

1 **Spatially resolved soil solution chemistry in a central European** 2 **atmospherically polluted high-elevation catchment**

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6 **Revised Introduction**

7 During the second half of the 20th century, atmospheric deposition of reactive nitrogen (N) and sulfate
8 (SO_4^{2-}) caused persistent perturbations in temperate forest soils and water sheds across Europe (Blazkova,
9 1996; Alewell *et al.*, 2001; Verstraeten *et al.*, 2017). Intergovernmental cooperation to abate detrimental
10 sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions was implemented during the 1980s and resulted
11 in a significant decrease in the atmospheric deposition of soil-acidifying species. Reaction of SO_2 and
12 NO_x gases with water molecules in the atmosphere produced sulfuric and nitric acids (H_2SO_4 , HNO_3)
13 which were then entering ecosystems *via* wet and dry deposition. Industry restructuring and installation of
14 scrubbers in power plants significantly reduced industrial SO_2 emission rates by more than 90% in one of
15 the most polluted industrial regions of Central Europe, known as the “Black Triangle”, which includes
16 mountainous border regions of three countries, Czech Republic, East Germany and Poland (Fig. 1a;
17 Blazkova, 1996; Novak *et al.*, 2005). A decrease in soil solution SO_4^{2-} concentrations followed, and has
18 progressively lowered soil solution ionic strengths while contributing to a progressive raise in soil pH,
19 which may have in turn increased organic matter leaching by lowering the soil solution concentrations of
20 aluminum ions (Al^{3+}) (*e.g.*, Monteith *et al.* 2007).

21 Although also significantly decreased (Waldner *et al.*, 2014), atmospheric inputs of reactive N species in
22 excess to the nutritional demands of plants and microorganisms have prevailed across central Europe.
23 These have resulted in forest ecosystem perturbations consisting on a cascade of biogeochemical
24 reactions linked to soil N-saturation (Galloway *et al.*, 2003). For instance, despite a ~40 % reduction in
25 atmospheric N inputs (Kopacek *et al.* 2013), in the Czech Republic alone the value of the total nitrogen
26 deposition remained—during the last decade—in the range of 70,000–80,000 t per year as a result of the
27 production of NO_x emissions from transport, industrial production and energy generation (CENIA, 2017).
28 The unchanged figures despite significant efforts for controlling industrial emissions over the same period
29 is a societal concern since there is growing uncertainty on whether or not central European temperate
30 forest ecosystems will be in capacity to continue acting as major sinks for a 15-20% intensification in
31 anthropogenic emissions of reactive N to the atmosphere (Galloway *et al.* 2008). A detrimental effect of
32 unmanaged soil N-saturation in catchment areas is propagation of environmental effects to lacustrine
33 ecosystems (Kopacek *et al.* 1995).

34 N-saturation in soils is indicated by leaching and losses of nitrate (NO_3^-) below the rooting zone (Aber *et al.*,
35 1989; Perakis and Hedin, 2002; Perakis and Sinkhorn, 2011). Continuing mineralization of soil
36 organic N pools has been pointed out as the most probable reason for high N fluxes. Yet, the fate of
37 excess NO_3^- is not only controlled by belowground biogeochemical N cycling and remineralization
38 processes, but also by site-specific characteristics, such as the size and quality of subsoil carbon pools,
39 bedrock lithology, differential weathering and hydrological conditions (Lovett and Goodale 2011).
40 Altogether these parameters affect soil solution chemistries to produce complex spatial and temporal
41 trends at a catchment scale.

42 Given the number of interacting factors affecting soil solution chemistries, there is an intrinsic difficulty
43 associated to interpreting soil solution dataset. However, the chemical composition of soil solutions has
44 been proven useful to assess the mobility of anionic species and nutrients in soils and their leaching from
45 the soil profiles (Nieminen et al., 2016). It is thought reflective of equilibrium between atmospheric
46 deposition and soil physicochemical processes, including mineral weathering, sorption-desorption and
47 cation exchange, as well as biological processes such as remineralization and nutrient turnover (Smith,
48 1976; Scott and Rothstein, 2014). In consequence, soil solution chemistries are increasingly seen as
49 valuable indicators of perturbed forest ecosystems (Nieminen et al. 2016; Verstraeten et al., 2017).

50 Here, we interpret temporal and spatial relations between environmentally relevant chemical species in
51 soil solutions collected using nests of zero tension lysimeters in a small, central European high-elevation
52 catchment —U dvou loucek (UDL)— which formerly received high loads of atmospheric pollutants
53 which resulted in soil acidification and spruce die-back. Some 30 years after peak acidification, the soil
54 solutions at UDL were collected across an elevation gradient during a 2-year evaluation period. The
55 collected soil solutions include both capillary and percolating water in the mineral soil (*e.g.*, Nieminen et
56 al., 2011). We revisited our unpublished chemical records to: (i) evaluate how do they reflect concurrent
57 atmospheric deposition trends and stream water fluxes of acidifying species and base cations (after
58 Oulehle et al. 2017), and whether seasonal shifts observed on atmospheric deposition trends affected the
59 spatially and temporally variable base cation contents of our independently measured soil solution
60 chemistries; (ii) determine the effects of variable base cation content of soil solutions, soil granulometry
61 and aluminum contents over the belowground carbon (C) and phosphorus (P) allocation; and (iii) assess
62 to what extent does the chemistry of soil solutions varies along the topographic gradient.

63 Our small catchment has a low pedodiversity as it is situated entirely on base-poor, crystalline gneissic
64 bedrock in the north-eastern part of Czech Republic (Fig. 1a). This peculiarity simplifies our
65 interpretations (*cf.* Kram et al., 2012). Amongst 14 multi-decadal monitored small forested catchments of
66 the Czech' GEOMON network, UDL received the highest bulk atmospheric loads of a nitrogen and
67 sulfur. As a result, the catchment is P limited and purportedly N saturated, with the ongoing pollution
68 recovery process apparently altering concentrations and surface fluxes of other solutes via runoff (Oulehle
69 et al., 2017). Our combined dataset documents spatial heterogeneity of soil solutions in the form of
70 variable nutrient imbalances and offers further information to improve interpretations on the dynamics
71 and catchment-scale patterns of soil solutions in temperate forests undergoing recovery after peak
72 acidification.