Supplemental Information for Phosphorus sorption to aluminum-based water treatment residuals reacted with dairy wastewater: 2. X-ray absorption spectroscopy

Phosphorus, Al, and Si microfocused XRF mapping

As noted in the main text, Al-WTR and WW-Al/O-WTR samples were encased in optical epoxy and prepared for micro-XRF and micro-XAS analysis after being affixed to glass slides. Samples were cut and polished flat using a wet-wheel rock saw and grinder to expose the interiors of particles prior to analysis.

Micro-XRF and micro-XANES analyses of prepared samples were conducted on Beamline 14-3 at the Stanford Synchrotron Radiation Lightsource in Menlo Park, California, United States. As noted in the text, for the microfocused X-ray analyses, energy calibration was achieved by setting the top of the primary lazulite P $K$-edge peak to 2153.5 eV. The beamline monochromator was then set at 2160 eV in order to generate P, Si, Al, and Mg (data not shown) fluorescence signal for micro-XRF mapping. A single-element Vortex Si-drift solid-state detector (Canberra, Connecticut, United States) was used to collect an energy-dispersive X-ray fluorescence signal from each point, and the energy region corresponding to the P, Si, Al, and Mg fluorescence signal were separately analyzed to create the images shown in Figure 1 (P fluorescence), Figure 2 (Al fluorescence), and Figure 3 (Si fluorescence). Both the Al and Si fluorescence maps indicated that there were distinct particles in the WTR that were either Al-rich, Si-rich, or both. The Al-rich particles were likely aggregates of Al oxide, while the Si-rich particles may have been quartz (identified in the samples using X-ray diffraction).

Phosphorus $K$-edge XANES data collection, normalization, and linear combination fitting details

As noted in the main text, energy calibration was performed using lazulite, by setting the peak of the primary lazulite $K$-edge peak (the top of the “white line”) to 2153.5 eV. Spectra were collected from $\sim$2110 eV to $\sim$2240+ eV, with count times of 1 second at each point. Step size was 2.0 eV until 2140 eV, and 0.2 eV from 2140 to 2160 eV (the “edge region”). Step size was 0.5 eV in the immediate post-edge region, from 2160 to 2200 eV, and step size was 1.0 eV beyond 2200 eV.
Prior to analysis, multiple spectra (2-8, usually ~3-4) from each point were averaged, and truncated to a data region from ~2130-2200 eV. Linear functions were subtracted from the pre-edge and post-edge regions for normalization, and the “edge step” was normalized to 1 for linear combination fitting.

The data were fit across a region spanning approximately 2130-2140 eV to 2180-2190 eV. Bulk XANES spectra in Figure 5 were fit using the normalized XANES spectrum itself, while micro-XANES spectra such as those in Figure 4 were fit using the first derivative of each spectrum. Each type of fit used the same normalization and fitting parameters for each spectrum, in order to ensure comparability of results across multiple spectra and fits.

**Uncertainty of P K-edge XANES linear combination fitting**

Uncertainty can arise from a number of sources in XANES linear combination fitting analysis. For example, the choice of fitting parameters can lead to systematic error and differing results. However, as noted by Calvin (2012), as long as the choice of normalization parameters is consistent across samples and reference spectra, the uncertainty from normalization is not generally of primary concern.

Another source of potential uncertainty is statistical, and indeed, the Athena software package computes uncertainty estimates of fit results (listed in parentheses in Table 2). These must be adjusted as discussed in Calvin (2012), but in this case generally fall in the range of ±1-3% uncertainty in the normalized results.

For heterogeneous samples of natural origin, however (such as soils, sediments), the primary source of uncertainty is arguably the choice of standard spectra or model compounds used to fit the unknown spectra. It is not practically possible to meaningfully fit a P K-edge XANES spectrum of a soil sample with every species of P that is actually present in the sample. For example, in the fits reported here, P adsorbed on calcite was used to estimate the amount of Ca-associated P. This may actually represent poorly-crystalline Ca-P precipitates, or mixed Al/Ca-P precipitates, but one cannot capture the complexity of the entire sample. The same might be said of apatite-like spectra: they might represent apatite-like materials with a range of composition and crystallinity. Thus, one must make reasonable and prudent choices regarding model compounds and model spectra in the fit. Of practical importance in this case are the similarities between the spectrum of P adsorbed on Al oxide, and that of an Al oxide-humic P complex (as reported in Giguet-Covex et al., 2013). The Al oxide-humic P complex spectrum yields more conservative fit results, so was used in the final fitting results reported herein.

However, using the spectrum of P adsorbed on Al oxide also yields reasonable fit results, but with different proportions. The results vary by approximately 6-11%, suggesting that the choice of standard spectrum is the dominant source of uncertainty in this system. Combining the uncertainty arising from the choice of standard spectrum with uncertainties arising from normalization parameters and statistics yields a final, conservative uncertainty estimate of approximately ±10-15% for the P K-edge XANES fitting results. The fit results are not implausible (Figure 5).
Semi-quantitative XANES linear combination fitting of first-derivative of spectra

Figure 4 depicts example fits used to distinguish between apatite-like P, P on calcite, and P on Al oxide in Figures 1 through 3 in the text. Due to self-absorption, interference, or other issues with the post-edge region of the micro-XANES spectra, only the primary peak and edge region were usable in the fit.

Some investigators (e.g., Vogel et al., 2017) have used qualitative evaluation of P K-edge spectra in order to shed light on P speciation in spite of issues with data quality. A different, semi-quantitative approach was attempted in the present work: fitting of the first-derivative of the unknown spectra, which seems to be less sensitive to data quality issues.

There is a great deal of P speciation information contained in the pre-edge region, primary K-edge peak, and immediate post-edge region of P XANES spectra. For example, in the pre-edge region, there is a feature that is diagnostic of Fe-associated P (Beauchemin et al., 2003). The position of the primary K-edge peak can also provide information regarding organic versus inorganic P species (Giguët-Covex et al., 2013; Brandes et al., 2007), and subtle differences in peak position may help to distinguish between mineral P species. In the immediate post-edge region, Ca-associated P spectra often have a “shoulder” on the primary K-edge peak (e.g., Beauchemin et al., 2003; Ingall et al., 2011; Figure 5). The “shoulder” on apatite-like P spectra is quite pronounced, while the spectra of other Ca-P species have a less-pronounced post-edge feature (e.g., P adsorbed on calcite in Figure 5 and Giguët-Covex et al., 2013). The spectrum of P adsorbed on Al oxide has none of these features (Figure 5; Beauchemin et al., 2003; Giguët-Covex et al., 2013).

This wealth of speciation information in the pre-edge, edge, and immediate post-edge region allows the categorization of spectra based on the first derivative of the micro-XANES spectra semi-quantitatively, as in Figure 4. However, there is significantly less information available than when fitting the full spectra (e.g., Figure 5). Consequently, estimates of statistical uncertainty (e.g., Table 2) may be unreliable, so this method should be considered semi-quantitative without further testing. Nonetheless, the prevalence of unambiguously and exclusively Al-associated P on Al-rich particles (yellow triangles in Figures 1B, 2B and 3B) provide supportive evidence of the validity of the methodology.
References


Calvin, S. 2013. XAFS for Everyone. CRC Press.

