 to $3.7 \mu\text{mol}/\text{m}^2$) at pH 6. A sample of gibbsite with phosphate adsorbed at near-maximum capacity (12 mmol/kg or $1.3 \mu\text{mol}/\text{m}^2$) at pH 6 was also analyzed. Data were collected in fluorescence mode using a Ge(111) monochromator and a He-purged sample chamber designed to house a Passivated Implanted Planar Silicon (PIPS) detector.

Figure 2 shows that P K-XANES spectra for phosphate adsorbed on gibbsite and goethite have different features. For an adsorbed P level of 10 or 12 mmol/kg, a shoulder on the high-energy side of the white line peak is apparent, regardless of whether the adsorbent is goethite or gibbsite. In view of the infrared spectroscopic results of Parfitt et al. (1977), one could tentatively assign the prominent shoulder in the spectra for

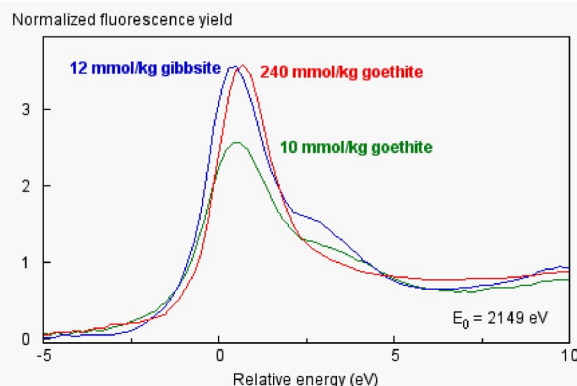


Figure 2. Phosphorus K-XANES spectra for phosphate adsorbed on gibbsite [$\alpha\text{-Al}(\text{OH})_3$] and goethite [$\alpha\text{-FeOOH}$]. Note the prominent shoulder on the high-energy side of the white-line peak for adsorbed P levels of 10 and 12 mmol/kg.

PO_4 on gibbsite to the presence of bidentate-bonded phosphate. If so, then the shoulder on the XANES spectrum for PO_4 on goethite would also suggest bidentate bonding, consistent with infrared spectroscopy evidence of Tejedor-Tejedor and Anderson (1990). At the higher level of adsorbed PO_4 on goethite (Fig. 2), the high-energy shoulder has diminished and the white-line peak has increased in intensity, indicating a different molecular configuration of adsorbed phosphate.

Comparing a range of adsorbed PO_4 concentrations on goethite (Fig. 3), the prominence of the shoulder on the high-energy side of the white line peak diminished systematically with increasing level of adsorbed PO_4 . The white line peak intensity increased between 10, 20, and 480 mmol P/kg, but was essentially constant for levels between 20 and 120 mmol P/kg goethite. The spectral changes indicate that there are multiple species of phosphate associated with the

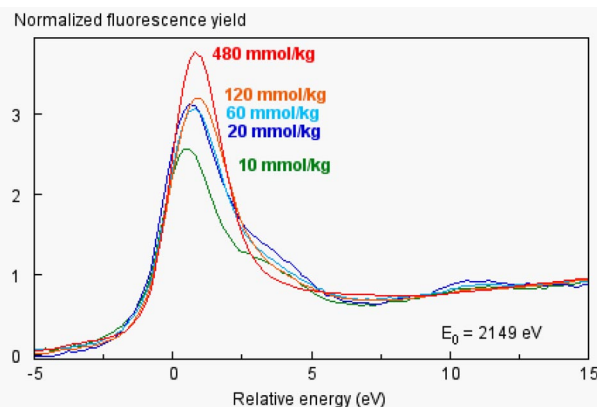


Figure 3. Phosphorus K-XANES spectra for phosphate adsorbed on goethite at different levels.

goethite surface at pH 6, depending on level of adsorbed PO_4 . Whether or not the protonation state of the bound phosphate is affecting the XANES results cannot be determined from these data. Infrared spectroscopy data of Tejedor-Tejedor and Anderson (1990) indicated that the pK_a for deprotonation of the bidentate phosphate species on goethite decreased from ~6 to ~3.7 as adsorbed P decreased from 190 to 100 mmol/kg (2.4 to 1.2 $\mu\text{mol}/\text{m}^2$). If protonation effects are not significant at a constant pH of 6, then our XANES spectra are more consistent with the notion that bidentate phosphate species were dominant at low levels of phosphate adsorption, and monodentate species (or other surface species) occurred at higher levels of adsorption.

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Association of Lead with Soil Manganese Oxides

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It is well established that manganese oxide nodules and concretions, found in various environments, accumulate heavy metals. In fact, mining of oceanic Mn nodules has been proposed because of their high concentration of Cu, Co and Ni. Manganese oxides produced by freshwater *Leptothrix discophora* bind high concentrations of Pb (Nelson et al. 1999). Terrestrial Mn oxides also are high in many metals. Recent work at the NSLS has shown that added Pu will associate with Mn oxide minerals in volcanic tuff (Duff et al. 1999). The study of soil Mn oxides has been difficult because of low concentrations and difficulties in sample handling (Bartlett and James 1980).

In the aerobic soils we have studied, Mn tends to be found in discrete, concentrated areas usually 50 μm or less in diameter (see Figs 2-7). Most soil Mn is in the oxide form, primarily Mn(IV) but with an uncertain contribution from Mn(III). Earlier work showed that soil Mn oxides sorb added Cr(III) and oxidize it to more mobile and toxic Cr(VI) (Bartlett and James 1979). Subsequent studies by many researchers have shown an interaction of soil Mn with a number of metals, including Pu and As. Soil Mn oxides have also been shown to oxidize a number of contaminant organics, with some suggestion of catalyzing oxidative polymer-

ization (Shindo and Wang 1982). Although often found in relatively low concentration, the environmental reactions of soil Mn oxides are significant and more information is needed about their structure and reactivity.

As mentioned, analysis of soil Mn oxides is difficult. Determining the structure by x-ray diffraction is hampered by the fact that even pure mineral Mn oxides are relatively disordered and give broad peaks. Interference by other soil minerals is strong and Mn peaks are not distinguishable without concentration of the sample. In addition, soil Mn oxides are sensitive to environmental change and easily reduce upon drying (Bartlett and James 1980, Ross et al. 2001a). This observation may be counterintuitive but the redox status of Mn in the environment has a delicate poise. Synchrotron-based x-ray spectroscopic methods appear ideal for studying these oxides. Unfortunately, photoreduction appears to occur during XANES spectroscopy of moist soils (Ross et al. 2001b). These effects, however, are not extremely rapid and useful data can be obtained before significant change occurs in the oxides.

We have been studying soils from northwestern Vermont that are both high in Mn and high in Cr oxidizing ability. These soils are found near the Champlain

thrust fault and developed either over high-pH glacial till or high-lime bedrock. The soils presented here are interesting in that they are moderately high in Mn (Holiday 0.14%, Beech-O 0.16%, Pease 0.79% - our highest soils are 1.8%) and they are relatively acidic. They are in forested areas that are shallow to bedrock and subsequently have high organic carbon content (Holiday 24.4%; Beech-O 27.2%; Pease 24.1%) and low pH (Holiday 5.4; Beech-O 5.1; Pease 4.6). This high carbon content is significant in terms of Pb sorption in that it is generally assumed that Pb is strongly bound to the organic fraction in soils. One of our objectives in working with these soils is to determine if there is a relationship between Cr oxidation and sorption of other metals using information provided by XANES spectroscopy.

Manceau et al. (1992) and Schulze et al. (1995) showed that Mn XANES spectroscopy of Mn oxide minerals reveals differences due both to oxidation state and coordination environment. Minerals with tunnel structure and less edge sharing tend to have lower edge absorption peaks and more distinct pre-edge features. Because most "higher" oxides of Mn contain some Mn(III) and because of the above effects on peak shapes, it is difficult to model oxidation state. However, the separation between Mn(II) and Mn(IV) is clear, and our Mn K α XANES spectra confirm that the soil oxides are primarily Mn(IV) (Fig. 1). The similarity to birnessite, a layer-structured Mn oxide, suggests a similar local environment for the soil Mn oxides. The pre-edge peaks for the soil oxides and birnessite also match. For the higher pH soils that we have studied, the absorption edge is shifted to higher energies (data not shown). Indeed, there is an excellent correlation between edge position and soil pH with soils above pH 7 having an edge about 1 eV higher. This is logical in

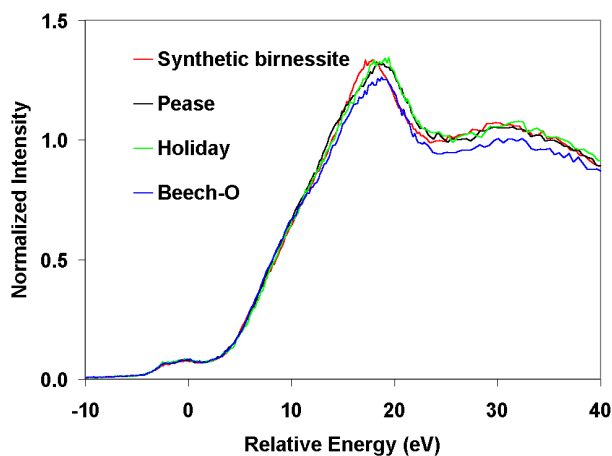


Figure 1. Mn K α XANES of synthetic birnessite and three soil samples. Energy is relative to the pre-edge peak of a Mn(VII) standard

that the higher pH promotes a more complete oxidation to Mn(IV). We have not yet been able to discern a relationship between features of the XANES spectra and the soils' relative ability to oxidize Cr. There are a number of potentially interfering substances in the complex soil environment, including reducing organics and other metals.

Using the x-ray microprobe at beamline X26A at the NSLS, we mapped the metal distribution in these soils using SXRF. Samples were observed with and without added Pb using a spot size of ~20 x 20 μ m. For the Pb treatment, moist soils were treated on an equal Mn-weight basis with Pb at a concentration of either 1.0 or 0.1 mmol L⁻¹. Samples were rinsed with Ca solutions to remove readily exchangeable Pb and then air-dried prior to x-ray analysis. Complete spectra were collected from areas of metal concentration, selected by visual inspection of the 2-D images. Peaks in the spectra were fitted and used to estimate point concentrations of metals (SNRLXRF).

It is clear from the results (Figs. 2-7) that Pb is associated with Mn in both untreated and treated soil. Weight percent estimates were calculated based on the assumption of relatively uniform distribution of trace elements (i.e., Zn, Ti), confirmed by visual assessment of SXRF scans. Soil trace element abundance, determined by HF digestion, was used to calibrate spectral data. Sample densities of 2.65-5.0 g/cm³ were iteratively fit with little change in weight percent estimates. Similarly, estimates varied little with change in sample thickness from 100 to 300 μ m. However, because of the number of assumptions, some uncertainty remains as to the exact concentrations. Statistical correlations (Table 1) show a strong relationship between Pb and Mn counts. The correlations with Fe, the other major oxide present, are much lower and usually not significant.

Whether or not Pb is sorbed on the same sites that oxidize Cr(III) is still not completely clear. Competitive sorption experiments showed that pretreatment with Pb reduced the soils' ability to oxidize Cr(III). However, these three acidic soils showed much less of a decrease than higher pH soils and synthetic birnessite. Similar

Table 1. Simple correlation between Pb and Mn or Fe counts.			
		Mn vs. Pb	Fe vs. Pb
		r	r
Holiday	untreated	0.98	0.01
	1 mM Pb	0.79	0.09
Beech-O	untreated	0.81	0.57
	0.1mM Pb	0.84	0.16
Pease	untreated	0.70	0.07
	0.1 mM Pb	0.81	0.44

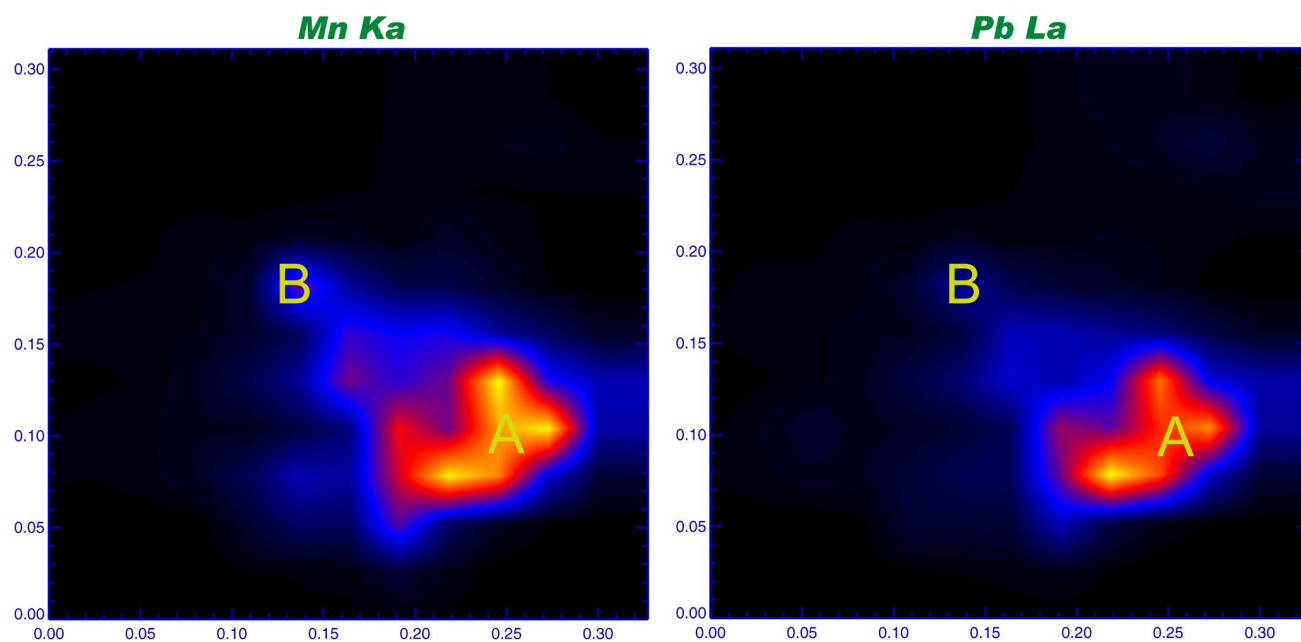


Figure 2. 2-D scans (0.63 x 0.63 mm) of untreated Holiday soil. Estimated weight percent at (A) Mn = 0.03, Pb=0.01; at (B) Mn=0.09, Pb=0.01.

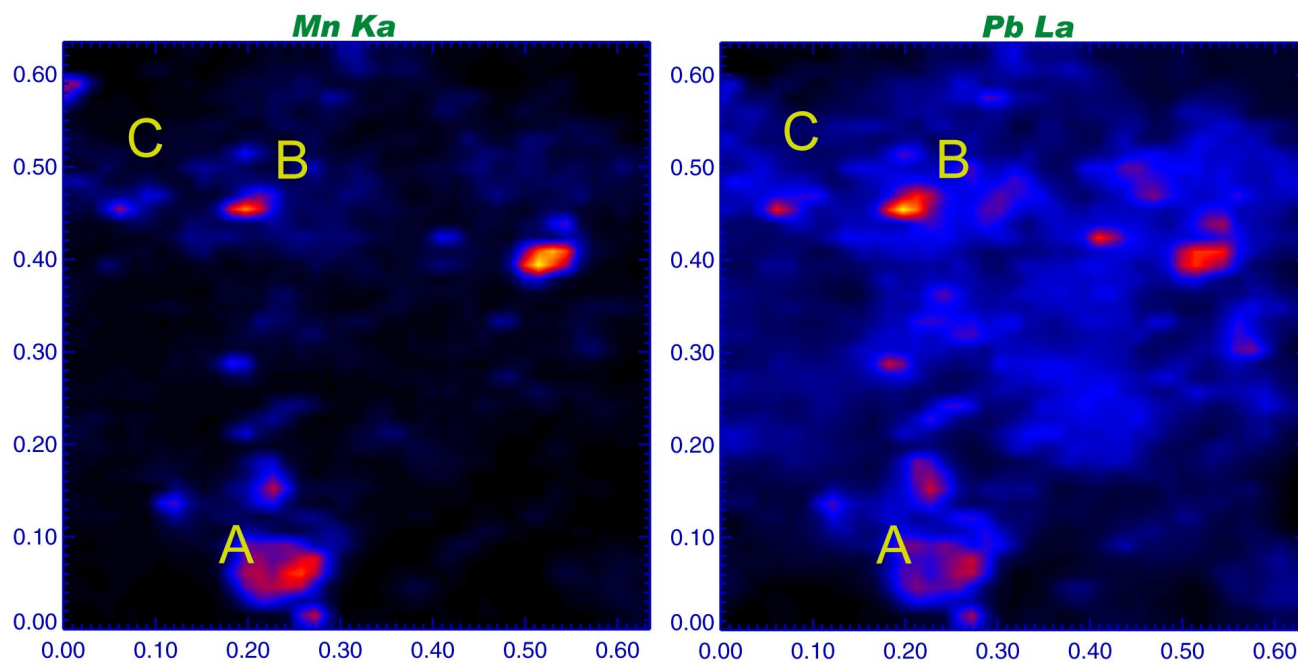


Figure 3. 2-D scans (0.63 x 0.63 mm) of Holiday soil treated with 1 mM $\text{Pb}(\text{NO}_3)_2$. Estimated weight percent at (A) Mn = 0.29, Pb=0.46; at (B) Mn=0.06, Pb=0.26; at (C) Mn=0.11, Pb=0.31.

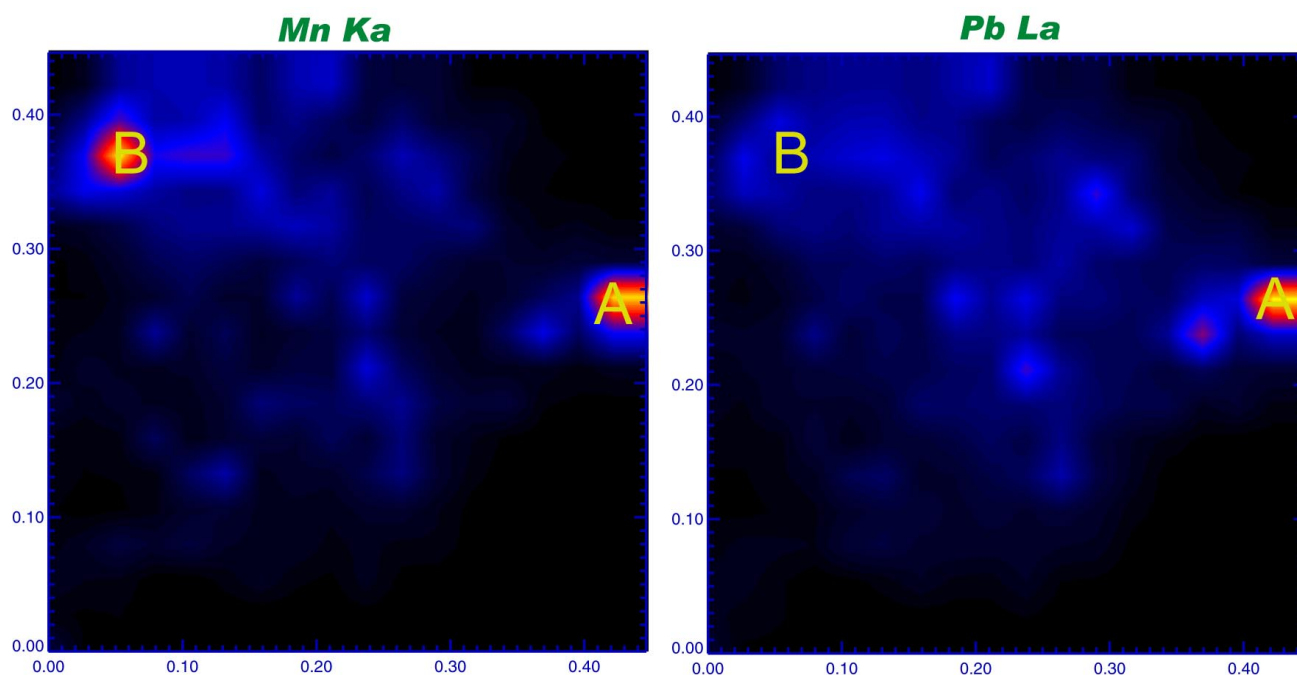


Figure 4. 2-D scans (0.45 x 0.45 mm) of untreated Beech O soil. Estimated weight percent at (A) Mn=0.07, Pb=0.01; at (B) Mn=0.20, Pb=0.03.

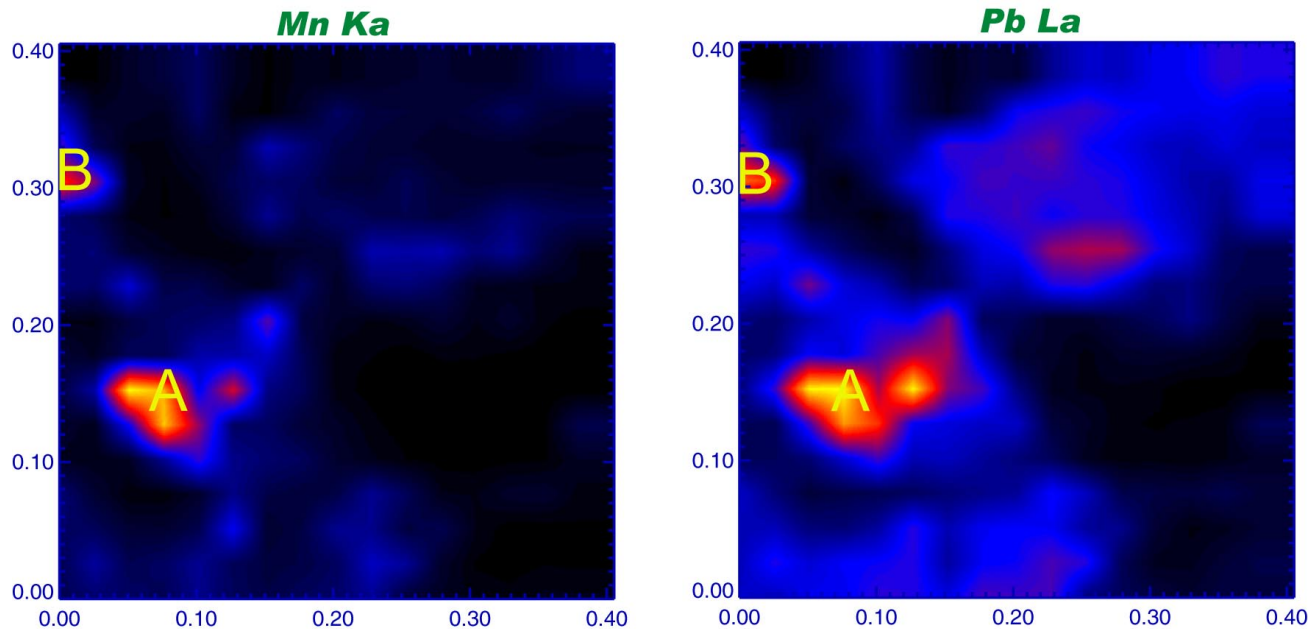


Figure 5. 2-D scans (0.4 x 0.4 mm) of Beech O soil treated with 0.1 mM $\text{Pb}(\text{NO}_3)_2$. Estimated weight percent at (A) Mn = 0.11, Pb=0.07; at (B) Mn=1.07, Pb=0.23.

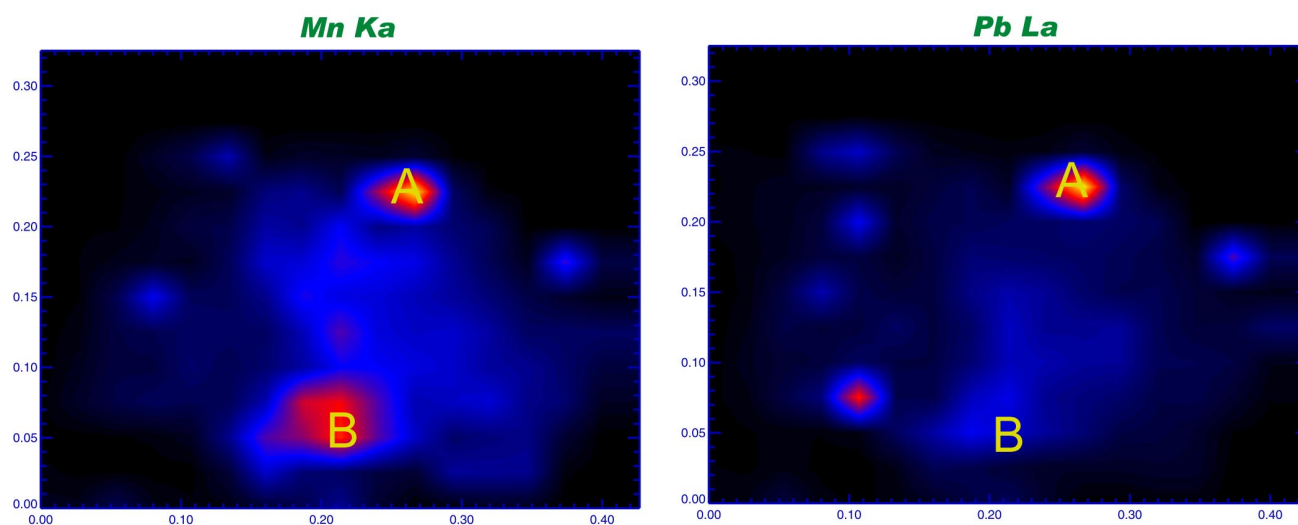


Figure 6. 2-D scans (0.42 x 0.32 mm) of untreated Pease soil. Estimated weight percent at (A) Mn = 1.33, Pb= 0.04; at (B) Mn=1.56, Pb=0.01.

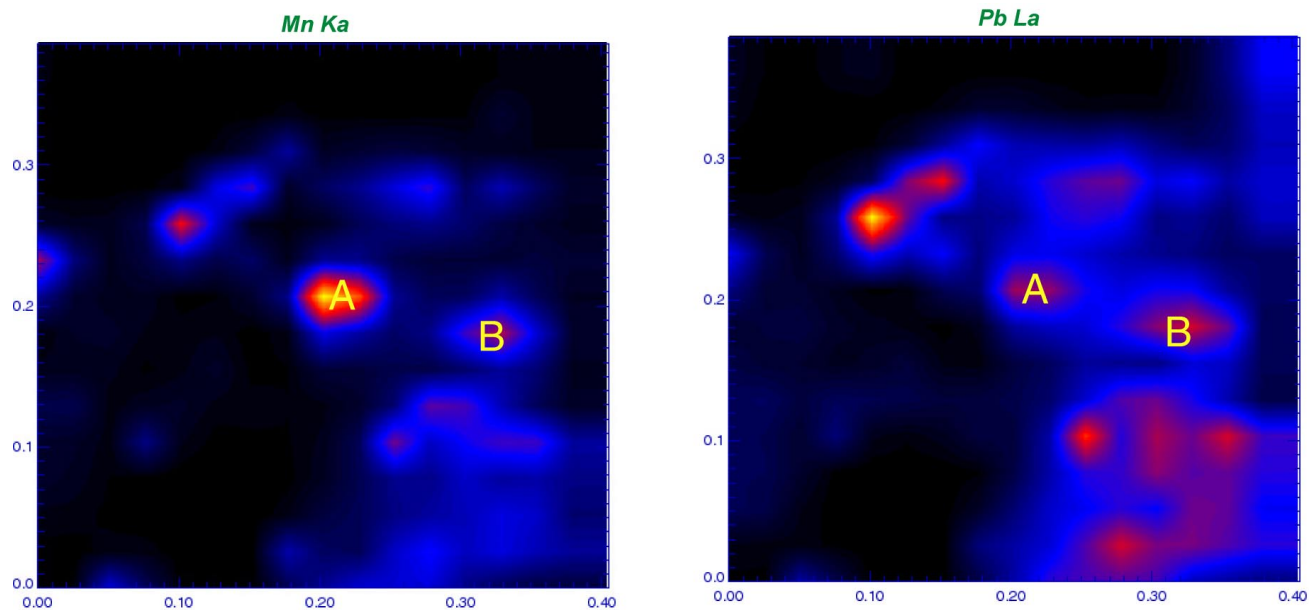


Figure 7. 2-D scans (0.40 x 0.38 mm) of Pease soil treated with 0.1 mM $Pb(NO_3)_2$. Estimated weight percent at (A) Mn = 0.82, Pb=0.10; at (B) Mn=1.26, Pb=0.20.

trends in relative decrease in Cr oxidation were found in competitive experiments with Co(II), Mn(II), or Cu(II). More work is needed, including EXAFS experiments, to elucidate the structure of soil Mn oxides and the nature of their reactive sites. This work adds to the evidence that soil Mn oxides are important reactive sites that may control the behavior of contaminant metals.

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