

Ultrahigh-resolution mass spectral analysis of dissolved organic matter in rainfall, throughfall and soil water in temperate forest stands, western Japan

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This study aimed to clarify alternations of the quality of dissolved organic matter (DOM) in rainwater moving through temperate forests. For this, we compared the molecular composition of dissolved organic matter (DOM) between bulk deposition (rainfall), throughfall and soil water in Japanese cypress (*Cryptomeria japonica*) and Japanese stone oak (*Lithocarpus edulis*) stands, which were regarded as coniferous and broad-leaved stands, respectively, during a rain event. Analyses of ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry revealed that the number of DOM molecular species detected was significantly greater in throughfall and soil water than in rainfall ($p < 0.05$). In contrast, the number of molecular species did not significantly differ between throughfall and soil water ($p > 0.05$). There were no significant differences in the number of molecular species in both throughfall and soil water between coniferous and broad-leaved stands ($p > 0.05$). These results suggest that a diverse array of DOM molecules are provided from the tree canopies and soils to the rainwater in both stands. Approximately 52%–59% of the total molecular species in throughfall samples ($n = 6$) were unique to throughfall. Additionally, approximately a half of the total molecular species in soil water samples ($n = 5$) were unique to soil water. The classification of molecular species into seven biomolecular classes using a van Krevelen diagram revealed that throughfall samples contained many of lipid and protein molecules compared to rainfall and soil water samples, whereas approximately 70% of the total molecular species in soil water were lignin-like molecules. The analysis of multidimensional scaling revealed that molecular species were significantly differentiated between rainfall, throughfall and soil water ($p < 0.05$). These results indicate that there are diverse molecules unique to throughfall and soil water and that the quality of DOM drastically changes in rainwater as it moves through temperate forests.

Keywords: Biomolecules, Carbon dynamics, Forest type, FT-ICR MS, Molecular diversity