Understanding DOC Mobilization Dynamics through High Frequency Measurements in a Headwater Catchment

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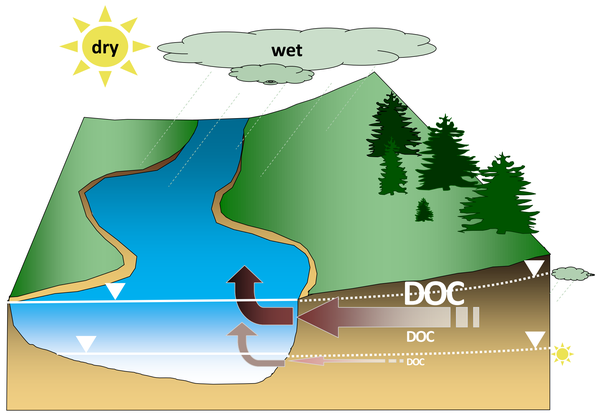
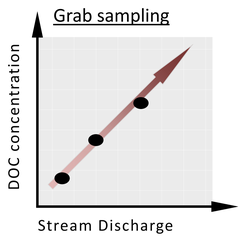
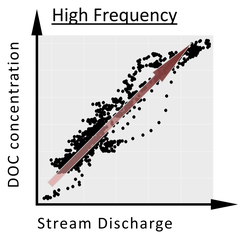
Introduction



- Increasing DOC exports from catchments impact the ecology and quality of downstream waters
- Riparian zones are the most dominant source zones for in-stream DOC in a temperate climate
- High-flow events (snowmelt, heavy rain) drive DOC deliverance to streams
- Hydrological and biogeochemical controls of mobilization and transport in riparian zones are complex and still elusive
- **High frequency, *in situ* sensing** techniques provide new insights into dominant mobilization mechanisms and source zones of DOC





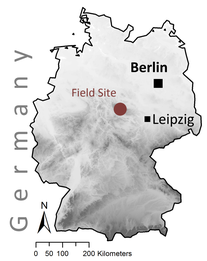
Objectives

i) Investigate the **hydrologic** and **biogeochemical controls** for the **mobilization** and **transport** of DOC from riparian soils to the streams

ii) Evaluate how **concentration** and **composition** of DOC change during **events** and varying **seasonal** conditions

iii) Extract the most decisive factors which are needed to explain the variance of DOC concentration and composition in streams

The Rappbode Field Site



- Harz Mountains (540 m a.s.l.)
- Temperate climate
  - Mean temperature: 6.9 °C
  - Annual precipitation: 1200 mm
- Drainage area: 2.58 km²
  - Forest: 77 %
  - Grasslands: 11.2 %
- Groundwater-influenced soils: 25 %
- Drainage density: 2.91 km/km²

Processing of in situ UV-vis Absorption Spectra (220 nm - 720 nm)

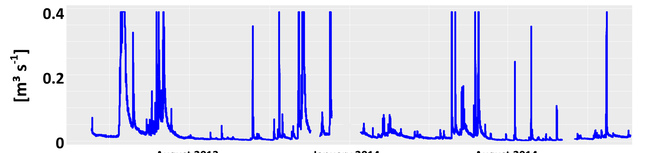
- DOC concentration (from PLS Regression)
- Spectral Slope (275 nm - 295 nm)
- Specific UV Absorption: $SUVA_{254} = \frac{SAC_{254nm}}{DOC\ conc.}$

Modeling DOC concentration, SUVA and Spectral Slope

- Explaining time series variance
- Linear Regression model selection and validation
  - Akaike's Information Criterion
  - Variance Inflation Factor
  - Nash Sutcliffe Eficiency (NSE)

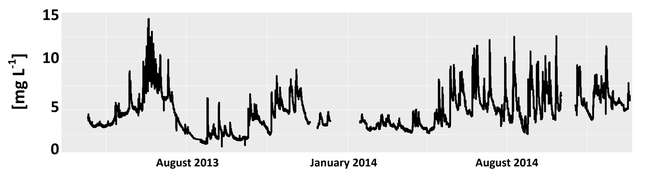
1.5 Year High-Frequency Data Set (15 min)

- Discharge derived from water level*

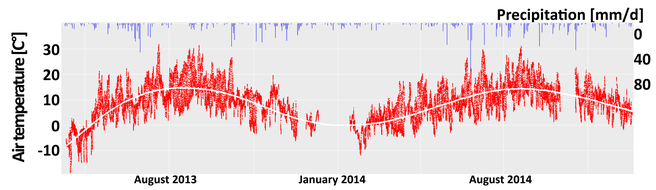


*Note: Discharge peaks cut above 0.38 m³ s⁻¹ based on maximum observed discharge.

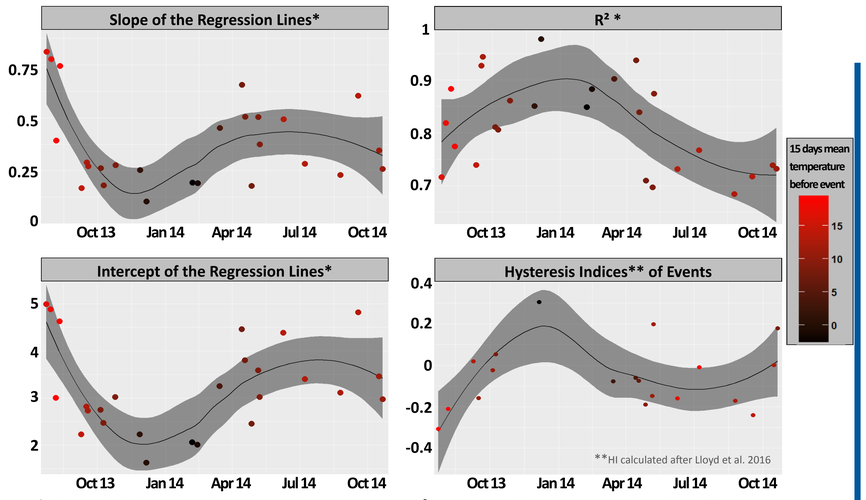
- In-situ DOC concentration derived from UV-vis spectra



- Weather Data



Event-based patterns in DOC mobilization

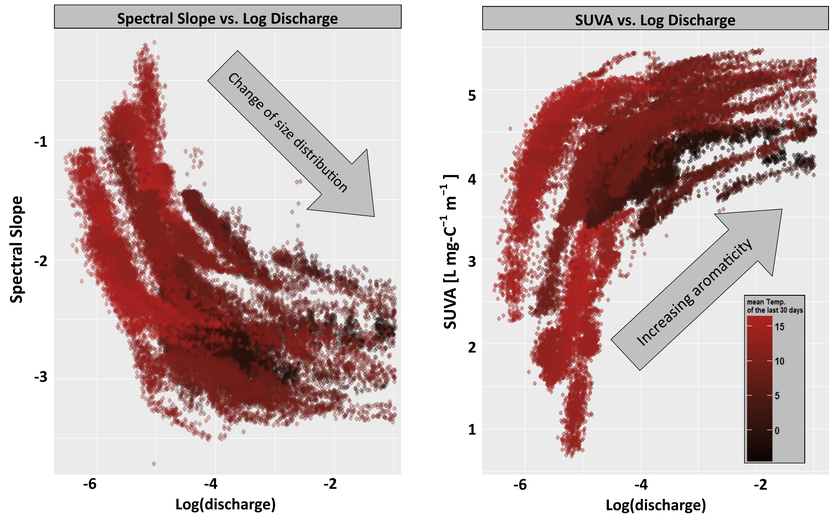


* Each point indicates one discharge event. Slope, Intercept and R² were calculated from linear regressions of log DOC vs. log discharge. Hysteresis analysis was conducted in non-log space.

- Seasonal trends for the Slope, Intercept and R² of the Regression lines, Hysteresis Index and Spectral Slope (not shown) with maxima in winter and summer
- Best explanation by 15 days mean temperature before event (r = > 0.52)

⇒ Indicate shift in mobilization mechanisms over the seasons

DOC quality variation in the stream

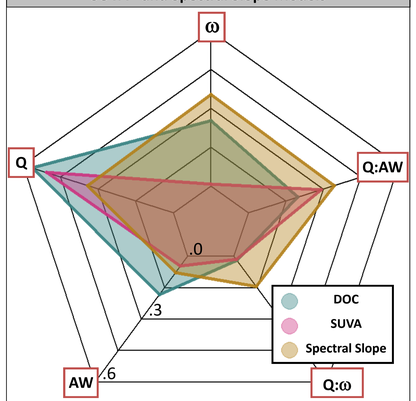


- In-stream DOC quality varies with discharge and antecedent temperature
- Systematical change of DOC quality with increasing discharge:
  - Change in DOC-compound size distribution and increasing aromaticity
  - Less variability: Convergence of SUVA values and Spectral Slope

⇒ Indicates a shift in the activated source zones with rising discharge

Linear Regression Modeling

Comparison of the (scaled) DOC concentration -, SUVA - and Spectral Slope Models



Q: Discharge

AW: Antecedent Wetness conditions of the last 30 days (= cum. rainfall – cum. evapotranspiration)

ω : $= \frac{\text{mean Discharge of the last month}}{\text{mean Temperature of the last month}}$

- All models use the same parameters
- NSE of DOC: 0.62, SUVA: 0.52, Spectral Slope: 0.37

⇒ Different parameter loadings allow for mechanistic interpretations

Conclusions

- The variations in DOC concentration and quality can be explained by four variables: discharge (Q), temperature (Temp) antecedent wetness (AW), and the antecedent discharge-temperature ratio (ω)
- These variables can be linked to event-based DOC source activation (discharge) and more seasonal controls (AW, ω) of DOC production

Outlook

- **Link stream-DOC** concentration and composition with riparian **groundwater** flow and discharge generation
- Fingerprint DOC compounds in the stream and riparian zone
- Derive a mechanistic model of catchment-scale DOC export which includes the better understanding of DOC mobilization and transport

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