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Changes in soil DOC affect reconstructed history and projected future trends in surface water acidification

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Over the last two decades there has been growing evidence of widespread increasing concentrations of dissolved organic carbon (DOC) in surface waters in several regions in Europe and North America. Two main drivers have been proposed to explain this observation: climate change entailing changed humidity and temperature which alter rates of microbial processes and reductions in acid deposition which lead to decreased concentrations of strong acid anions and alter rates of decomposition and solubility of organic matter in soil. The question of historical DOC concentrations is therefore important for quantifying present-day acidification and possible future recovery of the surface waters. Due to the paucity of historical data, estimates of pre-acidification chemical and biological status usually come from modeling applications. Lack of process-understanding and of consensus upon what has been driving the observed DOC trends makes modeling uncertain and model outcomes are subject to controversy. Here we apply the MAGIC model to the long-term observed soil and streamwater chemistry data from an anthropogenically acidified small Lysina catchment, Czech Republic, to illustrate the importance of choice of source of DOC during recovery from acidification.

The annual mean streamwater DOC concentration increased from 15.6-16.9 mg L-1 (1993-1994) to 21.8-24.5 mg L-1 in 2010-2011, an average annual increase of 0.6 mg L-1 year-1 ($p<0.001$). Even stronger DOC trends were observed for soilwater draining the organic soil horizons. Mean annual DOC increased from 41-42 mg L-1 in 1993-1994 to 67-74 mg L-1 in 2010-2011 below the organic horizon (at 5 cm depth below the surface), an annual increase of 2.7 mg L-1 year-1 ($p<0.001$). At 15 cm depth below the surface, in the uppermost mineral horizon (E), the DOC concentrations increased from 31-34 mg L-1 to 68-73 mg L-1, an annual increase of 1.9 mg L-1 year-1 ($p<0.005$)

Pre-industrial (1850′s) and future (2060) streamwater chemistry was estimated using the MAGIC model for three different dissolved organic carbon (DOC) levels and sources. The highest pH = 5.7 for 1850′s as well as for 2060 (pH = 4.4) was simulated given the assumption that streamwater DOC concentration was constant at the 1993 level. A scenario accounting for an increase of DOC as an inverse function of ionic strength (it has declined as a result of decreasing acidic deposition) of soilwater and streamwater resulted in much lower pre-industrial pH=4.9 and future recovery to pH=4.1 if only stream riparian zone was taken as a DOC source. If upland soilwater (where significant DOC increase was observed at –5 cm and –15 cm) was also included, DOC was partly neutralized by base cations within the soil and pre-industrial pH=5.3 and future pH = 4.2 were estimated. The observed DOC riverine flux was 2 – 4 times higher than the potential carbon production of the riparian zone. Thus modelling pre-industrial pH based on the assumption that stream DOC changes are solely attributable to changes in the riparian zone appears likely to result in a substantial under-estimate of pre-industrial and future steamwater pH.