

Origin of fluorescent dissolved organic matter in forested headwater stream during base-flow period

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In this study, we focus on fluorescent dissolved organic matter (FDOM) such as humic substances (HSs) and aromatic amino acids, which constitutes the main portion of streamwater DOM. Our objective is to estimate the origin of streamwater FDOM during baseflow period, by comparing its composition with soil infiltration water, saturated groundwater and bedrock spring water.

Our study site is Inokawa watershed (watershed area 503 ha) in The University of Tokyo Chiba Forest. We collected stream water samples and bedrock spring water at 142 points in the watershed in 2009, 2010 and 2012, and also soil waters and groundwater in Fukuroyamasawa Experimental Watershed (2ha) which is one of most headwater hollows. Rainwater was collected at the weather station in the watershed. The water samples were filtered with 0.45mm membrane filters and analyzed for DOC concentration by wet-oxidation method, and Excitation-Emission Matrix (EEM) using 3D-spectrofluorometry. EEMs were compiled and further analyzed by Parallel Factor Analysis based on Murphy et al., (2013), and decomposed into five components with distinctive fluorescence spectra. Chemical characteristics of components were identified by comparing their spectral shapes with previous studies as follows: C1 as humic acid type HS-like, C2 as fulvic acid type HS-like, C3 as microbial-derived HS-like, C4 as tryptophane-like and C5 as tyrosine-like.

Groundwaters and bedrock spring waters were classified into three groups based on the ratio of three HS-like components, as C1-dominant group, C2-dominant group and C3-dominant group. Although groundwater in Fukuroyamasawa watershed belonged to C1-dominant group, and showed seasonal change in DOC concentration, the composition of HS-like components of groundwaters and bedrock spring waters in three groups were temporally relatively stable. This suggests that these groups can be used as end-members in identification of the origin of streamwater FDOM.

Ratios of three HS-like components in streamwaters fell in between groundwater groups and soil waters in about half of the samples. In other samples, however, ratios could not be explained by mixing of such hillslope end-members. FDOM of those streamwaters had higher abundance of C1 and C2, and also relatively higher DOC concentrations, suggesting that it was originated not only from soil and/or groundwater in the hillslope, but also from organic materials in the stream such as deposited litters, woody debris and/or other organic-containing sediments. As to aromatic amino acid-like components, streamwater FDOM tended to have lower C5/C4 ratio relative to hillslope waters, and often had C5 undetectable, suggesting that C5 was more labile than C4 in stream environment.

This study showed that HS in streamwater is produced not only in hillslope but also in stream itself, and in-stream produced HS can show different fluorescence spectral characteristics from hillslope-produced HS.

Keywords: fluorescent dissolved organic matter (FDOM), forested watershed, streamwater chemistry, excitation-emission matrix (EEM), parallel factor analysis (PARAFAC)