Molecular level characterization of soil organic matter by using XRD and FTICR-MS

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Soil organic matter (SOM) includes metabolites and decomposed products of plants/organism and those products having different degrees of humification (or darkness). The SOM plays important roles associated with crop productivity and carbon sequestration. To understand the dynamics/functions of SOM, chemical structure of SOM is to be clarified. The molecular recalcitrance of SOM is one of their stabilization mechanisms in soils. Condensed aromatic components that could derive from char have been considered as the recalcitrant components. Here, we highlight our studies on the chemical characterization of soil humic acids (HAs), especially for condensed aromatic components.
Materials and methods
Humic acids (HAs) were prepared from ten Japanese soils to cover varying degrees of humification according to NAGOYA method. The degree of humification of HAs was evaluated with the absorbance at 600 nm per mg C mL^{-1} (A_{600}/C) and the ratio of absorbances at 400 and 600 nm on a logarithmic scale [$\log(A_{400}/A_{600})$]. Based on these two variables, HAs were classified into four types: Rp < P < B < A, with the degree of humificaiton increasing in this order.
The XRD profile was measured following to Fujimoto and Shiraishi (2004). The XRD profiles were analyzed by using Carbon Analyzer DiHiGa Series 2007 software (Ryoka Systems Inc., Tokyo). The composition of carbon layer planes on a weight basis was obtained by fitting the XRD profile to theoretical profiles. The FTICR-MS was performed according to Sleighter and Hatcher (2008). The molecular formulas assigned were examined using the van Krevelen diagram and Kendrick mass defect (KMD) analysis that focusing on condensed aromatic structure.
Results
1) The 11 band analysis indicated that the radius size of the carbon layer planes in HAs ranged from 0.48–1.68 nm, corresponding to 4- to 37-ring condensed aromatics.
2) The contents of the total and larger carbon layer planes were larger in HAs with both darker color and larger aromatic carbon content.
3) The number of molecular formulas in the condensed aromatic region increased with increasing degree of humification (from Type Rp to Type A HAs), as well as the sum of the peak magnitudes of those formulas.
4) The KMD analysis indicated that the largest number of the rings in potential condensed aromatic components increased in the order: Types Rp and P (7) < Type B (9) < Type A (10) HAs.

Keywords: soil organic matter, X-ray diffraction, condensed aromatics

