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FT-ICR MS と 3 次元励起蛍光スペクトル測定を用いたヒノキ森林生態系を循環する溶存有機物のキャラクタリゼーション
Characterization of dissolved organic matter using FT-ICR MS and fluorescence spectrometry in a Japanese cypress forest

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In forest ecosystem, DOM plays important roles such as: being a main energy source of microorganisms which control material cycles in the pedosphere; making complex with iron, aluminum, other trace metals, or organic pollutants and affects their mobility or toxicity in the hydrosphere. Thus, DOM is one of the important materials for water quality. In Japan, forest covers about 70% of the land and stores large amount of freshwater supporting human life. Forest also stabilizes the freshwater supply to river and controls the water quality. Therefore, it is important to study the chemical characteristics of DOM and its alteration processes in forest ecosystem. Recently, Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS) was developed and applied to molecular-level study of DOM. FT-ICR MS has quite high resolution power and makes it possible to calculate the molecular formula from the charge to mass ratio (m/z) of the peaks detected. We further can estimate the molecular class of the each peak from its elemental ratio of O/C and H/C. The objective of this study was to apply FT-ICR MS to the DOM in a cypress forest ecosystem and try to elucidate the cycling of DOM and alteration processes in the ecosystem. Samples were collected from Shiso, Hyogo-pref., Japan in July 2011. Main vegetation of the experimental field was 50 years' Hinoki cypress (*Chamaechparis obtusa*) and the soil type was Andosol. We collected rainfall, throughfall, stem flow, soil waters (middle of A-horizon: 10 cm, bottom of A-horizon:25 cm, middle of B-horizon: 40 cm, bottom of B-horizon: 60 cm), and stream waters. All samples were filtered by precombusted GF/F filters. The filtrated samples were subjected to dissolved organic carbon (DOC) measurement and three dimensional excitation-emission matrix fluorescence spectroscopy analysis. After C18 solid phase extraction, FT-ICR MS analysis was applied. We calculated the expected molecular formula for m/z values of the peaks and made the van Krevelen diagrams by plotting the atomic ratios of H/C and O/C of the formula. In rainfall samples, low DOC concentration (1.3 mgC/L) and no clear fluorescence peak were observed. Both of these increased at throughfall (13.0 mgC/L), stem flow (31.7 mgC/L) and middle of A horizon (28.7 mgC/L). Both DOC concentration and humic-like peak intensity decreased greatly from the middle to bottom of A horizon (2.5 mgC/L). The active aluminum in A horizon consists of Andosol likely adsorbed DOM especially humic substances and removed it from the soil water. From the van Krevelen diagrams, especially in throughfall, stemflow, and soil water samples, great number of mass peaks appeared in the lignin region($0.7 < H/C < 1.5$, $0.1 < O/C < 0.67$) with high relative intensities. The number of mass peaks which corresponded to the protein region ($1.5 < H/C$, $0.3 < O/C < 0.67$) decreased as the water percolated deeper through the soil. Polar molecules with high O/C ratios might be decomposed more rapidly or removed preferentially by adsorption. In contrast, mass peaks in the lignin and the lipid regions ($1.5 < H/C$, $0.1 < O/C < 0.3$) remained even in deeper B horizon soil water.

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