Distinctive pools and chemical species of phosphorus among density fractions of allophanic and non-allophanic Andisols

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Andisols with abundant aluminum (Al) and iron (Fe) oxyhydroxides are characterized by a high phosphorus (P) retention capacity. Such property leads to a significant inhibition of plant growth in Andisols unless properly managed. Andisols are classified into two types in accordance with the difference in the clay mineral compositions. One type is referred to as allophanic Andisols, in which allophane and imogolite are present in the clay fraction. The other type is referred to as non-allophanic Andisols, in which Al- and Fe-humus complexes and 2:1 phyllosilicates are predominant. Based on the result of chemical extraction, it has been suggested that these clay minerals appear to contribute to P retention capacity of Andisols. Separating the different soil minerals in accordance with their density can limit the number of P-bearing phases, facilitating characterization of species and accumulating pools of P. The objective of this study was to characterize the species and distinctive pools of P in allophanic and non-allophanic Andisols using density separations in combination with sequential extraction and solution 31P nuclear magnetic resonance (NMR) spectroscopy.

Allophanic and non-allophanic Andisols collected from Tsukuba and Osaki, respectively, were fractionated by sodium polytungstate into five density levels including 1.6-1.8, 1.8-2.0, 2.0-2.25, 2.25-2.5, and > 2.5 g cm\(^{-3}\). Phosphorus in each density fraction was extracted sequentially by deionized water, 0.5 M NaHCO\(_3\), 0.1 M NaOH and 1.0 M HCl. After the extracts were filtered, the concentration of inorganic P (P\(_i\)) in all fractions was determined colorimetrically with a molybdenum blue method. The concentration of total P (P\(_t\)) in each fraction was determined by the same method after the solution was treated using H\(_2\)SO\(_4\)-persulphate digestion. The concentration of organic P (P\(_o\)) was calculated as the difference between P\(_t\) and P\(_i\) of each fraction.

The total concentration of P was similar in the allophanic and non-allophanic Andisols (6.2 g kg\(^{-1}\)). A large proportion of P\(_i\) and P\(_o\) in the bulk and each density fraction was extracted by NaOH, indicating that P in both Andisols was mainly associated with Al and Fe (oxy)hydroxides. The density fraction that accumulates P was contrastingly different between allophanic and non-allophanic Andisols where over 90% of P\(_i\) and P\(_o\) in the former was accumulated in the >2.0 g cm\(^{-3}\) fraction, whereas about 70% of P\(_i\) and P\(_o\) in the latter was found in the <2.0 g cm\(^{-3}\) fraction. According to the 31P-NMR analysis, ortho-P monoesters were the primary organic P species for the allophanic and non-allophanic Andisols, although it was 2-folds more abundant in the latter than the former. In the non-allophanic Andisols, myo-inositol hexakisphosphate, an ortho-P monoester, was accumulated in the 1.8-2.25 cm\(^{-3}\) fraction.

Keywords: phosphorus, NMR, chemical speciation