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Resolution of photo chemically induced changes of dissolved organic matter as function of cumulated radiation in a sample of a humic-rich and forested stream

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Photochemical processing is a major transformation pathway for allochthonous and autochthonous dissolved organic matter (DOM). DOM consists of thousands or even millions of different molecules and the isomer-resolved identification molecular structures is still far from any analytical realization. The highest analytical resolution of DOM can be achieved on a molecular mass basis via Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). With this technique, the molecular elemental compositions of thousands of DOM components can be assessed, given that they are extractable from water (via e.g. solid phase extraction, SPE-DOM) and ionizable (e.g. via electrospray ionization).

Increasing levels of DOC in drinking water reservoirs pose serious challenges for drinking water processing. Photochemical processes potentially influence the DOM quality in the reservoir water. The photo degradation and / or the photo production of DOM components in surface freshwater as function of cumulated radiation was rarely investigated. In order to fill this gap we performed an irradiation experiment with water from a shaded forest stream flowing into a large reservoir (Muldenberg, Germany). DOC concentration, UV absorption, excitation-emission-matrices (EEMs) including calculated PARAFAC components and fluorescence indices, and FT-ICR MS derived molecular formulas of SPE-DOM were recorded at 13 different time points. The cumulated radiation was recorded during six days of solar irradiation (sunny days in August at 50.401847 deg. latitude and 12.380528 deg. longitude). Changes in relative peak intensity of DOM components as function of cumulated radiation were evaluated both by Spearman`s rank correlation and linear regression.

We found components with different types of photo reaction behavior. Relative aliphatic components like $C_9H_{12}O_5$ were identified as photo products showing a monotonous mass peak intensity increase with irradiation time. Highly unsaturated and oxygen-rich components like $C_{15}H_6O_8$ showed a more or less monotonous intensity decrease indicating photo degradation. Many similar components were positively correlated to the humic-like fluorescence intensity and the humification index (HIX). The strong degradation of these components can explain the high

loss of fluorescence intensity and the drop of the HIX in our experiment. As a result of the high temporal resolution in our experiment (i.e. intensity change as function of cumulated irradiation) we found another type of photo reaction. Components like $C_{15}H_{16}O_8$ showed first increasing and then decreasing intensity indicating the formation of intermediate products.

In general, the river DOM from the forested catchment area showed high potential for photochemical transformations which probably occur in the sunlight exposed predam of the drinking water reservoir.