

Dissolved organic matter transformations control longitudinal shifts in organic acidity in a peat bog-fed stream

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1. Introduction

Headwater streams draining peatland ecosystems are major contributors of dissolved organic matter (DOM) into the environment. As DOM travels through river systems, it undergoes compositional changes, which have been described across scales and climate zones. However, how these changes are propagated into the acid-base properties of these streams remains largely unknown. Here we investigate the effect of DOM longitudinal transformations on organic acidity controls in a temperate, highly acidic peat bog-fed stream in the Czech part of the Ore mountains.

2. Study location, data and analytical methods

Study location

A 22.4 km² upper catchment of Rolava River, left tributary of Eger River, Ore Mts.

High-frequency in situ measurements

System of automatic stations measuring water table depth, water temperature, precipitation, and pH in a 10-minute step

One station located in the headwater bog (B1), three stations positioned along the first 11 km of the Rolava watercourse (R7, R6, R1, Fig. 1)

Field sampling based on hydrological conditions

A total of 25 sampling campaigns during 2025 scheduled to capture the following hydrological conditions: 1) snowmelt, 2) rainfall, 3) summer low flows, 4) stormflow events

Analytical methods

DOC measurements

Titration under N₂ atmosphere

UV-Vis spectroscopy

High-performance size exclusion chromatography

4. DOC, optical properties and molecular weights of DOM

- Continuous longitudinal decrease in DOC, aromaticity and molecular weights of DOM
- Upstream, more aromatic and higher molecular weight moieties were tied to late spring and summer, downstream to autumn
- Longitudinal increase of <3 kDa fraction (hydrophilic carbohydrate fraction) and noticeable decrease of fraction >30 kDa (humic like hydrophobics)

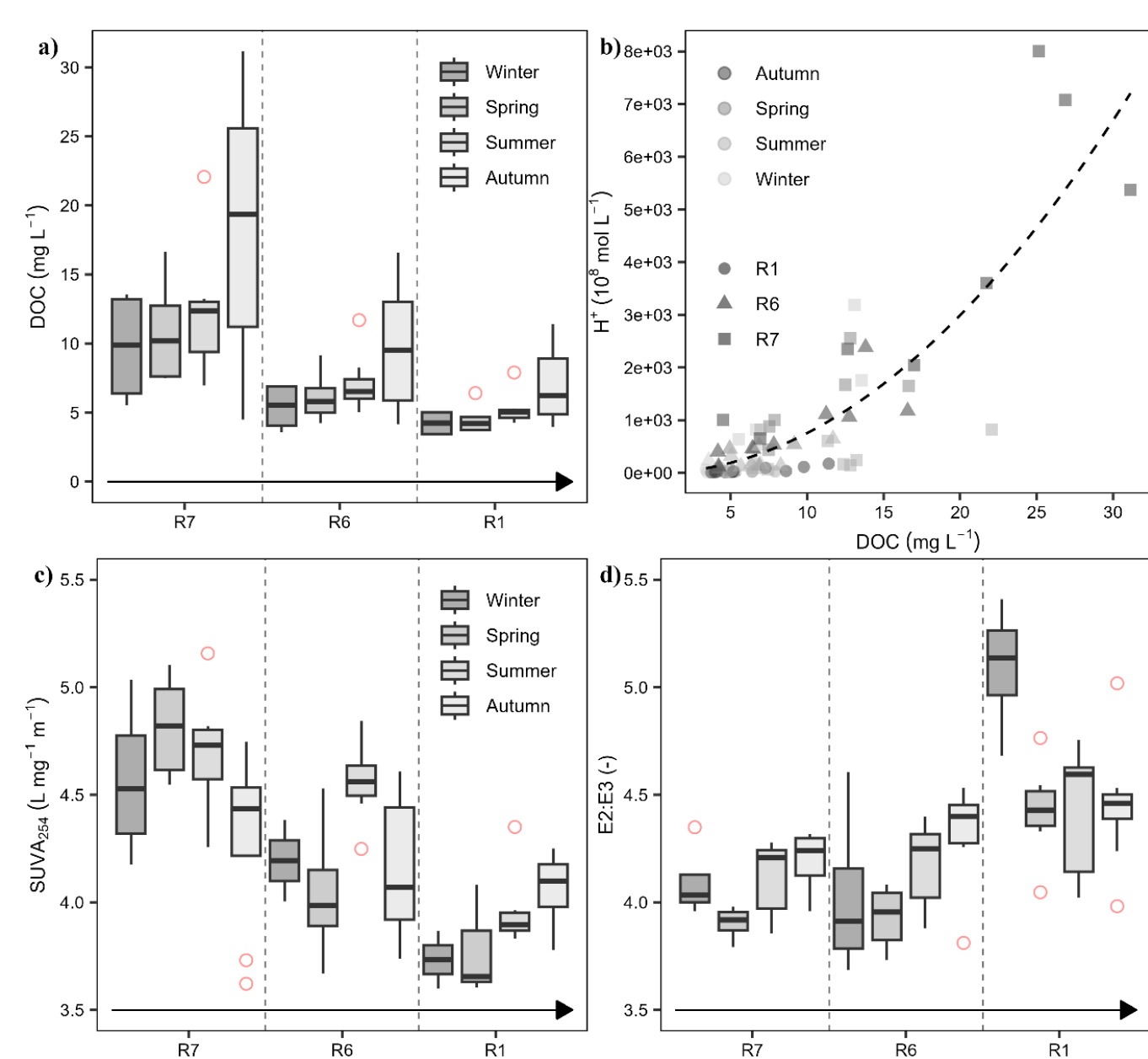


Fig. 5 – Seasonal DOC shifts along the longitudinal profile (solid black line with arrow), (a), mutual relationship between H⁺ ions and DOC (b), and complete opposite behavior of aromaticity and molecular weight proxies (c, d). Red hollow points highlight outliers.

6. Conclusions

- The longitudinal shift from a pH-controlled to a DOC-controlled system was validated under both variable and constant charge densities.
- The fading longitudinal relationships between pH and the apparent molecular weights of dissolved organic matter and between pH and ANC_{4.5} support the transition from a pH to a DOC-controlled system.
- Although DOC fluctuations upstream are higher than downstream, DOC continues to originate from peat (a stable source) as suggested by higher aromaticity and lower seasonal fluctuations of apparent molecular weights. On the other hand, the downstream DOC input is linked to variable mineral soil horizons, leading to lower aromaticity and higher fluctuations in its molecular properties.



Fig. 2 – Experimental station R7

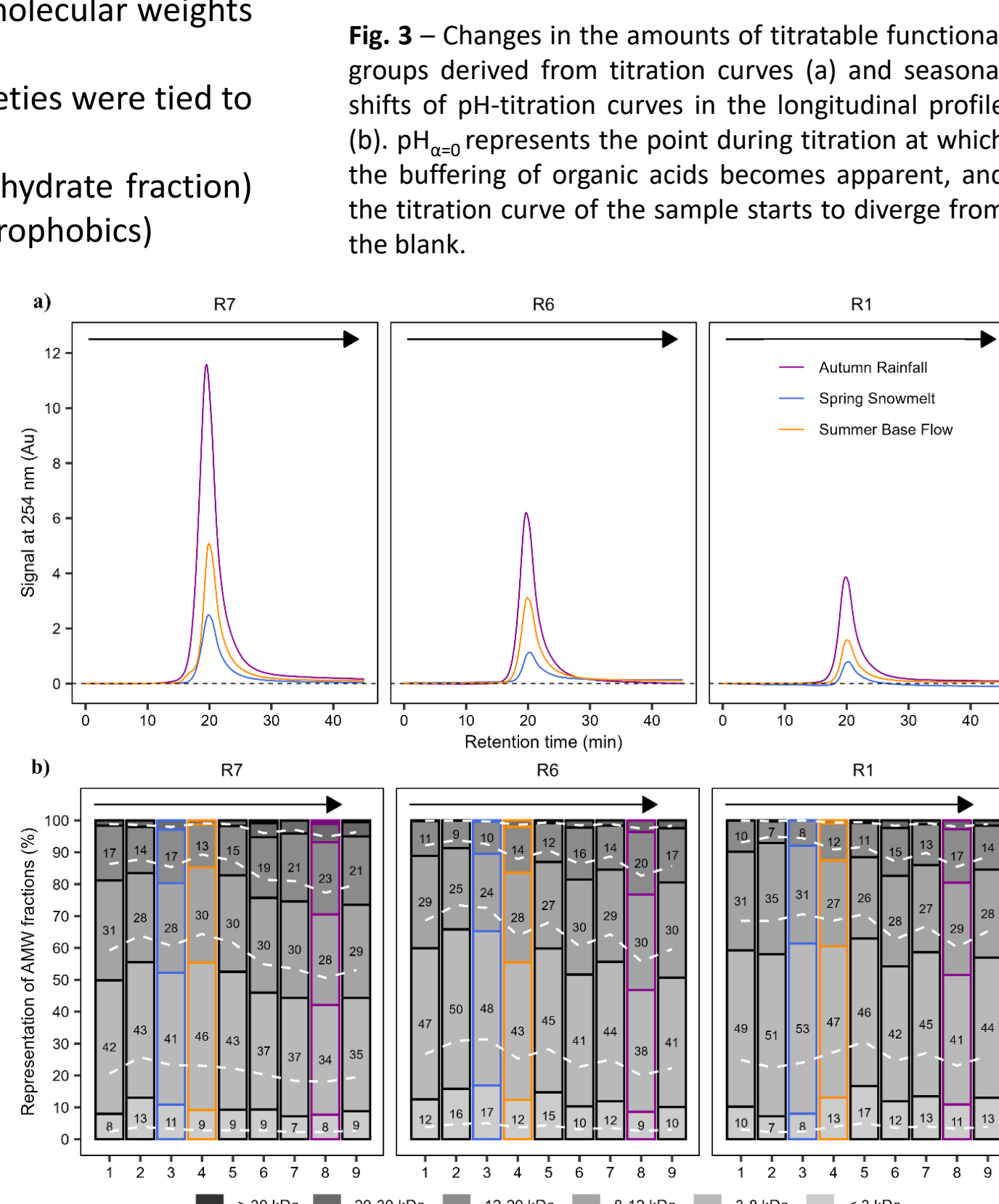


Fig. 6 – HPSEC chromatograms during different hydrological conditions (snowmelt, base flow, R-R event) along the longitudinal profile (black solid line with an arrow), (a). Dashed horizontal line refers to baseline. Different strength signals correspond to different DOC input values. Part (b) offers more detailed information regarding the AMW intervals for all samples (n = 27, 9 per location) and its shifts in longitudinal profile (solid black line with an arrow). White dashed line highlights seasonal dynamics of each fraction. X-axis refers to the sampling dates 1: 07.02.2025, 2: 13.02.2025, 3: 05.03.2025, 4: 30.06.2025, 5: 15.08.2025, 6: 26.09.2025, 7: 06.10.2025, 8: 07.10.2025, 9: 13.12.2025.

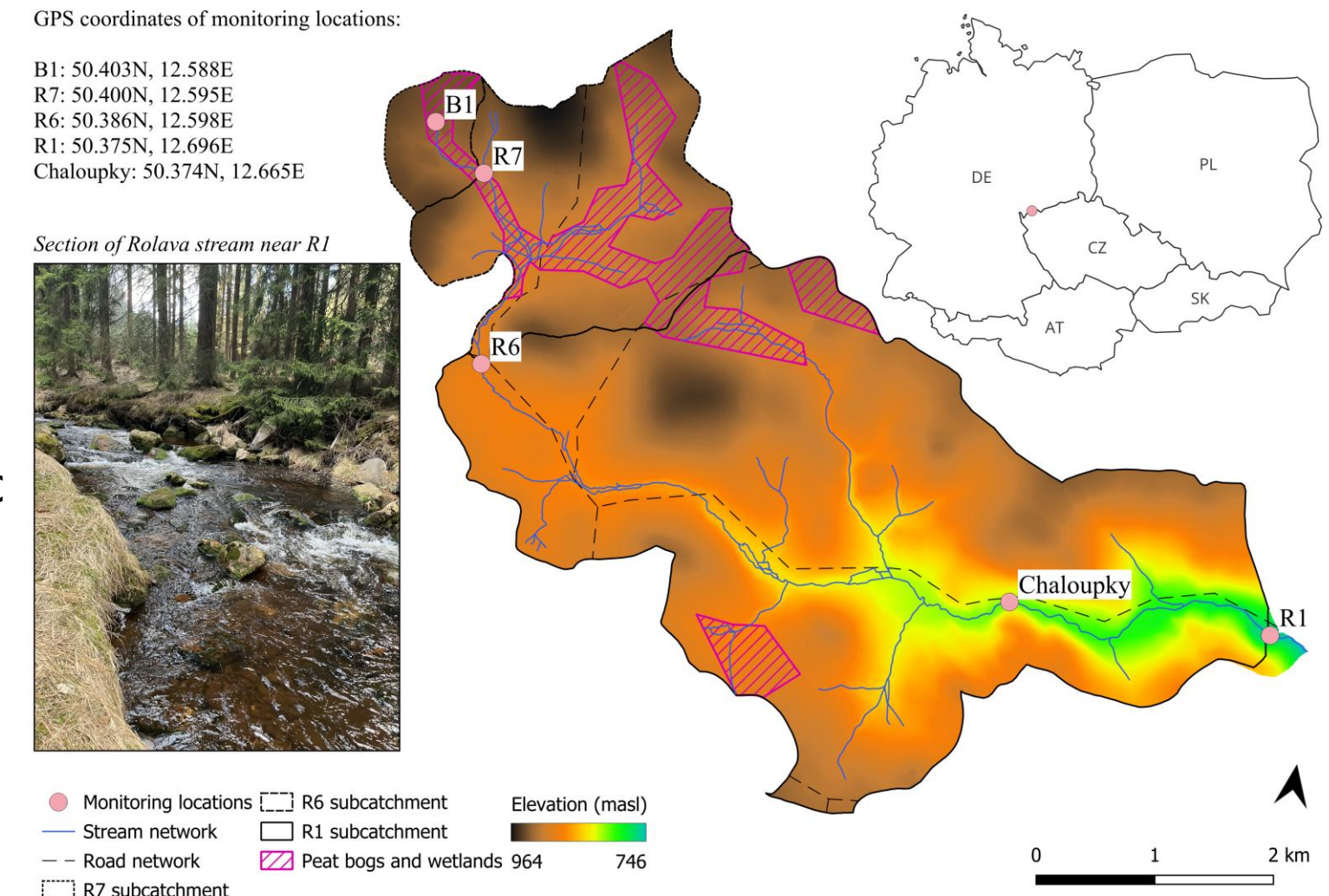


Fig. 1 – Overview of the study location

3. -COOH groups dominate upstream, -OH groups downstream

- Poor neutralization capacity in the whole longitudinal profile
- Upstream, the buffering system is controlled by organic acids with prevalent -COOH groups
- Downstream, the buffering system is a combination of poor bicarbonate buffer with organic acids with prevalent -OH groups

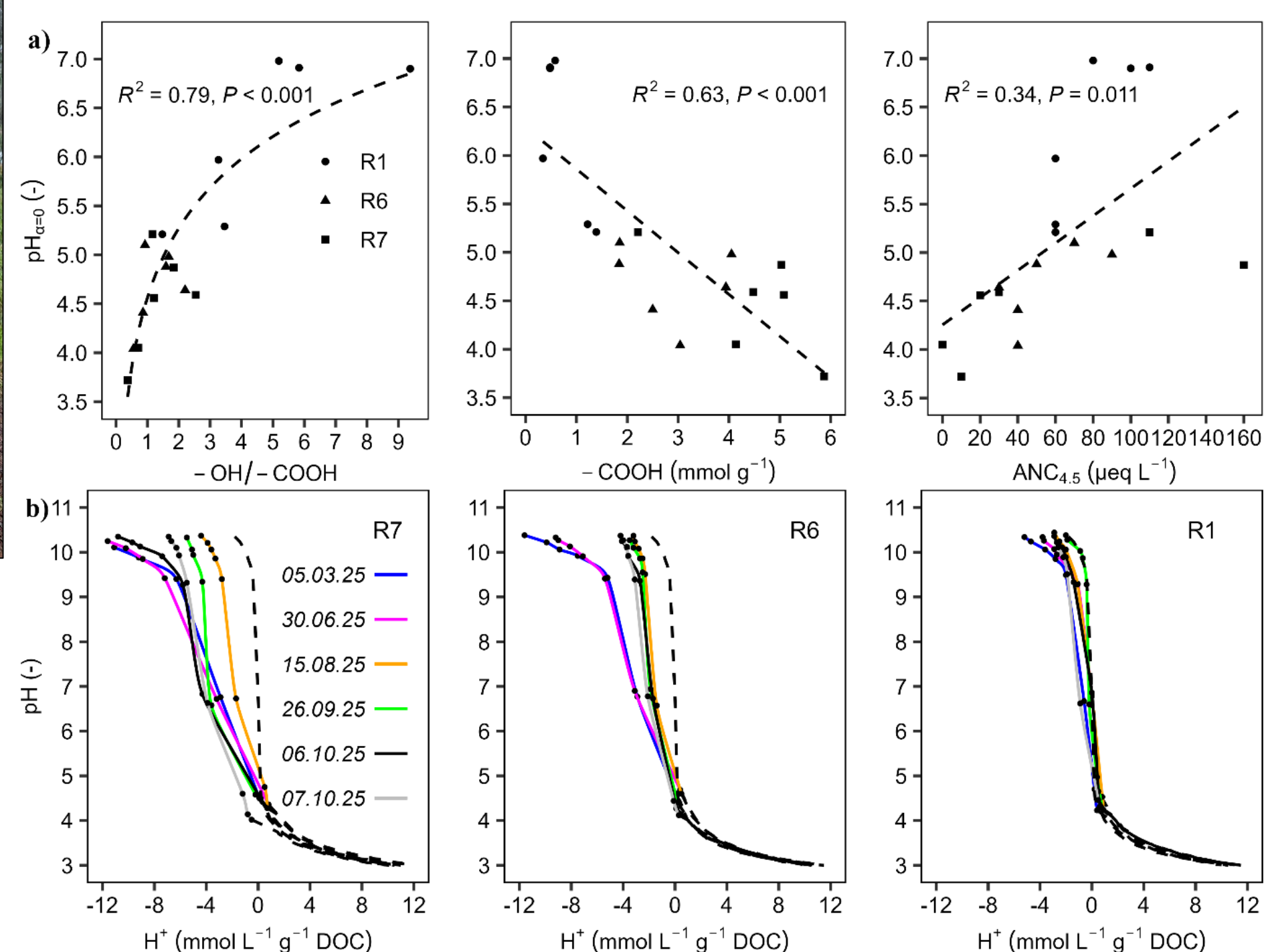


Fig. 3 – Changes in the amounts of titratable functional groups derived from titration curves (a) and seasonal shifts of pH-titration curves in the longitudinal profile (b). pH_{tr_{ao}} represents the point during titration at which the buffering of organic acids becomes apparent, and the titration curve of the sample starts to diverge from the blank.

5. Longitudinal shifts and controls on organic acidity

- Dissociation of -COOH groups -> -COO⁻, while -OH groups remain protonated
- Contribution of RCOO⁻ to ANC_{4.5} is system dependent
- Upstream driven by dissociation of organic acids, pH-controlled system
- Downstream controlled by DOC quantity – fading effect of less acidic -OH groups

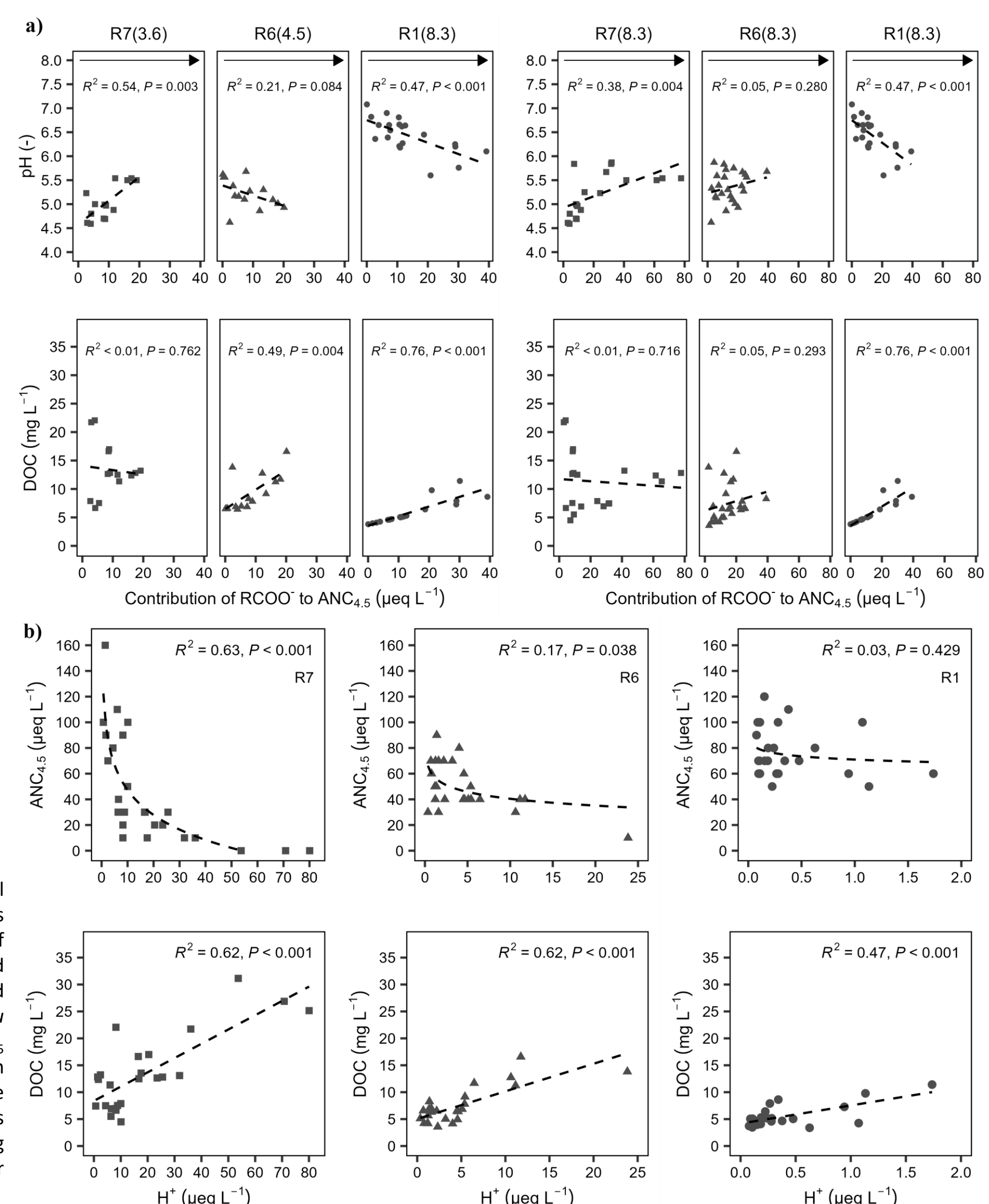


Fig. 7 – Controls on longitudinal dynamics of organic acidity as indicated by a): system shifts of contribution of organic anions to acid neutralization capacity and DOC, and b): relationship between *in situ* measured pH (expressed as H⁺), ANC_{4.5} and DOC. Black solid line with an arrow indicates longitudinal profile direction. Number in parentheses reflects used charge density (μeq mg DOC⁻¹), which was either variable or constant.

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