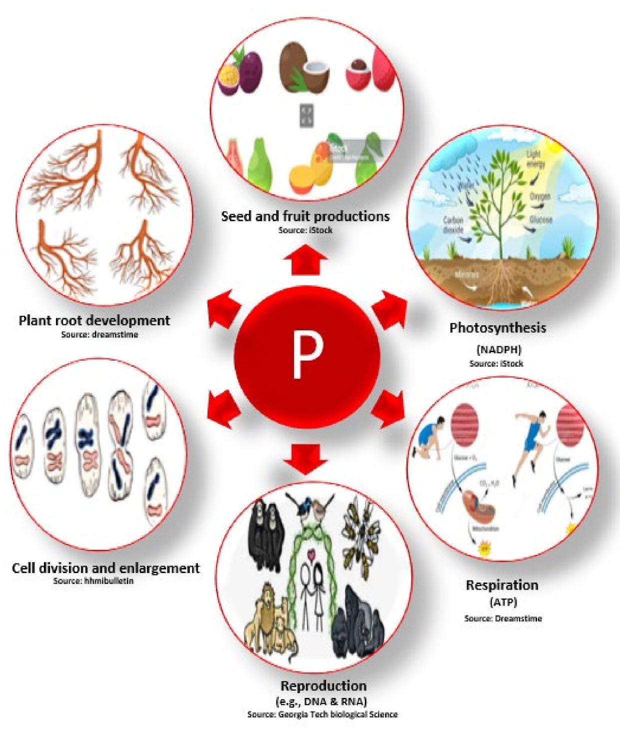
Investigating Legacy Phosphorus Availability in Acidic, Organic, and Calcareous soils

MD Anik Mahmud (md.mahmud@ufl.edu) [1], Caroline Buchanan Fisher[1], Xue Bai[1], Abul Rabbany[1], Shin-Ah Lee[2], Rebecca Muenich[3], Luke Gatiboni[4], Owen Duckworth[4], Juan Claudio Nino[5], Andy Ogram[1], Jonathan Judy[1], and Jehangir Bhadha[1]

[1]University of Florida, Soil, Water, and Ecosystem Sciences; [2]University of Florida, Environmental Engineering Sciences; [3]University of Arkansas, Biological and Agricultural Engineering; [4]North Carolina State University, Crop and Soil Sciences, [5]University of Florida, Materials Science and Engineering

Introduction



Phosphorus (P) is an essential nutrient

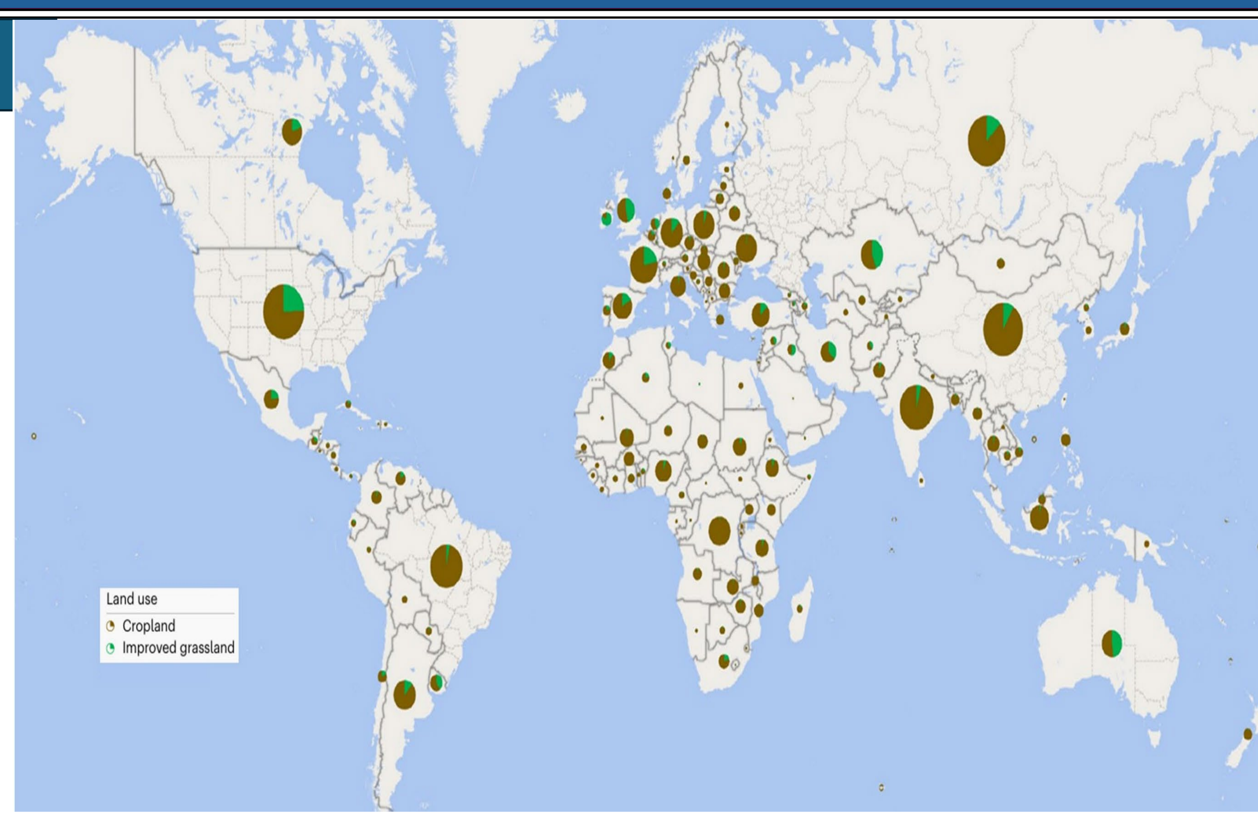


Figure 1: Legacy P global distribution map in (3.510 Gt, in the top 20–30 cm depth) in cropland and improved grassland

(McDowell et al., 2020)

- **Global P reserves: 74 x 10^9 metric tons, yet > 40% of world arable lands lacks plant-available P**

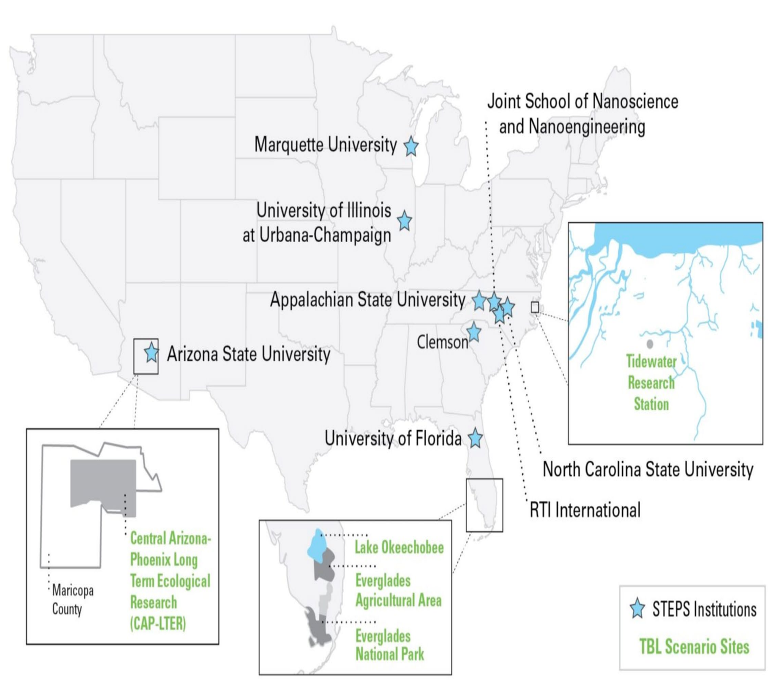
Source: Mineral commodity summaries 2024

- **Globally, applied P fertilizer rate: 16.5 X 10^6 metric tons y^{-1}**

- **Estimated legacy P build-up: 10 x 10^6 metric tons y^{-1}, which can provide 100 years of P demand**

(Doydora et al., 2020)

Our understanding of chemical forms of legacy P in soils is lacking



Science and Technologies for Phosphorus Sustainability (STEPS) 25-in-25 vision:

25% reduction in dependence on mined phosphates and 25% reduction in losses within 25 years

Figure 2: STEPS collaborators and key P research sites in the USA

Methods & Materials

Acidic soils

TP = 1,303 mg/kg
M3P = 336 mg/kg
(25% of total P)

Organic soils

TP = 1,036 mg/kg
M3P = 40 mg/kg
(4% of total P)

Calcareous soils

TP = 1,081 mg/kg
M3P = 187 mg/kg^{-1}
(17% of total P)

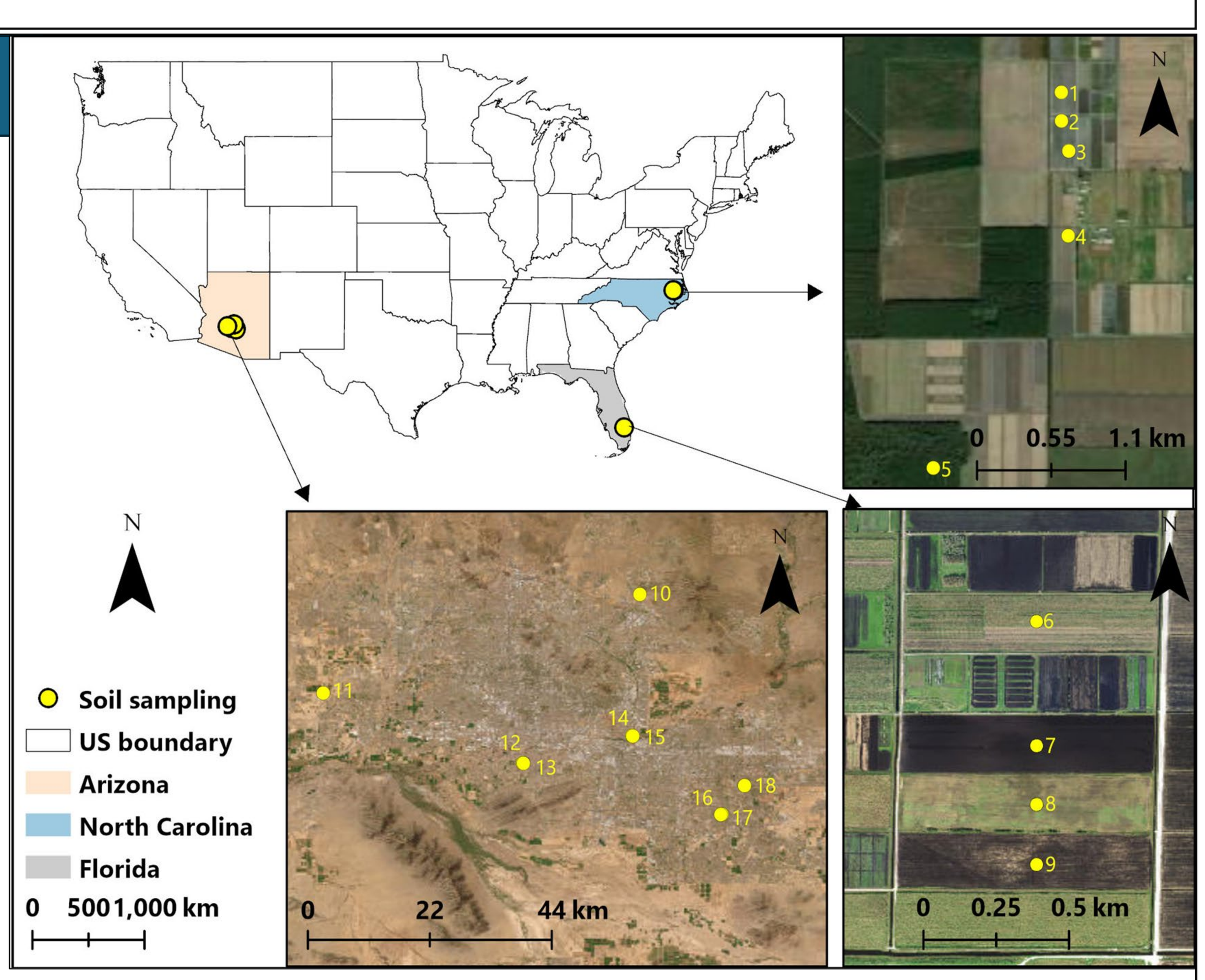
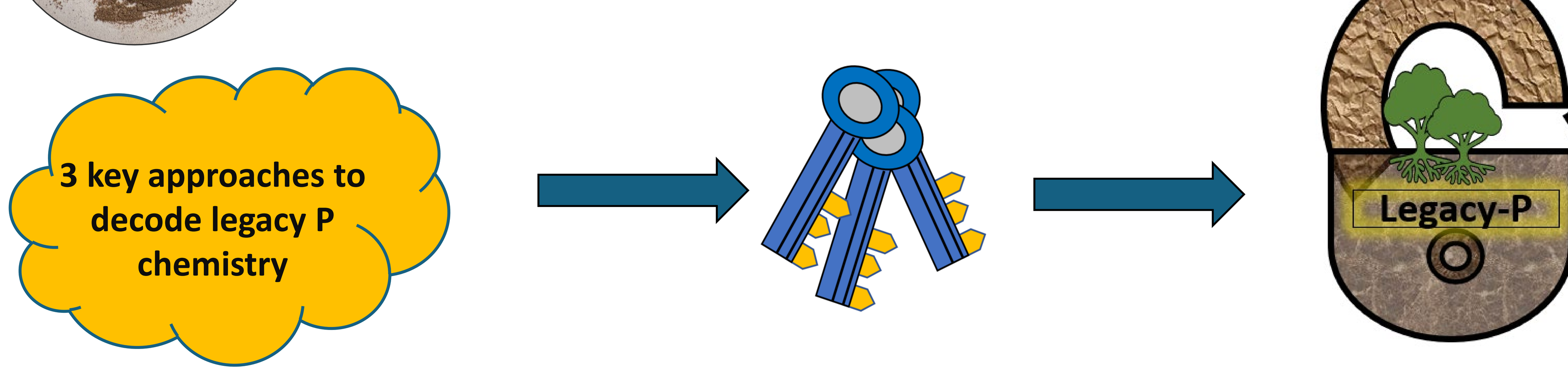


Figure 3: A map presenting sampling sites of three types of soils, including acidic soils (1-5), organic soils (6-9), and calcareous soils (10-18)



#1 **Hedley Fractionation and Total Soil P Storage Capacity by ICP-OES and UV-vis spectrometer**

#2 **Solution-state ^{31}P Nuclear Magnetic Resonance (NMR) to identify different functional P groups in soils**

#3 ***K*-edge Xray Absorption Near Edge Spectroscopy (XANES) to identify inorganic and mineral-bound P in soils**

UV-vis spectrometer #1

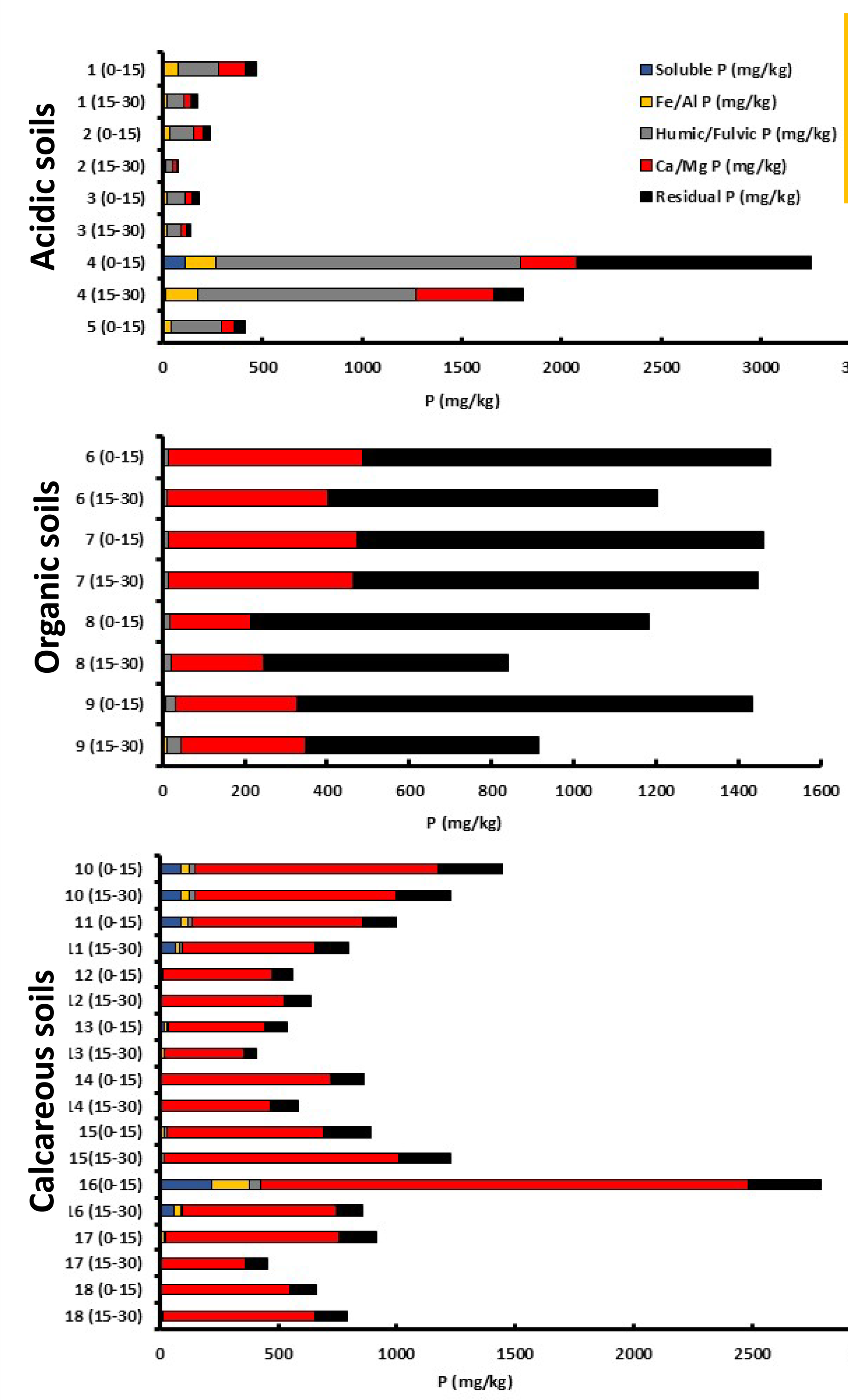
Bruker Avance III HD 600 MHz NMR Spectrometer at Advanced Magnetic Resonance Imaging and Spectroscopy (AMRIS) Facility at UF #2

ICP-OES #1 & #2

Beamline (2.1-5.0) keV capable of P *K*-edge XANES analysis #3

Figure 4: Three keys to decode legacy-P chemistry in acidic, organic and calcareous soils

Results & Discussion



Acidic soils were primarily **P sinks** and dominated by **Humic/fulvic P fraction**

Organic soils were primarily **P sinks** and dominated by **residual P fraction**

Calcareous soils were **P sinks and sources** and dominated by **Ca/Mg P fraction**

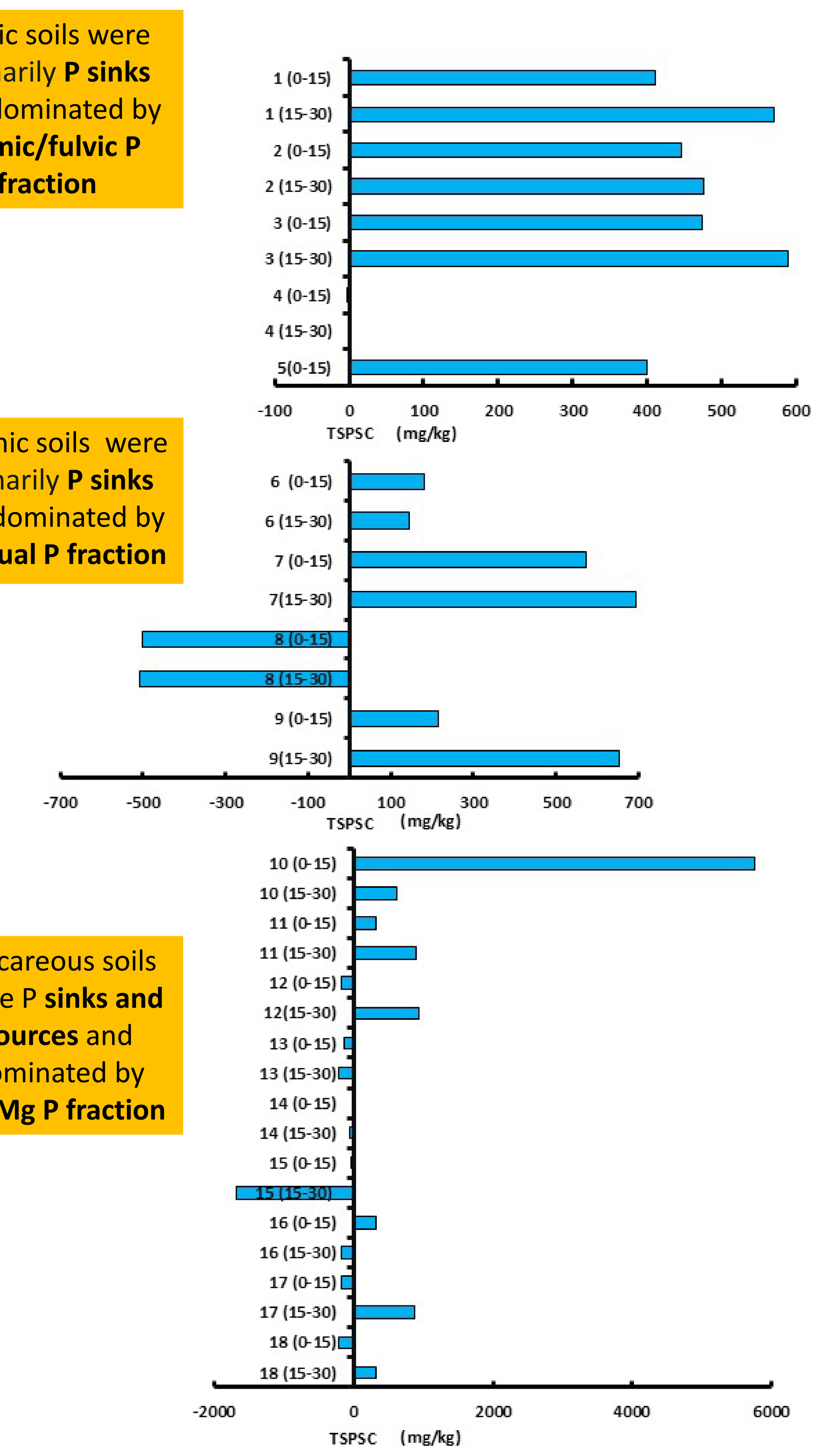


Figure 5: Hedley P fractionations of three soil types. Each soil has two depths: 0-15 cm and 15-30 cm, except sample 5

Figure 6: Total Soil phosphorus storage capacity (TSPSC) of three soil types. Each soil has two depths: 0-15 cm and 15-30 cm, except sample 5

Orthophosphate | Monoester | Diesters | Pyrophosphate | Polyphosphate | Phosphonates

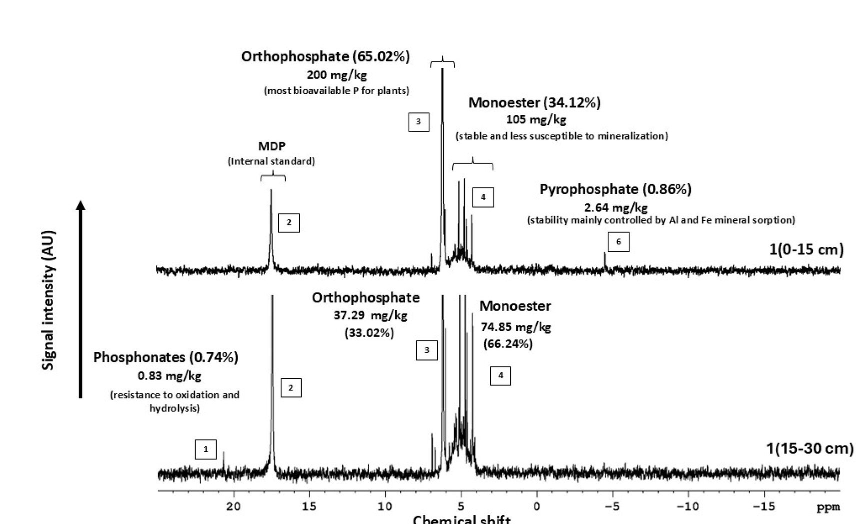
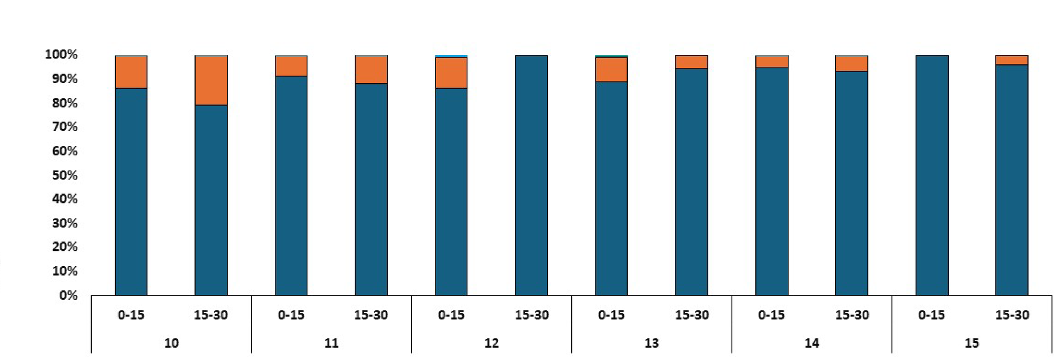
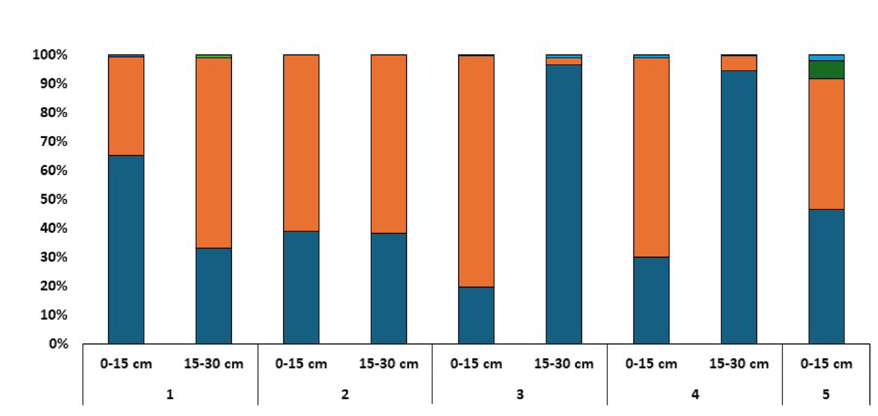


Figure 7: NMR Spectra of an acidic soil sample

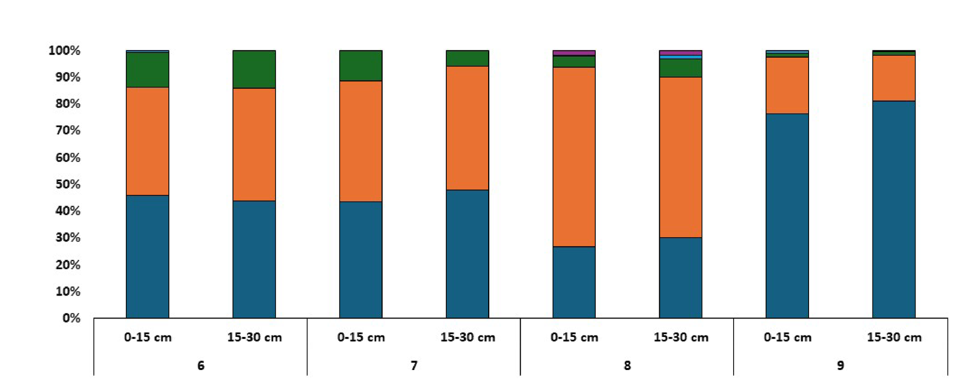


Calcareous soils

Acidic and calcareous soils were dominated by **bioavailable** orthophosphate and **organic** monoesters, while Organic soils were dominated by organic **monoesters and diesters**



Acidic soils



Organic soils

Figure 8: Different P functional compounds identified in three soil types. Each soil has two depths: 0-15 cm and 15-30 cm, except sample 5

Preliminary results show no pre-edge feature at 2148.9 eV, indicating the **absence of Fe(III)-P bonds** in all samples. Organic (8) and calcareous (15) soils resemble **hydroxyapatite**, while acidic soils (4) align with **Na-phytic acid** reference spectra

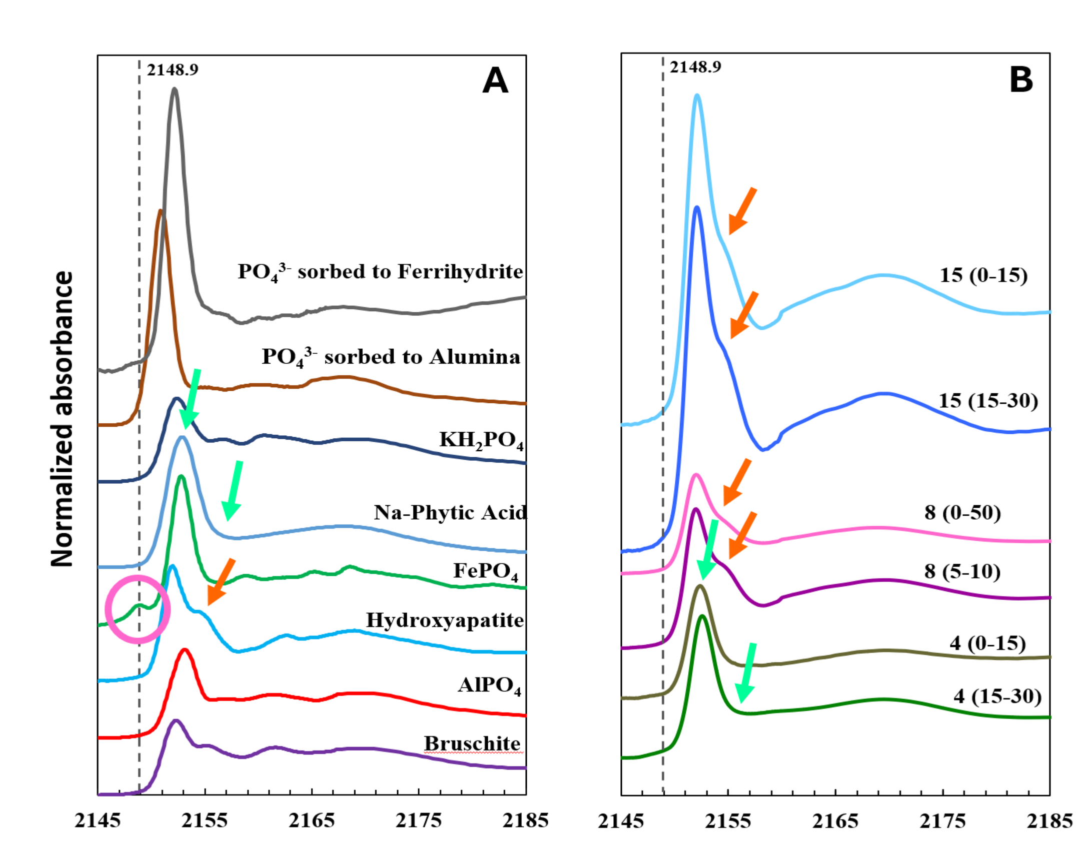


Figure 9: XANES K-edge spectra of (A) P reference minerals and (B) three soil types

Conclusions

- **Acidic soils** functioned primarily as a P sink, with legacy P dominated by humic/fulvic fractions. NMR analysis revealed prevalent bioavailable orthophosphate and organic monoester

- **Organic soils** acted primarily as a P sink, with legacy P dominated by residual fractions. NMR analysis revealed prevalent monoester and diester

- **Calcareous soils** acted as both a P sink and source, with legacy P dominated by Ca/Mg fractions. NMR analysis revealed prevalent orthophosphate and monoester