



## An interdisciplinary approach on the controls of stream biogeochemistry in a mesoscale catchment – A journey from the landscape sources to the outlet.

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The landscape types and hydrology of a catchment are the dominant controls of stream water biogeochemistry. Soils are sources of most stream solutes, while the hydrology is the medium of transport. These concepts and understandings have been well established at the headwater catchment scales but much is still unknown about the interaction at the larger meso-scale. In larger catchments, there are changing hydrological flow pathways and longer water residence time which alters the sources, fates, and transport of stream chemistry. Understanding these processes hold the key to conceptualizing processes that control water chemistry in larger rivers. In this work, the small-scale process based concepts of groundwater and surface water interactions are integrated to model DOC concentrations in a meso-scale catchment using an interdisciplinary approach.

First, stream water DOC concentrations are modeled using a landscape mixing-model based on three end-members (peat, till and fine sorted sediments). In headwater catchments ( $<10\text{ km}^2$ ), this was successfully used to predict stream concentrations ( $\text{RMSE}=2.6$ ). However, at the outlet of the meso-scale catchment ( $69\text{ km}^2$ ), the residuals were high especially during baseflow ( $\text{RMSE}=9.1$ ), indicating that simple mixing of water does not apply at this scale. The instream processing of DOC calculated from photo-oxidation and bacterial utilization of DOC cannot explain this over prediction at the outlet of the catchment.

The systematic change in the residuals with discharge indicates that change in flow paths control DOC during baseflow. The over predicted DOC concentration suggests that another source of water affects the signal. DOC and base cations (BC) are used as tracers in a mass balance model to show groundwater input. Both DOC and BC shows large input of groundwater (70% and 80% respectively) during baseflow. Despite uncertainties in input fluxes due to measured concentrations errors, discharge measurements errors and uncertain groundwater concentrations, both tracers show comparable results.

Quantifying the groundwater input into the catchment is also done by applying the hydrograph separation technique. The specific discharge of a headwater catchment ( $0.47\text{ km}^2$ ) is compared with the specific discharge of the meso scale catchment ( $69\text{ km}^2$ ), which verifies the groundwater input shown by the tracers. The hydrograph separation technique shows 80% more water in the meso scale catchment compared to the headwater catchment during baseflow. These results all indicate that there is a shift in source of water in the catchment from surface flow paths during high and intermediate flow conditions to deeper groundwater paths during low flow conditions. With groundwater dominating the stream during baseflow, the streams show characteristics of a mixture of both surface and groundwater chemistry. This has many implications for water resource managers, groundwater and surface water modeling and river basin management.