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Catchment scale molecular composition of hydrologically mobilized dissolved organic matter

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Increasing concentrations of dissolved organic matter (DOM) in rivers of temperate catchments in Europe and North Amerika impose new technical challenges for drinking water production. The driving factors for this decadal increase in DOM concentration are not conclusive and changes in annual temperatures, precipitation and atmospheric deposition are intensely discussed. It is known that the majority of DOM is released by few but large hydrologic events, mobilizing DOM from riparian wetlands for export by rivers and streams. The mechanisms of this mobilization and the resulting molecular composition of the released DOM may be used to infer long-term changes in the biogeochemistry of the respective catchment.
Event-based samples collected over two years from streams in three temperate catchments in the German mid-range mountains were analyzed after solid-phase extraction of DOM for their molecular composition by ultra-high resolution mass spectrometry (FT-ICR MS). Hydrologic conditions, land use and water chemistry parameters were used to complement the molecular analysis. The molecular composition of the riverine DOM was strongly dependent on the magnitude of the hydrologic events, with unsaturated, oxygen-enriched compounds being preferentially mobilized by large events. This pattern is consistent with an increase in dissolved iron and aluminum concentrations. In contrast, the relative proportions of nitrogen and sulfur bearing compounds increased with an increased agricultural land use but were less affected by the mobilization events. Co-precipitation experiments with colloidal aluminum showed that unsaturated and oxygen-rich compounds are preferentially removed from the dissolved phase. The precipitated compounds thus had similar chemical characteristics as compared to the mobilized DOM from heavy rain events. Radiocarbon analyses also indicated that this precipitated fraction of DOM was of comparably young radiocarbon age. DOM radiocarbon from field samples showed that also the event-mobilized DOM had higher radiocarbon content.
Overall, hydrology not only controls the quantity of exported carbon from temperate catchments but also strongly influences the molecular composition by mobilizing distinct compound classes in conjunction with dissolved iron and aluminum. From these results future compositional changes in temperate river DOM can be assessed, given an expected increase in the magnitude of hydrologic events, and technical advice for drinking water production may be inferred.