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Patterns of streamwater dissolved organic carbon (DOC) in a spruce catchments with felsic, mafic and ultramafic substrate from 1993 to 2024

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Transport of DOC in freshwater ecosystems plays a major role in the global carbon cycle. In the last three decades, streamwater DOC has been increasing, potentially due to a decline in acidic deposition, leading to a decrease in ionic strength of precipitation and soilwater, subsequently increasing solubility of soil humic substances [1,2]. For over thirty years, monitoring of three Czech catchments in the Slavkov Forest (50°N, 12.7°E, altitude 690-949 m) has documented enormous reduction in atmospheric load of sulfur, from 30 to 1.5 kg/ha/yr. We investigated geochemically contrasting catchments: Lysina (LYS, since 1990, 27 ha, Podzol on felsic leucogranite), Na Zelenem (NAZ, since 2002, 55 ha, with Cambisol on mafic amphibolite), and Pluhuv Bor (PLB, since 1992, 22 ha, Stagnosol on ultramafic serpentinite). At each of these catchments we measured ions and DOC in precipitation, throughfall and soilwater monthly and in streamwater weekly. Different rates of calcium and magnesium weathering [3], generated contrasting values of streamwater discharge-weighted annual mean pH (LYS 4.05, NAZ 6.30, PLB 7.05). pH values gradually rose (LYS 0.05 pH/decade; NAZ 0.17 pH/decade; PLB 0.12 pH/decade). Slow pH increase happened due to buffering capacity of humic and fulvic acids, which prevented faster rise. Changes in streamwater chemistry were driven mainly by decreases of deposition derived sulfate concentrations. The most pronounced increase of discharge-weighted DOC concentrations was at PLB (0.96 mg/L/yr, $p<0.01$, from 15 to 44 mg/L). Lower, but similar relative increases were observed at LYS (0.32 mg/L/yr, $p<0.01$, 17-27 mg/L) and NAZ (0.33 mg/L/yr ($p<0.01$, 7-14 mg/L). Annual runoff of water decreased markedly at LYS and NAZ due to warming and consequent higher evapotranspiration. However, mean runoff at PLB (270 mm/yr) did not show decline due to spruce decline caused by gradual bark beetle infestation and corresponding evapotranspiration decline. Fluxes of streamwater DOC increased significantly at PLB, by 2.4 kg/ha/yr in the study period. Our work informs about recovery of anthropogenically acidified ecosystems and how DOC increases are supported among geochemically contrasting catchments.

[1] Monteith *et al.* (2023) *Sci.Advances* 9(3)*,* eade3491. [2] Hruska & Kram (2024) *Water* 16*,* w16162220. [3] Kram *et al.* (2012) *Appl.Geoch.* 27*,* 1854-1863.