

A multi-technique approach to assess chemical speciation of phosphate in soils

Dalton Belchior Abdala (1), Marcos Rodrigues (2), Wilfrand Herrera (2), and Paulo Sergio Pavinato (2)

(1) Brazilian Synchrotron Light Laboratory, São Paulo, Brazil, daltonabdala@gmail.com, (2) Luiz de Queiroz College of Agriculture, ESALQ/University of São Paulo

Soil scientists see chemical characterization of phosphorus (e.g., chemical speciation) as a winning strategy to increase phosphorus use efficiency in agriculture, to understand the fate of applied P fertilizer in soils and to devise strategies to minimize P losses to the environment.

Phosphorus (P) is majorly presented in soils as phosphate, bound to mineral components of soils such as Al-, Ca- and Fe-(hydr)oxides or associated with organic molecules, being thus generally referred to as organic phosphates. In addition, because of the turnover of P between plants and microbes, it delivers P back to soils as a mixture of species with high spatial and chemical heterogeneity, adding complexity to the determination of the P species contained in environmental samples. Therefore, due to the variety of forms that phosphate can present in soils, its precise chemical characterization can only be achieved using a set of analytical techniques. Although established methodologies (e. g., soil test P, sequential chemical fractionation, P isotherms) have been useful to subsidize information for the establishment of policies and guidelines for soil management and P fertilizers use, they have failed to provide detailed information on P chemistry and reactivity in soils in a more satisfactory manner, which are critical to predict P bioavailability to plants and loss potential to the environment. More recently, the association of wet chemistry analysis with spectroscopy and microscopy techniques has arguably represented the most successful means to chemically speciate phosphate in soils. This is because using qualitative (chemical speciation), quantitative (chemical fractionation) and spatial (microscopy) data allows for triangulation of information, thereby reducing bias and increasing validity of the results.

The analysis framework that we propose in this study includes the use of (i) sequential chemical fractionation of soil P to determine the partitioning of P within the different P pools considered in the fractionation protocol, (ii) two synchrotron-based X-ray absorption spectroscopic techniques, XANES and EXAFS, for chemical characterization of the P forms and mineralogy of Fe-(hydr)oxides present in a sample, and (iii) Scanning Electron Microscopy and Energy-Dispersive spectroscopy, SEM/EDS, to provide complimentary information to corroborate and aid in the interpretation of our P XANES data.

It was shown that the combination of techniques can assist us not only in the determination of the P chemical species present in a given material, but also to better understand the complex and dynamic processes to which P is subjected in soils. The association of spectroscopy (XANES and EXAFS) and microscopy (SEM/EDS) with wet chemistry data in this study was key to shift our understanding of the relationship between P and other soil mineral components from a macroscopic into a microscopic one. This represents a strong driving force to integrate the results of multi-analytical techniques into a more complete understanding of the systems under study.

In addition, we provide a library of reference spectra for P K-edge XANES containing P sorbed to single and binary mixtures of mineral analogues intended to assist in the identification of P sorbed species commonly found in soils and sediments.

Key-words: P K-edge XANES, Fe K-edge EXAFS, sequential chemical fractionation, soil phosphorus