



## **Non-linear, connectivity and threshold-dominated runoff-generation controls DOC and heavy metal export in a small peat catchment**

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Peat soils act as important carbon sinks, but they also release large amounts of dissolved organic carbon (DOC) to the aquatic system. The DOC export is strongly tied to the export of soluble heavy metals. The accumulation of potentially toxic substances due to anthropogenic activities, and their natural export from peat soils to the aquatic system is an important health and environmental issue. However, limited knowledge exists as to how much of these substances are mobilized, how they are mobilized in terms of flow pathways and under which hydrometeorological conditions.

In this study, we report from a combined experimental and modelling effort to provide greater process understanding from a small, lead (Pb) and arsenic (As) contaminated upland peat catchment in northwestern Germany. We developed a minimally parameterized, but process-based, coupled hydrology-biogeochemistry model applied to simulate detailed hydrometric and biogeochemical data. The model was based on an initial data mining analysis, in combination with regression relationships of discharge, DOC and element export. We assessed the internal model DOC-processing based on stream-DOC hysteresis patterns and 3-hourly time step groundwater level and soil DOC data (not used for calibration as an independent model test) for two consecutive summer periods in 2013 and 2014. We found that Pb and As mobilization can be efficiently predicted from DOC transport alone, but Pb showed a significant non-linear relationship with DOC, while As was linearly related to DOC.

The relatively parsimonious model (nine calibrated parameters in total) showed the importance of non-linear and rapid near-surface runoff-generation mechanisms that caused around 60% of simulated DOC load. The total load was high even though these pathways were only activated during storm events on average 30% of the monitoring time – as also shown by the experimental data. Overall, the drier period 2013 resulted in increased nonlinearity, but exported less DOC ( $115 \text{ kg C ha}^{-1} \text{ yr}^{-1} \pm 11 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ ) compared to the equivalent but wetter period in 2014 ( $189 \text{ kg C ha}^{-1} \text{ yr}^{-1} \pm 38 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ ). The exceedance of a critical water table threshold (-10 cm) triggered a rapid near-surface runoff response with associated higher DOC transport connecting all available DOC pools, and with subsequent dilution. We conclude that the combination of detailed experimental work with relatively simple, coupled hydrology-biogeochemistry models allowed not only the model to be internally constrained, but also provided important insight into how DOC and tightly coupled heavy metals are mobilized.