ESRF	**Experiment title:** Phosphorus fate, behavior and bioavailability in long-term phosphate fertilizer and soil management trials in the Brazilian Cerrado	**Experiment number**: EV-420
Beamline: ID21	**Date of experiment**: from:11 February 2022 to: 14 February 2022	**Date of report**: 11 September 2022
Shifts: 9	**Local contact(s)**: Luis Carlos Colocho Hurtarte (luis.colocho@esrf.fr)	*Received at ESRF:*

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Report:

Context: We carried out P K-edge XANES measurements in soil samples of two long-term experiments in Brazilian Savanna (Cerrado). In experiment 1 we aimed to assess the bioavailability of legacy P after 17 years of P fertilization and after 8 years of P fertilizer suppression. In experiment 2 we aimed to assess the P species in soil samples from cropland after 20 years of continuous fertilization under different fertilizer management and two annual P rates.

Samples: In experiment 1 we analyzed 72 soil samples referred to two soil management systems (conventional-CT and no-tillage-NT), two P sources (triple superphosphate-TSP and phosphate rock-PR, 35 kg ha^{-1} yr^{-1} P), and two methods of application (sowing furrow-F and broadcasted-B), plus soil under a native Cerrado forest (control-Sav). We sampled the soil after the initial 17 years (2011) and again after 8 years of P fertilizer suppression (2019). Soil samples were collected at the following depths: 0-2.5; 2.5-5; 5-10; and 10-20 cm (D1, D2, D3, and D4). In experiment 2 we analyzed 30 soil samples that comprise more than 20 consecutive years under two soil management systems (NT and CT); with three annual rates (0, 50, and 100 kg ha^{-1} of P_2O_5) as TSP and PR sources broadcasted on the surface. The soil was sampled in the depths: of 0-5 (D1), 5-10 (D2), and 10-20 cm (D3) in 2021. Furthermore, high-resolution maps of P, Al, and Si were obtained from an undisturbed soil sample of experiment 2, using synchrotron-based micro-X-ray fluorescence spectrometry (μ-XRF) and P K-edge μ-XANES was also performed.

Results: In Experiment 1, P-Fe and P-Al are the main species across all treatments and increased over time (77% in 2011 and 88% in 2019). P-Ca and organic-P species were depleted under CT but were still found in NT after 8 years without fertilization. Overall, NT showed a higher bioavailability of legacy P with PR as a phosphorus source (Figure 1).

In Experiment 2, the main P species found were the P-Fe and P-Al. However, P-Org also was found in the topsoil, mainly in the NT system. The P-Ca was detected in PR trials, especially in the NT, because in CT the soil is disturbed every year and the fertilizer is homogenized with the soil. The consequence of the CT systems is the increase in the surface contact between soil clay particles and fertilizers. This promotes the solubility of fertilizer (less P-Ca) but also increases the formations of P-Fe and P-Al species, that are less bioavailable to crops (Figure 1).

In Figure 2, the μ-XRF map and μ-XANES showed that P hotspots and P-Hap abundance confirmed the location of fertilizer grain. In the soil/fertilizer interface we found P-HAp transforming to dicalcium phosphate (P-Ca, 5-

17%) and P adsorbed on gibbsite (P-Al, 32-44%). Inside the soil aggregate, further from the fertilizer, P adsorbed on ferrihydrite (P-Fe) was also found (18-47%). The results showed short distance range transformations of P into less available species (P-Fe and P-Al). Our methodology allowed us to better understand the mechanisms controlling the fate of P from the fertilizers in tropical soils. This knowledge is useful to improve P fertilization efficiency for crops

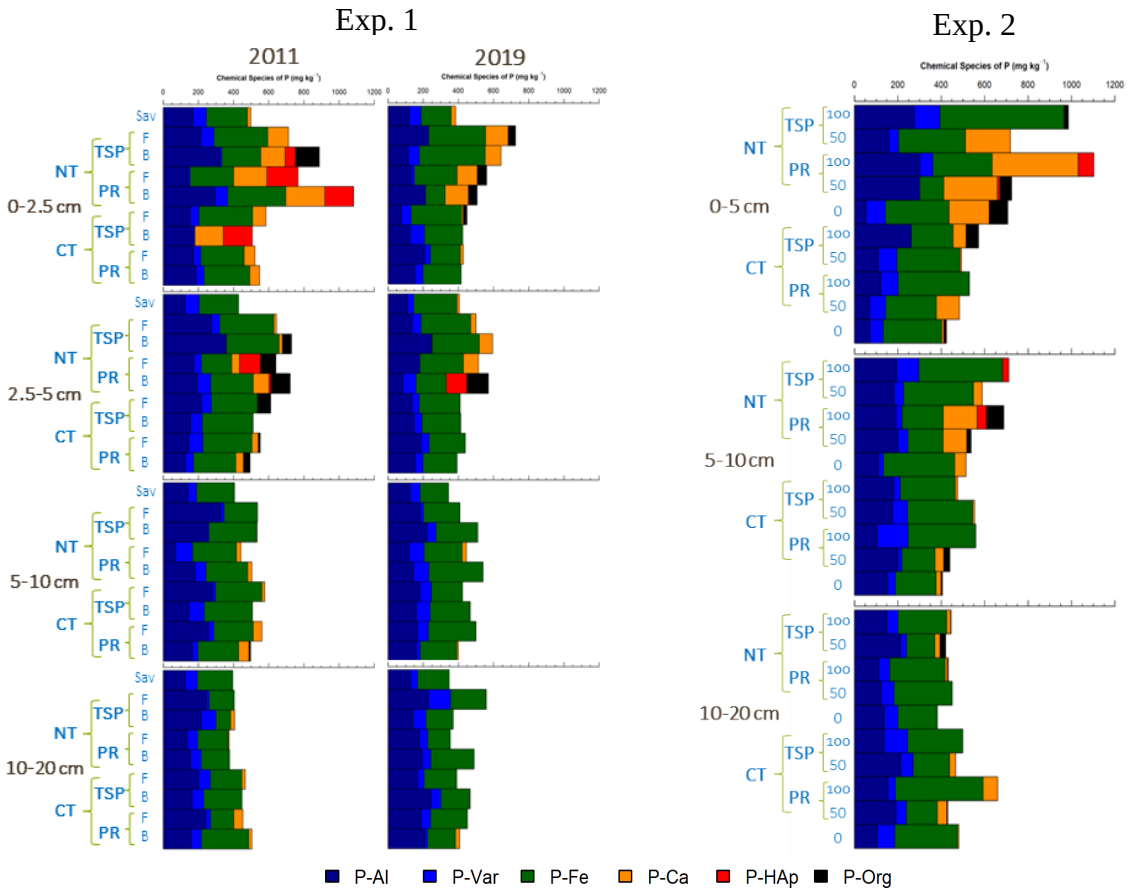

Figure 1. P species in different soil depths of experiments 1 and 2 under two soil management systems (NT and CT), two sources of P (TSP and PR), and two application management (F or B). P-Al = phosphate adsorbed on gibbsite, P-Var = variscite mineral, P-Fe = phosphate adsorbed on ferrihydrite, P-Ca = $CaHPO_4$, P-HAp = hydroxyapatite mineral, P-Org = inositol hexaphosphate

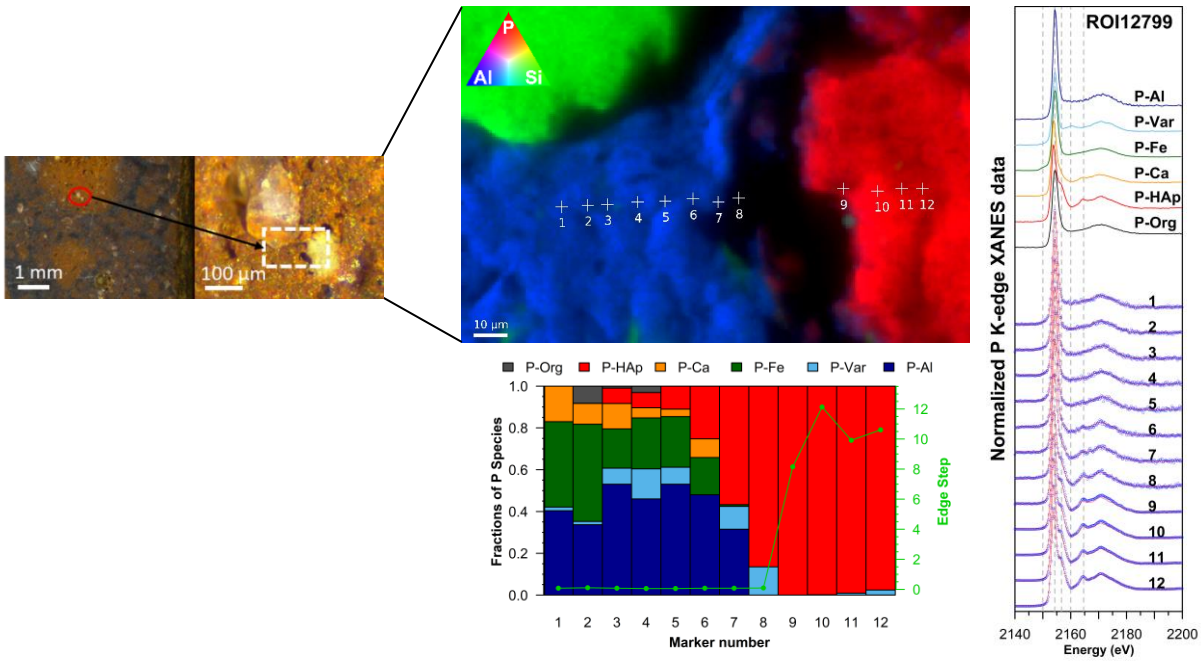

Figure 2. Al, P, and Si distribution and P species, based on µ-XRF map and µ-XANES spectra of an undisturbed soil sample experiment 1.

Dissemination: These results will be presented at the Sustainable Phosphorus Summit in November, Raleigh-NC (https://steps-center.org/p-week/). The manuscripts are being prepared for publication.