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# Speciation and distribution of phosphorus in environmental samples using the ID21 beamline, at the ESRF

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Phosphorus (P) is an essential nutrient for life, phosphates being elementary blocks of DNA, ATP and phospholipids. P is thus one of the main fertilizer inputs for agricultural soils. Excessive P inputs are nevertheless damaging for the environment as leaching of extra P directly increases the amount of P in natural aquatic systems, potential destabilizing the ecosystems. In this way, anthropogenic P present in domestic wastewaters or at a larger scale accumulated in coastal marine environments, has received increasing attention in recent years [1], [2].

P is present in many environments and also under numerous forms (dissolved, in the structure of minerals, organic, bound or adsorbed to mineral or organic substrates). Despite growing interest, the geochemical cycle of P is only partially understood.

ID21 (ESRF) [3] is a beamline dedicated to micro-X-ray fluorescence (μ-XRF) and micro-X-ray absorption spectroscopy (μ-XANES) in the tender X-ray domain (2-9.2 keV). The X-ray beam can be focused using KB mirrors to achieve a beam spot of about 0.4 x 0.6 (H x V) μm² with a flux of $4.5 \times 10^9$ph/s at P K-edge (2.15 keV).

μ-XRF provides spatial P-distribution and elemental co-localization with a micron resolution. The shape of the P XANES spectra is characteristic of species or at least groups of species. In particular, inorganic-P, organic-P and adsorbed-P are easily distinguished from each other and minerals with structural P present unique P XANES features. The identification of P-bearing species is based on a comparison with XANES spectra recorded on references and the relative abundance of P-species in a mixture can be determined using linear combination fitting (Fig. 1).
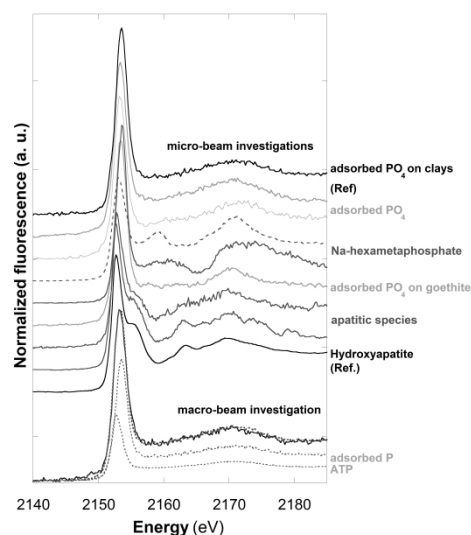


*Figure 1*. Phosphorus K-edge XANES spectra on soil samples. Bottom: Linear combination fit of a macro-beam spectrum. Top: μ-beam XANES spectra and comparison with references.

Here, the advantages, and the limits of μ-XANES for P speciation and distribution investigations will be discussed using a variety of examples from different aspects of the P geochemical cycle. A first example concerns soil genesis after the glacial retreat in mountain ecosystems, in which evidence is provided for an increase in P species diversity with time, due to pedogenetic processes [4]. The second example is related to agricultural soil samples and action of fertilizers. Analyses on undisturbed agricultural soil samples showed the predominance of adsorbed-P on organic matter together with the concentration of P in small hot spots (0.5-10 μm large), related to the presence of minor P species like apatite, polyphosphates or phosphates adsorbed on iron oxides (Fig. 1). A third set of experiments, conducted on sludges precipitated in sewage water treatment after $FeCl_3$ injection, aims at better understanding P removal mechanism through the determination of the P-bearing phases formed at different stages of the process. In the last example, P is investigated in Baltic Sea sediments to better understand marine burial of P. XRF maps evidenced the accumulation of P in biogenic stuctures and its association with Mn.

The use of complementary techniques like solid state NMR or XANES at the Fe, Mn or Ca edge can be applied to obtain a global view of the P species in a sample. μ-XANES is a useful tool in the field of Earth and Environmental Sciences, providing P spatial distribution and speciation and highlighting both major and minor phases.

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