



	Experiment title: Identification of phosphorus species in soils treated with inorganic or organic manures for 170 years	Experiment number: EV-219
Beamline:	Date of experiment: from: 29/09/2016 08:00 to: 05/10/16 08:00	Date of report: 03/03/2017
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Report:

Background and Aims

Phosphorus (P) is a nutrient that is essential for agricultural production and food security. As a finite resource, its future use needs to be more efficient as reserves deplete and prices increase. The P cycle needs to be tighter, and the utilisation of P in fertilisers and manures needs to be better understood, through increased understanding of the mechanisms of fixation, bioavailability and loss through the soil. Most studies investigating P have not identified the chemical species present due to methodological issues, and few studies have utilized synchrotron techniques. In particular, little is known about the micro-scale P speciation and distribution within soils and how that is linked to agricultural practices in fertiliser type and application.

In this experiment, our aim was to investigate a well-equilibrated soil system with contrasting inputs to improve our knowledge of the mechanisms of P mobility in soils using the μ -FTIR and μ -XRF/XANES capabilities at ID21. This combines the advantages of the two methods, with μ -XRF/XANES providing P distribution, inorganic P speciation and to a limited extent, organic P, and μ -FTIR as an additional tool to further differentiate organic P.

Experimental

The Broadbalk experiment at Rothamsted Research is the longest scientific experiment in the world and has some unchanged treatments. As a result, the soils are in a long-term equilibrium with respect to the inputs and losses of P, which offers unique insights unattainable from other recently-established experiments. Fifteen soil samples were selected from the experiment based on their age (5 time points: 1865, 1914, 1944, 1987 and 2012)

and treatments (3 treatments that reflect contrasting P inputs: inorganic P fertiliser, P as farmyard manure, and no P addition). All samples had been dried and sieved to 2mm.

Small soil particles/microaggregates were compressed in a diamond compression cell to make a thin film while partially preserving the structure. UV fluorescence images were acquired to identify areas rich in organic matter, and μ -FTIR spectra were acquired from selected areas. Subsequently, it was electrostatically transferred to ultralene film for imaging by μ XRF above the P K-edge, and μ XANES spectra were acquired from areas rich in P, poor in P (multiple spectra averaged) and also high in organic matter (as identified by UV fluorescence). Bulk P XANES were also acquired by expanding the beam to 300 \times 300 μ m.

Results

One of the major challenges was in the sample preparation methodology. The compression method, which had given acceptable results in previous experiments (at 2 different facilities, albeit for different soils), had not been satisfactory for an μ FTIR map collection from the entire sample. The compressed sections were too thick for transmission IR, especially when silicate were present in the spectra. To partially circumvent this issue, the approach of combining the UV fluorescence images and μ FTIR spectra from selected areas was adopted (Figure 1a).

The μ XRF images clearly showed that there was microscale, heterogeneous distribution of P within all soil samples, with microscale “hot spots” of high local P signals among “diffuse” low P signal observed throughout. The μ -XANES spectra indicated that the local hot spots were largely composed of inorganic, ordered P (e.g. apatite), while the diffuse P spectra were more representative of organic P (Figure 1b, c). A more detailed analysis is currently in progress and the report will be updated when the data is collated in a publication.

We also initiated a sample preparation method based on a method that was developed by Kopittke et al. (unpublished), where moist soil particles were cryo-sectioned at -50°C with a diamond blade on-site. While the method was technically challenging, successful 0.5 μ m sections were obtained from which good quality μ FTIR map was obtained (Figure 1 d-f) and shows significant promise as an effective sample preparation method for correlative μ FTIR and μ XANES spectroscopy.

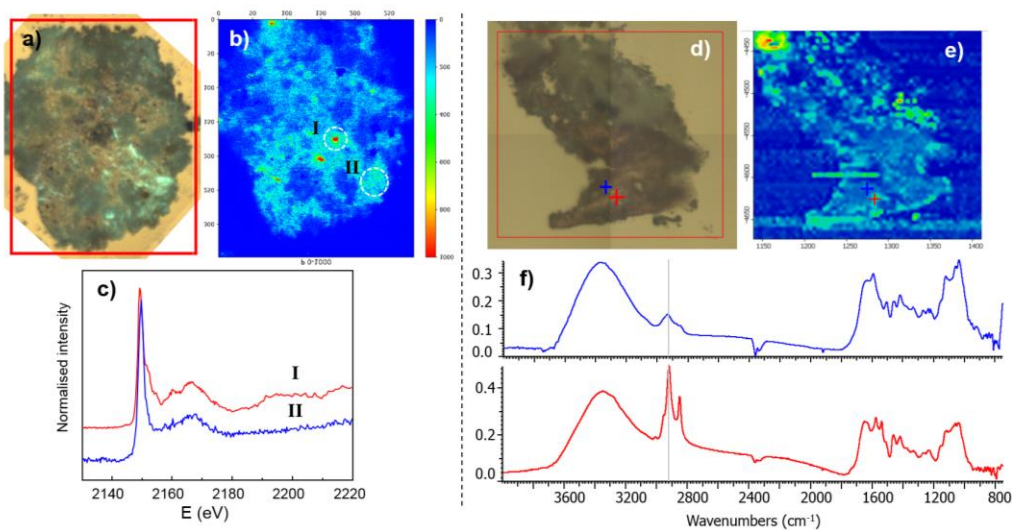


Figure 1. LHS: a) Visible microscope image of compressed soil particle with UV fluorescence image overlaid (emerald colour); b) μ XRF image of P K-line emission with P hot spot I and diffuse P II; c) corresponding μ XANES spectra. **RHS:** d) Visible microscope image of 0.5 μ m section of soil, e) corresponding IR absorption intensity map at 2916 cm^{-1} , and f) two μ FTIR spectra from corresponding cross-hairs in d) and e). (NB: μ XRF and μ FTIR from different sections).