Phosphorus L2,3-edge NEXAFS spectroscopy for the quantification of organic and inorganic P compounds in agro-industrial byproducts and soils

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Phosphorus (P) is an essential element for life on Earth that moves through its global cycle in different forms and associations. In contrast to inorganic P forms, organic P forms in soils and sediments have been historically unaccounted for due to the difficulty to accurately determine organic P forms in association with complex materials like soils and sediments. 31P NMR spectroscopy currently is the most reliable technique for bulk P speciation in soils and sediments. However, it does not account for all of the P present in soils and sediments, because alkaline extraction is required as pre-treatment, which does not completely recover soil- or sediment-bound P. During recent decades, synchrotron-based X-ray absorption spectroscopy (XAS) techniques (XANES, NEXAFS) have emerged as powerful tools for a direct, non-invasive P speciation in soils and sediments, permitting bulk and microspatial speciation analyses. Until now, most P XAS studies on soils and sediments have been conducted in the energy range of the P K-edge, which is well suited for the identification and quantification of different inorganic P species, but not for organic P species. XAS studies conducted at the P L-edge, which is a feature-rich edge for both organic and inorganic P forms are still scarce, because spectrum deconvolution is difficult. Thus, in this work we aim to apply XAS at the P L-edge for the quantification of different inorganic and organic P forms in soils and other environmentally important samples. First, we developed a data workflow to yield Linear Combination Fitting (LCF) results using known standard mixtures, then we analysed different soil samples and compared the P speciation obtained by XAS with results obtained by 31P NMR spectroscopy. Background subtraction and normalization were achieved by subtracting a polynomial background from the spectra and normalizing to the highest peak, using our R package "LCF". The results obtained for standard mixtures with known composition showed that NEXAFS spectroscopy performed at the P L-edge has a high accuracy for the quantification of inorganic P (apatite), P-monoesters, P-diesters and phosphonates. However, it underestimates polyphosphates, especially when mixed with P-monoesters. The underestimation is possibly due to the large similarity between P-monoester and polyphosphate spectra. We also observed spectral distortions caused by the Si L-edge, which we could account for by subtracting an appropriate polynomial background to our data. To prove the feasibility of our technique for the P speciation of environmental samples, we analysed soil samples and agro-industry by-products and their EDTA-extracts by P L-edge NEXAFS, and compared the P speciation results with those obtained by 31P NMR spectroscopy. In conclusion, P L2,3-edge NEXAFS spectroscopy is a potentially powerful tool for P speciation in geosciences, when combined with microscopy or as standalone spectroscopy.